

Pittsburg State University

## Pittsburg State University Digital Commons

---

Electronic Theses & Dissertations

---

Spring 5-10-2019

### SYNTHESIS AND CHARACTERIZATION OF CORN OIL BASED POLYOL AND ITS APPLICATION FOR RIGID FLAME RETARDANT POLYURETHANE FOAMS

Sneha Ramanujam

Pittsburg State University, [sramanujam@gus.pittstate.edu](mailto:sramanujam@gus.pittstate.edu)

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

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

---

#### Recommended Citation

Ramanujam, Sneha, "SYNTHESIS AND CHARACTERIZATION OF CORN OIL BASED POLYOL AND ITS APPLICATION FOR RIGID FLAME RETARDANT POLYURETHANE FOAMS" (2019). *Electronic Theses & Dissertations*. 338.

<https://digitalcommons.pittstate.edu/etd/338>

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).

SYNTHESIS AND CHARACTERIZATION OF CORN OIL BASED POLYOL AND ITS APPLICATION  
FOR RIGID FLAME RETARDANT POLYURETHANE FOAMS

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

Sneha S. Ramanujam

Pittsburg State University

Pittsburg, Kansas

May, 2019

SYNTHESIS AND CHARACTERIZATION OF CORN OIL BASED POLYOL AND ITS APPLICATION  
FOR RIGID FLAME RETARDANT POLYURETHAN FOAMS

Sneha S. Ramanujam

APPROVED:

Thesis Advisor

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

Committee Member

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

Committee Member

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

Committee Member

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

## **Acknowledgments**

I would like to begin my acknowledgments with a sincere thanks to my thesis advisor Dr. Ram Gupta who has been a pillar of support and encouragement. He believed in my abilities and offered to help me during my hurdles. I am so grateful to him for his kindness, generosity, and for being the most crucial part in my success in the master's program. I would also like to thank my committee members Dr. Pawan Kahol, Dr. Khamis Siam, and Dr. Anuradha Ghosh for their acceptance of my thesis proposal. I am grateful to Dr. Bobby Winters, Department chair and Dr. Peter Dvornic, former department chair, in providing me a graduate research assistantship position. I am thankful to the Kansas Corn Commission for providing support to complete this work. I am thankful to Dr. Santimukul Santra, who offered me a position in his lab for the first two semesters. I would also like to thank Dr. Tuhina Banerjee in helping me learn important aspects of research. I am really thankful to my labmate Camila Zequina for her immense support in helping me understand the laboratory work. I would also like to thank my friends Tanuja Tummala, Varun Doddapaneni, Saloni Darji, and Hamid Reza Givehchi, who were beside me through thick and thin during this program.

I would like to thank my friends in India, who gave me emotional support in this journey. Finally, I would like to dedicate the success throughout my life to my family, who gave me this identity, who is the sole reason for all my successes, and who make me live my life with hope and wanting better for tomorrow.

# SYNTHESIS AND CHARACTERIZATION OF CORN OIL BASED POLYOL AND ITS APPLICATION FOR RIGID FLAME RETARDANT POLYURETHAN FOAMS

An Abstract of the Thesis By  
Sneha Ramanujam

A novel bio-based polyol was synthesized using corn oil and 2-mercaptoethanol via thiol-ene reaction as an alternative to petroleum-based polyol for the synthesis of polyurethane foams. The polyol was analyzed using wet chemical techniques to obtain a hydroxyl number and the viscosity of the polyol. Infrared spectroscopy and gel permeation chromatography were used to confirm the structural properties of the foams. Flame-retardant polyurethane foams were prepared by the addition of different concentrations of dimethyl methyl phosphonate (DMMP) in the final foam composition. The effect of DMMP on the thermo-mechanical properties of the polyurethane foams was analyzed. The TGA analysis showed improved stability of the final char with the addition of DMMP in the foams. All the foams maintained a well-defined cellular structure and over 95% of closed cell content. The horizontal burning test showed reduced burning time and weight loss from 115 s and 38 wt% for the neat foams to 3.5 s and 5.5 wt% for DMMP containing foams (1.94 wt% P). The combustion test using a cone calorimeter showed a considerable reduction in heat release rate and total heat release. Thus, our study shows that corn oil-based polyol can be used to produce renewable polyol for industrially producible rigid polyurethane foams. The addition of a small amount of DMMP could result in a significant reduction in flame retardant properties of the polyurethane foams.

## TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION.....	1
1.1. Polyurethanes: Importance and applications.....	1
1.2. Polyurethanes using bio-based materials .....	2
1.3. Major issues with polyurethanes .....	3
1.4. Flame retardant polyurethanes foams .....	4
1.5. Types of flame retardant materials .....	5
1.6. Synthesis of polyurethane.....	6
1.7. Objective of the Thesis .....	9
II. EXPERIMENTAL DETAILS.....	11
2.1. Starting Materials.....	11
2.1.1 Polyols.....	11
2.1.2 Isocyanate.....	12
2.1.3 Catalyst.....	13
2.1.4 Surfactant.....	15
2.1.5 Blowing agent.....	16
2.1.6 Fire Retardants.....	17
2.1.7 Photo initiator.....	18
2.2. Synthesis of Corn oil-based Polyols.....	19
2.3. Characterization of Polyol.....	21
2.3.1. Phthalic anhydride/pyridine (PAP) method.....	21
2.3.2. Viscosity.....	23
2.3.3. Acid value.....	24
2.3.4 Fourier Transform Infrared Spectroscopy (FT-IR).....	24
2.3.5 Gel Permeation Chromatography.....	25
2.3.6. <sup>13</sup> C Nuclear Magnetic Resonance.....	25
2.4. Preparation of Flame Retardant Rigid Polyurethane Foams.....	25
2.5. Characterization of the Rigid Polyurethane Foams.....	27
2.5.1. Apparent density.....	27
2.5.2. Closed-cell content.....	28
2.5.3. Compression test.....	28
2.5.4. Thermogravimetric Analysis (TGA).....	28
2.5.5. Horizontal burning test.....	29
2.5.6. Cone calorimetry.....	29
2.5.7. Scanning electron microscope.....	30

III. RESULTS AND DISCUSSION.....	31
3.1. Properties of polyol.....	31
3.1.1. <i>Acid Value</i> .....	31
3.1.2. <i>Hydroxyl number</i> .....	32
3.1.3. <i>Viscosity</i> .....	32
3.1.4. <i>Fourier Transform Infrared Spectroscopy (FT-IR spectra)</i> .....	33
3.1.5. <i>Gel permeation chromatography</i> .....	33
3.2. Properties of corn oil-based polyurethane foams.....	37
3.2.1. <i>Apparent Density</i> .....	38
3.2.2. <i>Closed Cell Content</i> .....	39
3.2.3. <i>Compression Strength</i> .....	40
3.2.4. <i>Microstructural Properties of the Foams</i> .....	42
3.2.5. <i>Thermogravimetric analysis (TGA)</i> .....	44
3.2.6. <i>Horizontal burning test</i> .....	48
3.2.7. <i>Combustion test</i> .....	51
IV. CONCLUSION.....	53
REFERENCES.....	55
APPENDICES.....	70
APPENDIX A - List of conference presentations.....	71
APPENDIX B - List of Publications.....	72
APPENDIX C - Published work on polyurethane.....	73

## LIST OF TABLES

TABLE		PAGE
Table 1.1	Physical properties in testing different types of polyurethane.....	9
Table 2.1	Formulation for preparation of phosphorus-containing polyurethane foams.....	27



## LIST OF FIGURES

FIGURE		PAGE
Figure 1.1	Depicts various materials manufactured using polyurethane compound.....	2
Figure 1.2	Shows building and property loss due to the flammability issue of polymers used in the construction of the building.....	4
Figure 1.3	Reaction between isocyanate and alcohol.....	7
Figure 1.4	Reaction between isocyanate and carboxylic acid group.....	7
Figure 1.5	Reaction between isocyanate and water.....	8
Figure 2.1	Example of a chemical structure of polyol .....	11
Figure 2.2	Corn oil.....	12
Figure 2.3	Structure of Mercaptoethanol.....	12
Figure 2.4	Chemical structure of 4,4'-Methylenediphenyl diisocyanate.....	13
Figure 2.5	Chemical structure of dibutyltin dilaurate (DABCO® T-12) and bis-2-dimethyl-aminoethyl ether (Niax™ A-1).....	15
Figure 2.6	Blowing reaction with the use of chemical blowing agent i.e. water.....	17
Figure 2.7	Chemical Structure of Dimethyl methyl phosphonate (DMMP).....	18
Figure 2.8	Chemical structure of 2-hydroxy-2-methyl propiophenone.....	19
Figure 2.9	Overall representation of the synthesis of polyol using thiol-ene reaction.....	20
Figure 2.10	The chemical reaction involving the synthesis of CO-ME.....	21
Figure 2.11	The mechanism involved in thiol-ene synthesis of CO-ME polyol....	22
Figure 2.12	Images of (A) Shimadzu IR Affinity-1 spectrophotometer, (B) AR 2000 dynamic stress rheometer,(C) Gel permeation chromatography.....	26
Figure 2.13	Images of (A) Ultrapycnometer, Ultrafoam 1000, (B) Q-Test 2-tensile machine, (C) Phenom G2 Pro scanning electron microscope, (D) TGA Q500, (E) Horizontal burning test instrument, (F) Cone calorimeter.....	30
Figure 3.1	FT-IR graph of corn oil, 2-mercaptoethanol, and corn oil-based polyol (CO-ME polyol).....	34
Figure 3.2	GPC graphs of corn oil, 2-mercaptoethanol, and corn oil-based polyol (CO-ME polyol).....	36
Figure 3.3	C MNR of corn oil, 2-mercaptoethanol, and corn oil-based polyol (CO-ME polyol).....	36
Figure 3.4	Photographs of the synthesized polyurethane foams with various concentration of DMMP (a) 0%P, (b) 0.25%P, (c) 0.51%P, (d) 1%P, (e) 1.48%P, (g) 1.93%P, and 2.37%P, as a flame-retardant additive.....	37

Figure 3.5	Density of corn oil-based polyurethane foams.....	39
Figure 3.6	Closed cell content of corn oil-based polyurethane foams.....	40
Figure 3.7	Compression strength of corn oil-based polyurethane foams.....	41
Figure 3.8	SEM images of the polyurethane foams containing various amount of DMMP (a) 0%P, (b) 0.25%P, (c) 0.51%P, (d) 1%P, (e) 1.48%P, (f) 1.93%P, and (g) 2.37%P.....	43
Figure 3.9	TGA curves of polyurethane foams with different amount of DMMP (a) 0%P, (b) 0.25%P, (c) 0.51%P, (d) 1%P, (e) 1.48%P, (f) 1.93%P, and (g) 2.37%P. The gathered transition of all the foams is represented in (h).....	46
Figure 3.10	TGA for polyurethane foams in nitrogen and air environment of 0.51%P (a) & (b) and 1.9%P (c) & (d) are represented, respectively. The gathered transition is represented in (e).....	47
Figure 3.11	(a) Percentage weight loss after burning and (b) burning time of corn oil-based polyurethane foams.....	49
Figure 3.12	Photographs of the foams before and after burning test of corn oil-based polyurethane foams.....	50
Figure 3.13	(a) Heat release rate and, (b) Total heat release versus time for the foams containing 0 wt% and 1.5 wt% P.....	52

## CHAPTER I

### INTRODUCTION

#### 1.1. Polyurethanes: Importance and applications

Polyurethanes are polymers with repeated urethane moiety which show numerous properties with wide applications.<sup>1</sup> They are generally made from diols or polyols (compounds with at least two reactive hydroxyl groups) and poly-isocyanates using addition polymerization.<sup>2,3</sup> Polyurethane represents around 7% of the worldwide polymer market.<sup>4</sup> It is important to study polyurethane because of its extensive use in commercial manufacturing units such as automotive, transportation, packaging, medical and so on.<sup>5-8</sup> Largely, polyurethane is classified into flexible foams (50%), rigid foams (30%), and also as coatings, adhesives, elastomers, and sealants (20%). Flexible foams are utilized for furniture, automotive seats, and mattresses while rigid foams are used in insulation and construction materials (**Figure 1.1**).<sup>9,10</sup> Its influence on the medical industry is tremendous where polyurethane is utilized in the production of catheters, surgical drapes, medical dressings, and as injection molds. The most renowned medical application of polyurethane is in the making of pacemaker leads.<sup>8</sup> It is also one of the key components in building construction where it is being used in the production of thermal

insulators, vibration insulators, electrical insulators, furniture, and refrigerators.<sup>11</sup> The other uses of polyurethanes are in the making of rigid and flexible foams, gaskets, wheels for carts, elevators, synthetic fibers, adhesives, and electronic instruments.<sup>12</sup>



**Figure 1.1.** Depicts various materials manufactured using polyurethane compound  
(These images were adopted from Google for demonstration purpose only)

## 1.2. Polyurethanes using bio-based materials

Polyurethanes are generally prepared by the catalytic breaking of oil or natural gas liquids. The most popularly used oil for the synthesis of such polymers is petroleum<sup>13</sup>

but the production of polymers from petrochemical industries faces the danger of energy crisis. Living in an era where polymers are a boon, it is a definite objective for scientists to find an alternative to produce such polymers. Recently, the most intense investigation has been undertaken to replace the petrochemical-based production of polyurethane.<sup>14</sup> The best alternative would be the use of bio-based materials for polymer synthesis. Such bio-based polymers are synthesized from vegetable oil derivatives which have hydroxyl, amine, silane, isocyanate, isothiocyanate, and epoxy terminal.<sup>15</sup> The major sources for such oil derivatives are soybean oil, castor oil, corn oil, canola oil, sunflower oil, and orange oil.<sup>16-28</sup> The merits of using vegetable oil are in the oil's chemical structure because it has many reactive centers which could be altered and functionalized as desired. Bio-based polymers' biodegradable property makes them more attractive to use considering the rising environmental alarms.<sup>29</sup>

### **1.3. Major issues with polyurethanes**

There has been an increasing demand for polyurethane because of its applicability as foam in the production of many household essentials, and also due to its insulating property. In general, polyurethanes do not possess adequate flame retardancy and are easily susceptible to fire, mainly due to the organic nature of the polyurethane and its exposure to air owing to its large surface area (**Figure 1.2**). This restricts the use of polyurethane in flammable applications. Therefore the development of polyurethanes with resistance to combustion would permit the use of these polymers safely, especially

when used in the production of adhesives, coatings, fibers, elastomeric compounds, and cellular materials.<sup>30-33</sup> Research has found that the use of aromatic polyols and the existence of an isocyanate ring on the polymer structure had relatively reduced the combustibility.<sup>34,35</sup> Additionally, a highly cross-linked polymer along with high-density polymer has also been found to have lesser flammability issues.<sup>36,37</sup>



**Figure 1.2.** Shows building and property loss due to the flammability issue of polymers used in the construction of the building (These images were adopted from Google for demonstration purpose only)

#### **1.4. Flame retardant polyurethane foams**

When polyurethane is open to ignition, it rapidly catches fire and emits an enormous amount of smoke and heat, ultimately leading to devastating consequences.<sup>38</sup> In the year 2017, National Fire Protection Association (NFPA) took a survey on fire occurrence and its consequences in the United States, and as per their reports, there were about 1.3 million fire incidents, bringing about 3,400 and 15,000 citizen deaths and injuries respectively with a property loss of about \$23 billion.<sup>39</sup> These overwhelming statistics highlight the importance of developing flame retardant polyurethane foams

with adherence to the stringent safety regulations.<sup>40</sup> One of the ways to make the polyurethane flame retardant is by the addition of fire retardants to the chemical composition or foaming composition of the polymer. With this addition to the polyurethane, the ignitability is declined drastically.<sup>36</sup>

### **1.5. Types of flame retardant materials**

There are two types of flame retardants used in making polyurethane less burnable. First is the traditional flame retardant, which is added as an additives. These non-reactive flame retardants (additive flame retardants) are not added during the synthesis of polymer foaming process; instead, they are incorporated as an additive at the end. This type of flame retardant is economical but carries a major limitation of moving out of the polymer framework when added physically to the foam.<sup>40,41</sup> This leads to an adverse interaction between the polymer structure and the additives, which may weaken the physical characteristics of polymer.<sup>42-45</sup> Therefore, the use of the reactive flame retardant which is halogenated has been adapted. In contrast to additive flame retardants, reactive flame retardants are combined during the polymer synthesis and thereby get incorporated in the structure of the polyurethane. This polymer has high mechanical strength and is also robust.<sup>46,49</sup> European Union guidelines do not recommend the use of such flame retardants, mainly because of the emission of undesired gases on the surroundings of such halogenated flame retardants.<sup>41</sup> To overcome this problem, phosphorus-containing reactive flame retardants (also called halogen-free flame

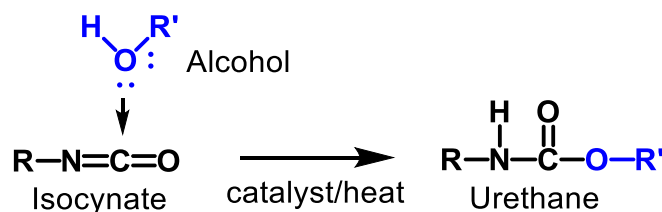
retardants) are of great interest because of their great efficacy as well as owing to their advantage of not producing any lethal gases during a fire.<sup>48-51</sup> The phosphorus-containing flame retardants generally used are DOPO, cyclic phosphates, and phosphine oxide.<sup>51-56</sup> Recently, a new candidate has been added to this list of flame retardants, Intumescent flame retardants, and has been found to be a good replacement for the poisonous halogenated flame retardants. These flame retardants swell up and form char during a fire, which acts as a barrier between ignition zone and polymer, and protects the material from the fire.<sup>57</sup> Scientists are mainly focused on studying polyolefins as intumescent flame retardants.<sup>58-62</sup> The investigated polyolefins so far are polypropylene, polystyrene, polyethylene, and poly(ethylene-co-vinyl acetate), and they showed promising results in attaining anticipated flame retardancy capacity.<sup>63-66</sup>

## 1.6. Synthesis of polyurethane

Three major steps are involved in the synthesis of polyurethane as described below:

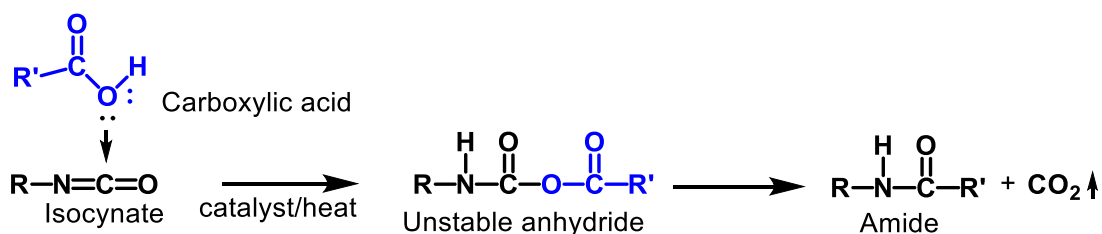
i) The first is the slow reaction between isocyanate and alcohol containing the group, which leads to the formation of urethane (**Figure 1.3**). To accelerate this reaction, heating and catalyst are used. Catalysts such as stannous octoate, dilaurate, and bismuth carboxylates could be used.<sup>67</sup>





**Figure 1.3.** Reaction between isocyanate and alcohol

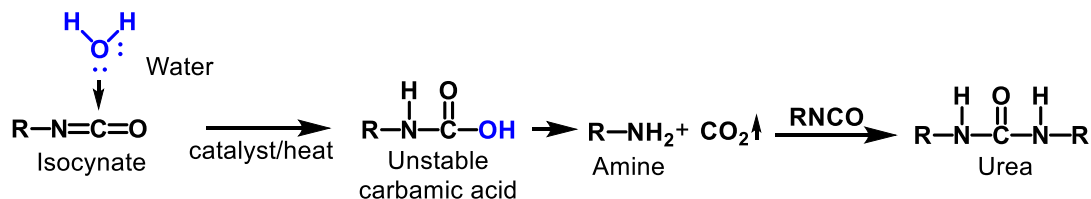
ii) The next reaction is a fast exothermic reaction, which does not require any use of a catalyst, It is a reaction between isocyanate and carboxylic acid group leading to the formation of amide as given in **figure 1.4**.



**Figure 1.4.** Reaction between isocyanate and a carboxylic acid group

iii) The last reaction is between isocyanate and water, which leads to the formation of urea. The important characteristic of this reaction is the formation of unstable carbamic acid as an intermediate, which further gets degraded to amine and carbon dioxide. The carbon dioxide released acts as a blowing agent, helping the foaming of polyurethane during the synthesis, whereas the amine formed during degradation again involves in the synthesis of urea formation by combining with other free isocyanates in the reaction. This final reaction is catalyzed by a tertiary amine group. Similar type of reaction is also possible when isocyanate reacts with a carboxylic acid. This reaction

between isocyanate and carboxylic acid will produce an unstable intermediate as anhydride, which dissociates into an amine group and release carbon dioxide as in **figure 1.5**.



**Figure 1.5.** Reaction between isocyanate and water

There are two other reactions that are possible, one is the reaction between isocyanate and urethane leading to the allophanate formation which happens between 120 to 140 °C whereas the other reaction occurs between isocyanate and urea forming biuret linkages at the temperature of 100 °C.<sup>68</sup>

The physical property of the polyurethane formed depends on the characteristics of the polyols used in the synthesis. For instance, the polyols with just two to three hydroxyl groups containing a high molecular weight of 2000 to 10000 g mol<sup>-1</sup> will lead to a formation of an elastic polyurethane compound while polyols with a high number of hydroxyl functional group with a low molecular weight between 300 to 1000 g mol<sup>-1</sup> lead to forming a cross-linked rigid polyurethane.<sup>3</sup>

**Table 1.1. Physical properties in testing different types of polyurethane**

<b>Polyurethane compounds</b>	<b>Physical properties</b>
Solid polyurethane	Flexibility, rigidity and durability test, tensile extension at break, tear strength, resistance to solvent, dynamic, and thermal property. <sup>67</sup>
Rigid Polyurethane foam	Thickness, liquid immersion, closed cell content, durability test, rigidity, heat conductance, compression robustness, size toughness, heat degradation, and flammability. <sup>69</sup>
Flexible Polyurethane foam	Thickness, durability test, cell size, tensile extension at break, tear strength, flexibility, compressive stress, indentation force deflection, and flow of air. <sup>69</sup>

### **1.7. Objective of the thesis**

The main focus of this work is to synthesize a polyurethane foam using a novel polyol with unmodified corn oil. For the synthesis of this polyol a one-step, solvent free, and cost-effective thiol-ene chemistry was employed. Different experiments to evaluate the important characteristics of a synthesized polyol such as acid value, hydroxyl number, viscosity, molecular structure, and molecular weight were performed. The flame

retardancy of polyurethane foams was improved using DMMP. The effect of different concentration of DMMP addition on the physicommechanical and thermal property of the polyurethane foams was studied in detail. Structural, thermal, flame retardancy, and mechanical properties of these polyurethane foams were studied in detail using apparent density, closed cell content, compression test, thermogravimetric analysis, horizontal burning test, cone calorimetry, and scanning electron microscopy techniques.

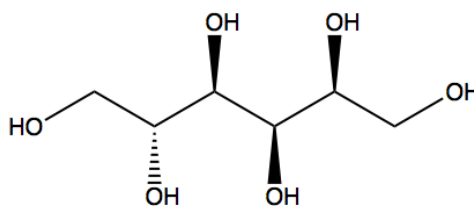
## CHAPTER II

### EXPERIMENTAL DETAILS

#### 2.1. Starting Materials

##### 2.1.1. Polyol

Polyol, also called sugar alcohol, is an organic compound with multiple hydroxyl groups. There are numerous kinds of polyols that could be used for the synthesis of polyurethane. The property of polyurethane synthesized is dependent on the physical characteristics of the polyol being used during the synthesis.



**Figure 2.1.** Example of a chemical structure of polyol

In this study, a bio-based polyol was synthesized using corn oil and 2-mercaptoethanol. Corn oil was purchased from the local Walmart. 2-Mercaptoethanol (molecular formula:  $C_2H_6OS$ ), clear, colorless liquid, soluble in water with the molecular

weight of 78.13 g/mol, decomposition temperature at 315 deg F, and viscosity of 343 cP, was purchased from Acros Organic. Jeffol SG-360, which is a sucrose-based polyol, was also used in the synthesis of polyurethane. It was purchased from Huntsman, USA and it was used without any modification. Jeffol SG-360 has a molecular weight of 730 g/mol, an OH content of 360 mg KOH/g, the functionality of 4.7, an equivalent weight of 156, viscosity of 3,500 cps@25°C, and specific gravity of 1.08@25 °C.



**Figure 2.2.** Corn oil

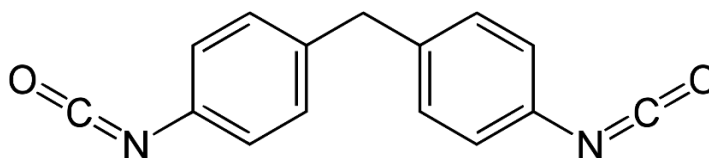


**Figure 2.3.** Structure of Mercaptoethanol

### 2.1.2. Isocyanate

The isocyanate is compound with a functional group  $R-N=C=O$  (-NCO) which react with a polyol to give polyurethane polymers. Isocyanates that could be used are methylene diphenyl diisocyanate, toluene diisocyanate, and their derivatives. In this study, isocyanate used was Rubinate M isocyanate, the chemical name of Rubinate M isocyanate is 4,4'-Methylenediphenyl diisocyanate (MDI). Rubinate M isocyanate was purchased from Huntsman, USA and it was used without any further purification. 4,4'-Methylenediphenyl diisocyanate (MDI) is miscible in water, and it is also soluble in acetone, benzene, kerosene, and nitrobenzene. Rubinate M isocyanate has an equivalent

weight of 135, a functionality of 2.70, NCO content of 31%, a viscosity of 210 cps at 25°C, specific gravity of 1.23 at 25°C. The chemical structure of MDI is shown below:



**Figure 2.4.** Chemical Structure of 4,4'-Methylenediphenyl diisocyanate

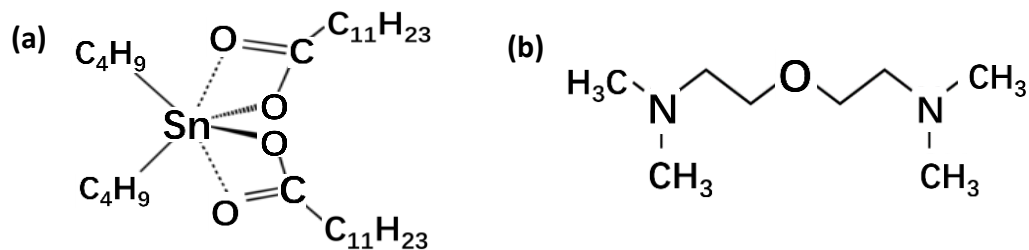
### 2.1.3. Catalyst

A catalyst can be used in any chemical reaction in order to expedite the rate of the reaction. It does not alter the chemical structure of the reactants/product in the reaction and it can be removed unchanged at the end of the reaction. Catalysts have a substantial effect on the different types of polymer synthesis such as free-radical, cationic, and anionic polymerization reactions. The selection of catalyst determines the time taken and the properties of the polymer formed. This also applies to the synthesis of polyurethane, which is prepared by an additional polymerization reaction. The use of a catalyst in this study was considered to be crucial because the reaction between isocyanate and polyol/water is considered to be comparatively slow. In this study, the choice of catalyst is majorly significant because of the impact it may have on the property of the polyurethane compound synthesized, which is used commercially for wide applications such as construction, automobile manufacturing, packaging, and so on.<sup>70</sup>

Two kinds of catalysts are generally utilized for the formation of polyurethane foam such as organometallics and amine catalysts. The blowing reaction of the polyurethane synthesis is effected by the amine catalyst. Tertiary amines are the amine catalyst, among which 1,4-diazobicyclo[2,2,2]octane (DABCO) is broadly used in the synthesis of polyurethane. It catalyzes both gelling and blowing reactions but one major limitation of tertiary amines is their instability and unpleasant odor.<sup>71,72</sup> The gelling reaction of the polyurethane is catalyzed by organometallics, although it may also have some influence on the blowing reaction.<sup>72,73</sup>

In this study, DABCO® T-12 catalyst received from Air Products, USA was used. DABCO® T-12 is dibutyltin dilaurate which assists in the production of flexible and rigid polyurethane foams, coatings, adhesives, and sealants. They are light yellow liquid with a viscosity of 125 g/cm<sup>3</sup> and specific gravity of 1.03 g/cm<sup>3</sup> at 25°C. Niax™ A-1 is another catalyst which was used, considered to be the most active catalysts in polyurethane foam synthesis. It was purchased from OSi Specialties, USA. Niax™ A-1 is used especially in the synthesis of high-density unfilled foam, filled foam, high-load-bearing flexible foam, low-density foam, and high resilience molded foam. These catalysts were used as such without undergoing any chemical modifications.





**Figure 2.5.** Chemical structure of (a) dibutyltin dilaurate (DABCO® T-12) and (b) bis-2-dimethyl-aminoethyl ether (Niax™ A-1)

#### 2.1.4. Surfactant

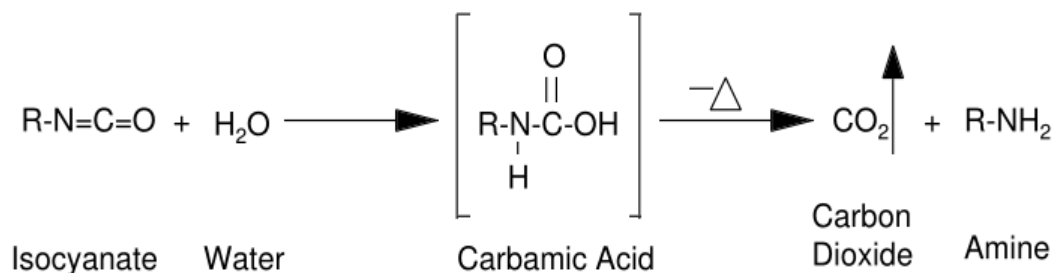
Surfactant decreases the interfacial tension between two immiscible compounds in which it is dissolved. They may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. The main use of surfactants in the polymerization reaction is to enhance the miscibility of the incompatible reactants, thereby promoting uniformity in polyurethane formation and also enhancing its property by improving its stability. The stability is mainly maintained by the ability of the surfactant in preventing the defoaming effect of the polymer formed. They also strengthen the foam, thereby controlling the closed cell feature and pore size of the foams.<sup>74-76</sup> It is also helpful in preventing the formation of blemishes such as pinholes and sink marks.<sup>77</sup> The surfactant should act within minutes in order to obtain effective foam stability and it defoam.<sup>74</sup> When there is no equilibrium between the foaming and surfactant ability it can lead to surface film rupture and defoaming. A variety of surfactants are available in the synthesis of polyurethane foam, which includes nonionic and cationic surfactants.<sup>78,79</sup> The usage of a low molecular weight surfactant in polyurethane synthesis may cause erode and

delaminate the polyurethane surface.<sup>80</sup> In this experiment, Tegostab B-8404, a silicone surfactant which offers foam stability in the synthesis of rigid polyurethane foam, was utilized. It was purchased from Evonik and used without modifications.

#### **2.1.5. Blowing agent**

The release of gas is a crucial part of foam formation. There are two types of gas formation methods that happens based on the type of blowing agent employed. Chemical gas formation and physical gas formation are those two kinds of gas formation methods involved in polyurethane foaming process with the use of chemical and physical blowing agent respectively. Water has been the most commonly used chemical blowing agent since the beginning polyurethane foams manufacturing. The other chemical blowing agent includes boric acid and enolizable organic compounds. Later, in the mid-90s, the usage of the physical blowing agent was adopted because of its ease information of low-density polyurethane foams. Some examples of physical blowing agents include C5-hydrocarbons, liquefied CO<sub>2</sub>, and azeotropes/halogenated azeotropes. But, use of physical blowing agent was later banned owing to CFC-11 content. After this ban, using only water as a blowing agent in the polyurethane foam synthesis was adopted.<sup>74</sup>

The mechanism of the foaming process involves two concurrent reactions which are the release of carbon dioxide gas and the formation of amine substituents. In this work, water was added as a blowing agent in preparing polyurethane foam. Water reacts with isocyanate groups to generate carbon dioxide and urea like illustrated below.<sup>81</sup>



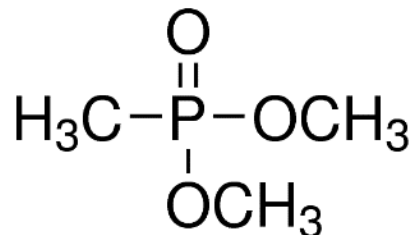
**Figure 2.6.** Blowing reaction with the use of chemical blowing agent i.e. water

#### 2.1.6. Fire retardant

The addition of fire retardant to the polyurethane formation reduces the combustibility of foam. There is an extensive choice of fire retardants available in the market which falls into two broad classifications-- reactive and non-reactive flame retardants. The solids flame retardants include graphite, melamine and/or aluminum trihydrate. The other products are phosphate, phosphonate, or phosphate containing compounds. The halogen fire retardants with bromine or chlorine act in the gas phase and interfere with free radical processing of combustion, while phosphorous retardants act in the solid phase and promote the formation of char, which acts as a barrier in the interface between fire and polymer.

In this study, an additive flame retardant, Dimethyl methyl phosphonate (DMMP) obtained from Sigma-Aldrich, USA was used. DMMP is used in the synthesis of flame retardant high phosphorous containing unsaturated polyester resin. DMMP has a vapor

pressure of <0.1 mmHg ( 20 °C), the refractive index of  $n_{20/D}$  1.413(lit.), a boiling point of 181 °C, and density of 1.145 g/mL at 25 °C.<sup>74</sup>

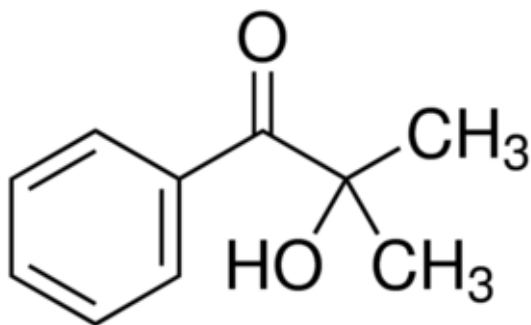


**Figure 2.7.** Chemical Structure of Dimethyl methyl phosphonate (DMMP)

#### 2.1.7. Photoinitiator

Photoinitiators are compounds that absorb UV light and initiate the polymerization reaction. When irradiated, these photoinitiators dissociate to reactive species, which assist in the initiation of the reaction. The polyurethane materials that are formed by the initiation of photoinitiation possess the advantage of manufacturing chemical resistant and tough polyurethane foams. Still, they face few hitches in applications like compatibility issues, discoloration, and bad odor.<sup>82</sup> The conversion and rate of photopolymerization are based on the amount of photoinitiators used and intensity of light irradiated, which is attributed to increased free radical generation.<sup>83,84</sup> Some of the most widely used photoinitiators in the polyurethane synthesis are hydroxycyclohexyl phenyl ketone and 2-hydroxyl-2-methyl-1- phenylpropane-1-one.<sup>85-87</sup>

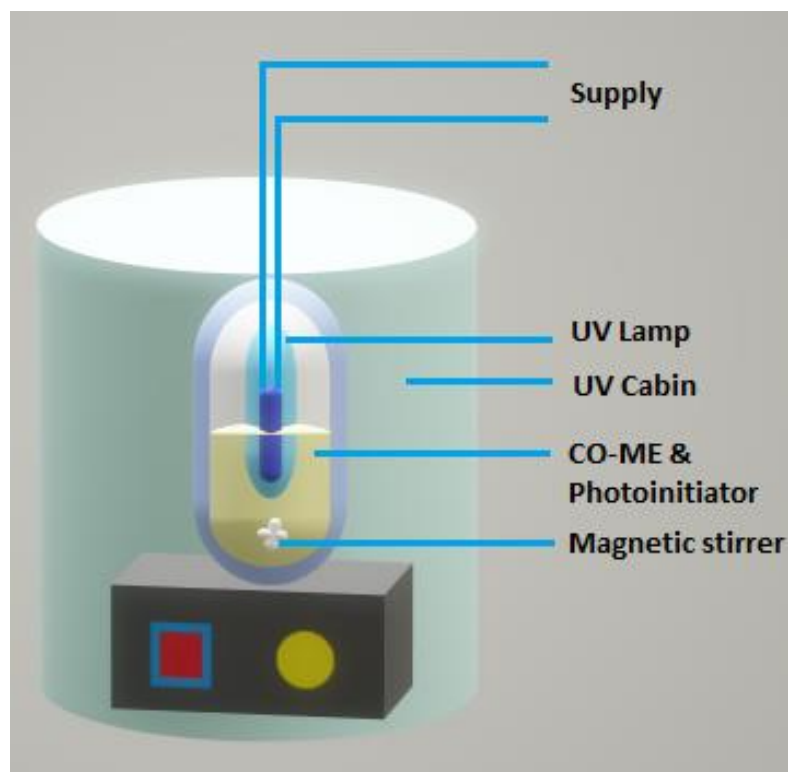
In this work, 2-hydroxy-2-methyl propiophenone was added as the photoinitiator. It was received from Sigma-Aldrich, USA. It has a refractive index of  $n_{20/D}$  1.533, boiling point of 102-103 °C/4 mmHg, and density of 1.077 g/mL at 25°C.



**Figure 2.8.** Chemical structure of 2-hydroxy-2-methyl propiophenone

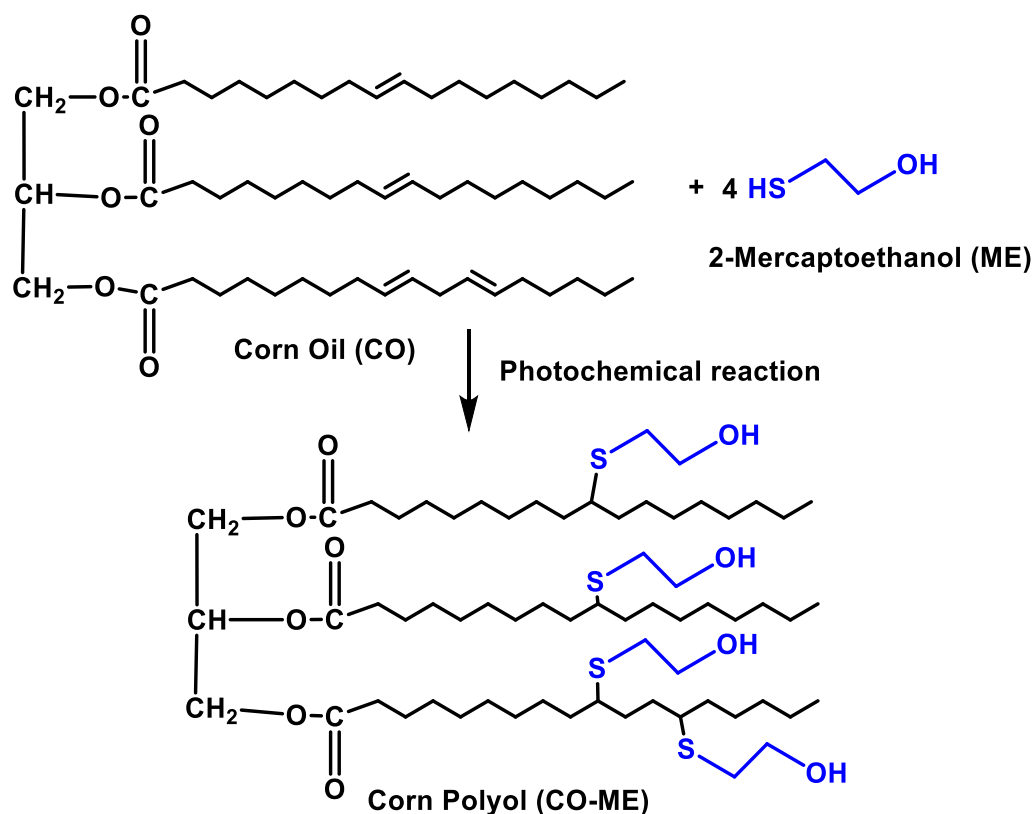
## 2.2. Synthesis of Corn Oil-Based Polyol

Corn oil-based polyol was obtained by the reaction between corn oil and 2-Mercaptoethanol using a thiol-ene reaction under UV irradiation as shown in **figure 2.9**. First, 200 g of corn oil (CO) was allowed to react with 149 g of 2-mercaptoethanol (ME) in a molar ratio of 1:4. Then, 2-hydroxy-2-methyl propiophenone (photoinitiator) of 2.5 wt% was added to this thiol-ene reaction, which was carried out at room temperature. The reaction was proceeded with vigorous stirring (using a magnetic stirrer at 300 rpm) for 6 h under ultraviolet radiation with irradiation intensity of 365 nm. By the end of the reaction, the excess unreacted 2-mercaptoethanol was removed by purification using a high vacuum.



**Figure 2.9.** Overall representation of the synthesis of polyol using thiol-ene reaction

Synthesis of corn oil-based polyol is a reaction between corn oil (CO) and 2-mercaptoethanol (ME) as represented in **figure 2.10**. Thiol group (-SH) in 2-mercaptoethanol (ME) gets dissociated to thiyl radical when exposed to UV radiation with the help of a photoinitiator. The reactive thiyl radical formed then reacts with the -C=C- of corn oil (CO) and leads to the formation of an intermediate carbon-centered species. This carbon-centered radical is transferred to another thiol group to form another reactive thiyl radical to propagate another such reaction. Once the carbon-centered radical has been transferred from the intermediate, we obtain corn polyol (CO-ME) eventually as given in the given **figure 2.11**.



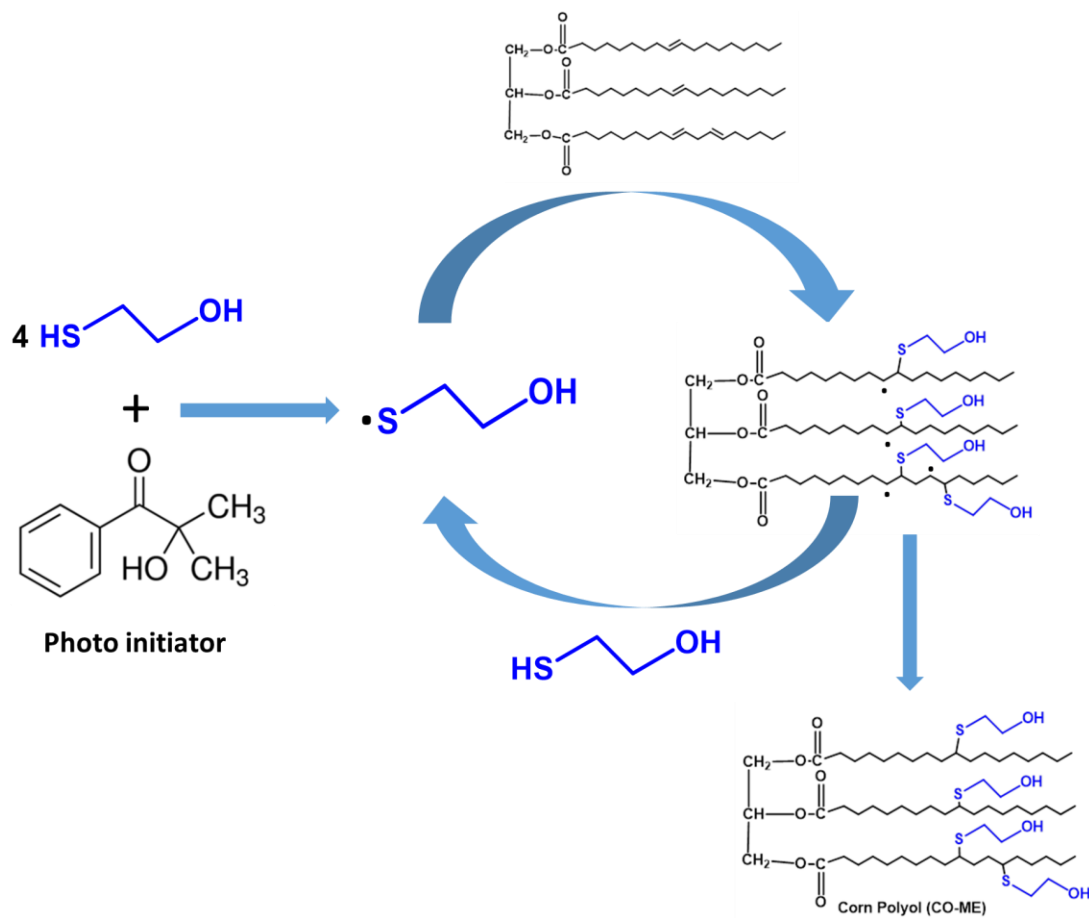
**Figure 2.10.** The chemical reaction involving the synthesis of CO-ME

### 2.3. Characterization of Polyol

The synthesized CO-ME polyol was characterized using the following methods:

#### 2.3.1. Phthalic anhydride/pyridine (PAP) method:

This method is used to determine the number of hydroxyl group present in the synthesized polyol. Since the hydroxyl group is involved to react with the isocyanate group, it is essential to measure the OH content of the polyol before initiating the synthesis of polyurethane foams. This PAP method uses the standard ASTM D 4274 in analyzing the hydroxyl number.



**Figure 2.11.** The mechanism involved in the thiol-ene synthesis of CO-ME polyol

The OH number determining the volume was determined before ( $v_o$ ) and after titration ( $v$ ) of the sample in hydroxyl reagent using 1.0 N NaOH solution. These measured volumes are then applied in the below equation.

$$\text{OH\#} = \frac{56.11 \times 1.00 \times (v_o - v)}{w} \text{ (mg KOH/g) ..... (1)}$$

To prepare the hydroxyl reagent, 148g of phthalic anhydride and 4g of imidazole was dissolved in 1000mL of pyridine. 10mL of this prepared reagent with 0.4mg of the



sample was added in a closed bottle and allowed to sit in an oven at 100 °C. The mixture was shaken every 15 minutes and after 70 mins it was allowed to cool down. To this solution, 10mL of water and 20mL isopropanol of HPLC grade was added along with 3-5 drops of phenolphthalein indicator and stirred. This initial volume was recorded as  $v_0$ . This solution was titrated with 1.0 N of NaOH solution until the color of the solution turned pink, and the volume was measured as  $v$ . These two volumes,  $v_0$  and  $v$ , were incorporated in the equation to calculate the hydroxyl number.

### **2.3.2. Viscosity:**

Viscosity is a property of the material which defines the flow of the material against any resistance. Measurement of viscosity is considered to be very crucial because it determines the property of the polymer synthesized. Viscosity should be measured over a range of shear rates or stresses. In large scale, the viscosity should be high at low shear rates to prevent the collapse of the material and low at high shear rates to be easily treated during manufacturing. For this experiment, the viscosity of the polyol AR 2000 dynamic stress rheometer (TA Instruments, USA) at 25 °C with a linear increase in shear stress from 1 to 2000 Pa was utilized. This rheometer has a cone-plate at an angle between 2° and a cone diameter of about 25mm. High viscosity directly correlates to a high molecular weight of the polyol. Low viscosity enables the thorough mixing of the polyol to the polymeric matrix.

### 2.3.3. Acid value:

The acid value is the measure of potassium hydroxide that has been used in the neutralization of 1g of the sample. This is the direct determination of the number of carboxylic acid group in the compound. IUPAC2.201 was used as the standard indicator method in determining the acid value of the synthesized polyol. For this measurement, 3g of the sample was taken in a 125mL conical flask. This sample was dissolved in a solvent mixture of 30mL. 500mL of isopropanol; 500mL of toluene and 3mL of phenolphthalein indicator (10 g/L) was used in the preparation of the solvent mixture. This solution with the sample in the conical flask was titrated against 0.1 N KOH until the color of the solution turned pink. The volume of the solution after the endpoint was measured and applied in the below equation to obtain the acid value.

$$\text{Acid Value} = \frac{56.11 \times 0.100 \times V}{w} \text{ (mg KOH/g) ..... (2)}$$

### 2.3.4. Fourier Transform Infrared Spectroscopy (FT-IR):

FT-IR is an ideal infrared spectroscopy method. When IR radiation passes through the sample, it absorbs energy and represents a spectral fingerprint of the molecular structure of the sample. Thereby, changes in the peak representing the change in the functional group during the proceeding of the reaction could be observed. The FT-IR spectrum of the polyol was obtained using a Shimadzu IR Affinity-1 spectrophotometer at room temperature.

### **2.3.5. Gel Permeation Chromatography**

Gel Permeation Chromatography also is known as size exclusion chromatography and is often used in the analysis of the molecular weight of the polymer. In this experiment, this method was used in the determination of polyol molecular weight using a system by Waters (Milford, MA, USA). The system consists 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 maintained at 1 ml/ min at 30 °C. The solvent tetrahydrofuran was used as eluent and the rate of the eluent was sustained at 1mL/min at 30 °C.

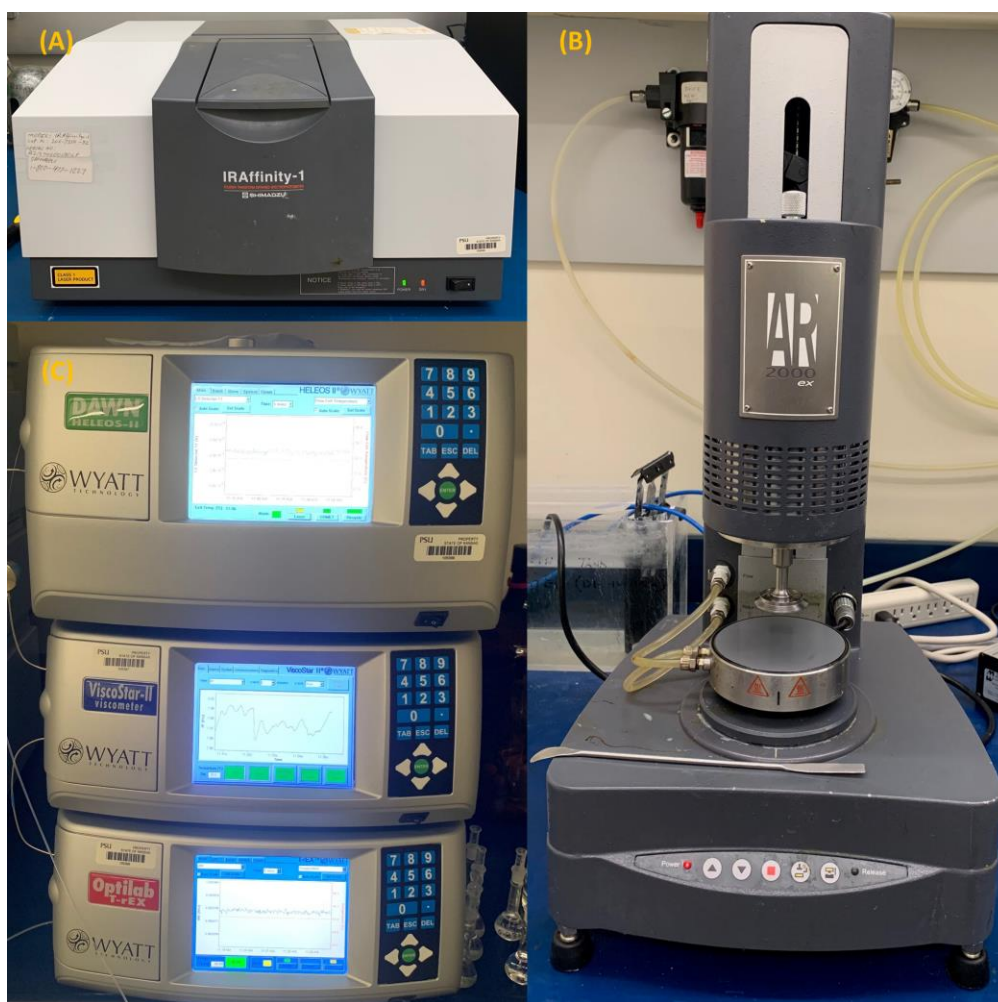
### **2.3.6. $^{13}\text{C}$ Nuclear Magnetic Resonance:**

A Bruker DPX-300 spectrometer (Billerica, MA, USA) was used to acquire the  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance spectra. Deuterated chloroform  $\text{CDCl}_3$  was used as a solvent and tetramethyl silane as internal reference. The experiments were carried out at 300 MHz and eight scans for proton NMR at room temperature.

## **2.4. Preparation of Flame Retardant Rigid Polyurethane Foam**

Synthesized polyol, isocyanate, surfactant, catalyst, and water were used in the preparation of rigid polyurethane foam. Different compositions of phosphorus were used in synthesis as shown in Table 2.1. Different compositions of all the ingredients and stirred vigorously (3,000 rpm). After thorough mixing of the ingredients into a homogenous

mixture, MDI of 32.07 g was added to it and stirred again at 3,000 rpm to form a polyurethane foam. As per the percent of phosphorous added in the preparation of each foam, they were designated as P-0 wt%, P-0.26 wt%, P-0.51 wt%, P-1 wt%, P-1.5 wt%, P-1.9 wt% and P-2.4 wt%. These foams were then allowed to rest at room temperature until the growth stopped and it formed into a complete rigid foam. This was followed by a curing process of about one week where the foam sat at room temperature.



**Figure 2.12.** Images of (A) Shimadzu IR Affinity-1 spectrophotometer, (B) AR 2000 dynamic stress rheometer, and (C) Gel permeation chromatography

**Table 2.1.** Formulation for preparation of phosphorus-containing polyurethane foams.

Compounds	P-0	P-0.26	P-0.51	P-1	P-1.5	P-1.9	P-2.4
	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Jeffol-360	10	10	10	10	10	10	10
CO-ME	10	10	10	10	10	10	10
DMMP	0	0.5	1	2	3	4	3
Tegostab B-8404	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Niax-A1	0.14	0.14	0.14	0.14	0.14	0.14	0.14
T-12	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Water	0.8	0.8	0.8	0.8	0.8	0.8	0.8

All the weights are in grams.

## 2.5. Characterization of Rigid Polyurethane Foams

After the foam cured, it was cut into cylindrical shapes of 45 mm × 30 mm (diameter × height) for further characterization. Various characterization techniques were used as given below:

### 2.5.1. Apparent density

The apparent density of the foams was measured according to the standard ASTM D 1622. It is essential for the foam density to fall between the range of 30 to 50 kg/m<sup>3</sup> as per the industrial standards. Apparent density was measured as an average between the

densities of the top and middle portion of the foam. To determine this, a cylindrical foam of 45mm x 30mm (diameter x height) was cut and weighted.

#### **2.5.2. Closed-cell content**

The closed-cell content of the foams was measured using Ultrapycnometer (Ultrafoam 1000) according to ASTM D 285. It is an essential characteristic to confirm the thermal insulation capability of the foam. The higher the closed cell content the higher the thermal insulation capacity of the foam.

#### **2.5.3. Compression test**

The compressive strength at 10 % strain was determined by using a Q-Test 2-tensile machine (MTS, USA) according to ASTM D 1621. It is an important parameter to be determined to ensure the mechanical strength of the foam. For the compression test, the foam samples were cut in the dimension of 50 mm × 50 mm × 25 mm (length × width × height). The compressive force was applied at a strain rate of 30 mm/min, parallel to the direction of the foam.

#### **2.5.4. Thermogravimetric analysis (TGA)**

TGA Q500 was used to analyze the thermal behavior of the foams. The thermogravimetric analysis was performed under a nitrogen atmosphere by heating the foams from room temperature to 600 °C with a heating rate of 10 °C/min. Thermal

stability was ensured by measuring the weight loss at the respective temperature, thereby the maximum probable temperature the foam could withstand was found.

#### **2.5.5. Horizontal burning test**

It is very essential to study the flame retardancy property used in the polyurethane synthesis. Therefore, the horizontal burning test of cellular polymeric material was performed using the standard ASTM D 4986-98. This test was performed by burning the sample in the flame for almost 10s. The standard sample size of 150 mm length, 50 mm width, and 12.5 height was used for the test. Burning time was recorded and weight difference before and after exposing the sample to flame was noted.

#### **2.5.6. Cone calorimetry**

To understand the amount of heat and smoke released during the combustion in a real-time scenario cone calorimetry analysis was performed. Total heat release and heat release rate of the samples were analyzed. The test was performed by complying to the ISO 5560 standard which recommends cutting the test specimen into the size of 100 mm × 100 mm × 25 mm (length × width × height) and exposing it to the external flux of 35kW/m<sup>2</sup>. This combustion test was performed using a standard cone calorimeter (fire testing technology).

### 2.5.7. Scanning Electron Microscopy

Cell morphology such as microstructural and cell size distribution characteristics of the foam was detected using a Phenom G2 Pro scanning electron microscope (SEM) (Netherlands). All the foam samples were gold sputtered before imaging to avoid the charging effect during imaging.



**Figure 2.13.** Images of (A) Ultrapycnometer, Ultrafoam 1000, (B) Q-Test 2-tensile machine, (C) Phenom G2 Pro scanning electron microscope, (D) TGA Q500, (E) Horizontal burning test instrument, (F) Cone calorimeter



## **CHAPTER III**

### **RESULTS AND DISCUSSION**

#### **3.1. Properties of Polyol**

The physical characteristics of the polyol such as acid value, hydroxyl number, viscosity, and its structural assembly are important to determine because those characteristics decide the reactivity of polyol with the isocyanate group. The chemical assembly of the polyol was determined using FT-IR, GPC, and NMR. GPC also determines the molecular weight of the compound. The details of the methods used for determining the property of the polyol is described below.

##### **3.1.1. Acid value**

The acid value is used for determining the number of potassium hydroxide (KOH) in milligrams used to neutralize one gram of polyol. The important reason to measure the acid value is that it may interfere in the gelling of the reaction by decreasing the catalyst activity. This is mainly because of the acid-base neutralization it may cause. Therefore, the lower the acid value, the better the reactivity of the compounds during the foaming process.

The synthesized corn oil-based polyol (CO-ME) showed an acid value of 1.77 mg KOH/g, which shows that the reactivity of the polyol was appropriate due to its low acid value.

### **3.1.2. Hydroxyl Number**

The hydroxyl number is to determine the number of hydroxyl group present in the polyol for the reactivity with the isocyanate. It is the measure of the number of milligrams of KOH which is chemically equivalent to the number of hydroxyl functional groups per unit weight of the polyol. The higher the hydroxyl number, the higher the reactivity of the polyol during the foaming process to make polyurethanes.

The synthesized corn oil-based polyol (CO-ME) showed a hydroxyl number of 176 mg KOH/g. Since the hydroxyl number was higher it shows that this synthesized corn-oil based polyol is the right candidate to be used in the preparation of polyurethane foam.

### **3.1.3. Viscosity**

Viscosity is the measure of the resistance of a substance to the force applied. This is used to determine the intermolecular strength between the molecules in the polyol. If the viscosity is found to be higher, that is a direct indicator that the polyol has higher molecular weight with the high number of functional groups. This helps to enhance the reactivity of the polyol with the isocyanate group but the homogenous mixing of the polyol might not be attained.

In this experiment, a low viscosity of about 1.33 Pa.s. was found, which allowed for proper mixing of the polyol in the reaction mixture as well as it allowed ease during the processing of the polyurethane foam.

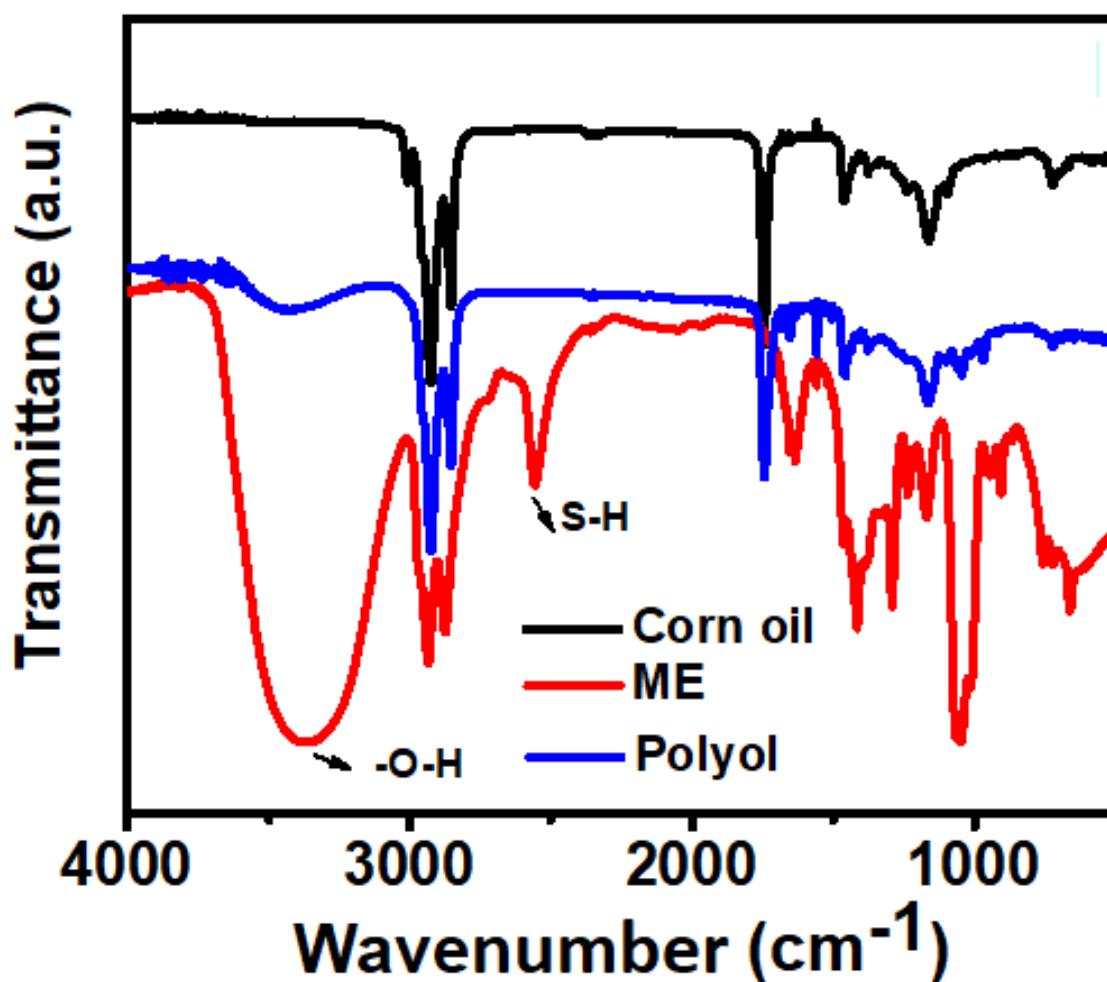
#### **3.1.4. Fourier Transform Infrared Spectroscopy (FT-IR spectra)**

The structural characteristics of the synthesized polyol were studied using FT-IR spectra, which aids understanding of the reaction mechanism by presenting the spectrum of the raw materials and the final polyol as shown in **figure 3.1**. The peak intensity around  $3,432\text{ cm}^{-1}$  in the polyol suggests the presence of hydroxyl groups (-OH), which is the most important property of polyol to react with isocyanate in forming a urethane. The peak around  $2551\text{ cm}^{-1}$  in **figure 3.1** is the characteristic peak of S-H stretching of 2-mercaptoethanol. The disappearance of this peak in the FT-IR spectrum of the polyol suggests that 2-mercaptoethanol has been utilized for the polyol synthesis, and thus indicates that the reaction has been carried out. All the FT-IR spectrum peaks were close to the previous studies.<sup>88,89</sup> Thus, from the FT-IR analysis, we conclude that the reaction was completed as desired.

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

Gel permeation chromatography was used to determine the relative molecular weight of the polymer by separating them based on their size. The compounds with higher molecular weight elute first since they have less retention time in the porous beads

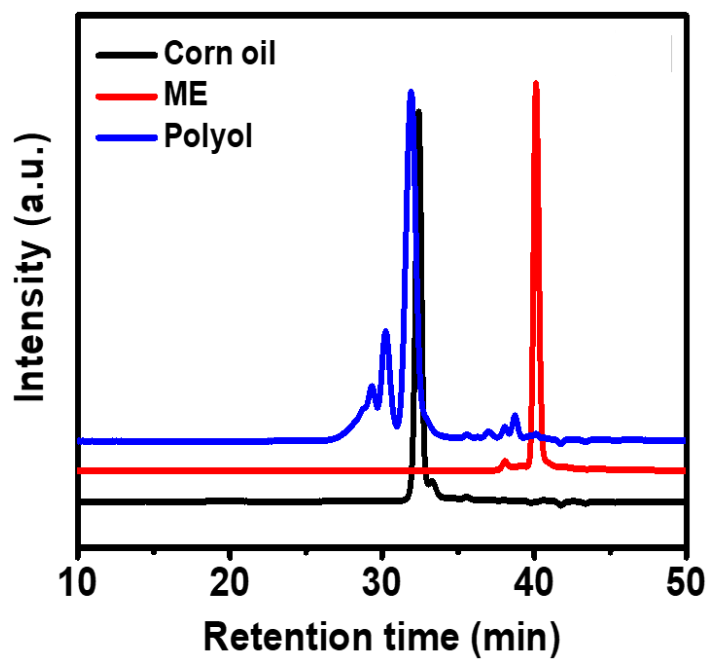
packed in the column. This is followed by elution of the low molecular weight substances, which possess high retention time because they are trapped in the pores easily, which assists in examining the proceedings of the reaction by the changes observed in the molecular weight of the reacting species as the reaction proceeds until the final polyol was obtained.



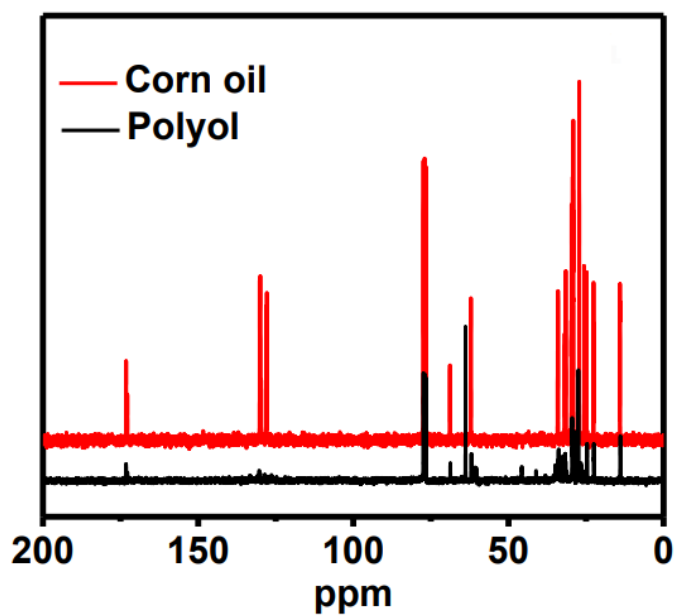
**Figure 3.1.** FT-IR graph of corn oil, 2-mercaptoethanol, and corn oil-based polyol (CO-ME polyol)

As shown in **figure 3.2**, the reactants for polyol synthesis such as corn oil and 2-mercaptoethanol were observed to have a retention time of 33 minutes and 40.5 minutes, respectively. The retention time of polyol was 30 minutes, which is comparatively shorter than its reactants' retention time. The peak observed around 32 minutes in the polyol is probably because of a few unreacted double bonds which are present in the inner structure of the corn oil. Since, there was no retention peak of 2-mercaptoethanol in the polyol, it suggests that all 2-mercaptoethanol was utilized for the formation of polyol, and the reaction proceeded. It also suggests that the final polyol does not possess any impurities of the reactants.

The synthesized polyol was further characterized using proton and carbon NMR. The disappearance of the signal around 5.4 ppm corresponding to =C-H confirms the attachment of the thiol group to the double bond.  $^{13}\text{C}$  NMR of corn oil and polyol is shown in **figure 3.3**. Corn oil shows a signal around 128 ppm which corresponds to C=C. The disappearance of this peak in polyol confirms the thiol-ene reaction.



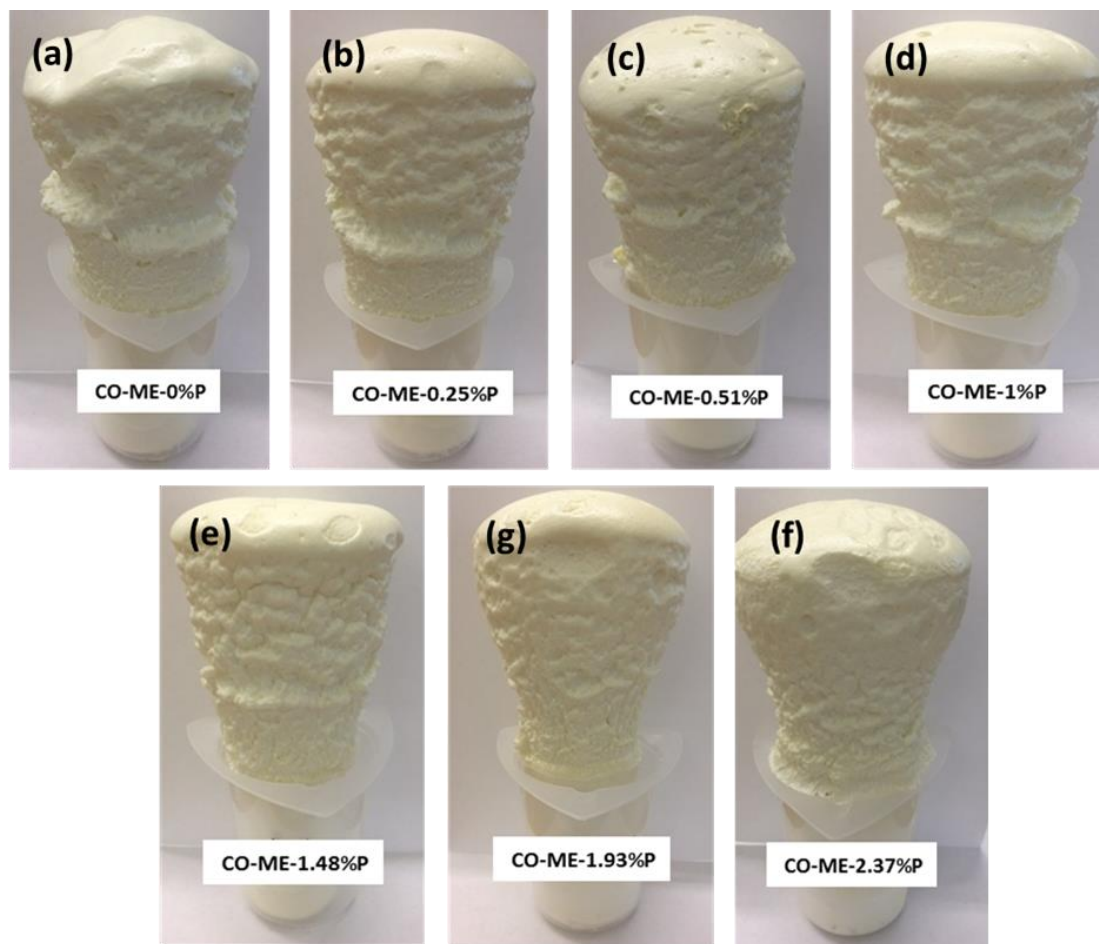
**Figure 3.2.** GPC graph of corn oil, 2-mercaptoethanol, and corn oil-based polyol (CO-ME polyol)



**Figure 3.3.** <sup>13</sup>C NMR of corn oil, 2-mercaptoethanol, and corn oil-based polyol (CO-ME polyol)

### 3.2. Properties of Corn Oil-Based Polyurethane Foams

Corn oil-based polyol, thus synthesized with the most desired physical characteristics was used in the preparation of polyurethane foams with different proportion of DMMP. The visual images of the synthesized foams can be seen in **figure 3.4**. All the foams showed uniform growth and well-defined structure suitable for industrial application.



**Figure 3.4.** Photographs of the synthesized polyurethane foams with various concentration of DMMP (a) 0%P, (b) 0.25%P, (c) 0.51%P, (d) 1%P, (e) 1.48%P, (g) 1.93%P, and 2.37%P, as a flame-retardant additive

Further, the foam was examined for its physical characteristics such as apparent density, closed-cell structure, compression strength, microstructural and cell size distribution, thermogravimetric analysis, horizontal burning test, and combustion test for understanding their physical, mechanical, and thermal strength. These tests performed on the foam are described in detail below.

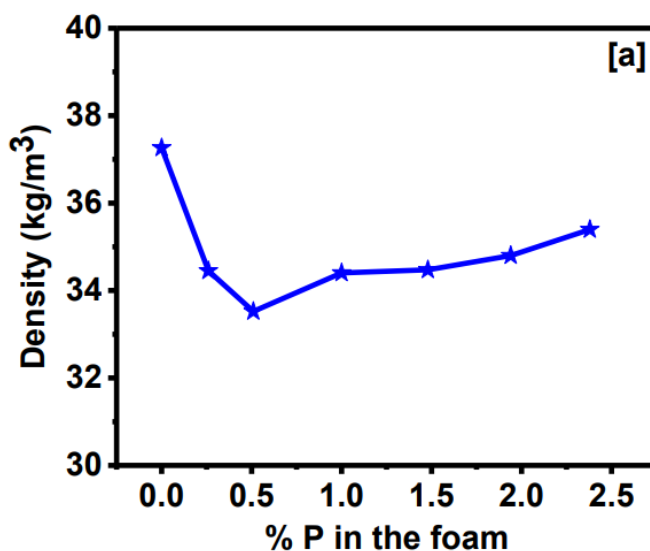
### **3.2.1. Apparent density**

The measurement of apparent density is essential because it is the direct indicator of the physical and the mechanical strength of the foam. Moreover, the density of the polyurethane foam also decides its application. The industrial standard density for the purpose of commercial usage is accepted from the range of 30 to 50 kg/m<sup>3</sup>.<sup>90</sup> The density was calculated using the average density from cylindrical and square-shaped test specimen, which is shown in **Figure 3.5**. The highest density was observed in foams with 0% DMMP, whereas the lowest density was observed in the foam with 0.51% DMMP. The density of all preparations of foam with varying percentages of DMMP was between the range of 33 to 37 kg/m<sup>3</sup>, which proves that the addition of DMMP did not significantly change the density of the foams. The average density of 35 kg/m<sup>3</sup> shows that the tested foams maintained the industrial weight standard, enabling them to be used in the preparation of commercial products.



### 3.2.2. Closed cell structure

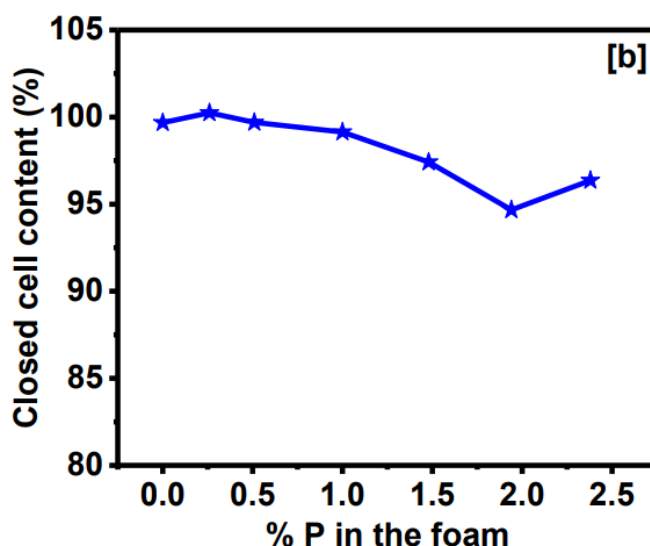
Closed cell content is one more exam done to access the physical property of polyurethane foam. It helps to determine the thermal insulation capability of the foam. For a foam to possess excellent thermal stability, it is necessary for the foam to possess closed cell content,<sup>89</sup> which forms a rigid polyurethane foam with low thermo-conductivity. The percentage of closed cell content of all the synthesized polyurethane foams is depicted in **figure 3.6**. The foam with maximum closed cell content is the one with 0% DMMP whereas the foam with least closed cell content is the foam with 2.37%



**Figure 3.5.** Density of corn oil-based polyurethane foams

DMMP. The range of closed cell content between which all the foams fall is 95-100%. This shows that, irrespective of the percentage of DMMP present, all foams showed higher than 95% closed cell content. This indicates that they all possess well defined rigid foam

properties.<sup>91,92</sup> In addition to this, it provides high thermal strength by preventing rapid heat transfer between the cells. The air between these cells acts as an insulator thereby restricting the easy access to oxygen while burning to lead to improved insulation property. The obtained data from the closed cell content showed all the foams with highest closed cell content ensuring outstanding thermal resistance.

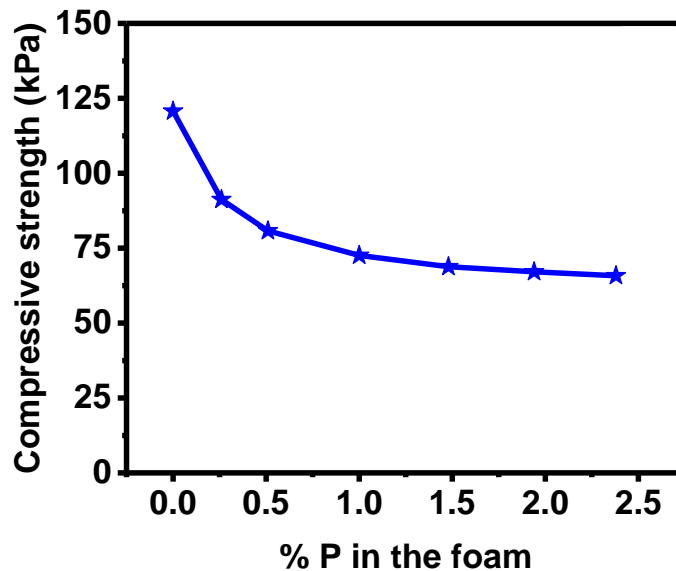


**Figure 3.6.** Closed cell content of corn oil-based polyurethane foams

### 3.2.3. Compression strength

The compression test was performed to understand the mechanical property of the foam with the addition of DMMP. The compression strength study was performed for all the foams containing a different concentration of phosphorus and are shown in **figure 3.7**. It is evident that there is a gradual depression in the compression strength as the percent of the DMMP increases. As visible in the **figure 3.7**, the compression strength of

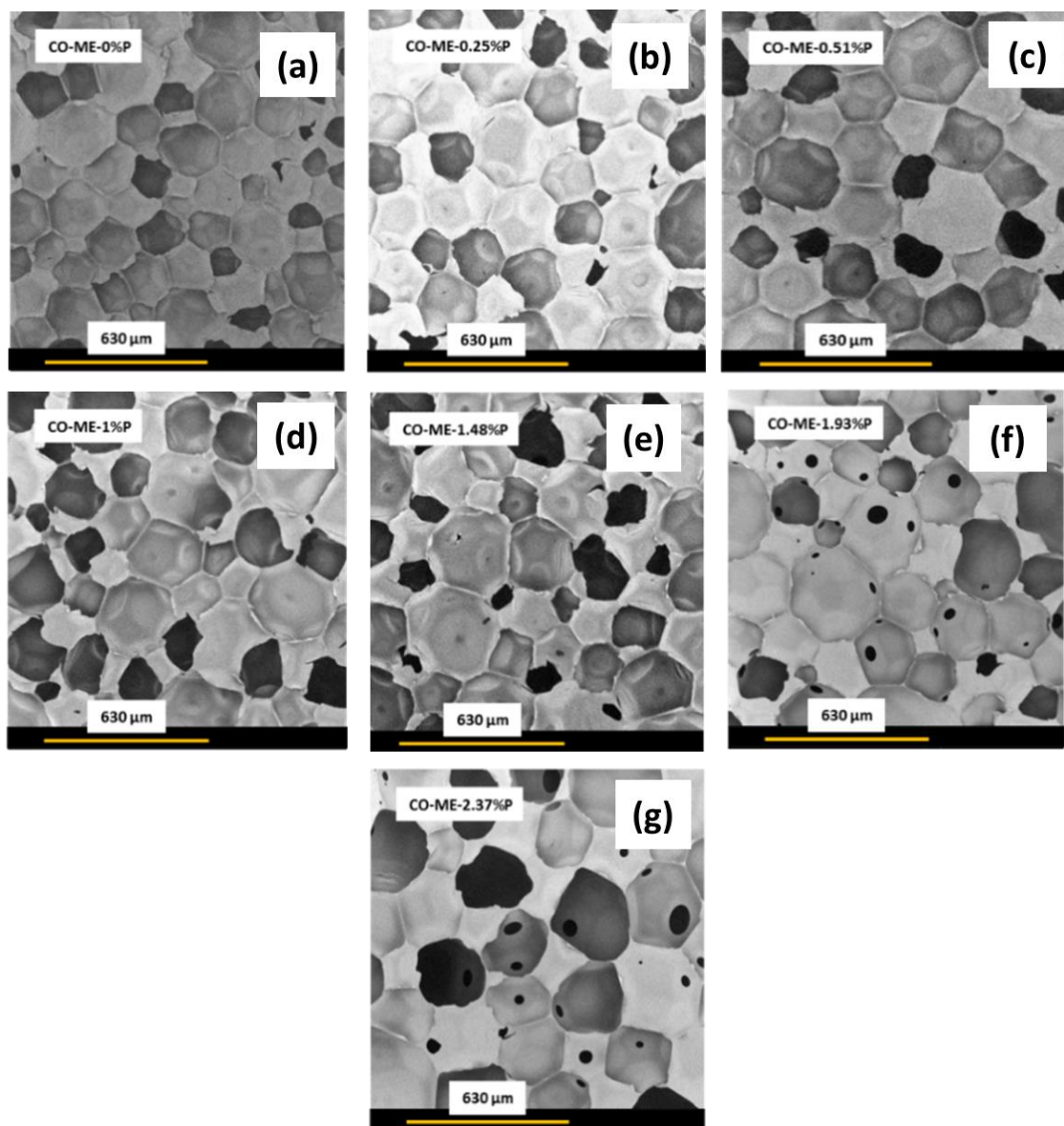
the foam without DMMP is approximately 120 kPa, and with an addition of 0.5% DMMP, the compression strength dropped to 81 kPa, which is almost a 32.5% decrease. The lowest compression strength is observed in the foam with the highest percent of DMMP used. The overall compression strength of all foams lies between the ranges of 70 to 123 kPa. The detected decline in the mechanical strength is possibly related to the inconsistency of DMMP within the reaction mixture. This incompatibility could be due to the plasticizing effect of DMMP resulting in an increased cellular size and a decrease in compressive properties. Similar results were witnessed in other studies.<sup>93</sup> In this experiment, it was found presented that the addition of DMMP decreases the mechanical strength of the polyurethane foam.



**Figure 3.7.** Compression strength of corn oil-based polyurethane foams

#### 3.2.4. Microstructural and cell size distribution

To find the microstructural and cell size distribution within the foam, a scanning electron microscope (SEM) was utilized. SEM images of all the foams with different concentrations of DMMP were performed and are represented in **figure 3.8**. As per **figure 3.8 a**, it was observed that the foams without DMMP show an average cell size of about 250  $\mu\text{m}$  with a uniform circular shape. As the concentration of DMMP increased, a slight increase in cell size was observed. The cell size increased up to 320  $\mu\text{m}$  as shown in **figure 3.8 (f, g)** with 1.93 and 2.37% DMMP, respectively. These effects are comparable to the results in previous studies.<sup>89,94</sup> The addition of DMMP showed a slight alteration in the uniformity of the circular shape of the foams. This irregularity in cell shape is clearly visible in the foams with 1.93 and 2.37% DMMP as in **figure 3.8 (f, g)**. In spite of the cellular structure, all the foams maintained promising physicomechanical characteristics. These SEM images showing tremendous density which further confirms the previous results for high compression strength and closed cell content.



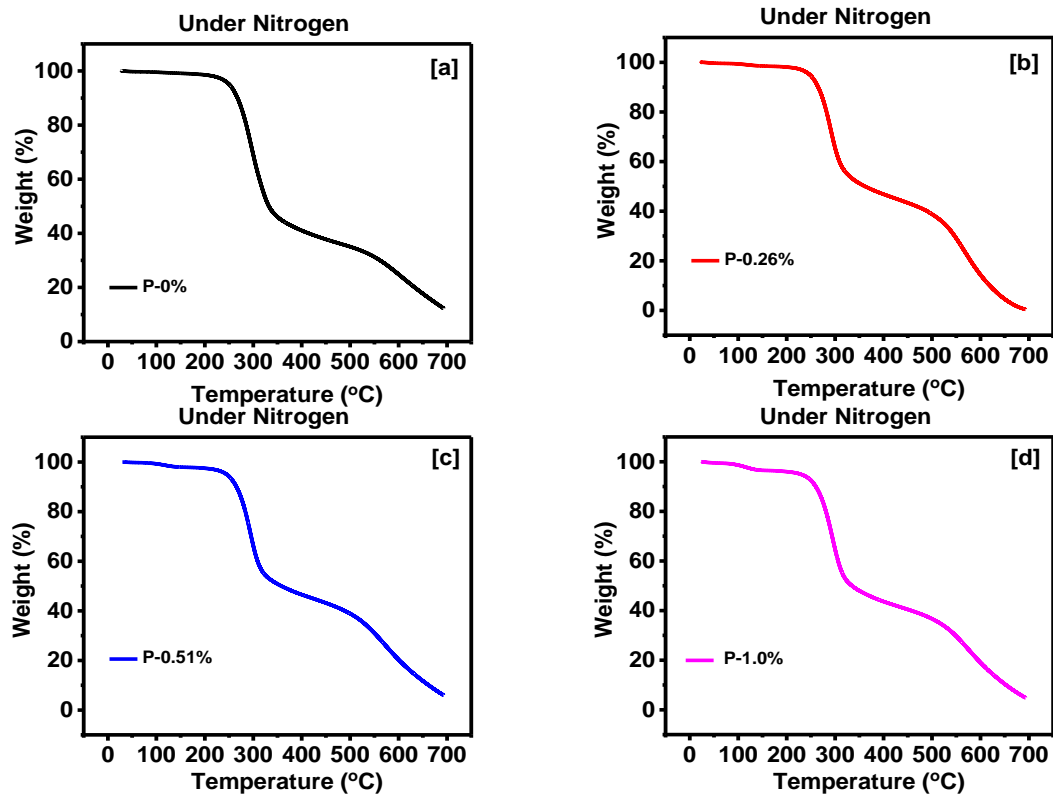
**Figure 3.8.** SEM images of the polyurethane foams containing various amount of DMMP (a) 0%P, (b) 0.25%P, (c) 0.51%P, (d) 1%P, (e) 1.48%P, (f) 1.93%P, and (g) 2.37%P

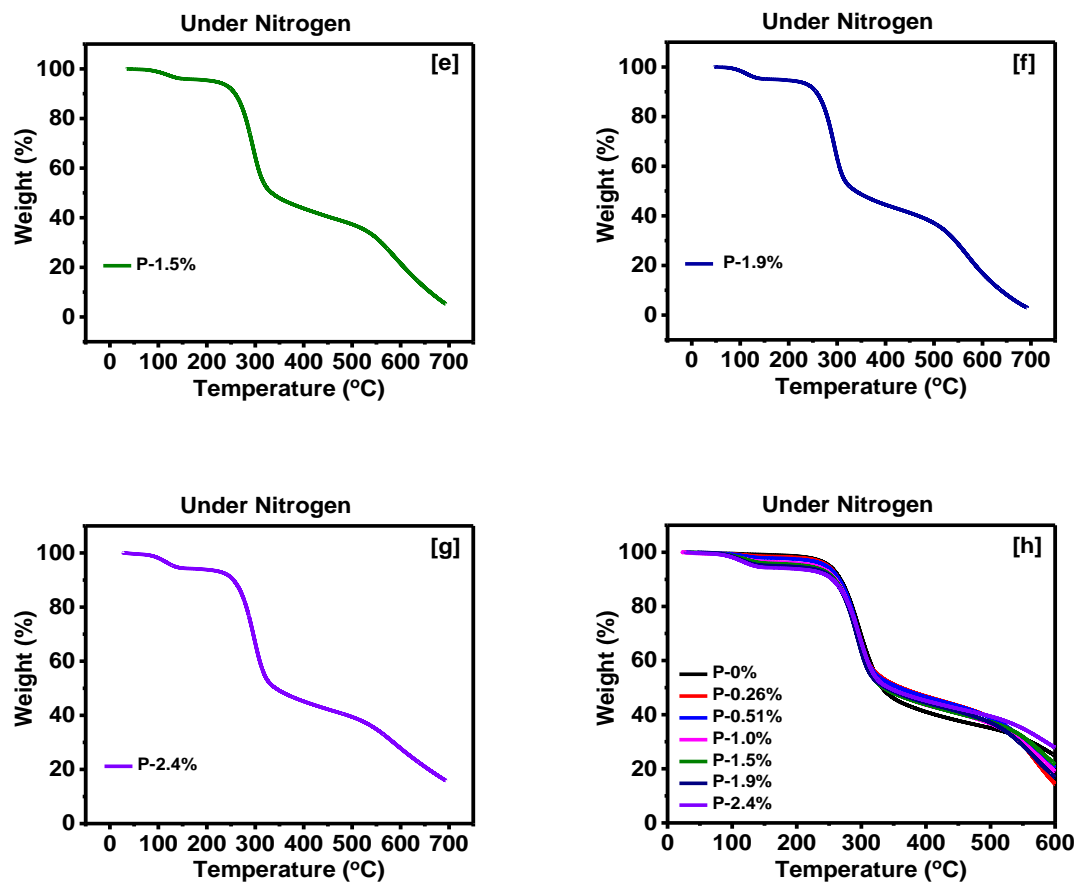
### 3.2.5. Thermogravimetric analyses (TGA)

Thermal properties of polyurethane foams were studied using thermogravimetric analyses (TGA) and derivative thermogravimetric analyses (DTGA) to understand the thermal stability by learning the transition behavior of the foams. The weight loss with respect to the increased temperature can be observed in **figure 3.9**.

Polyurethane foams without DMMP showed three transitions in the temperature vs weight curve obtained from the TGA. This is owing to decomposition of the main chain, pyrolysis of polyol and isocyanate, and degradation of the char layer. As given in **figure 3.9**, the transitions were observed around the temperature of 325, 360 and 475°C. Similar results were also discussed in other similar studies.<sup>95,96</sup> However, with the addition of DMMP in the polyurethane synthesis, there was an extra transition observed. There was an early degradation of the foams that was observed, with the transition being observed around the temperatures of 100-150°C (as in **figure 3.9 c-g**) corresponding to volatilization of DMMP.<sup>94</sup> This peak increases with the increase in DMMP concentration which actually improves the char stability. This is more evident in the later decomposition peak around 360°C and 475°C. These outcomes were comparable to other studies.<sup>97-99</sup> The volatilization of DMMP results in decomposition of less stable -P-O-C- a bond which further assists in the formation of a char layer that inhibits fire.<sup>100</sup> **Figure 3.9** shows improvement in final char content of the foams as the amount of DMMP was raised, suggesting formation of stable char that could act as a barrier for improving flame retardancy. This could be correlated with improved flame retardancy observed in the

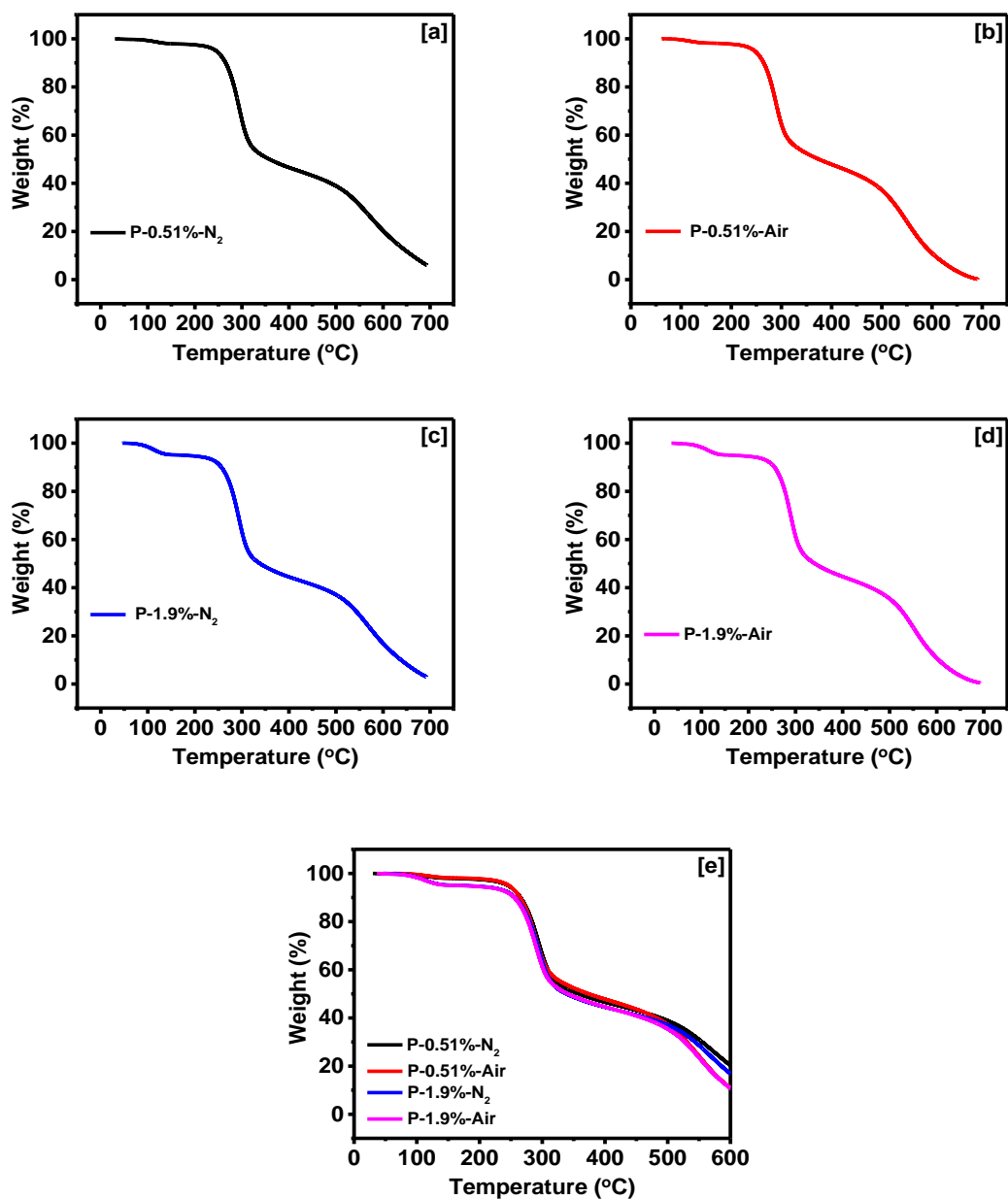
horizontal burning test and combustion test discussed in the later section. The thermal behavior of two samples containing 0.51% and 1.9% of phosphorus was compared in nitrogen and air atmosphere. As in seen in **figure 3.10**, the thermal decomposition behavior in nitrogen and air atmosphere is similar, with little difference in residual content at high temperature.





**Figure 3.9.** TGA curves of polyurethane foams with different amount of DMMP (a) 0%P, (b) 0.25%P, (c) 0.51%P, (d) 1%P, (e) 1.48%P, (f) 1.93%P, and (g) 2.37%P. The gathered transition of all the foams is represented in (h)





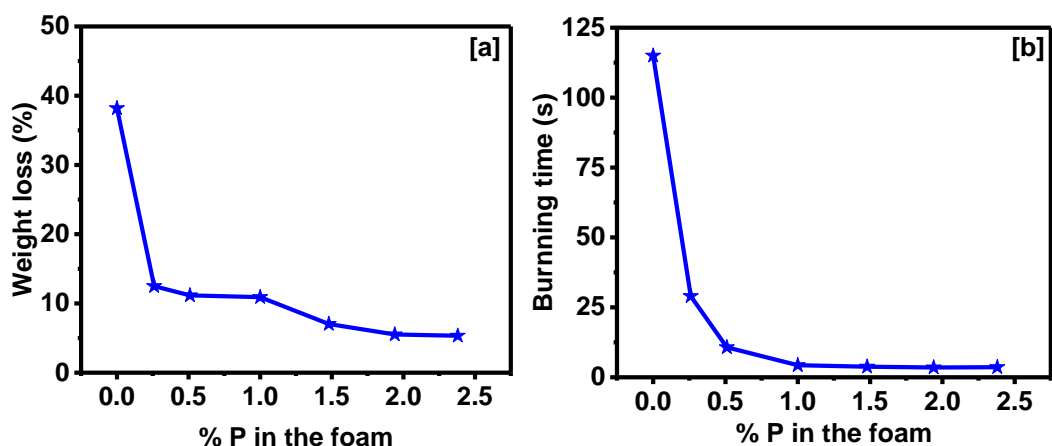
**Figure 3.10.** TGA for polyurethane foams in nitrogen and air environment of 0.51%P (a) & (b) and 1.9%P (c) & (d) are represented, respectively. The gathered transition is represented in (e)

### 3.2.6. Horizontal burning test

The flame-retardant properties of the foams were studied using a horizontal burning test as per ASTM D 4986-98. The reason this test was performed was to determine the on-field fire retardancy characteristics of the foam. **Figure 3.11** shows the details of the overall test results of performing the horizontal burning test. This test was performed by holding the foams horizontally as they were subjected to a continuous flame for 10 s. Burning time along with respective weight loss were recorded and shown **figure 3.11 (a,b)**. The foams with no DMMP showed a burning time of 115 s and a weight loss of 38 wt%. There was a significant drop in the burning test and weight loss with an addition of 0.26% of DMMP 13 wt% weight loss and 28 s. The maximum weight loss was observed in the foam with a 1.94 wt% of DMMP, which showed 5.5 wt% weight loss with 3.5 s burning time. The burning time of foams was almost constant with the addition of DMMP over 1.5 wt% of DMMP as shown in **figure 3.11 (b)**. The least weight loss was observed with the foam prepared with the DMMP of 2.4 wt%. Ranaweera et al. synthesized rigid polyurethane foams using limonene polyol and studied flame retardant properties by addition of different amounts of DMMP.<sup>94</sup> The foams containing 6 wt% of DMMP showed the lowest burning time of 19 s. Similarly, in our previous report, we observed that 1.7 wt %P foams prepared using DMMP as a flame retardant showed burning time and weight loss of ~5 s and ~5 wt%, respectively.<sup>89</sup> However, the current study shows improved flame retardant properties as compared to previous results. This further proves that the flame

retardancy capacity of the corn-oil based polyol synthesized polyurethane foam is highly resistant to fire.

The optical images of the burnt foams with different concentrations of phosphorus within the foams is shown in **figure 3.12**. The improved flame retardancy could be due to the two-way active contribution of DMMP including a condensed and vapor phase.<sup>89</sup> Firstly, the formation of the intumescent barrier char layer over the surface of the foams prevents the combustible media, oxygen and thermal energy to propagate. Secondly, radical phosphorus species such as  $\text{PO}^*$ ,  $\text{PO}_2^*$  and  $\text{OHPO}^*$  help in inhibition of  $\text{H}^*$  and  $\text{OH}^*$ .<sup>101</sup> Thus, with the addition of small amount of DMMP, efficient flame retardancy can be achieved.



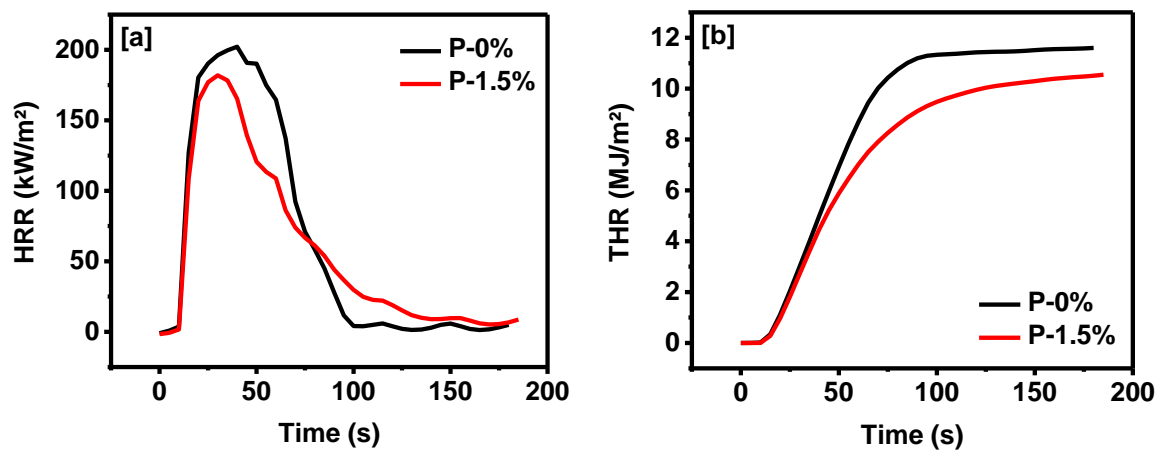
**Figure 3.11.** (a) Percentage weight loss after burning and (b) burning time of corn oil-based polyurethane foams



**Figure 3.12.** Photographs of the foams before and after burning test of corn oil-based polyurethane foams

### 3.2.7. Combustion test

The combustion test was performed using a cone calorimeter to study the flame-retardant characteristics of the foams in detail. A control foam and foam containing 1.5 wt% phosphorus were exposed to the flame test. **Figure 3.13 (a,b)** shows the heat release rate (HRR) and total heat release (THR) behavior of the foams. Total heat release for the foam containing 1.5% phosphorous showed a 21% reduction in THR, compared to the control foam. There was also a notable decrease in the HRR from 200 kW/m<sup>2</sup> to 150kW/m<sup>2</sup> with an addition of 1.5%P. This proves that the addition of phosphorus has a significant impact in influencing the flame retardancy of the foams. The major reason was found to be the protective char formed due to the addition of DMMP. This has been the foremost reason for the improvement of the flame retardancy of foam and reduction of the heat transfer to the underlying layer.<sup>102,103</sup> Hence, from the overall study it can be concluded that addition of DMMP within the foam matrix could improve the flame retardant properties of the foams.



**Figure 3.13.** (a) Heat release rate and, (b) Total heat release versus time for the foams containing 0 wt% and 1.5 wt% P.

## **CHAPTER IV**

### **CONCLUSION**

In the present study, the flame-retardant polyurethane foams were synthesized using corn oil derived polyol and DMMP. From the overall study, we conclude that high purity polyol can be synthesized using a single-step thiol-ene reaction. The synthesized polyol was tested before being used in the polyurethane synthesis. The hydroxyl number was found to be higher with 176 mg KOH/g. Similarly, the low acid value of 1.77 mg KOH/g represented the higher reactivity. The homogeneity in mixing of the polyol with the reaction mixture was ensured because of the low viscosity of 1.33 Pa.s. The absence of peak representing the elongation of S-H of 2-mercaptoethanol in the FT-IR proves the reaction proceeded. Similarly, in the gel permeation chromatography, the disappearance of the retention peak indicates 2-mercaptoethanol was consumed in the polyol synthesis. The foams prepared using as-synthesized polyol resulted in uniform cellular structure, higher closed cell content (> 95%), moderate compression strength (81-120 kPa) and appropriate density (~35 kg/m<sup>3</sup>). Addition of DMMP resulted in improved flame-retardant properties of the foams. With a small addition of DMMP, the tested foams showed a significant reduction in self-extinguishing time, heat release rate and total heat

release. It was observed that the foams without DMMP showed a higher burning time of 115 s with a weight loss of 38%, while foams containing 1.94 wt% P showed a reduced burning time of 3.5 s and weight loss of 5.5 wt%. Similar behavior was observed from the cone test, where the foams containing DMMP showed a reduced peak heat release rate and a total heat release, thereby improving the flame retardancy of the polyurethane foams.



## REFERENCES

- (1) Xu, J.; Jiang, J.; Hse, C.-Y.; Shupe, T. F. Preparation of Polyurethane Foams Using Fractionated Products in Liquefied Wood. *J. Appl. Polym. Sci.* **2014**, *131* (7), 40096.
- (2) Chen, R.; Zhang, C.; Kessler, M. R. Polyols and Polyurethanes Prepared from Epoxidized Soybean Oil Ring-Opened by Polyhydroxy Fatty Acids with Varying OH Numbers. *J. Appl. Polym. Sci.* **2015**, *132*
- (3) Tersac, G. Chemistry and Technology of Polyols for Polyurethanes. Milhail Ionescu. Rapra Technology, Shrewsbury, UK. *Polym. Int.* **2007**, *56*, 820.
- (4) Plastics – the Facts 2012: An analysis of European plastics Production, Demand and Waste Data for 2011, *Plastics Europe*, **2012**, pp. 5–10.
- (5) Alavi Nikje, M. M.; Noruzian, M.; Tamaddon Moghaddam, S. Investigation of Fe<sub>3</sub>O<sub>4</sub>/AEAP Supermagnetic Nanoparticles on the Morphological, Thermal and Magnetite Behavior of Polyurethane Rigid Foam Nanocomposites. *Polimery* **2015**, *60*, 26–32.
- (6) Badri, K. H.; Ahmad, S. H.; Zakaria, S. The Production of a High-Functionality RBD Palm Kernel-Based Polyester Polyol. *J. Appl. Polym. Sci.* **2001**, *82*, 827–832.
- (7) Chian, K. S.; Gan, L. H. Development of a Rigid Polyurethane Foam from Palm Oil. *J. Appl. Polym. Sci.* **1998**, *68*, 509–515.
- (8) Teo, A. J. T.; Mishra, A.; Park, I.; Kim, Y.-J.; Park, W.-T.; Yoon, Y.-J. Polymeric Biomaterials for Medical Implants and Devices. *ACS Biomater. Sci. Eng.* **2016**, *2*, 454–472.

- (9) G. Woods, Flexible Polyurethane Foams, *Applied Science Publishers*, London, **1982**.
- (10) Z. Wirpsza, Polyurethanes: Chemistry, Technology and Applications, *Ellis Horwood Ltd.*, New York, **1994**.
- (11) Shea, J. J. Polymeric Foams: Mechanisms and Materials [Book Review]. *IEEE Electr. Insul. Mag.* **2005**, *21*, 56–56.
- (12) Global Polyurethane (PU) Market size & Share, *2025 Industry report*; **2017**.
- (13) Mol, J. Industrial Applications of Olefin Metathesis. *J. Mol. Catal. A Chem.* **2004**, *213*, 39.
- (14) Luo, X.; Xiao, Y.; Wu, Q.; Zeng, J. Development of High-Performance Biodegradable Rigid Polyurethane Foams Using All Bioresource-Based Polyols: Lignin and Soy Oil-Derived Polyols. *Int. J. Biol. Macromol.* **2018**, *115*, 786–791.
- (15) Ionescu, M.; Radojčić, D.; Wan, X.; Petrović, Z. S.; Upshaw, T. A. Functionalized Vegetable Oils as Precursors for Polymers by Thiol-Ene Reaction. *Eur. Polym. J.* **2015**, *67*, 439–448.
- (16) Ji, D.; Fang, Z.; He, W.; Zhang, K.; Luo, Z.; Wang, T.; Guo, K. Synthesis of Soy-Polyols Using a Continuous Microflow System and Preparation of Soy-Based Polyurethane Rigid Foams. *ACS Sustain. Chem. Eng.* **2015**, *3*, 1197–1204.
- (17) Zhang, C.; Madbouly, S. A.; Kessler, M. R. Biobased Polyurethanes Prepared from Different Vegetable Oils. *ACS Appl. Mater. Interfaces* **2015**, *7*, 1226–1233.

- (18) Palaskar, D. V.; Boyer, A.; Cloutet, E.; Alfos, C.; Cramail, H. Synthesis of Biobased Polyurethane from Oleic and Ricinoleic Acids as the Renewable Resources via the AB-Type Self-Condensation Approach. *Biomacromolecules* **2010**, *11*, 1202–1211.
- (19) Gupta, R. K.; Ionescu, M.; Radojcic, D.; Wan, X.; Petrovic, Z. S. Novel Renewable Polyols Based on Limonene for Rigid Polyurethane Foams. *J. Polym. Environ.* **2014**, *22*, 304–309.
- (20) Gupta, R. K.; Ionescu, M.; Wan, X.; Radojcic, D.; Petrović, Z. S. Synthesis of a Novel Limonene Based Mannich Polyol for Rigid Polyurethane Foams. *J. Polym. Environ.* **2015**, *23*, 261–268.
- (21) Schimpf, V.; Ritter, B. S.; Weis, P.; Parison, K.; Mülhaupt, R. High Purity Limonene Dicarboxylate as Versatile Building Block for Sustainable Non-Isocyanate Polyhydroxyurethane Thermosets and Thermoplastics. *Macromolecules* **2017**, *50*, 944–955.
- (22) Ugarte, L.; Gómez-Fernández, S.; Peña-Rodríguez, C.; Prociak, A.; Corcuera, M. A.; Eceiza, A. Tailoring Mechanical Properties of Rigid Polyurethane Foams by Sorbitol and Corn Derived Biopolyol Mixtures. *ACS Sustain. Chem. Eng.* **2015**, *3*, 3382–3387.
- (23) Montero de Espinosa, L.; Meier, M. A. R. Plant Oils: The Perfect Renewable Resource for Polymer Science?! *Eur. Polym. J.* **2011**, *47*, 837–852.
- (24) Lu, Y.; Larock, R. C. Soybean-Oil-Based Waterborne Polyurethane Dispersions: Effects

of Polyol Functionality and Hard Segment Content on Properties. *Biomacromolecules* **2008**, *9*, 3332–3340.

(25) Wang, H. J.; Rong, M. Z.; Zhang, M. Q.; Hu, J.; Chen, H. W.; Czigány, T. Biodegradable Foam Plastics Based on Castor Oil. *Biomacromolecules* **2008**, *9*, 615–623.

(26) Liu, D.; Tian, H.; Zhang, L.; Chang, P. R. Structure and Properties of Blend Films Prepared from Castor Oil-Based Polyurethane/Soy Protein Derivative. *Ind. Eng. Chem. Res.* **2008**, *47*, 9330–9336.

(27) Poussard, L.; Mariage, J.; Grignard, B.; Detrembleur, C.; Jérôme, C.; Calberg, C.; Heinrichs, B.; De Winter, J.; Gerbaux, P.; Raquez, J.-M.; et al. Non-Isocyanate Polyurethanes from Carbonated Soybean Oil Using Monomeric or Oligomeric Diamines To Achieve Thermosets or Thermoplastics. *Macromolecules* **2016**, *49*, 2162–2171.

(28) Ugarte, L.; Gómez-Fernández, S.; Peña-Rodríguez, C.; Prociak, A.; Corcuera, M. A.; Eceiza, A. Tailoring Mechanical Properties of Rigid Polyurethane Foams by Sorbitol and Corn Derived Biopolyol Mixtures. *ACS Sustain. Chem. Eng.* **2015**, *3*, 3382–3387.

(29) Maisonneuve, L.; Chollet, G.; Grau, E.; Cramail, H. Vegetable Oils: A Source of Polyols for Polyurethane Materials. *OCL* **2016**, *23*, D508.

(30) Zhang, Y.; Shang, S.; Zhang, X.; Wang, D.; Hourston, D.J., Influence of the composition of rosin-based rigid polyurethane foams on their thermal stability. *Journal of Applied Polymer Science.* **1996**, *59*, 1167-1171.

- (31) Goods, S. H.; Neuschwanger, C. L.; Henderson, C. C.; Skala, D. M. Mechanical Properties of CRETE, a Polyurethane Foam. *J. Appl. Polym. Sci.* **1998**, *68*, 1045–1055.
- (32) Singh, H.; Jain, A. K. Ignition, Combustion, Toxicity, and Fire Retardancy of Polyurethane Foams: A Comprehensive Review. *J. Appl. Polym. Sci.* **2008**.
- (33) Amrollahi, M.; Sadeghi, G. M. M. Evaluation of Adhesion Strength, Flammability, and Degradation of HBCD-Containing Polyurethane Adhesives. *J. Appl. Polym. Sci.* **2008**, *110*, 3538–3543.
- (34) Buszard, D.; Dellar, R. Fire and Cellular Polymers; *Elsevier: London*, **1984**, p 265.
- (35) VITKAUSKIENĖ, I.; MAKUŠKA, R.; STIRNA, U.; CABULIS, U. Thermal Properties of Polyurethane-Polyisocyanurate Foams Based on Poly(Ethylene Terephthalate) Waste. *Mater. Sci.* **2011**, *17*.
- (36) Zarzyka, I. Foamed Polyurethane Plastics of Reduced Flammability. *J. Appl. Polym. Sci.* **2018**, *135*, 45748.
- (37) Levchik, S. V.; Weil, E. D. Thermal Decomposition, Combustion and Fire-Retardancy of Polyurethanes—a Review of the Recent Literature. *Polym. Int.* **2004**, *53*, 1585–1610.
- (38) Chen, H.-B.; Shen, P.; Chen, M.-J.; Zhao, H.-B.; Schiraldi, D. A. Highly Efficient Flame Retardant Polyurethane Foam with Alginate/Clay Aerogel Coating. *ACS Appl. Mater. Interfaces* **2016**, *8*, 32557–32564.

(39) Ben Evert. Summary for Policymakers. In *Climate Change 2013 - The Physical Science Basis*; Intergovernmental Panel on Climate Change, Ed.; *Cambridge University Press: Cambridge, 2018*; pp. 1–30.

(40) Laufer, G.; Kirkland, C.; Morgan, A. B.; Grunlan, J. C. Exceptionally Flame Retardant Sulfur-Based Multilayer Nanocoating for Polyurethane Prepared from Aqueous Polyelectrolyte Solutions. *ACS Macro Lett.* **2013**, *2*, 361–365.

(41) Ashford, P. Polyurethane *World Congress* **1997**, 612.

(42) Gao, L.-P.; Wang, D.-Y.; Wang, Y.-Z.; Wang, J.-S.; Yang, B. A Flame-Retardant Epoxy Resin Based on a Reactive Phosphorus-Containing Monomer of DODPP and Its Thermal and Flame-Retardant Properties. *Polym. Degrad. Stab.* **2008**, *93*, 1308–1315.

(43) Zhang, C.; Huang, J. Y.; Liu, S. M.; Zhao, J. Q. The Synthesis and Properties of a Reactive Flame-Retardant Unsaturated Polyester Resin from a Phosphorus-Containing Diacid. *Polym. Adv. Technol.* **2011**, *22*, 1768–1777.

(44) Ebdon, J. R.; Price, D.; Hunt, B. J.; Joseph, P.; Gao, F.; Milnes, G. J.; Cunliffe, L. K. Flame Retardance in Some Polystyrenes and Poly(Methyl Methacrylate)s with Covalently Bound Phosphorus-Containing Groups: Initial Screening Experiments and Some Laser Pyrolysis Mechanistic Studies. *Polym. Degrad. Stab.* **2000**, *69*, 267–277.

(45) Kandola, B. K.; Krishnan, L.; Ebdon, J. R. Blends of Unsaturated Polyester and Phenolic Resins for Application as Fire-Resistant Matrices in Fibre-Reinforced Composites: Effects

of Added Flame Retardants. *Polym. Degrad. Stab.* **2014**, *106*, 129–137.

(46) Shieh, J.-Y.; Wang, C.-S. Synthesis of Novel Flame Retardant Epoxy Hardeners and Properties of Cured Products. *Polymer (Guildf)*. **2001**, *42*, 7617–7625.

(47) Frigione, M.; Maffezzoli, A.; Finocchiaro, P.; Failla, S. Cure Kinetics and Properties of Epoxy Resins Containing a Phosphorous-Based Flame Retardant. *Adv. Polym. Technol.* **2003**, *22*, 329–342.

(48) Liu, Y. L. Flame-Retardant Epoxy Resins from Novel Phosphorus-Containing Novolac. *Polymer (Guildf)*. **2001**, *42*, 3445–3454.

(49) Xiong, Y.-Q.; Zhang, X.-Y.; Liu, J.; Li, M.-M.; Guo, F.; Xia, X.-N.; Xu, W.-J. Synthesis of Novel Phosphorus-Containing Epoxy Hardeners and Thermal Stability and Flame-Retardant Properties of Cured Products. *J. Appl. Polym. Sci.* **2012**, *125*, 1219–1225.

(50) Wang, Y.; Yang, X.; Peng, H.; Wang, F.; Liu, X.; Yang, Y.; Hao, J. Layer-by-Layer Assembly of Multifunctional Flame Retardant Based on Brucite, 3-Aminopropyltriethoxysilane, and Alginate and Its Applications in Ethylene-Vinyl Acetate Resin. *ACS Appl. Mater. Interfaces* **2016**, *8*, 9925–9935.

(51) Dai, K.; Song, L.; Jiang, S.; Yu, B.; Yang, W.; Yuen, R. K. K.; Hu, Y. Unsaturated Polyester Resins Modified with Phosphorus-Containing Groups: Effects on Thermal Properties and Flammability. *Polym. Degrad. Stab.* **2013**, *98*, 2033–2040.

(52) Lin, Y.; Yu, B.; Jin, X.; Song, L.; Hu, Y. Study on Thermal Degradation and Combustion

Behavior of Flame Retardant Unsaturated Polyester Resin Modified with a Reactive Phosphorus Containing Monomer. *RSC Adv.* **2016**, *6*, 49633–49642.

(53) Wazarkar, K.; Kathalewar, M.; Sabnis, A. Flammability Behavior of Unsaturated Polyesters Modified with Novel Phosphorous Containing Flame Retardants. *Polym. Compos.* **2017**, *38*, 1483–1491.

(54) Bai, Z.; Song, L.; Hu, Y.; Yuen, R. K. K. Preparation, Flame Retardancy, and Thermal Degradation of Unsaturated Polyester Resin Modified with a Novel Phosphorus Containing Acrylate. *Ind. Eng. Chem. Res.* **2013**, *52*, 12855–12864.

(55) Lin, Y.; Jiang, S.; Gui, Z.; Li, G.; Shi, X.; Chen, G.; Peng, X. Synthesis of a Novel Highly Effective Flame Retardant Containing Multivalent Phosphorus and Its Application in Unsaturated Polyester Resins. *RSC Adv.* **2016**, *6*, 86632–86639.

(56) Dai, K.; Song, L.; Hu, Y. Study of the Flame Retardancy and Thermal Properties of Unsaturated Polyester Resin via Incorporation of a Reactive Cyclic Phosphorus-Containing Monomer. *High Perform. Polym.* **2013**, *25*, 938–946.

(57) Bourbigot, S.; Le Bras, M.; Duquesne, S.; Rochery, M. Recent Advances for Intumescent Polymers. *Macromolecular Materials and Engineering*, **2004**.

(58) Bras, M. Le; Bugajny, M.; Lefebvre, J.-M.; Bourbigot, S. Use of Polyurethanes as Char-Forming Agents in Polypropylene Intumescent Formulations. *Polym. Int.* **2000**, *49*, 1115–124.



- (59) Wang, D.-Y.; Cai, X.-X.; Qu, M.-H.; Liu, Y.; Wang, J.-S.; Wang, Y.-Z. Preparation and Flammability of a Novel Intumescent Flame-Retardant Poly(Ethylene-Co-Vinyl Acetate) System. *Polym. Degrad. Stab.* **2008**, *93*, 2186–2192.
- (60) Xie, R.; Qu, B. Expandable Graphite Systems for Halogen-Free Flame-Retarding of Polyolefins. I. Flammability Characterization and Synergistic Effect. *J. Appl. Polym. Sci.* **2001**, *80*, 1181–1189.
- (61) Xie, F.; Wang, Y.-Z.; Yang, B.; Liu, Y. A Novel Intumescent Flame-Retardant Polyethylene System. *Macromol. Mater. Eng.* **2006**, *291*, 247–253.
- (62) Wang, D.-Y.; Liu, Y.; Wang, Y.-Z.; Artiles, C. P.; Hull, T. R.; Price, D. Fire Retardancy of a Reactively Extruded Intumescent Flame Retardant Polyethylene System Enhanced by Metal Chelates. *Polym. Degrad. Stab.* **2007**, *92*, 1592–1598.
- (63) Hu, X.-P.; Li, Y.-L.; Wang, Y.-Z. Synergistic Effect of the Charring Agent on the Thermal and Flame Retardant Properties of Polyethylene. *Macromol. Mater. Eng.* **2004**, *289*, 208–212.
- (64) Liu, Y.; Deng, C.-L.; Zhao, J.; Wang, J.-S.; Chen, L.; Wang, Y.-Z. An Efficiently Halogen-Free Flame-Retardant Long-Glass-Fiber-Reinforced Polypropylene System. *Polym. Degrad. Stab.* **2011**, *96*, 363–370.
- (65) Yan, Y.-W.; Chen, L.; Jian, R.-K.; Kong, S.; Wang, Y.-Z. Intumescence: An Effective Way to Flame Retardance and Smoke Suppression for Polystyrene. *Polym. Degrad. Stab.*

**2012**, 97, 1423–1431.

(66) Wang, D.-Y.; Cai, X.-X.; Qu, M.-H.; Liu, Y.; Wang, J.-S.; Wang, Y.-Z. Preparation and Flammability of a Novel Intumescent Flame-Retardant Poly(Ethylene-Co-Vinyl Acetate) System. *Polym. Degrad. Stab.* **2008**, 93, 2186–2192.

(67) Oertel, G. Polyurethane Handbook Chemistry-Raw Materials-Processing Application-properties. *Munich Vienna New York, Carl Hanser Verlag.* **1993**; 56-63, 428-432.

(68) Sendijarevic, V. Polyurethanes Chemistry. *Presented at Troy Polymers Inc, Troy, Michigan, USA.* October **2008**.

(69) Klempner, D. and Sendijarevic, V. Handbook of Polymeric Foams and Foam Technology. **2004**; 94-138. *Munich, Carl Hanser Verlag.*

(70) Dworakowska, S.; Bogdał, D.; Zaccheria, F.; Ravasio, N. The Role of Catalysis in the Synthesis of Polyurethane Foams Based on Renewable Raw Materials. *Catal. Today* **2014**, 223, 148–156.

(71) Silva, A. L.; Bordado, J. C. Recent Developments in Polyurethane Catalysis: Catalytic Mechanisms Review. *Catal. Rev.* **2004**, 46, 31–51.

(72) D. Randall, D. Lee, S. The Polyurethanes Book, *Wiley Ltd., New York*, **2002**.

(73) Woods, G. Flexible Polyurethane Foams, *Applied Science Publishers, London*, **1982**.

(74) Nguyen Dang, L.; Le Hoang, S.; Malin, M.; Weisser, J.; Walter, T.; Schnabelrauch,

M.; Seppälä, J. Synthesis and Characterization of Castor Oil-Segmented Thermoplastic Polyurethane with Controlled Mechanical Properties. *Eur. Polym. J.* **2016**, *81*, 129–137.

(75) Ebdon, J. R.; Price, D.; Hunt, B. J.; Joseph, P.; Gao, F.; Milnes, G. J.; Cunliffe, L. K. Flame Retardance in Some Polystyrenes and Poly(Methyl Methacrylate)s with Covalently Bound Phosphorus-Containing Groups: Initial Screening Experiments and Some Laser Pyrolysis Mechanistic Studies. *Polym. Degrad. Stab.* **2000**, *69*, 267–277.

(76) Frigione, M.; Maffezzoli, A.; Finocchiaro, P.; Failla, S. Cure Kinetics and Properties of Epoxy Resins Containing a Phosphorous-Based Flame Retardant. *Adv. Polym. Technol.* **2003**, *22*, 329–342.

(77) Akindoyo, J. O.; Beg, M. D. H.; Ghazali, S.; Islam, M. R.; Jeyaratnam, N.; Yuvaraj, A. R. Polyurethane Types, Synthesis and Applications – a Review. *RSC Adv.* **2016**, *6*, 114453–114482.

(78) Zheng, J.; Luo, J.; Zhou, D.; Shen, T.; Li, H.; Liang, L.; Lu, M. Preparation and Properties of Non-Ionic Polyurethane Surfactants. *Colloids Surfaces A Physicochem. Eng. Asp.* **2010**, *363*, 16–21.

(79) Motamedi, M.; Tehrani-Bagha, A. R.; Mahdavian, M. The Effect of Cationic Surfactants in Acid Cleaning Solutions on Protective Performance and Adhesion Strength of the Subsequent Polyurethane Coating. *Prog. Org. Coatings* **2014**, *77*, 712–718.

(80) Akindoyo, J. O.; Beg, M. D. H.; Ghazali, S.; Islam, M. R.; Jeyaratnam, N.; Yuvaraj, A.

R. Polyurethane Types, Synthesis and Applications – a Review. *RSC Adv.* **2016**, *6*, 114453–114482.

(81) Zhang, C.; Huang, J. Y.; Liu, S. M.; Zhao, J. Q. The Synthesis and Properties of a Reactive Flame-Retardant Unsaturated Polyester Resin from a Phosphorus-Containing Diacid. *Polym. Adv. Technol.* **2011**, *22*, 1768–1777.

(82) Han, W.; Lin, B.; Zhou, Y.; Song, J. Synthesis and Properties of UV-Curable Hyperbranched Polyurethane Acrylate Oligomers Containing Photoinitiator. *Polym. Bull.* **2012**, *68*, 729–743.

(83) Sun, F.; Shi, J.; Du, H. guang; Nie, J. Synthesis and Characterization of Hyperbranched Photosensitive Polysiloxane Urethane Acrylate. *Prog. Org. Coatings* **2009**.

(84) Zhang, Y.; Asif, A.; Shi, W. Highly Branched Polyurethane Acrylates and Their Waterborne UV Curing Coating. *Prog. Org. Coatings* **2011**, *71*, 295–301.

(85) Kim, J.; Im, H.; Kim, C. K. Characteristics of Sonar Encapsulant Materials Fabricated from Electron-Beam-Irradiated Polyurethane Elastomers Coated with UV-Curable Polyurethane Acrylates. *Ind. Eng. Chem. Res.* **2013**, *52*, 1908–1915.

(86) Yu, Y.; Liao, B.; Li, G.; Jiang, S.; Sun, F. Synthesis and Properties of Photosensitive Silicone-Containing Polyurethane Acrylate for Leather Finishing Agent. *Ind. Eng. Chem. Res.* **2014**, *53*, 564–571.

- (87) Cheng, J.; Cao, Y.; Jiang, S.; Gao, Y.; Nie, J.; Sun, F. Synthesis and Performances of UV-Curable Polysiloxane–Polyether Block Polyurethane Acrylates for PVC Leather Finishing Agents. *Ind. Eng. Chem. Res.* **2015**, *54*, 5635–5642.
- (88) Chen, M. J.; Shao, Z. B.; Wang, X. L.; Chen, L.; Wang, Y. Z. Halogen-Free Flame-Retardant Flexible Polyurethane Foam with a Novel Nitrogen-Phosphorus Flame Retardant. *Ind. Eng. Chem. Res.* **2012**, *51*, 9769.
- (89) Zhang, C.; Bhoyate, S.; Ionescu, M.; Kahol, P. K.; Gupta, R. K. Highly Flame Retardant and Bio-Based Rigid Polyurethane Foams Derived from Orange Peel Oil. *Polym. Eng. Sci.* **2018**, *58*, 2078–2087.
- (90) Shea, J. J. Polymeric Foams: Mechanisms and Materials. *IEEE Electr. Insul. Mag.* **2005**, *21*, 56.
- (91) Bhoyate, S.; Ionescu, M.; Kahol, P. K.; Chen, J.; Mishra, S. R.; Gupta, R. K. Highly Flame-Retardant Polyurethane Foam Based on Reactive Phosphorus Polyol and Limonene-Based Polyol. *J. Appl. Polym. Sci.* **2018**, *135*, 46224.
- (92) Bhoyate, S.; Ionescu, M.; Kahol, P. K.; Gupta, R. K. Sustainable Flame-Retardant Polyurethanes Using Renewable Resources. *Ind. Crops Prod.* **2018**, *123*, 480.
- (93) Levchik, S. V.; Weil, E. D. Thermal Decomposition, Combustion and Fire-Retardancy of Polyurethanes—a Review of the Recent Literature. *Polym. Int.* **2004**, *53*, 1585–1610.
- (94) 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*, 1.

(95) Bhoyate, S.; Ionescu, M.; Radojicic, D.; Kahol, P. K.; Chen, J.; Mishra, S. R.; Gupta, R. K. Highly Flame-Retardant Bio-Based Polyurethanes Using Novel Reactive Polyols. *J. Appl. Polym. Sci.* **2018**, *135*, 46027.

(96) Zhang, L.; Zhang, M.; Zhou, Y.; Hu, L. The Study of Mechanical Behavior and Flame Retardancy of Castor Oil Phosphate-Based Rigid Polyurethane Foam Composites Containing Expanded Graphite and Triethyl Phosphate. *Polym. Degrad. Stab.* **2013**, *98*, 2784.

(97) Liu, W.; Tang, Y.; Li, F.; Ge, X. G.; Zhang, Z. J. TG-FTIR Characterization of Flame Retardant Polyurethane Foams Materials. *IOP Conf. Ser. Mater. Sci. Eng.* **2016**, *137*, 012033.

(98) Xi, W.; Qian, L.; Huang, Z.; Cao, Y.; Li, L. Continuous Flame-Retardant Actions of Two Phosphate Esters with Expandable Graphite in Rigid Polyurethane Foams. *Polym. Degrad. Stab.* **2016**, *130*, 97.

(99) Hejna, A.; Kirpluks, M.; Kosmela, P.; Cabulis, U.; Haponiuk, J.; Piszczyk, Ł. The Influence of Crude Glycerol and Castor Oil-Based Polyol on the Structure and Performance of Rigid Polyurethane-Polyisocyanurate Foams. *Ind. Crops Prod.* **2017**, *95*, 113.

- (100) Lorenzetti, A.; Modesti, M.; Besco, S.; Hrelja, D.; Donadi, S. Influence of Phosphorus Valency on Thermal Behaviour of Flame Retarded Polyurethane Foams. *Polym. Degrad. Stab.* **2011**, *96*, 1455.
- (101) Pettigrew, A. Halogenated Flame Retardants; **1993**.
- (102) Pan, H.; Wang, W.; Pan, Y.; Song, L.; Hu, Y.; Liew, K. M. Formation of Layer-by-Layer Assembled Titanate Nanotubes Filled Coating on Flexible Polyurethane Foam with Improved Flame Retardant and Smoke Suppression Properties. *ACS Appl. Mater. Interfaces* **2015**, *7*, 101.
- (103) Chen, Y.; Jia, Z.; Luo, Y.; Jia, D.; Li, B. Environmentally Friendly Flame-Retardant and Its Application in Rigid Polyurethane Foam. *Int. J. Polym. Sci.* **2014**, *1*.

## **APPENDICES**



## **APPENDIX A - List of Conference Presentations**

- (1) **Ramanujam, S.**; Zequine, C.; Bhoyate, S.; Neria, B.; Kahol, P.K.; Gupta, R. K. One Step Synthesis of Novel Biobased Polyol for Highly Flame-Retardant Polyurethane Foams. PSU Research Colloquium, Pittsburg, KS, April 10<sup>th</sup> **2019**
- (2) **Ramanujam, S.**; Santimukul, S; Banerjee, T. Magnetic relaxation nanosensors (MRnS) for rapid detection and one-step differentiation between subtypes of influenza. ACS National Meeting & Exposition, March 31 – April 4, **2019**, Orlando, FL
- (3) **Ramanujam, S.**; Banerjee, T.; Santimukul, S. Multimodal detection of ebola virus using a novel magneto-plasmonic nanosensor. 2018 Midwest Regional Meeting, 21-23<sup>rd</sup> Oct **2018**, Iowa State University, Ames, Iowa
- (4) **Ramanujam, S.**; Banerjee, T.; Santimukul, S. Magneto-plasmonic nanosensors for the multiparametric detection of ebola virus. Pentasectional meeting, 21<sup>st</sup> April **2018**, The University of Tulsa, Tulsa, Oklahoma
- (5) **Ramanujam, S.**; Shelby, T.; Banerjee, T.; Zegar, I.; Santimukul, S. Magnetic Nanosensors for the detection of ZIKA Virus. PSU Research Colloquium, Pittsburg, KS, April 11<sup>th</sup> **2018**

## **APPENDIX B - List of Publications**

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

### APPENDIX C - Published Work on Polyurethanes

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