SIMULATION AIDED ANALYSIS AND EXPERIMENTAL STUDY OF
POLYURETHANE POLYMERIZATION REACTION AND FOAMING PROCESS

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Doctor of Philosophy

by

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The undersigned, appointed by the dean of the Graduate School, have examined the
dissertation entitled

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POLYURETHANE POLYMERIZATION REACTION AND FOAMING PROCESS

presented by Harith H. Al-Moameri, a candidate for the degree of doctor of philosophy,
of Chemical Engineering, and hereby certify that, in their opinion, it is worthy of
acceptance.

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________________________________________________________________________

Associate Professor Thomas Greg Engel
To my amazing and outstanding wife, Rusul Al-Itbi.
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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................ ii

LIST OF FIGURES ................................................................................................................... viii

LIST OF TABLES ..................................................................................................................... xiv

ABSTRACT ............................................................................................................................... xvii

CHAPTER 1. INTRODUCTION ................................................................................................. 1

CHAPTER 2. SIMULATION OF LIQUID PHYSICAL BLOWING AGENTS FOR FORMING RIGID URETHANE FOAMS ........................................................................ 5

2.1 Abstract ............................................................................................................................... 5

2.2 Introduction .......................................................................................................................... 5

2.3 Methodology ....................................................................................................................... 10

2.3.1 Materials and recipes ................................................................................................... 10

2.3.2 Physical blowing agents ............................................................................................... 11

2.4 Experimental Procedure .................................................................................................... 13

2.5 Results and Discussion ..................................................................................................... 15

2.5.1 Gel reaction ..................................................................................................................... 15

2.5.2 Foam reaction .................................................................................................................. 17

2.6 Conclusion ......................................................................................................................... 22

CHAPTER 3. SIMULATION BLOWING AGENT PERFORMANCE, CELL MORPHOLOGY, AND CELL PRESSURE IN RIGID POLYURETHANE FOAMS ............................................................................. 24

3.1 Abstract ............................................................................................................................... 24

3.2 Introduction .......................................................................................................................... 24

3.3 The Physical System and Assumptions ............................................................................. 26
CHAPTER 4. IMPACT OF THE MAXIMUM FOAM REACTION TEMPERATURE ON REDUCING FOAM SHRINKAGE ........................................ 51

4.1 Abstract ........................................................................................................ 51
4.2 Introduction .................................................................................................... 51
4.3 Methodology .................................................................................................. 55
  4.3.1 Experimental design .................................................................................. 55
4.4 Materials and recipes ...................................................................................... 56
  4.4.1 Gel experiments ....................................................................................... 56
  4.4.2 Foam experiments ..................................................................................... 58
  4.4.3 Scanning electron microscopy (SEM) ....................................................... 59
4.5 Results and discussion .................................................................................... 60
  4.5.1 Catalyst loading study ............................................................................. 64
  4.5.2 Density and shrinkage study ..................................................................... 69
4.6 Conclusion ...................................................................................................... 74
BIBLIOGRAPHY .............................................................................................................. 212

VITA .................................................................................................................................. 225
LIST OF FIGURES

Figure 2-1 Temperature profile of polyurethane gel reaction ........................................... 16
Figure 2-2 Concentration profile of isocyanate and alcohol moieties, isocyanate and alcohol monomer, and polymer .......................................................... 16
Figure 2-3 Experimental and simulation results of temperature profile, PDP, and tack-free time of rigid polyurethane foams blown by different physical blowing agents. .......... 18
Figure 2-4 Comparison of simulated foam heights blown by different blowing agents. . 19
Figure 2-5 Experimental and simulation percentage and of blowing agent remaining in the foam resin ......................................................................................... 21
Figure 2-6 % losses of blowing agents during mixing ......................................................... 21
Figure 3-1 Algorithm for simulating urethane foam formation including cell growth..... 28
Figure 3-2 Schematic diagram of bubbles in the resin phase. ............................................ 33
Figure 3-3 Experimental and simulation results of temperature profile, height profile, and tack-free time of rigid polyurethane foams blown by different physical blowing agents. 38
Figure 3-4 Simulation results of resin viscosity of foams by different physical blowing agents. .................................................................................................................. 39
Figure 3-5 Experimental and simulation data of foam height using physical blowing agent at two different loadings. ................................................................. 40
Figure 3-6 Experimental and simulation data of foam height using water as blowing agent at two different loadings. ................................................................. 41
Figure 3-7 Experimental and simulation data of foaming reaction temperature using water at two different loadings. ................................................................. 42
Figure 3-8 Simulation foam height using chemical and physical blowing agents at two different loadings. ................................................................. 43
Figure 3-9 Simulation of bubble radius. ................................................................. 44
Figure 3-10 Microscope image of foams blown by a) 6 and b) 8 g of n-Pentane. ........ 44
Figure 3-11 Resin viscosity versus constant/polymer concentration (Const./Cp)........ 45
Figure 3-12 Bubble Pressure simulation ................................................................. 46
Figure 3-13 Simulation results of bubble pressure, vapor pressure and temperature...... 47
Figure 4-1 Temperature profile of PU gel reaction control ......................................... 61
Figure 4-2 Temperature profile of PU gel reaction using A205 .................................. 62
Figure 4-3 Effect of preheating monomers of PU gel reaction using A205 or A205/glycerol as polyol on the maximum heat of reaction ........................................... 63
Figure 4-4 Effect of preheating monomers of PU foaming reaction using A205 or A205/glycerol as polyol on the maximum heat of reaction ........................................... 64
Figure 4-5 Temperature profile of A205 at ambient temperature (22°C) to achieve low catalysts loading ........................................................................... 65
Figure 4-6 Temperature profile of A205 at 35°C to achieve low catalysts loading ........ 66
Figure 4-7 Temperature profile of A205 at 45°C to achieve low catalysts loading ........ 66
Figure 4-8 Temperature profiles of PU gel reaction of the using the control (V490), A205, or A205/Glycerol as polyol ........................................................................... 67
Figure 4-9 Temperature profiles of PU foaming reaction using A205 as polyol .......... 68
Figure 4-10 Urethane concentration from the polymer-polymer reaction ............... 70
Figure 4-11 The relationship between the peak temperature of foaming reaction and shrinkage percentage for foams using the control, A205 and A205/Glycerol at different preheating temperatures with full catalyst loadings................................................................. 71
Figure 4-12 The relationship between the peak reaction temperature of foaming reaction and shrinkage percentage for foams using the control, A205 and A205/Glycerol at different preheating temperatures and different catalyst loadings.............................. 72
Figure 4-13 The relationship between the peak reaction temperature and percent density change for foams using the control, A205 and A205/Glycerol at different preheating temperatures and different catalyst loadings................................................................. 72
Figure 4-14. Scanning electron micrographs of the cut section of the foams showing the cell morphology ........................................................................................................................................... 74
Figure 5-1 Experimental data and simulation results of reaction temperature, viscosity profile, isocyanate moieties and polyol moieties of V360 (left) and V490 (right) using intra-molecular movement approach ................................................................. 90
Figure 5-2 Ratio of the rate of diffusion to the rate of reaction for inter-molecular diffusion ........................................................................................................................................... 91
Figure 5-3 Concentration profile of the encounter complex during the reaction suing inter-molecular movement (solid line) and viscosity profile (dash line). ......................... 92
Figure 5-4 Experimental data and simulation results of reaction temperature, viscosity profile, isocyanate moieties and polyol moieties of V360 (left) and V490 (right) using intra- and inter-molecular movement approach ........................................................................ 93
Figure 5-5 Ratio of the rate of diffusion to the rate of reaction for inter- and intra-molecular movement.................................................................................................................. 94
Figure 5-6 Concentration profile of the encounter complex during the reaction using inter-and intra-molecular movement (solid line) and viscosity profile of the resin (dash line). ................................................................. 94

Figure 5-7 Experimental data and simulation results of reaction temperature, viscosity profile, isocyanate moieties and polyol moieties of V360 (left) and V490 (right) using intra- and inter-molecular movement as a collision frequency faction............................... 96

Figure 5-8 Experimental and simulation results of temperature profile, height profile, and tack-free time of rigid polyurethane foams blown by different physical blowing agents. 98

Figure 6-1. Simulation results of the previous model........................................ 108

Figure 6-2. Simulation results of reaction temperature and resin viscosity profiles of DEG and TEG reactions.............................................................. 120

Figure 6-3. Simulation results of reaction temperature and resin viscosity profiles of V490 reactions................................................................. 121

Figure 6-4. Simulation results of reaction temperature and resin viscosity profiles of V360................................................................. 122

Figure 6-5. Simulation results of reaction temperature and resin viscosity profiles of PolyG and Jeffol R315x reactions........................................ 123

Figure 6-6. Values of the frequency factor of primary alcohol moieties reactions. ....... 126

Figure 6-7. Simulation results of reaction temperature and resin viscosity profiles of polyol mixtures reactions................................................................. 127

Figure 6-8. Impact of catalyst on reaction temperature of V360.................................. 128

Figure 6-9. Simulation results of 1-Pentanol and 2-Pentanol reactions......................... 130
Figure 6-10. Simulation results of reaction temperature at different power of T of Equation 6-7

Figure 7-1 Schematic view of step-growth and chain-growth polymerization assuming A and B are bifunctional monomers.

Figure 7-2 Illustration of different moieties.

Figure 7-3 Reaction temperature and resin viscosity profiles of polyurethane homogeneous reaction.

Figure 7-4 Resin viscosity vs. reaction temperature for homogeneous and catalytic gel reactions.

Figure 7-5 Reaction temperature (a) and resin viscosity (b) profiles of polyurethane catalytic reactions considering step growth mechanism.

Figure 7-6 Analysis of $k_{\text{coupling}} / k_0$.

Figure 7-7 Effect of $K_{\text{coupling}}/K_{\text{decoupling}}$ ratio on urethane formation and reaction temperature profile.

Figure 7-8 Comparison of simulation with and without considering Hougen-Watson equation.

Figure 7-9 Reactions rates at different reaction times.

Figure 7-10 Comparison of the simulation of reaction temperature of the three approaches with experimental data using two catalyst loadings.

Figure 7-11 Comparison of the temperature profile of Approaches 2 and 3 at indices 1.1 and 2.

Figure 7-12 Comparison of catalyst profile different simulation mechanism approaches.
Figure 7-13 Polymer concentration at the different efficiencies of polymer-polymer reactions. .......................................................... 165

Figure 8-1. Visual representation of concentrations profile of isothermal polymerization reactions. .......................................................... 184

Figure 8-2. Visual representation of concentrations profile of isothermal polymerization reactions. .......................................................... 185

Figure 8-3. Impact of fraction intra-reactions on polymer concentration and gel point time. .......................................................... 188

Figure 8-4. Visual representation of degree of polymerization profile. ...................... 189

Figure 8-5. Visual representation of temperature profile........................................ 193

Figure 8-6. Visual representation of viscosity profile of resin during the reaction. ...... 194

Figure 8-7. Impact of catalyst loading on reaction temperature. .......................... 196

Figure 8-8. Block diagram of the simulation program of Table 8-4.......................... 201

Figure 8-9. Block diagram of advanced simulation............................................. 202
LIST OF TABLES

Table 2-1 Gel and Foaming recipes of rigid polyurethane gel and foam .................... 11
Table 2-2 Specifications of Voranol 360 and isocyanate .............................................. 11
Table 2-3 Amount of each blowing agents used in the foaming formulation ............... 12
Table 2-4 Antoine constants, critical pressure, and critical temperature for the physical blowing agents [20]. ........................................................................................................ 13
Table 2-5 Physical properties, ozone depletion potential, and global worming potential of the blowing agents ........................................................................................................ 13
Table 2-6 Material balance of the physical blowing agents ........................................... 22
Table 3-1 Foaming recipes of rigid polyurethane foam................................................. 34
Table 3-2 Specifications of Voranol 360 and PMDI. ...................................................... 34
Table 3-3 Amounts of blowing agents and PMDI. ....................................................... 35
Table 3-4 Physical properties, ozone depletion potential (ODP), and global worming potential (GWP) of the PBAs. .................................................................................. 35
Table 4-1 Specifications of V490, A205, and isocyanate............................................. 58
Table 4-2 Gel reaction Recipe of the control, A205, and A205/Glycerol mixture .......... 58
Table 4-3 Foam reaction Recipe of the control, A205, and A205/Glycerol mixture ...... 60
Table 4-4 Catalysts loadings of the A205 gels and foams at different preheating temperatures ..................................................................................................................... 67
Table 4-5 Values of % shrinkage and % density change for A205 foams at different preheating temperature and catalysts loadings ...................................................... 73
Table 5-1 Expressions of the diffusion and reaction steps .............................................. 81
Table 5-2 Specifications of V360, V490, and PAPI ...................................................... 88
Table 5-3 Recipes for polyurethane gel reaction ................................................................. 88

Table 5-4 Kinetic and parameters used in the simulation code. ........................................ 99

Table 6-1. Number of parameters needed for simulating polyurethane reactions ............ 110

Table 6-2. Number of parameters needed for simulating polyurethane reaction
considering heuristics and constitutive equations ............................................................ 111

Table 6-3. Comparison of equations used in the previous and current simulation .......... 113

Table 6-4. Number of parameters needed for simulating polyurethane reaction
considering the heuristics and constitutive equations of the current approach .......... 115

Table 6-5. Isocyanate and Polyols Properties ................................................................. 116

Table 6-6. Recipes of homogeneous reaction of different polyols ............................... 117

Table 6-7. Comparison of the fractional content of alcohol moieties using current and
previous approaches .......................................................................................................... 124

Table 6-8. Number of parameters needed for simulating polyurethane reaction
considering the heuristics and constitutive equations of the current approach .......... 125

Table 6-9. Comparison of the activation energies of different catalysts used by the current
and previous approaches .................................................................................................. 129

Table 7-1. Step-growth polymerization reactions .............................................................. 139

Table 7-2. Chain growth reactions of three possible approaches .................................. 142

Table 7-3. Stoichiometry of Approach#1. ....................................................................... 143

Table 7-4. Stoichiometry of Approach#2. ....................................................................... 144

Table 7-5. Stoichiometry of Approach#3. ....................................................................... 145

Table 8-1. Polyurethane basic reactions .......................................................................... 178
Table 8-2. Concentration profiles and initial conditions that define a simplified liquid polymer reaction system .......................................................... 179

Table 8-3. MatLab code for simulating isothermal polymerization reaction ............... 182

Table 8-4. Script of MatLab code for simulating near-adiabatic polymerization reaction ........................................................................................................ 191

Table 8-5. Function of MatLab code for simulating near-adiabatic polymerization reaction ........................................................................................................ 192

Table 8-6. Example of simulation-based questions ................................................. 197

Table 8-7. Example of simulation question and different testing levels of learning ...... 199

Table 8-8. List of advanced topics, approach method, and their corresponding learning and operational utility ............................................................................... 200
ABSTRACT

A MatLab simulation model was developed to simulate polymerization reactions, gel point times and foam formation. The simulation is based on the simultaneous solution of typically 25-80 ordinary differential equations that describe elementary reactions, energy balances, and mass transfer. Laboratory polymerization experiments were performed to evaluate the accuracy of the simulations, including setting up experimental systems and measurement of temperature, height, and viscosity profiles of the urethane systems.

The performance of physical and chemical blowing agents were simulated with mass transfer of the blowing agent estimated as a function of reaction temperature and resin viscosity. The simulation code of polyurethane reactions allows the studying of variables that are impossible to obtain in labs like the rate of foam’s cell growth and pressure inside the cells. Also, simulation provides insight into mechanisms such as how attaining a reasonable maximum reaction temperature is important to properly cure foams and avoid foam shrinkage.

The impact of mass transfer limitation of the reacting moieties was successfully simulated based on three fundamental approaches. Further modeling shows the ability to reduce the number of parameters used for simulating urethane reactions by considering the viscosity dependent term for the frequency factor of Arrhenius equation.

Finally, the simulation studies of this research provide fundamental insights into the mechanism of homogeneous and catalytic reactions. This research process places high demands on identifying and testing highly-impactful fundamental mechanisms during polymerization that have not previously been identified.
CHAPTER 1. INTRODUCTION

From an engineering perspective, simulation of urethane polymerization reactions is a great opportunity in the polymer area based on a) the current $20 billion market expected to grow to over $50 billion in the next couple of decades and b) the stage of the technology where formulation development is substantially an art but the capability exists to convert it to a science.

Also, simulation requires less resources. Compared to the traditional lab work, simulation needs less resources (no lab, no materials, and no man power). In addition, simulation is faster, more accurate, and simulation provide more variables that cannot be obtained from labs.

Simulation thermoset reactions was the subject of interest of many researchers. Most of the simulation approaches assumed empirical or semi-imperial equation and/or constant values of some kinetic and/or thermodynamic variables. Other simulation approached considered only the reactions before the gel point time and for specific formulation.

The simulation project presented in this paper is based on fundamental approaches of mass transfer, heat transfer, and reaction kinetics to calculate the rate of changes of concentrations, foam height, bubble radius, and rate of mass transfer as an ordinary differential equation solved by ODE45 MatLab function.

The work presented in this dissertation builds upon a foundation of five years of effort of MatLab programming to simulate gel times, concentration profiles, and temperature profiles of polyurethane-forming reactions. In Chapters 2, the simulation code of the
gelling reactions was extended to simulate the rate of evaporation of liquid physical blowing agents including methyl format and C5-C6 hydrocarbons. Evaporation of the blowing agent was modeled as an overall mass transfer coefficient times the difference in activity of the blowing agent in the gas foam cells versus the resin walls of the cells. Successful modeling hinged upon the use of a mass transfer coefficient that decreased to near zero as the foam resin approached its gel point. The fitted parameters allowed for interpretations of the final disposition of the blowing agent, especially, if the blowing agent successfully led to larger foam cells versus being entrapped in the resin.

Blowing agent simulation was improved such that the overall mass transfer coefficient was a function of the change of resin viscosity and reaction temperature during foaming (Chapter 3). The research was improved by studying the performance chemical and physical blowing agents and their mixtures. In addition, the simulation provides the opportunity to measure and study variables that were impossible to obtain through experimentation, like cell growth during foaming and the pressure inside the cells.

A simulation aided study designed to identify how to avoid foam shrinkage of soy-based polyols rigid urethane foam was performed in Chapter 4. Foam shrinkage was mainly due to the inadequate curing of the resin due to lower maximum-attained temperatures. Preheating of the monomers prior to reaction and using glycerol as a co-reagent were the two approaches considered in this research for increasing maximum reaction temperature toward faster curing and reducing foam shrinkage.

The impact of the mass transfer rate of the reacting moieties on reaction rate was simulated for rigid urethane polymerization reaction (Chapter 5). It was important to
consider this phenomena since the polyol and isocyanate monomers have relatively high viscosities and the reaction of these monomers leads to more increase in viscosity. Three approaches were adopted to simulate this phenomenon. The first approach considered the rate of inter-molecular diffusion as a reaction step. The result shows that the reaction stops at the gel point since diffusion is limited. The second approach considered the intra-molecular movement in parallel with the rate of intermolecular diffusion. Reaction temperature was successfully simulated and the results show that the reaction is reaction rate limited before the gel point and diffusion rate limited after the gel point. The third approach incorporates the sum of the intermolecular and intramolecular movements as a pre-exponential factor in Arrhenius equation. This approach uses fewer parameters and fewer differential equations.

A follow-up study on the second approach was done in Chapter 6 to facilitate the reduction in the number of parameters needed to simulate thermoset polymerization reactions and dropping the hindered secondary alcohol moieties that have been suggested in a previous study. The same pre-exponential factor was used for catalytic reactions and the impact of catalyst was reflected in lower activation energies. The study reduces the number of fitted parameter from 80 to 8 and provides a more fundamental simulation method of thermoset reactions.

In Chapter 7, the experimental results for the gel reactions were improved by considering step-growth mechanism polymerization for homogeneous reactions and chain-growth mechanism for catalytic reactions. The research provides a powerful tool for predicting if a catalyst is interacting with only alcohol moieties or with the alcohol and the isocyanate moieties.
The impact of the successful development of polyurethane reaction simulation science would be the replacement of up to 90% of laboratory product development with a simulation that will often be ready for pilot scale (or semi-commercial scale) production right from the simulator.

Chapter 8 provides an educational research to highlights the ability to of using simulation as a powerful tool to achieve higher levels of education. A Matlab simulating code for polyurethane polymerization reaction was presented as an example to achieve parameters and variables that are impossible to attain from traditional polymer or kinetic textbooks.

This dissertation work was turned into four peer-reviewed published papers and three papers under review.
CHAPTER 2. SIMULATION OF LIQUID PHYSICAL BLOWING AGENTS FOR FORMING RIGID URETHANE FOAMS

2.1 Abstract

A computer-based simulation for rigid polyurethane foam-forming reactions was compared with experimental data for six blowing agents including methyl formate and C₅-C₆ hydrocarbons. Evaporation of blowing agent was modeled as an overall mass transfer coefficient times the difference in activity of the blowing agent in the gas foam cells versus the resin walls of the cells. Successful modeling hinged upon use of a mass transfer coefficient that decreased to near zero as the foam resin approached its gel point. Modeling on density agreed with experimental measurements. The fitted parameters allowed for interpretations of the final disposition of the blowing agent, especially, if the blowing agent successfully led to larger foam cells versus being entrapped in the resin. The only component-specific fitted parameters used in the modeling was the activity coefficient that was lower for methyl formate than the value used for hydrocarbons.

2.2 Introduction

The market demand of polyurethane (PU) is growing every year due to its versatile application. Average annual growth rates reach 5% with over 12 million metric tons of its raw material consumed globally.[1] The applications of polyurethane range from rigid insulation in buildings and refrigerators, cushions for furniture, and elastomeric wheels and tires.[2]
Polyurethane foams are produced from the reaction of polyol(s) and isocyanate (Equation 2-1) in the presence of, catalysts, surfactants, fire retardants, and physical and/or chemical blowing agent.[3]

\[
\begin{align*}
RNCO & + R'CH_2OH & \rightarrow RNCOOCH_2R' \\
\text{Isocyanate} & \quad \text{Alcohol} & \quad \text{PU} \\
\end{align*}
\]

\textit{Equation 2-1}

Foam is generated by using a blowing agent that is able to yield a cellular gas-filled structure. Liquid blowing agents are typically mixed with the liquid polyol monomers prior to mixing with the isocyanate monomer. The blowing agent is what transforms a solid plastic or elastomer to a foam. For physical blowing agents, the heat generated by exothermic reactions evaporates the blowing agent. Successful foam formation requires the successful synchronizing of temperature increase, which causes the blowing agent to evaporate, with the increase viscosity, which is key to stabilizing the gas cells. The blowing agent controls the density, the cellular microstructure, and morphology of the foam which are critical to the end-use and performance.[4, 5]

Commonly, water is used as a chemical blowing agent since it reacts with isocyanate to form carbon dioxide (Equation 2-2 and Equation 2-3). The heat generated from this exothermic reaction and the exothermic polymerization reaction are used to evaporate another added physical blowing agent (PBA) to provide more gas for foaming and some desired properties to the foam.[6, 7]

\[
\begin{align*}
RNCO & + H_2O & \rightarrow RNHCOOH \\
\text{Isocyanate} & \quad \text{Water} & \quad \text{Carbamic Acid} \\
\end{align*}
\]

\textit{Equation 2-2}
\[
\text{RNHCOOH} \rightarrow \text{RNH}_2 + \text{CO}_2 + \text{Heat} \quad \text{Equation 2-3}
\]

Carbamic Acid \hspace{1cm} \text{Amine} \hspace{1cm} \text{Carbon Dioxide}

Physical blowing agents can be defined as low boiling point inert liquids.[8] Heat and temperature increases from exothermic reactions cause the physical blowing agents to evaporate in-situ.[9] Amount and type of the physical blowing agent impacts foam density by creating and expanding gas cells. More blowing agent tends to create a lower-density foam with impact on foam properties such as compressive strength and thermal conductivity.[10]

Modeling foam height and temperature profiles have attracted the attention of many research workers. Baser and Khakhar [11, 12] predicted both temperature and density of polyurethane foams blown by chemical and physical blowing agents (water and R-11) based on mass and energy balance, rate of viscosity increase, kinetic parameters, and thermodynamic relations.

Cell size distributions in foams blown with either water or Freon were correlated with energy balance equations and the rate of evaporation of the blowing agent by Niyogi et al.[13] After that, Niyogi et al.[14] developed a model that combined equations of energy balance, kinetics of the reactions of isocyanate with water and polyol, and nucleation and growth of CO\textsubscript{2} bubbles to predict bubble size and distribution of polyurethanes foams blown by water as a chemical blowing agent.

Later, Tesser et al.[15] developed the mathematical modeling of Rojas et al.[16] by improving the vapor-liquid phase equilibrium of the blowing agent and the polymer mixture and using the kinetic parameters of the polyol and isocyanate and different
amounts of blowing agent. Modesti et al.[17] develop a theoretical model to predict temperature profile, foam density, and other physical-mechanical properties using oligomeric isocyanate and a mixture of polyether polyols blown by either water, methyl formate, or n-pentane.

This work differs from previous because the simulation is based, to a first approximation, only on pure component parameters and dozens of differential equations capable of simulating performances of mixtures and able to predict performance based on pure component parameters. Shen et al.[18] expanded the code of simulation code of Zhao et al.[19] to predict foam density of polyurethane foams blown by different concentrations of water and methyl formate.

Shen’s code was based on an assumption of equilibrium between blowing agent in the resin walls of the gas cells with the gas in the cells. Equation 2-4 summarizes the modified Raoult’s law which is a practical estimate of the equilibrium condition that sets the activity of the blowing agent in the vapor phase equal to the activity in the liquid phase.

\[
x_{Ri} \gamma_i P_{sat} = y_i P
\]

\textbf{Equation 2-4}

Where \(x_{Ri}\) and \(y_i\) are mole fractions of blowing agent in the liquid and gas phases respectively, \(P\) is the total pressure (assumed to be equals to 1 atm.), \(\gamma\) is the activity coefficient. The activity coefficient is set to the same value for the hydrocarbons; a lower value is used for methyl formate. The activity coefficient is a fitted parameter, but methods are available to predict the activity coefficient.
In the work presented by this paper, an approach using a mass transfer driving force is used which includes the rapid decrease in the mass transfer coefficient as the gel point is approached. The driving force of evaporation of the physical blowing agent is expressed as a differential equation that has been solved with other differential equations of polyol-isocyanate reactions in the computer code.

\[ \frac{dC_{PBA}}{dt} = -K C_{PBA} (\gamma X_{liq} - X_{Ri}) \]  

Equation 2-5

Where \( C_{PBA} \) is the concentration of the physical blowing agent, \( K \) is the overall mass transfer coefficient, \( X_{liq} \) is the molar concentration and the equilibrium molar concentration of the physical blowing agent in the liquid phase. The overall mass transfer coefficient includes the impact of surface area. At the onset of the reaction, the value of \( K \) increases both due to increasing surface area and increasing temperature. As polymerization proceeds, crosslinking has an increasing impact on viscosity leading to a decrease in polymer concentration and rapid increase in viscosity. Noting that the concentration of polymer in the system qualitatively followings these important trends, the mass transfer coefficient was estimated as being equal to a fitted constant, \( k_1 \), times the polymer concentration (\( C_{Polymer} \)).

\[ K = k_1 C_{Polymer} \]  

Equation 2-6

Also, the polymer concentration can be used to estimate the polymer degree of polymerization (PDP) according to the following equation:

\[ PDP = \frac{M_{iso and polyol}^0 - M_{iso and polyol}^t}{M_{polymer}} \]  

Equation 2-7
Where $M_{iso\ and\ polyol}^0$ and $M_{iso\ and\ polyol}^t$ are moles of isocyanate and polyol initially and at time $t$ respectively and $M_{polymer}$ is moles of polymer.

The work presented here can be distinguished from previous work due to the ability to estimate the rapid decrease in the overall mass transfer coefficient as the concentration of polymer goes to zero. The models for both the activity coefficients and mass transfer coefficients would be characterized as semi-fundamental since the models follow known fundamental trends. Model performances versus experimental data are compared for six different blowing agents.

### 2.3 Methodology

#### 2.3.1 Materials and recipes

Table 2-1 summarizes gel and foaming formulations at an isocyanate index of 110%. Amounts of polyol, catalyst, surfactant, fire retardant, and isocyanate were kept constant for all the rigid polyurethane foams. RUBINATE M isocyanate and Voranol 360 were manufactured by Huntsman Company and Dow Chemical, respectively. N, N-dimethylcyclohexylamine is a gelling catalyst, Momentive L6900 is the surfactant, and Tris (1-chloro-2-propyl) Phosphate (TCPP) was used as a fire retardant.

Experiments were performed to evaluate the performance of different blowing agents with the moles of each blowing agent kept constant. Table 2-2 shows the specifications of Voranol 360 and Rubinate M isocyanate (thereafter referred as PMDI) used in the gel and foaming formulation. Voranol 360 (V360) is identified as having 5% secondary and 95% hindered secondary moiety fraction according to the previous study[19].
Table 2-1 Gel and Foaming recipes of rigid polyurethane gel and foam

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight, g</th>
<th>Gel Formulation</th>
<th>Foaming Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-side materials</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voranol 360</td>
<td>43.5</td>
<td>43.5</td>
<td></td>
</tr>
<tr>
<td>Dimethylcyclohexylamine (Cat8)</td>
<td>0.44</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>Momentive L6900</td>
<td>0.6</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>TCPP</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Physical blowing agent</td>
<td>0</td>
<td>see Table 2-3</td>
<td></td>
</tr>
<tr>
<td>A-side material</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMDI</td>
<td>41.7</td>
<td>41.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-2 Specifications of Voranol 360 and isocyanate

<table>
<thead>
<tr>
<th>Property</th>
<th>V360</th>
<th>PMDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm$^3$</td>
<td>1.081</td>
<td>1.23</td>
</tr>
<tr>
<td>Average molecular weight</td>
<td>728</td>
<td>340</td>
</tr>
<tr>
<td>Functionality</td>
<td>4.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Hydroxyl number, mg KOH.g$^{-1}$</td>
<td>360</td>
<td>-</td>
</tr>
<tr>
<td>Equivalent weight</td>
<td>155.55</td>
<td>134</td>
</tr>
<tr>
<td>Viscosity, mPa.s at 25°C</td>
<td>3500</td>
<td>150-220</td>
</tr>
<tr>
<td>NCO content by weight, %</td>
<td>-</td>
<td>31.4</td>
</tr>
<tr>
<td>Vapor pressure, mm Hg at 25°C</td>
<td>-</td>
<td>&lt;10-5</td>
</tr>
<tr>
<td>Specific heat, g.cal/g at 25°C</td>
<td>-</td>
<td>0.43</td>
</tr>
</tbody>
</table>

2.3.2 Physical blowing agents

Equal moles of six different physical blowing agents was tested with recording of height profiles. Experiments were performed with 0.0975 moles of blowing agent with Table 2-3 summarizing the respective mass loadings.
A modified Antoine equation was used to estimate vapor pressure of each blowing agent as a function of reaction temperature according to Equation 2-8.

$$\ln \left( \frac{P_{\text{sat}}}{P_c} \right) = (1 - x)^{-1}[Ax + Bx^{1.5} + Cx^3 + Dx^6]$$  \hspace{1cm} \text{Equation 2-8}

where \( x = (1 - T/T_c) \), \( T_c \) is the critical temperature in Kelvins, \( P_{\text{sat}} \) is the vapor pressure in bars, and \( P_c \) is the critical pressure in bars. This equation provides a wide temperature range of 220-487 K which covers the foaming reaction temperature change. Values of A, B, C, and D constants and critical temperature and pressure of the physical blowing agents are provided in Table 2-4. For simulation purposes, the latent heat of evaporation of the physical blowing agents is calculated using Giacalone equation [20]

Table 2-5 summarizes the physical properties of the blowing agents along with their ozone depletion potential and global worming potential. Researchers are actively pursuing blends and new blowing agents [21-24] to both improve rigid polyurethane foam properties like thermal conductivity, compressive strength, and fire resistance and to decrease environmental impact. A key aspect of the present work is to establish the accuracy of

---

**Table 2-3 Amount of each blowing agents used in the foaming formulation**

<table>
<thead>
<tr>
<th>Physical blowing agent</th>
<th>Weight, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Formate</td>
<td>5.856</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>7.042</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>7.042</td>
</tr>
<tr>
<td>cyclo-Pentane</td>
<td>6.842</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>8.411</td>
</tr>
<tr>
<td>cyclo-Hexane</td>
<td>8.214</td>
</tr>
</tbody>
</table>
simulation to predict the performance of blowing agents so that simulation can play a role in faster and better evolution of blowing agents in urethane foams.

Table 2-4 Antoine constants, critical pressure, and critical temperature for the physical blowing agents [20]

<table>
<thead>
<tr>
<th>Component</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>T_{min}</th>
<th>T_{max}</th>
<th>P_{c}</th>
<th>T_{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl formate</td>
<td>-6.99601</td>
<td>0.89328</td>
<td>-2.52294</td>
<td>-3.16636</td>
<td>220</td>
<td>487.2</td>
<td>60</td>
<td>487.2</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>-7.28936</td>
<td>1.53679</td>
<td>-3.08367</td>
<td>-1.02456</td>
<td>195</td>
<td>469.7</td>
<td>33.7</td>
<td>469.7</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>-7.12727</td>
<td>1.38996</td>
<td>-2.54302</td>
<td>-2.45657</td>
<td>220</td>
<td>460.4</td>
<td>33.9</td>
<td>460.4</td>
</tr>
<tr>
<td>cyclo-Pentane</td>
<td>-6.51809</td>
<td>0.38442</td>
<td>-1.11706</td>
<td>-4.50275</td>
<td>289</td>
<td>511.7</td>
<td>45.1</td>
<td>511.7</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>-7.46765</td>
<td>1.44211</td>
<td>-3.28222</td>
<td>-2.50941</td>
<td>220</td>
<td>507.5</td>
<td>30.1</td>
<td>507.5</td>
</tr>
<tr>
<td>cyclo-Hexane</td>
<td>-6.96009</td>
<td>1.31328</td>
<td>-2.75683</td>
<td>-2.45491</td>
<td>288</td>
<td>553.5</td>
<td>40.7</td>
<td>553.5</td>
</tr>
</tbody>
</table>

Table 2-5 Physical properties, ozone depletion potential, and global warming potential of the blowing agents

<table>
<thead>
<tr>
<th>PBA</th>
<th>Boiling Point, °C</th>
<th>Molecular weight</th>
<th>ΔH_{vap}, J mol^{-1}</th>
<th>Vapor Pressure, Kpa, 20°C</th>
<th>Surface Tension, 20°C (mN m^{-1})</th>
<th>ODP</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl formate</td>
<td>31.8</td>
<td>60.05</td>
<td>27648.65</td>
<td>63.51</td>
<td>21.384</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>36.1</td>
<td>72.15</td>
<td>26363.35</td>
<td>57.9</td>
<td>15.82</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>27.85</td>
<td>72.15</td>
<td>25372.42</td>
<td>76.99</td>
<td>16.05</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>cyclo-Pentane</td>
<td>49.26</td>
<td>70.15</td>
<td>26378.72</td>
<td>35.3</td>
<td>23</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>68</td>
<td>86.18</td>
<td>29543.3</td>
<td>17.3</td>
<td>18.43</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>cyclo-Hexane</td>
<td>80.7</td>
<td>84.16</td>
<td>30108.86</td>
<td>12.9</td>
<td>24.95</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

2.4 Experimental Procedure

Gel and foaming experiments were performed using the recipes shown in Table 2-1 to prepare polyurethane gels and foams using different physical blowing agents. Experiments consisted of the following steps:
• The B-side components are weighted and added together as a B-side into a closed 150 ml glass beaker and mixed until the mixture mixed well.

• The beaker is left open for two minute for degassing and then weighted to measure the weight of physical blowing agent lost during mixing.

• The B-side mixture is poured into a plastic cap and the A-side component is added.

• The mixture mixed with a 2000 rpm mixer for 10 seconds.

• For gel, the mixture is left in the cup and reaction temperature is recorded.

• For rigid polyurethane foam, the mixture is quickly poured into a wooden box with aluminium foil lining to measure temperature and height profiles.

• The foaming mixture is allowed to expand until foam temperature started to cool down.

LabView soft-ware was used to measure gel and foam reaction temperature and foam height using type-K thermocouple and ultrasound device attached through a national instrument SCB-68 box to a national PCI 6024E data acquisition card. The LabView soft-ware is recording the time-temperature and time-height data in the computer as x-y axis.

A high-speed mixer blade attached to a floor-model drill press was used to mix the chemicals.

The tack-free time is measured for the rigid polyurethane foams prepared using the different physical blowing agents. It can be defined as the span time between pouring the A- and B- side mixture in the foaming box and the time when the surface of the foam does not show stickiness when touched with a spatula [8].
As a test to determine if blowing agent remained in the resin phase after formation of foam, foams were crashed and the resulting resin was placed in an oven for three hours at a temperature of 150°C. The reduction in mass that occurred as a result of this was attributed to entrapped resin that evaporated as a result of the higher temperatures, time of exposure, and exposed surface areas.

2.5 Results and Discussion

2.5.1 Gel reaction

Gel reaction temperature profiles were measured and used as a control (benchmark) to assist in interpreting the data for the foam reactions; the gel reaction is the polymerization without blowing agent. Figure 2-1 shows a good fit of the model to the data using previously published kinetic and thermodynamic parameters for V360 [19].

Figure 2-2 shows how the simulation can generate profiles for alcohol moiety, isocyanate moiety, isocyanate monomer, and polymer concentrations. Those concentrations were used to calculate reaction temperature and polymer concentration by solving the kinetic reaction equations. Polymer concentration increases at the beginning of the reaction and then reduces to a very low number due to the polymer-polymer crosslinking as is prevalent when polyols of high functionality are used in formulations.

Crosslinking of polymers to a concentration that approaches zero is the indication of the gel point. For foam systems, this gel point should occur at a time similar to the tack-free time.
Figure 2-1 Temperature profile of polyurethane gel reaction Symbol “Δ” represent experimental data and solid line represents simulation.

Figure 2-2 Concentration profile of isocyanate and alcohol moieties, isocyanate and alcohol monomer, and polymer. Lines from top to bottom represent concentration profile of isocyanate moieties, alcohol moieties, isocyanate monomer, and polymer.
2.5.2 Foam reaction

Figure 2-3 compares temperature and height profiles for the six different blowing agents. As compared to the gel reaction, the foam reactions are slower due to the evaporative cooling caused by the blowing agents.

The simulation results show good agreement with both the temperature and height profiles. The tack-free times are indicated by vertical lines that correlate well with the increase in degree of polymerization. The height of the foam is essentially constant after the tack-free time is reached.

As the polymer degree of polymerization increases and the polymer become more viscous, the foam stops expanding and the remaining amount of the physical blowing agent is entrapped in the resin phase walls of the foam cells (versus the gas phase in the cells).

For the cyclohexane solvent (Figure 2-3f), the simulation’s temperature profile deviates from experimental data. This is attributed to the large amount of cyclohexane used in the foaming formulation that quenched the reactions and the high heat of evaporation, which are both attributed to the higher molecular weight of cyclohexane. Despite the issues with the temperature profile, the simulation’s height profile is accurate.

Figure 2-4 shows a comparison of the simulated height profile for the different physical blowing agents to allow a better direct comparison of the performances. The following observations can be noted for the hydrocarbon blowing agents:

- Foam height increased with decreasing boiling point.
- Foam height increases with decreasing latent heat of vaporization of the blowing agent.

Figure 2-3 Experimental and simulation results of temperature profile, PDP, and tack-free time of rigid polyurethane foams blown by different physical blowing agents. Symbols “▲” and “∆” represent experimental data of temperature and height profiles respectively. Solid lines represent simulation results for temperature and height. Dashed line and dot line represent PDP and tack-free time.
The blowing agents evaporate as a result of the heat of reaction. As the temperature of the reaction mixture increases, the blowing agents with lower boiling points evaporate first while many highly reactive alcohol moieties are available to keep the exotherm going. Lower heats of vaporization result in lower impacts on the temperature profiles.

![Graph showing comparison of foam heights blown by different blowing agents.](image)

**Figure 2-4** Comparison of simulated foam heights blown by different blowing agents. Lines from high to low height represent height profiles of foams blown by iso-Pentane, n-Pentane, cyclo-Pentane, Methyl Formate, n-Hexane, and cyclo-Hexane respectively.

There are a compounding of effects that lead to lower heights for the higher boiling point blowing agents, including: a) higher heats of evaporation result in greater impacts on temperature, b) the resin is more viscous at the later times which resists expansion for blowing agents that evaporate at later times, and c) at the later reaction times the ability of the reaction to continue is hindered both by the absence of the more-reactive alcohol moieties, viscosity hindering mobility of moieties, and a greater fraction of the moieties are attached to polymer chains which further exasperates the impact of viscosity on the mobility of reactive moieties.
Methyl formate tends to be less efficient toward cell expansion than hydrocarbons of similar volatility. This is attributed to the lower activity coefficient of methyl formate in the resin phase.

One of the factors not taken into account is mass transfer rate. For the methyl formate system, uncertainty in the mass transfer rate creates an uncertainty in the activity coefficient; which when combined, explain the deviation in the fit to methyl formate data. Future work is focusing on modeling and understanding the impact of mass transfer rates and how increasing viscosities and temperatures cause huge changes in mass transfer rates.

The simulation code predicts that substantial amounts of blowing agent remain in the foam. The weight loss of crushed foam samples is compared to the fraction remaining in the foam by Figure 2-5. Higher mass losses from the resin correlate with higher residual amounts of the higher boiling point blowing agents. Less evaporates in the crushed samples than anticipated based on simulation primarily due to a) some blowing agent will remain in the crushed foam even after evaporation in the oven and b) some blowing agent is lost during mixing of monomers (mixing is open to atmosphere, blowing agent is added to the B-side before mixing). The loss of blowing agent during mixing was independently measured as summarized by Figure 2-6.
Figure 2-5 Experimental and simulation percentage and of blowing agent remaining in the foam resin

Figure 2-6 shows the effect of the boiling point of the physical blowing agent on the percent loss during monomer mixing with the other components of the B-side components. As the boiling point temperature increases, the losses during mixing decrease for all the C₅ and C₆ hydrocarbons. Methyl formate has lower losses due to evaporation which can be attributed to a lower activity coefficient for methyl formate.

Figure 2-6 % losses of blowing agents during mixing
The experimental measurements in combination with simulation results enable an estimate of the ultimate fate of the blowing agents. Table 2-6 shows the material balance of the physical blowing agents. The results indicate that appreciable amounts of blowing agent are entrapped in the resin and do not contribute to expansion.

These amounts are not indicative of commercial foams since commercial foams have been optimized for performance rather than formulated for fundamental insight. Nevertheless, the data show that entrapment in the resin phase can lead to substantial losses in efficacy of the blowing agent. The data also show that this entrapment can be predicted; hence, simulation can be an important and effective tool in developing new blowing agents.

Table 2-6 Material balance of the physical blowing agents

<table>
<thead>
<tr>
<th>PBA</th>
<th>Amount of PBA evaporated during mixing</th>
<th>Amount that remained in resin phase</th>
<th>Amount that escaped to surrounding air</th>
<th>Amount that went into cells to form a foam</th>
<th>Amount that remained entrapped in the resin phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl formate</td>
<td>0.061</td>
<td>0.199</td>
<td>0.123</td>
<td>1.811</td>
<td>3.696</td>
</tr>
<tr>
<td>N-Pentane</td>
<td>0.223</td>
<td>0.149</td>
<td>0.117</td>
<td>3.014</td>
<td>3.567</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>0.347</td>
<td>0.126</td>
<td>0.115</td>
<td>3.457</td>
<td>3.015</td>
</tr>
<tr>
<td>cyclo-Pentane</td>
<td>0.208</td>
<td>0.162</td>
<td>0.10</td>
<td>2.627</td>
<td>3.760</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.190</td>
<td>0.172</td>
<td>0.220</td>
<td>2.210</td>
<td>5.639</td>
</tr>
<tr>
<td>cyclo-Hexane</td>
<td>0.054</td>
<td>0.536</td>
<td>0.213</td>
<td>1.065</td>
<td>6.362</td>
</tr>
</tbody>
</table>

2.6 Conclusion

The simulation of foam-forming reactions was effective for providing insight into mechanisms of efficiency and lack of efficiency of physical blowing agents for forming foams. A blowing agent overall mass transfer coefficient that rapidly decreases as the
reacting system approached its gel point (tack-free time) was the most critical aspect of the simulation that led to both insight and quantitative predication of performance.

For the hydrocarbon blowing agents, a single fitted parameter was able to transfer prediction from one system to another. That single fitted parameter accounted for both the activity coefficient and a constant used in an equation for the overall mass transfer coefficient. This validates the fundamentally-correct nature of the simulation which validates the ability of the simulation to be extrapolated to other systems including mixtures of blowing agents.

A major source of inefficiency of blowing agents was identified as the entrapment of blowing agent in the resin phase. Future work will include the use of established methods for estimating activity coefficients and mass transfer in liquids to improve the accuracy of the simulation and to gain further insight in many chemical and physical processes occurring during foam-forming reactions.
CHAPTER 3. SIMULATION BLOWING AGENT PERFORMANCE, CELL MORPHOLOGY, AND CELL PRESSURE IN RIGID POLYURETHANE FOAMS

3.1 Abstract

A series of over 30 differential equations were solved to model experimental data on urethane foam formation. Methyl formate and C₅–C₆ hydrocarbons were used as physical blowing agents, and water was used as a chemical blowing agent. The rate of evaporation of the physical blowing agents was estimated using an overall mass-transfer coefficient times the difference in activity in the gas phase inside the bubbles and in the resin walls of the bubbles. The rate of CO₂ diffusion was expressed as the overall mass-transfer coefficient times the rate of CO₂ generation. The overall mass-transfer coefficient was found to decrease to near zero as the gel point of the resin was approached. Only one fitted parameter was used for the overall mass-transfer calculation for all blowing agents. The simulation results for foam height agree with the experimental data. Bubble growth and bubble pressure were simulated for the first time as compared to the available literature.

3.2 Introduction

Rigid polyurethane foams are generally produced by the reaction of the isocyanate group and the alcohol groups in polyols in the presence of selected catalysts, surfactants, fire retardants, and physical and/or chemical blowing agents [3], as described by the following equation:
Foaming is caused chemically or physically or by a combination of the two. The gas produced from the blowing agents fills the cellular structure of the bubbles. Water is used as a chemical blowing agent because it reacts with the isocyanate group to generate carbon dioxide gas according to the reactions:

\[ \text{RNCO} + \text{H}_2\text{O} \rightarrow \text{RNHCOOH} \]  \hspace{1cm} \text{Equation 3-2}

Isocyanate \hspace{1cm} Water \hspace{1cm} Carbamic Acid

\[ \text{RNHCOOH} \rightarrow \text{RNH}_2 + \text{CO}_2 + \text{Heat} \]  \hspace{1cm} \text{Equation 3-3}

Carbamic Acid \hspace{1cm} Amine \hspace{1cm} Carbon Dioxide

Physical blowing agents (PBAs) are widely used in polyurethane formulations. In general, physical blowing agents are inert compounds that evaporate during foaming. The heat generated from the exothermic reactions of the isocyanate group with polyols and water drives the evaporation process. A mixture of chemical and physical blowing agents can be used to advantage over either type of agent alone. Chemical blowing provides more heat that helps to increase the peak reaction temperature, which, in turn, provides better final foam properties. [25-27] Physical blowing agents are able to provide additional gas during foaming, add some desired properties to the foam, [5, 28] and have the advantage of not consuming isocyanate.

Synchronizing the amounts of chemical and physical blowing agents with the reaction temperature and resin viscosity is a key aspect of optimizing the blowing performance. The
blowing agent diffuses from the liquid phase to the gas phase inside the generated bubbles to expand the urethane polymer, and this portion of blowing agent causes bubbles growth. When the resin becomes more viscous as a result of the formation of the polymer and cross-linking, the overall mass-transfer coefficient decreases, and the blowing agent stops diffusing.

Cell structure and orientation determine the final properties of the foam. Foaming is a complex process, as many variables simultaneously influence the rheological properties and the microstructure of the cells. [29]

The foaming process can be described in four steps. The first step is gas dissolution, in which a gas/polymer solution is formed. The second step is cell nucleation (bubble formation), which starts after the solubility of the dissolved blowing agent gas is exceeded. In this study, bubble nucleation is assumed to be homogeneous. The mechanical agitation of the A- and B-side mixtures provides microbubbles of air that serve as sites for bubble growth. The third step is bubble growth, in which blowing-agent gas diffuses from the liquid–gas interface into the bubbles. The final step is the stabilization of the cell bubbles.

The present research focuses on the ability to simulate the performance of chemical and physical blowing agents and their mixtures. The computer program simulates temperatures, concentrations, diffusion coefficients, bubble/cell radii, and the pressure inside the cells.

3.3 The Physical System and Assumptions

As the polyol–isocyanate and water–isocyanate reactions take place in the foaming mixture, the temperature of the mixture rises, and when the partial pressure exerted by the blowing agents exceeds the total pressure of the system, the solution becomes
supersaturated. A further buildup of supersaturation leads to the nucleation of bubbles, which can be assisted by intense agitation. The time at which the first nuclei have a visible impact is referred to as the cream time, which occurs a few seconds after nucleation. Thereafter, the bubbles grow through diffusion of the blowing agent from the liquid phase into the bubble phase. To simplify this process in the simulation code, the following assumptions were made:

1. Foam bubbles have a spherical geometry at all times, and gravitational effects are neglected.
2. The interaction of the growing bubble with its neighbors and with the boundaries of the liquid resin is neglected because growing bubbles are influenced almost exclusively by diffusion from thin shells surrounding them. [30]
3. The gas phase inside the bubble is ideal.
4. Nucleation is homogeneous, is not simulated, and occurs at a site density set in the program. [31]
5. Thermodynamic equilibrium is maintained at all times at the gas–liquid interface.
6. No blowing agent is lost during foaming. [18, 32]
7. Adiabatic conditions apply in the simulation. According to this assumption, all of the conditions are spatially uniform, and gelation occurs at the same instant throughout the mold. Hence, the bubbles stop growing in the entire mold at the same time.
8. No bubbles collapse or become distorted (from collisions or other causes).
9. Bubble motion is neglected.
10. Any volume change due to liquid-phase mixing is neglected.
11. Heats of reaction are constant over the range of temperatures considered (about 25–130 °C).

### 3.4 Mathematical Formula

The simulation code for the urethane reaction is shown in the algorithm of Figure 3-1. Recipes, initial conditions, and database equations are the input to FoamSim, which uses the ODE45 function, which calls on the derivatives in the ReacSim function and solves the ordinary differential equation (ODE) initial condition problem as a function of time.

![Figure 3-1 Algorithm for simulating urethane foam formation including cell growth](image)

The derivatives in ReacSim include the rate of change of temperature; the foam height; the bubble radius; and the numbers of moles of polyol, isocyanate, and blowing agents. The blowing agent (BA) function receives the temperature, numbers of moles, foam height,
and bubble radius from ReacSim and calls on the viscosity function to estimate viscosity. The BA function uses this information to estimate rates of change in foam height and bubble radius, returning these values to ReacSim in iterative steps of solution.

3.4.1 Overall mass transfer coefficient

Mass transfer is described by Fick’s law

\[ J_A = -D_{AB} \left( \frac{dC_A}{dz} \right) = -D_{AB} \left( \frac{\Delta C_A}{\Delta z} \right) \]  

Equation 3-14

The kinetic theory for diffusion in liquids is not as well defined as that for diffusion in gases. Liquid diffusion is believed to depend primarily on hydrodynamics and activated states. [33] Albert Einstein in 1905[34] and Marian Smoluchowski in 1906[35] suggested an equation that enables determination of the liquid phase diffusivity in more easily measured parameters. The simple form is

\[ D_{AB} = K_B T \left( \frac{\mu_A}{F_A} \right) \]  

Equation 3-15

If the particle has a spherical shape and no-slip possibility at the fluid interface, Equation 3-15 can be written as:

\[ D_{AB} = \frac{K_B T}{6\pi \eta a} \]  

Equation 3-16

Practical applications of the mass-transfer coefficient encounter increased complexity due to discontinuous interfaces between phases and convection. [36] For convection, an overall mass-transfer coefficient is used because of its simplicity and reasonable accuracy.
when the boundary layers do not change considerably over the course of the process. The overall mass transfer coefficient can be defined by

\[ N_A = -K \Delta C \]  

Equation 3-17

Assuming that all of the resistance is mainly in the liquid phase, the diffusion flux will equal to the bulk flux, and the overall mass-transfer coefficient can be expressed as

\[ K = \frac{K_B T}{6\pi \eta a \Delta z} \]  

Equation 3-18

As part of the modeling and simulation process for urethane foaming, the product of the molecular radius \((a)\) and the boundary-layer thickness \((\Delta z)\) is set as a fitted parameter. One value of this product provided a reasonable fit for the six physical blowing agents evaluated in this study. The resin viscosity was calculated using the group contribution method. [37]

For carbon dioxide diffusion, Einstein’s equation was used to calculate the overall mass-transfer coefficient with a value of \((a.\Delta z)\) specific to carbon dioxide.

As compared to previous studies, the present work is different in multiple ways. Several studies[13, 38, 39] have assumed a constant diffusion coefficient; however, because of changes of more than 100 °C in temperature and several orders of magnitude in viscosity, such an approach would be fundamentally flawed in a reacting urethane system. Tuladhar and Mackley[40] assumed that the diffusivity varied between \(10^{-10}\) and \(10^{-14}\) m²/s, but even this variation is too small to represent the physical processes in a urethane reaction system. Ramesh and Malwitz[41] used an equation derived from the penetration theory with a constant diffusion coefficient for the bubble growth dynamics in olefinic foams, which is also inaccurate for the large ranges of temperatures and viscosities in a urethane system.
3.4.2 Rate of blowing agent evaporation

The steps involved in simulating the rate of bubble growth are summarized by Equation 3-5 through Equation 3-11 in Figure 3-1. In this sequence of equations, the overall mass-transfer coefficient is estimated for the specific temperature and viscosity of the calculation increment. In addition to estimating the overall mass-transfer coefficient, (a) the activity coefficient is set as a fitting parameter and assumed as a function of polymer concentration (Equation 3-5), (b) the total mass transfer area is calculated using Equation 3-10, (c) the vapor pressure is calculated using the modified Antoine equation, and (d) the modified Raoult’s law is used to estimate the equilibrium mole fraction of the liquid blowing agent using Equation 3-9.

These intermediate calculations are then used to estimate the rate of evaporation of the physical blowing agent(s) in Equation 3-12 with specific application of the overall mass-transfer equation (Equation 3-18). The rate of bubble growth is estimated by an equation independent of the rate of evaporation.

3.4.3 Bubble growth modelling

The density of nucleation sites is specified based on typical cell densities of that formulation as based on previous experimental results. Here, the term cell refers to the final structure in the foam formed by bubbles that grow and ultimately set. A microscope by Renishaw was used to measure the radii of the cells in the foams. Assuming ideal-gas behavior and a very small volume of urethane compared to the volume of the blowing gas, the number of nucleating sites was calculated using the following equation:
\[ N_C = \frac{V_F}{V_C} = \frac{V_F}{\frac{4\pi}{3} r_f^3} \quad \text{Equation 3-19} \]

Equation 3-20 is used to calculate the rate of increase of the bubble radius during foaming (for the derivation, see references [41-43])

\[ P_g = P_L + \frac{\sigma}{2r} + 4\eta \left( \frac{dr}{dt} \right) \left( \frac{1}{r} - \frac{r^2}{S^3} \right) \quad \text{Equation 3-20} \]

The resin radius \((S)\) is assumed to be constant and equal to the final bubble radius.

The surface tension term is assumed to have a minimal effect on bubble pressure and can be neglected. [44] By rearranging Equation 3-20, we obtain (Equation 3-13 is used later instead of this equation as shown in the results)

\[ \frac{dr}{dt} = \left( P_g - P_L \right) / \left[ 4\eta \left( \frac{1}{r} - \frac{r^2}{S^3} \right) \right] \quad \text{Equation 3-21} \]

The atmospheric pressure \((P_g)\) is calculated using the ideal gas law (Equation 3-6). An imperial equation using the polymer concentration that approximates resin viscosity (Equation 3-13) is used in this estimate rather than the actual viscosity.

As part of the ODE45 solution process, all of the ODEs are solved simultaneously through the ReacSim sub-function using the Runge–Kutta method.

Figure 3-2 illustrates the simulation of the bubbles in the resin phase. The bubbles are assumed to have a spherical shape inside the resin phase. The layer surrounding the bubbles has a mixture of resin and gas, the bubbles encapsulate gaseous blowing agent, and all of the bubbles are surrounded by the resin.
Figure 3-2 Schematic diagram of bubbles in the resin phase.

3.5 Materials and Recipes

Voranol 360 (V360), catalyst(s), surfactant, fire retardant, blowing agent, and isocyanate were used in the foaming formulation as listed in Table 3-1. PAPI isocyanate (hereafter referred to as PMDI) and V360 were manufactured by Dow Chemical. V360 is identified as having 5% secondary and 95% hindered secondary moieties according to a previous study. [19] Table 3-2 lists the specifications of V360 and the PMDI used.

N,N-Dimethylcyclohexylamine (Cat8) was used as a gelling catalyst, N,N,N,N",N"-pentamethyldiethylenetriamine (Cat5) was used as the foaming catalyst, Momentive L6900 was used as a surfactant, and tris(1-chloro-2-propyl)phosphate (TCPP) was used as a fire retardant.
Table 3-1 Foaming recipes of rigid polyurethane foam.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight, g</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B-side materials</strong></td>
<td></td>
</tr>
<tr>
<td>Voranol 360</td>
<td>45</td>
</tr>
<tr>
<td>Dimethylcyclohexylamine (Cat8)</td>
<td>see Table 3-3</td>
</tr>
<tr>
<td>Pentamethyldiethylenetriamine</td>
<td>see Table 3-3</td>
</tr>
<tr>
<td>(Cat5)</td>
<td></td>
</tr>
<tr>
<td>Momentive L6900</td>
<td>0.6</td>
</tr>
<tr>
<td>TCPP</td>
<td>2</td>
</tr>
<tr>
<td>Blowing agent</td>
<td>see Table 3-3</td>
</tr>
<tr>
<td><strong>A-side material</strong></td>
<td></td>
</tr>
<tr>
<td>PMDI (1.1 index)</td>
<td>see Table 3-3</td>
</tr>
</tbody>
</table>

Table 3-2 Specifications of Voranol 360 and PMDI.

<table>
<thead>
<tr>
<th>Property</th>
<th>V360</th>
<th>PMDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>1.081</td>
<td>1.23</td>
</tr>
<tr>
<td>Average molecular weight</td>
<td>728</td>
<td>340</td>
</tr>
<tr>
<td>Functionality</td>
<td>4.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Hydroxyl number, mg KOH·g⁻¹</td>
<td>360</td>
<td>-</td>
</tr>
<tr>
<td>Equivalent weight</td>
<td>155.55</td>
<td>134</td>
</tr>
<tr>
<td>Viscosity, mPa·s at 25°C</td>
<td>3500</td>
<td>150-220</td>
</tr>
<tr>
<td>NCO content by weight, %</td>
<td>-</td>
<td>31.4</td>
</tr>
<tr>
<td>Vapor pressure, mm Hg at 25°C</td>
<td>-</td>
<td>&lt;10-5</td>
</tr>
<tr>
<td>Specific heat, g·cal/g at 25°C</td>
<td>-</td>
<td>0.43</td>
</tr>
</tbody>
</table>

The amounts of polyol, cat8, surfactant, and fire retardant were kept constant in all foam experiments to evaluate the performance of the blowing agents. The amounts of the physical blowing agent were kept at 0.1 mole to compare their efficiency. Table 3-3 summarizes the mass loadings of each blowing agent with the corresponding amounts of PMDI and catalysts.
Table 3-3 Amounts of blowing agents and PMDI.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Blowing agents</th>
<th>Weight, g</th>
<th>PMDI (1.1 index)</th>
<th>Cat8</th>
<th>Cat5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methyl Formate</td>
<td>6.005</td>
<td>43</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>n-Pentane</td>
<td>7.215</td>
<td>43</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>iso-Pentane</td>
<td>7.215</td>
<td>43</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>cyclo-Pentane</td>
<td>7.015</td>
<td>43</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>n-Hexane</td>
<td>8.618</td>
<td>43</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>cyclo-Hexane</td>
<td>8.416</td>
<td>43</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>n-Pentane</td>
<td>6</td>
<td>43</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>n-Pentane</td>
<td>8</td>
<td>43</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Water</td>
<td>0.5</td>
<td>51.2</td>
<td>0.12</td>
<td>0.32</td>
</tr>
<tr>
<td>10</td>
<td>Water</td>
<td>1</td>
<td>59.46</td>
<td>0.12</td>
<td>0.32</td>
</tr>
<tr>
<td>11</td>
<td>Water/n-Pentane</td>
<td>0.5/4</td>
<td>51.2</td>
<td>0.12</td>
<td>0.32</td>
</tr>
<tr>
<td>12</td>
<td>Water/n-Pentane</td>
<td>0.5/5</td>
<td>51.2</td>
<td>0.12</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Table 3-4 summarizes the physical properties of the physical blowing agents. The current simulation is the key for faster and more accurate evaluations of the performance of the blowing agents and their blends.

Table 3-4 Physical properties, ozone depletion potential (ODP), and global worming potential (GWP) of the PBAs.

<table>
<thead>
<tr>
<th>PBA</th>
<th>Boiling Point, ºC</th>
<th>Molecular Weight</th>
<th>(\Delta H_{vap}, \text{ J mole}^{-1})</th>
<th>Vapor Pressure, Kpa, 20ºC</th>
<th>ODP</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl formate</td>
<td>31.8</td>
<td>60.05</td>
<td>27648.65</td>
<td>63.51</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>36.1</td>
<td>72.15</td>
<td>26363.35</td>
<td>57.9</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>27.85</td>
<td>72.15</td>
<td>25372.42</td>
<td>76.99</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>cyclo-Pentane</td>
<td>49.26</td>
<td>70.15</td>
<td>26378.72</td>
<td>35.3</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>68</td>
<td>86.18</td>
<td>29543.3</td>
<td>17.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>cyclo-Hexane</td>
<td>80.7</td>
<td>84.16</td>
<td>30108.86</td>
<td>12.9</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
3.6 Experimental Procedure

Foaming experiments were performed for the different foaming systems in Table 3-1 and Table 3-3. The B-side components were weighed and mixed in a closed 150 mL beaker. The beaker was left open for 2 min for degassing and then weighed to measure the amount of blowing agent lost during mixing. The B-side mixture was then poured into a plastic cup to mix it with the A-side component with a 2000 rpm mixer blade attached to a floor-model drill press for 10 s. The mixture was quickly poured into a wooden box (base area of 11.5 × 11.5 cm²) with an aluminum-foil lining and allowed to expand until the temperature started to decrease. Foaming temperature and height profiles were measured using LabView software with a type-K thermocouple and an ultrasound device attached through a National Instruments SCB-68 box to a National Instruments PCI 6024E data acquisition card. The LabView software recorded the time−temperature and time−height data as x−y axes.

The tack-free time was measured for all of the foams by measuring the time when the surface of the foam did not show stickiness when touched with a spatula.[8]

A microscope by Renishaw was used to examine the average radius of the foam bubbles prepared at different loadings of blowing agent. Foams were cut using a razor blade into 5 × 5 × 1 cm³ slices. The bubble structure of the foams was observed parallel to the free-rise direction.
3.7 Results and Discussion

3.7.1 Simulating blowing agent performance

Experimental data on reaction temperature and foam height profiles for the foams blown using six different physical blowing agents (experiments 1–6) were simulated, and the results are shown in Figure 3-3. The heat generated from the exothermic polyol–isocyanate reaction evaporates the blowing agent while reactive alcohol moieties are available to maintain the exothermic reaction. The simulation results show good agreement with the experimental data for both temperature and height.

Methyl formate tends to have a low efficiency compared to other blowing agents with similar volatilities. This is attributed to the lower activity coefficient in the resin phase. For the foam blown by cyclohexane (Figure 3-3f), the simulated temperature deviates from the experimental data, whereas the height profile shows good agreement with the experimental data. This can be attributed to the large amount of cyclohexane in the foaming formulation and to its high heat of vaporization. The reasons for obtaining low efficiencies from high-boiling-temperature blowing agents are that the high heat of vaporization that has a great impact on the temperature and higher boiling temperatures lead to bubble formation and expansion at greater extents of reaction where the viscosity is higher, causing more resistance to bubble expansion and slower diffusion of gases into the bubbles.
Figure 3-3 Experimental and simulation results of temperature profile, height profile, and tack-free time of rigid polyurethane foams blown by different physical blowing agents. Symbols “♦” and “◊” represent experimental data of temperature and height profiles respectively. Solid lines represent simulation results for temperature and height. Dashed line represents tack-free time.

The tack-free times of the different foams show good agreement with both foam height and resin viscosity as corresponding to when the viscosity of the foam reaches a high value (gel) and the foam stops expanding.
Figure 3-4 shows the simulated viscosities of foams blown by different blowing agents. As the viscosity of the foam increases, the mass transfer of the blowing agent from the resin phase to the gas phase inside the bubbles decreases, the foam stops expanding, and the remaining amount of blowing agent is entrapped in the resin phase.

![Graph showing simulated viscosities of foams blown by different blowing agents](image)

**Figure 3-4 Simulation results of resin viscosity of foams by different physical blowing agents.** Dash lines from left to right represent viscosity of foams blown by Methyl Formate, n-Hexane, and iso-Pentane.

Figure 3-5 shows the experimental data and the superimposed simulation of the height profiles using two different loadings of n-pentane as the blowing agent (experiments 7 and 8).

The heat of the urethane-forming reaction causes the evaporation of n-pentane, and the bubbles expand, causing the foam to rise as the reaction proceeds with time. As the viscosity increases rapidly when the gel point is approached, diffusion of the blowing agent into the cell essentially ends, and the rate of increase in height stops.
Figure 3-5 Experimental and simulation data of foam height using physical blowing agent at two different loadings. Symbol "♦" and "◊" represent experimental results of foam height using 8 g and 6 g of n-Pentane respectively. Solid lines represent simulation results. Dash lines and dot lines from left to right represent resin viscosities and tack-free times of the foams blown by 6g and 8 g of n-Pentane respectively.

The water-blown reaction is summarized in Figure 3-6 for two different loadings of water in the foaming formulation (experiments 9 and 10). The results show that, as the water loading in the formulation increases, more carbon dioxide is generated, and a higher foam is obtained.

The water–isocyanate reaction is faster than the polyol–isocyanate reaction, and this leads to the conclusion that all water present in the formulation reacts to generate carbon dioxide. For the water system, a doubling of the amount of water almost doubles the height of the foam. Entrapment of carbon dioxide in the resin phase is less of a problem than entrapment of physical blowing agents.
Figure 3-6 Experimental and simulation data of foam height using water as blowing agent at two different loadings. Symbol "♦" and "◊" represent experimental results of foam height using 1 g and 0.5 g of water respectively. Solid lines from top represent simulation results for foam height. Dash and dot lines from left to right represent viscosities and tack-free times of the foams blown by 0.5 g and 1 g of water respectively.

Figure 3-7 shows temperature profiles of the two different loadings of water. Peak temperatures are reached at about 300 s as compared to 450–500 s for the physical blowing agents (see Figure 3-3). The exothermic reaction of water and isocyanate increases the reaction temperature, which leads to an increase in the rates of reactions of alcohol moieties and isocyanate.
A mixture of PBA (n-pentane) and water was used. The good match of the simulation results with experimental data on height and viscosity profiles is illustrated in Figure 3-8 (experiments 11 and 12). The reaction with water provides more heat to the system, and the higher temperature of the system supports faster evaporation of n-pentane. However, the higher temperature increases the rate of the reaction of the alcohol moiety to produce urethane, which leads to a faster increase in viscosity, which, in turn, decreases the diffusion rate of both CO$_2$ and n-pentane from the liquid phase to the gas phase in the bubbles.
Figure 3-8 Simulation foam height using chemical and physical blowing agents at two different loadings. Symbol ”♦” and “◊” represent experimental data of foam height using 0.5 g of water and 4 g and 5 g of n-Pentane respectively. Solid lines represent simulation results. Dash and dot lines from left to right represent viscosities and tack-free time for the foams blown by 0.5 g of water and 4 g and 5 g of n-Pentane respectively.

3.7.2 Bubble radius simulation

The dynamics of bubble growth as a function of bubble expansion time is illustrated by Figure 3-9. The model assumes spherical bubble growth upon nucleation and retention of a spherical shape for the entire period of growth. The simulation results show that, as more blowing agent is present in the formulation, larger bubbles are obtained. The interpretation of the trend of increasing bubble radius is empowered by the rate of increasing foam height. Bubble collisions affect the shapes and numbers of bubbles generated and the density of the foam; however, the current simulation does not take into account bubble collapse and bubble collision. The simulation results for bubble radius agree with the measured radius from the microscope image in Figure 3-10 (0.0145 and 0.0213 cm, respectively).
Figure 3-9 Simulation of bubble radius. Solid and dash lines form top represent bubble radius and foam height using 8g and 6g of n-Pentane as blowing agent respectively.

Figure 3-10 Microscope image of foams blown by a) 6 and b) 8 g of n-Pentane.

Figure 3-11 shows a comparison of the trends in viscosity and polymer concentration. The two trends show good agreement in the time range of bubble growth. This good agreement is used to support using Equation 3-13 instead of Equation 3-21.
3.7.3 Bubble Pressure simulation

The pressure generated from the evaporated physical blowing agent and/or the CO$_2$ generated from the water–isocyanate reaction was calculated assuming ideal gas behavior. The results in Figure 3-12a shows that the pressure starts increasing when the viscosity of the resin reaches a high value and the blowing agent cannot expand the bubbles. Figure 3-12b shows that, at the time when the pressure starts increasing, the blowing agent stops diffusing into the gas phase inside the bubbles, which leads to the conclusion that the increase in pressure is due only to the continued increase in temperature of the system.
In addition to being useful for simulating foam formation, the algorithm and program are able to simulate the pressure in the cells as the foam cools. Of particular interest for such simulations are (a) the extent to which a vacuum forms in the cells and (b) the extent to which the blowing agent will condense. Condensation of a blowing agent can be problematic if it has the propensity to soften the resin. These results are summarized in Figure 3-13, where the Antoine equation is used to estimate the total pressure inside the bubbles. The results show that, when the foam cools, the pressure inside the bubble...
decreases, and the blowing agent vapor condenses when its vapor pressure becomes less than the pressure inside the bubbles. This phenomenon causes a vacuum pressure inside the bubble that can lead to foam shrinkage if the urethane polymer cannot withstand the vacuum forces. These results substantiate earlier findings on how the setting of a rigid foam resin is critical to prevent shrinkage. [25]

![Figure 3-13 Simulation results of bubble pressure, vapor pressure and temperature. Solid, dash, and dot lines represent the pressure inside the bubble, vapor pressure, and reaction temperature respectively.](image)

### 3.8 Conclusions

By simulating urethane foam formation, it is possible to estimate the pressure of gases in the foam’s cells and the extent to which gelling entraps blowing agent in the resin before it can diffuse into the cells. One fitted parameter interpreted as the product of the boundary-layer thickness and the molecular radius was successfully used to estimate the overall mass transfer coefficient for the six physical blowing agents of this study. These results provide
a fundamental consistency that validates the model and supports use of the model to extrapolate performance outside the range of blowing agents evaluated.

The rapid reduction in mass transfer leads to part of the blowing agent being entrapped in the resin phase. During simulation, the rapid onset of viscosity led to near-zero diffusion coefficients and an end to cell growth; experimentally, this corresponded to an end of foam expansion with an associated end of the increase in height of the foam in the mold.

Simulated pressures ranged from a 1.18 atm peak pressure at a time coinciding with the maximum temperature to about 0.75 atm after the foam had cooled to ambient temperature. The results can be used to estimate whether a physical blowing agent will condense in the cells upon cooling.

### 3.9 Nomenclature

- $\Delta z$: Boundary layer thickness (cm)
- $a$: Molecular radius (cm)
- $A_f$: Total mass transfer area ($\text{cm}^2$)
- $C_A$: Concentration of species A (mole/cm$^3$)
- $C_{\text{PBA}}$: Concentration of the blowing agent in the liquid phase (mole/cm$^3$)
- $D_{AB}$: Diffusivity of component A in B (cm/s)
- $H$: Foam height (cm)
- $H_0$: Initial foam height (cm)
- $J_A$: Mass flux of species A (mole/cm$^3$.s)
\( K \quad \text{The overall mass transfer coefficient (cm/s)} \)

\( K_B \quad \text{Boltzmann constant} \)

\( n_{0\text{PBA}} \quad \text{Initial number of moles of blowing agent in the liquid phase (mole)} \)

\( N_A \quad \text{Bulk flux (mole/cm}^3\text{.s)} \)

\( N_C \quad \text{Number of nucleating sites} \)

\( n_g \quad \text{Number of moles of blowing agent in the gas phase (mole)} \)

\( n_i \quad \text{Number of moles (mole)} \)

\( n_p \quad \text{Number of moles of Polymer (mole)} \)

\( n_{\text{PBA}} \quad \text{Number of moles of blowing agent in the liquid phase (mole)} \)

\( P_0 \quad \text{Atmospheric pressure (1 atm)} \)

\( P_g \quad \text{Pressure inside the bubble (atm)} \)

\( P_{\text{sat}} \quad \text{Vapor pressure of physical blowing agent (atm)} \)

\( r \quad \text{Bubble radius (cm)} \)

\( r_0 \quad \text{Initial radius (cm)} \)

\( r_f \quad \text{Final radius of the bubble (cm}^3\text{)} \)

\( S \quad \text{Resin radius (cm}^3\text{)} \)

\( T \quad \text{Temperature (K)} \)

\( T_0 \quad \text{Initial temperature (K)} \)

\( u_A/F_A \quad \text{Mobility of a particle A} \)
\( V_F \)  Final volume of the foam (cm\(^3\))

\( x \)  Mole fraction of physical blowing agent in the liquid phase

\( x^* \)  Equilibrium mole fraction of physical blowing agent in the liquid phase

\( y \)  Mole fraction of physical blowing agent in the gas phase

\( \alpha_1, \alpha_2 \)  Constants

\( \gamma \)  Activity coefficient

\( \eta \)  Viscosity of resin (cp)

\( \sigma \)  Surface tension
CHAPTER 4. IMPACT OF THE MAXIMUM FOAM REACTION TEMPERATURE ON REDUCING FOAM SHRINKAGE

4.1 Abstract

One of the obstacles to displacing petroleum-based polyols with soy-based polyols in rigid urethane foam formulations is foam shrinkage, especially at displacements greater than 50%. The shrinkage is a result of partial vacuums forming in the closed-cell foam as reaction temperatures dissipate. It was hypothesized that the shrinkage was in part due to inadequate curing of the foam which was due to lower maximum-attained temperatures during the near-adiabatic foaming process. Foam formulation studies were performed to evaluate the correlation of peak temperature foam shrinkage. Two approaches were evaluated to increase peak temperatures: (a) preheating of the monomers prior to reaction and (b) use of bio-based glycerol as a co-reagent to increase the mixture hydroxyl number and respective maximum temperatures. The results show that as the maximum reaction temperature increases, foam shrinkage decreases. Both preheating and use of a glycerol co-reagent were effective for increasing peak temperatures and decreasing shrinkage. Experimental results were supplemented with a simulation of the foaming process to better understand the fundamental phenomena and to evaluate the effectiveness of the simulation to evaluate approaches to better utilize bio-based monomers in thermoset polymers.

4.2 Introduction

Polyurethanes (PU) are one of the highest value polymer markets because of their versatility and high-performance in applications ranging from furniture cushions to
building insulation. 12 million metric tons of PU is consumed globally with an average annual growth rate of 5%.[1, 29] A 2007 US Presidential Green Chemistry Challenge award went to the development of soy-based polyols for use in PUs. Due to the high value of polyols, the good performance of soy-based polyols, and the size of the PU market; the PUs industry represents one of the largest sustainable green chemistry markets.

The major chemicals applied in the manufacture of PU foams are polyols, isocyanate, physical and chemical blowing agents, gel and blowing catalysts, surfactant, and cross linker.

The PU reaction is described in Equation 2-1 (where R contains additional isocyanate moieties and R₀ contains additional hydroxyl moieties) in which the isocyanate is reacting with alcohol groups in the polyol(s) to produce the PU. To get foam, PU is expanded by either physical or chemical blowing agents or both. Water is normally used as a chemical blowing agent to produce carbon dioxide gas. The water–isocyanate reactions are described in Equation 2-2 and Equation 2-3.

\[
\text{RNCO} + R'\text{CH}_2\text{OH} \rightarrow \text{RNHCOOCH}_2R' \quad \text{Equation 4-1}
\]

Isocyanate Alcohol PU

\[
\text{RNCO} + \text{H}_2\text{O} \rightarrow \text{RNHCOOH} \quad \text{Equation 4-2}
\]

Isocyanate Water Carbamic Acid

\[
\text{RNHCOOH} \rightarrow \text{RNH}_2 + \text{CO}_2 + \text{Heat} \quad \text{Equation 4-3}
\]

Carbamic Acid Amine Carbon Dioxide
In polymer chemistry, polyols are defined as the polymeric compounds containing at least two hydroxyl functional groups. These polyols will typically have molecular weights between 500 and 5000. The properties of polyols, such as hydroxyl number, functionality, and molecular weight, play a significant role in determining the final properties of foams.[4] Polyols are characterized by functionality, hydroxyl number, and equivalent weight[45] as well as other properties that may be more specific to application.

PU producers are seeking to replace petrochemical based polyols by “greener” renewable materials due to the increasing in crude oil price and the strong public desire for environmentally friend products. Soy-based material is an excellent choice because it provides environmental and costing benefits in addition to performing well in PU polymers.[46, 47] Several excellent soy-based polyols are commercially available.

Partial substitution of petroleum-based polyols with bio-based polyols was studied by several researchers.[48-50] Fan measured different properties of PU rigid foams with partial substitution of soybean oil-based polyol.[51] The results show that a 50% substitution is the best to achieve good foam properties.

Tan et al.[52] studied cell structure, cell size, density, thermal conductivity, and compressive strength when replacing polypropylene-based polyol with soy-based polyol. The results show that the density was within 5% of the controls, except that the density of foams from 100% soy-based polyol was 17% higher.

A reoccurring results of research on using soy-based polyols in PU foams is that displacing > 50% of the petroleum based polyol in the formulation leads to deteriorating performance.
The goal of this work is to better understand how to fully displace petroleum-based polyols in a rigid foam formulation with bio-based polyols. A205, which is prepared by reaction of epoxidized soybean oil with ethylene glycol in the presence of catalyst, is used in this study.[53, 54]

It is hypothesized that the lower hydroxyl number of A205 led to lower peak temperatures during reaction and that the lower peak temperatures led to inadequate curing. Insufficiently cured foams may have inadequate strength to resist the tendency to shrink caused by partial vacuums which form in closed cells of rigid foams—closed cells are important for good insulating properties. An understanding of the fundamental cause for inferior performance of a foam is an important step toward providing variations in formulations and processes (e.g. preheating) to fix the problems.

The soy-based polyol industry has undergone a significant evolution during the past two decades. In the early 1990’s, a few customers were content with simply displacing 5–10% of the polyol in the formulation where, often times, the soy-based component acted more like an inert component or plasticizer than a monomer. During the next 15 years, several good performing soy-based monomers were developed and have become commercial; however, the mind-set of much of the industry was to require “drop-in” substitutions for the commercial petroleum-based polyols.

Soy-based drop-ins for petroleum-based polyols is a particularly problematic goal since petroleum-based polyols are custom-built from 2 to 4 carbon oxides (ethylene, propylene, and butylene oxide) to attain specific structures known to deliver the desired performance.
The cost-effective soy-based polyols retain much of the soybean oil backbone, and so, it is simply not possible to custom-design structures.

An alternative approach to “drop-in” substitutes is the combination of soy-based polyols and simulation software to rapidly identify how to modify a PU formulation to provide similar performance. Simulation is necessary because PU formulations tend to have many more degrees of freedom as used to specify the thermoset formulation as compared to thermoplastic formulations. Typically, eight or more degrees of freedom are used in specifying foams that include monomer selection and their concentrations, two or more homogeneous catalysts, blowing agent(s), and additives. The status of PU foam formulation is more of an art than a science. Simulation can be used to transform the industry to more of a science than an art, and can be an important enabling technology to green chemistry in the PU industry.

The simulation presented in these studies is based on a simultaneous solution of over two dozen ordinary differential equations[19] for the many reaction and physical processes that occur in the foaming process. Simulation of the reaction temperature quantifies the factors impacting peak temperature and to assists in identifying conditions that produce desired temperature profiles.

### 4.3 Methodology

#### 4.3.1 Experimental design

Gel and foaming experiments were performed to create PU gel and foams as described in the following steps:
1. Weighed masses of polyols, fire retardant, catalysts, surfactant, chemical blowing agent, and the physical blowing agent are added together as a B-side in a plastic cup and mixed for 10 to 15 second in a 2000 rpm mixer.

2. Via a syringe (weighed before and after), isocyanate (as Asi) is added to the mixture and the new mixture is mixed with a 2000 rpm mixer for 10 seconds.

3. The mixture of A and B-sides is quickly poured into wooden mold (11.4 x 11.4 x 21.6 cm) with aluminum foil lining to measure temperature profile.

A thermocouple is inserted into the center of the foaming PU. Temperatures and times were recorded by LabVIEW software.

To control preheating of monomers and all items contacting the PU reaction mixture, a temperature-controlled oven equipped with mixing capabilities through a rotating shaft that enters the oven's top. The oven is used to preheat A and B-sides, mixing blade, the thermocouple, and the foaming box with foil inside for about one hour. A 35 and 45°C were chosen as pre-heating temperatures because they provide enough distinct results for evaluating the impact of preheating and high enough to avoid blowing agent from evaporation.

4.4 Materials and recipes

4.4.1 Gel experiments

Control – a commercially available 490 hydroxyl number polyol (V490) was selected as a control in this study.
A205 Gels – A205 polyol is synthesized by reaction of epoxidized soybean oil with ethylene glycol in the presence of toluene sulfonic acid in a controlled temperature of 161 °C. The epoxy number of A205 is around 1.3 and its water content is 0.2%. The amount of A205 is calculated so that it has the same total moles of hydroxyl functional group as the control.

A205/glycerol study – adding glycerol as a polyol co-reagent (hydroxyl number = 1829 (ref. [56])) was used as an alternative method to increase the maximum reaction temperature of the A205 polyol.

Glycerol has a 66.67% primary and 33.33% secondary alcohol moiety fractions. The amount of glycerol is calculated so the resulting A205/glycerol mixture has the same total moles of hydroxyl functional group as the control. Glycerol was chosen because it is available as bio-based.

An isocyanate index of 1.1 is used in all the gel systems above except for the control (0.9) to avoid excessively high peak temperatures.

The properties of the control, A205, and isocyanate are summarized in Table 4-1. Table 4-2 provides the recipe of the gel reaction using the control, A205, and A205/glycerol mixture.
Table 4-1 Specifications of V490, A205, and isocyanate

<table>
<thead>
<tr>
<th>Property</th>
<th>V490</th>
<th>A205</th>
<th>Isocyanate (PMDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>1.11</td>
<td>-</td>
<td>1.23</td>
</tr>
<tr>
<td>Average molecular weight</td>
<td>460</td>
<td>-</td>
<td>340</td>
</tr>
<tr>
<td>Functionality</td>
<td>4.3</td>
<td>-</td>
<td>2.7</td>
</tr>
<tr>
<td>Hydroxyl number, mg KOH/g</td>
<td>484.8</td>
<td>200</td>
<td>-</td>
</tr>
<tr>
<td>Equivalent weight</td>
<td>115</td>
<td>280.5</td>
<td>134</td>
</tr>
<tr>
<td>Viscosity, mPa.s at 25°C</td>
<td>6180</td>
<td>-</td>
<td>150-220</td>
</tr>
<tr>
<td>NCO content by weight, %</td>
<td>-</td>
<td>-</td>
<td>31.4</td>
</tr>
<tr>
<td>Vapor pressure, mm Hg at 25°C</td>
<td>-</td>
<td>-</td>
<td>&lt;10-5</td>
</tr>
<tr>
<td>Specific heat, gm.cal/gm.at 25°C</td>
<td>-</td>
<td>-</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Table 4-2 Gel reaction Recipe of the control, A205, and A205/Glycerol mixture.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight, gm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
</tr>
<tr>
<td>B-side materials</td>
<td></td>
</tr>
<tr>
<td>V490</td>
<td>32.2</td>
</tr>
<tr>
<td>A205</td>
<td>0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0</td>
</tr>
<tr>
<td>Dimethylcyclohexylamine (Cat8)</td>
<td>0.12</td>
</tr>
<tr>
<td>Pentamethyldiethylenetriamine (Cat5)</td>
<td>0.32</td>
</tr>
<tr>
<td>A-side material</td>
<td></td>
</tr>
<tr>
<td>Isocyanate (PMDI)</td>
<td>41.58</td>
</tr>
</tbody>
</table>

4.4.2 Foam experiments

While the final PU application is as a foam, gel tests were performed to evaluate performance without the added reaction and physical process complexities of foam processes. Evaluation of both provides for greater insight and certainty.
Foam experiments were performed for the three gel formulations by adding blowing agents and blowing catalysts. The amounts of the fire retardant, surfactant, and the blowing agent are the same for all the systems. Also, a 1.1 isocyanate index is used for all the system except for the control (0.9) to avoid excessively high peak temperatures. The amounts of catalysts used are also the same except for the gels and foams with the preheating attempt (catalysts loading studies). The recipes of these foams are shown by Table 4-3.

Foam shrinkage is measured using water displacement method. This method provides good accuracy for measuring the volume of un-regular shapes. Since the foam prepared is a closed-cell, the amount of water absorb by the foam is neglected. Foams were cut in regular shapes to measure the initial volume, and then the water displacement method was used to measure the new volume after shrinkage. Foam density was measured using the volume and weight of the foam samples.

4.4.3 Scanning electron microscopy (SEM)

Scanning Electron Microscopy (FEI Quanta 600) is used to examine foam cells morphology of the control, A205 prepared at ambient temperature, and A205/glycerol. Foams were cut using a razor blade into a 10 x 10 x 1 mm slices and attached to the stub using conductive carbon tape. Slices were sputter coated with thin layer of platinum and imaged at an accelerating voltage of 5 kV and 80x magnification. The cellular structure of the foams was observed parallel to the free-rise direction.
Table 4-3 Foam reaction Recipe of the control, A205, and A205/Glycerol mixture

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight, gm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B-side materials</strong></td>
<td><strong>Control</strong></td>
</tr>
<tr>
<td>V490</td>
<td>32.2</td>
</tr>
<tr>
<td>A205</td>
<td>0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0</td>
</tr>
<tr>
<td>Dimethylcyclohexylamine (Cat8)</td>
<td>0.12</td>
</tr>
<tr>
<td>Pentamethylenetetramine (Cat5)</td>
<td>0.32</td>
</tr>
<tr>
<td>Momentive L6900</td>
<td>0.6</td>
</tr>
<tr>
<td>TCPP</td>
<td>2</td>
</tr>
<tr>
<td>Water</td>
<td>1.04</td>
</tr>
<tr>
<td>Methyl Formate</td>
<td>2.4</td>
</tr>
<tr>
<td><strong>A-side material</strong></td>
<td></td>
</tr>
<tr>
<td>Isocyanate (PMDI)</td>
<td>48.06</td>
</tr>
</tbody>
</table>

4.5 Results and discussion

Figure 4-1 and Figure 4-2 show the experimental and simulated temperature profiles for the gel reaction control and gel reaction with 100% displacement of the control polyol with A205. The initial temperature of 22 °C indicates no preheating was used.

Whereas the model line for the control formulation was generated using kinetic and physical parameters (preexponential factors, activation energies, and heat of reactions) as previously reported,[19] the model line for A205 was based on parameters fitted the data and a hydroxyl number obtained by titration of the polyol. The fitted parameters included fraction of primary, secondary, and hindered secondary of alcohol moieties. This approach was previously published[57] and represents a method that both reduces the number of parameters needed to characterize a polyol and provides for immediate insight into the
reactivity and structure of the polyol. Fractions of 50% primary, 50% secondary, and zero hindered secondary moiety fractions provided the best-fit characterization of A205.

Since repeating the experimental data show very slight change from system to system, there is no reason to expect significant changes when repeating experiments in the next experiments.

Figure 4-1 Temperature profile of PU gel reaction control. Symbols “♦” represent experimental data and the solid line represents simulation results.

Once the A205 polyol was characterized (fit of Figure 4-2), the fitted parameters were used in the simulation program to project the impact of preheating and glycerol addition on performance. The simulation results and experimental data are provided by Figure 4-3 and Figure 4-4. There was good agreement between what was predicted by the simulation software and the superimposed experimental data for the gel reactions.
Preheating leads to substantial increases in initial reaction rates and more-rapid attaining of maximum temperature. In addition, increasing the initial temperature increases the maximum temperature of the reacting mixture. The presence of glycerol leads also to increase the initial reaction rates because it has highly reactive primary hydroxyl group and high heat of reaction.

The trend of the temperature profiles of the A205 is prominently different than that of the control (V490). This is likely attributed to using ethylene glycol as a reagent in the synthesis of A205. If only one of the alcohols of ethylene glycol reacts, the other remains as a primary hydroxyl with a high reaction rate; it is likely that this primary hydroxyl (corroborated by fitted parameters) is present and leads to high reaction rates. Also, the existence of ethylene glycol in synthesizing leads to a special A205 structure and/or reaction activity.
Figure 4-3 illustrates how higher hydroxyl numbers (V490 and glycerol) as well as preheating lead to higher peak temperatures. The hydroxyl numbers are 484.8, 205.24, and 1829 for V490, A205, and glycerol.

The gel simulation results fully corroborate the temperature trends and the maximum temperatures. The slight variation in the trends results from the uncertainties in heat capacities and heats of reaction.

As compared to gel reactions, temperature rises for foam forming reactions are faster and this attributed to the heat of reaction between water and isocyanate. For the foam reactions, the simulation predicts the temperature rise to be faster for several of the systems than the experimental data (Figure 4-4). A further inspection reveals that when the model predicts substantial temperature increases (e.g. > 30% of the maximum temperature
increase) in the first 50 seconds, the model projects a more rapid rate of increase than the data. This can be attributed to the fact that the model is based on Arrhenius-type reaction kinetic models, and in highly viscous reaction systems mass transfer can limit reaction rates as opposed to limits on reaction rates.

![Graph showing temperature vs time](image)

**Figure 4-4** Effect of preheating monomers of PU foaming reaction using A205 or A205/glycerol as polyol on the maximum heat of reaction. Symbols “♦, ●, ▲, ■, ×” represent experimental data using V490, A205 at ambient temp., 35, and 45˚C, and A205/Glycerol respectively. Lines from higher to lower peak temperature represent simulation results using V490, A205 at 45˚C, A205/Gly. at amb. temp., A205 at 35˚C, A205 at amb. temp. respectively.

Addition of diffusion rate limitations to reaction kinetics is outside the scope of this work, and so, an alternative approach was taken. The alternative approach consisted of adjusting recipes (lowering catalyst concentrations) to mixtures where diffusion would not limit reaction rates.

### 4.5.1 Catalyst loading study

The soy-based A205 is more reactive than the control petroleum based polyol. This insight reveals a previously unknown benefit of the soy-based polyol; the higher intrinsic
reactivity would allow lower catalyst loadings to be used. Catalysts are a major contributor to the costs of many urethane foams.

Quantifying the extent to which the amount of catalyst for the A205 gels and foams can be reduced was performed using the simulation software. Catalyst loadings were reduced until the temperature reaches its half value (half of increase at peak temperature) at the same time when the temperature profile of the control reached its half value. Figure 4-5, Figure 4-6, and Figure 4-7, show how the amounts of catalysts are achieved for different initial preheating temperature. Table 4-4 shows the different amounts of catalysts loadings obtained at different preheating temperatures.

![Temperature profile of A205 at ambient temperature (22°C) to achieve low catalysts loading. Lines from higher to lower peak temperature represent simulation results using V490, A205 at ambient temp. with full catalyst loadings, and A205 at ambient temp. using low catalyst loadings respectively.](image)
Figure 4-6 Temperature profile of A205 at 35°C to achieve low catalysts loading. Lines from higher to lower peak temperature represent simulation results using V490, A205 at 35°C temp. using full catalyst loadings, and A205 at ambient temp. using low catalyst loadings respectively.

Figure 4-7 Temperature profile of A205 at 45°C to achieve low catalysts loading. Lines from higher to lower peak temperature represent simulation results using V490, A205 at 45°C temp. using full catalyst loadings, and A205 at ambient temp. using low catalyst loadings respectively.
Table 4-4 Catalysts loadings of the A205 gels and foams at different preheating temperatures

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Weight, gm</th>
<th>At ambient temp. (22°C)</th>
<th>At 35°C</th>
<th>At 45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylcyclohexylamine (Cat8)</td>
<td>0.072</td>
<td>0.036</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>Pentamethyldiethylenetriamine (Cat5)</td>
<td>0.192</td>
<td>0.096</td>
<td>0.032</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4-8 present both experimental and simulation temperature profiles of the gel reaction using the control, A205, or A205/glycerol as polyol at different preheating temperature and the new catalyst loadings of Table 4-4. Figure 4-9 shows foaming experiments for the new catalyst loadings.

![Figure 4-8 Temperature profiles of PU gel reaction of the using the control (V490), A205, or A205/Glycerol as polyol. Symbols “♦,●,○,□,∆,×” represent experimental data using V490, A205 at ambient temp. with full catalyst loading, A205 at ambient temp., 35, and 45˚C with low catalysts loading, and A205/Glycerol respectively. Lines from higher to lower peak temperature represent simulation results using V490, A205/Gly. at amb. temp., A205 at 45˚C with low cats, A205 at 35˚C with low cats, A205 at amb. temp. with full cats, and A205 at amb. temp. with low cats loading respectively.](image-url)
For foam-forming system, simulation is in better agreement with data when half temperature times are greater than 100 seconds. The simulation is successful both quantifying the impacts on reaction temperature profiles at conditions where mass transfer does not slow down the reaction. Even when mass transfer is the rate limiting step, the simulation provides qualitative trends.

![Temperature profile graph](image)

**Figure 4-9 Temperature profiles of PU foaming reaction using A205 as polyol. Symbols “◊ △ □” represent experimental data at ambient temp., 35, and 45°C respectively with low catalyst loadings. Lines from higher to lower peak temperature represent simulation results using A205 at 45°C with low cats, A205 at 35°C with low cats, and A205 at amb. temp. with low cats respectively.**

The following advantages were realized for simulation as a tool for use in urethane formulation development, simulation provided:

- Insight into when mass transfer limitations on reaction kinetics become limiting.
- Insight into the type of hydroxyl functional groups (primary versus secondary) and how these groups impact reaction.
- A quantification of the trade-off between pre-heating and catalyst addition to achieve desired reactivity profiles.
- A quantification of peak temperatures of the foam as a function of formulation.

### 4.5.2 Density and shrinkage study

It was observed that the foam of the A205 formulation of Figure 4-4 exhibited considerable shrinking (with associated increase in foam density) during the time frame of 30 minutes to 6 days. A first method to reduce shrinkage, no cutting of the foam was performed until after day five; this led to a substantial reduction in shrinkage but not an elimination of shrinkage.

The foams prepared from A205 at ambient temperature (with full catalysts loading) have low peak temperatures (Figure 4-9) and high shrinkage due to the low hydroxyl number of the polyol. An advantage of the lower hydroxyl number is a reduced isocyanate content in formulations (green chemistry). Disadvantages include reduced peak temperatures and less crosslinking in the polymer.

Preheating to 35 and 45°C (with full catalysts loading) reduced the shrinkage. Figure 4-10 illustrates how the percent shrinkage appears to be directly related to the maximum reaction temperature. Increases in peak temperature lead to faster reaction rates and more-complete curing during the time frame when shrinkage occurs.

To verify how the higher peak temperature leads to more complete curing, Figure 4-10 shows the urethane moieties resulting from polymer–polymer reactions for the different systems. The polymer–polymer reactions constitute a crosslink density and ultimate curing. Later onset of the crosslinking or a lower crosslinking density results in a foam that can
shrink when the temperature of the foam cools. By comparing this figure with the results shown in Figure 4-3, it's obvious that at higher peak reaction temperature more urethane moieties produced from the polymer–polymer reaction and this is interpreted to faster crosslinking.

![Figure 4-10 Urethane concentration from the polymer-polymer reaction. Lines from higher to lower concentration represent simulation results using V490, A205 at 45°C, A205/Gly. at ambient temperature, A205 at 35°C, and A205 at ambient temperature respectively.](image)

This exemplifies how the “setting” of the foam is different from the “curing” of the foam. Setting of the foam occurs when an adequate resin structure exists to prevent collapse; however, that resin structure may still be too weak to withstand the vacuum forces that can form inside the closed cells. Curing can lead to further crosslinking and a sufficiently strong resin to withstand the vacuum forces without shrinkage. In addition to time and temperature to attain an adequate amount of curing, foam formulation must provide enough cross-linking capability and rigidity (hard segments, high glass transition temperature) for a rigid resin structure.
Figure 4-11 shows the relationship between percent shrinkage and the maximum reaction temperature for the A205 foams at different preheating temperatures and different catalyst loadings. It is obvious that the foams with the full catalyst loadings have less shrinkage due to the higher maximum reaction temperature and higher catalyst content that may have crosslinking effect.

![Graph showing the relationship between percent shrinkage and maximum reaction temperature for A205 foams]

Figure 4-11 The relationship between the peak temperature of foaming reaction and shrinkage percentage for foams using the control, A205 and A205/Glycerol at different preheating temperatures with full catalyst loadings.

Figure 4-12 compares densities of the A205 foams at different preheating temperatures and different catalysts loading. Differences in density between foams of different catalysts loadings decrease with increased preheating.

Table 4-5 summarizes the values of percentage shrinkage and both density measurements. The values show that foams tend to have less changing in density (see Figure 4-13) and less shrinkage values when using higher hydroxyl number polyols like V490 and A205/glycerol.
Figure 4-12 The relationship between the peak reaction temperature of foaming reaction and shrinkage percentage for foams using the control, A205 and A205/Glycerol at different preheating temperatures and different catalyst loadings.

Figure 4-13 The relationship between the peak reaction temperature and percent density change for foams using the control, A205 and A205/Glycerol at different preheating temperatures and different catalyst loadings.

Simulation results effectively predicted the impact of preheating and glycerol addition on the peak reaction temperature of the foams. Simulation also quantified the trade-off
between preheating and more catalyst addition. At this point in its development, simulation is not able to predict shrinkage from fundamentals; however, empirical correlations based on trends of Figure 4-10 and Figure 4-11 are possible.

Table 4-5 Values of % shrinkage and % density change for A205 foams at different preheating temperature and catalysts loadings

<table>
<thead>
<tr>
<th>Polyol used in foaming recipe</th>
<th>Max. Reaction Temp.</th>
<th>% Shrinkage</th>
<th>Initial Density</th>
<th>Final Density</th>
<th>% Density Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>V490 at amb</td>
<td>129.3</td>
<td>2.03</td>
<td>0.39</td>
<td>0.423</td>
<td>8.09</td>
</tr>
<tr>
<td>A205 at amb</td>
<td>95.8</td>
<td>26.92</td>
<td>0.175</td>
<td>0.212</td>
<td>21.53</td>
</tr>
<tr>
<td>A205 at 35˚C</td>
<td>106.9</td>
<td>17.58</td>
<td>0.114</td>
<td>0.125</td>
<td>9.33</td>
</tr>
<tr>
<td>A205 at 45˚C</td>
<td>114.9</td>
<td>3.74</td>
<td>0.109</td>
<td>0.113</td>
<td>3.14</td>
</tr>
<tr>
<td>A205 at amb low cats</td>
<td>94.1</td>
<td>37.97</td>
<td>0.144</td>
<td>0.215</td>
<td>49.35</td>
</tr>
<tr>
<td>A205 at 35˚C low cats</td>
<td>98.6</td>
<td>24.89</td>
<td>0.181</td>
<td>0.235</td>
<td>29.87</td>
</tr>
<tr>
<td>A205 at 45˚C low cats</td>
<td>110.4</td>
<td>5.27</td>
<td>0.242</td>
<td>0.259</td>
<td>6.86</td>
</tr>
<tr>
<td>A205/Glycerol</td>
<td>127.2</td>
<td>2.69</td>
<td>0.459</td>
<td>0.475</td>
<td>3.54</td>
</tr>
</tbody>
</table>

The SEM images in Figure 4-14 shows that the cell structure of A205 prepared at ambient temperature has substantially more open-cell content and distorted cell structure as compared with the control. Increasing peak reaction temperature eliminates the distorted cell structure and result in a high closed cell content.

It should be noted that the foams studied in this investigation were cured prior to cutting. The foam skin sealed the exterior and allowed for open cell content to have minimal impact on shrinkage and to allow water displacement to provide accurate density measurement.
Figure 4-14. Scanning electron micrographs of the cut section of the foams showing the cell morphology

4.6 Conclusion

Simulation was a valuable tool in being able to develop formulations that allow 100% of the soy-based polyol to be used while avoiding shrinkage. The simulation quantified how higher reactivity of the soy-based polyol can be translated to lower catalyst loadings. Preheat can also be used to reduce catalyst loadings. Further studies are needed to evaluate the impact of these new formulations on thermal conductivity and compressive strength.
For these formulations, the maximum reaction temperature (peak temperature) attained during reaction was a critical performance metric that translated to reduced shrinkage of the foam. Two different methods were used to increase the peak temperature of reaction: (a) preheating the monomers to a 35 and 45°C temperature which increased the initial rates of reaction and lead to a faster and higher maximum temperature and (b) adding glycerol to the bio-based polyol to increase its hydroxyl number and the heat of reaction.

This is one of the first (if not the first) applications of simulation of the foaming process to assist in formulation modification to allow the use of bio-based polyols. Historically, the PU industry has pursued drop-in bio-based solutions to avoid the costs of reformulating PU recipes. Simulation provides a new and powerful green chemistry tool to reduce the costs of adopting new bio-based polymers in thermoset formulations.
CHAPTER 5. IMPACT OF INTER- AND INTRA-MOLECULAR MOVEMENTS ON THERMOSET POLYMERIZATION REACTIONS

5.1 Abstract

The large increase in viscosity during thermoset reactions leads to reduced frequencies of reacting moiety collisions with respective reduced reaction rates. Molecular diffusion substantially ends after the gel point; however, reactions continue after the gel point through mechanisms involving local movement (and reacting moiety contact) of polymer sections/branches which is referred to as intra-molecular movement. The impact of inter-and intra-molecular movements was simulated for polyurethane reactions to better understand the impact of mass transfer on polymerization reactions.

Inter-molecular reaction mechanisms are dominant prior to the gel point, and intra-molecular mechanisms are dominant after the gel point. Representing the Arrhenius pre-exponential factor as a sum of a viscosity-dependent term and a viscosity-independent term was identified as the most efficient method to model this phenomenon. Good agreement of simulation results for reaction temperature, foam height, and viscosity profile with the experimental data were obtained.

5.2 Introduction

Toward the goal of having a reasonably small set of kinetic parameters to describe urethane-forming reactions from dozens of polyols, Ghoreishi et al [57] developed a group contribution approach to characterize the reactivity of polyols in terms of concentration of primary, secondary, and hindered secondary alcohol moieties. Subsequent analysis of this
approach questioned the basis of characterizing two different types of secondary alcohol moieties. In addition, unexpected deviations from model predictions occurred in the form of slower reaction rates in higher viscosity polyols than projected by this model.

Thus, a hypothesis was then put forth that in these systems, the reaction rates were viscosity dependent; and an objective was put forth to eliminate the need to classify certain alcohol moieties as “hindered” secondary. A further objective was to have a model that corrected previous deficiencies where the model was not able to predict that higher viscosity polyols would have slower reaction rates. This paper is on research to identify a fundamental basis to incorporate the impact of viscosity on reaction kinetics for polymer forming systems. Ultimately, this fundamental pursuit is one of better understanding the role of mass transfer on reaction kinetics for systems where the viscosity changes by several orders of magnitude during reaction.

Diffusion-controlled (or diffusion-limited) reaction is defined as the reactions that occur quickly and the rate of reaction depends on the rate of diffusion of the reactants through the reaction medium. As the reacting species diffuses to each other, they form a complex that reacts quickly to product. For inter-molecular collision of reacting moieties, diffusion rate is proportional to the time it takes to bring the reactive moieties (or the reactive part in the moieties) into contact to allow reaction. Diffusion-controlled reaction is rare in the gas phase where the rate of diffusion of gas molecules is very high compared to the rate of reaction. However, this phenomenon is more important in liquids, especially when the viscosity is high and the diffusion of the molecules becomes slow.
During reactions, which form thermoset polymers, the viscosity of the resin increases due to the formation of product polymer and crosslinking, which causes reduction in the diffusion rate of the reactants. In this stage, the diffusion step becomes the limiting (controlling) step of this reaction. An associated theory was developed first by Smoluchowski, [58] Collins and Kimball,[59] Noyes [60], and discussed in details by Rice [61].

The diffusion and reaction of a simple irreversible reaction of two reactive moieties, A and B, can be represented by the three steps of Equation 5-1:

- Diffusion of A and B to a proximity at which attractive chemical forces become dominant to form the pseudo species (AB)*, and either
- Dissociation of the pseudo species (AB)* if the species A and B diffuse apart without reacting or
- Reaction of the pseudo species (AB)* to form product.

\[ A + B \xrightarrow{k_{df}} (AB)^* \xrightarrow{k_{rxn}} P \]

Equation 5-1

(AB)* is described as an active complex if it is at the saddle point of the potential energy surface of A and B or as a collision complex if there is no interaction between A and B. The term “encounter complex” has been used to cover the above two cases [62].

Polyurethane forming reactions can be particularly insightful for studying the impact of diffusion on reaction rates because formulations are available that react from flowing liquid to solid in a couple minutes. Polyurethane (PU) is a chain of organic units joined by
urethane links. Isocyanate moieties reacting with alcohol moieties to produce urethane [3, 8, 9]. The general reaction is described in Equation 5-2.

\[
RNCO + R'CH_2OH \rightarrow RNHCOOCH_2R' \quad \text{Equation 5-2}
\]

Isocyanate    Alcohol    PU

The structure and the molecular size of the isocyanate and polyol have a significant impact on the polyurethane produced [7]. Other additives such as catalysts, cross-linkers, and light stabilizers also have an impact of the polymerization reaction of polyurethane [2, 19, 63].

5.3 Modeling Approaches

Two different approaches are presented in this paper to provide insight into mechanisms and, ultimately, an effective method to more-accurately simulate urethane-forming reactions. The first approach assumes that the reactive moieties diffuse together forming the encounter complex which may either disassociate or react. This approach is described as the inter-molecular movement of the reactive moieties. The second approach considers an intra-molecular movement (bending and rotation without breaking of covalent bonds) in parallel to the inter-molecular movement with the rate of inter- and intra- movement as additive in the collision frequency factor in Arrhenius equation.

5.3.1 Intermolecular diffusion

Alberty and Hammes [64] demonstrated that diffusion can be modeled in a power-law rate expression where the rate constant is related to diffusivities according to Equation 5-3.

\[
k_{d\text{(inter)}} = 4\pi NR^* (D_A + D_B) \quad \text{Equation 5-3}
\]
The Equation 5-4 expression of diffusivity suggested by Albert Einstein [34] and Marian Smoluchowski [35] can be used to calculate the diffusivity of A and B moieties in the reaction medium.

\[ D_A = \frac{K_BT}{6\pi r_A \mu}, \quad D_B = \frac{K_BT}{6\pi r_B \mu} \]  

Equation 5-4

By substituting Equation 5-4 into Equation 5-3, the equation of diffusion rate constant becomes:

\[ k_d = 4\pi NR^* \left( \frac{1}{r_A} + \frac{1}{r_B} \right) \left( \frac{K_B T}{\mu} \right) = 4\pi NR^* \left( \frac{1}{r_A} + \frac{1}{r_B} \right) \left( \frac{T}{\mu} \right) \]  

Equation 5-5

To simplify this equation, the molecular radii of the reactive moieties are assumed to be equal and the critical distance necessary to form the encounter complex is assumed to be equal to two times the molecular radius of the reacting moieties [62]. These assumptions reduce Equation 5-5 to:

\[ k_d(\text{inter}) = A_1 \left( \frac{T}{\mu} \right) \]  

Equation 5-6

Where T at Kelvins and resin viscosity at centipoises.

Reaction temperature and resin viscosity are the key parameters that impact rate of diffusion (in liquid phase). Equation 5-6 identifies that the rate of diffusion increases as the reaction temperature of the resin increases and decreases as the viscosity increases. In the limit of slow reaction, backward diffusion rate (rate of moieties dissociation) is assumed equal to the forward diffusion rate.
In order to simulate the effect of the diffusion rate of the moieties on the reaction rate, the mechanism of Equation 5-2 is divided into three rate steps as provided in Table 5-1. For purposes of simulation, these steps were assumed for all urethane reactions proposed by Ghoreishi [57].

<table>
<thead>
<tr>
<th>Diffusion and reaction and steps</th>
<th>Rate expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + B $\xrightarrow{k_{df}}$ (AB)*</td>
<td>$r_{(AB)^*} = k_{df} [A][B]/V^2$</td>
</tr>
<tr>
<td>(AB)* $\xrightarrow{k_{db}}$ A + B</td>
<td>$r_{(AB)^<em>} = -k_{db} [(AB)^</em>]/V$</td>
</tr>
<tr>
<td>(AB)* $\xrightarrow{k_{rxn}}$ P</td>
<td>$r_P = k_{rxn} [(AB)^*]/V$</td>
</tr>
</tbody>
</table>

Forward diffusion is expressed as second order rate based on the concentration of A and B components. Backward diffusion and reaction steps are expressed as first order rates based on (AB)* concentration.

5.3.2 **Intramolecular movement**

In addition to molecular diffusion, intra-molecular movement is also considered to describe the movement of the reacting moieties due to a molecule's local movement. The rate of intra-molecular movement is assumed proportional to the square root of the reaction temperature (Equation 5-7).

$$k_{d(intra)} = A_2 \ T^{0.5} \quad \text{Equation 5-7}$$

The constant $A_2$ is set as one fitted parameter that leads to better temperature profile for the region after the gel point. By adding inter- and intra- molecular movement, the total diffusion rate becomes:
\[ k_d = A_1 \left( \frac{T}{\mu} \right) + A_2 T^{0.5} \quad \text{Equation 5-8} \]

As compared to a mechanism that only considers the reaction step, this approach increases the number of parameters necessary to model the process from two (the Arrhenius parameters) to four (the Arrhenius parameters plus \( A_1 \) and \( A_2 \)).

5.3.3 Incorporating mass transfer into frequency factor

Basic kinetic theory identifies that for reaction to occur, two conditions must be met: a) the reactive moieties must collide and b) the collision must be of sufficient energy to overcome barriers. For the Arrhenius (Equation 5-9), the limit of no activation energy yields Equation 5-10:

\[ k = A e^{-\frac{E}{RT}} \quad \text{Equation 5-9} \]

\[ \lim_{E \to 0} (k) = A \quad \text{Equation 5-10} \]

An interpretation of the situation where there is zero activation energy is that all collisions of the reactive moieties lead to reaction. Hence, the pre-exponential term, \( A \), is related to collision frequency, \( Z \), which is a measure of the frequency of collisions.

Recognizing that inter- and intra- molecular movement are parallel and additive paths to collision for reaction, the frequency factor should include a driving force for collision according to Equation 5-11.

\[ Z \propto r_{\text{reactive collision}} \propto (r_{\text{interMT}} + r_{\text{intraMT}}) \quad \text{Equation 5-11} \]

A mechanism to quantify this driving force for reactive collision is to multiply these rates by a probability of successful reaction as a result of collision which is referred to as
the steric hindrance factor \( \rho \). This probability would vary depending upon the accessibility of the part of a moiety that can react where a primary moiety would have a higher probability than a secondary moiety. This mechanism results in Equation 12:

\[
A = \rho Z = \rho (r_{\text{interMT}} + r_{\text{intraMT}})
\]

Equation 5-12

Substituting this result into Equation 5-8 and Equation 5-9 yields Equation 5-13:

\[
k = \rho \left( A_1 \frac{T}{\mu} + A_2 T^{0.5} \right) e^{\frac{-E}{RT}} = \left( A_1' \frac{T}{\mu} + A_2' T^{0.5} \right) e^{\frac{-E}{RT}}
\]

Equation 5-13

Here, \( \rho \) dependents on both whether the moiety is primary, secondary, or tertiary and the type of reaction. This approach requires three fitted kinetic parameters as compared to modeling diffusion separate which requires a total of four parameters.

Several researchers have proposed modeling, equations, and approaches of viscosity impact on the molecular diffusion of reacting components to better understand reaction limits. Wang et al identified reaction diffusion as the limiting step for termination in their system [65].

In an investigation of the effect of cross-linking agent concentration on reaction-controlled termination for different acrylate polymeric systems, the reaction diffusion parameter (rate of termination to the rate of propagation) was found to increase when the concentration of the cross-linking agent increases, which agrees with the hypothesis that increasing viscosity leads to decreasing diffusion rate [66].

Guzman et al used a mathematical model to simulate the effect of diffusion on linear step growth polymerization using the Hatta number and a dimensionless ratio of reaction
and diffusion rates. This study found that diffusion limitation narrows molecular weight distribution [67]. In this work the Hatta number was expressed as an empirical function of chain length. While establishing a correlation, the approach failed to produce a fundamental approach that can be applied to other systems.

Abrams et al used analytical and simulation techniques to discuss the influence of confinement (inter versus intra moieties) in internal diffusion-reaction processes of polymer chains. The study showed that confinement can accelerate the polymer-polymer reactions processes in different ways as it impacts the internal cyclization.[68]

Different polyurethane systems were studied by Verhoeven et al to investigate the effects of reaction condition and diffusion limitation on the reaction kinetics. The results showed that the interfacial diffusion of the reacting species was hindered by the presence of bulky oligomer molecules (causes increasing resin viscosity). This leads to the straightforward conclusion of high viscous polymer reactions are diffusion limited [69].

Yan et al simulated chain extension reactions to study the impact of diffusion in high molecular weight polymeric solution. A reptation theory was adopted to consider the diffusive behavior of different chains. The study showed that diffusion can impede the growth reaction of the polymer chains and leads to lower molecular weight polymers [70].

Wang et al [71] proposed a simulation model for diffusion-limited reaction of highly branched macromolecular polymer units. The model assumes a 3D reactive bond fluctuation lattice in which each monomer occupies a cubic cell. Wang showed that increasing the degree of polymerization leads to more compact polymer that occupies less
space in the lattice. This study based on a non-fundamental exponential expression between
gyration and degree of polymerization.

Rabea and Zhu modeled the impact of diffusion of the reaction kinetics for radical
polymerization at high polymer conversions by solving differential equations of rate of
diffusion and reactions. The results show that the radical chains are trapped at high
conversions and polymerization terminated at high viscosity [72].

Liu et al [73] used a simple expression to simulate reaction kinetics of stepwise
polymerization in the diffusion-controlled regime using Monte Carlo simulation and
scaling analysis. Degree of polymerization was assumed to be related to the reaction time
and initial concentration. Simulation results show a transition from reaction control to
diffusion control regimes that are predicted by Flory’s assumptions. The assumption does
not provide good representation of the degree of polymerization as it is greatly depending
on the rate of diffusion and reaction of moieties.

These works included simplifying assumptions such as: a) assuming constant rate of
reaction (including initiator reaction with monomer, decomposition, and propagation), b)
not including the impact of changes in temperature, termination rate and diffusion rate
during reaction, and c) using empirical (or semi-empirical) equations for rates of diffusion
and reaction. While these works identified the impact of diffusion on polymerization
reactions, the results are highly specific to the systems studied and any advance in
underlying theory is limited in its broader impact.

The previous publications as cited in the previous paragraphs included simplifying
assumptions such as: a) assuming constant rate of reaction (including initiator reaction
with monomer, decomposition, and propagation), b) not including the impact of changes in temperature, termination rate and diffusion rate during reaction, and c) using empirical (or semi-empirical) equations for rates of diffusion and reaction. While these works identified the impact of diffusion on polymerization reactions, the results are highly specific to the systems studied and any advances in underlying theory are limited in their broader impact.

The novelty of this work relative to previous publications on this topic is:

- Two fundamental approaches were successfully used to evaluate the impact of mass transfer on polymer reactions, one based on mass transfer being a separate step in the overall reaction scheme and a second based on illustrating how the Arrhenius equation’s frequency factor fundamentally accounts for the mass transfer/collision step of reactions.
- Modeling was performed through the gel point where there was a transition from mass transfer due to movement of molecules relative to one another to only movement of segments of molecules (bending and rotation without breaking of covalent bonds).
- Collision of moieties was reflected as the addition of inter-molecular and intra-molecular movement terms in the frequency factor of the Arrhenius equation.
- Modeling was performed with over 50 ordinary differential equations to account for the elementary reactions and processes.
- Simulation included gas generation and verification with the profile of decreasing foam density with time during foam-forming reactions.
The fundamental nature of the research presented in this paper, including approaches to accounting for mass transfer in the frequency factor of reaction rates, has the prospect of being widely applicable to a number of polymerization reactions.

Simulation was based on the code of Zhao, Ghoreishi, and Al-Moameri [19, 25, 57, 74-76] for the reaction kinetics and blowing agents. Group contribution simulation presented by Fu [37] was used for viscosity calculations.

5.4 Experimental

Two urethane recipes including two different polyols were used in experimental studies to provide data for comparing to modeling results. PAPI (Standard Polymeric MDI - Huntsman Company), Voranol 490 (V490 - Dow Chemical), and Voranol 360 (V360 - Dow Chemical) were used as isocyanate and polyols respectively. Isocyanate index was kept at 1.1 for all gel reactions. N, N-dimethylcyclohexylamine (thereafter referred as Cat8) is a gelling catalyst, Momentive L6900 is the surfactant, and Tris (1-chloro-2-propyl) Phosphate (TCPP) is a fire retardant. Table 5-2 provides the specification of V360, V490, and the PAPI.

Recipes were mixed in a paper cup using 2000 rpm mixer blade attached to a floor-model drill press for 10 seconds. Mixing rate was kept the same for all gel experiments as it may affect the viscosity profiles [77]. The cup was put into a polyurethane foam box to insulate the gel system and reduce the heat loss. Reaction temperature was measured using LabView soft-ware with type-K thermocouple attached through a national instruments SCB-68 box to a national PCI 6024E data acquisition card.
Table 5-2 Specifications of V360, V490, and PAPI

<table>
<thead>
<tr>
<th>Property</th>
<th>V360</th>
<th>V490</th>
<th>PAPI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>1.081</td>
<td>1.11</td>
<td>1.23</td>
</tr>
<tr>
<td>Average molecular weight</td>
<td>728</td>
<td>460</td>
<td>340</td>
</tr>
<tr>
<td>Functionality</td>
<td>4.5</td>
<td>4.3</td>
<td>2.7</td>
</tr>
<tr>
<td>Hydroxyl number, mg KOH.g⁻¹</td>
<td>360</td>
<td>484.4</td>
<td>-</td>
</tr>
<tr>
<td>Equivalent weight</td>
<td>155.55</td>
<td>115</td>
<td>134</td>
</tr>
<tr>
<td>Viscosity, mPa.s at 25°C</td>
<td>3500</td>
<td>6180</td>
<td>150-220</td>
</tr>
<tr>
<td>NCO content by weight, %</td>
<td>-</td>
<td>-</td>
<td>31.4</td>
</tr>
<tr>
<td>Vapor pressure, mm Hg at 25°C</td>
<td>-</td>
<td>-</td>
<td>&lt; 10-5</td>
</tr>
<tr>
<td>Specific heat, g.cal/g.at 25°C</td>
<td>-</td>
<td>-</td>
<td>0.43</td>
</tr>
</tbody>
</table>

The thermocouple was placed in the middle of the foaming box to reduce error associated with heat loss to the surroundings. The thermocouple provides an immediate measurement of reaction temperature. The LabView software records the time-temperature and time-height data in the computer as x-y data. A Cole-Parmer basic viscometer was used to measure viscosity profiles of the polyurethane gel. All experiments were carried out at ambient temperature in order to avoid deviations in reaction kinetics and molecular weights of the polymer [78]. Table 5-3 shows the gel formulation.

Table 5-3 Recipes for polyurethane gel reaction

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V490</td>
</tr>
<tr>
<td>B-side</td>
<td></td>
</tr>
<tr>
<td>Polyol</td>
<td>31</td>
</tr>
<tr>
<td>Cat8</td>
<td>0.34</td>
</tr>
<tr>
<td>Momentive L6900</td>
<td>0.4</td>
</tr>
<tr>
<td>TCPP</td>
<td>2</td>
</tr>
<tr>
<td>A-side</td>
<td></td>
</tr>
<tr>
<td>PAPI (1.1 index)</td>
<td>40</td>
</tr>
</tbody>
</table>

88
Foam forming data from a previous publication were used to evaluate the simulation approaches of this paper in foam-forming reactions.

5.5 Results and Discussions

The simulation code of Ghoreishi et al [57] was modified by replacing a single elementary reaction step of an A moiety reacting with a B moiety with the three elementary steps summarized in Table 5-1. Figure 5-1 shows the experimental results of temperature and viscosity profiles versus the simulation results for the two recipes in Table 5-3. When the movement of the moieties is described as only an inter-molecular diffusion rate, the reaction stops at the gel point. At the gel point, the viscosity goes to infinity, which results in a) a rate of zero mass transfer, b) no further reaction, c) no further temperature increase, and d) no further increase in foam height.

The good fitting of the simulation results of reaction temperature and viscosity profiles in the region before the gel point indicates that the Table 5-1 rate expressions are accurate up to the gel point time.
Figure 5-1 Experimental data and simulation results of reaction temperature, viscosity profile, isocyanate moieties and polyol moieties of V360 (left) and V490 (right) using intra-molecular movement approach. Circles, squares, solid line, and dash line refer to experimental data and simulation results of temperature and viscosity respectively in the top figures. Solid line, and dash line refer to isocyanate moieties and polyol moieties respectively in the down figures.

The simulation allows the ratio of the diffusion rate to the reaction rate to be estimated and is reported in Figure 5-2. The rapid increase in resin viscosity causes the rate of diffusion to decrease rapidly, in comparison, the rate of reaction increasing following to Arrhenius equation. The result shows that the rate of diffusion is always greater than the rate of reaction in the region before the gel point and decreases rapidly to zero at the gel point.
Figure 5-2 Ratio of the rate of diffusion to the rate of reaction for inter-molecular diffusion. Solid line and dash line represent the ratio and viscosity profile respectively.

Figure 5-3 shows an example for the simulated concentration profile of the encounter complex (AB)* during the reaction. The results show that the concentration of the encounter complex is increasing instantly due to the high rate of diffusion at the beginning of the reaction and then decreasing as the driving force for formation of the encounter complex decreases.

It was hypothesized that movement of sections of a polymer molecule would allow reaction without a net movement of polymer molecules relative to each other. This suggested an intra-molecular mechanism for movement and collision.
Figure 5-3 Concentration profile of the encounter complex during the reaction using inter-molecular movement (solid line) and viscosity profile (dash line).

The rate of intra-molecular movement was added to the inter-molecular diffusion (see Equation 5-8) to include movement of the reacting moieties by this second mechanism. As mathematically specified in Equation 8, when viscosity goes to infinity the contribution from inter-molecular diffusion goes to zero while the intermolecular term is un-effected.

Figure 5-4 shows simulated temperature and viscosity profiles as superimposed over experimental data. Parameters $k_{df}$ and $k_{db}$ were optimized to provide a fit to the data. Data and simulation agreed, showing reaction temperature continuing increase after the gel point due to the intra-movement of the moieties. Concentrations of alcohol and isocyanate moieties decrease until all the alcohol moieties consumed.
Figure 5-4 Experimental data and simulation results of reaction temperature, viscosity profile, isocyanate moieties and polyol moieties of V360 (left) and V490 (right) using intra- and inter-molecular movement approach. Circles, squares, solid line, and dash line refer to experimental data and simulation results of temperature and viscosity respectively in the top figures. Solid line, and dash line refer to isocyanate moieties and polyol moieties respectively in the down figures.

The ratio of the total rate of diffusion to the rate of reaction (Figure 5-5) decreases throughout the reaction time. Prior to the gel point, many monomers that diffuse together diffuse apart before reacting. After the gel point, rate of diffusion becomes essentially zero while reaction rates proceed through mechanisms of movement of polymer segments as opposed to movement of the entire polymer.
Figure 5-5 Ratio of the rate of diffusion to the rate of reaction for inter- and intra-molecular movement. Solid line and dash line represent the ratio and viscosity profile respectively.

Concentration profile of the encounter complex shown by Figure 5-6 is similar to the inter-molecular diffusion profile, except for Figure 5-6 shows a low but significant rate of reaction after the gel point. This concentration is an example of one encounter complex in the urethane reaction.

Figure 5-6 Concentration profile of the encounter complex during the reaction using inter-and intra-molecular movement (solid line) and viscosity profile of the resin (dash line).
The approach of incorporating a power law expression for diffusion successfully provided a good fit to the data (Figure 5-4) where one set of kinetic parameters worked well for two polyol reagents having significantly different viscosity.

The second approach to simulation uses the Equation 5-13 frequency factor for both homogenous and catalytic reactions. The modified "A" term of the Arrhenius equation was applied to the reaction of monomers, and so, the use of representing the monomer reaction as the three steps of Table 5-1 was avoided. As summarized in Table 5-4, only one value for $A_1$ and one value for $A_2$ were used for all reactions (including the same values for homogeneous and catalytic reactions).

Also, in this second simulations both Voranol 360 to Voranol 490 were modeled as having 100% secondary alcohol as compared to previous work where both the alcohol moieties were considered a mix of secondary and hindered secondary moieties. This approach represents a simplification of the model and is designed to test the hypothesis that what was characterized as "hindered" secondary alcohols was actually an artifact of reaction rates slowing due to viscosity increases and associated decreases in diffusion rates.

The simulation results of reaction temperature and viscosity profiles (Figure 5-7) show good agreement with experimental data of the gel reaction. A good fits to the data support several advances in understanding of these processes, including: a) both inter- and intra-molecular movements are critical reaction steps in polymer-forming reactions, b) the frequency factor term can be successfully used to simulate the mass transfer step of these liquid phase polymer-forming reactions, c) the same frequency factor term can be used for catalytic and non-catalytic paths where the impact of the catalyst is reflected in the
activation energy, and d) the "hindered" secondary alcohol term of previous works leading to this simulation study are not necessary.

Figure 5-7 Experimental data and simulation results of reaction temperature, viscosity profile, isocyanate moieties and polyol moieties of V360 (left) and V490 (right) using intra- and inter-molecular movement as a collision frequency fraction. Circles, squares, solid line, and dash line refer to experimental data and simulation results of temperature and viscosity respectively in the top figures. Solid line and dash line refer to isocyanate moieties and polyol moieties respectively in the down figures.

This approach uses fewer parameters to describe the reactions than previously, while providing a better fit to the data. Also, the parameters extrapolate well from one system to another (same parameters for two polyols of considerably different properties). These observations suggest that the elementary steps as used in the model are fundamentally correct.
This second approach was used to redo the simulation of the foam-forming reactions presented by Al-Moameri [74]. The results show better agreement with reaction temperature profiles for the regions before and after the gel points (gel points are where the foam height ceases to increase in height when temperatures continue to increase). All of the improved fits of Figure 5-8 were attained with a single set of $A'_1$ and $A'_2$ parameters (see Table 5-4). This further supports that an approach of simulating the pre-exponential term as the sum of a viscosity dependent and a viscosity independent diffusion term is fundamentally correct.

For the foam blown by cyclo-Hexane (Figure 5-8f), the maximum reaction temperature deviates from the experimental date. This is attributed to the fact that the foam only raised to about half of its height and the surface area to foam volume become smaller and causes lower heat transfer to the surrounding. The simulation results have been corrected by increasing the overall mass transfer coefficient to get better simulation results (the long-dashed line).

The previous simulation approach of Al-Moameri was only able to provide a single inflection point in the temperature profile before peak temperature was reached. Two inflection points are evident in some of the systems, especially n-hexane which has inflection points at about 120 and 300 s.

Previously, the presence of two inflection points was considered an anomaly. The new simulation results provide an explanation for this phenomena--initial reaction rates are fast due to low viscosity, but slow as viscosity increases; then, higher temperatures lead to faster reaction rates that ultimately slow due to decreasing reagent concentrations.
Figure 5-8 Experimental and simulation results of temperature profile, height profile, and tack-free time of rigid polyurethane foams blown by different physical blowing agents. Symbols “♦” and “◊” represent experimental data of temperature and height profiles respectively. Solid lines represent old simulation results for temperature and height. Dot line represent tack-free time. Dashed line represents new simulation using the Equation 8 frequency factor approach.
Table 5-4 list the kinetic parameters used in the simulation approaches for inter-and intra-molecular movements and the frequency factor.

**Table 5-4 Kinetic and parameters used in the simulation code.**

<table>
<thead>
<tr>
<th>Kinetic Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-exponential factor</td>
<td></td>
</tr>
<tr>
<td>Homogeneous reaction (Primary/secondary/tertiary)</td>
<td>0.38 / 0.15 / 0.0125</td>
</tr>
<tr>
<td>Catalytic reaction (Primary/secondary/tertiary)</td>
<td>500 / 58 / 37</td>
</tr>
<tr>
<td>Activation energy (J/mol)</td>
<td></td>
</tr>
<tr>
<td>Homogeneous reaction (Primary/secondary/tertiary)</td>
<td>40000 / 42000 / 54000</td>
</tr>
<tr>
<td>Catalytic reaction (Primary/secondary/tertiary)</td>
<td>37000 / 40000 / 42000</td>
</tr>
<tr>
<td>Heat of reaction of alcohol moieties (J/mol)</td>
<td></td>
</tr>
<tr>
<td>Primary alcohol moieties</td>
<td>68000</td>
</tr>
<tr>
<td>Secondary alcohol moieties</td>
<td>68000</td>
</tr>
<tr>
<td>Hindered-secondary</td>
<td>68000</td>
</tr>
<tr>
<td>Overall heat transfer coefficient (W/m²/K)</td>
<td>1.0</td>
</tr>
<tr>
<td>Inter- and intra- molecular movement constants (Equation 5-8)</td>
<td></td>
</tr>
<tr>
<td>$A_1$</td>
<td>2.216*1010</td>
</tr>
<tr>
<td>$A_2$</td>
<td>200</td>
</tr>
<tr>
<td>Frequency factor constants (Equation 5-13)</td>
<td></td>
</tr>
<tr>
<td>$A'_1$</td>
<td>0.45</td>
</tr>
<tr>
<td>$A'_2$</td>
<td>15.5*10-3</td>
</tr>
</tbody>
</table>

5.6 Conclusions

Bimolecular chemical reactions require both mass transfer toward molecular collision and energy states sufficient to overcome an activation energy. Two approaches were
successfully used to simulate the impact of large changes of mass transfer rates on reaction profiles for a rigid urethane foam formulation.

A first approach comprising diffusion and reaction as sequential mechanisms described by sequential power law rate expressions illustrated that reactions are reaction-limited in the region before the gel point and diffusion limited after the gel point. When considering only the inter-molecular diffusion mechanism that depended on viscosity, simulation incorrectly predicted the temperature of the mixture to cease to increase after the gel point. Incorporation of an intra-molecular mechanism in parallel with inter-molecular diffusion successfully simulated temperature profiles. The intra-molecular movement mechanism is consistent with observations. As with most aspects of science, the starting point on a theory and approach may not be an ultimate proof; but it provides a path for advancing the science with ultimate proof being a latter milestone.

A second approach was based on the observation that the impact of mass transfer on reaction rates can be isolated to changes in the Arrhenius pre-exponential factor. More specifically, the pre-exponential term can be represented as the sum of the two fundamentally different approaches/terms for reacting moiety collision; an inter-molecular viscosity-dependent term plus an intra-molecular term. This approach relies on fewer parameters and on solving fewer differential equations.

Both approaches are able to provided fundamental insight (and fitted parameters) into experimental temperature profiles, which exhibited two inflection points prior to achieving a maximum reaction temperature. The use of diffusion-dependent reaction mechanisms is critical to simulate polymerization; and it is suggested that incorporation of diffusion
mechanisms in the Arrhenius pre-exponential factor is the most efficient method to simulate the impact of diffusion and viscosity on reaction rates.

It was further demonstrated that the use of kinetic parameters for "hindered" secondary alcohols is not necessary when reaction rates include a viscosity dependence. Hence, an advance to previous modeling/simulation publications leading to this work is that the alcohols in a polyol may be fully characterized as fractions of secondary and primary alcohols which add to 1.0. In this work, as is the case for many polyols, the polyols were characterized as having 100% secondary alcohols.

The frequency factor values are independent of the actual encounter complex where the impact of catalyst is reflected in lower activation energies catalyst encounter complexes. The values of the fitted parameters for inter and intra-molecular movement in Arrhenius equation are in agreement with fundamental mechanisms and impacts on the frequency factor and activation energy

5.7 Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu)</td>
<td>Resin viscosity, cp</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Stearic factor</td>
</tr>
<tr>
<td>(A)</td>
<td>Pre-exponential term in Arrhenius equation</td>
</tr>
<tr>
<td>(A_1, A_2, A_1', A_2')</td>
<td>Constants</td>
</tr>
<tr>
<td>(D_A)</td>
<td>Diffusivity of component A, cm/s</td>
</tr>
<tr>
<td>(D_B)</td>
<td>Diffusivity of component B, cm/s</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>E</td>
<td>Activation energy</td>
</tr>
<tr>
<td>$K_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$k_{db}$</td>
<td>Rate constant of backward diffusion</td>
</tr>
<tr>
<td>$k_{df}$</td>
<td>Rate constant of forward diffusion</td>
</tr>
<tr>
<td>$k_{d(\text{inter})}$</td>
<td>Rate constant of inter-molecular movement</td>
</tr>
<tr>
<td>$k_{d(\text{intra})}$</td>
<td>Rate constant of intra-molecular movement</td>
</tr>
<tr>
<td>$k_{rxn}$</td>
<td>Rate constant of reaction.</td>
</tr>
<tr>
<td>$N$</td>
<td>Avogadro’s number</td>
</tr>
<tr>
<td>$R$</td>
<td>Ideal gas constant</td>
</tr>
<tr>
<td>$R^*$</td>
<td>Critical distance between “A” and “B” necessary to form the encounter complex (AB)*</td>
</tr>
<tr>
<td>$r_A$</td>
<td>Molecular radius of A</td>
</tr>
<tr>
<td>$r_B$</td>
<td>Molecular radius of B</td>
</tr>
<tr>
<td>$T$</td>
<td>Reaction temperature, K</td>
</tr>
<tr>
<td>$Z$</td>
<td>Collision frequency</td>
</tr>
</tbody>
</table>
CHAPTER 6. VISCOSITY-DEPENDENT FREQUENCY FACTOR FOR MODELING POLYMERIZATION KINETICS

6.1 Abstract

Impacts of mass transfer limitations due to the large increase of resin viscosities during thermoset polymer reactions were reflected in the frequency (pre-exponential) factor of Arrhenius equation. By representing the frequency factor as the sum of a viscosity-dependent and a viscosity-independent terms to account the impact of inter- and intra-molecular diffusion/movement of the reacting moieties in the resin, the same pre-exponential factor was able to be used for catalytic and non-catalytic paths. Impacts of catalysts were reflected in lower activation energies. Temperature profiles of urethane gel reactions were used to characterize the reactivities of different polyols based on the fractional content of primary (versus secondary) hydroxyl moieties. This approach reduces the number of fitted parameter needed for simulation and provides a more fundamental, efficient, and robust method to simulate thermoset reactions. The simulation results of reaction temperature show good agreement with the experimental data.

6.2 Introduction

Polyurethane demand is growing 5% every year due its versatile and high-performance in many applications.[1, 8, 79] Thermosetting reaction of polyurethane is a complex process with over a dozen degrees of freedom. For these reasons, there is a desire to use simulation to predict key parameters used to design processes for making polyurethane devices such as car seat cushions and refrigerator insulation.
Generally, polyurethane is a matrix of organic chains joined by urethane molecules and is produced from the reaction of alcohol and isocyanate groups.[4, 7, 9] The general gelling reaction of polyurethane can be written as:

$$RNCO + R'CH_2OH \rightarrow RNHCOOCH_2R'$$  \textbf{Equation 6-1}

Isocyanate                Alcohol                PU

where R and R’ are long organic chains that contain additional isocyanate and alcohol moieties. The chemical structure and the properties of the polyl and the isocyanate, in addition to the other additives, determine the final properties of the final polyurethane polymer.[6] Polyurethane foam is produced by adding chemical and/or physical blowing agent to the formulation.[5] In the current research, the impact of viscosity on the mass transfer limitation were studied for gel reactions. Previous studies[32, 74] identify how to simulate the performance of blowing agents when provided parameters that characterize the gel reactions.

The kinetics of polyurethane reaction has been the subject of interest of many researchers. Grepinet et al [80] develops a method to characterize the kinetic parameters of the reaction of Toluene diisocyanate (TDI) and poly(propylene glycol) using H1-NMR. This method was able to determine six individual rate constants and to study the influence of the temperature using SIMULBATCH soft-ware.

Deng and Martin [81] treated the intra-diffusion of the thermosetting polymer chains as a process parallel to the diffusion of the ionic species and developed a model for estimating the average diffusion coefficient in the curing system based on the dielectric measurement of the ionic conductivity and the dipole relaxation time. The study provided an insight for
the relation between diffusion-controlled cure kinetics and structure-property for thermoset reactions.

Liu et al [73] suggest a concise expression of reaction kinetics of stepwise polymerization in diffusion controlled regime using Monte Carlo simulation and scaling analysis. The simulation study shows two regions for reaction-controlled and diffusion-controlled. The suggested expression relates the average degree of polymerization to the initial concentration and reaction time through a power law dependence.

Krol [82] developed a mathematical model of a complex system of ordinary differential equations for the reaction of TDI and 1,4-butandiol by following Flory’s assumptions for 32 subsequent and parallel polyurethane reactions. The model assumed different reactivates for the isocyanate groups. Good agreement was obtained with the experimental data.

Li et al [83] monitored the absorption of the isocyanate group by Fourier transform infrared spectroscopy (FTIR) to study the curing processes of polyurethane reaction using a model of two exponential fittings for the rate of reactions of different formulations. The results were showing reaction and diffusional regions.

Nagy et al [84] studied the reaction different isocyanates with alcohols by high-performance liquid chromatography (HPLC) and electrospray ionization mass spectrometry (ESI-MS). The rate constant of the reactions was assumed as temperature dependent and the activation energies was determined.
These studies were limited to specific recipes, non-catalyzed reactions, and did not study the impact of viscosity increase on reaction kinetics.

The simulation of polyurethane reactions of Ghoreishi et al [57] was based on the characterization of the reactivity of alcohol moieties of the polyols in terms of the fractional content of the primary, secondary and hindered secondary (tertiary) alcohol moieties concentration. The approach provided a good simulation results of some polyols, however, there was deviations when higher or lower viscosity polyols were reacting. The higher viscosity leads to slower reaction rates.

Toward the goal of considering the impact of viscosity on reaction kinetics, Al-Moameri et al [85] developed two fundamental approaches to model mass transfer limitations of the reactive moieties during reaction. The first approach was based on modeling the diffusion step using a power-law expression similar to that used for reactions and where the moieties are diffusing to form an encounter complex that might react to product or diffused apart. The second approach considered the rate of change of viscosity in the Arrhenius pre-exponential factor. The work concluded that a) both inter- and intra- molecular movements are critical reaction steps in polymer-forming reactions, b) the frequency factor term can be successfully used to simulate the mass transfer step of these liquid phase polymer-forming reactions, c) the same frequency factor term can be used for catalytic and non-catalytic paths where the impact of the catalyst is reflected in the activation energy, and d) the "hindered" secondary alcohol term of previous works leading to this simulation study are not necessary.
The shortcomings of this research were: it was limited to two known polyols that are having high concentration of secondary alcohols moieties, and the research did not adequately summarize how the approach reduces the number of parameters needed to simulate polymerization. The current research is a follow-up work to the second approach.

6.3 Background

6.3.1 Shortcomings of previous simulation

During thermoset polymerization, the viscosity is often increase several orders of magnitude starting from hundreds or few thousands centipoises. [58, 86] Ghoreishi et al's simulating approach is able to predict reaction temperature profiles of various polyols in urethane formations with a method that assigned a fractional content of “hindered” secondary alcohol moieties. Al-Moameri et al [85] concluded that "hindered secondary polyols" were not a separate type of moiety, but rather, an artifact of the slow reaction due to viscosity increases that leads to substantial decrease in diffusion rates and subsequently reaction rates. It was hypothesized that inaccuracies encountered with Ghoreishi et al's simulations when extrapolating reaction rate constants from one system to another were due to differences in viscosity, and that use of constant pre-exponential factor of Arrhenius equation was insufficient approach to extrapolate the modeling toward using other polyols with a wider range of viscosity. Figure 1 shows how the previous modeling failed to extrapolate well from pentanols and V360 systems having higher viscosities.
Figure 6-1. Simulation results of the previous model. Symbols and lines, from right to left, refer to experimental and simulation results of Jeffol, V490, and TEG respectively.

6.3.2 Parameters for simulation

In general, many parameters were needed to simulate the reactions of polyurethane reactions. These parameters are a) the physical properties of the reacting monomers and the produced urethane polymer which are obtained from literatures or suppliers and b) thermodynamic and kinetic parameters which are either obtained from literatures, external experiments, or fitted to get better simulation results. For a polyurethane gel reaction of one polyol reacting with isocyanate in the presence of a catalyst, Equation 6-2 lists the possible reactions of two multifunctional alcohol and isocyanate monomers:

\[
\begin{align*}
A + B & \rightarrow P \\
PA + B & \rightarrow P \\
A + PB & \rightarrow P \\
PA + PB & \rightarrow P
\end{align*}
\]  

Equation 6-2

For these reactions, Table 6-1 shows that 68 fitted parameters were needed for simulation out of 80 parameters assuming constant physical properties (density, heat capacity, heat of reaction) in the range of reaction temperature (22-160°C).
Heuristics and constitutive equations were adopted to reduce this large number of parameters to a more reasonable number. These heuristics were:

- Heat of reaction of alcohol and isocyanate moieties was the same regardless if the alcohol moiety is primary, secondary, or hindered secondary.
- The frequency factors and the activation energies of non-catalytic and catalytic reactions of alcohol moieties with the isocyanate are the same regardless if the alcohol or the isocyanate moieties were attached to a monomer or to a polymer.

Constitutive equations are defined as the relations between two physical quantities for a material. A constitutive equation for calculating the hydroxyl number from polyol molecular weight and functionality were used to reduce the number of parameters.

\[
OH\# = \frac{(56.1 \times 1000) \times \text{Functionality}}{\text{Molecular weight}}
\]  
Equation 6-3

For the viscosity modeling where a group contribution method was used, six fitted parameters were needed for calculating the viscosity of the polyol, isocyanate, and the urethane polymer as shown in Equation 6-4 where \(i\) refers to polyol, isocyanate, or polymer.

\[
\ln \left[ \frac{\mu_i}{\rho M} \right] = A_i + \left( \frac{B_i}{T} \right)
\]  
Equation 6-4
Table 6-1. Number of parameters needed for simulating polyurethane reactions

<table>
<thead>
<tr>
<th>Parameters needed</th>
<th>Source</th>
<th>Number of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Obtained</td>
<td>3</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Obtained</td>
<td>2</td>
</tr>
<tr>
<td>Functionality</td>
<td>Obtained</td>
<td>2</td>
</tr>
<tr>
<td>Hydroxyl number</td>
<td>Obtained</td>
<td>1</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>Obtained</td>
<td>3</td>
</tr>
<tr>
<td>Overall transfer coefficient</td>
<td>Obtained</td>
<td>1</td>
</tr>
<tr>
<td>Viscosity (group contribution parameters)</td>
<td>fitted</td>
<td>6</td>
</tr>
<tr>
<td>Fraction alcohol moieties</td>
<td>fitted</td>
<td>2</td>
</tr>
<tr>
<td>Heat of reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>isocyanate in monomer + alcohol in monomer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in polymer + alcohol in monomer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in monomer + alcohol in polymer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in polymer + alcohol in polymer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>Activation energy of non-catalytic reaction of the moieties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>isocyanate in monomer + alcohol in monomer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in polymer + alcohol in monomer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in monomer + alcohol in polymer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in polymer + alcohol in polymer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>Activation energy of catalytic reaction of the moieties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>isocyanate in monomer + alcohol in monomer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in polymer + alcohol in monomer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in monomer + alcohol in polymer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in polymer + alcohol in polymer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>Frequency factor of non-catalytic reaction of the moieties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>isocyanate in monomer + alcohol in monomer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in polymer + alcohol in monomer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in monomer + alcohol in polymer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in polymer + alcohol in polymer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>Frequency factor of catalytic reaction of the moieties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>isocyanate in monomer + alcohol in monomer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in polymer + alcohol in monomer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in monomer + alcohol in polymer</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>isocyanate in polymer + alcohol in polymer</td>
<td>fitted</td>
<td>3</td>
</tr>
</tbody>
</table>
Two constitutive equations were used for relating the fitted parameters of the urethane polymer to the polymer degree of polymerization as shown in Equation 6-5.

\[
\begin{align*}
A_{\text{polymer}} &= -0.9 \text{ PDP} - 21.43 \\
B_{\text{polymer}} &= 500 \text{ PDP} + 7085
\end{align*}
\]

Equation 6-5

The heuristics and the constitutive equations reduced the number of fitted parameters by less than one third (from 68 to 19) as shown in Table 6-2.

**Table 6-2. Number of parameters needed for simulating polyurethane reaction considering heuristics and constitutive equations**

<table>
<thead>
<tr>
<th>Parameters needed</th>
<th>Source</th>
<th>Number of Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Obtained</td>
<td>3</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Obtained</td>
<td>2</td>
</tr>
<tr>
<td>Functionality</td>
<td>Obtained</td>
<td>2</td>
</tr>
<tr>
<td>Hydroxyl number</td>
<td>Calculated</td>
<td>0</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>Obtained</td>
<td>3</td>
</tr>
<tr>
<td>Overall transfer coefficient</td>
<td>Obtained</td>
<td>1</td>
</tr>
<tr>
<td>Viscosity (group contribution parameters)</td>
<td>fitted</td>
<td>4</td>
</tr>
<tr>
<td>Fraction alcohol moieties</td>
<td>fitted</td>
<td>2</td>
</tr>
<tr>
<td>Heat of reaction</td>
<td>fitted</td>
<td>1</td>
</tr>
<tr>
<td>Activation energy of non-catalytic reaction of the moieties</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>Activation energy of catalytic reaction of the moieties</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>Frequency factor of non-catalytic reaction of the moieties</td>
<td>fitted</td>
<td>3</td>
</tr>
<tr>
<td>Frequency factor of catalytic reaction of the moieties</td>
<td>fitted</td>
<td>3</td>
</tr>
</tbody>
</table>

To follow-up the approach presented earlier by Al-Moameri et al [85] on considering the pre-exponential factor of Arrhenius equation as a frequency factor, the common form of Arrhenius equation for each polymerization reaction was revised to the following form to include the impact of inter- and intra- molecular diffusion.
Inter-molecular diffusion was assumed to proportional to reaction temperature and reversely with resin viscosity. Intra-molecular movement was assumed to be proportional to the reaction temperature. This assumption provides better simulation results compared to the previous assumption where it was proportional to the square root temperature.

$$k = \left( A'_1 \frac{T}{\mu} + A'_2 T \right) e^{-\frac{E}{RT}}$$ \hspace{1cm} \text{Equation 6-6}

Equation 6-6 was re-written in the following form where $A'$ depends whether the alcohol moieties are primary of secondary.

$$k_h = A' \left( \frac{T}{\mu} + A_1 T \right) e^{-\frac{E_E}{RT}}$$ \hspace{1cm} \text{Equation 6-7}

Using this equation in this form for non-catalytic and catalytic reactions increase the number of fitted parameters of Table 6-2. Several constitutive equations and heuristics were adopted to reduce the fitted parameters. These heuristics were:

- The fraction of the hindered secondary alcohol moieties presented in previous simulation were dropped.
- A constitutive equation was assumed to relate the fitted parameters $A'$ and $A_1$.
- The frequency factors of the catalytic path were set to be equal to the frequency factors of the non-catalytic path.
- The fitted parameter $A'$ for the reaction of the primary alcohol moieties is set as six times the frequency factor of the reaction of the secondary alcohol moieties.
- The activation energy for the secondary alcohol moieties reaction was set as 1500 greater than the that for the primary alcohol moieties reaction for catalytic and non-catalytic paths.
Table 6-3 shows a comparison of the equations used in this approach and the set of equations used in the previous simulations. The equations show that any urethane system of one polyol and one catalyst can be simulated using this approach if the fraction of primary alcohol moieties and the activation energy of the catalytic reaction of the primary alcohol moieties is known in addition to chemical and physical properties of the polyol and isocyanate. The other kinetic parameters are related to each other.

Table 6-3. Comparison of equations used in the previous and current simulation

<table>
<thead>
<tr>
<th>Kinetic expression</th>
<th>Previous simulation</th>
<th>Current simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency Factor (non-catalytic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frequency Factor (catalytic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate constant of homogeneous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate constant of catalyst reactions</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Kinetic expression</th>
<th>Previous simulation</th>
<th>Current simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency Factor (non-catalytic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frequency Factor (catalytic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate constant of homogeneous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate constant of catalyst reactions</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

113
Table 6-4 shows that how the current approach of the current research reduces the number of fitted parameters needed for the gel reaction of polyurethane catalytic polymerization from 19 (as shown in Table 6-2) to 9.

The novelty of this work relative to previous publications on this topic were:

1. The current simulation provides a fundamental approach for considering the impact of mass transfer limitation in the calculation of the pre-exponential factor of Arrhenius equation.
2. The number of fitted parameters of reaction rate constant needed to simulate polyurethane gelling reaction were successfully reduced.
3. For a gel reaction of one polyol with isocyanate in the presence of one catalyst, the number of differential equations of the rate expressions were reduced to 9.
4. The approach of the current research can successfully extrapolate to include different formulation of different viscosities.
Table 6-4. Number of parameters needed for simulating polyurethane reaction considering the heuristics and constitutive equations of the current approach

<table>
<thead>
<tr>
<th>Parameters needed</th>
<th>Source</th>
<th>Component</th>
<th>Test</th>
<th>Number of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Obtained</td>
<td>Polyol/Isocyanate</td>
<td>Reported</td>
<td>3</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Obtained</td>
<td>Polyol/Isocyanate</td>
<td>Reported</td>
<td>2</td>
</tr>
<tr>
<td>Functionality</td>
<td>Obtained</td>
<td>Polyol/Isocyanate</td>
<td>Reported</td>
<td>2</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>Obtained</td>
<td>Polyol/Isocyanate</td>
<td>Reported</td>
<td>3</td>
</tr>
<tr>
<td>Overall transfer coefficient</td>
<td>Obtained</td>
<td>System (box)</td>
<td>Reported</td>
<td>1</td>
</tr>
<tr>
<td>Viscosity (group contribution parameters)</td>
<td>fitted</td>
<td>Independent</td>
<td>Viscosity</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>parameters depend on moiety</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fraction alcohol moieties</td>
<td>fitted</td>
<td>Polyol</td>
<td>Rxn study</td>
<td>1</td>
</tr>
<tr>
<td>Heat of reaction</td>
<td>fitted</td>
<td>Moiety</td>
<td>Rxn study</td>
<td>1</td>
</tr>
<tr>
<td>Activation energy of non-catalytic reaction</td>
<td>fitted</td>
<td>Moiety</td>
<td>Rxn study</td>
<td>1</td>
</tr>
<tr>
<td>Activation energy of catalytic reaction</td>
<td>fitted</td>
<td>Moiety</td>
<td>Rxn study</td>
<td>1</td>
</tr>
<tr>
<td>Frequency factor of non-catalytic reaction</td>
<td>fitted</td>
<td>Moiety</td>
<td>Rxn study</td>
<td>1</td>
</tr>
<tr>
<td>Frequency factor of catalytic reaction</td>
<td>fitted</td>
<td>Moiety</td>
<td>Rxn study</td>
<td>0</td>
</tr>
</tbody>
</table>
6.4 Experimental

6.4.1 Materials

PAPI (standard polymeric MDI) from Dow Chemical Co. was the isocyanate (A side) used in this study, Voranol 360 from Dow Chemical Co., Voranol 490 Dow Chemical Co., Poly G76-635 from FSI, Jeffol R-315x from FSI, DEG from Sigma-Aldrich and TEG from Alfa Aesar were the six Polyols (B side) used in this study, and the specifications of each one are shown in Table 6-5. N,N-Dimethylecyclohexyl-amine (DMCHA) as catalyst8, N,N,N’,N”,N”-Pentamethyldiethylene-triamine (PMDETA) as catalyst5 both from FSI and DABACO BL-17 Catalyst from Air Products were used as amine based catalyst, (Fomrez UL-29) from Galata Chemicals LLC was used as tin based catalyst in this study. Momentive L6900 was used as surfactant, Tris (1-chloro-2-propyl) Phosphate (TCPP) was used as fire retardant and the amount of the surfactant and fire retardant were kept at 0.15% (mass fraction), the isocyanate index was kept at 1.1 for all reactions. Table 6-6 shows the recipes of the homogeneous reactions. Reaction temperature and viscosity change were obtained as temperature-time profiles and viscosity-time profiles.

<table>
<thead>
<tr>
<th>Property</th>
<th>PMDI</th>
<th>DEG</th>
<th>TEG</th>
<th>V360</th>
<th>V490</th>
<th>R315x</th>
<th>PolyG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g cm³</td>
<td>1.23</td>
<td>1.118</td>
<td>1.125</td>
<td>1.081</td>
<td>1.11</td>
<td>1.07</td>
<td>1.08</td>
</tr>
<tr>
<td>Average molecular weight</td>
<td>369.9</td>
<td>106.12</td>
<td>150</td>
<td>728</td>
<td>460</td>
<td>534</td>
<td>600</td>
</tr>
<tr>
<td>Functionality</td>
<td>2.7</td>
<td>2</td>
<td>2</td>
<td>4.5</td>
<td>4.3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Hydroxyl number, mg KOH g⁻¹</td>
<td>134</td>
<td>1057</td>
<td>747.2</td>
<td>360</td>
<td>484.8</td>
<td>315</td>
<td>274</td>
</tr>
<tr>
<td>Viscosity, mPa s at 25°C</td>
<td>150-220</td>
<td>35.7</td>
<td>49</td>
<td>3500</td>
<td>6180</td>
<td>2153</td>
<td>275</td>
</tr>
<tr>
<td>NCO content by weight, %</td>
<td>31.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vapor pressure, mm Hg at 25°C</td>
<td>&lt; 10-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 6-6. Recipes of homogeneous reaction of different polyols

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>DEG</th>
<th>TEG</th>
<th>V360</th>
<th>V490</th>
<th>PolyG</th>
<th>Jeffol</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-side materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyol</td>
<td>10</td>
<td>10</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>TCCP</td>
<td>0.06</td>
<td>0.04</td>
<td>0.07</td>
<td>0.07</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>L6900</td>
<td>0.06</td>
<td>0.04</td>
<td>0.07</td>
<td>0.07</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>A-side materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMDI</td>
<td>28.4</td>
<td>20.07</td>
<td>24.1</td>
<td>26.9</td>
<td>25.6</td>
<td>16.9</td>
</tr>
</tbody>
</table>

6.4.2 Gel preparation and data collection

The following steps were used in the gel experiments:

1. (B-side components) Polyols, catalysts, surfactant and fire retardant were added into a paper cup, then the B-side components were mixed for 10 s.

2. After that, pre-weighed isocyanate (A-side material) by syringe to reduce weight loss, then added and mixed with (B-side components) at the same speed for 10 seconds.

3. Finally, the mixture left in the paper cup covered by polyurethane foam to insulate the reaction and to reduce the heat loss and reaction temperature is recorded or poured into a viscometer cup and viscosity is recorded.

All experiments were carried out at room temperature in order to avoid deviations in reaction kinetics and molecular weight of the polymer.[77] A high speed mixer blade (2,000 rpm) attached to a floor-model drill press was used to mix the chemicals, mixing
rate was kept constant for all experiments as it may affect the viscosity profiles.[78] LabVIEW soft-ware was used to monitor the reaction temperature versus reaction time with a type-k thermo-couple attached through a National Instruments SCB-68 box to a National Instruments PCI 6024E data acquisition card and Cole-Parmer Basic Viscometer used to measure viscosity in a wide range of centipoise (cp).

After surrogate primary and secondary polyol molecules were used to identify Arrhenius parameters of Table 3 for primary and secondary alcohol moieties, the fraction of primary alcohol moieties (parameter) was used to optimize this parameter to kinetic data on a polyol's reaction in the recipe of Table 6-6. In the solving of the ordinary differential equations of the model (and subsequent simulations), the concentrations of primary and secondary alcohol moieties were independently followed based on the initial conditions defined by Equation 6-8 and Equation 6-9.

\[
C_{0P,Bmol} = X_{P,0} \cdot C_{0Bmol} \quad \text{Equation 6-8}
\]
\[
C_{0S,Bmol} = (1 - X_{P,0}) \cdot C_{0Bmol} \quad \text{Equation 6-9}
\]

### 6.5 Results and Discussion

The kinetic equations used by Zhao et al [19, 63, 87] for calculating reactions rate constants for polyurethane polymerization reaction were revised using the modified Arrhenius equation of Equation 6-7 with fraction of primary alcohol moieties (X_{P,0}) in polyol monomers (no hindered secondary moieties) being the only polyol-dependent parameter determined from kinetic data. Heat of reactions and heat capacities of the primary and secondary alcohol moieties were assumed equal and have been adopted from the previous studies [57].
Unlike the previous study of Ghoreishi [57] where 1-Pentanol was used as a reference for obtaining the kinetic parameters of the fraction content of primary alcohol moieties, the current study uses DEG and TEG due to: a) the more-readily available data on viscosity and b) the gel points of DEG and TEG formulations that allow parameters $A'$ and $A_1$ to be decoupled. Figure 6-2 shows the experimental data and simulation results of the gel reaction of DEG and TEG.

Compared to the results of the previous simulation, the Figure 2 simulation shows considerably better agreement with experimental data of reaction temperature and resin viscosity with slight deviation at the time of the maximum reaction temperature. These data were used to identify the parameters $A'$, $A_1$, and $E_P$ for primary alcohol moieties reacting with PMDI.
Figure 6-2. Simulation results of reaction temperature and resin viscosity profiles of DEG and TEG reactions. Circles and triangles refer to experimental data of reaction temperature and resin viscosity. Straight and dash lines refer to simulation results. Long dash line refers to simulation of the previous model.

To determine parameters for secondary moieties, V490 was assumed of having a 100% secondary alcohol moiety. The fit of the model to data are presented by Figure 6-3; the fitted parameters were $E_S$ and $A_S' = A'/6$. This fit is better than previous results despite the use of only two parameters.
Figure 6-3. Simulation results of reaction temperature and resin viscosity profiles of V490 reactions. Circles and triangles refer to experimental data of reaction temperature and resin viscosity. Straight and dash lines refer to simulation results. Long dash line refers to simulation of the previous model.

In total, five parameters were fit to the surrogate molecules selected to represent 100% primary alcohol and 100% secondary alcohols. From this basis, different polyols were specified by a best fit of $X_{P,0}$ to the data, and each catalyst was ultimately fitted to one parameter; that being the activation energies associated with that catalyst for primary moieties, $E_{P,i}$, for catalyst "i". It was observed that $E_{S,i} = E_{P,i} + 1500$ provided a good fit to the data. This class of reactions (polyols reacting with PMDI) is specified by 3 frequency factor parameters and 1 + $Y$ activation energies for a series including $Y$ catalysts.

Contour plots for different systematic content of fractional alcohol content of V360 are shown in Figure 6-5. Contour plots provide a useful method to identify how the performance of different polyols at different fractional content of alcohol moieties. Temperature profile is becoming faster at higher primary alcohol moiety content and slower as the secondary alcohol moiety content increases.
Figure 6-4. Simulation results of reaction temperature and resin viscosity profiles of V360. Circles and triangles refer to experimental data of reaction temperature and resin viscosity. Straight and dash lines refer to simulation results of reaction temperature and viscosity. Top and bottom dash lines refer to simulation assuming $X_{P,0} = 0.25$ and $X_{P,0} = 0$, respectively. Long dash line refers to simulation of the previous model.

Simulation was tested assuming $X_{P,0} = 0$ fractional content of primary alcohol moieties and a slower increase in temperature was obtained. A second test of $X_{P,0} = 0.25$ shows a model temperature profile with temperature increases faster than the data. The best fit for V360 was obtained at a $X_{P,0} = 0.11$. The new simulation shows good agreement with the previous simulation of Ghoreishi et al [57].

Simulation results of PolyG and Jeffol R315x are shown in Figure 6-5. PolyG simulation shows good agreement with the experimental data and previous simulation. Fractional content of $X_{P,0} = 0.25$ provides a good fit to the experimental data.

Experimental results of Jeffol R315x show a rapid increase in reaction temperature as compared to other polyols. This variation may likely due to catalyst content, either added
to the polyol are incorporated into the polyol mixture. A value of $X_{P,0} = 0.75$ was used which takes into account this inherent catalytic activity. Simulation of the current code shows better results compared to the previous simulation. Table 6-7 summarizes the fractional content of alcohol moieties of each polyol.

![Simulation results of reaction temperature and resin viscosity profiles of PolyG and Jeffol R315x reactions.](image)

**Figure 6-5.** Simulation results of reaction temperature and resin viscosity profiles of PolyG and Jeffol R315x reactions. Circles and triangles refer to experimental date of reaction temperature and resin viscosity. Straight and dash lines refer to simulation results of reaction temperature and viscosity. Long dash line refers to simulation of the previous model.
Table 6-7. Comparison of the fractional content of alcohol moieties using current and previous approaches

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Current simulation</th>
<th>Previous simulation</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Primary</td>
<td>Secondary</td>
<td>Primary</td>
<td>Secondary</td>
<td>Hindered secondary</td>
</tr>
<tr>
<td>V490</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>V360</td>
<td>0.11</td>
<td>0.89</td>
<td>0</td>
<td>0.05</td>
<td>0.95</td>
</tr>
<tr>
<td>Jeffol R315x</td>
<td>0.75</td>
<td>0.25</td>
<td>0.65</td>
<td>0</td>
<td>0.35</td>
</tr>
<tr>
<td>PolyG</td>
<td>0.25</td>
<td>0.75</td>
<td>0</td>
<td>0.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 6-8 summarizes all the parameters needed for current approach simulation and how the number of fitted parameters reduced from those in Table 6-2.

Figure 6-6 summarizes how the values of the frequency faction of primary alcohol moieties reactions depend on temperature (which changes with time) and depend on the gel point. The inter-molecular diffusion term increases when the viscosity decreases in the region before the gel point and decreases to zero at the gel point. The intra-molecular diffusion term increases with increasing reaction temperature. What may appear as subtle differences in frequency factors can have a significant impact on adiabatic reaction systems.
Table 6-8. Number of parameters needed for simulating polyurethane reaction considering the heuristics and constitutive equations of the current approach. IO indicates the information was "independently obtained" for information other than kinetic data. Fitted parameters include the fitted parameters for both primary and secondary moieties and reflect that \( E_{S,i} = E_{P,i} + 1500 \).

<table>
<thead>
<tr>
<th>Parameters needed</th>
<th>Source</th>
<th>Component</th>
<th>Test</th>
<th>Number of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>IO</td>
<td>Polyol/Isocyanate</td>
<td>Reported</td>
<td>3</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>IO</td>
<td>Polyol/Isocyanate</td>
<td>Reported</td>
<td>2</td>
</tr>
<tr>
<td>Functionality</td>
<td>IO</td>
<td>Polyol/Isocyanate</td>
<td>Reported</td>
<td>2</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>IO</td>
<td>Polyol/Isocyanate/ Urethane</td>
<td>Reported</td>
<td>3</td>
</tr>
<tr>
<td>Overall transfer coefficient</td>
<td>IO</td>
<td>System (box)</td>
<td>Reported</td>
<td>1</td>
</tr>
<tr>
<td>Viscosity (group contribution parameters)</td>
<td>IO</td>
<td>Independent parameters depend on moiety</td>
<td>Viscosity study</td>
<td>4</td>
</tr>
<tr>
<td>Heat of reaction</td>
<td>IO</td>
<td>Moiety</td>
<td>Rxn study</td>
<td>1</td>
</tr>
<tr>
<td>Fraction primary alcohol moieties of Z polyols</td>
<td>Fitted</td>
<td>Polyol</td>
<td>Rxn study</td>
<td>Z</td>
</tr>
<tr>
<td>Activation energy of non-catalytic reaction</td>
<td>Fitted</td>
<td>Moiety</td>
<td>Rxn study</td>
<td>1</td>
</tr>
<tr>
<td>Activation energy of &quot;Y&quot; catalyst</td>
<td>Fitted</td>
<td>Moiety-Catalyst</td>
<td>Rxn study</td>
<td>Y</td>
</tr>
<tr>
<td>Frequency factor of non-catalytic reaction</td>
<td>Fitted</td>
<td>Moiety</td>
<td>Rxn study</td>
<td>1</td>
</tr>
<tr>
<td>Frequency factor of catalytic reaction</td>
<td>Fitted</td>
<td>Moiety</td>
<td>Rxn study</td>
<td>0</td>
</tr>
</tbody>
</table>
The successful simulation of the reaction of different polyols were tested for the reaction of two different mixtures of polyols as shown in Figure 6-7. The first mixture of 50% V360 and 50% V490 shows good agreement with experimental data of temperature profile. Experimental data of viscosity profile shows variation compared to simulation result which may due to slight error in experiment measurement. The second mixture of 50% V490, 25% Jeffol R315x, and 25% PolyG shows that simulation is slower than experimental data. This is attributed to the content of Jeffol R315x which shows a faster reaction temperature as shown in Figure 6-5.
Figure 6-7. Simulation results of reaction temperature and resin viscosity profiles of polyol mixtures reactions. Circles and squares refer to reaction temperature data of mixtures 1 and 2. Triangles and diamonds refer to viscosity data of mixtures 1 and 2. Straight and dash lines refer to simulations of reaction temperatures and viscosities.

The simulation of the current code was extended to study the effect of catalyst in the polymerization reaction of polyurethane. The same frequency factor for non-catalytic path were used for the catalytic path and the impact of catalysts loading where reflected in lower activation energies. This approach provides a more fundamental understanding on catalyst rule in chemical reactions.

Four different catalyst were studied and simulated successfully. Figure 6-8 shows the impact of three amine catalyst (Cat8, Cat5, and DBTDL BL-17) and one Tin catalyst (Formez UL-29) at two loadings. Table 6-9 compares previous and current values of the activation energies for these catalysts. The simulation results of these catalysts show a variation compared to experimental results and previous simulation results of Zhao el al. These variations are likely attributed to a) the fewer number of parameters used by this approach and b) to the fact that catalytic reactions are following chain growth mechanisms.
as opposed to step growth mechanism suggested by the simulation. The Tin catalyst shows more deviation to the experimental data of the current and previous simulations. This is attributed to the non-linear relation of the increase in catalytic rate and the catalyst loadings[63].

![Graphs showing temperature over time for different catalysts and loadings.](image)

Figure 6-8. Impact of catalyst on reaction temperature of V360. Triangles, circles, and squares refer to catalyst loading of 0.05, 0.1, and 0.2 respectively. Straight and dash lines, from right to left, refer to simulation results of low and high loadings of the current and previous simulations respectively.

The values of $A'$ in Equation 6-7 for primary and secondary alcohol moieties were tested for simulating 1-Pentanol and 2-Pentanol. 1-Pentanol has one primary alcohol moiety (100% primary alcohol content) and 2-Pentanol has one secondary alcohol moiety (100% secondary alcohol content). Toluene was added as a solvent to reduce the heat of the reactions. Average values of the viscosities (based on experimental measurement) were
used to calculate the frequency factors. The fit of the simulation to data is summarized by Figure 6-9.

Table 6-9. Comparison of the activation energies of different catalysts used by the current and previous approaches

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Current simulation</th>
<th>Previous simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EP (J. mole⁻¹)</td>
<td>ES (J. mole⁻¹)</td>
</tr>
<tr>
<td>Cat8</td>
<td>18500</td>
<td>40000</td>
</tr>
<tr>
<td>Cat5</td>
<td>20000</td>
<td>35000</td>
</tr>
<tr>
<td>BL-17</td>
<td>20500</td>
<td>38000</td>
</tr>
<tr>
<td>UL-29</td>
<td>16500</td>
<td>40000</td>
</tr>
</tbody>
</table>

The results are remarkably accurate considering that the simulation lines are purely predictive based on Equation 7 parameters fit to DEG and TEG. Numeric values of the frequency factors for 1-pentanol and 2-pentanol (as calculated upon substitution of temperature and viscosity values into Equation 7) were initially at 2.3 due to the lower viscosity of these alcohols in the toluene diluent. These compare to 0.61 for DEG and accurately extrapolate the fitted parameters for DEG and V490 to 1-pentanol and 2-pentanol. Due to the low viscosity of the formulations, the inter-molecular diffusion term of Equation 6-7 is dominant. A slight variation in the new code for the two systems were observed which might be due to a) using average viscosity for calculating rate constants or b) error in the experiment results due to the evaporation of Toluene at higher reaction temperatures.
Figure 6-9. Simulation results of 1-Pentanol and 2-Pentanol reactions. Circles and triangles refers to experimental data of temperature and viscosity in the presence of 20% Toluene. Squares and diamonds refers to experimental data of temperature and viscosity in the presence of 50% Toluene. Straight lines refer to current simulation.

The rate of intra-molecular movement was assumed to be proportional to reaction temperature as shown in Equation 6-7. Different values of the power of temperature were tested to provide the best fit to the data. Unlike the previous simulation of Al-Moameri et al[85] where the power was assumed 0.5, a power of 1 was found to provide the optimum value as shown in Figure 6-10.
Figure 6-10. Simulation results of reaction temperature at different power of $T$ of Equation 6-7.

### 6.6 Conclusions

Arrhenius equation theory suggests that the frequency factor term is primarily dependent upon diffusion (which impacts frequency of collision) and steric hindrance (which impacts the efficiency of collisions in a manner independent of moiety energy surfaces). However, over a century of data on liquid phase reactions has left the impression that frequency factors are unique to molecules of reaction as opposed to a more-broader factor. The work presented in this paper has identified how a common frequency factor term can be shared over a range of polyol reagents; this observation was made possible because of the manner in which the viscosity of urethane thermoset reactions can change by orders of magnitude during reaction.

This finding is significant from many perspectives because it:
• Reduces the number of parameters needed to simulate reaction profiles over a class of reagents such as various polyols in urethane reactions,

• Can provide a “base case” of trends in reaction rate constants of a range of molecules that can be used to identify more fundamentally-correct activation energies and perturbations from expected behavior (that can be used to gain further insight), and

• Generally advance theory, insight, and consistency when pursing the attaining of the maximum information from reaction rate data.

For the urethane reactions of this study the number of parameters needed to perform simulation was reduced, where:

• This approach allowed alcohol moiety characterizations to be reduced to primary and secondary where a previous category of “hindered secondary” was dropped; the conclusion being that a phenomenon associated with hindered secondary alcohols was actually due to variations in viscosity.

• What was previously “6Y + 6” fitted parameters for frequency factor and activation energies for a homogenous reaction and Y catalysts (for primary, secondary, and hindered secondary moieties) has become 3 frequency factor terms and “Y + 1” activation energies (for primary and secondary alcohols).

• The use of common frequency factor terms has led to consistent trends in activation energies where better catalysts provide lower activation energies.

• This work will lead to a revision of previously published kinetic parameters by these authors.
In this paper, the rate of inter-molecular movement (the rotational movements of segments) was assumed to be proportional to the reaction temperature to a power between 0.5 and 1.0 where a power of 1.0 was identified as providing the better fit to data. Also, the reaction rate constant for the reaction of primary alcohol moieties were set at six times the reaction rate constant of the secondary alcohol moieties. These studies provide a basis where a single activation energy for a new catalyst (possibly from a single data point) for this system can provide a reasonable characterization of the catalyst and simulation of the catalyst’s impact. As more accurate simulations are needed; these base case parameters can be supplemented similar to the way the Van der Waals equation supplements the ideal gas law.

From a broader perspective, it is common practice to ignore the temperature dependence of the frequency factor; this can lead to errors in the activation energy by forcing all temperature dependence upon the activation energy term. This masking meaningful trends in activation energies can stunt the advancement of science.

### 6.7 Nomenclature

- $C_{0,Bmol}$: Initial concentration of B moieties
- $C_{0P,Bmol}$: Initial concentration of primary B moieties
- $C_{0S,Bmol}$: Initial concentration of secondary B moieties
- $X_{P,0}$: Initial reaction primary alcohol moieties
- $\mu$: Resin viscosity
- A, B: Alcohol and isocyanate moieties in monomers
$A_1', A_2', A', A_1$  Constants in frequency factor expression

$A_p, A_s, A_{hs}$  Fractional content of primary, secondary, and hindered secondary alcohol moieties in a polyol.

$A_{p,c}, A_{s,c}, A_{hs,c}$  Pre-exponential factor of Arrhenius equation for catalytic path

DEG  Diethylene glycol

$E_p, E_s, E_{hs}$  Activation energies of primary, secondary, and hindered secondary alcohol moieties of non-catalytic rate constant expression.

$E_p, E_s, E_{hs}$  Activation energies of primary, secondary, and hindered secondary alcohol moieties of catalytic rate constant expression.

$k_p, k_s, k_{hs}$  Rate constant of the reaction of primary, secondary, and hindered secondary alcohol moieties in non-catalytic reactions

$k_{p,c}, k_{s,c}, k_{hs,c}$  Rate constant of the reaction of primary, secondary, and hindered secondary alcohol moieties in catalytic reactions

M  Molecular weight

$P_A, P_B$  Alcohol and isocyanate moieties in polymer

PDP  Polymer degree of polymerization

PU  Polyurethane

T  Reaction temperature

TEG  Triethylene glycol

$\rho$  Density
CHAPTER 7. SIMULATION APPROACHES FOR THE MECHANISMS OF THERMOSET POLYMERIZATION REACTIONS

7.1 Abstract

Detailed modeling and simulation of the reaction of alcohol and isocyanate moieties to form urethane has provided a reason to question conventional opinions that this is a step-growth polymerization process. In particular, industrial formulations are dominated by catalytic mechanisms, and these chain mechanisms have the potential to change the polymer growth mechanism. The research of this paper evaluates experimental data of reaction temperature and resin viscosity of urethane gel reactions which substantiate a chain-growth mechanism. One of the artifacts of a chain growth mechanism is the rapid appearance of relatively large molecules which reduce gel point times earlier what would occur with step-growth mechanisms.

7.2 Introduction

Thermoset urethane polymerization is a complex reaction with a dozen degrees of freedom. Generally, polyurethane gel is produced from the reaction of alcohol and isocyanate moieties. Catalysts are typically added to formulations to increase reaction rates. The kinetic parameters and reaction mechanism of urethane reaction have been the subject of interest for many researchers and have been studied using chromatography, intrinsic fluorescence, NMR, mathematical modeling, and simulation:[84, 88-92] however, none of these provide a robust description to this complex polymerization.
At the early stages of the reaction of a multifunctional polyol and isocyanate, the reactive moieties in the monomers react to form polymer molecules. Later reactions are dominated by the reactive moieties in polymers reacting with other reactive moieties in another polymer of the same polymer. As these reactions proceed, polymer chains increase and cross-link to form large three-dimensional matrices. The viscosity of the resin increases with increasing molecular weight of the chains eventually reaching a gel point.

On the molecular level, the gel point is the where cross-linking has occurred to such an extent that the large fraction of the mixture is cross-linked to form a large three-dimensional molecule[93]. In this condition, the mixture undergoes a phase transition from liquid to solid phase.

Carothers [94, 95] was the first to point out that large molecules can be formed even at lower extents of reaction. Paul Flory [96-101], a 1974 Nobel laureate on this subject, developed initial theories of gelation and cross-linking. His approach targeted analytical solutions of equations, rather than computer simulations. Paul Flory based this theory on the following three assumptions (considering A and B are multifunctional monomers):

- All reactions occur between A and B.
- All functional groups on a branch unit are equally reactive.
- There are no intramolecular reactions.

This theory was extended by Stockmayer[16] using different mathematical methods that incorporate Flory’s assumption with the advantage of calculating molecular size distribution. However, this approach is not applicable beyond the gel point and only predicted extent of reaction at the gel point—not gel point time. Walling [17] followed
Flory’s assumptions and Stockmayer equations to predict the gel-point in the addition polymerization of a mixture of monomers.

Flory’s assumption of no intramolecular reaction becomes increasingly invalid with increasing monomer functionalities. As functionality increases, the number of unreacted monomers on polymer increases, and since these unreacted monomers are in close proximity (on the same molecule), they will tend to react in intra-polymer reactions.

A gel theory by Raphael et al has introduced in 1997 called “Olympic gel” to account for intra-molecular reactions in estimating the gel point as the reaction leads to the formation of polymer rings using the power of the tree approximation diagram [18]. The gel point is assumed only a function of polymer rings concentration. A year after, Suematsu [19] developed a new theory of polymer gelation that takes into account the delay of the gel point and change of functionality due to ring formation. The calculations are based on calculating the total polymer ring concentration and the extent of intermolecular reaction making use of Taylor series expansions.

The gel point can be defined as the instant at which the average molecular weight of the polymer diverges to infinity. Since the gel point is the endpoint during thermoset processing, it is of particular interest toward this practical application.

While the mechanism of urethane non-catalytic reactions superficially appears to be a step-growth mechanism, different mechanisms are possible with different urethane catalysts. Catalyst molecules interact with the alcohol and/or with the isocyanate moieties to provide highly active sites that react at higher rates. Both catalytic and non-catalytic
reactions will occur in parallel, they were simulated toward providing a fundamentally correct simulation.

The novelty of the current simulation is a) use of computer simulation of the reaction of multifunctional monomers to predict the gel point, b) considering intra-molecular reactions toward better prediction of the gel point, c) simulating polyurethane non-catalytic and catalytic reactions and d) comparing three different approaches for possible catalytic interaction mechanisms. Accounting for non-isothermal reactions, intra-molecular reactions, and chain growth mechanisms produces a degree of rigor far greater than is possible with analytical solutions and provides for estimates of gel point times as well as conversions.

7.3 Modeling Approaches

7.3.1 Non-catalytic reactions:

Possible non-catalytic reactions of two multifunctional alcohol and isocyanate monomers are listed in Table 7-1. The first of Flory’s assumptions is implicit by not including reactions beyond those provided. The second of Flory’s assumptions is that the reaction rate constants of these four reactions are equal. This assumption neglects a) different reactivates of primary versus secondary alcohols moieties, b) diffusion rates impacts on reaction rates, and c) impact of chain length on the reactivity of alcohol and isocyanate moieties.
<table>
<thead>
<tr>
<th>Rxn.</th>
<th>Reaction</th>
<th>Rate Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A + B → P</td>
<td>( r_1 = k_1 f_A C_A f_B C_B )</td>
</tr>
<tr>
<td>2</td>
<td>A + P_B → P</td>
<td>( r_2 = k_2 f_A C_A P_B )</td>
</tr>
<tr>
<td>3</td>
<td>B + P_A → P</td>
<td>( r_3 = k_3 P_A f_B C_B )</td>
</tr>
<tr>
<td>4</td>
<td>P_A + P_B → P</td>
<td>( r_4 = k_4 P_A P_B )</td>
</tr>
</tbody>
</table>

Flory’s assumption of no intra-molecular reactions impacts the manner in which the fourth reaction of Table 7-1 impacts the rate at which the polymer concentration decreases, which impacts the gel point time and conversion. The simulation approach of this paper considers the ratio of intra versus inter reactions as a function of degree of polymerization.

### 7.3.2 Catalytic Reactions

Simulations were performed with a chain-growth mechanism for catalytic reactions versus a step-growth polymerization for non-catalytic reactions. Figure 7-1 shows a schematic view of step growth versus chain growth polymerization mechanisms. [69, 84, 89, 91, 102]. [103] Chain growth produces fewer polymers of higher molecular weight at the same conversion.
While Ghoreishi et al. assumed catalyst interaction with alcohol and isocyanate moieties, the current research considers alternative approaches for different possible catalyst interactions with the alcohol (hereafter referred to as A) and isocyanate (hereafter referred to as B) moieties. These approaches are:

The first approach assumes that the catalyst has the same possibility to interact with either A and B moieties. In order to simplify the number of reactions, it is assumed that if the A moiety attached to catalyst reacts with B moiety, the catalyst transfers from the reacted A moiety to another B moiety and vice versa.

The second approach also assumes the possibility of a catalyst to react with A and B moieties independent of its previous complex. As the A moiety attached to catalyst reacts with B moiety, the catalyst randomly attaches is either A or B moieties in the mixture.

Approach#3 assumes the catalyst interacts only with the alcohol moieties in the mixture. This approach reduces the possible number of reactions from 26 to 15.

Table 7-2 lists the catalytic reactions of the three approaches and Table 7-3 to Table 7-5 summarize the stoichiometry of each component in each approach. Figure 7-2 illustrates the definition of the moieties used in these approaches.

**Figure 7-2 Illustration of different moieties**
<table>
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<tr>
<th>Rxn</th>
<th>Approach#1</th>
<th>Approach#2</th>
<th>Approach#3</th>
</tr>
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<tbody>
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<td>$A + M \rightarrow AM$</td>
<td>$B + M \rightarrow BM$</td>
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<tr>
<td>6</td>
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<tr>
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<td>$P_B + M \rightarrow PM$</td>
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### Table 7-3. Stoichiometry of Approach#1.

| Comp.  | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | 14  | 15  | 16  | 17  | 18  | 19  | 20  | 21  | 22  | 23  | 24  | 25  | 26  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| A_{mon}| -1  | -1  | 0   | 0   | -1  | 0   | 0   | 0   | -1  | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   | 0   |
| B_{mon}| -1  | 0   | 0   | -1  | 0   | 0   | -1  | 0   | 0   | -1  | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   |
| P     | 1   | 0   | 0   | 1   | -1  | *p_{eff} | 0   | 0   | -1  | 0   | 0   | -1  | 0   | 0   | -1  | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   |
| A_{moi}| -1  | -1  | -1  | -1  | 0   | -1  | 0   | 0   | -1  | 0   | 0   | -1  | 0   | 2   | -2  | 0   | -1  | 0   | -1  | 0   | 0   | 0   | 1   |
| B_{moi}| -1  | -1  | -1  | -1  | 0   | -1  | 0   | 0   | -1  | 0   | -2  | -2  | 0   | -1  | 0   | -1  | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   |
| M     | 0   | 0   | 0   | 0   | -1  | -1  | -1  | -1  | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   |
| AM    | 0   | 0   | 0   | 0   | 1   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   | -1  | 0   | 0   | 0   | 0   | 0   | 0   | -1  |
| BM    | 0   | 0   | 0   | 1   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| PMA   | 0   | 0   | 0   | 0   | 0   | 0   | 1   | 0   | -1  | 1   | 1   | 1   | -1  | 0   | 1   | 1   | 0   | -1  | 0   | 0   | 0   | 0   | 0   |
| PMB   | 0   | 0   | 0   | 0   | 0   | 0   | 1   | 1   | -1  | 0   | 1   | 1   | 0   | 0   | 1   | 0   | 1   | -1  | 0   | 0   | 0   | 0   | 0   |
| (PM)_{Amoi} | 0   | 0   | 0   | 0   | 0   | 0   | f_{PM_{a}} | f_{PM_{a}} | 0   | f_{PM_{a}} | f_{PM_{a}} | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| (PM)_{Bmoi} | 0   | 0   | 0   | 0   | 0   | 0   | f_{PB} | f_{PB}+1 | 0   | f_{PB} | f_{PB}+1 | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| U_{TOT} | 1   | 1   | 1   | 1   | 0   | 0   | 0   | 0   | 1   | 1   | 1   | 1   | 1   | 1   | 1   | 1   | 1   | mta | mtb | 1   | 1   | 0   | 0   | 0   | 0   |
| (P)_{Amoi} | f_{a}+1 | f_{a}+1 | f_{a}+1 | f_{a}+1 | -1  | -1  | 0   | -f_{PA} | -f_{PA} | -f_{PA} | -f_{PA} | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| (P)_{Bmoi} | f_{b}+1 | f_{b}+1 | f_{b}+1 | f_{b}+1 | -1  | -1  | 0   | -f_{PB} | -f_{PB} | -f_{PB} | -f_{PB} | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| U_{NC} | 1   | 1   | 1   | 1   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| U_{C} | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   | 1   | 1   | 1   | 1   | 1   | 1   | 1   | 1   | mta*p_{eff} | mtb*p_{eff} | 1   | 1   | 0   | 0   | 0   | 0   |
| PMD   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| Pb    | 1   | 0   | 0   | -1  | *p_{eff} | 0   | 0   | -1  | -1  | 0   | 0   | -1  | -1  | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 1   |
| Pc    | 0   | 0   | 0   | 0   | 0   | 1   | 1   | 0   | 0   | 0   | 0   | 1   | 1   | 1   | 1   | -1  | *p_{eff} | -1  | *p_{eff} | -1  | 0   | 0   | -1  | -1  | 0   |
Table 7-4. Stoichiometry of Approach#2.

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Table 7-5. Stoichiometry of Approach#3.
Each of the different functionalized moiety groups of Figure 7-2 impact one or more reactions of Table 7-2, and so, each of these must be calculated in virtual time during simulation. Key terms that are followed in virtual time during simulation with a brief explanation of how each is used in the simulation includes:

- **PDPC** – Average degree of polymerization of polymers formed by catalytic mechanisms impacts degree of inter versus intra polymerization. Also, these long chains substantially determine the mixture viscosity.

- **PDPh** – Average degree of polymerization of polymers formed by non-catalytic (non-catalytic) mechanisms are primarily small oligomers early in the reaction. These oligomers have less impact on viscosity than polymers formed by the chain mechanisms, and so, they must be followed separately to allow accurate estimation of viscosity.

- **mta** – Average number of A-moiety sites on a polymer functionalized by a catalyst molecule. This term is only used later in the simulation based on an equilibrium assumption for catalyst addition to moiety; after about 100 seconds.

- **mtb** – Average number of B-moiety sites on a polymer functionalized by a catalyst molecule.

The following paragraphs derive, define, and/or summarize the use of these terms. A complete summary of variables used in this simulation work is provided at the end of the paper.
PDP Terms and Their Use - It is useful at the earlier stages of thermoset polymeriation reactions to determine how catalysts impact increases in viscosity. Simulation provides the advantage of following polymer and urethane concentrations that are produced from non-catalytic and catalytic reactions separately. Polymer degree of polymerization (PDP) of the step (non-catalytic) and chain (catalytic) mechanisms were calculated by Equation 7-1 and Equation 7-2.

\[
PDP_h = 1 + \frac{U_{NC}}{P_h} \quad \text{Equation 7-1}
\]

\[
PDP_c = 1 + \frac{U_c}{P_c} \quad \text{Equation 7-2}
\]

These PDPs were used in this study to calculate the efficiency of intra-polymer reactions and to estimate resin viscosity during the reaction. Viscosity was calculated by the method of Fu et al.[37] based on the mixing rule where the mass fraction of each component was calculated from concentration profiles and the viscosity of each component was calculated using group contribution method. In the current research, the viscosity of polymer produces from non-catalytic and catalytic reactions separately based on their polymer degree of polymerization.

The efficiency of polymer-polymer intra-molecular reactions (P_{eff}) is defined as the fraction of polymer-polymer reactions that are ratio of inter-polymerization. In the “string’ model of a polymer introduced by Ghoreishi et al[55], the polymer has a length of k*PDP and a radius R1, the surface area of the string is \(2\pi R_1 k \text{PDP}\). The surface area of a sphere having the same volume as the string is \(4\pi \left[\frac{3}{4} R_1 k \text{PDP}\right]^{2/3}\). The ratio of the surface area
of the sphere to the surface are of the string is the lower value of an estimate of the fraction of inter-polymerization as provide by Equation 7-3.

\[
P_{\text{eff}} = \frac{4\pi \left[ \frac{3}{4} R_1^2 K \text{PDP} \right]^{2/3}}{2\pi R_1 K \text{PDP}} = C \cdot \text{PDP}^{-1/3} = \frac{C}{\text{PDP}^{1/3}}
\]  

Equation 7-3

Equation 7-3 has a fundamental basis at large PDP, but loses that significance at low PDP; this can be put in a form that has proper limits which would then be more fundamentally correct. The limits (heuristics) of this equation should be:

1. \( \lim_{\text{PDP} \to 1} P_{\text{eff}} = 1 \) and

2. \( \lim_{\text{PDP} \to \infty} P_{\text{eff}} = C / \text{PDP}^{1/3} \) (Assuming sphere shape)  or  \( \lim_{\text{PDP} \to \infty} P_{\text{eff}} = 1 \) (Assuming stretched string)

This leads to the conclusion that Peff is between 1.0 and 0.3333 depending on solubility of the polymer in the reacting mixture. The limit of Equation 3 is not correct at a PDP of 1; however, the rate of inter-polymerization is zero at this limit since polymer concentration starts at zero in the simulation. The error introduced as a result of this incorrect limit is considered negligible.

mta and mtb Terms and Their Use – As monomer concentrations decrease during simulation, a larger fraction of reactive moieties reside on polymers, and the need emerges to estimate the average number of catalyst molecules attached to a polymer. A Hougen-Watson equilibrium was used to estimate the average number of catalyst attached to the polymer. Resulting estimates of 90% of equilibrium concentration is provided by Equation
7-4 and Equation 7-5. These estimates are applied to reactions 17 and 18 of Ap.#1 and #2 (see Table 7-3 and Table 7-4) and reaction 11 of Ap.#3 (see Table 7-5).

\[
\begin{align*}
\text{mta} &= 0.9 \times M_t \frac{k \text{ (PM)}_A}{1 + k \text{ (PM)}_A + k \text{ (PM)}_B} = 0.9 \times M_t \frac{\text{(PM)}_A}{\text{(PM)}_A + \text{(PM)}_B} \quad \text{Equation 7-4} \\
\text{mtb} &= 0.9 \times M_t \frac{k \text{ (PM)}_B}{1 + k \text{ (PM)}_A + k \text{ (PM)}_B} = 0.9 \times M_t \frac{\text{(PM)}_B}{\text{(PM)}_A + \text{(PM)}_B} \quad \text{Equation 7-5}
\end{align*}
\]

Where \( k \gg 1 \) and \( M_t = M + AM + BM + PM_A + PM_B \).

By example, the rate expression of reaction 17 (Table 7-3) incorporates this estimate as repeated by Equation 6.

\[
\begin{align*}
\text{r}_{17} &= k_P \times \text{mta} \times \text{(PM)}_B \\
\text{Equation 7-6}
\end{align*}
\]

Similar applications of mta and mtb were applied for reaction 18 in Table 7-3, reactions 17 and 18 in Table 7-4, and reaction 11 in Table 7-5.

The average functionalities A and B moieties on polymer (\( f_{PA} \) and \( f_{PB} \)) were calculated as the concentration of A or B moieties on the polymer that does not have catalyst attached to it divided by the concentration of polymer (Equation 7-7). A similar approach is used for \( f_{PMA} \) and \( f_{PMB} \) as summarized by Equation 7-8.

\[
\begin{align*}
\text{f}_{PA} &= \frac{\text{(P)}_{Amoi}}{\text{P}} \quad \text{,} \quad \text{f}_{PB} = \frac{\text{(P)}_{Bmoi}}{\text{P}} \\
\text{f}_{PMA} &= \frac{\text{(PM)}_{Amoi}}{\text{PM}_A + \text{PM}_B} \quad \text{,} \quad \text{f}_{PMB} = \frac{\text{(PM)}_{Bmoi}}{\text{PM}_A + \text{PM}_B} \\
\text{Equation 7-7} \quad \text{Equation 7-8}
\end{align*}
\]

Atomic balances were used to check the consistencies of stoichiometries in Table 7-3 to Table 7-5. This balance is required for consistency for all the reactions except reactions
17-20 in Table 7-3 and Table 7-4 and reaction 11 in Table 7-5. It applies to a balance on the various forms of the catalyst as well as reactive moieties and respective products.

The rate of increasing reaction temperature was calculated using an energy balance assuming no blowing agent was present (gel reactions) in the formulation, constant heat of reaction, and neglecting the contribution to internal energy due polymer chains stretching. Heat generated and consumed from catalyst coupling and decoupling are assumed to be low, equal and ultimately cancelling. Equation 9 was used to calculate reaction temperature:

\[
\frac{dT}{dt} = \sum \Delta H_i \cdot r_i + UA \frac{dT}{n C_p}
\]  

Equation 7-9

MatLab’s ODE45 function was used to solve the differential equations of the rate of reactions. The initial concentration of the recipes and the thermodynamic and kinetic parameters are the input to the code to the ODE45 function which calls on a user function to calculate the rate of change of components and temperature. The reaction rate constant was calculated separately for non-catalytic and catalytic reactions based on Arrhenius equation parameters reported by Zhao et al.[25] for non-catalytic reactions and new fitted parameters for the catalytic reactions.

7.4 Modelling Heuristics

The following heuristics were adopted for the handling of reaction rates and component rate expressions in the program:

- Moiety equivalents (concentrations) are the driving force for reactions rather than molecule concentrations.
To generate concentration profiles and the gel point time; at a minimum, concentration profiles of moieties, monomers, and polymer(s) must be simulated by solving ordinary differential equations describing their rates of change.

If one moiety on a monomer reacts the monomer is consumed. As examples, the reactions of $A + M \rightarrow AM$ and $A + B \rightarrow P$ consume the monomers with indicated stoichiometries of 1 and -1.

Moieties complexed to a catalyst are considered separate and distinct from moieties not complexed.

The concentration of A moieties attached to a catalyst in the polymer is represented as $PM_A$ and the remaining A moieties in the polymer that are not attached to a catalyst are represented as $(PM)_A$.

Polymers are lumped into either step growth polymer or chain growth polymer. Each of these lumped categories has an average calculated concentration.

If a polymer has urethane linkages of both step and chain growth, the category of the last urethane added determines the category of the polymer (two polymer concentration profiles are generated by the simulation).

$PM_A$ reacts with two B monomers in the alternating catalyst model. One B monomer reacts with the A moiety and another complexes with the catalyst on in the polymer.

A monomer may have only one catalyst attached to a moiety on a monomer.

Molecule and moiety ODEs solved during simulation have units of moles/s. Concentrations used in rate expressions are calculated as moles divided by the total volume of liquid/resin using an ideal mixture.
• Heat capacity is calculated as the ideal sum of component heat capacities (units of J/K).

• Reactions are presented as elementary reactions (can be directly translated to reaction rate expressions).

• The rate constant of catalyst decoupling (kd) is assumed to be proportional to the rate constant of step growth rate constant (k0). The impact of this constant was studied. The approach was necessary because of lack of information on the impact of temperature on catalyst coupling and decoupling rates.

• The ratio of the rate constant of catalyst coupling (kc) and decoupling is set to 1000 if not otherwise stated.

Although the approach presented by this paper is adopting some assumptions, the conclusions can be applied without restraint.

7.5 Experimental Procedure

Voranol 360 (V360) from Dow chemicals and PAPI (standard polymeric MDI) from Huntsman company were used in this study as polyol (A) and isocyanate (B) respectively. Experiments of isocyanate index of 1.1 and 2 were compared to verify simulation results. Future studies were planned for studying and simulating the mechanisms of different types of catalyst. Momentive L6900 is the surfactant, and Tris (1-chloro- 2-propyl) Phosphate (TCPP) is a fire retardant. Amine catalyst, N, N-dimethylcyclohexylamine (thereafter referred as Cat8), were used as a gelling catalyst. The mechanism of this catalyst is studied in the current paper; however, different types catalysts (Tin or Bismuth) may result in a different mechanism. This paper focuses only on studying the mechanism of the amine
catalyst. No blowing agent is used in this study. The amount of the surfactant and fire retardant were kept at 0.15% (mass fraction).

Recipes were mixed together in a paper cup covered by a polyurethane foam to reduce the heat loss during the reaction. 2000 rpm mixing blade attached to a floor-model drill press were used to mix the recipes. The same mixing time for all experiment of 10 seconds was used to avoid any variation in viscosity profiles measurement[77]. A type-k thermocouple attached to a national instruments SCB-68 box to a national PCI 6024E data acquisition was used to measure temperature profile using LabView soft-ware. The LabView soft-ware provide an instant reading of the reaction temperature versus reaction time. Viscosity profile of the resin was measured by a Cole-Parmer basic viscometer. All reaction temperature and viscosity experiments were carried out at room temperature to avoid deviations in reaction kinetics and molecular weights of the polymer.[78]

7.6 Results and Discussion

The non-catalytic versions of the reactions in Table 7-1 were simulated and compared to experimental data. The good fitting of temperature and viscosity profiles in Figure 7-3 enable the assumption of step-growth mechanism for urethane non-catalytic reactions.
Figure 7-3 Reaction temperature and resin viscosity profiles of polyurethane homogeneous reaction.

Symbols “○” and “◊” refer to the experimental date of reaction temperature and resin viscosity. 

Solid and dash lines refer to simulation results of reaction temperature and resin viscosity

Additional studies at two catalyst loadings are compared to the Figure 3 non-catalytic data by Figure 7-4 illustrating how the viscosity of catalytic reactions increases faster at the lower reaction temperature. This is attributed to the chain growth mechanism for catalytic reactions. Under the assumption that the increases in temperature are proportional to the extents of urethane-forming reactions, the larger viscosities at the same extents of reaction (same temperatures) are attributed to the polymers of higher PDP formed by the chain mechanism.
Figure 7-4 Resin viscosity vs. reaction temperature for homogeneous and catalytic gel reactions.

Symbols “◊”, “○” and “∆” refer to homogeneous, catalyst loading of 0.1 and 0.2g.

Figure 7-5 shows simulation and experimental results of reaction temperature and viscosity profiles when considering a step-growth mechanism for the catalytic reactions. Temperature profiles show good agreement while viscosity data do not agree with the simulation. The faster gel point of the experimental data is due to the production of fewer polymer molecules with higher molecular weight resulting from the chain-growth mechanism.
Figure 7-5 Reaction temperature (a) and resin viscosity (b) profiles of polyurethane catalytic reactions considering step growth mechanism. Symbols “○” and “●” in (a) and “◊” and “♦” in (b) refers to 0.1 and 0.2 g loadings of cat8. Corresponding lines refer to simulation results.

A sensitivity analysis was performed to check the validity of the assumptions mentioned earlier for chain-growth simulation. The ratio of the rate constant of catalyst coupling to the rate constant of the non-catalytic reaction was analyzed, and the simulation results of Figure 7-6 show that higher ratios have a minor impact on temperature profile (and later for the viscosity profile). Simulations at values below a critical lower ratio reduce the rate of formation of complexed moieties which causes a lower temperature profile.
The ratio of the rate of coupling to decoupling of catalyst-moieties interaction was analyzed as summarized by the sensitivity analysis of Figure 7-7. At low ratios, simulation results of temperature profile are impacted because low ratios result in fewer catalyst complexes available to react. At higher ratios (about 300 and higher), the catalyst-moiety complex rapidly establishes near-equilibrium concentrations of complexed catalyst available for polymer propagation reactions. Increasing this ratio results in no impact on the temperature profile.

Urethane molecules from non-catalytic and catalytic reactions were tracked separately for different ratios of the rate of coupling-decoupling. As this ratio increases, more urethane forms from catalytic reactions. The sum of non-catalytic and catalytic urethane at different ratios is the same for different ratios except for the lower ratios.

Figure 7-6 Analysis of $k_{\text{coupling}} / k_0$. Continuous, dash, dash dot and long dash lines refer to the ratio of 100, 1000, 10000 and 100000.

157
Multiple catalyst complexes on polymer molecules (i.e., mta and mtb) are considered by applying the Hougen-Watson (H-W) equation for reversible, equilibrium interactions of catalyst sites. Figure 7-8 compares simulation results with and without considering multiple attachments to polymer molecules.

The results show that as polymer molecules become large and a larger fraction of the total of the reactive moieties are attached to these polymers, the probability of more than one catalyst attaching to the same polymer increases. After about 30% conversion,
significant errors can be induced in the simulation if mta and mtb values greater than 1.0 are not considered.

Figure 7-8 Comparison of simulation with and without considering Hougen-Watson equation. In (a), continuous and dot lines refer (PM)_{Amoi} and (PM)_{Bmoi} without considering H-W equation and dash and long dash lines refer (PM)_{Amoi} and (PM)_{Bmoi} with considering H-W equation. In (b), continuous and dash lines refer to temperature profile with and without considering H-W equation.

The data suggests that mta and mtb values of 1.0 or less is adequate at low conversions. This can be verified by tracking reaction rates of various reactions at different times during the simulation as summarized by Figure 7-9. The rates substantiate that monomer-
monomer reactions dominate early in the reaction. A Hougen-Watson rate expression has an impact after 100 seconds for this formulation of 0.2 g catalyst loading of this study.

In summary, the two assumptions of: a) mta and mtb values of 1.0 or less early in the reaction and b) equilibrium concentrations of complexing late in the reaction, jointly, substantially reduce the number of ODEs that need to be solved without introducing significant error.

Figure 7-9 Reactions rates at different reaction times. Black, white, gray, dotted, blocks and stripes columns refer to reactions 9, 12, 16, 17, 20 and 21 respectively.
Figure 7-10 compares the simulation results of two approaches (alternating and roaming) with the experimental data for a catalytic reaction of two catalyst loadings. These approaches 1 and 2 consider the catalyst to complex with both alcohol and isocyanate moieties; simulation results are only slightly different. The difference is considered within the error of the simulation.

Based on observing that Approach 1 and Approach 2 are substantially indistinguishable, only Approach 2 was considered in further comparison with Approach 3. The purpose of this comparison is to identify if simulation results (and experimentally obtained temperature profiles) can be used to gain insight into the mechanisms of catalysts (which can vary from catalyst to catalyst).

![Graph comparing simulation results and experimental data](image)

**Figure 7-10** Comparison of the simulation of reaction temperature of the three approaches with experimental data using two catalyst loadings. Symbols “○” and “◊” refer to experimental data using 0.1 g and 0.2 g catalyst loadings. Continuous, dot and dash lines refer to the simulation of Approaches 1, 2 and 3 when using 0.1 g (slower profile) and 0.2 g (faster profile) catalyst loadings.
The roaming catalyst approach (Approach #2) was compared to the alcohol-only mechanism approach (Approach 3) at an isocyanate index of 2. The roaming catalyst approach provides a good fitting to the experimental data of indices 1.1 and 2, while the alcohol-only approach deviates from both the data and roaming catalyst simulation at an index of 2.0. For the alcohol-only mechanism, additional alcohol monomer (above what can complex with the catalyst) serves as a diluent and can slow down the early reactions leading to different profiles.

Different temperature profiles of the two approaches provides a powerful tool for predicting whether a catalyst is interacting with either alcohol and isocyanate moieties or with only alcohol moieties.

![Figure 7-11 Comparison of the temperature profile of Approaches 2 and 3 at indices 1.1 and 2. Symbols “○” and “◊” refer to experimental data at 1.1 and 2 isocyanate indices. Continuous and dot lines refer to simulation of Approaches 2 and 3 at index 1.1 and dash and dot-dash lines refer to simulation of Approaches 2 and 3 at index 2](image-url)
The concentration of free (un-complexed) catalyst in the system can provide both insight into how the catalyst interacts with moieties and can verify consistency of in the limits of simulation with anticipated results. Figure 7-12 provides a comparison of the concentration profile of the catalyst of the different approaches for recipes of 1.1 isocyanate index. These profiles provide the following insights:

- Free catalyst concentration decreases rapidly at the beginning of the reaction due to the fast rate of catalyst-moietiy interactions.
- Free catalyst concentrations recover to initial values when all moieties in monomers and polymers have reacted.
- Free catalyst concentrations of Approach #3 (where catalyst attached to only alcohol moieties) recover to initial concentrations as alcohol moieties react to completion.
- Free catalyst concentrations of Approach#2 do not recover to initial concentrations since catalyst molecules are attached to the excess isocyanate moieties.

These profiles and insights can provide evidence to the validity of the simulation approaches.
Figure 7-12 Comparison of catalyst profile different simulation mechanism approaches. Continuous and dash lines refer to simulation catalyst concentration of Approach 1 and 3 respectively.

As the polymerization proceeds and polymer molecules become larger, the probability of intra-polymer reactions increase and lead to a faster gel point. Figure 7-13 provides a comparison of polymer concentrations when the efficiency of the polymer-polymer reaction is 1 (no intra-polymer reactions) versus intra-polymer efficiency of Equation 7-3 (assuming C = 3.5 for non-catalytic and catalytic). The results show polymer concentrations formed from non-catalytic and catalytic reactions decrease slower when considering intra-polymer reactions.

The simulation shows lower concentrations of polymers formed from catalytic reactions (chain-growth mechanism) as compared to the polymers formed from non-catalytic reactions. This is attributed to fewer molecules of polymers that having high PDP as compared to many short polymer chains formed from non-catalytic reactions (step-growth mechanism).
While low in concentration, the large polymers formed from the chain mechanism have a significant impact on viscosity, the catalysts introduce chain-growth mechanisms, and the change in viscosity versus temperature profiles resulting from different catalyst loadings can be thus understood.

![Figure 7-13 Polymer concentration at the different efficiencies of polymer-polymer reactions. Continuous and dash lines refer to efficiencies using Equation 7-3 versus P_eff=1](image)

**7.7 Conclusion Remarks**

In near-adiabatic ideal foaming processes, the temperature rise of a reacting formulation is proportional to the extent of reaction, and so, the viscosity will only be a function of temperature for systems having similar reaction mechanisms. Because differences in viscosity versus temperature profiles were observed for formulations with and without a catalyst, it was concluded that catalysts introduced different overall reaction mechanisms. It was hypothesized that catalysts can introduce a chain-growth mechanism for urethane-forming reactions resulting in faster increases in viscosity (versus temperature) than comparable step-growth non-catalytic reactions.
Chain-growth mechanisms lead to the formation of fewer polymers with higher molecular weights than step-growth mechanisms at similar extents of reaction. Even low concentrations of these large polymer molecules can lead to significant increases in viscosity. Reaction simulations were performed by solving the dozens of ordinary differential equations (ODEs) that represent the chain-growth versus step-growth mechanisms; these simulations allowed temperature and viscosity profiles to be estimated as a function of reaction rate constants of elementary reactions. A challenge of this simulation is reducing the hundreds of ODEs to a 15-30 ODEs without loss of accuracy.

A first method to reduce the number of ODEs was to assume that above a threshold ratio, the value of $k(\text{coupling})$ and the ratio of $k(\text{coupling})$ to $k(\text{decoupling})$ has minimal impact on simulation results. It was identified that at higher ratios the actual value of this ratio has minor impact on simulation results.

A second method to reduce the number of ODEs was related to the method of handling the prospect that more than one catalyst molecule may attach to the same polymer molecule. This was achieved by characterizing the initial polymerization as being dominated in a system where only on the catalyst may attach to a polymer molecule. At high conversions (and high degrees of polymerization), limiting catalyst attachment to one catalyst per molecules leads to an improper quenching of the reaction, and so, it is critical at later stages in the reaction to allow for multiple catalysts to attach to large polymer molecules. At these later stages of the reaction, an assumption of equilibrium between free catalyst concentration and attachment to moieties was identified as a sufficiently accurate representation.
To simulate the differences in viscosity profiles of step-growth versus chain-growth mechanisms, it is critical to distinguish between the different resulting molecular weight distributions of the polymers. For (non-catalytic) step-growth polymerization a single average degree of polymerization can be used. For a system with parallel step-growth and chain-growth mechanisms it is critical to estimate at least two average degrees of polymerizations; one for the step-growth mechanism and one for the chain-growth mechanism.

Based on these overall approaches, the following observations were made:

- Non-catalytic reactions tend to be faster at the initial stages of reactions in the presence of a large amount of free moieties (moieties that are not attached to catalyst). As the reactions proceed, catalytic reactions become dominant.

- The Hougen-Watson model was successfully applied to estimate the number of catalyst molecules attached to large polymer molecules at high extents of reaction.

- Accounting for intra-polymerization is essential to accurately predict gel points. Intra versus inter polymerization was distinguished through the use of factor dependent upon the polymer degree of polymerization.

- Urethane moieties produced from step versus chain mechanisms were successfully distinguished and identified as dependent on the ratio of the rate of coupling and decoupling of the catalyst.
• An important metric of consistency in the simulation was to confirm that after all moieties have reacted, the concentration of unbound catalyst recovers to its initial concentration as identified in the recipe.

• Simulations demonstrated that it is possible to use temperature profiles to distinguish between a catalyst mechanism where the catalyst only remains coupled with hydroxyl moieties (between reactions) versus a mechanism where the catalyst can remain coupled with either hydroxyl or isocyanate moieties.

• A roaming catalyst model gave similar simulation results as an alternating catalyst/moiet model for the recipe evaluated in this study (i.e. reactivity appeared to be the same whether the catalyst is attached to the A or the B moiety).

7.8 Nomenclature

(P)Amoi Concentration of A moieties attached to a polymer that does not have a catalyst attached to the polymer

(P)Bmoi Concentration of B moieties attached to a polymer that does not have a catalyst attached to the polymer

(PM)Amoi The other A moieties (in a polymer that is attached to catalyst) not attached to the catalyst.

(PM)Bmoi The other B moieties (in a polymer that is attached to catalyst) not attached to the catalyst.

\( \Delta T \) \( T_{ambient} - T_{reaction} \)

A Surface area of the gel
AM  Concentration of A moieties (in monomer) attached to the catalyst.

$A_{\text{moi}}$  Concentration of A moieties.

$A_{\text{mon}}$  Concentration of A monomer.

BM  Concentration of B moieties (in monomer) attached to the catalyst.

$B_{\text{moi}}$  Concentration of B moieties.

$B_{\text{mon}}$  Concentration of B monomer.

$f_A$  Functionality of monomer A.

$f_B$  Functionality of monomer B.

$f_{\text{intra}}$  Fraction of intramolecular reactions.

$k_1 - k_4$  Reaction rate constant of homogeneous reactions.

M  Concentration of catalyst.

$M_t$  Total concentration of catalyst in the mixture.

$P_{\text{eff}}$  Efficiency of polymer-polymer intra-molecular reactions.

P  Concentration of polymer.

$P_A$  Concentration of A moieties on polymer.

$P_{AB}$  Urethane polymer that has A and B moieties.

$P_B$  Concentration of B moieties on polymer.

$P_c$  Polymer concentration from catalytic reactions.

$P_{\text{DP}}$  Polymer degree of polymerization.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_h$</td>
<td>Polymer concentration from homogeneous reactions.</td>
</tr>
<tr>
<td>$P_{MA}$</td>
<td>Concentration of A moieties (in polymer) attached to catalyst.</td>
</tr>
<tr>
<td>$P_{MB}$</td>
<td>Concentration of B moieties (in polymer) attached to catalyst.</td>
</tr>
<tr>
<td>$P_{MD}$</td>
<td>Concentration of polymers freed from catalyst</td>
</tr>
<tr>
<td>$U$</td>
<td>Overall heat transfer coefficient</td>
</tr>
<tr>
<td>$U_C$</td>
<td>Concentration of catalytic extension of polymer</td>
</tr>
<tr>
<td>$U_{NC}$</td>
<td>Concentration of non-catalytic extension of polymer</td>
</tr>
<tr>
<td>$U_{TOT}$</td>
<td>Total urethane formed</td>
</tr>
</tbody>
</table>
CHAPTER 8. SIMULATION APPROACH TO LEARNING POLYMER SCIENCE

8.1 Abstract

Traditional engineering textbooks are substantially limited by approaches relying on analytical solutions where most of the applications are described by differential equations without simple analytical solutions. An alternative is to design a textbook around computer-program-based simulations, where the simulations progressively evolve through the textbook with the complexity of the content. Simulations can solve more-complex problems with immediate utility in practical applications, and the capabilities are able to achieve higher levels of Bloom’s Taxonomy with quiz-based methods that can be performed in a few minutes.

By example, the polymer engineering topic of thermoset polymerization has a global market of tens of billions of dollars; and yet, the textbook coverage of the subject is sparse due to the inability of simple analytical solutions to provide useful solutions to practical applications. This paper provides a foundation and approach for a simulation-based-learning textbook to cover the important topic of polymer engineering.

8.2 Traditional Versus Simulation Learning

Traditional approaches to learning polymer engineering has produced dozens of textbooks with emphases on the “Remember” (R) and “Understand” (U) levels of Bloom’s Taxonomy. The common subjects covered by traditional polymer textbooks including, but not limited to:
• common monomers and their structure, (R)
• classifications of polymers (thermosets versus thermoplastics), (R)
• definitions and identifications of key polymer properties (e.g., molecular weight, degree of polymerization, glass transition temperature, crystallinity, etc.), (R)
• types of polymerization reactions (addition, condensation, etc.), (U)
• common catalysts and typical catalyst mechanisms (chemistry perspective), (R)
• additives and their impact on the final properties of the polymer (e.g., fillers, surfactants, chain extenders, cross-linkers, etc.), (R)
• analytical methods for characterizing polymers (e.g., molecular weight analysis, molecular Structure, morphology, and physical properties), (R)
• equations for calculating properties or characterizations (e.g., degree of polymerization, the extent of reaction, equivalent weight, hydroxyl number), (U)
• mechanical properties of common polymers, (R)
• applications of common polymers, (R)
• methods of experimental investigation and manufacturing of polymers (e.g., cup foaming, small-box foaming, reaction injection molding, extrusion). (R)

This paper provides methods that can: a) attain higher levels of Blooms taxonomy, b) engage visible and active learning modes, and c) provide commercially important results. These simulation-based learning methods include activities of a) writing computer programs, b) evaluating problem statements to convert problems specifications to computer program input parameters, c) use of the computer programs to solve problems, and d) incremental addition to computer programming code to solve progressively more complex problems.
Computer programming efficiently summarizes information, and the underlying algorithms of computer code are creative by nature. This results in the achieve learning at “Analysis”, “Evaluation”, and “Creation” levels in exercises that can be completed in a matter of minutes. The following are specific examples of activities with an indication of the Blooms taxonomy level of learning associated with each activity:

1. Pre-written programs having less than 15 lines of code allow students to generate meaningful quantitative output in a matter of minutes with little background on the subject (Apply).

2. Generating concentration, temperature, and viscosity profiles (as a function of time) provide visible representation of reaction progress which helps students understand how polymer reactions proceed (Analysis).

3. Entering input parameters into the computer code to generate output of immediate practical value (e.g., gel point time) engages students in an active learning process (Evaluate).

4. Entering of input parameters can include “trial and error” (“pattern recognition” or other) input to optimize formulations or meet performance specifications (Evaluate).

5. Adding or modifying computer code to simulate increasingly complex phenomena (e.g., catalysis) achieves creation-level learning in exercise that can be completed in a few minutes (Create).

6. Extending computer simulation to predict physical properties of polymer devices (e.g., thermal conductivity, compressive strength) extends the creation process to visible association with devices/products with which the students are familiar (Create).
Active learning, visible learning, and achieving higher levels of learning all lead to improved retention by the students.

The simulation approach to learning allows more variables and properties to be related to the progress of the polymerization process. These variables and properties include:

- concentration profiles of monomers, moieties, and polymers;
- gel point time;
- degree of polymerization (DP) and polymer degree of polymerization (PDP);
- temperature and viscosity profiles;
- reaction rate constants (i.e., Arrhenius parameters);
- blowing agent concentrations and foam density; and
- mechanical properties (thermal conductivity, compressive strength, etc.).

8.3 Literature Survey on Simulation Learning

Chemistry and Chemical Engineering educators have been interested in incorporating software in student interactive learning since microcomputers were first available. Chau and Chung[104] developed four packages of a MatLab software (CHEMETRIC) for chemical technology student to provide better understanding to chemometric basic studies. The application of this software has found considerable success among chemistry and chemical engineering students in the different studying fields of like data calibration, experimental design, optimization of chemical measurement, and signal processing. The software provides questions and allows students to retake for three times.
LUCID (Learning and Understanding through Computer-based Interactive Discovery) software was incorporated for promoting student engagement in the learning process[105]. LUCID’s interactive models, easy-to-use tools, multilevel feedback, network reporting, peer assessment, and performance distributions significantly enhance the learning ability of students. The software provides interactive models to increases students’ engagement, interest, and team working.

Xie et al [106] described an open-source program called “Molecular Workbench” to simulated molecular dynamics and built a model capable of generating chemical reactions kinetics for classroom use. The software was limited to specific types of reactions that undergraduate students are familiar and ignore some chemical reaction aspects toward simplicity. The software generates dynamic 2D visual representations to assist students to reach the better understanding level to the connections between chemical reaction equations and atomic interactions.

A pre-laboratory session of interactive viscosity simulator was integrated to improve training in a chemistry laboratory[107]. Compared to the control students, the experimental group of students who participated in a pre-laboratory session was more confident during the experiment procedure of viscosity measurement and they understood better the theory behind the experiment.

The attitude of one hundred and fifteen undergraduate students to using visual media tools in the chemistry laboratory was investigated[108]. A 29-item scale was developed to obtain the students’ feedback and review. The video-recorded chemistry experiments led improves students’ learning and increases their interest general chemistry.
SimChemistry programming software was used as an active learning tool at the University College of Borås, Sweden[109]. The students were asked to write their own simulation program on molecular structure and interactions. The simulation outcomes led to a deep molecular-level understanding of the chemical concept, interactively engaging group work, and a much better ability to explain the concepts. Students interview showed that simulation created a good learning environment, close collaborations with active discussions, and many students preferred simulation learning over studying a textbook.

The effects of computer simulation on the solving ability of chemistry problems were studied[110]. Two chemistry experiments for the ammonia fountain and the ignition of a sulfur and oxygen mixture were simulated for a group of students. Students feedback on this study assumed that the major advantage of simulation was to help them selecting the proper application of the equations. The scores of a control and experimental samples of students demonstrate that using computer simulations was very helpful.

The impact of associating animations in organic chemistry on students’ comprehension was studied[111]. A designed test (Organic Chemistry Visualization Test) was utilized to measure student level of learning at the end of the class. The results reveal a positive impact of using animations along with traditional learning is an effective instructional tool for enhancing chemistry learning. The research ends up with a conclusion that teachers nowadays need to use more than traditional techniques to get the attention of students.

GeoGebra dynamic worksheets were created by Kostic et al[112] for solving quantitative composition problems. The software offers interactive connection concrete and abstract visual representations of the problem. The outcomes of using this software on
an experimental group of chemistry students were statistically significant. The results show better improvement of students’ ability to estimate quantitative relationships in a well thought-out manner, as well as to have critical anticipation about the obtained results.

This paper includes MatLab code for simulating thermoset polyurethane polymerization reactions; the initial code is based on Flory’s assumptions[96]. MatLab was adopted for this simulation because it is easy to learn, normally available for students in universities, and provides a program that can be readily extended to greater complexity.

While simulation reaction kinetics using MatLab have been published in many education papers, the current paper uniquely provides:

1. an alternative approach to learning polymer engineering,
2. programming code that provides immediate results and can be modified to simulate increasingly complex processes,
3. a visual presentation of how polymerization progresses in terms of a variety of meaningful properties, and
4. example problem statements that can be solved using simulation.

8.4 Discussion

Introduction to Thermoset Kinetics and Simulation - Polyurethane thermoset polymerization reaction has been chosen as an example for this polymer simulation. Polyurethane is a high-value thermoset polymer with a range of applications due to its high performance and versatility[6]. Typically, polyurethane is produced from the exothermic step-growth polymeric reaction of an isocyanate and a polyol monomers[4] according to Reaction Scheme 1.
RNCO + R'CH₂OH → RNCOOCH₂R \hspace{1cm} \textbf{Equation 8-1}

Isocyanate polyol PU

For polymeric reactions of organic materials, the rate of reaction is not dependent upon the concentration of compounds; but rather, the concentration of moieties (functional groups) of compounds. The moieties are defined as the functional groups (e.g. an alcohol moiety) within the polymer molecule that are responsible for polymer-bond-forming chemical reactions. To handle polymerization reactions (with a reasonable set of reactions), elementary reaction mechanisms and resulting kinetic expressions should be based on moieties rather than monomers (compounds). Table 8-1 lists the basic reactions and rate expressions of a multi-functional isocyanate and polyol monomers based on Flory’s assumption.

\begin{table}
\centering
\begin{tabular}{lll}
\hline
Rxn. # & Reaction & Rate Expression \\
\hline
1 & A + B → P & \( r_1 = k_1 f_A C_A f_B C_B \) \\
2 & A + P_B → P & \( r_2 = k_2 f_A C_A C_{P_B} \) \\
3 & B + P_A → P & \( r_3 = k_3 C_{P_A} f_B C_B \) \\
4 & P_A + P_B → P & \( r_4 = k_4 C_{P_A} C_{P_B} \) \\
\hline
\end{tabular}
\caption{Polyurethane basic reactions}
\end{table}

Initial theories of gelation and crosslinking were developed by Paul Flory, a 1974 Nobel laureate on this subject. In an approach targeting the analytical solution of equations, rather than a computer simulation, Paul Flory and Walter Stockmayer based this theory on the following three assumptions:

- All reactions occur between A and B.
• All functional groups on a branch unit are equally reactive.
• There are no intramolecular reactions.

The first of these assumptions is implicit by not including reactions beyond those provided in Table 8-1. The second of these assumptions is equivalent to the constraint that \( k_1 = k_2 = k_3 = k_4 \). The last assumption impacts the way Rxn #4 impacts the rate of change of polymer molecules (see Equation 8-3).

Table 8-2 shows a minimal set of concentrations (and their initial values) that must be calculated to simulate polymerization of polyurethane; these are calculated by solving the ordinary differential equations (ODEs) that describe their rates of change. Atomic balances allow addition concentrations of moieties on the monomers (\( C_{MA} \) and \( C_{MB} \)) and moieties on polymers (\( C_{PA} \) and \( C_{PB} \)) to be calculated as \( f_A C_A, f_B C_B, C_{Amoi} - f_A C_A, \) and \( C_{Bmoi} - f_B C_B \) respectively. It is necessary to calculate these latter four calculated quantities because they appear in the ODEs of Equation 8-2.

**Table 8-2. Concentration profiles and initial conditions that define a simplified liquid polymer reaction system**

<table>
<thead>
<tr>
<th>Component</th>
<th>Initial Condition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_A )</td>
<td>( C_{A0} )</td>
<td>Molarity of Monomer A</td>
</tr>
<tr>
<td>( C_B )</td>
<td>( C_{B0} )</td>
<td>Molarity of Monomer B</td>
</tr>
<tr>
<td>( C_P )</td>
<td>0</td>
<td>Molarity of Polymer</td>
</tr>
<tr>
<td>( C_{Amoi} )</td>
<td>( f_A C_{A0} )</td>
<td>Equivalence of Moiety A</td>
</tr>
<tr>
<td>( C_{Bmoi} )</td>
<td>( f_B C_{MB0} )</td>
<td>Equivalence of Moiety B</td>
</tr>
</tbody>
</table>
The rate expressions for the components of Table 2 are described in terms of the rate expressions of Table 1 by the Equation 8-2 ODEs.

\[ r_{A_{\text{mon}}} = \frac{dC_{A_{\text{mon}}}}{dt} = -r_1 - r_2 \]
\[ r_{B_{\text{mon}}} = \frac{dC_{B_{\text{mon}}}}{dt} = -r_1 - r_3 \]
\[ r_p = \frac{dC_p}{dt} = r_1 - r_4 \]
\[ r_{A_{\text{moi}}} = \frac{dC_{A_{\text{moi}}}}{dt} = -r_1 - r_2 - r_3 - r_4 \]
\[ r_{B_{\text{moi}}} = \frac{dC_{B_{\text{moi}}}}{dt} = -r_1 - r_2 - r_3 - r_4 \]

The solution of these ODEs is achieved through the initial value method of Matlab’s ODE45 function.

The simulations of this paper are introduced in two phases. The first phase is a basic simulation of isothermal reactions. This simulation provides output of a) concentration profiles of the monomers, polymer, and moieties; b) times at which the gel point occurs; c) impact of inter/intra polymer-polymer reactions on the gel point time; and d) profiles of the degrees of polymerization.

The second phase includes near-adiabatic reactions where the rate constants of reactions are calculated from the Arrhenius equation. To achieve near-adiabatic simulation a rate of change of temperature was added and an empirical equation was introduced to approximate viscosity as a function of degree of polymerization.
The following basis and heuristics were adopted for the Phase 1 computer code:

1. A 1-liter basis at a constant density.
2. Monomers concentration are followed where monomers are consumed when any moiety on the monomer reacts.
3. Polymers are indistinguishable once formed.
4. Polymer concentration is calculated but not used in any rate expression to avoid the propagation and compounding of any error in the polymer concentration.

**Simulation of Basic Isothermal Reactions** - Table 8-3 shows the coding of the program for a step-growth alternating copolymer formation. The global command in line 1 declares the variables and makes them available for the function file (floryrxn).

Lines 2 and 3 set the functionalities of the isocyanate and the polyol monomer respectively ($A_{\text{mon}}$ and $B_{\text{mon}}$). The vector in line 4 has the rate constants of the four reactions of Table 8-1. In this simulation example, the rate constants were assumed the same for all reactions and are not changing with temperature (isothermal conditions).

The vector $C_0$ has the initial recipes concentration (mol/l) of A monomer, B monomer, polymer, A moieties, and B moieties respectively. An isocyanate index of 1.1 was chosen for this example.
### Table 8-3. MatLab code for simulating isothermal polymerization reaction

<table>
<thead>
<tr>
<th>line #</th>
<th>Script</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><code>global fa fb k;</code></td>
</tr>
<tr>
<td>2</td>
<td><code>fa=3.5; %Functionality of Amon</code></td>
</tr>
<tr>
<td>3</td>
<td><code>fb=3.5; %Functionality of Bmon</code></td>
</tr>
<tr>
<td>4</td>
<td><code>k=[5E-3 5E-3 5E-3 5E-3]; %Rate constants</code></td>
</tr>
<tr>
<td>5</td>
<td><code>c0=[1.1 1 0 fa*1.1 fb*1]; %Initial conditions</code></td>
</tr>
<tr>
<td>6</td>
<td><code>[t,ct]=ode45('floryrxn',[0:1:250],c0) %Solves the ODEs</code></td>
</tr>
<tr>
<td>7</td>
<td><code>figure;plot(t,ct) %Plotting concentrations</code></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>line #</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><code>function ydot=floryrxn(tt,c);</code></td>
</tr>
<tr>
<td>2</td>
<td><code>global fa fb k intra;</code></td>
</tr>
<tr>
<td>3</td>
<td><code>CPA=c(4)-fa*c(1); %Amoi in polymer</code></td>
</tr>
<tr>
<td>4</td>
<td><code>CPB=c(5)-fb*c(2); %Bmoi in polymer</code></td>
</tr>
<tr>
<td>5</td>
<td><code>r1=k(1)*fa*c(1)*fb*c(2); %Monomer + monomer rxn</code></td>
</tr>
<tr>
<td>6</td>
<td><code>r2=k(2)*fa*c(1)*CPB; %Monomer A + polymer rxn</code></td>
</tr>
<tr>
<td>7</td>
<td><code>r3=k(3)*CPA*fb*c(2); %Polymer + monomer B rxn</code></td>
</tr>
<tr>
<td>8</td>
<td><code>r4=k(4)*CPA*CPB; %Polymer + polymer rxn</code></td>
</tr>
<tr>
<td>9</td>
<td><code>ydot(1)=-r1-r2; %Rate of change of Amon</code></td>
</tr>
<tr>
<td>10</td>
<td><code>ydot(2)=-r1-r3; %Rate of change of Bmon</code></td>
</tr>
<tr>
<td>11</td>
<td><code>ydot(3)=r1-r4; %Rate of change of polymer</code></td>
</tr>
<tr>
<td>12</td>
<td><code>ydot(4)=-r1-r2-r3-r4; %Moiet A accumulation</code></td>
</tr>
<tr>
<td>13</td>
<td><code>ydot(5)=-r1-r2-r3-r4; %Moiet B accumulation</code></td>
</tr>
<tr>
<td>14</td>
<td><code>ydot=ydot';</code></td>
</tr>
</tbody>
</table>
The Script file calls upon the ODE45 function (line 6) to solve the ODEs specified in the “floryrxn” function. The time span of 0 to 250 seconds is set in the ODE45 command line. Lines 7 in the Script is for drawing the concentration profiles.

The material balance of A and B moieties are shown in lines 3 and 4 in “floryrxn”. Lines 5 – 9 are the rate expressions of the basic reactions and the derivatives (lines 9 – 13) specify the ODEs describing the rates of change of the first five concentrations in Table 8-2.

The use of this code in a course on polymer engineering provides for the efficient specifying of a problem statement having an abundance of parameters and fundamental equations. And the program is able to transform these fundamental parameters and equations into meaningful visible output. This simulation approach far exceeds what is possible in traditional approaches putting forth equations which lack the tools needed to transform the equations into results to which the students can better relate.

The simulation results of Figure 8-1 show the concentration profiles of the monomers, moieties, and polymer. Monomers and moieties concentration are decreasing gradually from their initial conditions as they consumed with the reactions proceed.

Polymer concentration become negative at a time of about 62 seconds. This is not realistic; it is an artifact of the numeric method. The simulation results after the polymer concentration become negative are all in error.
Figure 8-1. Visual representation of concentrations profile of isothermal polymerization reactions.

The graph is specifically generated from the code of Table 8-3. The following lines of code are added after the plot line to create axis titles and legend: “xlabel('Time (s)'); ylabel('Concentration (mol/l)'); legend('A monomer','B monomer','Polymer','A moiety','B moiety’)”

One approach to prevent this error is to force a very small step size. An alternative approach is to set the ODE solver options so that the concentration variable cannot become negative by using the “odeset” function. To add this option, line 6 in the Script of Table 8-3 should be replaced by the following lines.

Script/Line#6: \[ \text{options} = \text{odeset('NonNegative',1:5)} \]

\[ \text{Script/Line#6b: } [t, ct] = \text{ode45('floryrxn',[0:1:250],c0, options)] } \] \hspace{1cm} \text{Equation 8-2}

Figure 8-2 illustrates concentration profiles for a code that incorporates the Equation 8-2 code.

The polymer concentration of zero represents the time at which polymer segments crosslink into one large molecule. This is the gel point; the time of which is an important specification in industrial processes.
Initially, the polymer concentration increases due to its formation. As more polymer is present and more of the reactive functional groups are attached to that polymer, polymer-polymer reactions occur leading to a decrease in polymer concentration. Eventually the crosslinking leads to a concentration that asymptotically approaches zero.

The results of Figure 8-1 and Figure 8-2 provide immediate output in a visible format that can provide improved learning and retention. The results also provide an approximate to the gel point time which is not possible without simulation. Unfortunately, an isothermal reaction is not realistic for these systems, and gel point estimates of practical value are only possible with the near-adiabatic code provided later in this paper.

Figure 8-2. Visual representation of concentrations profile of isothermal polymerization reactions. The graph is specifically generated from the code of Table 8-3 and Equation 8-2. The following lines of code are added after the plot line to create axis titles and legend: “xlabel('Time (s)'); ylabel('Concentration (mol/l)'); legend('A monomer','B monomer','Polymer','A moiety','B moiety')”
Flory’s assumptions limit both the accuracy and capabilities of simulation. The computer program code can be readily modified to deviate from these assumptions.

It is common practice in the urethane industry to use water as a blowing agent to make rigid foams. The mechanism for this includes water reacting with the A monomer (isocyanate) to make carbon dioxide gas. The additional reactions to generate carbon dioxide can be added to the simulation code—this is one example of the need to deviate from Flory’s first assumption.

Flory’s second assumption is also inaccurate for polyurethane systems. Polymer propagation rate constants will vary due to: a) primary versus secondary location of moieties, b) the impact of viscosity on reaction rates combined with the large changes in viscosity that occur during thermoset polymerization and c) variations in rate constant with the size of the polymer where it is expected that \( k_1 > k_2 \approx k_3 > k_4 \). The last of these is of least significance if the impact of viscosity (“b”) is taken into account.

Flory’s assumption of no intra-polymer reactions (third assumption) becomes increasingly inaccurate as the gel point is approached and with increasing functionalities of A and B monomers. As functionality increases, the number of unreacted monomers on a polymer increases, and since these unreacted monomers are in close proximity (on the same molecule) they will tend to react in intra-polymer reactions. Also, the reactions only proceed until the concentration of polymer is zero, at which point it would be deduced that all functional groups are in one molecule and all reactions are intra-molecular.
The topic of intra-molecular reactions is addressed by estimating the fraction of polymer-polymer reaction that is intra-molecular by introducing the fraction “intra” into the rate of change of the polymer concentration as summarized by Equation 8-3.

\[ r_P = \frac{dC_P}{dt} = r_1 - r_4(1 - \text{intra}) \quad \text{Equation 8-3} \]

Polymer self-reactions (intra-molecular) reduces the rate at which moiety reactions reach the gel point. The inclusion of this in the model will lead to higher critical extents of reaction at the gel point.

The impact of intra polymer-polymer reactions can be included in the programming code of Table 8-3 by replacing/adding the code of Equation 8-4. This example incorporates a constant for the value of intra; in practice this variable is a function of at least polymer degree of polymerization (PDP).

Script/floryrxn: \texttt{global fa fb k intra}

Script/Line#4b: \texttt{intra = 0.1; \%Fraction intra reactions}

floryrxn/Line#11: \texttt{ydot(3) = r1 - r4 * (1 - intra);} \quad \text{Equation 8-4}

The sensitive analysis of Figure 8-3 shows that increasing the fraction of intra polymer-polymer reactions increases the time at which the gel point is. The learning output of this figure are in how the fraction of intra polymers reactions impacts polymer concentration and gel point time.
Figure 8-3. Impact of fraction intra-reactions on polymer concentration and gel point time. The figure was generated by drawing polymer concentration of three runs using MS Excel.

The concentration profile of monomers and polymer allows the calculation of the average degree of polymerization (DP) during the reaction. This can be done by adding the Equation 8-5 lines of code to the code of Table 8-3. Similar code can be written to calculate average PDP.

Script/Line#7b: \[ dp = \frac{c0(1) + c0(2)}{ct(:,1) + ct(:,2) + ct(:,3)} \] \[ \text{Equation 8-5} \]

Script/Line#7c: figure; plot (t, dp) \[ \% \text{Plotting dp} \]

The first line of the Equation 8-5 code calculates the degree of polymerization from the definition of the initial concentration of monomers divided by the concentration of monomers and polymer during the reaction. The second line is for plotting the degree of polymerization profile as exemplified by Figure 8-4.
Virtual time estimates of degree of polymerization provide visible results (Figure 8-4) and with the profiles providing more-meaningful learning than single point estimates possible used in traditional textbook approaches.

**Simulation of Near-Adiabatic Reactions** - The Table 8-3 simulation code is a straightforward application of Flory’s assumptions, and as such, it is a good starting point for a textbook. Few if any polyurethane-forming reactions are isothermal; most are near-adiabatic. Near adiabatic implies that only a small fraction of the heat is lost before the gel point is reached due to low surface-area to volume ratios of molds used to make thermoset devices.

To simulate near-adiabatic polymerization, the Arrhenius equation (see Equation 8-6) is used to calculate the reactions rate constant of the reactions in Table 8-1.
\[ k = k_0 \times e^{-\frac{E_0}{RT}} \]  \hspace{1cm} \text{Equation 8-6}

Also, the rate of change of the temperature must be added as summarized by Equation 8-7 (based on the heat balance). The heat balance equation includes a term for the loss of heat to the mold.

\[
\frac{dT}{dt} = \frac{\sum (\Delta H_i r_i) + U Ar (T_s - T)}{m C_p} \hspace{1cm} \text{Equation 8-7}
\]

To simplify the simulation, the heat of reaction of A and B moieties in line 5 was assumed the same whether these moieties were attached to a monomer or a polymer. Thermodynamic properties in this simulation are assumed constants and not changing with temperature. Table 8-4 and Table 8-5 show the MatLab program coding of this simulation.

The overall heat transfer coefficient “U” (line 6) is approximated as a constant. The area (Ar) for heat transfer can be incorporated into U or considered separately. The ambient temperature “Ts” was added for heat loss calculation and separated from the initial condition (of monomers) temperature “T0”.

190
Table 8-4. Script of MatLab code for simulating near-adiabatic polymerization reaction

<table>
<thead>
<tr>
<th>line#</th>
<th>Script</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>\textbf{global} fa fb mCp Hrxn T0 k0 E0 Ts U Ar intra;</td>
</tr>
<tr>
<td>2</td>
<td>fa=3.5; %Functionality of Amon</td>
</tr>
<tr>
<td>3</td>
<td>fb=3.5; %Functionality of Bmon</td>
</tr>
<tr>
<td>4</td>
<td>mCp=1.5; %Total mass*Heat capacity</td>
</tr>
<tr>
<td>5</td>
<td>Hrxn=-70; %Heat of reactions</td>
</tr>
<tr>
<td>6</td>
<td>U=1; %Overall heat transfer coeff.</td>
</tr>
<tr>
<td>7</td>
<td>T0=295.15; %Initial temperature</td>
</tr>
<tr>
<td>8</td>
<td>Ts=295.15; %Ambient temperature</td>
</tr>
<tr>
<td>9</td>
<td>Ar=0.0025; %Surface area of the gel</td>
</tr>
<tr>
<td>10</td>
<td>E0=[40 40 40 40]; %Activation energy</td>
</tr>
<tr>
<td>11</td>
<td>k0=[1E4 1E4 1E4 1E4]; %Pre-exponential factor</td>
</tr>
<tr>
<td>12</td>
<td>intra=0; %percent intra reactions</td>
</tr>
<tr>
<td>13</td>
<td>c0=[1.1 1 0 fa<em>1.1 fb</em>1 T0]; %Initial conditions</td>
</tr>
<tr>
<td>14</td>
<td>options=odeset(’NonNegative’,1:5);</td>
</tr>
<tr>
<td>15</td>
<td>[t,ct]=ode45(’floryrxn’,[0:1:150],c0,options);</td>
</tr>
<tr>
<td>16</td>
<td>dp=(c0(1)+c0(2))/(ct(:,1)+ct(:,2)+ct(:,3)) %DP calc</td>
</tr>
<tr>
<td>17</td>
<td>figure;plot(t,ct(:,6)) %Plotting dp</td>
</tr>
</tbody>
</table>
Table 8-5. Function of MatLab code for simulating near-adiabatic polymerization reaction

<table>
<thead>
<tr>
<th>line#</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>function ydot=floryrxn(tt,c);</td>
</tr>
<tr>
<td>2</td>
<td>global fa fb k mCp Hrxn k0 E0 Ts U Ar intra;</td>
</tr>
<tr>
<td>3</td>
<td>for i=1:4</td>
</tr>
<tr>
<td>4</td>
<td>k(i)=k0(i)<em>exp(-E0(i)/(0.008314</em>c(6))); %rate constants calc.</td>
</tr>
<tr>
<td>5</td>
<td>end</td>
</tr>
<tr>
<td>6</td>
<td>CPA=c(4)-fa*c(1); %Amoi in polymer</td>
</tr>
<tr>
<td>7</td>
<td>CPB=c(5)-fb*c(2); %Bmoi in polymer</td>
</tr>
<tr>
<td>8</td>
<td>r1=k(1)<em>fa</em>c(1)<em>fb</em>c(2); %Monomer + monomer rxn</td>
</tr>
<tr>
<td>9</td>
<td>r2=k(2)<em>fa</em>c(1)*CPB; %Monomer A + polymer rxn</td>
</tr>
<tr>
<td>10</td>
<td>r3=k(3)<em>CPA</em>fb*c(2); %Polymer + monomer B rxn</td>
</tr>
<tr>
<td>11</td>
<td>r4=k(4)<em>CPA</em>CPB; %Polymer + polymer rxn</td>
</tr>
<tr>
<td>12</td>
<td>ydot(1)=-r1-r2; %Rate of change of Amon</td>
</tr>
<tr>
<td>13</td>
<td>ydot(2)=-r1-r3; %Rate of change of Bmon</td>
</tr>
<tr>
<td>14</td>
<td>ydot(3)=-r1-r4*(1-intra); %Rate of change of polymer</td>
</tr>
<tr>
<td>15</td>
<td>ydot(4)=-r1-r2-r3-r4; %Moity A accumulation</td>
</tr>
<tr>
<td>16</td>
<td>ydot(5)=-r1-r2-r3-r4; %Moity B accumulation</td>
</tr>
<tr>
<td>17</td>
<td>ydot(6)=(Hrxn*(-r1-r2-r3-r4)+U<em>Ar</em>(Ts-c(6)))/(mCp);</td>
</tr>
<tr>
<td>18</td>
<td>ydot=ydot';</td>
</tr>
</tbody>
</table>

The resulting output of temperature profile is shown in Figure 8-5. Temperature starts from the initial value of 295.15 K and increased as heat generated from the exothermic reactions. Initial slope of temperature profile is highly impacted by the assumed value of the pre-exponential factors of Arrhenius equation, curve hump is highly impacted by the
assumed value of activation energies, maximum reaction temperature depends on heat of reactions, and the slop of the last part of the temperature curve depends on the overall heat transfer coefficient.

Figure 8-5. Visual representation of temperature profile. The graph is specifically generated from the code of Table 8-4. The following lines of code are added after the plot line to create axis titles:

```
"xlabel('Time (s)'); ylabel('Temperature (K)')"
```

The learning outcome of simulating temperature profiles is a virtual-time realization of how values of thermodynamic and kinetic parameters impact the temperature. Temperature profiles contain valuable information, such as an approximation of extent of reaction, and can be readily verified in experimental studies.

An important addition to the Table 8-4 code is the calculation of viscosity. Studying viscosity change of thermoset polymerization reaction is highly important for a number of reasons (e.g., measure of progress of polymerization, flow dynamics in molds, practical realization of the gel point). From a simulation perspective, the viscosity is a key parameter
that ultimately impacts diffusion rates. Diffusion rates impact reaction rate constants and mass transfer for blowing agents from the resin phase to the bubbles/cells cause foam formation. Viscosity profiles can be added to the Table 4 code through use of an empirical equation based on the degree of polymerization such as provided by Equation 8-8.

\[
\text{vis} = 500 \times \text{dp} \times \exp(0.005 \times \text{dp} + 2.13 \times \text{dp}/c(t;6) + 0.32)
\]

Equation 8-8

Figure 8-6 provides visual presentation of viscosity profile. The viscosity of the resin is increasing several orders of magnitude during the reaction, eventually going toward infinity as DP goes to infinity. A variation of Equation 8-8 code would use PDP rather than DP with the choice of PDP versus DP being a topic of academic discussion.

Figure 8-6. Visual representation of viscosity profile of resin during the reaction. The graph is specifically generated from the code of Table 8-4 and considering Equation . The following lines of code are added after the plot line to create axis titles and legend: \("xlabel(\"Time (s)\")\; ylabel(\"Viscosity (cp)\")\). Axis limits of were set by adding \("axis([0,150,0,1E5])\)". 

194
Students can use this figure to understand the dramatic change of thermoset viscosity during the reaction and to identify the time at which the gel point occurs. The results provide an approximate to the gel point time that approaches realistic conditions and is thus useful for practical applications.

Catalysts are commonly used in polymerization reactions to increase the rates of reactions by reducing the activation energy required for the reactions. Catalytic reactions were reported to follow chain-growth mechanism as oppose to the step-growth mechanism of homogeneous reaction[103]; however, for simplicity, a step-growth mechanism is easier to incorporate[63]. Equation 8-9 code provides a method to incorporate step-growth catalysis to the code of Table 8-4.

![Equation 8-9](image)

Figure 8-7 provide a comparison of reaction temperature at different catalyst loadings. The increase in the rate of reactions result faster temperature profile. The learning outcome of this example is an improved understanding of the role of catalysis and how catalysts impact the rate of reactions and gel point time. Possible advanced assignments on this topic would include considering chain-growth mechanism for catalytic reactions.
Figure 8-7. Impact of catalyst loading on reaction temperature. The figure were generated by drawing reaction temperature of three runs using MS Excel.

**Example Textbook Problem Statements** - The key point of this paper is to identify how a textbook on polymer engineering can be designed around the use of simulation of polymer-forming reactions. Goals include attaining higher level learning outcomes and capabilities more-directly applicable to practical applications.

Instructors can give simulation based questions to students is a short question statement in common online learning platforms such as Canvas and Blackboard. Students are able to copy programming lines, paste them on MatLab on a script and functions, separate programming lines, and run the simulation in less than two minutes and few more minutes to add or modify some lines in the simulation to get the answer. Table 8-6 shows two questions for isothermal and near-adiabatic simulations with question statements and the answer in the form of polynomial equation.
A polymer-forming reaction network includes the following reactions: (1) A+B→P, (2) A+P→P, (3) B+P→P, and (4) P+P→P. The script file of the simulation program is:

global f Ts k0 E0 UAovmCp HovmCp; f=[3.5 3.5]; T0=295.15; Ts=295.15;
UAovmCp=0.002; HovmCp=-45; E0=[40 40 40 40]; k0=[1E4 1E4 1E4 1E4]; options
=odeset('NonNegative',1:5); [t,ct]=ode45('floryrxn',[0:1:150],[1.1 1 0 f(1)*1.1 f(2)*1
T0],options); and corresponding function: function ydot=floryrxn(tt,c);
global f Ts k0
E0 UAovmCp HovmCp; for i=1:4;k(i)=k0(i)*exp(-E0(i)/(0.008314*c(6)));end;
Pmoi=[c(4)-f(1)*c(1) c(5)-f(2)*c(2)];
r=[k(1)*f(1)*c(1)*f(2)*c(2) k(2)*f(1)*c(1)*Pmoi(2) k(3)*Pmoi(1)*f(2)*c(2)
k(4)*Pmoi(1)*Pmoi(2)]; ydot=[-r(1)-r(2);-r(1)-r(3);r(1)-r(4);sum(r);
sum(r);HovmCp*(-sum(r))+UAovmCp*(Ts-c(6))].

a) What is the concentration of A moieties after [X] seconds?

Answer as Polynomial equation: \[-1.125 \cdot 10^{-7} \cdot X^4 - 2.5 \cdot 10^{-7} \cdot X^3 + 0.000131 \cdot X^2 - 0.02098 \cdot X + 3.948; \ 20 < X < 60.\]

b) What is the gel point time if the intra polymer-polymer reactions is [Y]?

Answer as Polynomial equation: \[33.3333 \cdot Y^3 - 10 \cdot Y^2 + 12.66667 \cdot Y + 57.2; \ 0.1 < Y < 0.4.\]

c) What is maximum reaction temperature if the initial temperature is [Z]?(assume no intra reactions)

Answer as Polynomial equation: \[-4.20268 \cdot 10^{-8} \cdot Z^4 + 2.83596 \cdot 10^{-5} \cdot Z^3 - 0.0032 \cdot Z^2 + 305.7367507; \ 300 < Z < 315.\]

d) What is the degree of polymerization after [W] seconds? (assume no intra reactions)

Answer as Polynomial equation: \[0.0092 \cdot W^4 - 1.794666 \cdot W^3 + 122.35 \cdot W^2 - 3149.83 \cdot W + 24356; \ 40 < W < 60.\]
Table 8-7 provides example questions based on use of simulation code including questions that target different levels of learning. All questions use a common starting sentence that introduces the applicable program code.

The “Apply” questions applying a new value in the program and getting an answer from the solution. The “Analysis” requires multiple runs and reporting the difference. This comparison helps to analyze the database and to identify the impact of each variable. The “Evaluate” questions look for evaluating the reactions toward achieving an optimum condition. Questions in the “Create” level requires adding equations to get the profile of new variable.

An important advantage of the simulation code presented in this paper is the ability to incrementally expand the code to simulate the most common industrial applications. Table 8-8 lists advanced topics that are within the capabilities of extended simulation code.
Table 8-7. Example of simulation question and different testing levels of learning

A base-case near-adiabatic polymer-reaction simulation program (reacting at constant density) is based on Flory’s assumptions and includes the following code: fa (3.5), fb (3.5), k_o (1E4 1E4 1E4 1E4; l/mol/s), E_o (40 40 40 40), mCp = 1.5 (kJ/C for a 1-liter basis), H_rxn = -70 (kJ/mol, same for all reactions) and initial concentrations and T (1.1 0 fa*1.1 fb*1 295.15).

Apply

- What is the initial concentration of A moieties if the functionality of A monomer is 4?
- What is the concentration of A moieties at 100 seconds into the reaction?

Analysis

- What is the time at which gel point occurs (assuming no intra reactions)?
- What is the difference in maximum reaction time if the monomers were pre-heated to 310K?

Evaluate (Includes changes in program input based on feedback information from multiple simulations.)

- What is the minimum preheating temperature needed to achieve a peak reaction temperature of 150°C?
- What isocyanate index results the highest reaction temperature?

Create (Includes modifying code versus what is provided in Table 8-4)

- What is the gel point time if the fraction of intra reactions is 0.2?
- What is the gel point time if 0.1 grams of a step-growth catalyst is added that results in (and only in) a 20% reduction in activation energy (the rate constant has a unit of 1/g-catalyst)?
### Table 8-8. List of advanced topics, approach method, and their corresponding learning and operational utility

<table>
<thead>
<tr>
<th>Advanced topics (Method)</th>
<th>• Learning outcome (L) and operational utility (O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractions of primary and secondary moieties [57]. <em>(primary and secondary moieties reactions)</em></td>
<td>• Identify fractional content of primary vs secondary moieties. (L/O)</td>
</tr>
<tr>
<td></td>
<td>• Comparing different monomers. (O)</td>
</tr>
<tr>
<td>Chain growth mechanism for catalytic reactions [103]. <em>(catalyst coupling/decoupling reactions)</em></td>
<td>• Identifying the mechanism of catalytic reaction. (L)</td>
</tr>
<tr>
<td></td>
<td>• Chain-growth mechanism results higher viscosity. (L)</td>
</tr>
<tr>
<td></td>
<td>• Identifying catalyst-moiety attachment. (O)</td>
</tr>
<tr>
<td>Mass transfer limitation [85] <em>(impact of diffusion as reversible reaction or on the frequency factor)</em></td>
<td>• Impact of viscosity increase on rate of diffusion. (L)</td>
</tr>
<tr>
<td></td>
<td>• Identify reaction/diffusion limited regions. (L)</td>
</tr>
<tr>
<td></td>
<td>• Evaluating the effectiveness of similar reactive monomers of different viscosities. (L/O)</td>
</tr>
<tr>
<td>Chemical/physical blowing agent (BA) [32, 74]. <em>(Blowing agents fn - rate of BA evaporation)</em></td>
<td>• Calculating rate of diffusion and diffusion. (L)</td>
</tr>
<tr>
<td></td>
<td>• Identify fraction of BA diffuses vs retained. (L/O)</td>
</tr>
<tr>
<td></td>
<td>• Predicting cell diameter, pressure inside cells, foam density, and foam shrinkage. (L/O)</td>
</tr>
<tr>
<td>Viscosity profile of resin [37]. <em>(Viscosity fn - group contribution)</em></td>
<td>• Viscosity increase during the reactions. (L/O)</td>
</tr>
<tr>
<td></td>
<td>• Prediction of gel point time. (L/O)</td>
</tr>
<tr>
<td>Heat capacity profile. <em>(Heat capacity fn - group contribution)</em></td>
<td>• Heat of capacity increase during the reactions. (L)</td>
</tr>
<tr>
<td></td>
<td>• Impact of monomers heat capacities. (L/O)</td>
</tr>
<tr>
<td>Impact of surfactant. <em>(surface tension calculation)</em></td>
<td>• Impact of surfactant on blowing agent efficiency and cell diameter. (L/O)</td>
</tr>
<tr>
<td>Prediction of physical properties [87]. <em>(thermal conductivity and compressive strength fn)</em></td>
<td>• Factors impacting final properties of the foam. (L/O)</td>
</tr>
<tr>
<td></td>
<td>• Predicting the final properties of the foam. (O)</td>
</tr>
</tbody>
</table>
**Extended Simulation Capabilities** – As the complexity of the programming increases, the need to organize the program through use of functions and overall algorithms becomes increasingly important. Figure 8-8 is a block diagram showing the programming code of Table 8-4. For the example code of Table 4, the recipe and physical property estimates are provided in lines of code. The only function used in the program was ODE45 which solves the ordinary differential equation initial condition problem and returns concentrations and temperature profiles solution.

As the recipes and database become more comprehensive it is advantageous to place them in separate functions or databases that are called upon by the Script code. Recipes and database include initial monomer concentration, monomers functionalities, and kinetic and thermodynamic properties. “floryrxn” function calculates reaction rate constants, mass balance of moieties, rates of reactions, and rate of change of components.

![Block diagram of the simulation program of Table 8-4](image)

*Figure 8-8. Block diagram of the simulation program of Table 8-4*
Figure 8-9 provides a block diagram of a more advanced simulation. In this block diagram, ODE45 function calls on the derivatives of concentration profile, reaction temperature, and rate of blowing agent evaporation in the “floryrxn” function. In addition, ODE45 is exchanging concentrations and temperature of each iteration with the viscosity and heat capacity function of the resin and account its impact on reactions. This block diagram is subject to future extension to account the impact of surfactant and fire retardant on the reaction kinetics and/or on the final properties of the foam.

A well-written code allows the functions and database to be modified without impacting the Script or other functions.

![Block diagram of advanced simulation](image)

**Figure 8-9. Block diagram of advanced simulation**

### 8.5 Conclusions

Use of simulation code as a learning platform provides the ability to achieve higher level learning outcomes in problem statements that can be solved in a few minutes as compared to days or weeks in alternative platforms. For polymer engineering, simulation code is able
to achieve what is substantially not attainable in traditional textbook approaches. Examples outcomes simulation-based learning include estimating gel point times for non-isothermal polymer-forming processes, evaluating the impact of catalysts on gel point times, and evaluating how recipes may or may not reach critical maximum temperatures as needed to fully react the monomers in the recipe.

The paper has provided example code, example simulation output, example problem statements, and a summary of how the capabilities of the simulation can be incrementally expanded. The capabilities of this learning methodology represent an important and needed advance, especially on the topic of polymer engineering.

8.6 Acknowledgments

The authors thank the Higher Committee for Education Development (HCED) in Iraq for their financial support.

8.7 Nomenclature

<table>
<thead>
<tr>
<th>Equations symbols</th>
<th>Coding symbols</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>Ar</td>
<td>Base and lateral area of the gel (m²)</td>
</tr>
<tr>
<td>Amoi</td>
<td></td>
<td>Concentration of “A” moieties (mol/l)</td>
</tr>
<tr>
<td>Cₐ</td>
<td>Amon</td>
<td>concentration of “A” monomer (mol/l))</td>
</tr>
<tr>
<td>BA</td>
<td></td>
<td>Blowing agent</td>
</tr>
<tr>
<td>Bmoi</td>
<td></td>
<td>Concentration of “B” moieties (mol/l)</td>
</tr>
<tr>
<td>Cₐ</td>
<td>Bmon</td>
<td>concentration of “B” monomer (mol/l))</td>
</tr>
</tbody>
</table>
c Concentration (mol/l)
c0 Initial conditions (mol/l)
CMA Concentration of “A” on monomer
CMB Concentration of “B” on monomer
CPA CPA Concentration of A moieties in polymer (mol/l)
CPB CPB Concentration of A moieties in polymer (mol/l)
ct Output concentrations in the programming code (mol/l)
DP dp Degree of polymerization
E0 E0 Activation energy (kJ/mol)
fa fa Functionality of A monomer
fb fb Functionality of B monomer
Hrxn Hrxn Heat of reactions (kJ/mol)
ρintra intra Fraction intra polymer reactions
K0 K0 Pre-exponential factor of Arrhenius equation
mCp mCp Total mass*Heat capacity (kJ/K)
P Polymer concentration (mol/l)
PDP Polymer degree of polymerization
R 0.008314 Gas constant (kJ/K.mol)
ri ri Rate expression of reaction “i” (mol/l/s)
T Reaction temperature (K)
T0 T0 Initial temperature (K)
TS TS Ambient temperature (K)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>Overall heat transfer coefficient (kJ/mol/s)</td>
</tr>
<tr>
<td>dC/dt</td>
<td>Rate of change of component concentration of temperature</td>
</tr>
<tr>
<td>ydot</td>
<td>Rate of change of component concentration of temperature</td>
</tr>
</tbody>
</table>
CHAPTER 9. CONCLUSIONS AND FUTURE WORK

9.1 Conclusions of Current Research

A computer-based program on simultaneous solution of ordinary differential equations in combination with mass balance constraints was established to simulate polyurethane resin and foam forming reactions.

Simulating of polyurethane foaming reaction provides insight in the effectiveness of physical and chemical blowing agents. The results allow for conclusions based on agreement of simulated temperature and density profiles with experimental data. For a series of C₅ – C₆ physical blowing agents, a single fitted parameter for the product of the boundary-layer thickness and the molecular radius was included in the overall mass transfer coefficient and provided a fitted parameter applicable to the range of blowing agents. The single fitted parameter provides consistency that validates the model and supports extrapolating the other blowing agents.

A primary mechanism of loss of effectiveness of blowing agents was identified to be the entrapment in the resin phase. As the reaction system reaches its gel point, the rate of diffusion of the blowing agent decreased rapidly with part of the blowing agent entrapped in the resin matrix; this is the main reason for lack of effectiveness of some blowing agents. The carbon dioxide produced from water reactions tends to have high efficiency relative to physical blowing agents with lower fractions entrapped in the resin. Simulation allows estimating the pressure of the blowing agent gas inside the foam’s cells and the rate of growth of the foam’s cells.
The current simulation of polyurethane polymerization reactions and foaming process was used to assist in formulation modification to allow the use of 100% bio-based polyols while avoiding foam shrinkage. Maximum reaction temperature provided a benchmark that correlated with reduced shrinkage. Preheating monomers and adding glycerol to the bio-based polyol were both effective at increasing maximum reaction temperature. The first approach leads to an increase in the initial rates of reaction and leads to a faster and higher maximum temperature, and the second approach increases hydroxyl number and the heat of reaction. This simulation study provides a tool to better utilize bio-based polymers in thermoset formulations.

The impact of the rapid decrease in mass transfer due to viscosity increase during polyurethane polymerization reactions was successfully simulated using two approaches. The first approach considers the rate of diffusion and reaction of the reacting moieties as sequential mechanisms described by sequential power law rate expressions. This approach shows that simulation incorrectly predicts that reaction temperature stops increasing after the gel point when considering only inter-molecular diffusion mechanism. Reaction temperature was successfully simulated by incorporating intra-molecular mechanism in parallel with inter-molecular diffusion.

The second approach incorporated the impact of diffusion on reaction rates to changes in the Arrhenius pre-exponential factor. The pre-exponential was presented as the sum of inter-molecular diffusion (viscosity-dependent term) and intra-molecular term (temperature-dependent term). This approach relies on fewer parameters and on solving fewer differential equations. The two approaches were successfully able to exhibited two inflection points prior to achieving a maximum reaction temperature. This study has
demonstrated the "hindered" secondary alcohols can be dropped when reaction rates include a viscosity dependence. The same frequency factor was used for homogeneous and catalytic reactions where the impact of catalyst is reflected in lower activation energies.

The frequency factor of Arrhenius equation was identified as the summation of viscosity-dependent and temperature-dependent terms to account the impact of intermolecular diffusion and the rate of intra-molecular movement that leads to moiety collision. The manner in which viscosity of polyurethane thermoset reactions increases made it possible to share the same frequency factor over a range of polyol reagents. Intra-molecular movements (the rotational movements of segments) as assumed to be proportional to the reaction temperature to a power between 1.0 and 0.5. The rate constant for the reaction of primary alcohol moieties were set at six times the reaction rate constant of the secondary alcohol moieties. This research provides:

- an advance theory, insight, and consistency when pursuing the attaining of the maximum information from reaction rate data.
- a “base case” of trends in reaction rate constants of a range of molecules that can be used to identify more fundamentally-correct activation energies.
- the advantage of replacing the fraction of “hindered-secondary” alcohol moieties with a more fundamentally-correct approach of simulating the impact of viscosity in a inter-molecular diffusion term.
- for a reduced number of fitted parameters needed for simulating thermoset reactions over a class of reagents.
• increased consistency of trends in activation energies where better catalysts provide lower activation energies.

The observation of different viscosity versus temperature profiles of homogeneous and heterogeneous reactions leads to the conclusion that catalytic reactions introduces different polymerization mechanisms. For urethane-forming reactions, the faster viscosity versus temperature profile of catalytic reactions was hypothesized as due to a chain-growth mechanism as oppose to the step-growth mechanism of the homogeneous reactions. Chain-growth results in fewer polymer molecules with higher molecular weight as compared to the step-growth mechanism which results more polymers molecules with lower molecular weight at the same extent of reaction.

Dozens of ordinary differential equations (ODEs) of reactions rate equations and rate of change of components were solved simultaneously for chain-growth and step-growth mechanisms. The number of ODEs was reduced by considering a) the value of $k_{\text{coupling}}$ and the ratio of $k_{\text{coupling}}$ to $k_{\text{decoupling}}$ has minimal impact on simulation results above a threshold of high value, and b) an equilibrium between free catalyst concentration and attachment to moieties for handling the prospect that more than one catalyst molecule may attach to the same polymer molecule. Two average degrees of polymerizations were calculated to distinguish between the different resulting molecular weight distributions of the polymers resulting from the step-growth and chain-growth mechanisms to simulate the differences in viscosity profiles.

This research led to the following observations:
Homogeneous reactions tend to be faster at the initial stages of reactions and the catalytic reactions becomes dominant as the reactions proceeds.

The number of catalyst molecules attached to large polymer molecules at high extents of reaction can be successfully simulated by considering Hougen-Watson model.

Inter- and intra-polymerization were distinguished toward accurately predicting gel points.

Different ratios of the rate of coupling and decoupling of the catalyst result in different ratios of urethane moieties form step and chain mechanisms.

The simulation predicts high consumption of catalyst molecules which later recovered to the initial concentration after all moieties have reacted.

The mechanism of whether the catalyst is interacting with alcohol moieties versus the mechanism where the catalyst can remain coupled with either hydroxyl or isocyanate moiety was successfully distinguished in the simulation.

9.2 Recommendations for Further Research

The knowledge and insights gained form the simulation research of this project paved the way further studies by providing better understanding of thermoset reactions and foaming processes, applying simulation to assist optimizing formulation and predicting final properties. Future extension to the current simulation may include:

- Characterization of isocyanate moieties.
- Predicting final properties of the foam (compressive strength, thermal conductivity).
• Evaluating the impact of increasing maximum reaction temperature on thermal conductivity and compressive strength of the resulting foam.

• Studying the impact of surfactants and fire retardants.

• Identifying the mechanism of different catalyst attachments based on simulation where catalyst may interact with alcohol moieties or with both alcohol and isocyanate moieties.

• Modelling epoxy group fate in urethane formulation.

• Prediction/Correlation of glass transition temperature.

• Increasingly accurate prediction of foam failure and improved insight into modes of foam failure.

• Simulation of Bubble/cell bursting and closed cell content.
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VITA

Harith H. Al-Moameri was born in Baghdad, Iraq. He received his B.S. and M.S. in Chemical Engineering from the University of Baghdad, Iraq. During his Ph.D. study, he published four peer-review journal papers and submitted three papers as first author and he received the 2017 award of outstanding Ph.D. student from the Chemical Engineering department / University of Missouri-Columbia. Harith’s research has primarily focused on modeling and experimental study of polyurethane foaming reactions, reaction kinetics and polyurethane polymerization mechanisms. Impact of mass transfer limitation, initial reaction temperature, and gel point were also studied and a MatLab program was written to simulate polymerization and foaming reactions.