# DESIGN AND ENGINEERING OF BIOBASED AND SILOXANE POLYOLS FOR SUBSEQUENT SYNTHESIS OF FLEXIBLE POLYURETHANE FOAM

Ву

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#### ABSTRACT

# DESIGN AND ENGINEERING OF BIOBASED AND SILOXANE POLYOLS FOR SUBSEQUENT SYNTHESIS OF FLEXIBLE POLYURETHANE FOAM

By

#### Hugh Taylor MacDowell

Interest in more sustainable polyols for the creation of biobased flexible polyurethane foam has increased in recent years in the polymer industry. An alternative feedstock for conventional polyols can give options for companies in the event of supply shortages of petroleum products. Currently, a maximum of 20 weight percent of biobased polyol can be utilized in flexible polyurethane foam formulations. Dimerized fatty acids offer chemistry that increases the amount of biobased content introduced to existing flexible polyurethane formulations up to 50 weight percent.

Biobased poly(ester-ether) polyol has been synthesized by condensation reaction of a mixture of dimer and trimer acids with polyethylene glycol. The condensation reaction to produce biobased poly(esterether) polyol was scaled from a 5 L glass reactor to a 20 L Parr reactor. The resulting polyol was formulated with commercial polyether polyol to create a flexible polyurethane foam with 0 wt. %, 20 wt. %, and 50 wt. % biobased polyol. The synthesized polyurethane foams were subjected to density, tensile, tear, and wet compression set characterization in accordance with ASTM standards with all foams synthesized passing the test standards.

In addition to a biobased polyol, a siloxane polyol was synthesized with reaction of Aminopropylterminated polydimethylsiloxane and propylene carbonate for further formulation in polyurethane foam to aide in flexibility, mold release properties, and flammability resistance. A kinetic study was conducted to determine reaction rates and Arrhenius constants along with full characterization of the reaction product. Further polyurethane foam formulation was not successful, however a strategy to create a siloxane polyol that is miscible with biobased poly(ester-ether) polyol is outlined.

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#### **Chapter 1: Introduction**

#### 1.1 Thesis Organization

This thesis is organized into five different chapters, with each topic building on the work of each successive chapter.

Chapter One discusses the scope of the research conducted with a brief introduction into polyester and polyurethane synthesis. The production of the reactants used in the syntheses conducted will also be detailed.

Chapter Two details the development of a novel biobased polyester polyol derived from dimer fatty acid chemistry. A full characterization was conducted of the polyol made in three different reactors as part of the scale-up of the material.

Chapter Three describes the synthesis, characterization, and kinetics experiment conducted in the development of carbinol-terminated polydimethylsiloxane. This work expands on work previously conducted with carbonate and amine reaction.

Chapter Four discusses the synthesis and characterization of flexible polyurethane foam utilizing biobased polyol and silicon-based polyol. Both polyols were mixed with a commercial polyether triol as drop-in replacement technology. Biobased polyol was formulated in 0%, 20%, and 50% of the polyol mixture in the flexible polyurethane foam.

Chapter Five envisions future work to be conducted based on the research presented by previous chapters. The focus of this chapter is detailing development of a Dimer Acid – Polydimethylsiloxane polyol to be used in further flexible foam and thermoplastic polyurethane synthesis.

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#### 1.2 Objectives

The focus of this research is to develop and characterize novel biobased polyol, silicon polyol, and biobased flexible polyurethane foam. The polyols were developed as a drop in replacement for current polyurethane foam technologies to reduce the amount of fossil carbon present in existing polyurethane foam. Utilizing a biobased polyol instead of the conventional polyether polyol increases the sustainability, reduces the carbon footprint, and introduces a new feedstock for polyurethane foam production. Currently more than 1.5 billion pounds of flexible polyurethane foam is produced in the United States of America on an annual basis [1]. The main goal of this work was to show the biobased polyol content can be increased to 50% of the total polyol mixture by using a dimer fatty acid based polyol, which would displace more than 375 million pounds of petroleum based polyol in the USA annually.

Polyethylene glycol and dimer fatty acids will react via condensation reaction to form hydroxyl terminated molecules with a 1:1.5 molar ratio. Water generated during the reaction was removed to drive the reaction forward to near completion and reduce the acid content of the mixture. The resulting polyol was characterized for hydroxyl value, acid value, moisture content, and viscosity which are all important for further polyurethane foam synthesis.

In addition to the biobased polyol, a silicon based polyol was also investigated by the reaction of propylene carbonate and amino-terminated polydimethylsiloxane. Even though this molecule has been readily researched, non-solvent based reaction kinetics have not been fully developed [1]. The work presented offers a kinetic model for the reaction of propylene carbonate with amino-terminated polydimethylsiloxane in a solvent free environment.

Finally, flexible polyurethane foam was synthesized using the biobased polyol and silicon based polyol developed. The foam was created by water-blown synthesis utilizing various catalyst to regulate the

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blowing and gelling reaction. Box mold foam generated with 0%, 20%, and 50% biobased material was characterized by ASTM standards for flexible polyurethane foams [3].

# 1.3 Background

It is essential to describe the reactants used in the synthesis of the polyols to understand the benefits of the materials from a sustainability and performance viewpoint.

# 1.3.1 Dimer Fatty Acid

Dimer Fatty Acid has been used throughout the chemical industry in applications such as lubricants and viscosity increase agents [4,5]. Vegetable oils are most typically used as the feedstock of Dimer Fatty Acids. Viewing soy oil as a model triglyceride, it is composed of various fatty acids as shown in *Figure 1*.



Figure 1. Soy Oil Fatty Acid Composition

To form dimer acid, the ester linkage between the glycerol backbone and the fatty acids is first hydrolyzed and the glycerol is separated from the fatty acid molecules. The fatty acids are then heated with montmorillonite clay catalyst to form a mixture of dimer and trimer acids through Diels alder reaction [20]. The double bonds in the unsaturated fatty acids such as linoleic acid and linolenic acid rearrange to form the dimer and trimer acids as shown in *Figure 2* and *Figure 3* below.



Figure 2. Dimer Fatty Acid Structures



Figure 3. Trimer Fatty Acid Structure

### 1.3.2 Polydimethylsiloxane

Silicone is a tetravalent metalloid that creates similar bonding structures as carbon. However, silicon behaves differently than carbon in many ways such as rotational ability and bond energies. The Si-O bond has a lower barrier to rotation than a C-O bond which contributes to the flexible structures and low glass transition temperatures often displayed by several silicone materials [6]. Silicones are widely used in adhesive, sealant, and lubricant applications due to these flexural properties.

The Si-O-Si backbone in siloxanes have an associated bond energy of ~450 kJ/mol, whereas the repeating C-O-C bond (ether) has an associated bond energy of ~360 kJ/mol [7]. The increase in bond energy makes the molecule more thermolitically stable, giving the material a higher heat resistance before failure. High heat stability is advantageous for many polymers, especially polyurethane foam. The flexible nature of siloxane backbones coupled with the heat resistance can improve the flexibility of existing foams and increase flame retardency.

Chapter 2: Synthesis and Analysis of Biobased Dimer Acid and Polyethylene Glycol Polyol

# 2.1 Introduction and Literature Review

Vegetable oil derived Dimer Fatty Acids yield excellent possibilities for sustainable biobased chemistry due to the temperature stability, carboxylic functionality, and availability of the material. Dimer Acids have been found to be used in a variety of chemistries to produce lubricants, hot melt adhesives, and used to increase the viscosity of fluids through reaction with Polyethylene Glycol [4,5,8]. Many of the same synthesis methods used to create produce those products could be used to create a biobased flexible polyurethane foam polyol [9]. Most of the commercial flexible polyurethane foam polyols available are triols that utilize polyether chemistry. The most common reaction scheme of triol polyether polyol can be seen in *Figure 4* below.





The epoxide ring on the propylene oxide opens through radical addition reaction to first bind to the glycerol hydroxyl end groups, then the polyol builds molecular weight with further reaction of propylene oxide with the triol [9]. The majority of polyether triol polyols are produced using fossil carbon from petroleum feedstock. Vegetable oil derived polyols have been developed by functionalizing the

unsaturated carbon bonds in an attempt to reduce the amount of petroleum used in polyols and polyurethane synthesis [10]. One major limitation of functionalizing vegetable oil based polyols is that the molecular weight of the polyols produced is limited to the molecular weight of the initial triglyceride. Flexible polyurethane foam polyols incorporate a long amorphous section to polyurethane matrices due to their large molecular weight and subsequent low hydroxyl number. Polyester polyols synthesized using dimer fatty acid can provide an excellent alternative to oil derived polyols because the molecular weight can be readily changed through polycondensation reaction with diols.

### 2.2 Synthesis of Biobased Polyol

### 2.2.1 Materials

The materials used to perform the reaction include biobased dimer acid Radia 0955 (564 g/mol, f=2.02), biobased dimer/trimer acid mix Radia 0980 (747 g/mol, f=2.65), Polyethylene Glycol (200 g/mol, f=2), catalyst Titanium Butoxide, and ultra-high purity Nitrogen. The Radia 0955 and Radia 0980 were purchased from Oleon Incorporated. The Polyethylene Glycol and Titanium Butoxide were purchased from Sigma-Aldrich Corporation. Three different synthesis vessels were used for the scale-up of the biobased polyol. The first vessel was a 5 L 3-neck round bottom flask equipped with a Dean-Stark apparatus, a condenser, a thermometer, and a mechanical stirrer was used for the initial synthesis. The second vessel was a 2 L Parr reactor equipped with a condenser, a thermometer, pressure gauge, and a mechanical stirrer used for the final scale-up experiment.

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#### 2.2.2 Methods

The first set of condensation reactions to synthesize biobased polyol were conducted in a 5 L 3-neck round bottom flask charged with 120 grams (.21 mol) of Radia 0955, 365 grams (.49 mol) of Radia 0980, 335 grams (1.68 mol) of Polyethylene Glycol (PEG), and 5.15 grams of Titanium Butoxide. The reaction mixture was purged with Nitrogen for 15 minutes under constant stir. The vessel was sealed and the temperature was raised to 200°C for 3 hours under constant stir. The reaction mixture was then allowed to cool to 90°C. Vacuum was then applied for 1 hour under constant stir at 90°C to remove excess water. The second set of reactions were conducted in a 2 L Parr reactor charged with the reactor charged with 103 grams (.184 mol) of Radia 0955, 313 grams (.419 mol) of Radia 0980, 368 grams ( 1.84 mol) PEG, and 4.6 grams of Titanium Butoxide. The reactants were stirred at room temperature and purged with nitrogen for 20 minutes. The vessel was sealed and raised to 90°C under constant stir. The outlet valve to the condenser was opened and the mixture was heated to 215°C under constant stir for 4 hours. The vessel was then allowed to cool to 150°C and vacuum was applied to the reaction mixture for 1 hour while the temperature decreased to room temperature.

The third set of reactions were conducted in a 20 L Parr reactor with the reactor charged with 1.614 kg (2.88 mol) of Radia 0955, 4.883 kg (6.54 mol) of Radia 0980, 5.74 kg (28.7 mol) of PEG, and 0.075 kg of Titanium Butoxide. The reaction mixture was purged with nitrogen at room temperature under constant stir for 20 minutes. The temperature was then raised to 220°C for 4.5 hours under constant stir. The reaction mixture was allowed to cool to 150°C and vacuum was applied for 1 hour.

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#### 2.3 Characterization Methods

#### 2.3.1 Hydroxyl and Acid Value Titration

ASTM Test Method E1899-08 was used to measure hydroxyl value [11]. The hydroxyl group of the polyol is reacted with excess p-toluenesulfonyl isocyanate (TSI), to form an acidic carbamate. Water is added to convert unreacted isocyanate to sulfonamide, followed by direct potentiometric titration of the acidic carbamate with tetrabutylammonium hydroxide (Bu<sub>4</sub>NOH) in nonaqueous medium. The hydroxyl value was calculated as mgKOH/g-sample by the following equation in *Equation 1* below.

hydroxyl number (OH#) = 
$$\frac{(V_2 - V_1) \times N \times 56.1}{sample, g}$$

#### Equation 1. Hydroxyl Value Equation

Where N is the concentration of  $Bu_4NOH$  in meq/mL,  $V_1$  is the mL  $Bu_4NOH$  to first potentiometric end point,  $V_2$  is the mL  $Bu_4NOH$  to second potentiometric end point, sample (g) is the mass of the sample in grams, and 56.1 is the molecular mass of potassium hydroxide (KOH).

Lubrizol Test Method TP-AATM-109-01 was used to determine the acid value for the biobased polyol [12]. Samples of biobased polyol were dissolved in Isopropyl Alcohol (IPA) and 1% phenolphthalein solution was added. The sample was then titrated with 0.5N Potassium Hydroxide solution until a faint pink color remained in the sample container. Acid value was calculated by the equation in *Equation 2* below.

$$acid value = \frac{(mL sample - mL blank) \times N KOH \times 56.1}{g sample}$$

#### Equation 2. Acid Value Equation

Where "mL sample" is the volume of titrant needed to neutralize the sample, "mL blank" is the volume of titrant needed to neutralize the blank solution, "N KOH" is the molarity of KOH titrant, "56.1" is the molecular mass of potassium hydroxide, and "g sample" is the weight of the sample titrated.

### 2.3.2 Molecular Weight Calculation

The molecular weight of the biobased polyol was determined using a combination of the hydroxyl value titration data and the average functionality. The average functionality was calculated as seen in *Equation 3* below [13].

 $f_{av} = \frac{\sum (N_i \times f_i)}{\sum N_i}$ 

Equation 3. Average Functionality Equation

Where  $f_{av}$  is the average functionality,  $N_i$  is the moles of species i, and  $f_i$  is the functionality of species i. The molecular weight was calculated by the equation in *Equation 4* below.

 $m.w. = \frac{56100 \times f_{av}}{OH\#}$ 

Equation 4. Molecular Weight Equation

Where m.w. is the molecular weight of the biobased polyol, 56100 is the amount of milligrams in a mole of KOH,  $f_{av}$  is the average functionality of the biobased polyol, and OH# is the hydroxyl value number (mg KOH/g sample) of the biobased polyol.

### 2.3.3 Viscosity Measurements

Viscosity measurements were conducted using a Brookfield DV-E Viscometer, model LVDVE. The measurements were conducted at 20°C with spindle LV-1 at 30% to 70% torque. The spindle was placed into the sample to the height of the required depth markings on the spindle and did not touch the bottom or sides of the sample container.

# 2.3.4 Thermogravimetric Analysis

Thermogravimetric Analysis was conducted using a TA Instruments TGA-Q50. The degradation temperature was determined by ramping 10°C/min from room temperature to 550°C. The moisture content was found by ramping the temperature of the sample by 10°C/min to 105°C and held isothermal for 10 minutes. The PEG wt.% was found by ramping the temperature by 10°C/min to 250°C and held isothermal for 10 minutes.

# 2.3.5 Fourier Transform Infrared Spectroscopy Analysis

Fourier Transform Infrared Spectroscopy was conducted using a Shimadzu IRAffinity-1. The samples were analyzed from wavelengths ranging from 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.

# 2.4 Results and Discussion

# 2.4.1 Hydroxyl and Acid Value Titrations

The hydroxyl value for each of the biobased poly(ester-ether) polyol samples made in 5 L glass, 2 L Parr, and 20 L Parr reactors were determined by the method discussed in section 2.3.1. The results of the hydroxyl value characterization can be seen in *Table 1* below.

Poly(ester-ether) Polyol Hydroxyl Values	
Reactor Average OH Value (mgKOH/	
5L Glass	127
2L Parr	141
20L Parr	150

The hydroxyl values for each of the reactors were fairly consistent, with a standard deviation of 11.6, showing that the reaction is scalable without a significant change in overall hydroxyl value.

The acid value for each of the biobased poly(ester-ether) polyol samples made in 5 L glass, 2 L Parr, and 20 L Parr reactors was determined by the method discussed in section 2.3.3. The results of the acid value characterization can be seen in *Table 2* below.

Poly(ester-ether) Polyol Acid Values		
Reactor	Average Acid Value (mgKOH/g)	% Conversion
5L Glass	2.57	97.55%
2L Parr	2.44	97.68%
20L Parr	5.695	94.58%
Initial Reaction Mixture	105	

Table 2. Acid Values of Poly(ester-ether) Polyol

The acid values for each of the reaction vessels are significantly less than the starting reaction mixture acid value of 105 (mgKOH/g) which demonstrates almost complete reaction of the Dimer and Trimer acids. The standard deviation for the acid values from each of the reactors was found to be 1.84 (mgKOH/g), largely due to the better mixing efficiencies in the 5 L glass and 2 L Parr compared to the 20 L Parr. The average extent of reaction was found to be 96.6 % conversion calculated from the initial and final acid value.

## 2.4.2 Molecular Weight Calculation

The molecular weight of each of the polyol samples made in the three reactors was calculated using the hydroxyl value by the method described in section 2.3.2. The results of that calculation are shown below in *Table 3*.

Poly(ester-ether) Polyol Average Molecular Weight	
Sample	Mol. Wt. (g/mol)
5L Glass	932.5
2L Parr	839.5
20L Parr	789.1

Table 3.	Polv(ester-ether)	Polvol	Molecular	Weight
				i i cigii c

The average molecular weight of the polyol product was heavily dependent on the amount of PEG contained in the final product as will be discussed in section 2.4.4. The 20L Parr reactor polyol sample contained the most PEG, therefore had the highest hydroxyl value and lowest molecular weight.

### 2.4.3 Viscosity Measurements

Samples from the 5 L glass, 2 L Parr, and 20 L Parr reactor were analyzed for viscosity by the method described in section 2.3.4. The viscosities of the reactor polyol products have been tabulated in *Table 4* below.

Poly(ester-ether) Polyol Viscosity	
Sample	Viscosity (cP)
5L Glass	13426
2L Parr	11179
20L Parr	3483

Table 4. Viscosity Measurements of Biobased Poly(ester-ether) Polyol

The viscosities for the 5L glass and 2L Parr are comparable, with the 20L Parr viscosity being much lower than the other two reactors. The low viscosity in the 20L Parr is due to the additional PEG in the polyol that was not distilled during the final stage of the reaction and is shown in section 2.4.4 with TGA analysis.

## 2.4.4 TGA Moisture Analysis, PEG Percentage, and Degradation Temperature

The degradation temperature and moisture content was determined for samples from each of the reaction vessels by the method described in section 2.3.5. The degradation temperatures are tabulated in *Table 5*.

#### Table 5. Poly(ester-ether) Polyol Degradation Temperature

Poly(ester-ether) Polyol Degradation Temperature	
Sample	Degradation Temperature (°C)
PEG 200	247
Radia 0955	382
Radia 0980	438
5L Glass	426
2L Parr	426
20L Parr	426

The degradation temperature of the polyols formed in the various reactors are high enough to

withstand the heat generated during polyurethane foam synthesis. The moisture content for each of the

polyols from the different reaction vessels is shown in *Table 6* below.

Poly(ester-ether) Polyol Moisture Content			
Sample	Moisture Content (wt. %)		
5L Glass	1.61		
2L Parr	0.72		
20L Parr	1.36		

Table 6. Poly(ester-ether) Polyol Moisture Content

Moisture content in polyols is important for further reaction with isocyanate in polyurethane foam synthesis that will be discussed further in Chapter 4. It was important that the moisture content be reduced as to not hinder further polyurethane foam synthesis. All of the polyols met the goal of under 5% moisture needed to adequately formulate and synthesize polyurethane foam. The percentage of PEG in the resulting polyols is shown in *Table 7*.

### Table 7. Poly(ester-ether) Polyol PEG Percentage

Poly(ester-ether) Polyol PEG Percentage			
Sample	PEG (wt.%)		
5L Glass	10.2		
2L Parr	10.8		
20L Parr	15.1		

The weight percentage of PEG was comparable for the 5L glass and 2L Parr, explaining the similar final viscosities in section 2.4.2. However, the 20L Parr PEG percentage was much higher than the other reactors, leading to a much lower viscosity and a higher Hydroxyl Value.

# 2.4.5 FTIR Analysis

The reactants and the products of the biobased polyol synthesis were analyzed by FTIR as described in section 2.3.5.



Figure 5. FTIR Spectra of Radia 0955 Dimer Acid



Figure 6. FTIR Spectra of Radia 0980 Dimer/Trimer Acid

Radia 0955 and Radia 0980 have almost identical FTIR spectra as expected as shown in *Figure 5* and *Figure* 6. There is a characteristic carboxylic acid peak at 1700 cm<sup>-1</sup> and alkane peak at 2900 cm<sup>-1</sup> on both of the spectra of the Radia 0955 and Radia 0980 [14]. The structures of the dimer acids and trimer acids illustrating the carboxylic acid and alkane regions are shown in *Figure 7* and *Figure 8*.



Figure 7. Dimer Acid Chemical Structures



Figure 8. Trimer Acid Chemical Structure



Figure 9. FTIR Spectra of Polyethylene Glycol 200 Molecular Weight

The PEG spectra shows the characteristic broad hydroxyl peak from 3200-3500 cm<sup>-1</sup> and alkane peak at 2800 cm<sup>-1</sup> [16]. The structure of PEG illustrating the hydroxyl groups and alkane bonds is shown in *Figure* 10.



Figure 10. Polyethylene Glycol Chemical Structure



Figure 11. FTIR Spectra of Biobased Polyol Synthesized in 5L Glass Reactor



Figure 12. FTIR Spectra of Biobased Polyol Synthesized in 2L Parr Reactor



Figure 13. FTIR Spectra of Biobased Polyol Synthesized in 20L Parr Reactor

In each of the FTIR spectra of the three polyol reactions shown above in *Figure 11, Figure 12*, and *Figure 13*, the carbonyl peak shifted to ~1670 cm<sup>-1</sup> which is indicative of a polyester linkage [14]. All of the spectrums were similar, with only a slightly larger broad hydroxyl peak from 3200-3500 cm<sup>-1</sup> in the 20 L Parr reactor, most likely from a larger excess of PEG in the 20L Parr polyol than the other reactions. The model structure of the dimer acid and PEG polyol is shown in *Figure 14* below.



Figure 14. Model Biobased Poly(ester-ether) Polyol Chemical Structure

The chemical structure in *Figure 14* shows the polyester linkage between the dimer acid and PEG 200 and the hydroxyl functional ends groups of the polyol.

### 2.5 Conclusion

Biobased poly(ester-ether) polyol was synthesized and scaled from a 5 L glass reactor to a 20 L Parr reactor for further formulation in flexible polyurethane foam. The hydroxyl values for the resulting polyols formed in a 5 L glass reactor, 2 L Parr reactor, and 20 L Parr reactor were 127 (mgKOH/g), 141 (mgKOH/g), and 150 (mgKOH/g) respectively which are consistent with commercial polyols for semi-rigid polyurethane polyols commercially available. The molecular weight of each of the reactors used was an average of 853 (g/mol) as calculated from the hydroxyl values. The extent of reaction in each reactor was an average of 96.6 % as calculated from the acid value, with confirmation of a polyester linkage formed by the shift of the carbonyl peak to 1730 cm<sup>-1</sup> by FTIR analysis. The average moisture content of the polyol (1.23 wt.%) is applicable for further formulation for polyurethane foam synthesis. The consistent results of the characterization achieved from each of the reactors used illustrate the polyol is reproducible and easily scaled. Chapter 3: Synthesis and Analysis of Carbinol Terminated Polydimethylsiloxane Polyol

# 3.1 Introduction and Literature Review

Functionalized monomers and oligomers are vitally important for polymer synthesis, especially thermosetting materials such as polyurethanes. In addition, oligomers containing functional end groups can be used to enhance polymer properties in ways such as introducing branching or by changing the surface energy that can affect adhesion properties. The main functional group of interest in synthesizing a polyol for polyurethane applications is hydroxyl functionality. Cyclic carbonates have been used to introduce hydroxyl functionality to molecules through ring-opening reaction as shown in *Figure 15* below.



Figure 15. Aminolysis of Cyclic Carbonates

The reaction between amine functionalized molecules and cyclic carbonates to form a urethane linkage and change the amine functionality to hydroxyl has been studied for various carbonates and amine species [1]. The carbonate of most interest for this research is propylene carbonate because it is readily available, a liquid at room temperature, and has a relatively low cost compared to other cyclic carbonates [15]. Research has shown that cyclic carbonates such as propylene carbonate (PC) can be used to introduce hydroxyl functionality to aminopropyl-terminated polydimethylsiloxane (APDMS) [1]. However, the chemical kinetics of non-solvent reaction of PC and APDMS has not been thoroughly studied.

#### 3.2 Carbinol Terminated Polydimethylsiloxane Synthesis

#### 3.2.1 Materials – Synthesis

The materials used to perform the synthesis include Propylene Carbonate, Aminopropyl-Terminated Polydimethylsiloxane (1000 mol/g avg.), and ultra-high purity Nitrogen. The reaction was conducted in a 250 mL round bottom flask equipped with a thermometer in an oil bath. A purification process was used to wash the product and required the use of deionized water and sodium chloride. The purification process was conducted in a 1 L separatory flask.

#### 3.2.2 Method - Synthesis

A 250 mL round bottom flask was charged with 100 grams (.1 mol) of Aminopropyl-Terminated Polydimethylsiloxane (APDMS) and 21.44 grams (.21 mol) of Propylene Carbonate (PC). The reaction mixture was purged with ultra-high purity nitrogen for 15 minutes under constant stir. The reaction mixture was sealed and the temperature was raised to 70°C for 6 hours under constant stir. The product of the synthesis was cooled to room temperature and placed in a separatory flask. A solution to wash the product in a volume of 100 mL of 15 wt.% Sodium Chloride in deionized water was poured into the separatory flask, the flask was flipped 10 times, the mixture was left to separate for 30 minutes, and the water solution was drained from the product. The water washing process was repeated 5 times to remove excess PC.

#### 3.2.3 Materials – Kinetic Study

The materials used to perform the synthesis include Propylene Carbonate, Aminopropyl-Terminated Polydimethylsiloxane (5000 mol/g), and ultra-high purity Nitrogen. The reaction was conducted in a 250 mL round bottom flask equipped with a thermometer in an oil bath.

### 3.2.4 Method – Kinetic Study

A 250 mL round bottom flask was charged with 150 grams (.03 mol) of Aminopropyl-Terminated Polydimethylsiloxane (APDMS) and 7 grams (.069 mol) of Propylene Carbonate (PC). The reaction mixture was purged with ultra-high purity nitrogen for 15 minutes under constant stir. The reaction mixture was sealed and the temperature was raised to 74°C for 140 minutes under constant stir. Samples were taken of the reaction mixture every 5 minutes for the half hour, then every 10 minutes until the end. A second reaction using the same weight of reactants was conducted at 23°C, with samples taken every 20 minutes for the first hour, then samples taken every 30 minutes until 480 minutes. A third reaction using the same weight of reactants was conducted at 54 °C, with samples taken every 30 minutes until 240 minutes. The samples of the three reactions were placed in a freezer at -18 °C to limit further reaction until the samples were characterized.

#### 3.3 Characterization Methods

#### 3.3.1 Viscosity Measurements

Viscosity measurements were conducted using a Brookfield DV-E Viscometer, model LVDVE. The measurements were conducted at 20°C with spindle LV-1 at 30% to 70% torque. The spindle was placed into the sample to the height of the required depth markings on the spindle and did not touch the bottom or sides of the sample container during the measurements.

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#### 3.3.2 Thermogravimetric Analysis

Thermogravimetric Analysis was conducted using a TA Instruments TGA-Q50. A standard aluminum pan was placed on the scale and tared, sample of material was placed on the tared pan, and inserted into the oven. The temperature of the oven was raised by 10°C/min to 550°C. The developed graphs were analyzed for start of degradation and degradation temperature.

# 3.3.3 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy was conducted using a Shimadzu IRAffinity-1. The samples were analyzed from wavelengths ranging from 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.

#### 3.3.4 Nuclear Magnetic Resonance Analysis

The reaction reactants and the purified reaction product were placed in NMR tubes and dissolved in  $C_dCl_3$ . The samples were analyzed with an Agilent DDR2 500 MHz NMR spectrometer under HNMR conditions. The data from the analysis was compared to models generated by chemical structures developed by ChemDraw software.

### 3.3.5 Hydroxyl Value Titration and Molecular Weight Calculation

ASTM Test Method E1899-08 was used to measure hydroxyl value [11]. The hydroxyl group of the product is reacted with excess p-toluenesulfonyl isocyanate (TSI), to form an acidic carbamate. Water is added to convert unreacted isocyanate to sulfonamide, followed by direct potentiometric titration of the acidic carbamate with tetrabutylammonium hydroxide (Bu<sub>4</sub>NOH) in nonaqueous medium. The hydroxyl value was calculated as mgKOH/g-sample by the following in *Equation 5*.

hydroxyl number (OH#) = 
$$\frac{(V_2 - V_1) \times N \times 56.1}{sample, g}$$

#### Equation 5. Hydroxyl Value Equation

Where N is the concentration of  $Bu_4NOH$  in meq/mL,  $V_1$  is the mL  $Bu_4NOH$  to first potentiometric end point,  $V_2$  is the mL  $Bu_4NOH$  to second potentiometric end point, sample (g) is the mass of the sample in grams, and 56.1 is the molecular mass of potassium hydroxide (KOH).

The molecular weight of the reaction product was determined using a combination of the hydroxyl value titration data and the average functionality [13]. The average functionality was calculated by *Equation 6* below.

$$f_{av} = \frac{\sum (N_i \times f_i)}{\sum N_i}$$

Equation 6. Average Functionality Equation

Where  $f_{av}$  is the average functionality,  $N_i$  is the moles of species i, and  $f_i$  is the functionality of species i. The molecular weight was calculated by *Equation 7* below.

$$m.w. = \frac{56100 \times f_{av}}{OH\#}$$

#### Equation 7. Molecular Weight Equation

Where m.w. is the molecular weight of the product, 56100 is the amount of milligrams in a mole of KOH,  $f_{av}$  is the average functionality of the product, and OH# is the hydroxyl value number (mg KOH/g sample) of the product.

### 3.3.6 Amine Value Titration

The total amine value was determined by the ASTM test method D2074 [17]. A sample weight of 0.5 grams was dissolved in 50 mL of Isopropyl Alcohol. Bromophenol Blue indicator was added in the amount of 5 drops to the sample solution and titrated with 0.2 N Hydrochloric Acid solution until the solution turned from blue to yellow. The solution was constantly stirred with a magnetic stir bar during the titration.

### 3.4 Results and Discussion

### 3.4.1 Viscosity Measurements

The viscosity of the reactants and product were determined using a Brookfield viscometer by the method previously stated in section 3.3.1. The results of the viscosity measurements conducted on the reactants and products of the OHPDMS reaction and purification are shown in *Table 8*.

Carbinol PDMS Synthesis Viscosity			
Chemical	Viscosity (cP)		
Propylene Carbonate	298		
Aminopropyl PDMS	25		
Reaction Mixture	73		
Unwashed OHPDMS	338		
Washed OHPDMS	543		

 Table 8. Carbinol PDMS Synthesis Viscosity for Reactants and Products

The viscosity of the reaction mixture of PC and APDMS increased from 73 cP to 338 cP in the unwashed product OHPDMS. This increase is due to the formation of hydroxyl group on the OHPDMS that lead to more hydrogen bonding molecular interactions. The viscosity increased of the product increased from

338 cP to 543 cP after purification. The purification removed excess PC, increasing the average

molecular weight of the product and increasing hydrogen bonding molecular interactions.

# 3.4.2 Degradation Temperature

The degradation temperature of the reactants and the products were determined by thermogravimetric

analysis by the method previously stated in section 3.3.2. The results of the TGA characterization are

given in Table 9. The TGA data of the washed and unwashed OHPDMS is given in Figure 16 and Figure 17.

Table 9. Carbinol PDMS Synthesis Degradation Temperature for Reactants and Products

Carbinol PDMS Synthesis Degradation Temperature				
Chemical	Start of Degradation (°C)	Propylene Carbonate (wt.%)	Degradation	
			Temperature (°C)	
Propylene Carbonate	75	100	155.5	
Aminopropyl PDMS	200	0	358.2, 409.7, 459.3	
Unwashed OHPDMS	200	4.14	318.1, 370.4, 531.3	
Washed OHPDMS	200	1.78	304.4,368.6,494.6	



Figure 16. TGA of Unwashed OHPDMS



### Figure 17. TGA of Washed OHPDMS

The APDMS and OHPDMS samples had multiple degradation peaks due to the presence of carbon and silicon atoms in the structure. The majority of the PDMS containing samples degraded after 300°C, with the degradation peaks of the unwashed and washed OHPDMS at 96°C being from residual Propylene Carbonate in the samples.

# 3.4.3 Fourier Transform Infrared Analysis

Fourier transform infrared analysis was performed on the reactants and products of the OHPDMS reaction by the method described in section 3.3.3. The reactants used in the reaction yielded the FTIR spectras shown in *Figure 18* and *Figure 19* below.



Figure 18. Full FTIR Spectra of Propylene Carbonate



Figure 19. Full FTIR Spectra of Aminopropyl-Terminated PDMS

In *Figure 18*, the carbonyl peak can be seen at 1790 cm<sup>-1</sup> which is indicative of the cyclic carbonate structure in Propylene Carbonate. In *Figure 19* the siloxane peaks at 790 cm<sup>-1</sup>, 1000 cm<sup>-1</sup>, 1260 cm<sup>-1</sup> can be seen at the beginning of the spectra of Aminopropyl-Terminated PDMS [18]. The amine peak at 2900

cm<sup>-1</sup> and the siloxane peaks can be seen in the both the unwashed and washed OHPDMS products in *Figure 20* and *Figure 21* below.



Figure 20. Unwashed OHPDMS FTIR Spectra



Figure 21. Washed OHPDMS FTIR Spectra

In both of the washed and unwashed OHPDMS FTIR, a urethane peak at 1700 cm<sup>-1</sup> as seen in *Figure 22* below [6].



Figure 22. Washed and Unwashed OHPDMS Urethane Peak Comparison

The urethane peak present in both of the samples shows that reaction has occurred between PC and APDMS by forming a urethane linkage. Excess PC in the reaction product was removed during the wash purification as shown in *Figure 23* below and confirms the TGA analysis in section 3.4.2.



Figure 23. Washed and Unwashed OHPDMS Carbonyl Peak Comparison

The removal of the cyclic carbonyl peak in the washed sample shows that much of the excess PC has been removed from the reaction product. The purified product is important for further synthesis in polyurethane foam as PC can limit crosslinking reaction in the polyurethane matrix.

### 3.4.4 Nuclear Magnetic Resonance Analysis

The nuclear magnetic resonance analysis of the reactants and the purified product was conducted by the method described in section 3.3.4. The results of the propylene carbonate, aminopropyl-terminated PDMS, and purified OHPDMS product NMR analysis are shown below in *Figure 24*, *Figure 25*, *Figure 26*, *Figure 27*, and *Figure 28*.



Figure 24. NMR Spectra of Aminopropyl-Terminated Polydimethilsiloxane



Figure 25. NMR Spectra of Propylene Carbonate



Figure 26. Magnified NMR Spectra of Propylene Carbonate







Figure 28. Magnified NMR Spectra of Purified Carbinol-Terminated Polydimethylsolixane

The structures and NMR values that the NMR data was compared against are shown in *Figure 29*, *Figure 30*, and *Figure 31* below.



Figure 29. Aminopropyl-Terminated Polydimethylsiloxane Structure NMR Prediction



Figure 30. Propylene Carbonate Structure NMR Prediction



Figure 31. Carbinol-Terminated Polydimethylsiloxane Structure NMR Prediction

The largest peak seen on the APDMS NMR spectra is from the hydrogen of the silicon methyl group at .2 ppm which can also is present on the OHPDMS NMR spectra. The magnified propylene carbonate NMR spectra does not show any peak at 4.94 or 5.37 that would indicate partial degradation of the ring and hydroxyl protons. The magnified OHPDMS NMR spectra shows a large peak at 4.94 and no peaks at 5.37 which indicates all hydroxyl groups formed in the OHPDMS product were primary, contrary to work performed in earlier studies suggesting 70% of hydroxyl groups will be secondary (1). The result found in this study of only primary hydroxyl formation is most likely due to steric hindrance between the methyl group of propylene carbonate and the bulky APDMS chain which led to selective ring opening of the propylene carbonate on the opposite side of the methyl group.

### 3.4.5 Hydroxyl Value Titration

The hydroxyl value of the washed OHPDMS was found to be 65.8 (mgKOH/g sample) which is consistent with other commercial flexible polyurethane foam polyols as determined by the method described in section 3.3.5. The molecular weight of the washed OHPDMS was calculated from the titrated hydroxyl value by the equation shown before in *Equation 7*.

The molecular weight for the washed OHPDMS was found to be 1705.2 (g/mol). The determined molecular weight was higher than the expected molecular weight of 1204.2, which can be explained by either experimental error or an average molecular weight of APDMS that is larger in actuality than described by the manufacturer.

# 3.4.6 Amine Value Titration

Amine values were determined by the method described in section 3.3.6. The final amine value of the carbinol PDMS product was 0.55 mgKOH/g. The initial amine value of the reaction mixture determined to be 92.39 (mgKOH/g) and is significantly higher than the final amine value of the OHPDMS product.

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The extent of conversion was calculated by equation *Equation 8* below as 99.4% conversion based of the initial amine value of the reactants and the final amine value of the product [13].

Conversion % = 
$$\left(1 - \frac{Final Amine Value}{Initial Amine Value}\right) \times 100$$

Equation 8. Extent of Conversion Equation

## 3.4.7 Kinetics Study

A kinetic study was performed to determine rate law constant and activation energy of the OHPDMS reaction. Each of the samples taken during the three reactions at 74°C, 54°C, and 23°C were titrated for amine value. The density of OHPDMS was used to convert the Amine Value from titration to concentration of APDMS. The density of OHPDMS was found by weighing .1 mL of sample and determining g/mL. The result of the density measurements was found to be 1.065 (g/mL). The Amine Value was converted to APDMS concentration by the equation below in *Equation 9*.

$$[APDMS] = \frac{Amine \, Value \, \times \, \rho \, \times 1000}{56.1 \, \times f \, \times 1000}$$

#### Equation 9. APDMS Concentration from Amine Value Equation

Where [APDMS] is the concentration of APDMS in the solution in g/mol, Amine Value is the amine value of the sample in mgKOH/g sample,  $\rho$  is the density of the sample in g/mL, 1000 in the numerator is the conversion of mL to L, 56.1 is the molecular weight of KOH in g/mol, f is the functionality of APDMS which is 2, and 1000 in the denominator is the conversion of g to mg. In Figure 32, Figure 33, Figure 34 inverse concentration was plotted against time to generate a linear plot, indicating 2<sup>nd</sup> order reaction kinetics [19].



Figure 32. (1/[APDMS]) vs. Time During OHPDMS Synthesis at 23°C



Figure 33. (1/[APDMS]) vs. Time During OHPDMS Synthesis at 54°C



Figure 34. (1/[APDMS]) vs. Time During OHPDMS Synthesis at 74°C

In Figure 32, Figure 33, and Figure 34 the inverse plot fit the data of APDMS concentration vs. time with an R<sup>2</sup> value of .949, .960, and .984 respectively showing good agreement for the line of best fit and indicating 2<sup>nd</sup> order reaction.

The k value constant for each of the 1/[APDMS] vs. time plots were found by the linear line of best fit and the equation given in *Equation 10*.

$$\frac{1}{[APDMS]} - \frac{1}{[APDMS]_o} = kt$$

Equation 10. 2<sup>nd</sup> Order Reaction Rate Equation

Where [APDMS] is the concentration at time t, k is the reaction constant, t is time in minutes, and  $[APDMS]_{o}$  is the initial concentration. The k constants were determined for each reaction condition and plotted to determine the Arrhenius expression. The natural log of the k constants with respect to the inverse of the reaction temperature in Kelvin were plotted. A linear line of best fit was found in *Figure 35* to have a R<sup>2</sup> value of 0.98 showing good agreement of the data to a linear equation.



Figure 35. Arrhenius Plot of OHPDMS Reaction Kinetics

The activation energy ( $E_a$ ) and A constant were determined using the line of best fit from *Figure 35* and the equation shown below in *Equation 11*.

 $\ln k = (-E_a R) \left(\frac{1}{T}\right) + \ln A$ Equation 11. Logarithmic Form of the Arrhenius Equation

The activation energy ( $E_a$ ) was found to be 25.39 kJ/mol and the A constant was found to be 19.05 s<sup>-1</sup>. The A constant and activation can be used to determine the rate of reaction for a temperature in the range of room temperature to the degradation point of propylene carbonate and can be used for reactor design.

### 3.5 Conclusion

Carbinol-terminated PDMS was synthesized for further formulation in flexible polyurethane foams through the ring opening of propylene carbonate by reaction with aminopropyl-terminated PDMS and the reaction product was purified. The OHPDMS was found to have a viscosity of 543 cP, higher than both of the reactants due to the increase molecular weight and hydrogen bonding between hydroxyl end groups. The reaction was further confirmed by FTIR analysis with the formation of a peak at 1700 cm<sup>-1</sup> in the product indicative of a urethane linkage and the extent of reaction was found to be 99.4 % conversion by amine titration. It was found that the hydroxyl group on the OHPDMS formed was primary by NMR analysis. Hydroxyl value titration yielded the value of OHPDMS to 65.8 (mgKOH/g), consistent with commercially available flexible polyols, and the molecular weight was calculated from the titration data to be 1705.2 (g/mol). Amine titration was used in a kinetic study of the reaction to find 2<sup>nd</sup> order reaction kinetics with an E<sub>a</sub> of 25.39 kJ/mol which can be used for further scale up and process optimization in future work.

#### Chapter 4: Synthesis and Analysis of Flexible Polyurethane Foam

#### 4.1 Introduction and Literature Review

### 4.1.1 Polyurethane Reaction

Polyurethane materials are a major proportion of the total materials used in the polymer industry with versatility as a thermoset or thermoplastic. A major application for polyurethane thermosetting materials is in flexible and rigid polyurethane foam. Water blown polyurethane foam is formed by a reaction between isocyanate and polyol, along with a reaction between isocyanate and water as shown in *Figure 36* below [10].

$$HO-R'-OH + OCN-R-NCO \longrightarrow \begin{bmatrix} C-N-R-N-C-O-R'-O \\ \parallel & \parallel & \parallel \\ OH & HO \end{bmatrix}_{n}^{(1)}$$

$$2 H_{2}O + OCN-R-NCO \longrightarrow H_{2}N-R-NH_{2} + 2 CO_{2}$$

$$(2)$$

#### Figure 36. Polyurethane Chemical Reaction Schemes

In the first reaction in *Figure 36* the oxygen of the alcohol from the polyol attacks the partially positive carbon on the isocyanate to for a urethane linkage. The first reaction in *Figure 36* builds viscosity in the polyurethane foam mixture and eventually solidifies to for the polyurethane matrix of the foam. In the second reaction in *Figure 36*, the oxygen of the water attacks the partially positive carbon of the isocyanate to for a urea linkage and carbon dioxide. The carbon dioxide in the second reaction of *Figure 36* is released in the form of gas and blows the foam, which creates pores in the polyurethane matrix and reduces the density of the foam. The two main reactions in polyurethane foam synthesis are balanced by the amount of water introduced, as well as the addition of catalyst that promote both reactions. The balance of the two reactions is important because the foam will not rise and become too dense if there is not enough water or catalyst is added to the polyurethane mixture, while too much water or catalyst will disrupt the cell formation and collapse the foam.

4.1.2 Petroleum and Biobased Flexible Polyurethane Foams

The objective of the experimentation in this chapter was to reduce the amount of petroleum based polyether polyol in the flexible polyurethane foam synthesis by introducing a dimer fatty acid biobased polyol to the foam mixture. Other epoxidized vegetable oil based polyols have been used to effectively replace petroleum based polyol in foam mixtures in previous work up to 20% biobased polyol content [10, 21]. A flexible polyurethane foam with up to 50% biobased content was synthesized utilizing dimer fatty acid based polyol and characterized per ASTM standards for flexible polyurethane foam. The dimer fatty acid polyol is a drop-in replacement for existing polyether polyol and can be processed in the same manner as current polyurethane flexible foam.

### 4.2 Flexible Polyurethane Foam Synthesis

### 4.2.1 Materials

The materials used in flexible polyurethane foam synthesis include Pluracol 816 poly(ether) polyol from BASF, biobased poly(ester-ether) polyol synthesized in a 5 L glass reactor from Chapter 2, Tegostab B8734 silicone surfactant, Diethanolamine (DEOA) as a crosslinking agent, DABCO 33LV as a catalyst, Dabco BL19 as a catalyst, Voranol 4053 from Dow Chemical as a cell-opening agent, deionized water as a blowing agent, and polymeric Methylene Diphenyl Diisocyanate Suprasec 7007 from Huntsman. McLube 1038 was used a silicone mold release agent in box foam synthesis.

### 4.2.2 Free Rise Method

Free rise studies were conducted for a control foam formulation that used 100 wt.% Pluracol polyol, Pluracol mixed with 20 wt.% biobased poly(ester-ether) polyol, Pluracol mixed with 50 wt.% biobased poly(ester-ether) polyol, and Pluracol mixed with 20 wt.% biobased poly(ester-ether) polyol and 0.25-2 wt.% OHPDMS polyol. The polyol, Tegostab B8734, DEOA, 33LV, BL19, Voranol 4053, and D.I. water with a total mix weight of 40 grams were first mixed in a cup for 15 minutes by a pneumatic mixer. Suprasec 7007 was then added with an Isocyanate (ISO) index of 85 to the polyol mix. The reaction mixture was mixed until the foam started to rise in the cup, then removed from the mixer placed on a table to rise. All mixing and reaction was conducted in a fume hood while wearing appropriate personal protective equipment (PPE). PPE used during mixing included safety glass wear, face shield, laboratory coat, and elbow long neoprene gloves.

### 4.2.3 Box Mold Method

Once a formulation met criteria for the free rise study, a larger quantity was synthesized and placed in a box mold. The box mold was first coated with McLube 1038 and placed in an oven at 50°C to cure for 20 minutes. The polyol mixture was mixed for 15 minutes in total amount of 250 grams with a pneumatic mixer. After initial mixing of the polyol mixture, Suprasec 7007 was added in the amount of 85 ISO index. The isocyanate and polyol mixture was mixed until it started to rise in the container. The rising reaction mixture was poured into the box mold and the mold was sealed. The foam was left to rise in the mold for 20 minutes before opening. The box mold was disassembled to gently remove the foam and the foam was left to cure in a fume hood for 24 hours. All mixing and reaction was conducted in a fume hood with appropriate PPE worn.

### 4.3 Characterization Methods

### 4.3.1 Rise Profile

The free rise study reaction was timed starting with the addition of Suprasec 7007 to the polyol mixture with the cream time, rise time, and tack free time recorded. The cream time was decided when the reaction mixture began to thicken and turn opaque, the rise time was recorded when the reaction

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mixture stopped rising in the cup, and the tack free time was recorded when the foam did not stick to a nitrile glove when touched.

### 4.3.2 Tensile Strength Analysis

The tensile testing was conducted per ASTM D 3574, Test E [3]. The box mold foam samples were conditioned at room temperature and humidity for a minimum of 12 hours. Samples were cut after the skin of the foam bun was removed by cutting 10 mm of material from all of the sides of the mold product. Sheets were cut from the foam bun of 12.5 mm ± 1.5 mm with the thickness in the rise direction. Die A from ASTM D412 was used to stamp out a minimum of three samples using a hydraulic press making sure the samples had no obvious nicks or pores. The tensile test was performed using a United Testing Systems model SFM-20 ultimate tensile strength (UTS) equipment. The samples were run at 500 mm/min ± 50 mm/min after being clamped into the UTS equipment. The tensile strength was reported in kilopascals (kPa).

#### 4.3.3 Tear Strength Analysis

The tear strength testing was conducted per ASTM D 624 [22]. The samples were conditioned at room temperature and humidity for a minimum of 12 hours. After removing the skin by cutting each side of the foam bun by 10 mm, a sheet was cut from the foam bun of 10 mm  $\pm$  1.5 mm thickness with the rise direction in the direction of the thickness. Die C from ASTM D 624 was used to cut out at least three samples using a hydraulic press making sure the samples had no obvious nicks or pores. The samples were placed tested using a United Testing Systems model SFM-20 equipment at 500 mm/min  $\pm$  50 mm/min. The tear strength was reported as N/m using the equation seen in *Equation 12*.

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$$T = \frac{F}{t}$$

#### Equation 12. Tear Strength Equation

Where T is the tear strength (N/m), F is the maximum force to failure (N), and t is the measured thickness (m).

### 4.3.4 Wet Compression Set Analysis

Wet compression set testing was performed per ASTM D 3574, Test D [3]. The foam samples were conditioned at room temperature and humidity for a minimum of 12 hours. The skin of the foam bun was cut by removing 10 mm from each side of the bun. A minimum of three samples were cut 50 mm wide/long and 25 mm thick with the thickness being in the rise direction. The samples were kept in opaque bags if not tested within 24 hours. The exact dimensions of the foam samples were measured using a micrometer. After measurement, the foam samples were placed in a plate fixture and compressed to 50% of the original thickness. The fixture was immediately placed in a humidity chamber at 50°C  $\pm$  2°C and 95  $\pm$  5 % humidity for 22 hours  $\pm$  5 minutes. Once the test was complete and the samples removed from the humidity chamber, the samples were released from the plate fixture and conditioned at room temperature/humidity for 30-40 minutes. The final thickness of the samples were measured by a micrometer. The wet compression percentage was calculated using the equation in *Equation* 13.

% *Compression* = 
$$\frac{t_i - t_f}{t_i} \times 100$$

Equation 13. Wet Compression Percentage Equation

Where % Compression is the percentage of compression from the wet compression testing,  $t_i$  is the initial thickness of the sample,  $t_f$  is the final thickness of the sample, and 100 is a conversion factor for percentage.

### 4.3.5 Density Analysis

The density of each of the foams made was found using the samples from the wet compression testing prior to the testing of the samples [3]. The dimensions of each sample was measured by a micrometer and recorded. The weight of each sample was found using a digital scale. The density of the sample was calculated by the equation in *Equation 14* shown below.

$$\rho = \frac{m}{L \times w \times h}$$

Equation 14. Polyurethane Foam Density Equation

Where  $\rho$  is the density of the sample (kg/m<sup>3</sup>), m is the mass of the sample (kg), L is the length of the sample (m), w is the width of the sample (m), and h is the thickness of the sample (m).

#### 4.4 Results and Discussion

### 4.4.1 Rise Profile Results

The rise profile study was conducted per the method described in section 4.3.1. The results from the study for the control, 20 wt.% biobased polyol, and 50 wt.% biobased polyol formulations are shown in *Figure 37* below. A suitable free rise was not obtained for flexible foam formulations that contained OHPDMS polyol from 0.25-2 wt. % due to the immiscibility of the OHPDMS with the other polyols used in the formulation.



Figure 37. Control, 20 wt. %, and 50 wt. % Polyol Formulation Rise Profiles

All three formulations yielded rise profiles that met the conditions needed for scale-up in an industrial setting. The cream times were under 10 seconds, the rise time were around 1 minute, and the tack free times were at or under 300 seconds.

# 4.4.2 Tensile Strength Results

The tensile strength of each of the box foam samples prepared were tested using the method described in section 4.3.2. The results of the testing are recorded in *Table 10* shown below.

Table 10. Tensile Strength of Synthesized Flexible Polyurethane Foams Samples

Tensile Force Data			
Sample	Force (kPa)		
Control	145.29		
20% Biobased	211.90		
50% Biobased	227.99		
Requirement (min)	80		

All three samples met the requirement of a minimum of 80 kPa of tensile strength. The tensile strength increased with increased amount of biobased polyol content.

# 4.4.3 Tear Strength Results

The tear strength of each of the box foam samples prepared were tested using the method described in section 4.3.3. The results of the testing are recorded in *Table 11* shown below.

Tear Force Data		
Sample	Force (N/m)	
Control	655.86	
20% Biobased	920.33	
50% Biobased	1259.59	
Requirement (min)	450	

Table 11. Tear Strength of Synthesized Flexible Polyurethane Foam Samples

All three samples met the requirement of a minimum of 450 N/m of tear strength. The tear strength increased with an increase of biobased polyol content.

# 4.4.4 Wet Compression Set Results

The compression set data for all three box foam samples prepared were tested using the method described in section 4.3.4. The results for the wet compression set testing are recorded in *Table 12*.

Wet Compression Set Data			
Sample	Compression (%)		
Control	29.02%		
20% Biobased	33.92%		
50% Biobased	35.91%		
Requirement (max)	40.00%		

 Table 12. Wet Compression Set of Synthesized Flexible Polyurethane Foam Samples

All three samples met the requirement of a maximum of 40% compression after the wet compression set testing. The compression amount increased with an increase in the amount of biobased polyol content, showing that the biobased polyol is more susceptible to humidity and aging.

### 4.4.5 Density Results

The density data for each of the box foam samples prepared was determined by the method in section

4.3.5. The results from the density determination is tabulated in *Table 13* shown below.

Box Foam Density Data			
Sample	Density (kg/m <sup>3</sup> )		
Control	42.14		
20% Biobased	48.72		
50% Biobased	43.17		
Requirement Range	40-60		

Table 13. Densi	ty of S	Synthesized	Flexible	Polyurethane	Foam	Samples
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All three of the box foams synthesized fell within the range of typical flexible polyurethane foams used in seating applications.

### 4.5 Conclusion

Flexible polyurethane foam was formulated and synthesized using 0 wt.%, 20 wt.%, and 50 wt.% of biobased poly(ester-ether) polyol in commercially available poly(ether) polyol. The formulated foam was subjected to free rise study and yielded favorable results of cream time within 10 seconds, rise time within 60 seconds, and tack free time within 300 seconds for all formulations that were later used in box mold foam synthesis. The density of all three foams studied fell within the 40 (kg/m<sup>3</sup>) to 60 (kg/m<sup>3</sup>) range desirable for flexible polyurethane foam for seating applications. The tensile strength of the 0 wt.% biobased material, 20 wt.% biobased material, and 50 wt.% biobased material foam increased with increased amount of biobased material by 145.29 (kPa), 211.90 (kPa), 227.99 (kPa) respectively. The tear strength also increased with increase amount of biobased content, with a tear force of 655.86 (N/m), 920.33 (N/m), and 1259.59 (N/m) for 0 wt.% biobased material, 20 wt.% biobased material, and 50 wt.% biobased material respectively. All three of the foams passed the wet compression set testing, however the samples performed more poorly in the test as the biobased polyol amount increased in the foams. OHPDMS polyol was not successfully formulated to synthesize polyurethane foam due to miscibility issues with the other polyols in the formulation.

#### Chapter 5: Recommended Future Work

#### 5.1 Proposed Polydimethylsiloxane Polyol

### 5.1.1 Carbinol-Terminated PDMS and Dimer Acid Polyol Synthesis

The miscibility issues associated with the OHPDMS polyol synthesized in chapter 3 with the biobased poly(ester-ether) polyol synthesized in chapter 2 can be resolved with further reaction of the OHPDMS polyol. A polyester polyol synthesized from OHPDMS and dimer acid is proposed to increase the molecular weight of the OHPDMS and increase the miscibility of the OHPDMS with convention polyols. The OHPDMS/Dimer Acid polyol would be made by reacting OHPDMS and Dimer Acid by condensation reaction in a 1.5:1 molar ratio (OHPDMS:Dimer Acid) to yield a hydroxyl functional polyol with a degree of polymerization of 5 [13]. The condensation reaction would be conducted with 0.15 wt.% Titanium Butoxide as the condensation catalyst. The a two stage reaction would be conducted first at 160°C under constant stir and vacuum to remove water generated during the oligomerization, then the temperature would be increased to 200°C under constant stir and vacuum to polymerize the oligomers.

#### 5.1.2 Carbinol-Terminated PDMS and Dimer Acid Polyol Characterization

The OHPDMS/Dimer Acid polyol would be characterized by TGA, Viscometry, Acid Value Titration, and Hydroxyl Value Titration as detailed in chapter 2. The TGA analysis would yield both the moisture content and the degradation temperature of the polyol. Viscometry data would show an increase in viscosity of the product from the reactants if the molecular weight was increased through reaction. Acid value titration would show if there is any unreacted dimer acid, there should be a 0 acid value with the proposed molar ratio for the synthesis. Hydroxyl value titration would yield information needed for further polyurethane foam formulation and molecular weight could be calculated from the results.

#### 5.2 Proposed Polyurethane Synthesis and Characterization

#### 5.2.1 OHPDMS and Dimer Acid Polyol Flexible Foam Synthesis

OHPDMS/Dimer Acid polyol would be formulated into existing 20 wt.%-50 wt.% biobased poly(esterether) polyol flexible polyurethane foam formulation in 0.5 wt.% to 2 wt.%. The goal would be to add enough OPDMS/Dimer Acid polyol to coat the outside of a box mold polyurethane foam to aid in mold release properties. First, free rise studies would be conducted to find an optimum formulation with OHPDMS/Dimer Acid polyol with cream time, rise time, and tack-free time recorded. Next, a box mold foam would be synthesized to be used for testing.

#### 5.2.2 OHPDMS and Dimer Acid Polyol Flexible Foam Characterization

Flexible polyurethane foam formulated with 0.5 wt.% to 2 wt.% OHPDMS/Dimer Acid polyol would be characterized per methods in chapter 4. The tensile strength, tear strength, wet compression set, and density would be tested. In addition to the tests performed on past foams, Scanning Electron Microscopy would be used to analyze the skin and internal bun samples of the polyurethane foam synthesized by Energy Dispersive Spectroscopy (EDS). EDS analysis of the foam skin and internal bun samples should yield a higher proportion of silicon atoms on the skin than the internal bun sample, showing that the OHPDMS/Dimer Acid Polyol migrated to the surface of the polyurethane foam in the box mold. The mold release ability of the foam could increase with more silicon atoms on the surface of the bun due to differences in free energy from the silicon and the metal box mold. In addition, a force gauge could be used to remove a samples with and without OHPDMS/Dimer Acid polyol to show any enhanced mold release properties.

5.2.3 OHPDMS and Dimer Acid Polyol Thermoplastic Polyurethane Synthesis

Another application for the OHPDMS/Dimer Acid polyol could be to synthesize a novel thermoplastic polyurethane (TPU). The OHPDMS/Dimer Acid polyol proposed would be difunctional and could be reacted with difuctional isocyanate such as Methylene Diphenyl Diisocyanate. The diol and isocyanate would be mixed at room temperature in a 1:1 molar ratio (diol:isocyanate) under a blanket of nitrogen to limit the amount of moisture present during the reaction. Water can react with the isocyanate to form imperfections in the TPU backbone through undesirable side reaction products such as urea linkages.

5.2.4 OHPDMS and Dimer Acid Polyol Thermoplastic Polyurethane Characterization A TPU synthesized from OHPDMS/Dimer Acid diol would be characterized by TGA, DSC, melt index viscometry, and hydroxyl value titration. The TGA analysis would yield the degradation temperature of the TPU product. DSC would show the percent crystallinity, melting temperature, and the glass transition temperature of the TPU. Melt index viscometry would be used to determine the viscosity of the molten TPU which could help determine optimal processing conditions in further extrusion of the

TPU. The hydroxyl value could be used to determine the molecular weight of the TPU as there should be one hydroxyl group for every chain of polymer due to the molar ratios used during synthesis.

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APPENDIX

# List of Equations

Equation 1. Hydroxyl Value Equation

Equation 2. Acid Value Equation

Equation 3. Average Functionality Equation

Equation 4. Molecular Weight Equation

Equation 5. Hydroxyl Value Equation

Equation 6. Average Functionality Equation

Equation 7. Molecular Weight Equation

Equation 8. Extent of Conversion Equation

Equation 9. APDMS Concentration from Amine Value Equation

Equation 10. 2nd Order Reaction Rate Equation

Equation 11. Logarithmic Form of the Arrhenius Equation

Equation 12. Tear Strength Equation

Equation 13. Wet Compression Percentage Equation

Equation 14. Polyurethane Foam Density Equation

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