

Pittsburg State University

## Pittsburg State University Digital Commons

---

Electronic Theses & Dissertations

---

Spring 5-10-2019

### Highly Flame-Retardant Rigid Polyurethane Foams Prepared Using Corn Oil

Camila Muliterno Zequine

Pittsburg State University, [camilazequine@hotmail.com](mailto:camilazequine@hotmail.com)

Follow this and additional works at: <https://digitalcommons.pittstate.edu/etd>

 Part of the [Polymer and Organic Materials Commons](#)

---

#### Recommended Citation

Muliterno Zequine, Camila, "Highly Flame-Retardant Rigid Polyurethane Foams Prepared Using Corn Oil" (2019). *Electronic Theses & Dissertations*. 473.

<https://digitalcommons.pittstate.edu/etd/473>

This Thesis is brought to you for free and open access by Pittsburg State University Digital Commons. It has been accepted for inclusion in Electronic Theses & Dissertations by an authorized administrator of Pittsburg State University Digital Commons. For more information, please contact [digitalcommons@pittstate.edu](mailto:digitalcommons@pittstate.edu).

HIGHLY FLAME-RETARDANT RIGID POLYURETHANE FOAMS PREPARED USING CORN OIL

A Thesis Submitted to the Graduate School  
In Partial Fulfillment of the Requirements  
For The Degree of Master of Science

Camila Muliterno Zequine

Pittsburg State University

Pittsburg, Kansas

May 2019

HIGHLY FLAME-RETARDANT RIGID POLYURETHANE FOAMS PREPARED USING CORN OIL

Camila Muliterno Zequine

APPROVED:

Thesis Advisor

\_\_\_\_\_  
Dr. Ram Gupta, Chemistry Department

Committee Member

\_\_\_\_\_  
Dr. Khamis Siam, Chemistry Department

Committee Member

\_\_\_\_\_  
Dr. Pawan Kahol, Physics Department

Committee Member

\_\_\_\_\_  
Dr. Anuradha Ghosh, Biology Department

## ACKNOWLEDGMENTS

I would first like to express my sincere gratitude to Dr. Ram Gupta for giving me the opportunity to get a master's degree outside of my country. During these two years, he provided guidance, support, encourage and joy throughout my graduate studies at Pittsburg State University. All his patience and help made possible for me to complete my work and my objectives in the program. I am very grateful to Dr. Pawan Kahol and Dr. Khamis Siam for being active members of my thesis committee and providing support for research and educational activities. Financial supports from Kansas Corn Commission, Polymer Chemistry Program and Graduate College are gratefully appreciated. Thanks to Dr. Anuradha Ghosh for accepting her membership on the thesis committee. I would also like to thank Dr. Petar Dvornic, Dr. Jeanne Norton and Dr. Paul Herring for teaching me in the classroom, which will advantage for a whole life. Also, I would like to thank members of the Light, Energy, and Nanotechnology Research Group for their help, teachings and friendship.

Finally, I must express my gratitude to my parents, brother, whole family, partner and friends for their love and unfailing encouragement since the beginning of the journey. This accomplishment would not have been possible without them.

# HIGHLY FLAME-RETARDANT RIGID POLYURETHANE FOAMS PREPARED USING CORN OIL

An Abstract of the Thesis By  
Camila Muliterno Zequine

One of the biggest catastrophic problems worldwide is the structural fire that destroys properties, durable goods and lives. Polyurethanes are one of the most important polymers because of the widely used in industrial applications, such as thermal insulation, coating, construction, and automobiles. However, polyurethane foams have the disadvantage of being flammable. Most of the starting materials for the production of polyurethanes are derivate from petroleum-based resources, which generates environmental and governmental problems. In this study, bio-based rigid polyurethane foams were synthesized using corn oil. First, commercial corn oil was fully epoxidized to be used in the synthesis of flame-retardant rigid polyurethane foams using different concentrations of phosphorous containing polyol. Flame retardancy was tested on these foams and it was observed that phosphorous containing polyol from epoxidized corn oil provides excellent flame retardancy. It was observed burning time and weight loss decreased drastically for the foams containing only 1.5 wt% phosphorous. Second, commercial corn oil was partially epoxidized to be used in the synthesis of flame-retardant rigid polyurethane foams using different concentrations of phosphorous containing polyol. Partially epoxidation corn oil was converted to polyol using thiol-ene click chemistry. Flame retardancy for these foams was also studied and results showed that physicomechanical properties, such as density, closed cell content, and compressive strength maintained the range of industrial applications. The efficiency in flame-retardant

properties was achieved even for a small amount of phosphorous. From the overall study, the rigid polyurethane foams prepared using corn oil based-phosphorous containing polyol displayed high flame-retardancy.

## TABLE OF CONTENTS

CHAPTER	PAGE
<b>I INTRODUCTION</b>	<b>1</b>
1.1. Polyurethanes	1
1.2. Importance of Bio-based Foams	2
1.3. Drawbacks Faced by Polyurethane Foams	3
1.4. Flame-Retardants Polyurethane Foams	4
1.5. Purpose of This Research	5
<b>II CHARACTERIZATION DETAILS</b>	<b>6</b>
2.1. Characterization of the Polyols	6
2.1.1. Hydroxyl Number (OH)	6
2.1.2. Acid Value	7
2.1.3. Fourier Transform Infrared Spectroscopy (FT-IR)	8
2.1.4. Gel Permeation Chromatography (GPC)	8
2.2. Characterization of the Foams	8
2.2.1. Apparent Density	8
2.2.2. Closed Cell Content	9
2.2.3. Compression Strength	9
2.2.4. Scanning Electron Microscopy (SEM)	9
2.2.5. Horizontal Burning Test (HBT)	9
2.2.6. Cone Calorimetry	10
<b>III FLAME-RETARDANT RIGID POLYURETHANE FOAMS USING FULLY EPOXIDIZED CORN OIL</b>	<b>11</b>
3.1. Introduction	11
3.2. Experimental details	12
3.2.1. Materials	12
3.2.2. Synthesis of Fully Epoxidized Corn Oil	13
3.2.3. Synthesis of Polyol Using Fully Epoxidized Corn Oil	13
3.2.4. Preparation of Flame-Retardant Rigid Polyurethane Foams	14
3.3. Results and Discussion	16
3.4. Conclusion	27
<b>IV FLAME-RETARDANT RIGID POLYURETHANE FOAMS USING PARTIALLY EPOXIDIZED CORN OIL</b>	<b>29</b>
4.1. Introduction	29
4.2. Experimental Details	30
4.2.1. Materials	30
4.2.2. Synthesis of Partially Epoxidized Corn Oil	30
4.2.3. Synthesis of Polyol Using Partially Epoxidized Corn Oil	31
4.2.4. Preparation of Flame-Retardant Rigid Polyurethane Foams	34

4.3. <i>Results and Discussion</i>	35
4.4. <i>Conclusion</i>	46
<b>V SUMMARY OF THE THESIS</b>	<b>48</b>
<b>REFERENCES</b>	<b>50</b>
<b>APPENDIX</b>	<b>53</b>
7.1. <i>List of Conference Presentations</i>	54
7.2. <i>List of Publications</i>	57
7.3. <i>Published Work on Polyurethanes</i>	59
7.4. <i>Award received on Polyurethanes</i>	60



## LIST OF TABLES

TABLE		PAGE
Table 3.1	Formulation for preparation of phosphorus-containing polyurethane foams	15
Table 3.2	Cream time, rise time and tack-free time for the polyurethane foams	19
Table 4.1	Formulation used to prepare phosphorus-containing polyurethane foams	35

## LIST OF FIGURES

FIGURE		PAGE
Figure 1.1	Polyurethane synthesis	1
Figure 1.2	Civilian fire deaths in the United States	3
Figure 1.3	Polyurethane demand worldwide from 2011 to 2021, by application (in million metric tons)	4
Figure 3.1	Synthesis of epoxidized corn oil	13
Figure 3.2	Synthesis of polyol from epoxidized corn oil	14
Figure 3.3	(a) Adding MDI in pre-mix of corn oil-based polyol, (b) mixing the ingredient at 3,000 rpm, (c) foaming started after mixing for 10 seconds, (d) foam started raising, (e) foams keep raising and (f) fully prepared corn oil-based polyurethane foam	15
Figure 3.4	FT-IR spectra of the starting materials and corn oil-based polyol	17
Figure 3.5	GPC curve of the starting materials and corn oil-based polyol	17
Figure 3.6	Photographs of the prepared polyurethane foams	18
Figure 3.7	(a) Density and (b) closed cell content of various polyurethane foams prepared using corn oil	20
Figure 3.8	Compressive strength of various polyurethane foams	21
Figure 3.9	SEM images of various polyurethane foams	22
Figure 3.10	Scheme for horizontal burning test	23
Figure 3.11	(a) Burning time and, (b) weight loss for prepared rigid polyurethane foams	24
Figure 3.12	Digital images of the foams before and after burning test	25
Figure 3.13	(a) Thermal heat release (THR) and (b) thermal smoke release (TSR) data for the Foam-1 and Foam-4	27
Figure 4.1	Partial epoxidation of corn oil	31
Figure 4.2	Phosphorous based polyol using partially epoxidation of corn oil (PECO-DBP)	32
Figure 4.3	Thiol-ene reaction of PECO-DBP with thioglycerol	33
Figure 4.4	Thiol-ene reaction of PECO-DBP with thioglycerol and mercaptoethanol	34
Figure 4.5	FT-IR spectra of the synthesized compounds	37
Figure 4.6	GPC curves of the synthesized compounds	39
Figure 4.7	Density of the prepared corn oil-based polyurethane foams	40
Figure 4.8	Closed cell content of the prepared corn oil-based polyurethane foams	40
Figure 4.9	Compressive strength of the prepared corn-oil based polyurethane foams	41
Figure 4.10	SEM images of the prepared corn-oil based polyurethane foams	42

Figure 4.11	Burning time of corn-oil based polyurethane foams	43
Figure 4.12	Weight loss of corn-oil based polyurethane foams	43
Figure 4.13	Digital images of the foams before and after burning test	44
Figure 4.14	Heat release rate for various foams	45
Figure 4.15	Thermal heat release for various foams	45
Figure 4.16	Thermal smoke release for various foams	46



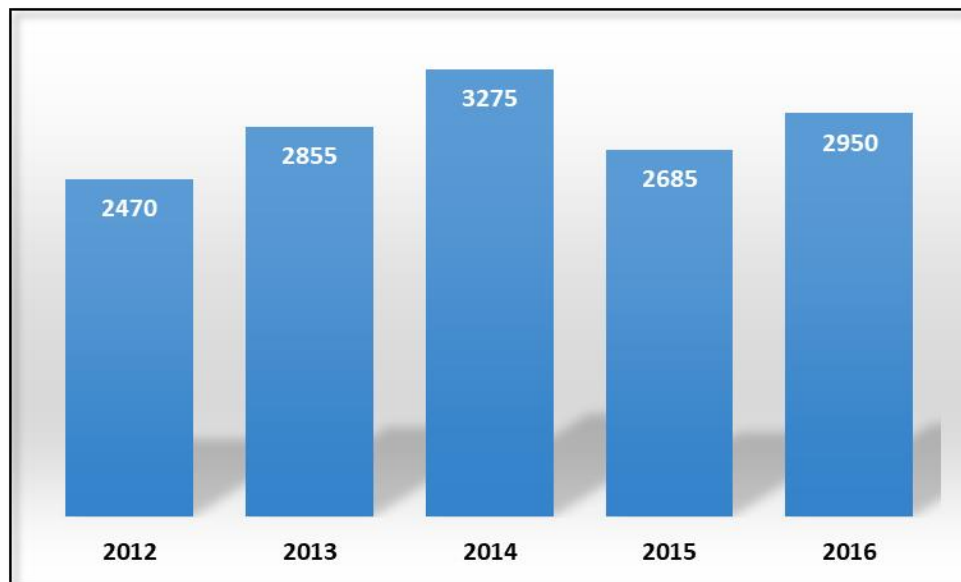
construction, thermal and electrical insulation.<sup>2,5,6</sup> The properties of the polyurethane are determined by the polyol used. Hence, new polyols have been developed using green sources, to combine excellent properties and environmental preservation in the polyurethane synthesis.<sup>3</sup> The polyurethane market size was 53 billion dollars in 2015 and is expected to grow with a rate of 7% for the next 10 years.<sup>7</sup> According to Research and Markets, industries such as BASF, Dow Chemical, Mitsui Chemicals are the major raw material providers which, together with other important industries, worldwide demanded was 16 million tons in 2016.<sup>8</sup>

## **1.2. Importance of Bio-Based Foams**

Most of the starting materials for the production of polyurethanes are derivate from petroleum-based resources, which are unsustainable. The depletion of the world's crude oil stock, environmental concerns, and price of crude oil are increasing significantly.<sup>1</sup> Sustainable solutions and efforts are dedicated to finding renewable sources for polyols to replace petroleum-based counterparts. Polyurethanes using bio-based materials are receiving attention because they can utilize cellulose, starch, sugar, vegetable oil (castor oil, canola oil, sunflower oil, corn oil) to switch to nonrenewable sources.<sup>5,9</sup> Vegetable oils are suitable candidates as with simple chemical modifications they can react with isocyanate to produce polyurethanes. Generally, chemical modifications produce multiple hydroxyl groups. The hydroxyl numbers generated in the vegetable oils control the crosslinking of the polyurethanes.<sup>1</sup>

### 1.3. Drawbacks Faced by Polyurethane Foams

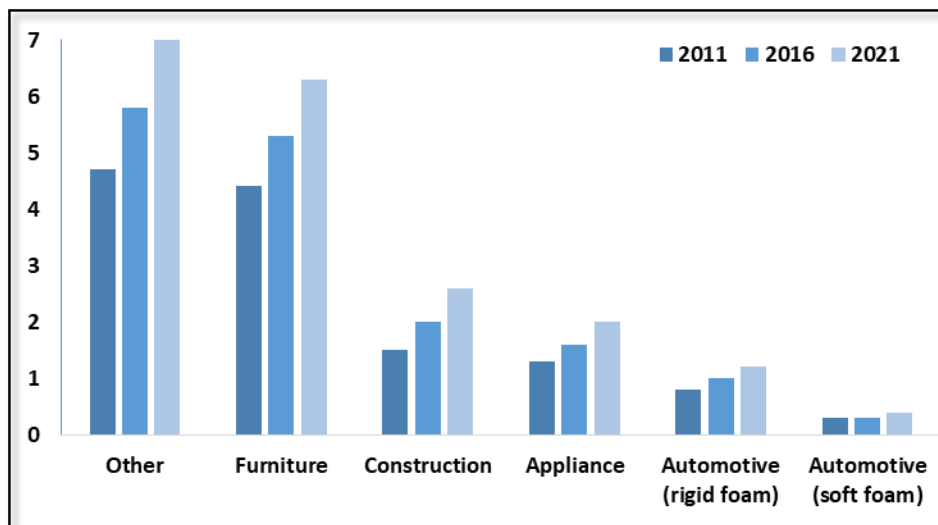
Polyurethane foams show high surface-to-mass ratio, high air permeability, open cell structure, and high oxygen, carbon, and hydrogen content in the polymer matrix.<sup>10</sup> These characteristics make polyurethane foams vulnerable to fire hazards. Due to easy ignition and high burning velocity, a small spark of fire would provide a significant disaster.<sup>9,10</sup> National Fire Protection Association estimates 1.3 million fires just in 2016. The most common accident with fire occurred in home structures and vehicles. These fires resulted in an increase of 3.4% of civilians died from the previous year. As evident in [Figure 1.2](#), fires have caused significant deaths long the years.<sup>11</sup>



**Figure 1.2:** Civilian fire deaths in the United States.

According to Center of Fire Statistics, in a study covering 31 countries, 18 thousands people died because of fires in 2015.<sup>12</sup> Data of U.S. Fire Administration shows 1305 civilian home fire fatalities in the first six months of 2018.<sup>13</sup> Polyurethane foams are widely used for thermal insulation in constructions, electrical insulation, coating in

furniture, and many household packings, <sup>2,7,9</sup> it is necessary to develop fire retardant polyurethanes. The growing demand for the polyurethanes (Figure 1.3), strongly suggest us to develop bio-based and flame retardant polyurethanes.<sup>15</sup>



**Figure 1.3:** Polyurethane demand worldwide from 2011 to 2021, by the application (in million metric tons).

#### 1.4. Flame-Retardants Polyurethane Foams

Flame-retardants can be classified by mechanisms and types. The mechanisms are a gas phase (free radical quenching), condensed phase (char forming), and endothermic.<sup>16</sup> The types of flame-retardants are divided into two groups: additive flame-retardants and reactive flame-retardants. Additive flame-retardants are compounds containing bromine, chlorine, dimethyl methyl phosphonate, melamine, and metal hydroxides.<sup>2</sup> They present no reactive groups such as OH, NH<sub>2</sub> or NCO.<sup>17,18</sup> Reactive flame-retardants are compounds that contain reactive functional groups and they participants during the polyurethane formation. This type of flame-retardants contain phosphorous, nitrogen, and silicone.<sup>19</sup>

By adding flame-retardant materials in the polyurethane foams during the preparation of these foams, the combustion cycle can be stopped and consequently the flammability will be controlled.<sup>2</sup> Rigid polyurethane foams are the main candidate for thermal insulation in the construction industry, because they show excellent properties such as thermal resistance, high compressive strength and closed cell content.<sup>9,20</sup> Among the flame-retardants compounds, phosphorous have received great importance and have shown good results. Thus, in this work, all the study was focused on synthesizing flame-retardant using the bio-based phosphorous compound to provide flame retardancy to the rigid polyurethane foams.

### **1.5. Purpose of This Research**

In this study, bio-based rigid polyurethane foams were synthesized using epoxidized corn oil. The flame-retardant was synthesized to study the relationship of phosphorus-based compounds over the flame retardancy of the foams. Furthermore, the flame-retardancy was studied over different quantity of epoxidized corn oil (fully and partially). Chapter two is dedicated to characterization techniques. All these studies are described in chapter three and four. In the third chapter, the study was focused on flame-retardant polyurethane foams using fully epoxidized corn oil. In the fourth chapter, the study was focused on flame-retardant polyurethane foams using partially epoxidized corn oil. The main objective of this research was prepared highly efficient flame-retardant rigid polyurethane foams using synthesized corn oil-based polyol, which is conferred from chapter five.



## CHAPTER II

### CHARACTERIZATION DETAILS

This chapter focuses on the analysis of synthesized corn oil-based polyol and polyurethane foams using standard characterization techniques. All the synthesized polyols were characterized to obtain hydroxyl number, acid value, molecular weight increase and functional characteristics of the polyols. While, foams were analyzed using apparent density, closed cell content, compression strength, scanning electron microscopy, horizontal burning test, and cone calorimetry.

#### 2.1. Characterization of the Polyols

##### 2.1.1. Hydroxyl Number (OH)

The hydroxyl number is defined as the quantitative value of the amount of hydroxyl groups available for the reaction with isocyanates. This number is expressed as milligrams of potassium hydroxide equivalent for one gram of the sample.<sup>21</sup> It is determined by the phthalic anhydride/pyridine (PAP) method according to ASTM D4274 standard. Hydroxyl reagent used in this method was a 2N phthalic anhydride solution in pyridine (1,000 ml). This reagent was prepared by dissolving 148 g of phthalic anhydride in 4 g of imidazole in pyridine. First, 10 ml of the hydroxyl reagent and 0.4 mg of sample

was added in 100 ml glass bottle with a magnetic bar. The bottle was capped and heated at 100 °C for 70 min (mixing every 15 minutes) and cooled down to room temperature. After that, it was added into the bottle 10 ml of water, 20 ml of isopropanol and 3 drops of the phenolphthalein indicator (10 g/l), and stirred. The first volume was recorded as  $v_0$ . This solution was titrated using 1.0 N NaOH until the solution turned pink. The new volume was recorded as  $v$ . For one hydroxyl group, one mole of KOH (56,100 mg of KOH) is consumed to neutralize the reaction. Considering 1.0 as the normality of the titrant,  $MW$  as the molecular weight of the polyol, the hydroxyl number could be calculated using the following equation:

$$\text{OH\#} = \frac{56.1 * 1.0 * (v_0 - v)}{MW} \text{ (mg KOH/g)}$$

### 2.1.2. Acid Value

The acid value is the amount of acidic groups in an oligo-polyol. It is important to control the acidity of oligo-polyols to avoid negativity effect of the reactivity in polyurethane synthesis.<sup>21</sup> According to IUPAC 2.201 standard, the acid value was determined using the indicator method. For this, it was prepared a solvent mixture using 500 ml of isopropanol, 500 ml of toluene and 3 ml of phenolphthalein indicator (10 g/l in 95% isopropanol). About 3 g of the test portion was put into a 125 ml conical flask and dissolved in 30 ml of the solvent mixture. This was titrated with 0.1 N KOH until the solution turned pink. Then, the acid value of polyol could be calculated using the following equation:

$$\text{Acid Value} = \frac{56.1 * 0.1 * V}{MW} \text{ (mg KOH/g)}$$

### **2.1.3. Fourier Transform Infrared Spectroscopy (FT-IR)**

FT-IR spectroscopy was used to understand the reaction process through the functional groups and structural peaks. FT-IR spectra were obtained using Shimadzu IR Affinity-1 spectrophotometer and the spectra of samples were recorded in a range of wave numbers from 4500 to 500  $\text{cm}^{-1}$ .

### **2.1.4. Gel Permeation Chromatography (GPC)**

Reduction in the retention time of GPC peaks, confirms the increase in molecular weight. GPC characterization was carried out using a Waters Gel Permeation Chromatograph (Waters Corporation, Milford, MA, USA) consisting of four 300 × 7.8 mm phenogel 5  $\mu$  columns with different pore sizes of 50, 102, 103 and 104 Å. Eluent solvent was tetrahydrofuran and the eluent rate was 1 ml/min at 30 °C.

## **2.2. Characterization of the Foams**

### **2.2.1. Apparent Density**

The apparent density of the foams was measured according to standard method ASTM D1622. The density of each foam was calculated as the average of the densities of the top and middle portions in the rising direction. A cylindrical foam with 45 mm of diameter and 30 mm of height was cut out. The foams were measured on a balance of  $\pm$  5 mg precision. The dimensions of the foams were measured and then the density could be calculated. Industrial standards for foam density ranges from 30 to 50  $\text{kg/m}^3$ .

### **2.2.2. Closed Cell Content (CCC)**

Ultracycrometer, Ultrafoam 1000 was used to analyze the closed cell content having specimen with cylindrical shape and dimensions of  $\varnothing 45$  mm x 30 mm, according to standard method ASTM D2856. Closed cell content is an important property because ensure good thermal insulation.

### **2.2.3. Compression Strength**

The compression strength of rigid polyurethane foams was measured using ASTM D1621 having specimen size of (L) 50 mm  $\times$  (B) 50 mm  $\times$  (H) 25 mm. The compressive strength at 10% strain was determined using the Q-Test 2-tensile machine made by MTS, USA. The compressive force of 30 mm/min was applied parallel to the direction of the foam.

### **2.2.4. Scanning Electron Microscopy (SEM)**

Cell morphology and cellular size of the foams were determined using the Phenom G2 Pro scanning electron microscope (Netherlands). The samples were pre-coated with gold using sputtering to avoid the charging effect during imaging.

### **2.2.5. Horizontal Burning Test (HBT)**

It is important to study fire behavior by testing the foams under real fire. Using standard ASTM D4986-98, fire retardancy was analyzed by the horizontal burning test. A test specimen of polyurethane foams with a size of (L) 150 mm  $\times$  (B) 50 mm  $\times$  (H) 12.5 mm was loaded over the holder and exposed to the open flame for 10 seconds. Burning time after the flaming and weight loss after burning was noted for all the foams.

### **2.2.6. Cone Calorimetry**

To understand the fire behavior, it is important to analyze the real-time fire with respect to the heat released and smoke produced out of the sample. Heat release rate (HRR), thermal heat release (THR) and thermal smoke release (TSR) were tested by using a standard cone calorimeter (Fire Testing Technology). For this, the test specimen was cut into a size of (L) 100 mm × (B) 100 mm × (H) 25 mm according to ISO 5560 standard and exposed to the external heat flux of 35 kW/m<sup>2</sup>.

## CHAPTER III

### FLAME-RETARDANT RIGID POLYURETHANE FOAMS USING FULLY EPOXIDIZED CORN OIL

#### 3.1. Introduction

Plant oils are an alternative resource to produce polymeric materials. They offer many advantages apart from their renewability, availability and relatively low prices, which make industrially attractive. Plant oils are mainly constituted for triacylglycerols that are highly functionalized molecules and have been used in the synthesis of cross-linked polymers.<sup>22</sup> Epoxidation is one of the most used methods for the functionalization of carbon-carbon double bonds.<sup>14</sup> Epoxidation of vegetable oil followed by oxirane ring-opening create polyols with different functionalities for polyurethanes. However, many agents used to prepared polyols by ring-opening of epoxidized vegetable oils are petroleum-based. Efforts have been dedicated to developing 100% bio-polyols.<sup>1</sup> Polyurethane foams are flammable and to minimize the flammability can be used different flame-retardants based on nitrogen, phosphorous, halogen, inorganic metal oxides and hydroxides. Flame-retardants based on halogens are widely used, but they can cause environmental and health concerns. Because of these concerns, some halogen-

containing compounds have been forbidden for many uses due to the emission of toxic gases and dense smoke. Hence, there is a demand for developing halogen-free flame retardant. Phosphorous containing flame-retardants suggests a good solution for that problem because they exhibit good flame retardancy with low toxicity and slow evolution of smoke.<sup>2,19,23,24</sup>

In this work, commercial corn oil was epoxidized to be used in the synthesis of polyol for further preparation of flame retardant polyurethane foams. Chemical and physical properties of the polyols were confirmed using characterization techniques. Our results confirmed that flame retardant using bio-based polyol provided higher flame retardancy in the foams using a small quantity of phosphorous.

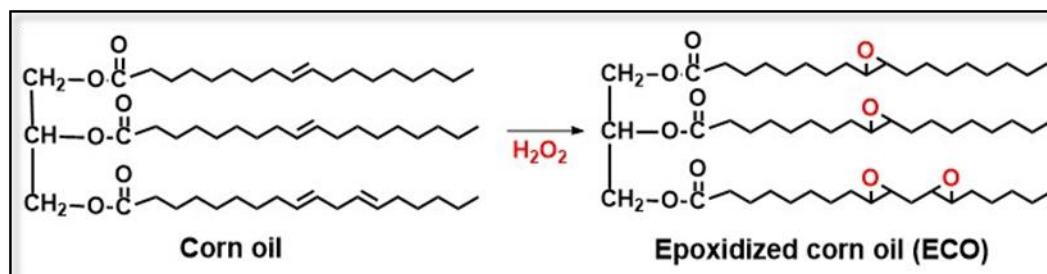
## **3.2. Experimental Details**

### **3.2.1. Materials**

Commercial corn oil was purchased from local Walmart, USA. Acetic acid, ion exchange resin, toluene, hydrogen peroxide, dibutyl phosphate, and triphenylphosphine were purchased from Acros Organic, USA. Sucrose-based polyether polyol (Jeffol SG-522) and methylene diphenyl diisocyanate (MDI, Rubinate M isocyanate) were purchased from Huntsman. DABCO T-12, NIAX A-1 and Silicon surfactant (Tegostab B-8404) were obtained from Air products, OSi Specialties and Evonik, respectively.

### 3.2.2. Synthesis of Fully Epoxidized Corn Oil

Corn oil was fully epoxidized by reacting with hydrogen peroxide. For this 500 g of corn oil, 71 g of acetic acid along with 125 g of ion exchange resin were added to a three-neck flask. In this, 250 g of toluene was added. The mixture was heated to 60 °C and then 225 g of hydrogen peroxide was added dropwise under stirring. The reaction was carried out at 70 °C for an additional 7 hours. After the reaction, the mixture was cooled to room temperature and ion exchange resin was separated by filtration. The organic phase was washed with water until pH 7.0. The solvent in the organic phase was removed by roto evaporator under low pressure followed high vacuum at 70 °C for about 2 hours. The reaction for the synthesis of epoxidized corn oil is given in [Figure 3.1](#).



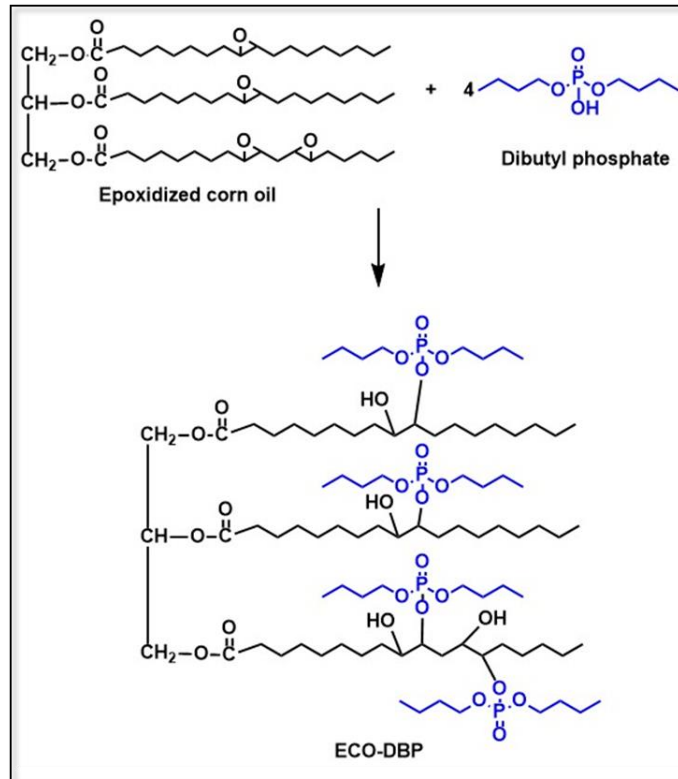
**Figure 3.1:** Synthesis of epoxidized corn oil.

### 3.2.3. Synthesis of Polyol Using Fully Epoxidized Corn Oil

For the synthesis of phosphorous-containing polyol from the epoxidized corn oil, 141 g of dibutyl phosphate and 3.5 g of triphenylphosphine as a catalyst were added to a 500 ml glass flask. The mixture was heated to 70 °C, and under continuous stirring 160 g of the epoxidized corn oil was added slowly in around 3 hours. After the addition of the epoxidized corn oil, the reaction was maintained at 75-80 °C for an additional 2 hours for



the digestion of the reactants. The reaction for the synthesis of phosphorous-containing polyol from the epoxidized corn oil is given in [Figure 3.2](#).



**Figure 3.2:** Synthesis of polyol from epoxidized corn oil.

#### 3.2.4. Preparation of Flame-Retardant Rigid Polyurethane Foams

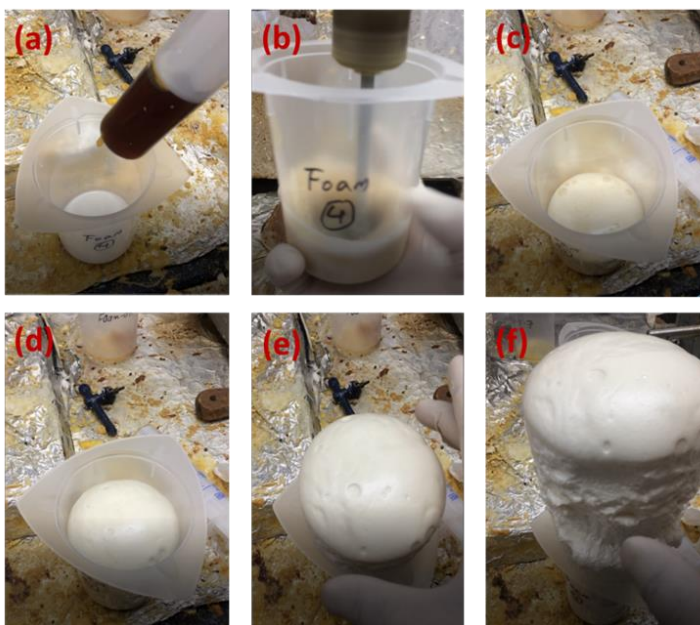
Polyurethane foams were prepared using polyols, diisocyanate, catalyst, surfactant, and a blowing agent. For this, a pre-mix containing polyols, catalyst, surfactant, and the blowing agent was prepared and in this MDI (diisocyanate) was added. All the ingredients were added according to [Table 3.1](#) to prepare the polyurethane foams with different concentrations of phosphorus. All the ingredients except MDI were added to a 500 ml cup and stirred vigorously (3,000 rpm) to mix them completely. After complete mixing, MDI was added to the mixture and stirred at 3,000 rpm to make polyurethane

foams. An illustrative example of the foaming process and the preparation of polyurethane foam is given in [Figure 3.3](#).

**Table 3.1:** Formulation for preparation of phosphorus-containing polyurethane foams.

Compounds	Foam-1 (P-0%)	Foam-2 (P-0.5%)	Foam-3 (P-1.0%)	Foam-4 (P-1.5%)	Foam-5 (P-2.0%)
Jeffol-522	20	15	12	10	8
ECO-DBP (corn oil based polyol)	0	4.46	8.86	14.1	21.2
Tegostab B-8404	0.4	0.4	0.4	0.4	0.4
Niax-A1	0.12	0.12	0.12	0.12	0.12
T-12	0.04	0.04	0.04	0.04	0.04
Water	0.8	0.8	0.8	0.8	0.8
MDI	38.97	32.7	30.95	30.7	32.86

All the weights are in grams.



**Figure 3.3:** (a) Adding MDI in pre-mix of corn oil-based polyol, (b) mixing the ingredient at 3,000 rpm, (c) foaming started after mixing for 10 seconds, (d) foam started raising, (e) foams keep raising and (f) fully prepared corn oil-based polyurethane foam.

### 3.3. Results and Discussion

Characteristics such as OH number, acid value, and chemical structure show the reactivity of the polyol. The hydroxyl number of the corn oil-based polyol was found to be 182 mg KOH/g. For this high OH number can be said that reactivity of the polyol is ensured during the foaming process. The formation of the epoxidized corn oil and its polyol was confirmed using infrared-spectroscopy (FT-IR) and gel permeation chromatography (GPC). FT-IR spectra of corn oil, epoxidized corn oil, and corn oil-based polyol are shown in [Figure 3.4](#). The presence of a new peak in the FT-IR spectra of epoxidized corn oil at  $826\text{ cm}^{-1}$  corresponds to an epoxy group, suggesting the success of the epoxidation reaction. The peak observed in the corn oil around  $3010\text{ cm}^{-1}$  corresponds to  $\text{=C-H}$  and  $\text{C=C}$  stretching. The disappearance of this peak in the epoxidized corn oil suggests epoxidation of the corn oil at double bonds. The peak around  $3450\text{ cm}^{-1}$  in the polyol suggests the presence of hydroxyl groups ( $\text{-OH}$ ). The peak corresponding to epoxide group disappeared in the polyol suggesting reaction of dibutyl phosphate at epoxide group.<sup>25</sup> Gel permeation chromatography curve provides the molecular weight distribution for the reacting species and for the product. It can be observed that retention time for obtained polyol was reduced with respect to corn oil and epoxidized corn oil suggesting the formation of higher molecular weight compound ([Figure 3.5](#)). Retention peak at 27 min represents the higher molecular weight polyol (ECO-DBP), which is lower than epoxidized corn oil (31 min), and corn oil (32 min) alone. These results for FTIR and GPC confirm that the obtained polyol was synthesized as desired.

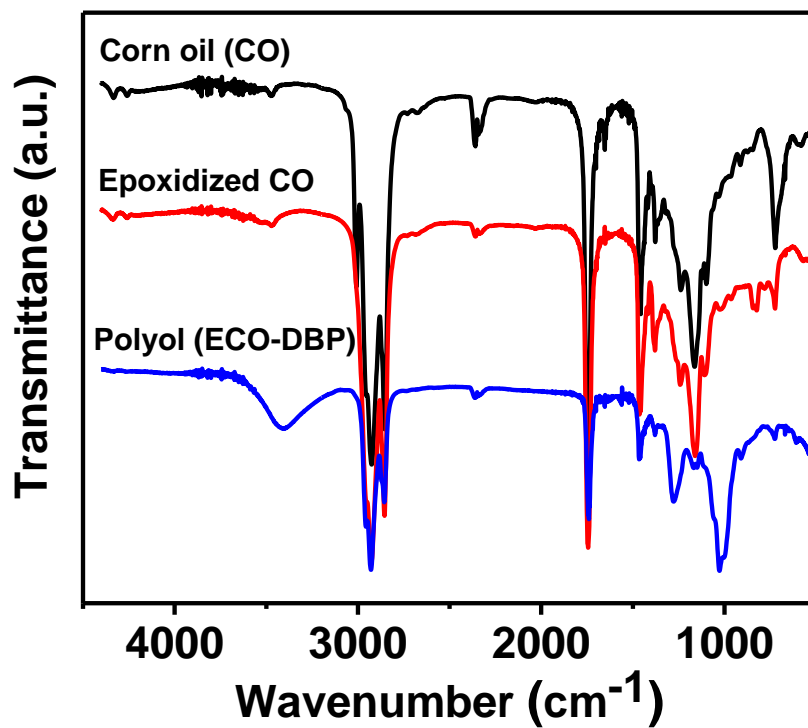


Figure 3.4: FT-IR spectra of the starting materials and corn oil-based polyol.

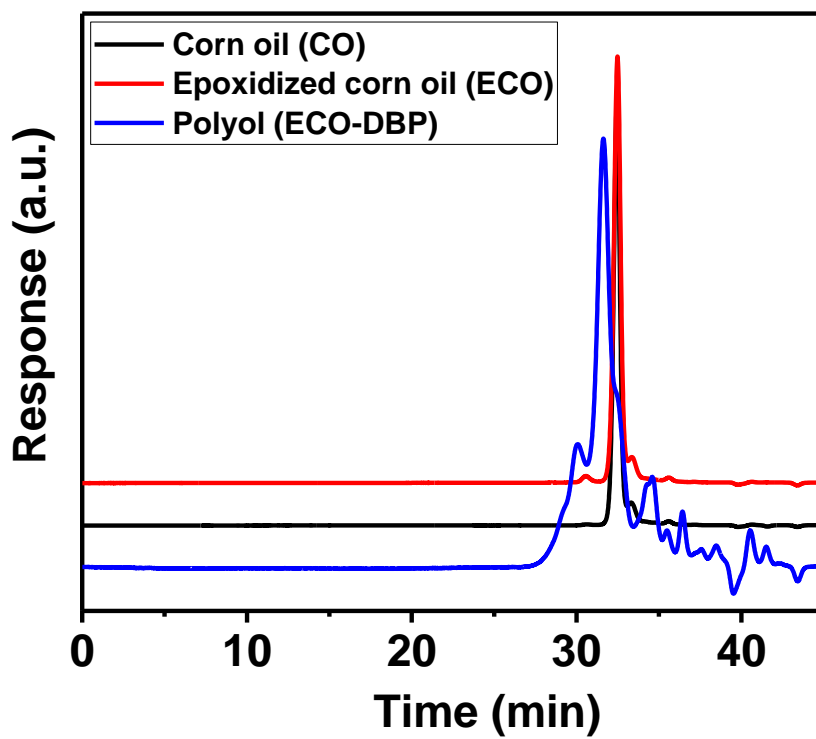
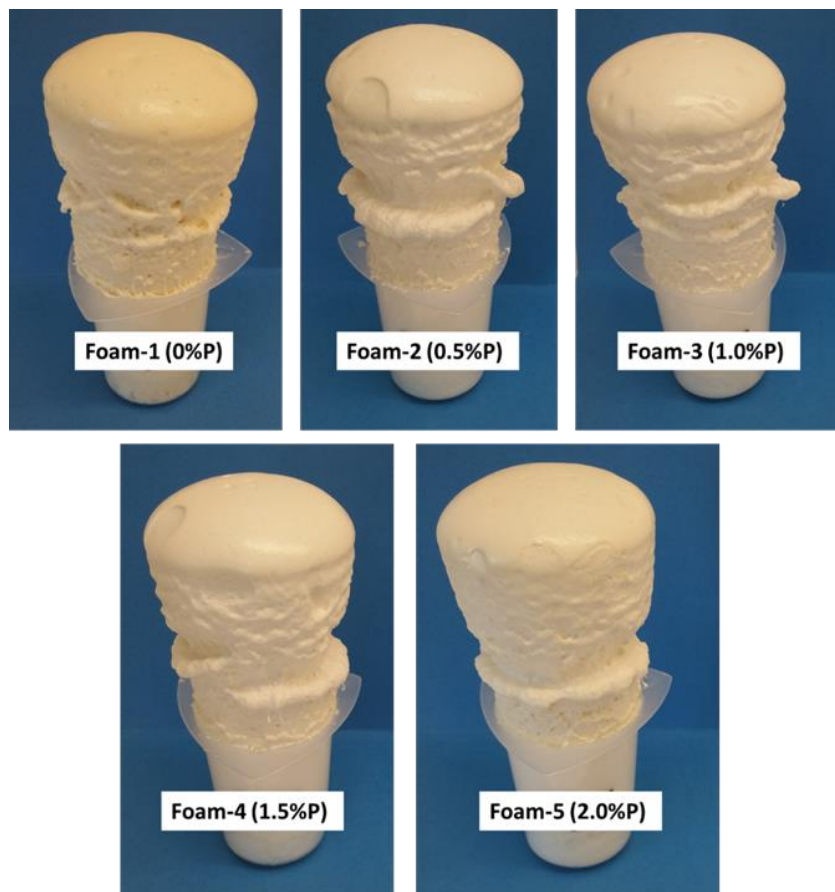


Figure 3.5: GPC curve of the starting materials and corn oil-based polyol.

The photographs of the prepared polyurethane foams are shown in [Figure 3.6](#). As seen in the foams' photographs, the corn oil-based polyurethanes grew very uniformly and expanded well, confirming its suitability for the industrial/commercial applications. The foaming cream, rise time and tack free times were of few seconds making them very suitable for thermal insulation applications where the rapid formation of foams are required ([Table 3.2](#)). After mixing all the ingredients, the called cream time is the time taken by the mixture to turn cream from the dark brown. Rise time is the time taken by the mixture to rise and form a stable network. The called tack free time is the time required for complete crosslinking of the foam lose its stickiness.<sup>2</sup>



**Figure 3.6:** Photographs of the prepared polyurethane foams.

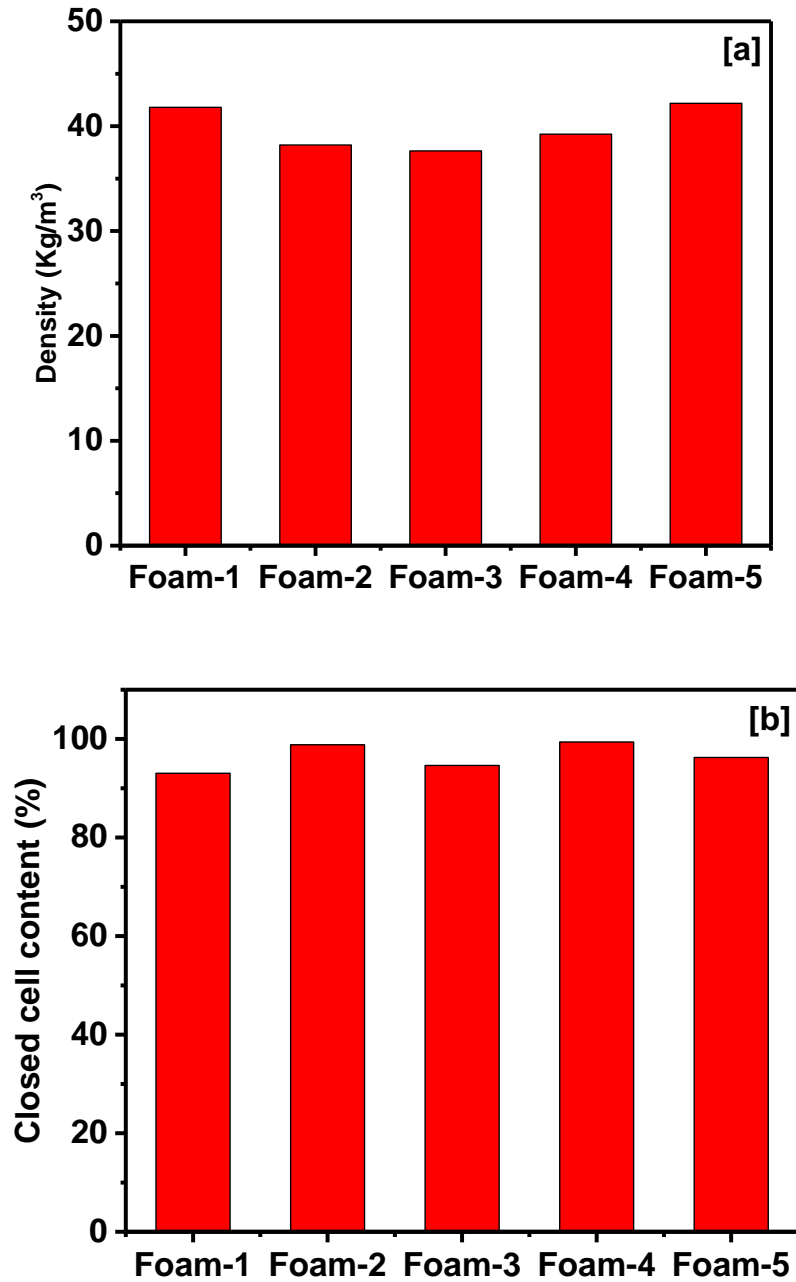
**Table 3.2:** Cream time, rise time and tack-free time for the polyurethane foams.

Name	Cream time	Rise time	Tack free time
Foam-1	6	12	16
Foam-2	7	11	16
Foam-3	6	12	17
Foam-4	6	12	16
Foam-5	7	11	16

All the times are in seconds.

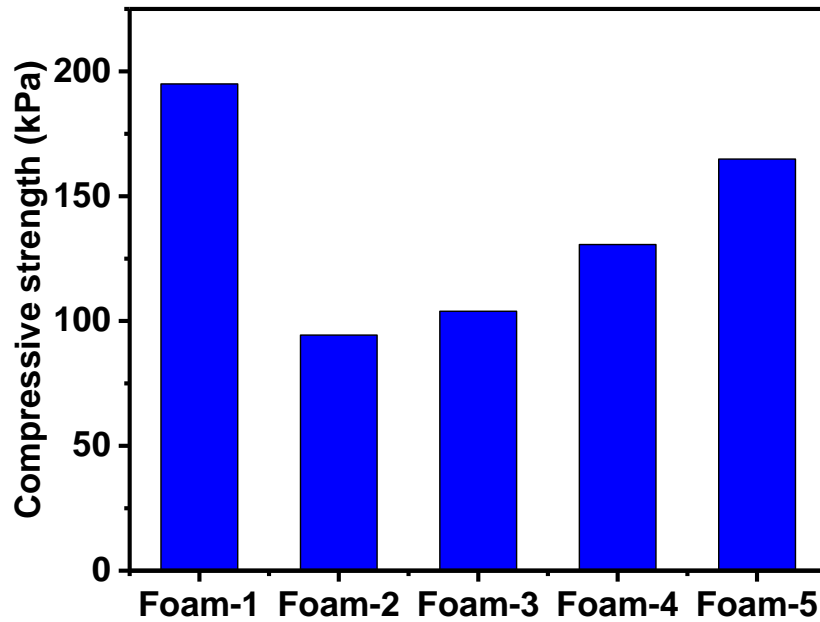
The density of the prepared polyurethane foams was measured using rectangular shaped foams. The density of all the prepared foams is given in [Figure 3.7\(a\)](#). The density of the foams is one of the important parameters to study for industrial applications.<sup>26</sup> Low-density foams are usually weaker in mechanical strength than high-density foams, and it will give a weight burden to the structure. As seen in [Figure 3.7\(a\)](#), the density of these foams was around  $40 \text{ kg/m}^3$ , which is in the range of industrial polyurethane foams ( $30$  to  $50 \text{ kg/m}^3$ ). According to Gaidukova et al, the density of rigid polyurethane foams containing bio-based and recycled components showed a range between  $37.7 \text{ kg/m}^3$  and  $52.5 \text{ kg/m}^3$ .<sup>27</sup> Overall observations suggest that all foams maintained their standard density for industrial foams.<sup>6</sup> The closed cell content of the polyurethane foam is another important characteristic and gives information about the average number of closed cells in the foam. For thermal barrier applications, it is important to have higher closed cell content in the foam. Elbers et al synthesized bio-based polyol via thiol-ene chemistry for rigid polyurethane foams, and found a closed cell content above 90%.<sup>4</sup> In this study, the overall closed cell content of corn oil-based foams was higher than 95%, which is comparable to industrial polyurethane foams. The closed cell content of various foams without corn oil-based polyol (Foam-1) and with corn oil-based polyol (Foam-2 to Foam-

5) is shown in [Figure 3.7\(b\)](#). It is worth noting that the closed cell content of the foams has improved after the addition of corn oil-based polyols during the preparation of the foams. The thermal insulation capability of the foams increases when the closed cell content is higher and the density is lower.



**Figure 3.7:** (a) Density and (b) closed cell content of various polyurethane foams prepared using corn oil.

To understand the addition of flame-retardants materials on the mechanical properties of the foams, compression strength study was obtained for rigid polyurethane foams with different concentration of phosphorus (Foam 2-5) and neat polyurethane foam (Foam-1, Phosphorus - 0%). [Figure 3.8](#) shows the compression strengths of the foams containing a different concentration of phosphorous. As seen in [Figure 3.8](#), initially the compressive strength of the foams decreased after addition of phosphorous containing polyol but started increases with the further addition of phosphorous containing polyol. This increase is due to the crosslinking in the reaction with phosphorous polyol that provides enough rigidity to the foams.

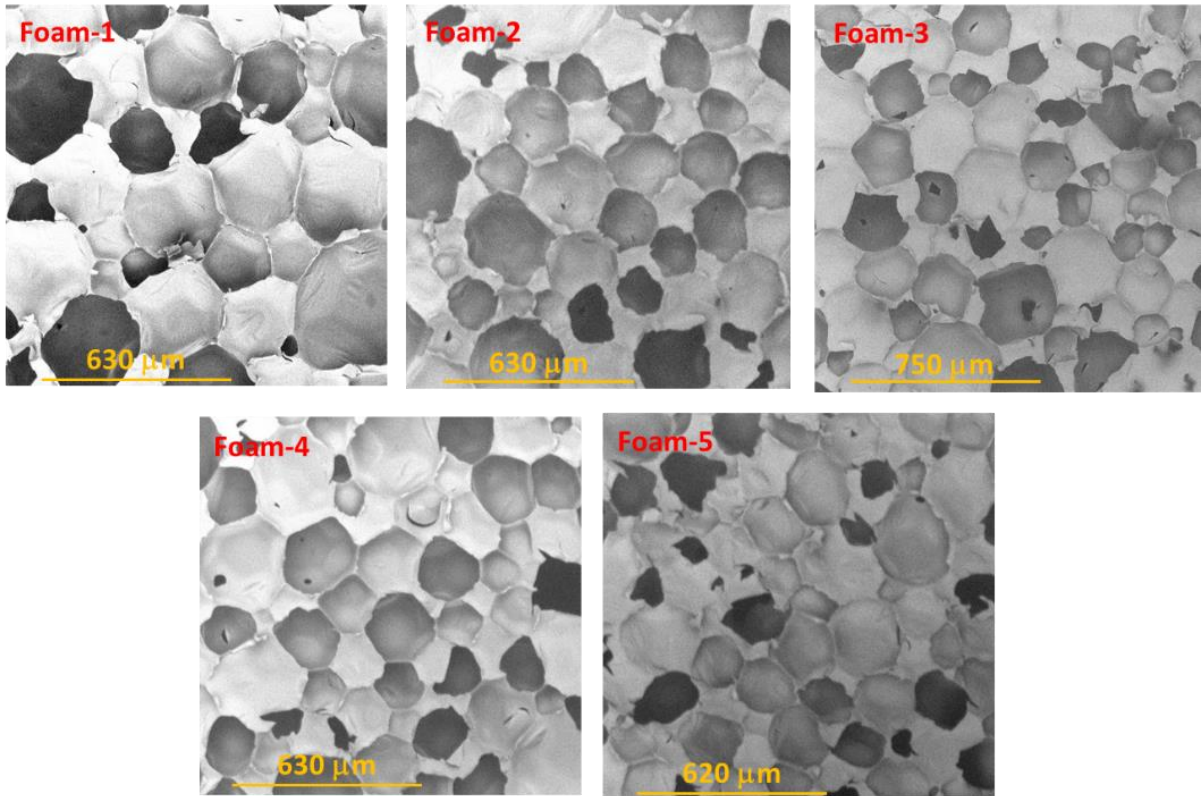


**Figure 3.8:** Compressive strength of various polyurethane foams.

The cellular morphology of the foams containing different concentrations of phosphorus was studied using scanning electron microscopy. [Figure 3.9](#) shows SEM images of the foams when increasing the phosphorus content. Foam without phosphorus



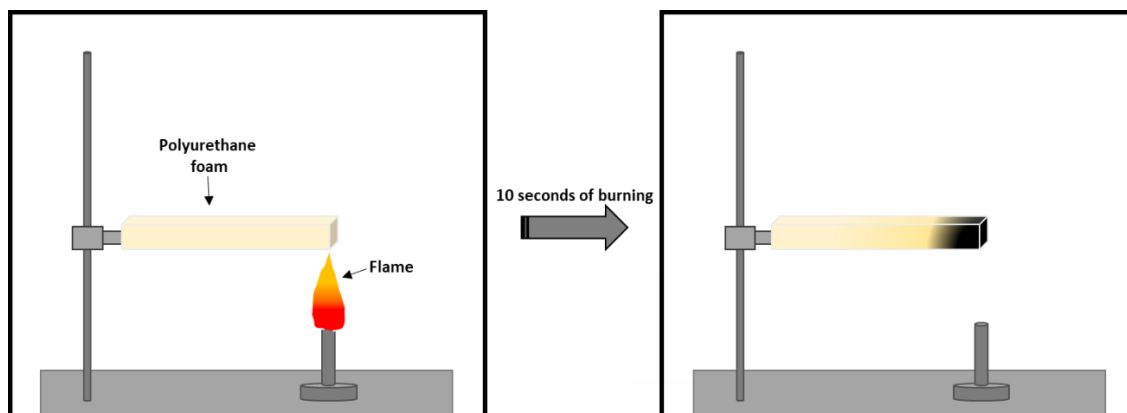
showed a cell size of about 300  $\mu\text{m}$ . The foams containing corn-oil based polyol showed little smaller cellular size. It should be noted that the addition of corn oil-based polyol did not affect much the closed cell structure of the foams.



**Figure 3.9:** SEM images of various polyurethane foams.

The horizontal burning test was performed to study the fire retardant behavior of the rigid polyurethane foams when subjected to fire.<sup>2</sup> Foams were held horizontally and subjected to a continuous flame for 10 seconds, as seen in the scheme in [Figure 3.10](#). It was recorded the burning time with respective weight loss. [Figure 3.11\(a, b\)](#) shows the burning time and respective weight loss of the foams with increasing phosphorus concentration. The foams without corn oil-based phosphorous polyol showed a burning time of 72 seconds with a corresponding weight loss of 56%. After addition of 0.5 wt%

phosphorous content in the corn oil-based polyol to make the foam, the burning time and weight loss reduced to 45 seconds and 26%, respectively. The burning time and weight loss for the foam containing 1.5 wt% phosphorous were 8.2 seconds 6.4%, respectively. Lowest burning time of 3.8 seconds was achieved when the phosphorus content in the foam was 2 wt%. Bhojate et al synthesized polyurethane foams based on reactive phosphorous polyol and limonene-based polyol. The burning time and weight loss of the foam containing 1.5% phosphorus were 11.2 s and 9.8%, respectively.<sup>2</sup> Figure 3.12 shows the photographs of the foams before and after performing the horizontal burning test. When increases the concentration of the phosphorus in the foams, the area of the burnt side of them decreases showing effective flame retardancy. It can be stated, from the observations, that corn oil-based polyol can be used to prepare highly flame retardant polyurethane foams.



**Figure 3.10:** Scheme for Horizontal Burning Test.

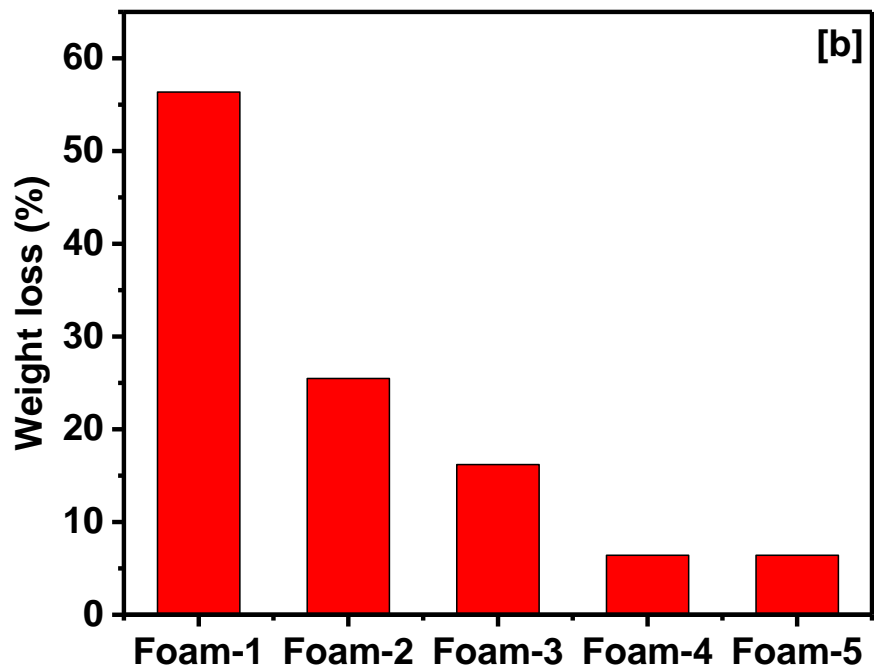
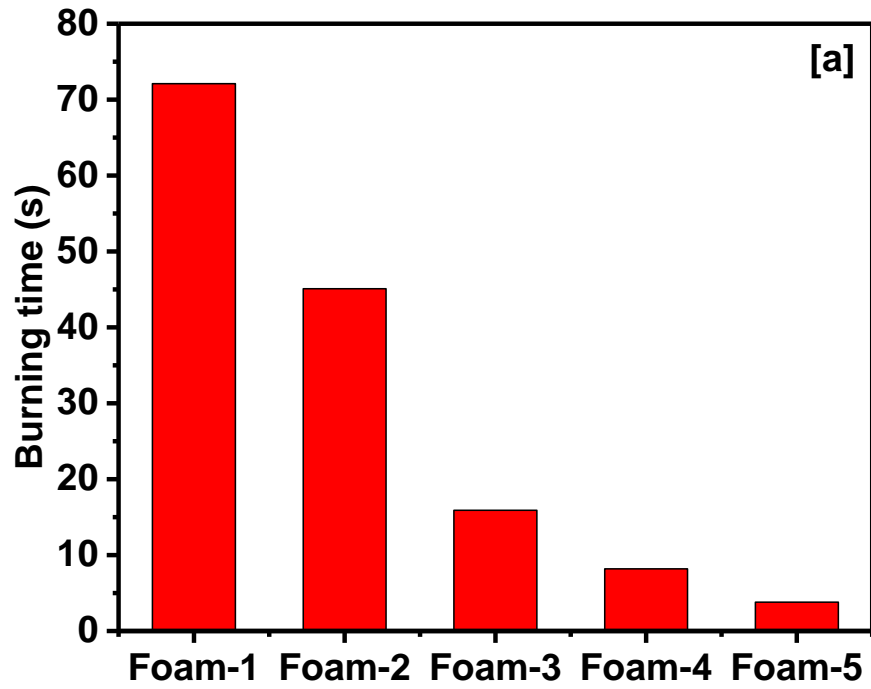
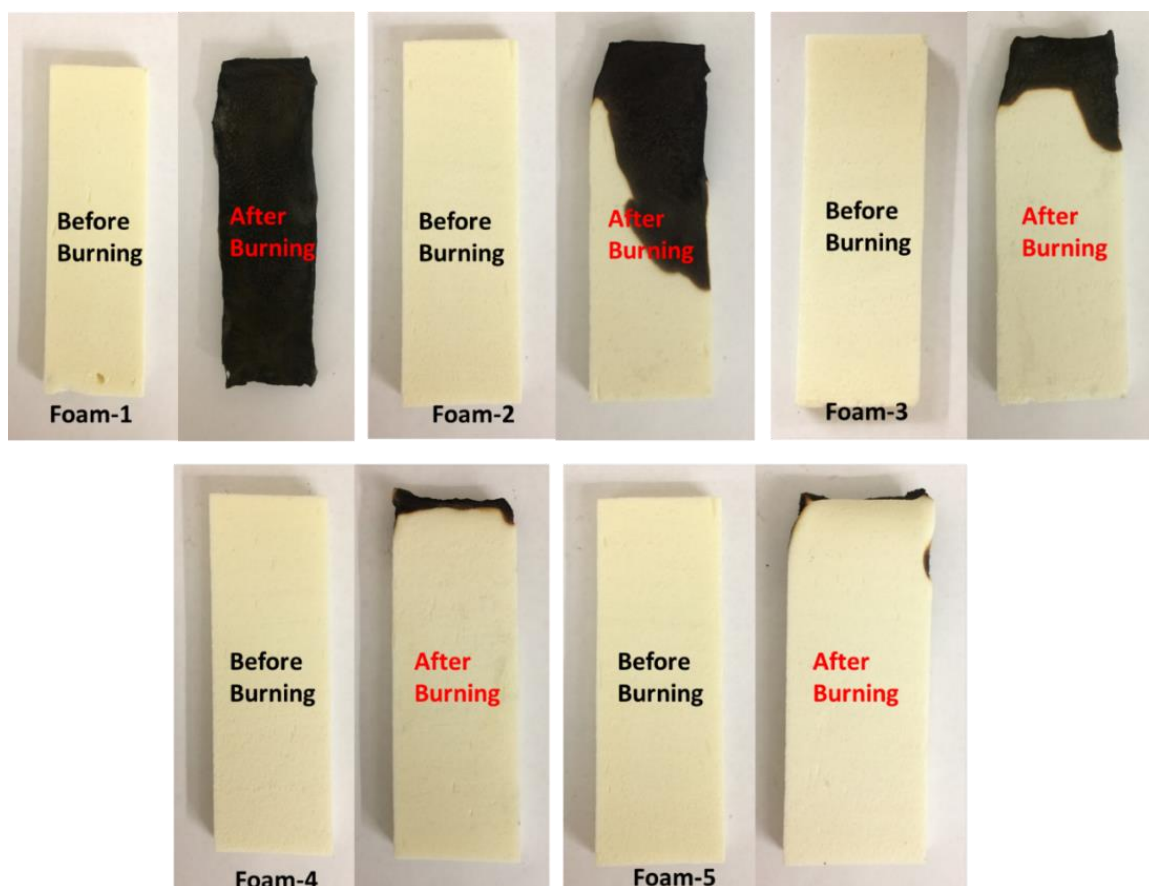


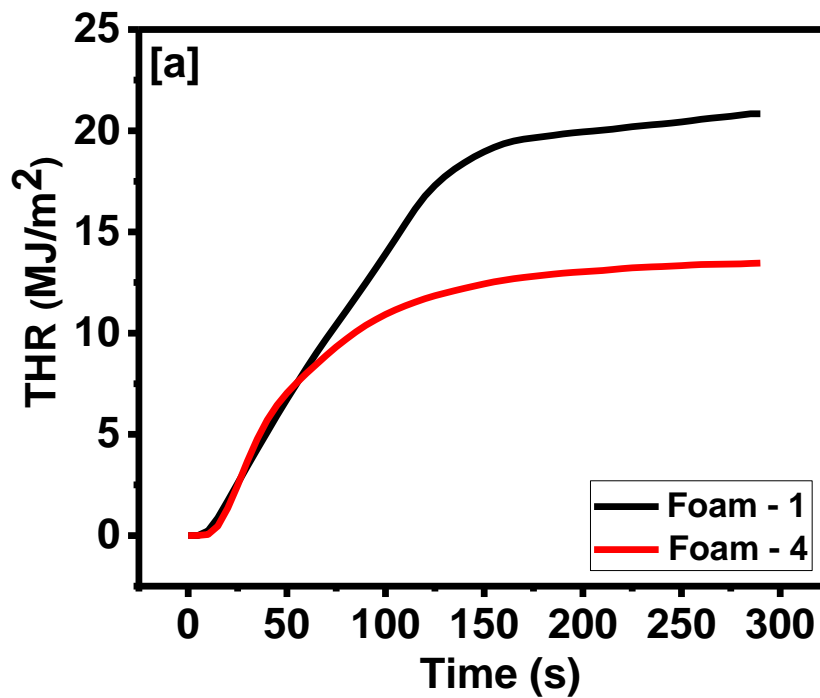
Figure 3.11: (a) Burning time and, (b) weight loss for prepared rigid polyurethane foams.

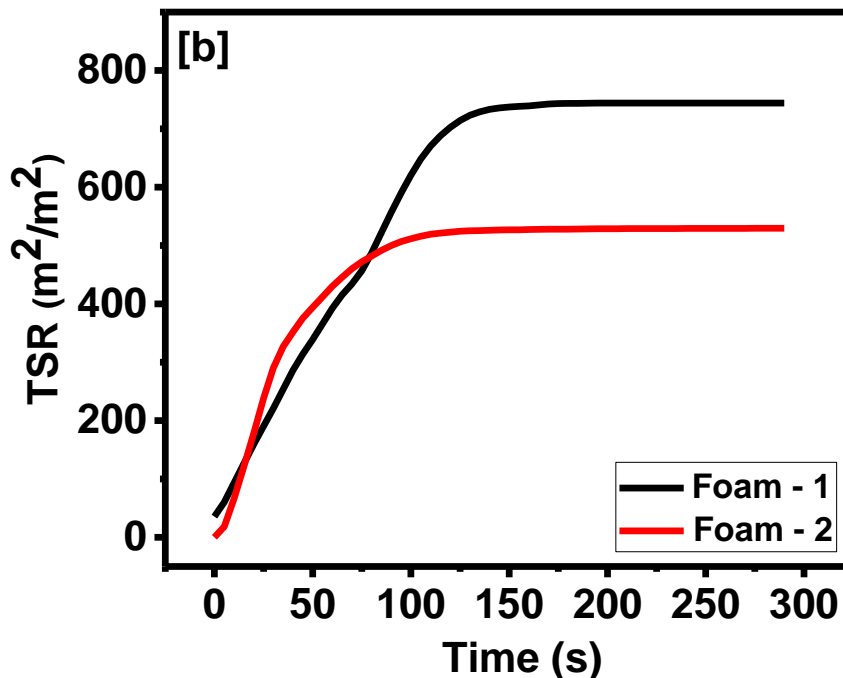


**Figure 3.12:** Digital images of the foams before and after burning test.

Cone calorimeter test was carried out on the foams to study the flame-retardant characteristics in detail. Foams with 1.5 wt% phosphorus (Foam-4) and the control (Foam-1, without corn oil containing polyol) were exposed to cone test. Thermal heat release and thermal smoke release are two important results obtained from cone calorimeter study. [Figure 3.13\(a, b\)](#) shows THR and TSR behavior for Foam-1 (control foam with no corn oil-based polyol) and Foam-4 (1.5 wt% phosphorus containing foam from corn oil). Thermal heat release for the Foam-4 showed an excellent reduction in the thermal heat released to compare to the Foam-1, as can see in [Figure 3.13a](#). It is possible that protective char formation makes the improvement in the flame retardancy for the Foam-

4 because reduces the mass and heat transfer of the underlying layer. For organic phosphinated polyurethane foams synthesized by Lorenzetti et al, the heat evolution decrease only 30% compared to reference polyurethane foam.<sup>24</sup> Figure 3.13b shows the thermal smoke release data for the Foam-1 and Foam-4. As seen in the Figure 3.13b, the thermal smoke release by corn oil containing foam is significantly lower than the control foam. Therefore, it can be concluded that corn oil based phosphorous containing polyol could be used to prepare high-quality polyurethane foams with significant higher flame retardancy.





**Figure 3.13:** (a) Thermal heat release (THR) and, (b) thermal smoke release (TSR) data for the Foam-1 and Foam-4.

### 3.4. Conclusion

Flame-retardant rigid polyurethane foams using fully epoxidized corn oil were synthesized. Bio-based polyurethane foams were synthesized using corn oil polyol containing flame-retardants based on different concentrations of phosphorous (0-2%). The presence of a new peak in the FT-IR spectra and the decrease in the retention time in the GPC suggests the success of the epoxidation reaction and of the obtained polyol. The density of the foams was around 40 kg/m<sup>3</sup>, which is in the range of standard industrial foams. The overall closed cell content of corn oil-based foams was higher than 95%, which is comparable to industrial polyurethane foams. The closed cell content of the foams improved after the addition of corn oil-based polyols during the preparation of the foams. Addition of phosphorous containing polyol increases the compression strength, which

suggests a consistent effect in the mechanical properties of the foams. After analyzing the cell morphology, can be concluded that the addition of corn oil-based polyol did not affect much the closed cell structure of the foams. The horizontal burning test performed, showed a decrease in burning time and weight loss from 72 s to 8.2 s, and from 56% to 6.4% when the concentration went from 0% to 1.5% of phosphorous. When the concentration went up to 2%, the burning time was to 3.8 s. Cone calorimeter test showed an excellent reduction in thermal heat release and thermal smoke release. Hence, it can be concluded that corn oil-based phosphorous containing polyol can be used to prepare high-quality polyurethane foams with significant higher flame-retardancy.

## CHAPTER IV

### FLAME-RETARDANT RIGID POLYURETHANE FOAMS USING PARTIALLY EPOXIDIZED CORN OIL

#### 4.1 Introduction

The previous chapter describes a study of flame-retardant rigid polyurethane foams using fully epoxidized corn oil. Now, chapter four will describe a study of flame-retardant rigid polyurethane foams using partially epoxidized corn oil. Considering the results obtained from the previous chapter, another synthesis using corn oil-based phosphorous polyol was performed to provide more enhanced flame retardancy to the polyurethane foams.

In this study, it was used thiol-ene click chemistry, which is a reaction between a thiol and an alkane, to synthesize partially epoxidized corn oil and further produce novel flame-retardant. Thiol-ene click reaction has been used as a new route for polyols because of some advantages such as high yields, simple reaction conditions and short reaction times.<sup>5</sup> It is a viable option to functionalize unsaturated compounds adding the thiol to the double bonds. Thiol-ene reaction is an effective reaction for crosslinking and oligomerization of vegetable oil.<sup>4,28</sup> Effect of phosphorous content from flame-retardant



polyol using partially epoxidized corn oil on physicochemical properties of the polyurethane foams were studied. Our results suggest that a small amount of phosphorous-based polyol could significantly reduce the flammability of the foams, maintaining the physicochemical properties.

## **4.2. Experimental Details**

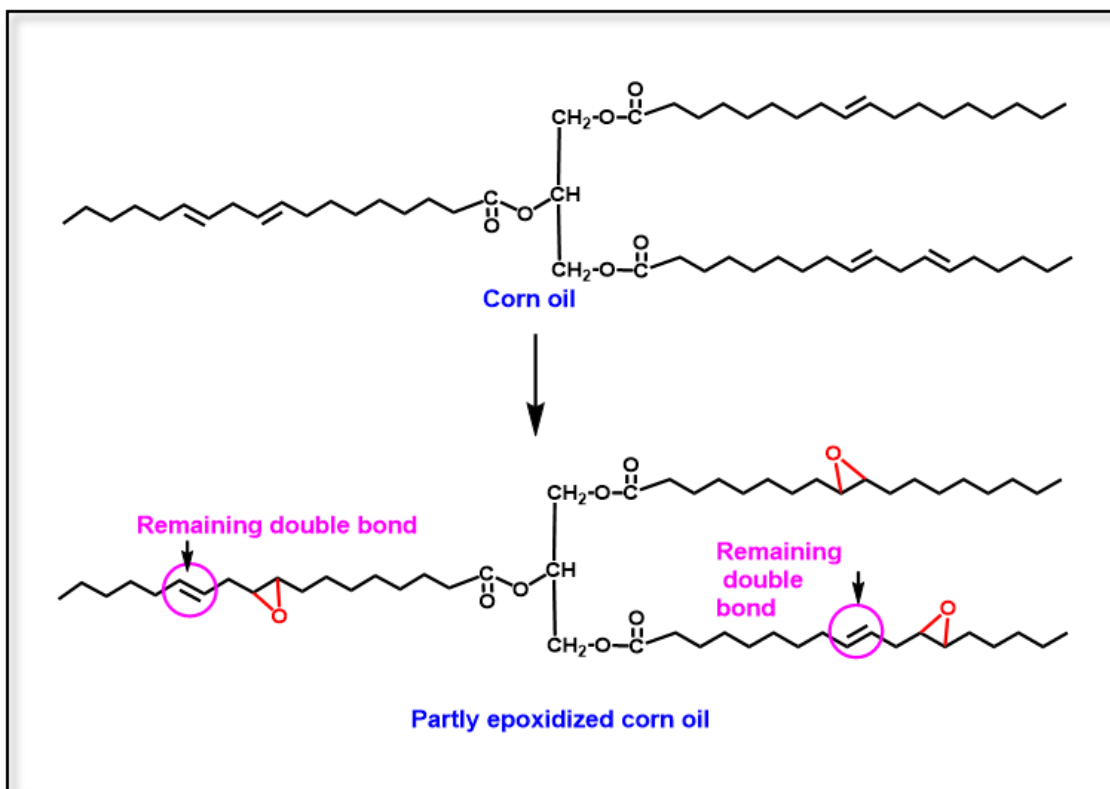
### **4.2.1. Materials**

Commercial corn oil was purchased from local Walmart, USA. Acetic acid, ion exchange resin (Amberlite IR-120 H), toluene, hydrogen peroxide, dibutyl phosphate, triphenylphosphine, thioglycerol, mercaptoethanol was purchased from Acros Organic, USA. DBTDL T-12 and NIAx A-1 catalyst were purchased from Air products and OSI Specialties, respectively. Silicon surfactant (Tegostab B-8404) was obtained from Evonik. Jeffol SG-360 (Sucrose polyol with OH# 360) and Rubinate M isocyanate (methylene diphenyl diisocyanate) were purchased from Huntsman.

### **4.2.2. Synthesis of Partially Epoxidized Corn Oil**

Corn oil was partially epoxidized using peroxyacetic acid. For this, 300 g of corn oil, 21 g of acetic acid, 75 g of ion exchange resin (Amberlite IR-120 H) and 150 g of toluene were added into a 3-neck flask equipped with a condenser and dropping funnel. 66.5 g of hydrogen peroxide was added to dropping funnel. The temperature of the system was set to 60 °C and under vigorous stirring hydrogen peroxide was dropped into the flask. After dropping was over, the temperature was raised to 70 °C and kept for 7 hours. The mixture was then cooled to room temperature and ion exchange resin was separated by filtration.

The organic phase was washed with water until pH 7.0. The solvent in the organic phase was removed by roto evaporator under low pressure followed by high vacuum at 70 °C around 2 hours. The partial epoxidation reaction is given in [Figure 4.1](#).

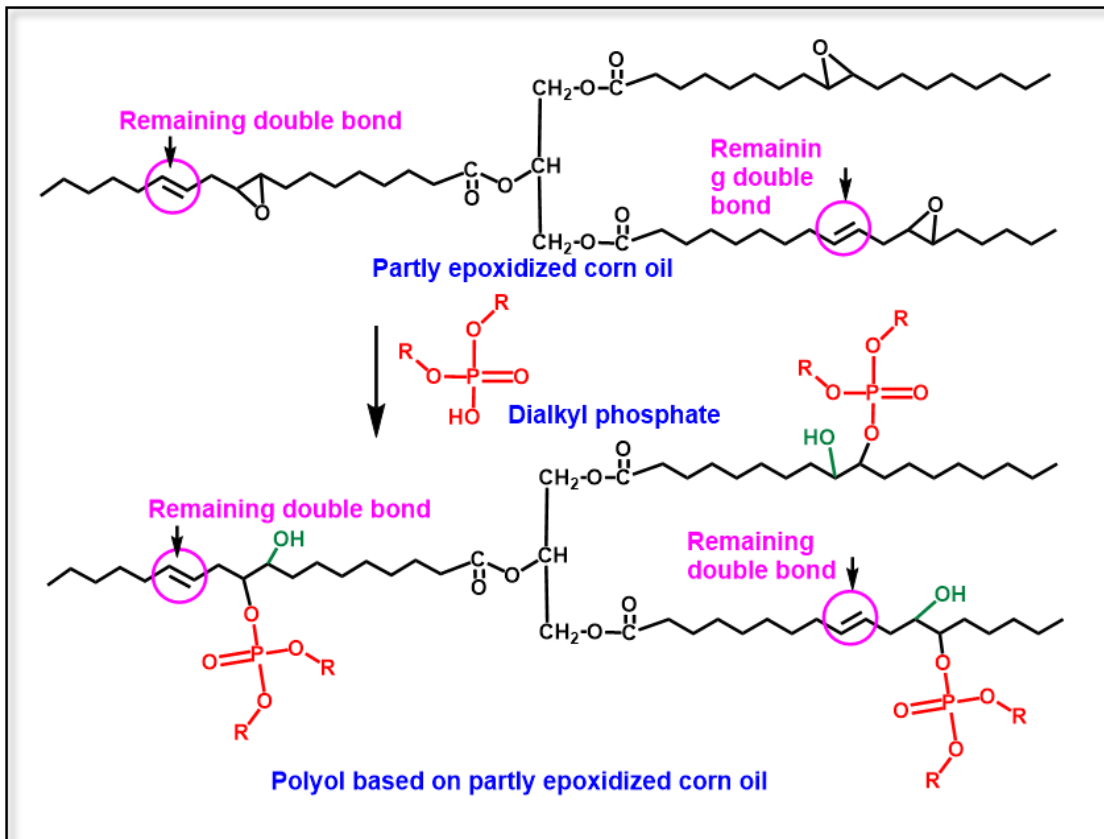


**Figure 4.1:** Partial epoxidation of corn oil.

#### 4.2.3. Synthesis of Polyol Using Partially Epoxidized Corn Oil

In the second step, partially epoxidized corn oil (PECO) was treated with dibutyl phosphate (DBP) to prepare phosphorous containing corn oil ([Figure 4.2](#)). For this, PECO was reacted with DBP in 3-neck flask equipped with a condenser and dropping funnel. Flask was charged with 101 g of DBP along with 3.7 g of triphenylphosphine and temperature was raised to 70 °C. 250 g of PECO was charged on to the dropping funnel and allowed to drop slowly into the mixture under vigorous stirring. After the addition,

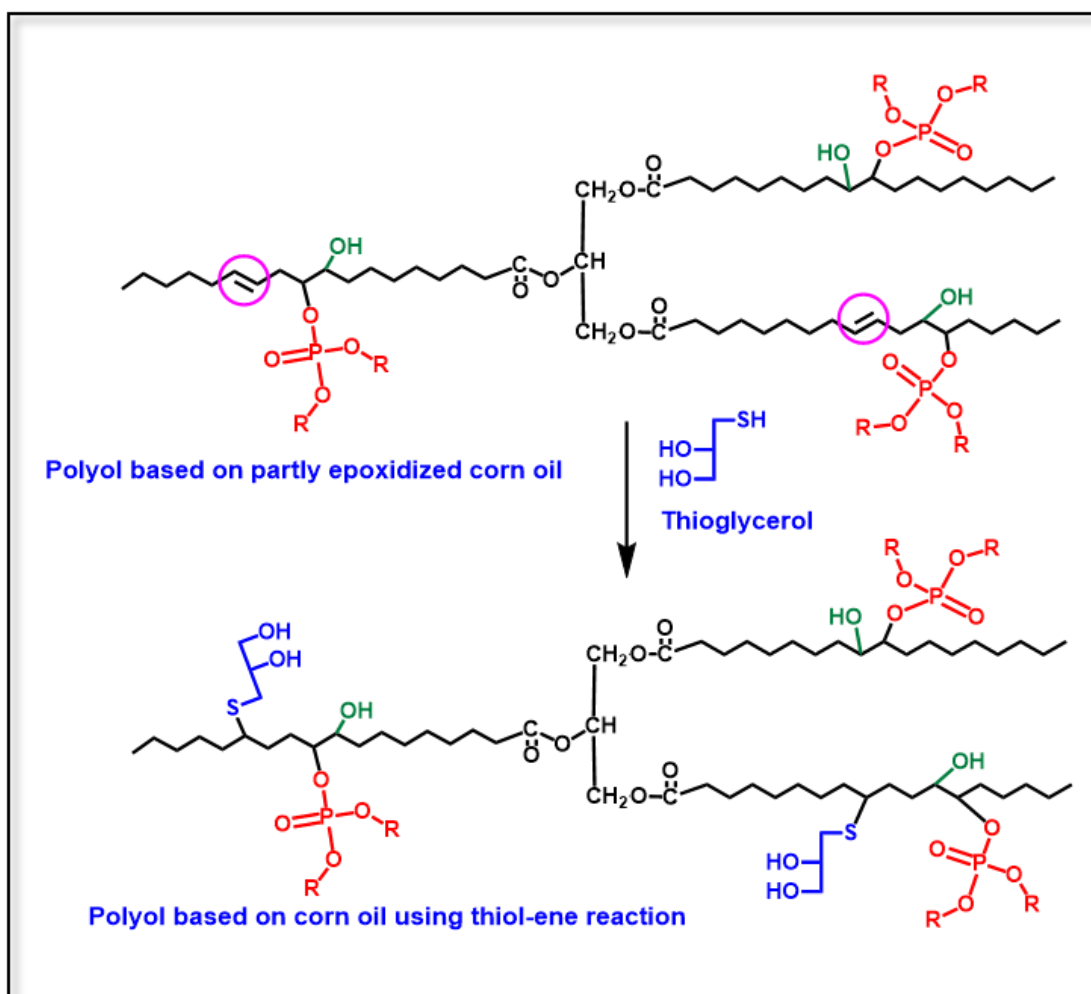
the temperature was kept at 75-80 °C for about 2 hours for digestion to obtain lower acid value.



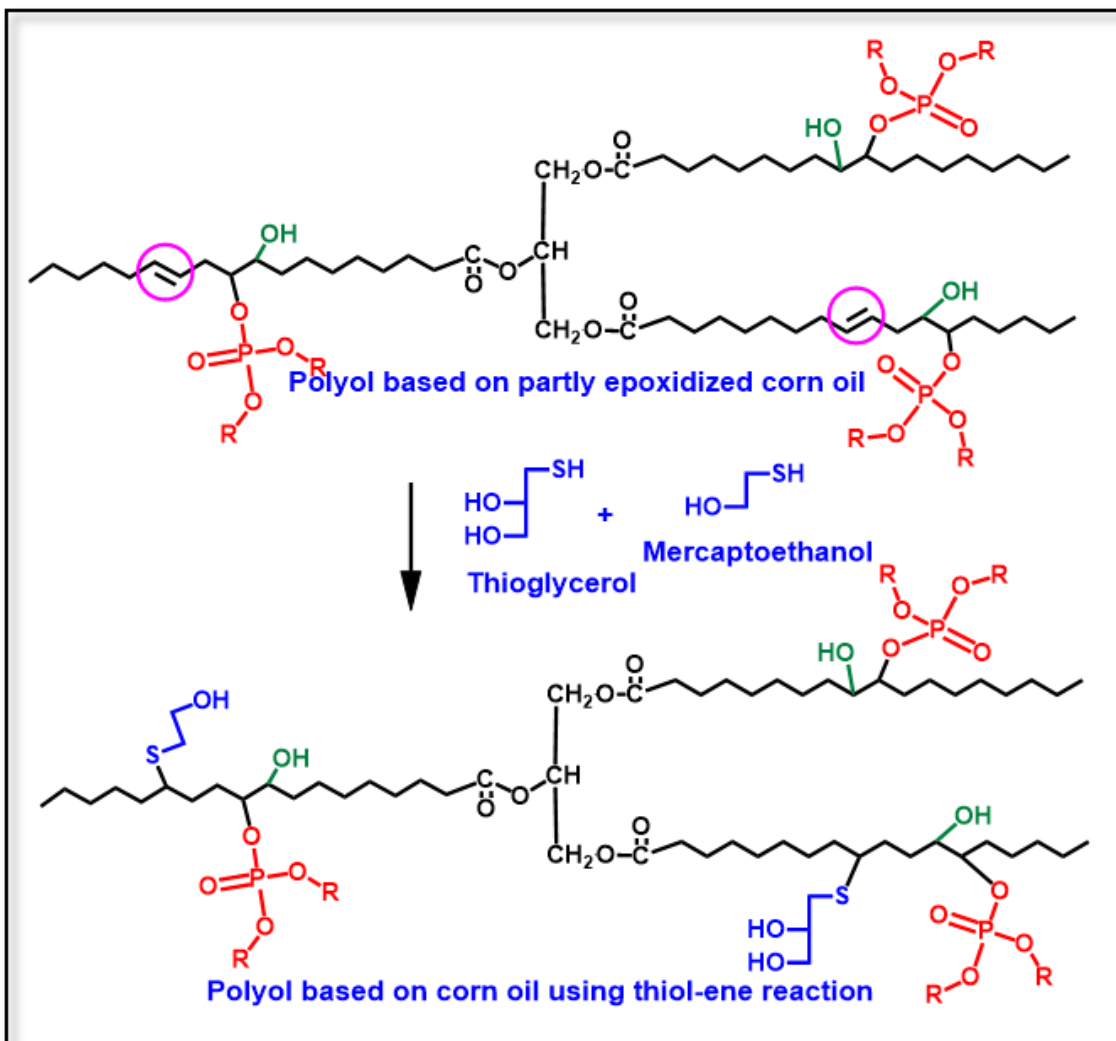
**Figure 4.2:** Phosphorous based polyol using partially epoxidation of corn oil (PECO-DBP).

The remaining double bonds in the partially epoxidized corn oil was reacted with thioglycerol to increase the functionality of the polyol (Figure 4.3). Thioglycerol was reacted using thiol-ene click chemistry. For this, 240 g of PECO-DBP was added along with 72.6 g of thioglycerol and 10.9 g of photoinitiator. The reaction was performed at room temperature under stirring for 6-8 hours under UV radiation.

The remaining double bonds in the partially epoxidized corn oil was further reacted with thioglycerol and mercaptoethanol to further increase the OH number of the polyol (Figure 4.4). This reaction was carried out using 300 g of PECO-DBP along with 22.8 g of mercaptoethanol, 31.5 g of thioglycerol and 12.5 g of photoinitiator. The reaction was performed at room temperature under stirring for 6-8 hours under UV radiation.



**Figure 4.3:** Thiol-ene reaction of PECO-DBP with thioglycerol.



**Figure 4.4:** Thiol-ene reaction of PECO-DBP with thioglycerol and mercaptoethanol.

#### 4.2.4. Preparation of Flame-Retardant Rigid Polyurethane Foams

Polyurethane foams were prepared using polyols, diisocyanate, catalyst, surfactant, and a blowing agent. All the ingredients were added according to [Table 4.1](#) to prepare the polyurethane foams with different concentrations of phosphorus. All the ingredients except MDI were added to a 500 ml cup and stirred vigorously (3,000 rpm) to

mix them completely. After complete mixing, MDI was added to the mixture and stirred at 3,000 rpm to make polyurethane foams.

**Table 4.1:** Formulation used to prepare phosphorus-containing polyurethane foams.

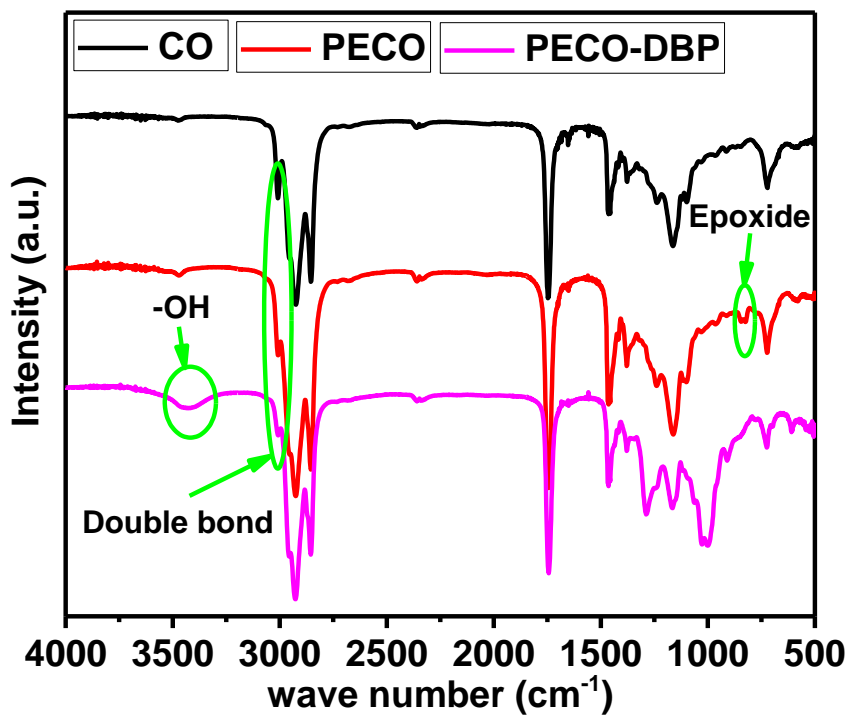
Compounds	Foam-1 (P-0%)	Foam-2 (P-0.819%)	Foam-3 (P-0.5%)	Foam-4 (P-0.54%)	Foam-5 (P-0.35%)
Jeffol SG-360	30	0	10	0	10
PECO-DBP-TG-ME	0	30	20	30	20
Silicon B 8404	0.56	0.56	0.56	0.56	0.56
Niax-A1	0.16	0.16	0.16	0.16	0.16
DBTDL (T-12)	0.06	0.06	0.06	0.06	0.06
Water	1.1	1.1	1.1	1.1	1.1
Rubinate M	44.6	28.16	0	38.6	40.61

All the weights are in grams.

### 4.3. Results and Discussion

The hydroxyl number of the partially epoxidized corn oil after reacting with dibutyl phosphate and thioglycerol was observed to be 54 and 282 mg KOH/g, respectively. This increased of the hydroxyl number ensure a high degree of reactivity of the polyol, showing that is essential to use thioglycerol for the reaction of partially epoxidized corn oil to make flame-retardants. The partial epoxidation of the corn oil and its reaction with dibutyl phosphate, thioglycerol, and mercaptoethanol was confirmed using infrared-spectroscopy and gel permeation chromatography. FT-IR spectra of corn oil, partially epoxidized corn oil and corn oil-based polyol are shown in [Figure 4.5](#). The presence of a new peak in the FT-IR spectra of partially epoxidized corn oil at  $826\text{ cm}^{-1}$  corresponds to

an epoxy group, and presence of a peak at  $3000\text{ cm}^{-1}$  due to remaining double bonds suggest that partially epoxidation of the corn oil. The peak around  $3450\text{ cm}^{-1}$  in the polyol suggests the presence of hydroxyl groups (-OH). The peak corresponding to epoxide group disappeared in the polyol after reaction with DBP suggesting reaction of DBP at epoxide group. Gel permeation chromatography curve provides the molecular weight distribution for the reacting species and for the product. It can be observed that retention time for obtained new compounds was reduced with respect to epoxidized corn oil suggesting the formation of higher molecular weight compound (Figure 4.6). Retention peak at 26 min represents the higher molecular weight polyol (PECO-DBP-TG-ME), which is lower than PECO-DBP (29 min), and PECO (32 min) alone. These results for FT-IR and GPC confirm that the obtained polyol was synthesized as desired.



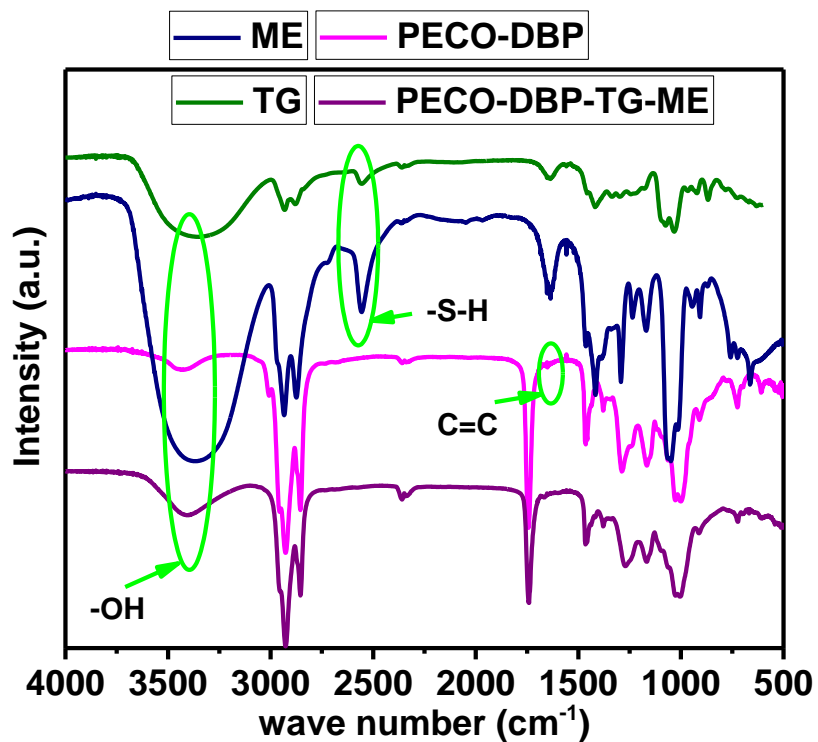
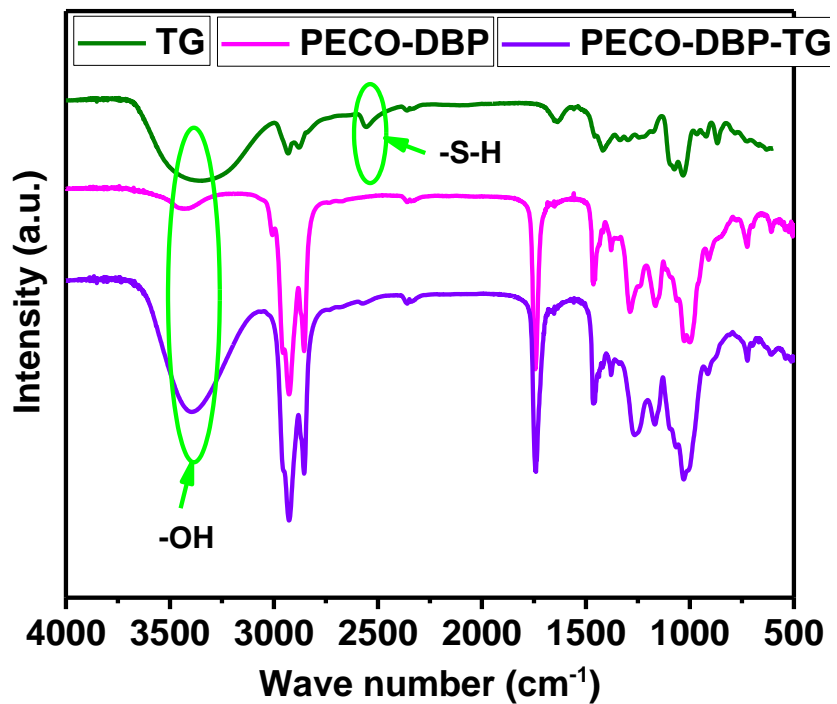
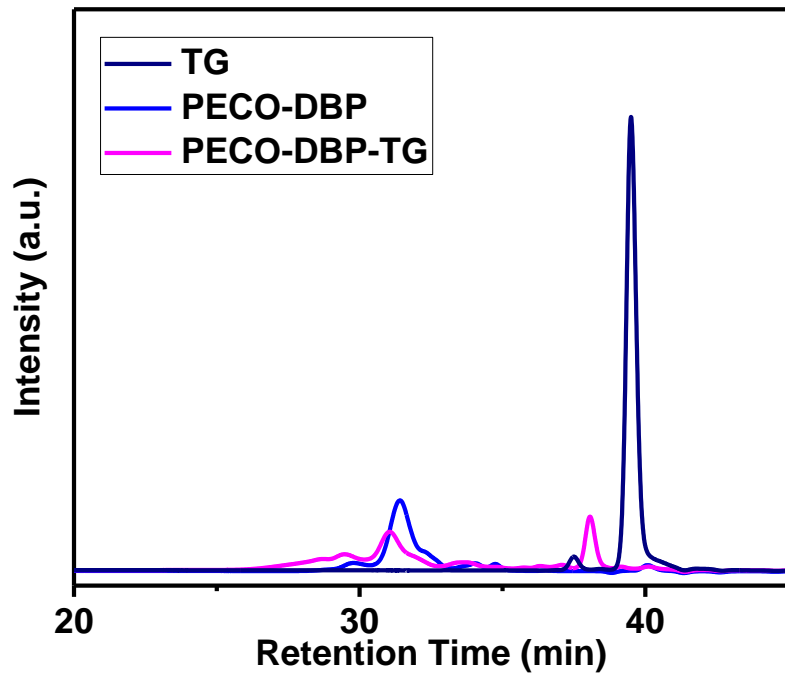
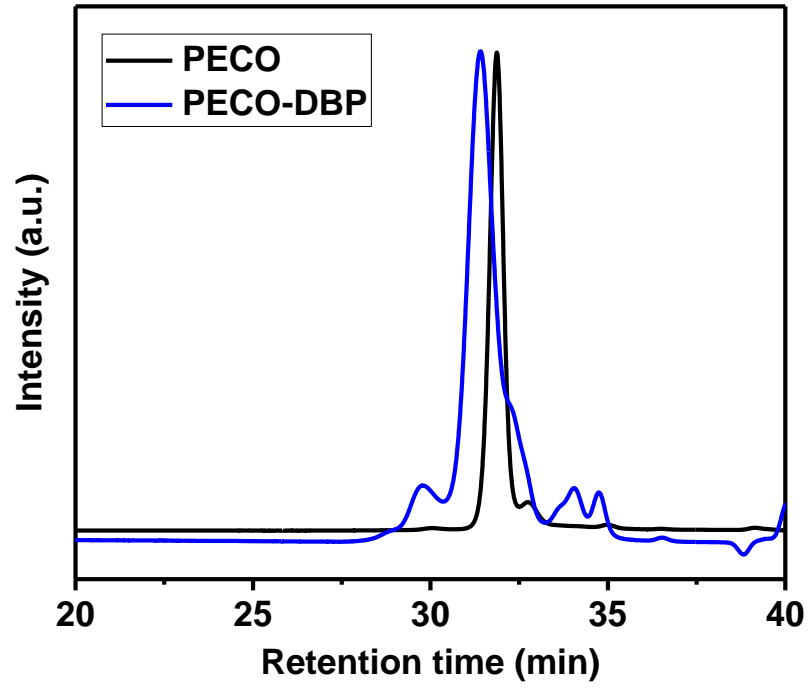
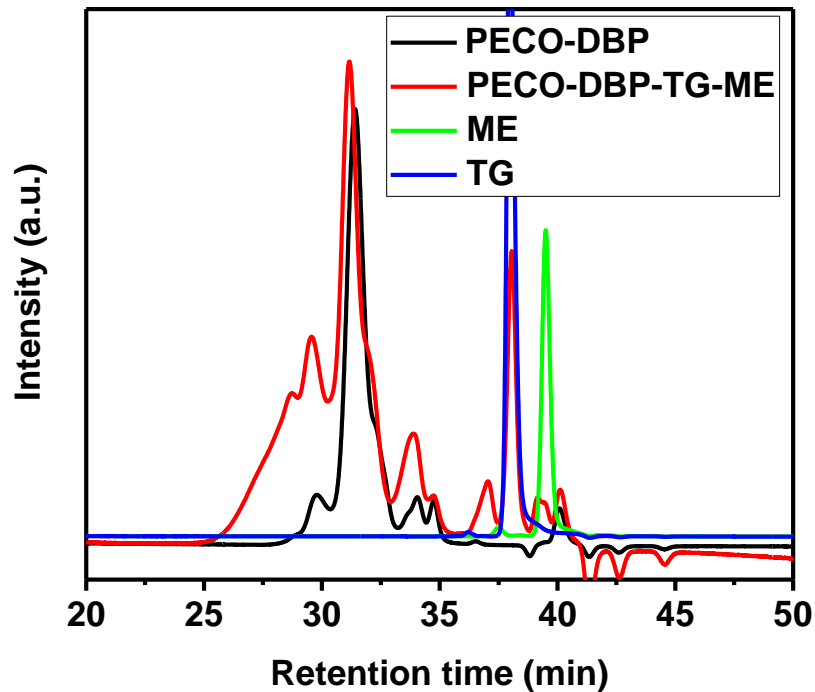


Figure 4.5: FT-IR spectra of the synthesized compounds.

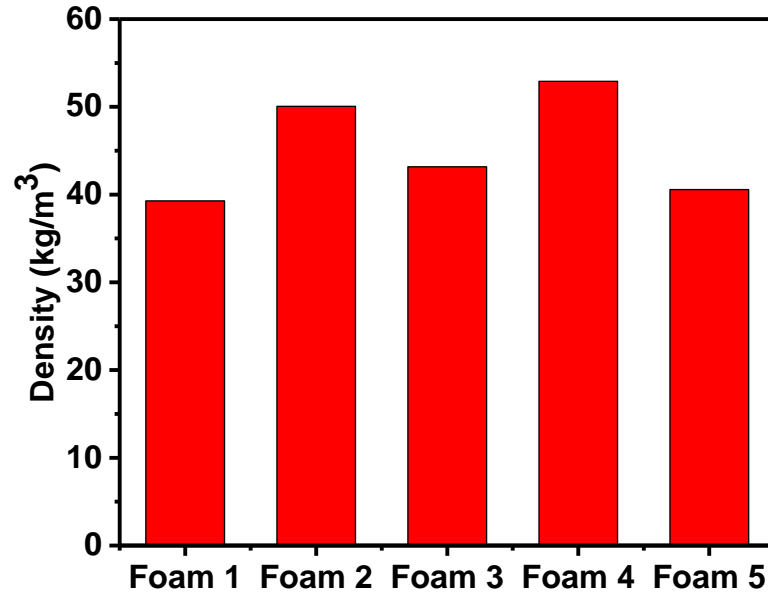




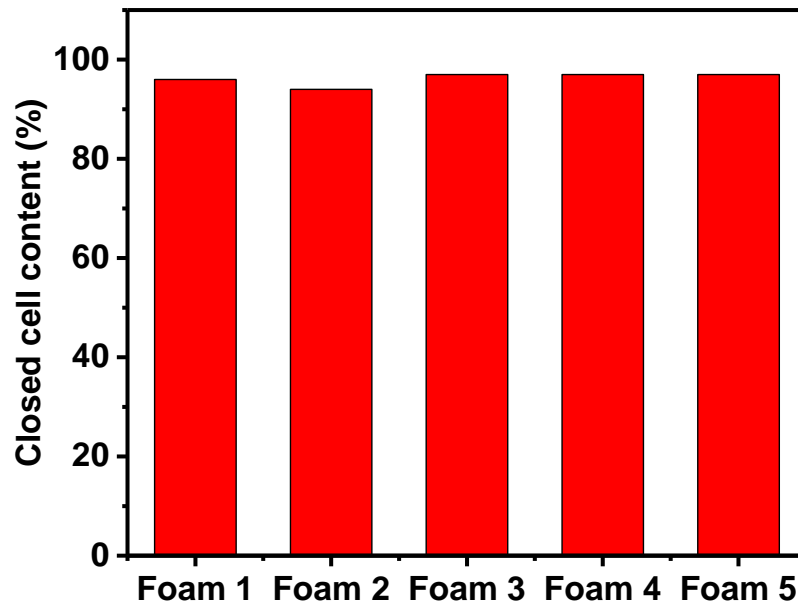


**Figure 4.6:** GPC curves of the synthesized compounds.

The density of all the prepared foams is given in [Figure 4.7](#). As seen in [Figure 4.7](#), the density of these foams was between 40-50 kg/m<sup>3</sup>, which is in the range of industrial polyurethane foams. The closed cell content of the polyurethane foam determines its suitability as thermal barriers ([Figure 4.8](#)). The overall closed cell content of all the foams was above 95%, which suggest that most of the cells are closed which makes them suitable to use a thermal insulator.



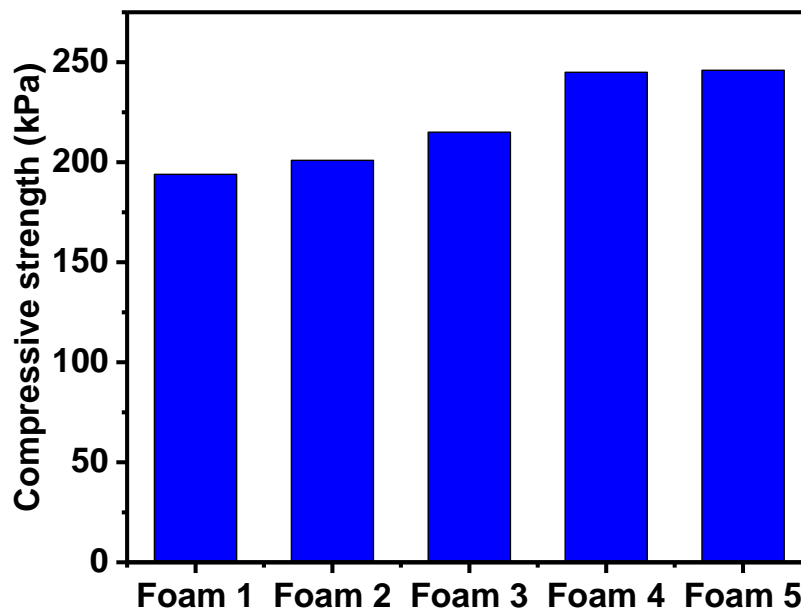
**Figure 4.7:** Density of the prepared corn oil-based polyurethane foams.



**Figure 4.8:** Closed cell content of the prepared corn oil-based polyurethane foams.

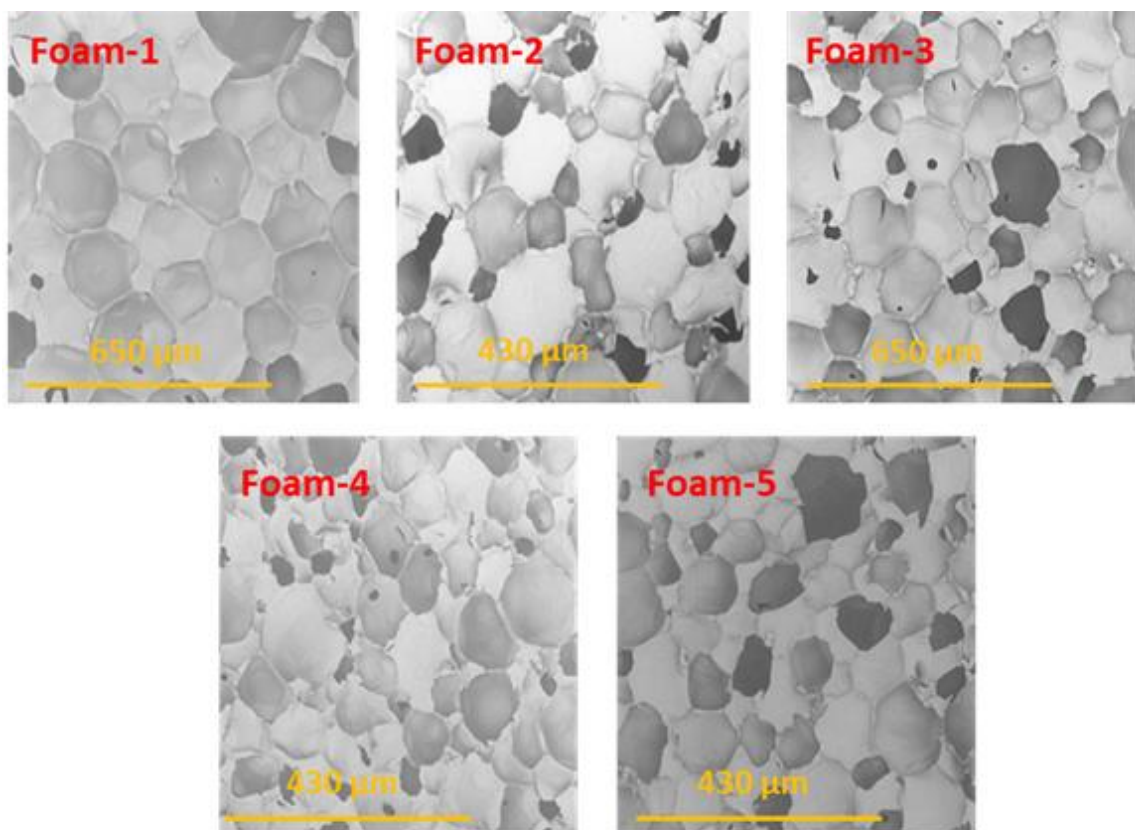
The compressive strength of the polyurethane foams synthesized using corn oil was compared with the polyurethane synthesized using commercial polyol. [Figure 4.9](#) shows the compressive strengths of the foams with the different phosphorus content. As

seen, the compressive strength of foams synthesized using corn oil is higher than that of commercial polyol.



**Figure 4.9:** Compressive strength of the prepared corn oil-based polyurethane foams.

The cellular morphology of the foams containing a different concentration of phosphorous was studied using scanning electron microscopy. [Figure 4.10](#) shows SEM images of the foams with various concentration of phosphorus. The flame-retardant behavior of the prepared foams was studied using horizontal burning test. For this, initially, foams were kept horizontal and exposed to a continuous flame for 10 seconds. Burning time with corresponding weight loss was recorded as seen in [Figure 4.11](#) and [4.12](#). As seen in the figures, there was a significant reduction in weight loss and burning time for the foams prepared using corn-oil based polyols. [Figure 4.13](#) shows the photographs of the foams before and after the burning test. As seen, the foams showed a significant reduction in the burning.



**Figure 4.10:** SEM images of the prepared corn-oil based polyurethane foams.

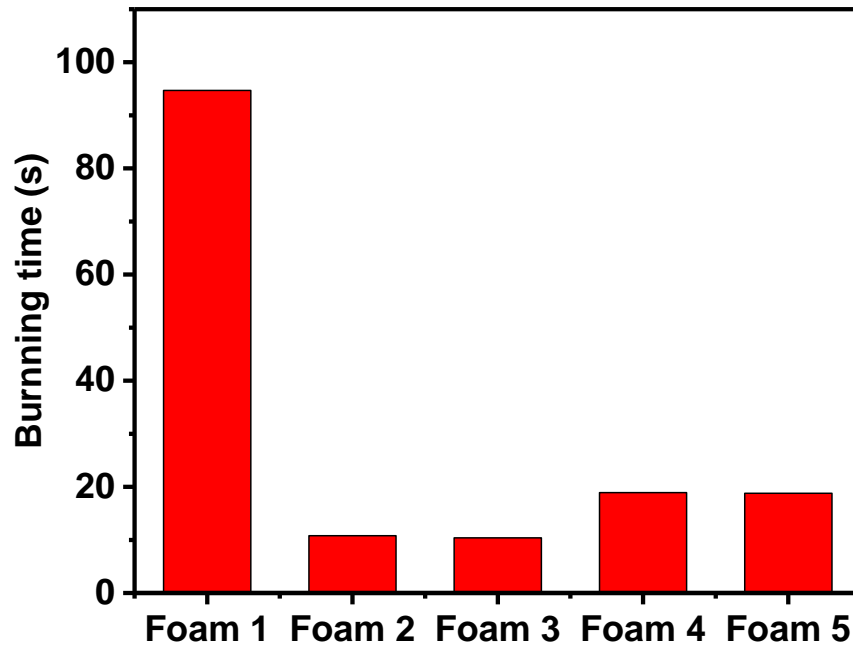


Figure 4.11: Burning time of corn oil-based polyurethane foams.

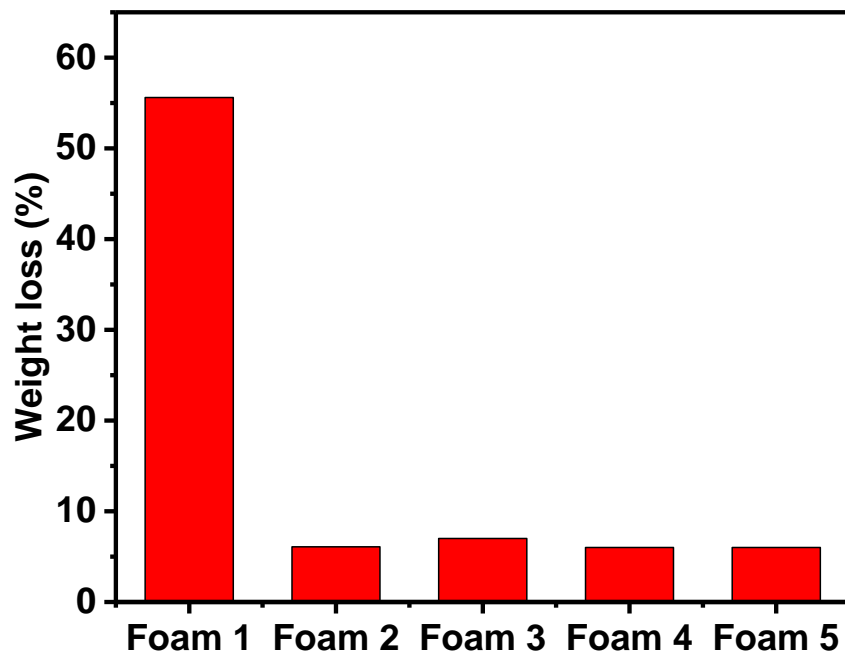
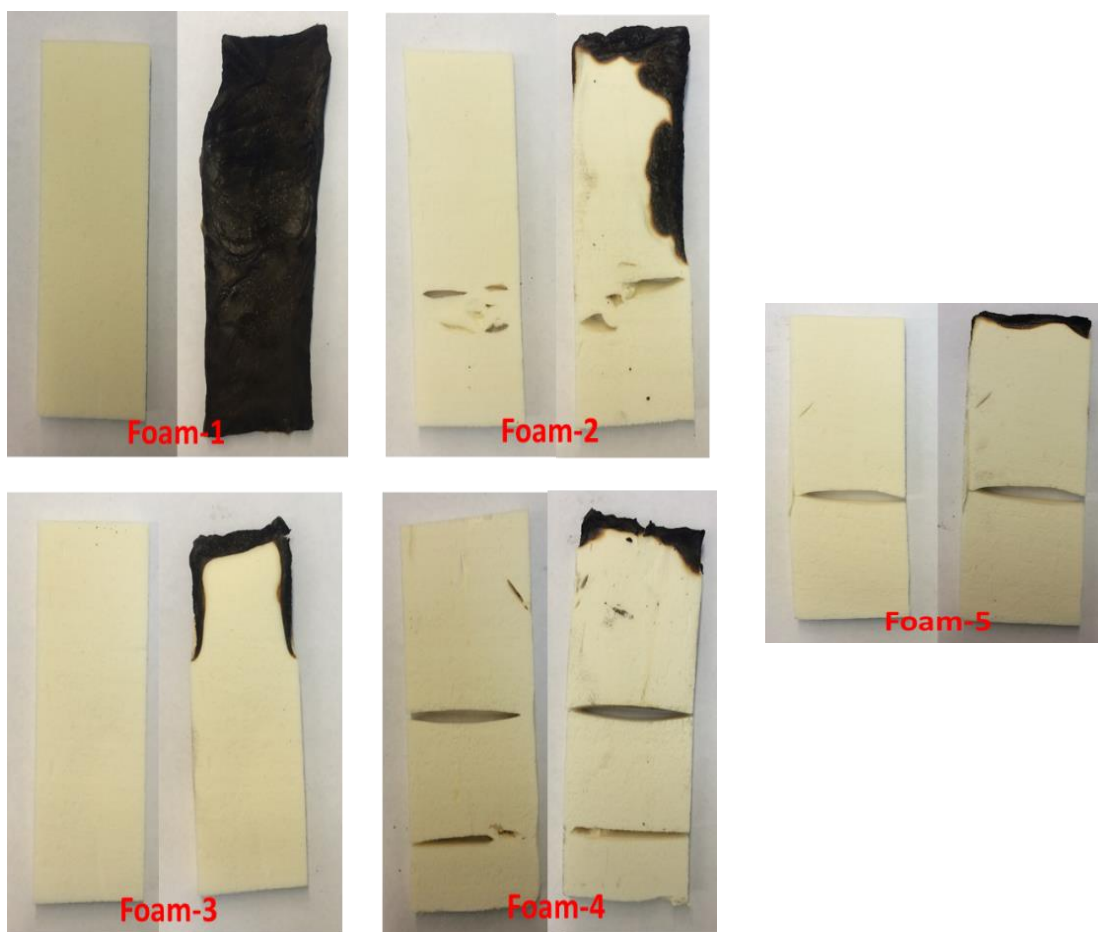


Figure 4.12: Weight loss of corn oil-based polyurethane foams.



**Figure 4.13:** Digital images of the foams before and after burning test.

Cone calorimeter test was carried out on the foams to study the flame-retardant characteristics detailed. Foam-1, 2 and 4 were subjected to a cone test. Heat release rate, thermal heat release and thermal smoke release were measured and shown in [Figures 4.14](#), [4.15](#) and [4.16](#), respectively. As seen in the graphs, HRR, THR, and TSR were significantly reduced by using phosphorous containing polyols in the foams.

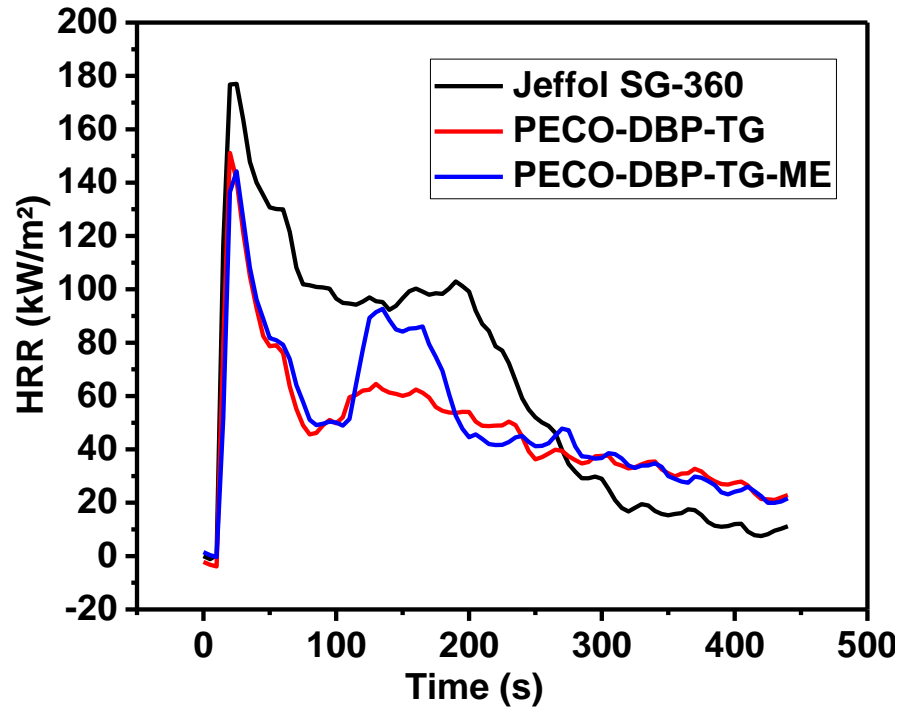


Figure 4.14: Heat release rate for various foams.

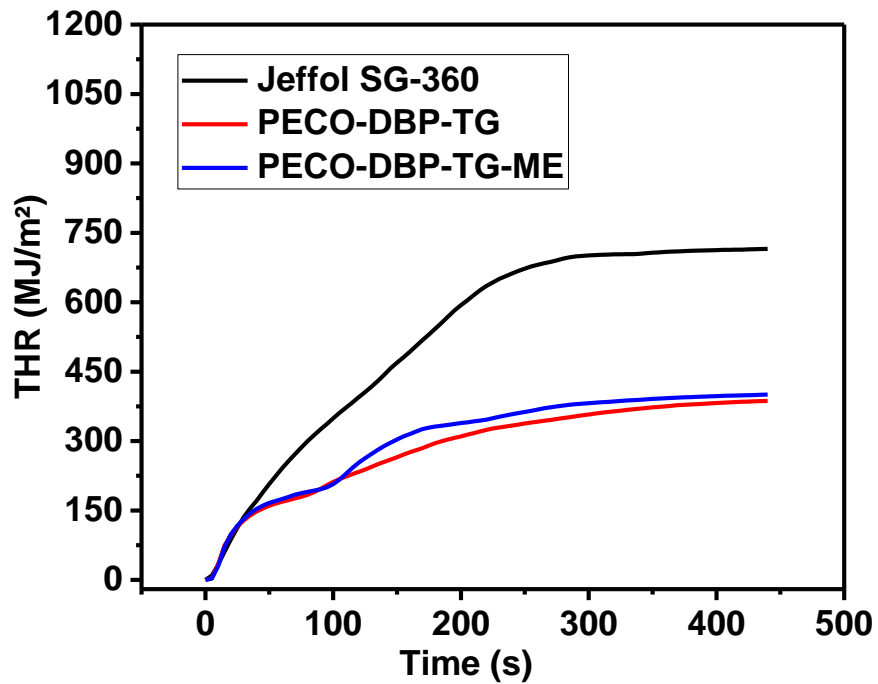


Figure 4.15: Thermal heat release for various foams.



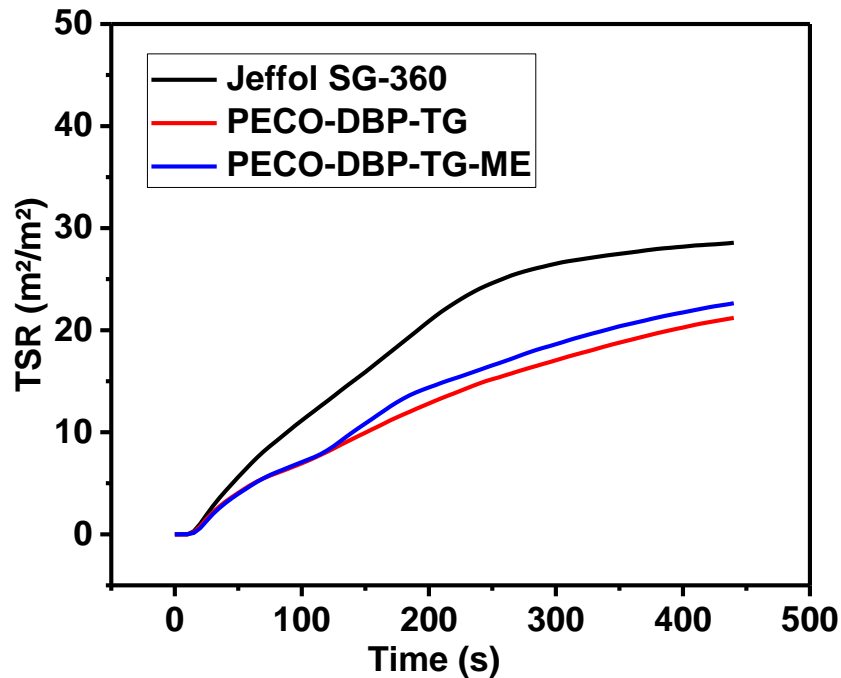


Figure 4.16: Thermal smoke release for various foams.

#### 4.4. Conclusion

Flame-retardant rigid polyurethane foams using partially epoxidized corn oil were synthesized. Bio-based polyurethane foams were synthesized using partially epoxidized corn oil polyol containing flame-retardants based on different concentrations of phosphorus (0, 0.189, 0.5, 0.54 and 0.35%). The partial epoxidation of the corn oil was confirmed with the presence of the new peak for the epoxy group and with the presence of remaining double bonds. The density of the foams was between 40-50 kg/m<sup>3</sup>, which is in the range of industrial polyurethane foams. The overall closed cell content of all the foams was above 95%, which suggest that most of the cells are closed which is favorable to use as a thermal insulator. The compressive strength of synthesized foams is higher than that of commercial polyol, suggesting high applicability. The horizontal burning test showed a significant reduction in the burning time and weight loss for the foams. Cone

calorimeter test was performed and showed a significant reduction in HRR, THR, and TSR by using phosphorous containing polyols in the foams. Thus, from an overall study, it can be said that partially epoxidized corn oil based phosphorous containing polyol can be used to prepare highly polyurethane foams with significant flame retardancy.

## CHAPTER V

### SUMMARY OF THE THESIS

Structural fire is a major issue for humanity, therefore, it is essential to develop flame-retardant polyurethane foams that can decrease the material loss and the deaths.

Chapter 1 describes the importance of bio-based foams and the importance of the development of flame-retardant polyurethane foams using bio-based compounds.

In chapter 2, there are the characterization techniques used to analyze the synthesized corn oil-based polyols and the foams.

In chapter 3, using corn oil fully epoxidized, it was synthesized corn oil based-phosphorous containing polyol. Foams containing 1.5% phosphorous showed excellent flame-retardant properties. The burning time and weight loss decreased significantly. The physicomechanical properties kept in the range of industrial standards. These suggest that corn oil-based phosphorous containing polyol can be used to prepare high-quality polyurethane foams with significant higher flame-retardancy.

In chapter 4, corn oil was partially epoxidized and then the corn oil-based phosphorous containing polyol was synthesized. The foams containing different amount of phosphorous was analyzed using all the same techniques in chapter 3. Flame

retardancy in all foams was ensured showing the effectivity of bio-based polyol in the synthesis of the foams.

In general, all the prepared foams containing flame-retardant polyol synthesized in this study showed excellent apparent density between 40-50 kg/m<sup>3</sup>, excellent closed cell content above 95%, and no significant effect on cell structure and cell size of the foams. The burning time and weight loss decrease significantly, and the cone calorimeter study showed a good reduction in HRR, THR, and TSR.

Considering all the results, it can be concluded that flame-retardant rigid polyurethane foams using fully and partially epoxidized corn oil-based phosphorous containing polyol can be used to provide excellent flame retardancy in many industrial and commercial applications, ensuring the safety for people and do not destroy the environment with the use of bio-based resources.

## REFERENCES

- (1) Zhang, C.; Madbouly, S. A.; Kessler, M. R. Biobased Polyurethanes Prepared from Different Vegetable Oils. *ACS Appl. Mater. Interfaces* **2015**, *7*.
- (2) Lu, Y.; Larock, R. C. Soybean-Oil-Based Waterborne Polyurethane Dispersions: Effects of Polyol Functionality and Hard Segment Content on Properties. *Biomacromolecules* **2008**, *9*.
- (3) Zhang, C.; Li, Y.; Chen, R.; Kessler, M. R. Polyurethanes from Solvent-Free Vegetable Oil-Based Polyols. *ACS Sustain. Chem. Eng.* **2014**, *2*.
- (4) Elbers, N.; Ranaweera, C. K.; Ionescu, M.; Wan, X.; Kahol, P. K.; Gupta, R. K. Synthesis of Novel Biobased Polyol via Thiol-Ene Chemistry for Rigid Polyurethane Foams. *J. Renew. Mater.* **2017**, *5*.
- (5) Yang, Z.; Feng, Y.; Liang, H.; Yang, Z.; Yuan, T.; Luo, Y.; Li, P.; Zhang, C. A Solvent-Free and Scalable Method to Prepare Soybean-Oil-Based Polyols by Thiol-Ene Photo-Click Reaction and Biobased Polyurethanes Therefrom. *ACS Sustain. Chem. Eng.* **2017**, *5*.
- (6) Shea, J. J. Polymeric Foams: Mechanisms and Materials. *IEEE Electr. Insul. Mag.* **2005**, *21*.
- (7) *Global Polyurethane (PU) Market Size & Share, 2025 | Industry Report*; 2017.
- (8) *Polyurethanes Market Research Reports - Research and Markets*; 2016.
- (9) Kirpluks, M.; Cabulis, U.; Avots, A. Flammability of Bio-Based Rigid Polyurethane Foam as Sustainable Thermal Insulation Material. *Insul. Mater. Context Sustain.* **2016**.

- (10) König, A.; Fehrenbacher, U.; Hirth, T.; Kroke, E. Flexible Polyurethane Foam with the Flame-Retardant Melamine. *J. Cell. Plast.* **2008**, *44*.
- (11) Haynes, H. J. G. *Fire Loss in the United States During 2016*; 2017.
- (12) *Center of Fire Statistics*; 2017.
- (13) Park, D. 1305 Civilian Fire Fatalities. *U.S. Fire Adm.* **2018**.
- (14) Li, Y. Y.; Luo, X.; Hu, S. Bio-Based Polyols and Polyurethanes. *Bio-based Polyols and Polyurethanes* **2015**.
- (15) • *Polyurethane Global Demand by Application 2021 | Statistic*; 2011.
- (16) Kearns, M. New Developments in Flame Retardants for Sustainable Fire Safety Solutions. *Technology* **2013**.
- (17) Zhang, A.; Zhang, Y.; Lv, F.; Chu, P. K. Synergistic Effects of Hydroxides and Dimethyl Methylphosphonate on Rigid Halogen-Free and Flame-Retarding Polyurethane Foams. *J. Appl. Polym. Sci.* **2013**, *128*.
- (18) Laoutid, F.; Bonnaud, L.; Alexandre, M.; Lopez-Cuesta, J.-M.; Dubois, P. New Prospects in Flame Retardant Polymer Materials: From Fundamentals to Nanocomposites. *Mater. Sci. Eng. R Reports* **2009**, *63*.
- (19) Thirumal, M.; Khastgir, D.; Nando, G. B.; Naik, Y. P.; Singha, N. K. Halogen-Free Flame Retardant PUF: Effect of Melamine Compounds on Mechanical, Thermal and Flame Retardant Properties. *Polym. Degrad. Stab.* **2010**, *95*.
- (20) Weil, E. D.; Levchik, S. V. Commercial Flame Retardancy of Polyurethanes. *J. Fire Sci.* **2004**, *22*.
- (21) Ionescu, M. *Chemistry and Technology of Polyols for Polyurethanes.*; Rapra

Technology, Shrewsbury, UK, 2007.

- (22) Montero De Espinosa, L.; Meier, M. A. R. Plant Oils: The Perfect Renewable Resource for Polymer Science?! *Eur. Polym. J.* **2011**, *47*.
- (23) Zhao, Q.; Chen, C.; Fan, R.; Yuan, Y.; Xing, Y.; Ma, X. Halogen-Free Flame-Retardant Rigid Polyurethane Foam with a Nitrogen-Phosphorus Flame Retardant. *J. Fire Sci.* **2017**, *35*.
- (24) Lorenzetti, A.; Modesti, M.; Gallo, E.; Schartel, B.; Besco, S.; Roso, M. Synthesis of Phosphinated Polyurethane Foams with Improved Fire Behaviour. *Polym. Degrad. Stab.* **2012**, *97*.
- (25) Rohman, A.; Che Man, Y. B. Quantification and Classification of Corn and Sunflower Oils as Adulterants in Olive Oil Using Chemometrics and FTIR Spectra. *Sci. World J.* **2012**, *2012*.
- (26) Ranaweera, C. K.; Ionescu, M.; Bilic, N.; Wan, X.; Kahol, P. K.; Gupta, R. K. Biobased Polyols Using Thiol-Ene Chemistry for Rigid Polyurethane Foams with Enhanced Flame-Retardant Properties. *J. Renew. Mater.* **2017**, *5*.
- (27) Gaidukova, G.; Ivdre, A.; Fridrihsone, A.; Verovkins, A.; Cabulis, U.; Gaidukovs, S. Polyurethane Rigid Foams Obtained from Polyols Containing Bio-Based and Recycled Components and Functional Additives. *Ind. Crops Prod.* **2017**, *102*.
- (28) Desroches, M.; Caillol, S.; Lapinte, V.; Auvergne, R.; Boutevin, B. Synthesis of Biobased Polyols by Thiol-Ene Coupling from Vegetable Oils. *Macromolecules* **2011**, *44*.

## **APPENDIX**



## APPENDIX

### 7.1. List of Conference Presentations

1. Sanket Bhoyate, **Camila Zequine**, P.K. Kahol, Ram K. Gupta, “Flame Retardant Polyurethane Foams using Corn Oil”, Kansas Corn Symposium, Four Points by Sheraton Conference Center, Manhattan, KS, USA, January 25, 2018.
2. Sanket Bhoyate, **Camila Zequine**, M. Ionescu, P. K. Kahol, Ram K. Gupta, “Industrially Producible High-Performance Corn-oil based Flame Retardant Rigid Polyurethane Foams”, Capitol Graduate Research Summit, Kansas State Capital Building, Topeka, KS, USA, February 20, 2018.
3. **Camila Zequine**, P.K. Kahol, Ram K. Gupta, “High-Performance Flexible Supercapacitors Obtained Via Recycled Jute: Bio-Waste to Energy Storage Approach”, PSU Research Colloquium, Pittsburg, KS, USA, April 11, 2018.
4. **Camila Zequine**, P.K. Kahol, Ram K. Gupta, “Cost Effective Ways to Fabricate Multifunctional Nanostructured Materials for Energy Applications”, PSU Research Colloquium, Pittsburg, KS, USA, April 11, 2018.
5. Sanket Bhoyate, **Camila Zequine**, P.K. Kahol, Ram K. Gupta, “Highly Flame Retardant Phosphorus Polyol for Rigid Polyurethane Foams”, 63<sup>rd</sup> Annual Oklahoma Pentasectional Meeting of the American Chemical Society, Tulsa, OK, USA, April 21, 2018.
6. **Camila Zequine**, Sanket Bhoyate, Khamis Siam, P.K. Kahol, Ram K. Gupta, “Nano-needle forest of nickel-cobalt sulfide for efficient multifunctional energy generation

- and storage”, 256<sup>th</sup> American Chemical Society National Meeting, Boston, MA, USA, August 20, 2018.
7. **Camila Zequine**, Khamis Siam, P.K. Kahol, Ram K. Gupta, “CuCo<sub>2</sub>S<sub>4</sub> Nanostructures as a Promising Material for Energy Storage Applications”, 2018 American Chemical Society Midwest Regional Meeting, Ames, IA, USA, October 22, 2018.
  8. Sanket Bhojate, **Camila Zequine**, Brooks Neria, P.K. Kahol, Ram K. Gupta, “A cost-effective way to develop highly flame retardant rigid polyurethane foams using corn oil”, 2018 American Chemical Society Midwest Regional Meeting, Ames, IA, USA, October 23, 2018.
  9. **Camila Zequine**, Xianglin Li, Fangzhou Wang, K. Siam<sup>1</sup>, P. K. Kahol, Ram K. Gupta, “Nanostructured CuCo<sub>2</sub>S<sub>4</sub> electrocatalyst for urea fuel cell and low-cost hydrogen production”, 2018 American Chemical Society Southwest Regional Meeting, Little Rock, AR, USA, November 9, 2018.
  10. **Camila Zequine**, Sanket Bhojate, Brooks Neria, P.K. Kahol, Ram K. Gupta, “Corn Oil: An Effective Precursor for Preparation of Highly Flame Retardant Rigid Polyurethane Foams”, 2018 American Chemical Society Southwest Regional Meeting, Little Rock, AR, USA, November 9, 2018.
  11. **Camila Zequine**, Fangzhou Wang, Xianglin Li, Pawan K. Kahol, Ram K. Gupta, “CuCo<sub>2</sub>S<sub>4</sub> Nanoballs: A solution to clean hydrogen generation and urea elimination from wastewater”, 2019 K-INBRE Symposium, Overland Park, KS, USA, January 20, 2019.
  12. Sanket Bhojate, **Camila Zequine**, Brooks Neria, Pawan K. Kahol, Ram K. Gupta, “One Step Synthesis of Corn-Oil based Polyols for Highly Flame Retardant Rigid

- Polyurethane Foams”, Kansas Corn Symposium, K-State Alumni Center, Manhattan, KS, USA, January 23, 2019. (Invited)
13. Xavier Martinez, Chen Zhao, **Camila Zequine**, Ram K. Gupta, Pawan K. Kahol, “Bio-Waste Generated in Corn Crops for High Performance Green Batteries and Supercapacitors”, Kansas Corn Symposium, K-State Alumni Center, Manhattan, KS, USA, January 23, 2019. (Invited)
  14. **Camila Zequine**, P.K. Kahol, Ram K. Gupta, “Molybdenum Oxides for Energy Generation and Storage Using Efficient Clean Method”, PSU Research Colloquium, Pittsburg, KS, USA, April 10, 2019.
  15. **Camila Zequine**, P.K. Kahol, Ram K. Gupta, “Nanosheets of  $\text{CuCo}_2\text{O}_4$  as a High-Performance Electrocatalyst in Urea Oxidation”, PSU Research Colloquium, Pittsburg, KS, USA, April 10, 2019.
  16. **Camila Zequine**, Khamis Siam, P.K. Kahol, Ram K. Gupta, “Molybdenum-based Metal Oxides for Overall Water Splitting and Supercapacitors”, 64th Annual Pentasectional Meeting of the American Chemical Society, Norman, OK, USA, April 13, 2019.

## 7.2. List of Publications

1. **Zequine, C.**, Ranaweera, C. K., Wang, Z., Singh, S., Tripathi, P., Srivastava, O. N., Gupta, B. K., Ramasamy, K., Kahol, P. K., Dvornic, P. R., Gupta, R. K. (2016). High performance and flexible supercapacitors based on carbonized bamboo fibers for wide temperature applications. *Scientific Reports*, 6, 1.
2. **Zequine, C.**, Ranaweera, C. K., Wang, Z., Dvornic, P. R., Kahol, P. K., Singh, S., Tripathi, P., Srivastava, O. N., Singh, S., Gupta, B. K., Gupta, G., Gupta, R. K. (2017). High-Performance Flexible Supercapacitors obtained via Recycled Jute: Bio-Waste to Energy Storage Approach. *Scientific Reports*, 7, 1.
3. Alqahtani, D. M., **Zequine, C.**, Ranaweera, C. K., Siam, K., Kahol, P. K., Poudel, T. P., Mishra, S. R., Gupta, R. K. (2019). Effect of metal ion substitution on electrochemical properties of cobalt oxide. *Journal of Alloys and Compounds*, 771, 951.
4. **Zequine, C.**, Bhoyate, S., Siam, K., Kahol, P. K., Kostoglou, N., Mitterer, C., Hinder, S. J., Baker, M. A., Constantinides, G., Rebholz, C., Gupta, G., Li, X., Gupta, R. K. (2018). Needle grass array of nanostructured nickel cobalt sulfide electrode for clean energy generation. *Surface & Coatings Technology*. 354, 306.
5. **Zequine, C.**, Bhoyate, S., Wang, F., Li, X., Siam, K., Kahol, P. K., Gupta, R. K. (2019). Effect of solvent for tailoring the nanomorphology of multinary  $\text{CuCo}_2\text{S}_4$  for overall water splitting and energy storage. *Journal of Alloys and Compounds*, 784, 1.
6. Darkwa, K., **Zequine, C.**, Kahol, P. K., Gupta, R. K. (2019). Supercapacitor Energy Storage Device Using Biowastes: A Sustainable Approach to Green Energy. *Sustainability*, 11, 414.

7. **Zequine, C.**, Wang, F., Li, X., Guragain D., Mishra S.R., Siam, K., Kahol, P. K., Gupta, R. K. (2019). Nanosheets of  $\text{CuCo}_2\text{O}_4$  as a High-Performance Electrocatalyst in Urea Oxidation. *Applied Sciences*, 9, 793.
8. Ramanujam, S., **Zequine, C.**, Bhoyate, S., Neria, B., Kahol, P. K., Gupta, R. K. (2019). Novel Biobased Polyol Using Corn Oil for Highly Flame-Retardant Polyurethane Foams. *Journal of Carbon Research*, 5, 13.
9. Dream, J., **Zequine, C.**, Siam, K., Kahol, P. K., Mishra, S. R., Gupta, R. K. (2019). Electrochemical Properties of Graphene Oxide Nanoribbons/Polypyrrole Nanocomposites. *Journal of Carbon Research*, 5, 18.

### 7.3. Published Work on Polyurethanes

1. Ramanujam, S., Zequine, C., Bhoyate, S., Neria, B., Kahol, P. K., Gupta, R. K. (2019).  
Novel Biobased Polyol Using Corn Oil for Highly Flame-Retardant Polyurethane Foams.  
Journal of Carbon Research, 5, 13.

#### **7.4. Award Received on Polyurethanes**

1. Sanket Bhoyate, C. Zequine, M. Ionescu, P. K. Kahol, Ram K. Gupta, “Industrially producible high-performance corn-oil based flame retardant rigid polyurethane foams”, Capitol Graduate Research Summit Champion Award, BIODIVERSITY, February 2018.