

# **POLYURETHANE RIGID FOAMS MODELING PROJECT**

---

A Thesis

presented to

the Faculty of the Graduate School

at the University of Missouri-Columbia

---

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

---

By

Yusheng Zhao

Dr. Galen Suppes, Thesis Advisor

MAY 2013

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

POLYURETHANE RIGID FOAMS MODELING PROJECT

presented by Yusheng Zhao,

a candidate for the degree of master of science,

and hereby certify that, in their opinion, it is worthy of acceptance.

---

Professor Galen Suppes

---

Professor Fu-hung Hsieh

---

Professor Sheila Baker

## ACKNOWLEDGEMENTS

Acknowledgements, first and foremost go out to the members of my committee: Drs. Galen Suppes, Fu-hung Hsieh, and Sheila Baker. I would like to express my special gratitude to my advisor, Dr. Galen Suppes for granting me the opportunity to work on this project as a group leader, and for his support, encouragement, and guidance in developing these experiments.

This work could not have been completed without the help of my co-researchers, and I would like to show my deepest appreciation to Ali Tekeei, Michael Gordon, and all the members in polyurethane foam research group for their support and dedication.

I would like to thank the United Soybean Board for financial support of the experimental studies used to validate the modeling work. Also thank FSI. Company providing foam formulas and technology support.

I would also like to thank my parents, Gengzhen Zhao and Huifang Wu for their unconditional love and support in my decision to pursue higher education.

And lastly I would like to thank my friends Chen Zhong, Sijia Hu and Yuxin Fang for all of their encouragement and support throughout the years.

Yusheng Zhao

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS .....	ii
LIST OF TABLES .....	v
LIST OF FIGURES .....	vi
ABSTRACT.....	viii
CHAPTER 1. INTRODUCTION .....	1
CHAPTER 2. MODELING REACTION KINETICS OF RIGID POLYURETHANE FOAMING PROCESS.....	5
2.1 Description of the model .....	5
2.2 Materials and methods.....	9
2.2.1 Materials .....	9
2.2.2 Experimental design and foaming formulation.....	10
2.2.3 Experimental procedures and data collection .....	11
2.3 Results and discussion.....	14
2.3.1 Data on repeatability .....	14
2.3.2 Single-polyol gel reaction modeling and kinetic parameter estimations .....	15
2.3.3 Prediction of mixture performance .....	19
2.4 Conclusion.....	24
CHAPTER 3. MODELING IMPACT OF CATALYST LOADING ON POLYURETHANE FOAM POLYMERIZATION .....	26
3.1 Introduction .....	26
3.2 Description of the model .....	29
3.3 Materials and methods.....	34
3.3.1 Materials .....	34
3.3.2 Experimental design.....	35
3.3.3 Foam preparation and data collection .....	36
3.4 Results and discussion.....	38
3.4.1 Data on repeatability .....	38
3.4.2 Evaluation on single polyol kinetics parameters .....	39

3.4.3 Prediction of polyols mixture temperature profiles .....	46
3.4.4 Evaluation on foam reaction kinetics parameters .....	47
3.4.5 Checking the consistency of the program .....	49
3.4.6 Impact of catalysts on foam reaction temperature .....	52
3.4.7 Impact of catalysts on gel reaction viscosity .....	54
3.5 Conclusion.....	56
<b>CHAPTER 4. EVALUATE REACTIONS WITH EXCESS ISOCYANATE IN POLYURETHANE FOAMING PROCESS .....</b>	<b>58</b>
4.1 Introduction .....	58
4.2 Background .....	58
4.3 Materials and methods.....	59
4.3.1 Materials .....	59
4.3.2 Experimental design and foaming formulation.....	60
4.3.3 Foam preparation and data collection .....	61
4.3.4 Standard test method for isocyanate groups in urethane materials or prepolymers.....	62
4.4 Results and discussion.....	64
4.4.1 Preliminary simulation.....	64
4.4.2 Isocyanate titration results .....	65
4.5 Conclusion.....	69
<b>BIBLIOGRAPHY .....</b>	<b>70</b>

## LIST OF TABLES

Table 2.1 Raw material properties .....	9
Table 2.2 Foaming formulation of rigid polyurethane foam.....	10
Table 2.3 Gel reaction recipes of single polyol and polyols mixture.....	11
Table 2.4 Fitted kinetic parameters based on single polyol gel reaction temperature profiles .....	18
Table 3.1 Raw material properties .....	34
Table 3.2 Recipes of single polyol gel reaction (poly G76-635) .....	39
Table 3.3 Recipes of single polyol gel reaction (poly V360).....	41
Table 3.4 Recipes of single polyol gel reaction (poly R315x).....	43
Table 3.5 Single polyol gel reaction kinetic parameters under different catalyst loadings .....	45
Table 3.6 Recipes of polyols mixture gel reactions .....	46
Table 3.7 Blow reaction kinetic parameters under different catalyst loadings .....	48
Table 3.8 Foaming formulation of rigid polyurethane foam.....	48
Table 4.1 Raw material properties .....	60
Table 4.2 Foaming formulation of rigid polyurethane foam.....	61
Table 4.3 Recipe used for isocyanate titration (poly G76-635).....	65
Table 4.4 Recipes with pentanol for isocyanate titration.....	67

## LIST OF FIGURES

Figure 2.1 Experimental system for internal temperature and foam height measurement .....	13
Figure 2.2 Internal temperature during the regular control foaming process of four times repeated test.....	14
Figure 2.3 Internal temperature of gel reaction in Poly G76-635 case .....	15
Figure 2.4 Internal temperature of gel reaction in Voranol 360 case .....	16
Figure 2.5 Internal temperature of gel reaction in Jeffol R315x case.....	17
Figure 2.6 Internal temperature of gel reaction in three polyols mixture case .....	20
Figure 2.7 Component concentrations of foam reaction in three polyols mixture case .....	21
Figure 2.8 Internal temperature of foam reaction in three polyols mixture case.....	23
Figure 2.9 Foam height of foam reaction in three polyols mixture case .....	23
Figure 3.1 Internal temperature during the regular control foaming process of four times repeated test.....	38
Figure 3.2 Internal temperature of poly G76-635 gel reaction with no catalysts .....	39
Figure 3.3 Internal temperature of poly G76-635 gel reaction under different catalyst loading conditions .....	40
Figure 3.4 Internal temperature of poly V360 gel reaction with no catalysts.....	41
Figure 3.5 Internal temperature of poly V360 gel reaction under different catalyst loading conditions .....	42
Figure 3.6 Internal temperature of poly R315x gel reaction with no catalysts.....	43
Figure 3.7 Internal temperature of poly R315x gel reaction under different catalyst loading conditions .....	44
Figure 3.8 Internal temperature of polyols mixture gel reaction under different catalyst loading conditions .....	47

Figure 3.9 Internal temperature of regular control blow reaction.....	49
Figure 3.10 Number of moles of components during polyols mixture foaming process .....	50
Figure 3.11 Components total volume change during polyols mixture foaming process .....	50
Figure 3.12 Components total heat capacity change during polyols mixture foaming process.....	51
Figure 3.13 Foam weight loss result during foaming process .....	52
Figure 3.14 Internal temperature of foam reaction under different catalyst5 loading conditions.....	53
Figure 3.15 Internal temperature of foam reaction under different catalyst8 loading conditions.....	54
Figure 3.16 Gel system viscosity data over time under three different catalyst8 loading conditions.....	55
Figure 3.17 Gel system viscosity data over time under three different catalyst5 loading conditions.....	55
Figure 4.1 Preliminary simulation result of isocyanate concentration during foaming process.....	64
Figure 4.2 Isocyanate titration results during gel reaction process.....	65
Figure 4.3 Preliminary simulation result of isocyanate titration during gel reaction process.....	66
Figure 4.4 Isocyanate titration results (pentanol) during gel reaction process .....	68



## **ABSTRACT**

Polyurethanes are very important polymers and have a surprising array of commercial applications. The polyurethane polymer-forming reaction occurs between an isocyanate and an alcohol. To make foams, the polyurethane polymer must be expanded or blown by the introduction of bubbles and a gas. A convenient source of gas was the carbon dioxide produced from the reaction of an isocyanate group with water.

A theoretical model was developed to simulate the polyurethane foaming process for a rigid foam. In the model, multiple ordinary differential equations were solved by MATLAB and the model was able to predict temperature profiles by inputting foam recipe information. This initial study on foam modeling focusses on reaction kinetic parameters that were fitted to experimental temperature data as a function of time. The modeling was able to accurately model temperature profiles of single-polyol polyurethane formulations and was able to accurately predict temperature profiles of mixtures based on pure component kinetic parameters. A primary goal of this work is to expedite the ability to develop new foam formulations by simulation - especially for incorporation of new bio-based polyols into formulations. In addition, there was a research program to predict the density of the foaming studies in the lab and then the results are to be used to revise the formulation to obtain a density identical to the base case.

The MATLAB model based on the simultaneous solution of several differential equations was developed further to include the impact of catalyst loading for the

reactions and physical processes of a urethane box foaming process. Experiments with different amounts of catalyst loading were conducted to fit the model parameters for this thermoset polymerization. The revised model improves the versatility of simulation for predicting temperature profiles, viscosity profiles, and densities during urethane foam-forming processes.

In addition, becoming knowledge on likely fates of unreacted isocyanate and developing experimental plan to evaluate reactions with excess isocyanate in solvents are significant. ASTM isocyanate titration was applied to measure isocyanate content in system during foaming process. Experiments with different amount of catalyst were carried out to verify accuracy of the model. Kinetics parameters relate to side reactions will be obtained by fitting modeling results to experimental data.

## CHAPTER 1. INTRODUCTION

Polyurethanes are used in a range of applications, including the manufacture of flexible, high-resilience foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting compounds, high performance adhesives, and surface coating. For the manufacture of polyurethane polymers, two bifunctional groups are needed as the reactants. Isocyanate groups and compounds with active hydrogen atoms have been used [1]. The structure and molecular size of these compounds influence the polymerization. In addition, additives such as catalysts [2], surfactants, blowing agents [3], cross linkers, flame retardants, light stabilizers, and fillers [4] are used to control and modify the reaction process and performance characteristics of the polymer.

In recent years, polyurethane (PU) foams have accounted for two-thirds of the total PU demand [5]. Therefore an increase in the understanding and ability to predict the polyurethane foaming process and resulting properties can enable superior formulation design, expedite development of new formulations, and enhance materials properties. This includes the ability to build upon previous work on understanding the impact on properties such as density, compressive strength, and thermal conductivity [6-9].

Ni has performed kinetic study with a titration method to determine the concentration of the isocyanate group as a function of time and estimated the rate constants of the reaction of isocyanate with water by linear regression [2]. Others

have worked on modeling to predict material properties in order to reduce time on performance tests. Conor Briody has developed a visco-hyperelastic numerical material model for simulating the uni-axial and shear behavior of polymer foams [10]. H. Jmal used a memory integer model and the difference-forces method to identify the Quasi-static behavior of polyurethane foam. Their model was able to identify the viscoelastic and global elastic parameters of the macroscopic integer model [11]. While the modeling of some specified properties of polyurethane foam has been widely studied, the modeling studies on the reaction process have been scarce.

Baser developed theoretical models for physical blowing agent blown rigid polyurethane foam formation [12] and water-blown polyurethane foams [13]. They carried out detailed experimental study to measure both temperature and density change during foam formation. However, they did not consider heat transfer to surroundings and the impact of thermocouples on temperature profiles. Tesser[14] optimized a model to include heat transfer and modify the description of the vapor-liquid equilibrium of the blowing agent and the polymeric phase by means of an extended Flory-Huggins equation that well describes the nonideal behavior of these reacting mixtures. Tesser did not consider mixtures of polyols nor the prediction of mixtures based on single-polyol parameters. Also, the work did not consider water as a chemical blowing agent, and attributed basically all lack of inefficiency of foam height to Flory-Huggins non-idealities.

The purpose of this paper is to provide a simplified engineering model for modeling complex polyurethane foaming reaction. Previous works were not able to

solve multiple ordinary differential equations [12-16] simultaneously by hand calculation. Therefore a MATLAB program was developed to solve these equations to model temperature profiles as a function of time during the foaming process and compare that to experimental data during the first 15 minutes of the foaming reaction. This program was able to easily predict temperature profiles of any foam recipes. In general, the dynamics of the foaming process has been studied using two approaches: (i) assuming the foam to be made up of many microscopic unit cells, and (ii) assuming the foam to be a single pseudo-homogeneous phase.

Gel reactions of three different polyols were performed individually to get the pure component activation energy, reaction rate constant, and heat of reaction. These values for pure polyols were used in the model to predict the performance of polyol mixtures including component concentrations, internal temperature and foam height. Experiments were performed to verify the veracity of the model. The rate constant pre-exponential factor, activation energy, and heat of reaction were varied as parameters to fit the model to the experimental data.

This work is an initial step toward being able to model and eventually predict temperature, density, degree of polymerization, closed cell content, thermal conductivity, and compressive strength as a function of time based only on the reagent and catalyst concentrations. Compared with the model previously developed [12-14], advantages of the present work include: a) predicting of mixture behavior based on pure component data, b) modeling of both chemical (water) and physical blowing agents, and c) a more-detailed foundation upon which a more-comprehensive foam

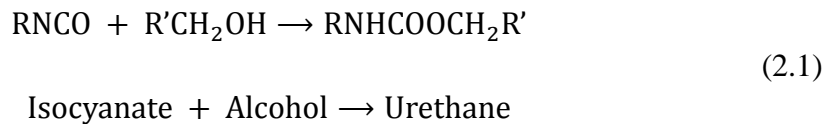
simulation package can be developed.

Chapters 2-4 of this thesis are presented as independent works. Chapter 2 is a paper published by Journal of Applied Polymer Science on Apr.17, 2013. It describes a basic reaction kinetics modeling of rigid polyurethane foaming process. Chapter 3 is a paper submitted to APPLIED CATALYSIS A: GENERAL and it is under review. It presents a revised modeling to include impact of catalyst loading on polyurethane foam polymerization. Chapter 4 is an initial work on the evaluation of reactions with excess isocyanate in polyurethane foaming process.

# CHAPTER 2. MODELING REACTION KINETICS OF RIGID POLYURETHANE FOAMING PROCESS

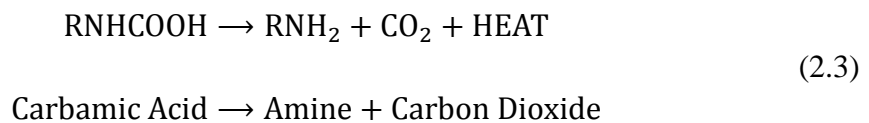
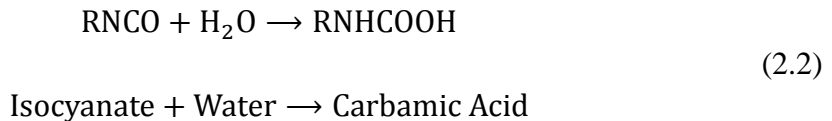
## 2.1 Description of the model

The polyurethane foaming process involves two competing reactions (gel reaction and blow reaction). The gel reaction, also sometimes called the polymerization reaction, involves the reaction of an isocyanate group with an alcohol group to give a urethane linkage as shown in Equation 2.1. Since polyurethane foams usually utilize polyfunctional reactants (typically difunctional isocyanate and trifunctional polyols), this reaction leads to the formation of a cross-linked polymer.



The reaction of a urethane group with an isocyanate group to form an allophanate group is another possible way to further cross-link the polymer. However, compared with gelation reaction this side reaction can be neglect [12-14, 17].

The blow reaction is a two-step reaction described by Equations 2.2 and 2.3. An isocyanate group reacts with water to yield a thermally unstable carbamic acid which decomposes to give an amine functionality, carbon dioxide, and heat.



The newly formed amine group reacts with another isocyanate group to give a

disubstituted urea. There are other secondary reactions, involving the formation of biuret and allophanate linkages which could lead to the formation of covalent cross-linking points. A common practice in literatures is to neglect these side reactions [12-14, 17]. This current work provided a base case simulation where the impact of these side reactions was neglected and where the impact can be further evaluated in subsequent studies.

For the reactions above, relationships between main variables are listed below.

Equations 2.4 and 2.5 represent the rates of gel and blow reaction;

$$r_{gel} = \sum_i k_{gel\ i} * c_{catgel} * c_{iso} * c_{OH\ i} = \sum_i r_{gel\ i} \quad (2.4)$$

$$r_{blow} = k_{blow} * c_{catblow} * c_{iso} * c_{water} \quad (2.5)$$

where  $c_{gel\ i}$  is the concentration of the gel associated with polyol  $i$ ,  $k_{gel\ i}$  is the reaction rate constant of gel  $i$ ,  $c_{catgel}$  is the concentration of gelling catalyst,  $c_{iso}$  is the concentration of isocyanate groups,  $c_{OH\ i}$  is the concentration of hydroxyl groups of polyol  $i$ ,  $r_{gel\ i}$  is the gel reaction rate of polyol  $i$ ,  $r_{gel}$  is the summation of gel reaction rates of polyol mixtures,  $r_{blow}$  is the blow reaction rate,  $k_{blow}$  is the reaction rate constant of blowing,  $c_{catblow}$  is the concentration of blowing catalyst,  $c_{water}$  is the concentration of water.

This model assumes the reactivity of hydroxyl functional groups depend upon the polyol of origin with the reactivity of unreacted groups not changing if the polyol becomes part of a urethane chain. A common theory is that the hydroxyl groups can vary considerably within the same molecule and as a function of degree of polymerization; however, such detailed modeling is not possible at this time. What



is possible is the ability to determine if this simplified model is able to represent the data within the standard deviation of the data.

Equations 2.6~2.10 relates the concentrations of isocyanate, polyol, water, urethane and carbon dioxide to the fundamental rate equations.

$$\frac{dc_{iso}}{dt} = -r_{gel} - r_{blow} \quad (2.6)$$

$$\frac{dc_{OH\ i}}{dt} = -r_{gel\ i} \quad (2.7)$$

$$\frac{dc_{water}}{dt} = -r_{blow} \quad (2.8)$$

$$\frac{dc_{ure}}{dt} = r_{gel} \quad (2.9)$$

$$\frac{dc_{CO2}}{dt} = r_{blow} \quad (2.10)$$

where  $c_{ure}$  is the concentration of urethane, and  $c_{CO2}$  is the concentration of carbon dioxide. Equation 2.11 shows the relationships of internal temperature versus time. As the volume changes, polymer chains stretch and the elastic energy stored in the chains during this deformation will contribute to the total internal energy. However in this case we neglect this contribution to internal energy and assume that the heat of reaction is a constant. The energy balance is given by

$$\frac{dT}{dt} = \frac{\sum_i \Delta H_{gel\ i} * r_{gel\ i} + \Delta H_{blow} * r_{blow} - \Delta H_{vap} * \left(-\frac{dn_{MFL}}{dt}\right) + UA\Delta T}{\sum(n * C_p)} \quad (2.11)$$

where U is the overall heat transfer coefficient from the surroundings. A is the surface area of the foam related to different foam height [18] which is the summation of base area and lateral area.  $\Delta H_{gel\ i}$  is the heat of gel reaction respect to polyol i,  $\Delta H_{blow}$  is the heat of blowing reaction,  $\Delta H_{vap}$  (27920 J/mol) is the enthalpy of

vaporization of methyl formate [19], for sake of simplicity it was assumed as a constant under different temperature.  $-\frac{dn_{MFL}}{dt}$  is the evaporation rate of methyl formate, and  $\sum(n * C_p)$  is the summation of heat capacities of all the chemicals used. Based on the heat capacity values under different temperatures [20, 21] we assume that heat capacity is a linear function of temperature and it increases 0.1% as temperature rising 1K degree in the study temperature range.

Equation 2.12, based on the ideal gas law, predicts foam height according to the volume of foam at different temperatures. Both carbon dioxide and methyl formate make a contribution to foam volume rise. The model allows for dynamic heat transfer primarily from the exposed top surface of the foam.

$$\frac{dh}{dt} = \frac{dV}{dt} * \frac{1}{A} = \left(\frac{22.4 * T}{273.15}\right) * \left(\frac{dn_{CO2}}{dt} + \frac{dn_{MFL}}{dt}\right) * \frac{1}{A} \quad (2.12)$$

where the bases of boxes had an area, A, which is 1.02 dm<sup>2</sup>. Equivalent volume of ideal gas at standard condition is 22.4 L/mol. Raoult's Law Equation was used in combination with heat and energy balances to solve the equilibrium between vapor and liquid phases of methyl formate. Details about foam height modeling and study on efficiencies of blowing agents will be discussed in future work.

These equations were combined in MATLAB to create the model for foam temperature as a function of time. Raw material concentrations can be input to the script file, and then the program will simulate the foaming process and show the temperature and concentration profiles.

## 2.2 Materials and methods

### 2.2.1 Materials

RUBINATE M (Standard Polymeric MDI) was the isocyanate used in this study and the petroleum-based polyols were Poly G76-635, Voranol 360 and Jeffol R315x from Huntsman Company and Dow Chemical Co. The specifications are shown in Table 2.1 [20, 21]. N,N-dimethylcyclohexylamine (DMCHA) and N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA) were used as the gelling catalyst and the blowing catalyst respectively. However, PMDETA was found also having impact on gel reaction based on experimental results. The efficiency of PMDETA on catalyzing gel reaction was about 80% respect to DMCHA. Momentive L6900 was used as the surfactant for rigid foams, TCPP was used as the fire retardant, and distilled water and methyl formate were used as the blowing agents.

*Table 2.1 Raw material properties*

<b>Component</b>	<b>Isocyanate</b>	<b>Polyol</b>	<b>Polyurethane</b>	<b>Water</b>	<b>Carbon Dioxide</b>	<b>Amine</b>
Heat Capacity (J/g-K)	1.799	1.57 ~1.8 9	1.4~1.5	4.19	0.846~0.939 (300K~400K)	1.55~ 1.64
Heat Capacity (J/equiv-K)	242.86	264. 86	362.5	75.42	39.6	128
<b>Product</b>	<b>Fn</b>	<b>Sp. Gravity @25°C</b>	<b>% NCO</b>	<b>Eq. Wt.</b>	<b>Viscosity cps@25°C</b>	
RUBINATE M	2.70	1.23	31.2	135	190	
<b>Product</b>	<b>Poly G76-635</b>		<b>Voranol 360</b>		<b>Jeffol R315x</b>	
<b>OH number</b>	635		360		315	
<b>Equivalent Weight</b>	88.3		155.8		178	

<b>Product</b>	<b>MW</b>	<b>Physical State</b>	<b>Boiling Point(°C)</b>	<b>Flash Point(°C)</b>	<b>LFL/UFL*</b>
Methyl Formate	60	Liquid	31.5	-19	5/20

## 2.2.2 Experimental design and foaming formulation

The experiment was comprised of two parts: gel reactions and foaming reactions. Gel reactions of three different polyols were performed individually to get the activation energy, reaction constant rate and heat of reaction. The values for pure polyols were used in the model to predict the performance of polyol mixtures in the gel reaction, and gelling experiments were performed to verify the accuracy of the model. Foam reaction of polyol mixtures was performed to get the kinetics parameters of blowing reaction.

Table 2.2 lists the regular control recipe used in foam reaction and Table 2.3 lists the recipes used in gel reactions for gathering kinetics parameters.

*Table 2.2 Foaming formulation of rigid polyurethane foam*

<b>B-side Materials</b>	<b>Weight/g</b>	<b>Moles of functional groups</b>
Poly G76-635	13.84	0.1567
Voranol 360	15.68	0.1006
Jeffol R315x	4	0.0225
Dimethylcyclohexylamine(Cat8)	0.12	
Pentamethyldiethylenetriamine(Cat5)	0.32	
Momentive L6900	0.6	
TCP	2	
Distilled Water (Blowing Agent)	1.04	0.1156
Methyl Formate (Blowing Agent)	2.4	
<b>A-side Material</b>		

RUBINATE M	61.548	0.4559
<b>Isocyanate Index</b>	1.15	

*Table 2.3 Gel reaction recipes of single polyol and polyols mixture*

	<b>G76-635</b>	<b>V360</b>	<b>R315x</b>	<b>Mixture</b>
Poly G76-635	19			13.85
Poly V360		33.55		15.68
Poly R315x			38.4	4.02
TCPP	2	2	2	2
L6900	0.6	0.6	0.6	0.6
Poly cat 8	0.12	0.12	0.12	0.12
Isocyanate	33.51	34.92	33.9	40.89
<b>Moles</b>				
Poly G76-635	0.2152			0.1569
Poly V360		0.2153		0.1006
Poly R315x			0.2157	0.0226
Isocyanate	0.2482	0.2587	0.2511	0.3029
Index	1.153	1.201	1.164	1.081

Moles of polyol and isocyanate were designed to lock in constant numbers in single polyol tests and recipe of mixture polyols was designed based on original foam recipe. Isocyanate indices in all runs were designed to lock in 1.15, however, there was deviation in actual numbers since it was uncontrollable when adding pre-weighted isocyanate.

### **2.2.3 Experimental procedures and data collection**

The following steps were used in both gel and foam experiments.

1. Polyols, water, blowing catalyst, gelling catalyst, and surfactant (B-side components) were added into a plastic cup successively.
2. The B-side components were mixed for 10-15 seconds.

3. The mixture was allowed to degas for 2 min.
4. Thereafter, pre-weighted isocyanate (A-side material) was added and mixed at the same speed for 7-10s.
5. The reacting mixture was then quickly poured into a box with aluminum lining, internal temperature was measured during foaming process and the foam was allowed to rise and sit at ambient conditions (25 °C) during curing.

All the B-side chemicals were added in the foam reaction while blowing agents and blowing catalyst were not added in the gel reaction. Since the volume of gel mixture is much smaller than that of foam, the fluid level in wood box is too low to gather accurate data while performing gel reaction. Instead of using wood box for both reactions, step 5 was not performed in gel reactions and temperature was directly measured in plastic cups which could give a more accurate profile.

A high speed mixer blade (540 rpm) attached to a floor-model drill press was used to mix the chemicals. LabVIEW software was used to monitor the temperature of the gel or foam reactions for the first 10 minutes with a type-k thermocouple attached through a National Instruments SCB-68 box to a National Instruments PCI 6024E data acquisition card. Figure 2.1 presents the experimental system for internal temperature and foam height measurement.

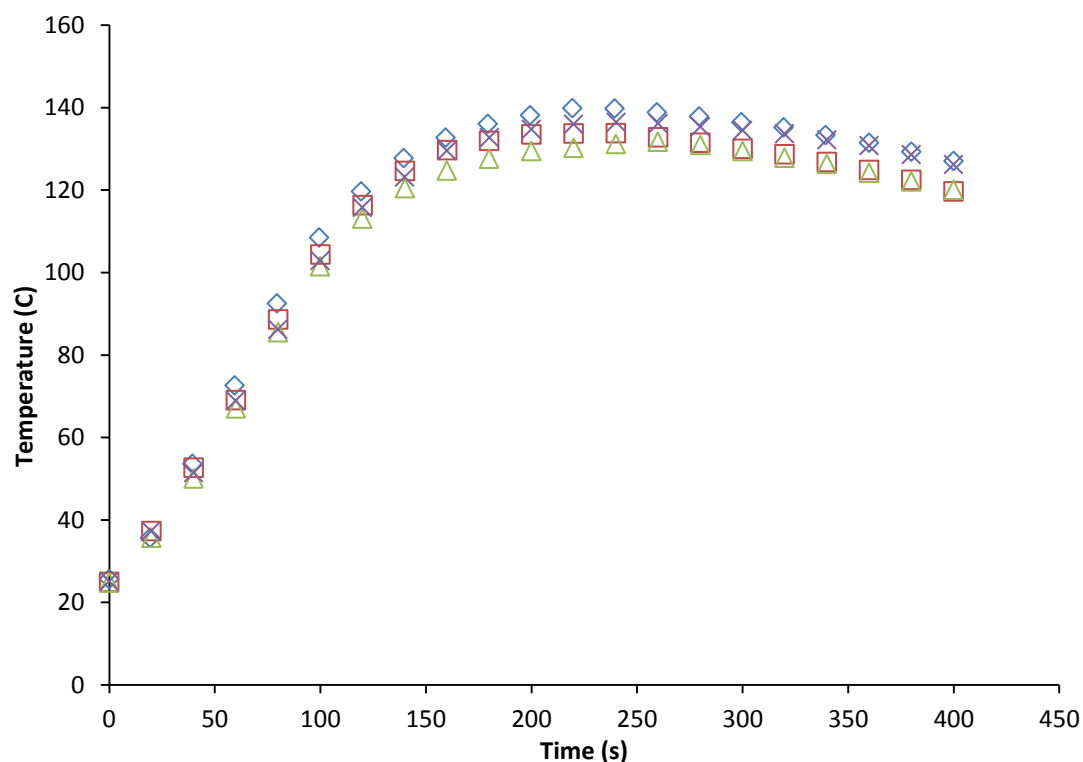


**Figure 2.1** Experimental system for internal temperature and foam height measurement

## 2.3 Results and discussion

### 2.3.1 Data on repeatability

Figure 2.2 shows the experimental data of internal temperature in the foaming process and the experiment was repeated four times under the same condition.



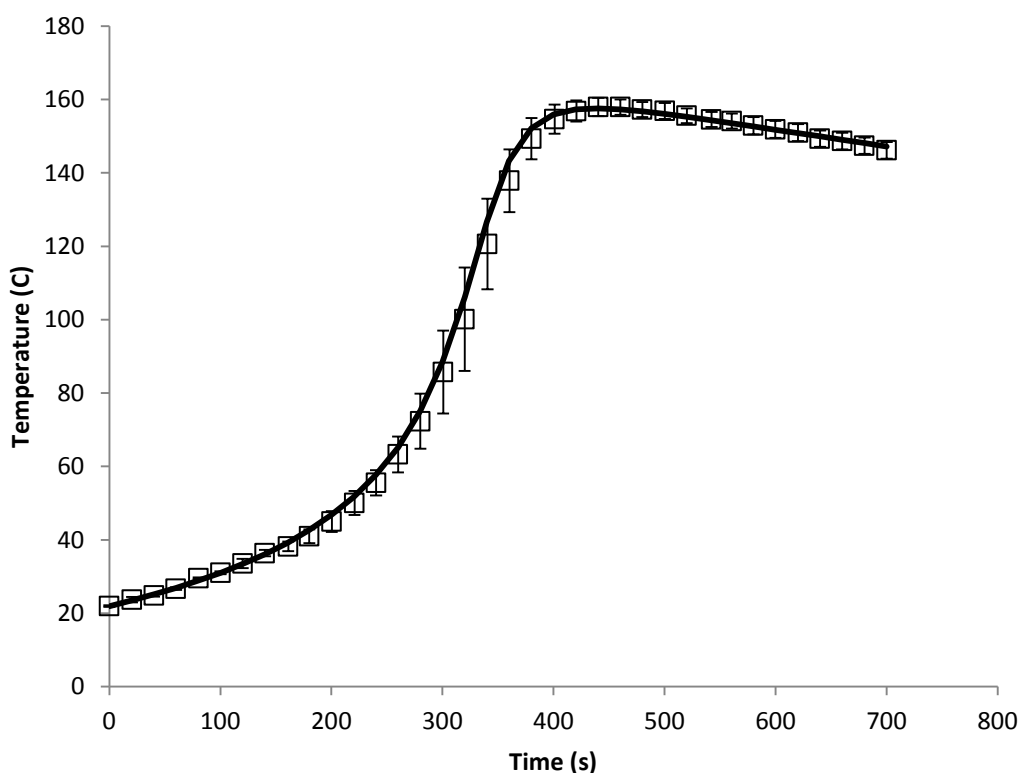
**Figure 2.2 Internal temperature during the regular control foaming process of four times repeated test. Four different symbols respectively represent four groups of data.**

Experimental deviation is attributed to a number of factors including minor variations in measuring/transfer of chemicals and the imperfect mixing. However, temperature profiles are substantially repeatable. The highest temperature and the corresponding time needed to reach the temperature were about 125-135°C and 200-250 seconds. The reduction in temperature toward the end is at least in part attributed to heat transfer from the sample to the surroundings.



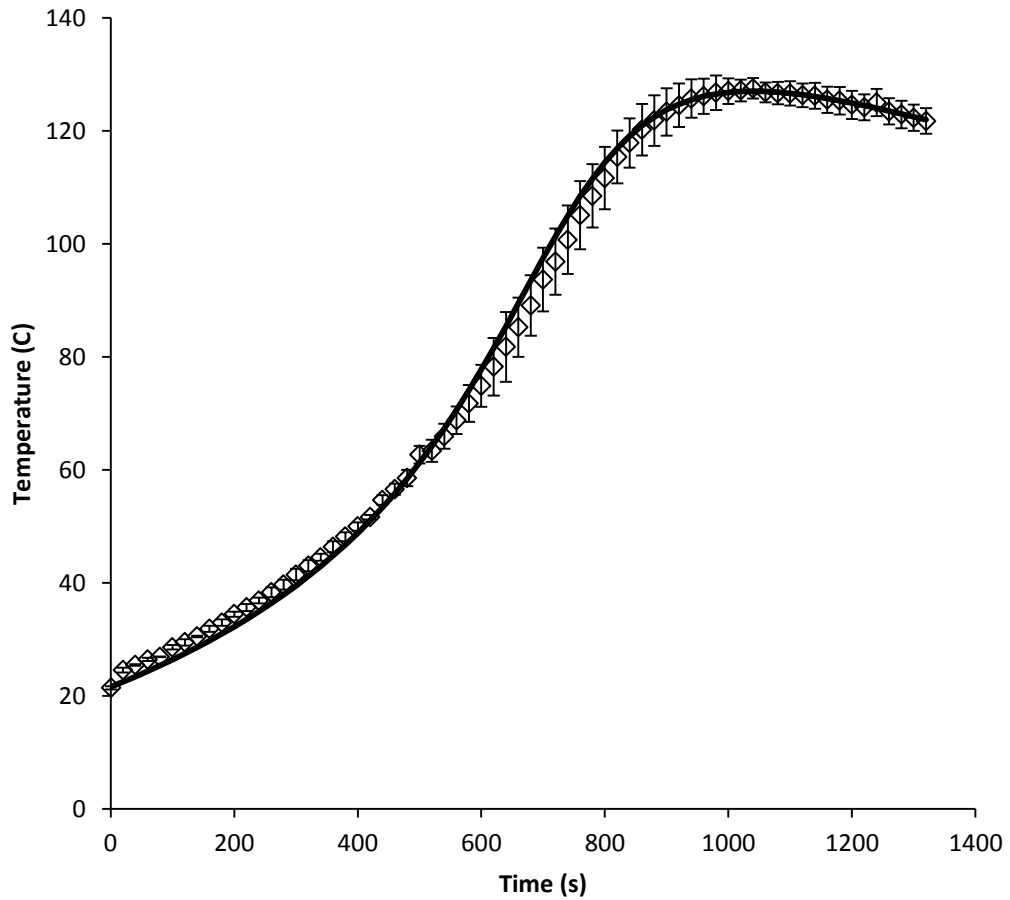
### 2.3.2 Single-polyol gel reaction modeling and kinetic parameter estimations

The internal temperature was measured during the gel reactions for each of three polyols. Recipes listed in Table 2.3 were used to perform each test. There was a slight difference between isocyanate indices for each test. Kinetic parameters in the model were manually adjusted to provide good fits to experimental data. The comparison of experimental data and modeling results for Poly G76-635 is shown in Figure 2.3, and the results of Voranol 360 and Jeffol R315x are shown by Figure 2.4 and Figure 2.5.



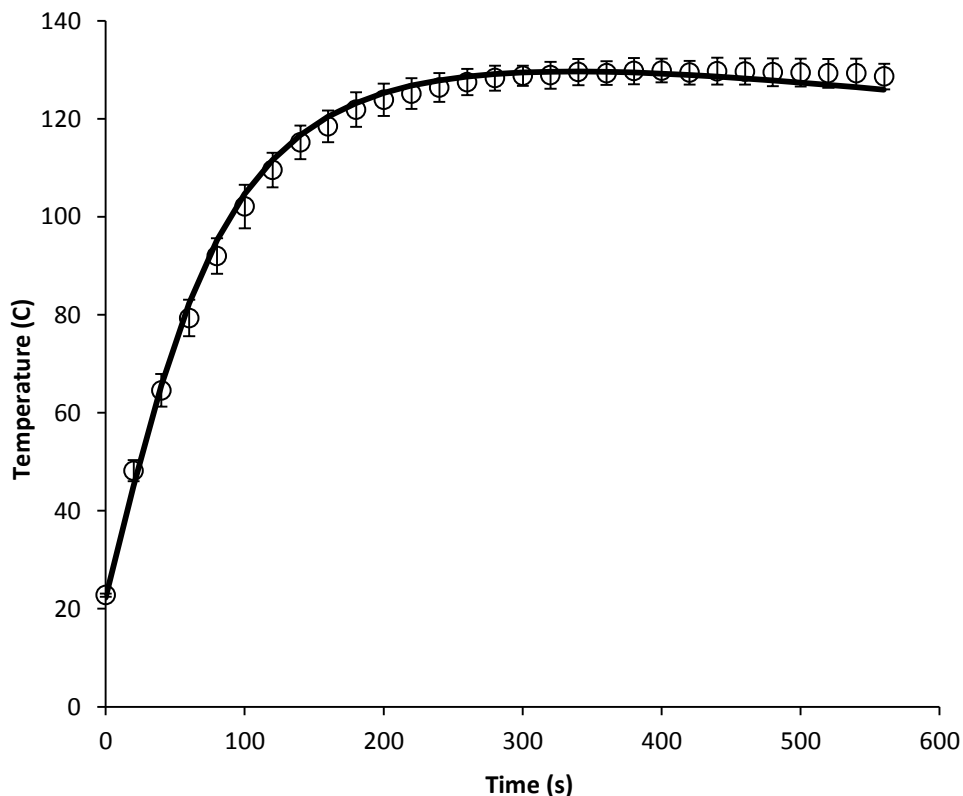
**Figure 2.3 Internal temperature of gel reaction in Poly G76-635 case. Symbol “□” represents the experimental data and solid line represents the modeling result.**

The highest temperature in the gel reaction of Poly G76-635 case was about 150 °C and the time needed to reach the temperature was about 450 seconds.



**Figure 2.4 Internal temperature of gel reaction in Voranol 360 case. Symbol “◇” represents the experimental data and solid line represents the modeling result.**

The highest temperature in the gel reaction of Poly V360 case was about 130 °C in about 1000 seconds. This reaction was faster than Poly G76-635 at low temperatures due to a fundamentally more-reactive hydroxyl group; this translates to a higher rate constant pre-exponential factor. The lower peak temperature can be attributed to the lower hydroxyl number of V360 whereby the additional polyol backbone effectively acts as solvent moderating changes in temperature.



**Figure 2.5 Internal temperature of gel reaction in Jeffol R315x case. Symbol “o” represents the experimental data and solid line represents the modeling result.**

The highest temperature in the gel reaction of Poly Jeffol R315x case was about 130 °C in about 350 seconds. The R315x polyol has a higher reactivity than V360 which can be attributed to a variety of factors including the nature of the hydroxyl groups and the presence of other functional groups or catalysts in the polyol. A hydroxyl number similar to that of V360 leads to a similar peak temperature.

Detailed values of revised kinetics parameters and the reference values in other literatures are listed in Table 2.4. Subscript 1 represents the kinetic parameters of the reaction between isocyanate and polyols. Subscript 2 represents the reaction between isocyanate and water. The units are provided per mole of isocyanate.

*Table 2.4 Fitted kinetic parameters based on single polyol gel reaction temperature profiles*

		Current Work Results	Reference Values
<b>Pre-Exponential Factor <math>k_{10}(25^{\circ}\text{C})</math></b>	Poly 76-635	59 ml/(mol*s*g catalyst)	1734.8 ml/(equiv*s) [13]
	Poly V360	65 ml/(mol*s*g catalyst)	
	Poly R315x	1900 ml/(mol*s*g catalyst)	
<b>Activation Energy <math>E_1</math></b>	Poly 76-635	50000 J/mol	40400 J/mol [13]
	Poly V360	40000 J/mol	
	Poly R315x	10000 J/mol	
<b>Heat of Reaction <math>\Delta H_1</math></b>	Poly 76-635	71000 J/mol	70750 J/mol [13]
	Poly V360	62000 J/mol	
	Poly R315x	59000 J/mol	
<b>Pre-Exponential Factor <math>k_{20}(25^{\circ}\text{C})</math></b>		800 ml/(mol*s*g catalyst)	1385 sec <sup>-1</sup> [13]
<b>Activation Energy <math>E_2</math></b>		40000 J/mol	32660 J/mol [13]
<b>Heat of Reaction <math>\Delta H_2</math></b>		65000 J/mol	86000 J/mol [13]

Table 2.4 summarizes the reaction parameters used to fit the model to the data. For comparison purposes, previously reported values for similar polyols are reported. The reaction conditions and chemicals used in this project were different from theirs in the references [13] so that the values in the model were adjusted based on experimental data in this study. The kinetic parameters for these three polyols are comparable to what has been previously reported. When reported on an alcohol equivalent basis, the heats of reaction are similar which reflects that heat release is directly related to the amount of alcohol groups reacting with isocyanate groups.

The activation energy and the pre-exponential factor for the R315x polyol were different than that of the others. This difference is reflected by the fundamentally different behavior summarized by Figure 2.5 where the temperature profile does not have an inflection point. One explanation is the possible presence of a built-in catalytic capacity of R315x which has a much higher reactivity at lower temperatures and was the decrease in reagent concentration counters any increased reactivity with increasing temperatures.

Based on a comparison to previously reported values (see Table 2.4), previously reported kinetic parameters are within the range of the values reported for the three polyols of this study. The heats of reaction observed in these studies are similar to values previously reported. A greater variation was observed with the blow reaction parameters. This may be due to that the program does not account for the impact from side reactions, especially the reaction between isocyanate and amine.

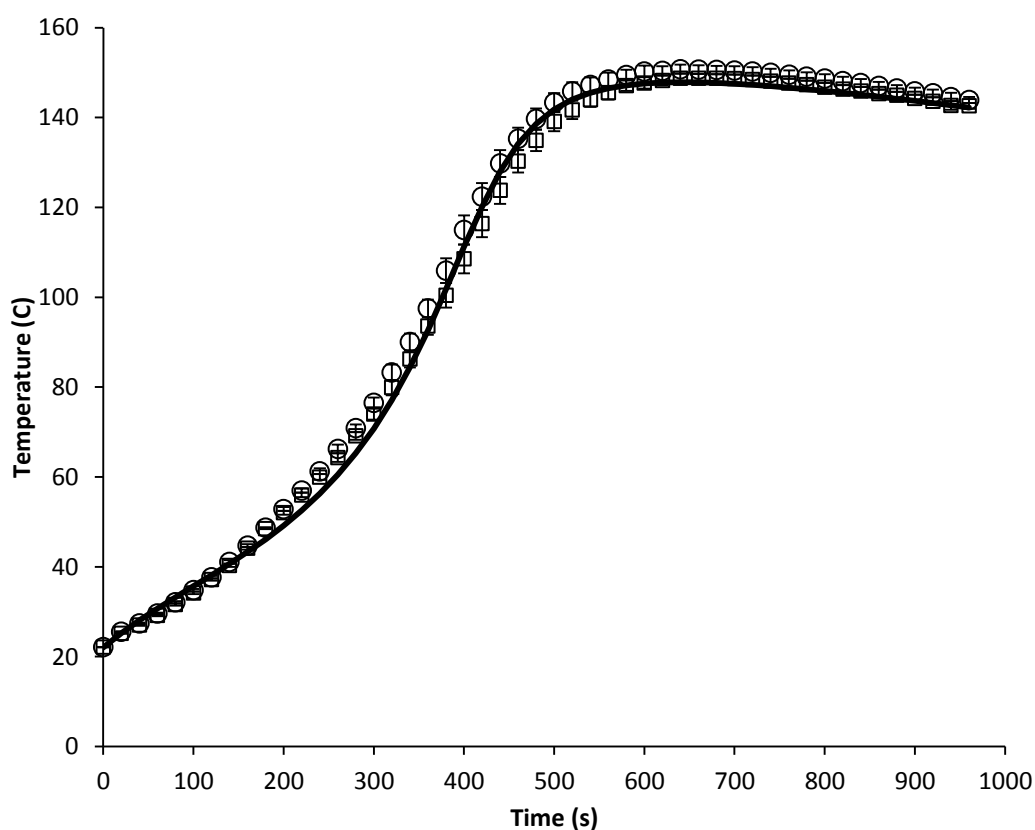
By plotting  $\ln(T-T_0)$  as a function of time, a straight line is obtained from which the slope of heat transfer coefficient can be evaluated. For all the runs, average values of  $U=3$  ( $W/m^2-K$ ) for gel reactions in plastic cups and  $U_f=1$  ( $W/m^2-K$ ) for foam reactions in wood box were used in the modeling.

### **2.3.3 Prediction of mixture performance**

The MATLAB model implicitly accounts for chemical mixtures by including the appropriate rate equation for each polyol that is present. The primary modes of interaction between the different polyols are their cumulative releases of heat of

reactions and cumulative consumption of isocyanate—both of these are implicitly accounted for in the model.

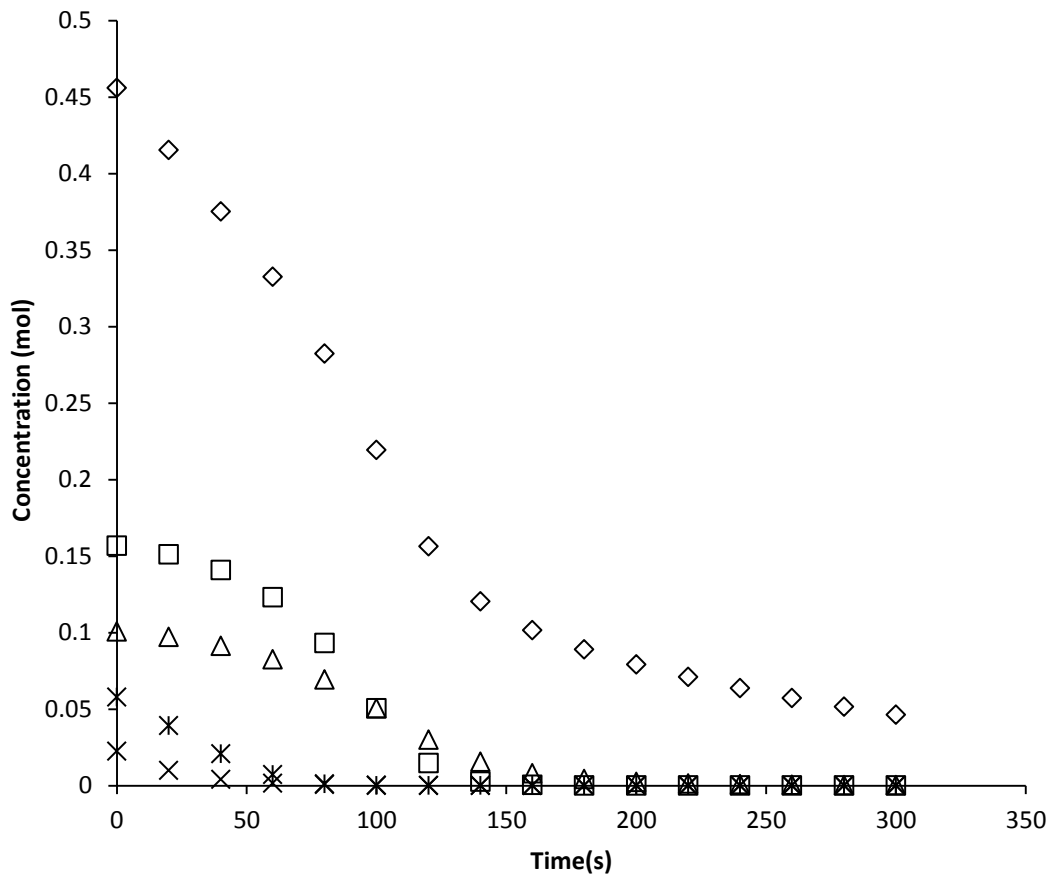
Figure 2.6 shows a good agreement between experimental data and the predicted performance based only on pure component properties. The data are well within the standard deviations.



**Figure 2.6 Internal temperature of gel reaction in three polyols mixture case. Symbol “□” and symbol “○” represent two different groups of experimental data and solid line represents the modeling result.**

These data validate the accuracy of this modeling approach as well as the utility of the modeling method. Here, as is the general case, the value of fundamentally based models is that they allow a limited amount of pure component data to be used to predict the performance of an infinite number of possible mixtures of the pure reagents.

Blowing catalyst and blowing agent (water and methyl formate) were added to the gel formation to create rigid foams and monitor the foaming processing. The isocyanate reacts with water to generate carbon dioxide which is blowing agent [22]. In addition, methyl formate is a blowing agent due to its high volatility (32 °C). Internal temperature and foam height were measured during the experimental process and compared with the modeling results to correct the kinetic parameters of blow reaction. Figure 2.7 shows the component concentrations estimated by the model during the foaming reaction.



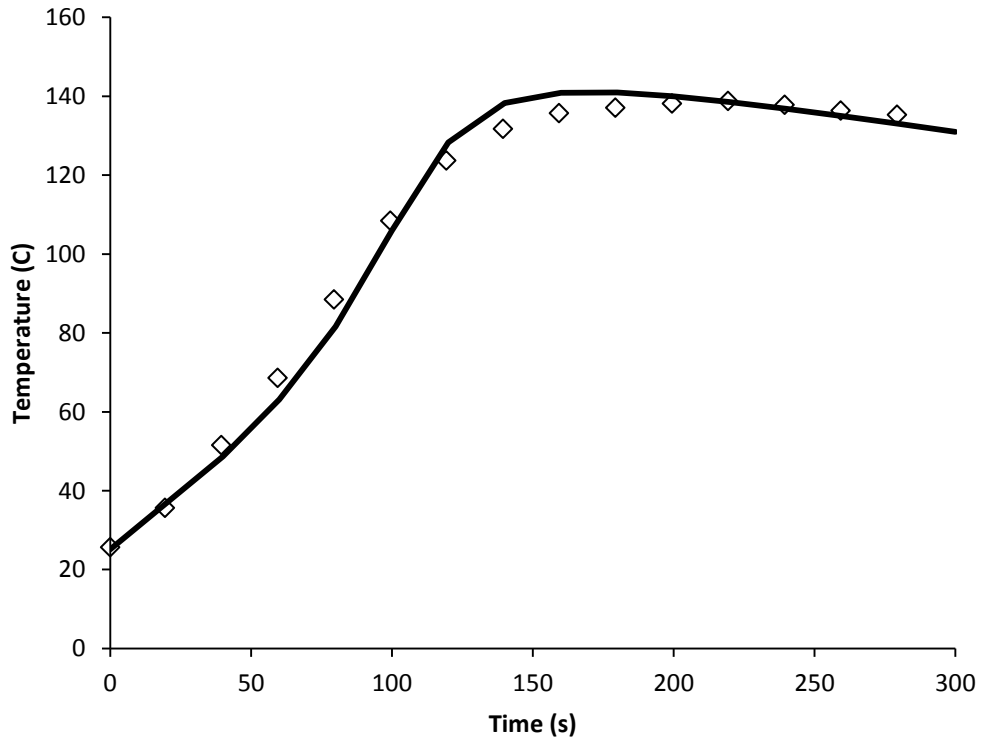
**Figure 2.7 Component concentrations of foam reaction in three polyols mixture case. Symbol “◇” represents the concentration of Isocyanate Rubinate M, symbol “□” represents Poly G76-635, symbol “△” represents Poly V360, symbol “×” represents Poly Jeffol R315x, and symbol “⌘” represents water.**

Excess isocyanate was used in the experiment to ensure that polyols and water react completely. Water was consumed in about 80 seconds and polyols were consumed at about 150 seconds. FTIR analyses of foams reveal that they contain no free isocyanate even when excess isocyanate is used in the formulation. However, the analyses were performed several days after the synthesis process, the excess isocyanate could react with moisture in air and therefore the isocyanate band will not appear in FTIR. The concentration profiles of Figure 2.7 show unreacted isocyanate present after reaction—this is a discrepancy between the model and observed phenomena.

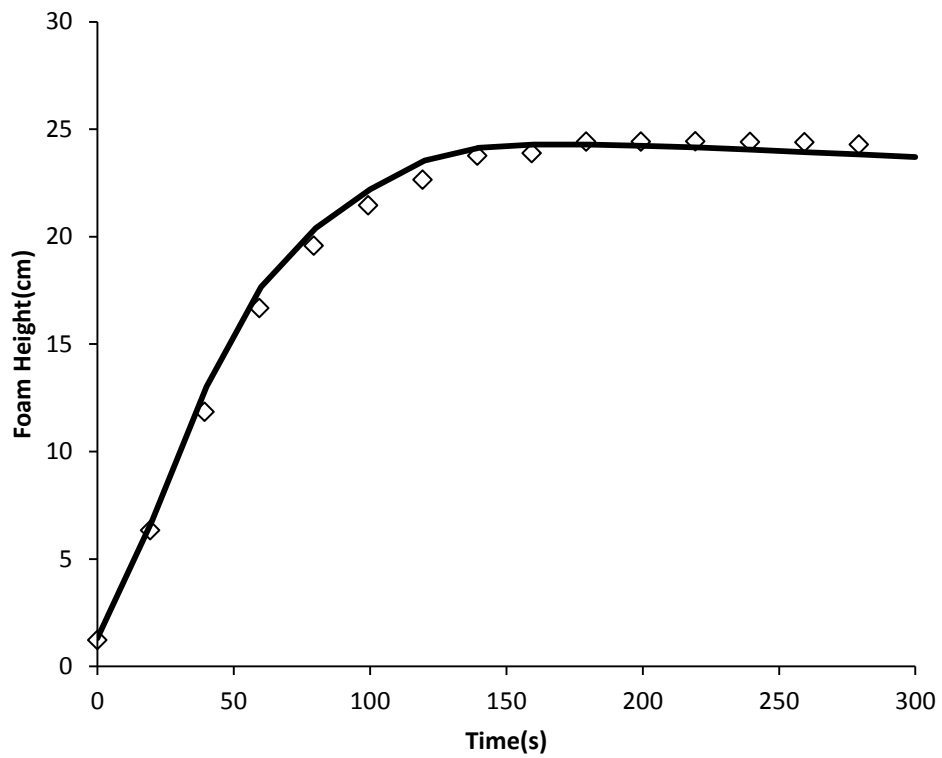
Formation of allophanates by excess isocyanate is projected but not verified and is a topic of scientific debate. While no answers are provided by this modeling, the model approach can be a useful approach to better understand the fate of excess isocyanate in urethane foam formulations.

Figure 2.8 and Figure 2.9 summarize the internal temperature and foam height profiles. As summarized by Figure 2.8, the peak foam temperature of 140 °C was attained at about 200 seconds. After this, convective cooling of the foam led to reductions in temperature. The rates of temperature rise were greater for the foaming reactions both because of the highly exothermic nature and would be accounted for in the model.





**Figure 2.8 Internal temperature of foam reaction in three polyols mixture case. Symbol “◇” represents the experimental data and solid line represents the modeling result.**



**Figure 2.9 Foam height of foam reaction in three polyols mixture case. Symbol “◇” represents the experimental data and solid line represents the modeling result.**

The maximum temperature substantially indicates the completion of reactions; and with the completion of the reactions, about 98% of the final height was attained. The difference between modeling and experimental data was attributed to a number of mechanisms through which blowing agent is less than 100% effective. Efficiencies of blowing agents were introduced to fit modeling result to experimental data. The efficiency of water was 85% and the efficiency of methyl formate was 45%. Details of efficiency calculation will be presented in the future since this work focused on temperature modeling.

## **2.4 Conclusion**

This work represents a modeling effort for the thermoset polyurethane reaction that goes beyond what have previously been achieved, including:

- Effective modeling of single-polyol gel-reaction temperature profiles including estimation of pre-exponential factors, Arrhenius activation energy, and heat of reaction with confirmation of accepted convective heat transfer coefficients for cooling.
- Prediction of the performance of mixtures of polyols based on pure component kinetic parameters.
- Estimation of concentration profiles based on kinetic parameters predicted from temperature profiles.

- And, estimation of foam density as a function of time with final foam height for this rigid foam being about 80% of what is estimated if all blowing agents were 100% effective.

This base model sets the foundation for future studies that will provide better insight into fundamental processes for thermoset reactions, have the potential to predict foam performance, and ultimately could provide a valuable mechanism to expedite new formulation development. These types of models would be particularly useful for expediting the rate at which new bio-based polyols can penetrate the market. The kinetic parameters and heat of reactions were in reasonable agreement with literature. It is to be noted that this work is part of an ongoing program with the goal of providing experimental data that can provide increasingly accurate values of kinetic parameters, fundamental mechanisms, and foam characteristics.

# **CHAPTER 3. MODELING IMPACT OF CATALYST LOADING ON POLYURETHANE FOAM POLYMERIZATION**

## **3.1 Introduction**

In the production of polyurethane foam, catalysts play an important role. Research results [23-25] show that the match between the gelatinizing rate and the foaming rate could be adjusted by specifying catalyst and changing catalyst amounts, thus the structure and properties of the polyurethane foam could be controlled. With a good selection of the catalyst, the desired profile in reaction, foaming, flow-ability, and foaming properties can be obtained [26]. Depending on concentration of catalysts in foaming recipe, the activity will be different [27, 28]. This activity relates to the catalysis of the gel and blow reaction [29], which has a great impact on the properties and functions of the foam [30].

Catalysts have a most important role in making urethane foams. If the gas formation takes place too fast in comparison to the gelation reaction, it would result in the cells opening before there is sufficient viscosity build-up to provide the foam struts with enough strength to uphold the foam, leading to the collapse of the foam [31]. On the other hand, if the gelation reaction is faster than the gas formation, it may result in foam with closed cells [32] and hindered expansion, which is not desirable. Catalysts have the critical purpose of fine-tuning the kinetics so that gas formation and gelation are properly synchronized.

The state of the art in developing new foam formulations is based on the

modification of established foam formulations by chemists who apply expertise in a qualitative sense. It would be highly desirable to elevate this process to a science including the simulation of the chemical reactions, physical processes, and ultimate the foam's physical properties. To date, such simulations have fallen short of what is needed for widespread application.

Baser developed theoretical models for physical blowing agent blown rigid polyurethane foam formation [12] and water-blown polyurethane foams [13]. They carried out detailed experimental study to measure both temperature and density change during foam formation. However, they did not consider heat transfer to surroundings and the impact of thermocouples on temperature profiles. Tesser [14] optimized a model to include heat transfer and modify the description of the vapor-liquid equilibrium of the blowing agent and the polymeric phase by means of an extended Flory-Huggins equation that well describes the nonideal behavior of these reacting mixtures. Tesser did not consider mixtures of polyols nor the prediction of mixtures based on single-polyol parameters. Also, the work did not consider water as a chemical blowing agent, and attributed basically all lack of inefficiency of foam height to Flory-Huggins non-idealities.

The following advances are needed to make foam simulation more useful and are beyond what has previously been attained:

- Simulate performance of mixtures of polyols,
- Simulate water reaction and physical processes for gas formation,

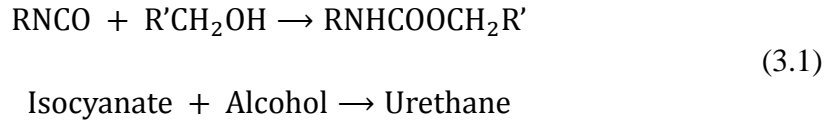
- Simulate impact of catalysts including the impact of catalyst concentration.
- Simulate the effectiveness with which gases lead to decreased foam density including impacts other than gas/vapor solubility (Flory-Huggins).
- A sufficiently fundamental basis so as to subsequently model physical processes (e.g. cell rupture) and the foam's physical characteristics (e.g. thermal conductivity).

The original work in Chapter 2 has initiated the first of several phases of modeling that will be necessary to attain these goals. That modeling work has included simulation of up to three polyols, a methyl formate physical blowing agent, and water reaction blowing agent. This work extends those initial studies to include modeling of homogeneous catalysts for these foam-forming reactions. In this modeling work the impact of temperature on process is important since temperatures will typically increase from 25 to in excess of 110 °C during foaming.

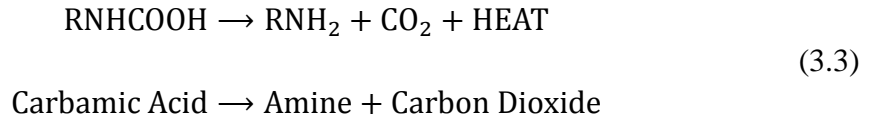
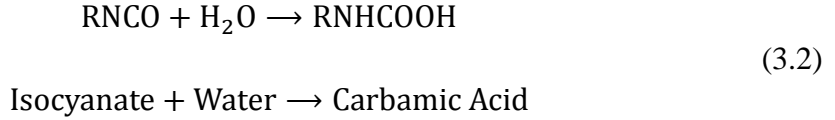
For urethane foams both physical blowing agents and gas-forming reactions are used for in-situ formation of gases that lead to foam cells. In water-blown foams, gel reaction and blow reaction occur simultaneously [33], and so, catalysts have the added role of controlling the gas formation in addition to controlling gelation rates. The goal of this project is to extend a newly developed thermoset polymerization model to include impact of catalyst concentration and combinations of catalysts.

### 3.2 Description of the model

This work investigates a urethane rigid foam process that uses both physical (methyl formate) and blowing-reaction blowing agents. The blowing reaction competing with gel reaction was summarized by the following schemes. The gel reaction creates urethane as described in Equation 3.1.



The blow reaction is a two-step reaction described by Equations 3.2 and 3.3.



The physical blowing process is based on the evaporation of volatile compound that typically has a boiling point between 30 and 70 °C. The elementary rate expressions [15, 34] for these reactions are summarized by Equations 3.4 and 3.5 along with the energy balance equation is expressed as Equation 3.6. These rate expressions are based on functional group concentration rather than molecule concentration. Also, the model assumes that the reactivity of any functional group can be represented by a single rate constant—this is a simplifying assumption that can be improved-upon as the accuracy of the simulation is improved.

$$r_{gel} = \sum_i \frac{dc_{gel\ i}}{dt} = \sum_i k_{gel\ i} * c_{cat\ gel} * c_{iso} * c_{OH\ i} \quad (3.4)$$

$$r_{blow} = k_{blow} * c_{catblow} * c_{iso} * c_{water} \quad (3.5)$$

where  $c_{gel\ i}$  is the concentration of the gel associated with polyol  $i$ ,  $k_{gel\ i}$  is the reaction rate constant of gel  $i$ ,  $c_{catgel}$  is the concentration of gelling catalyst,  $c_{iso}$  is the concentration of isocyanate groups,  $c_{OH\ i}$  is the concentration of hydroxyl groups of polyol  $i$ ,  $r_{gel\ i}$  is the gel reaction rate of polyol  $i$ ,  $r_{gel}$  is the summation of gel reaction rates of polyol mixtures,  $r_{blow}$  is the blow reaction rate,  $k_{blow}$  is the reaction rate constant of blowing,  $c_{catblow}$  is the concentration of blowing catalyst,  $c_{water}$  is the concentration of water.

$$\frac{dT}{dt} = \frac{\sum_i \Delta H_{gel\ i} * r_{gel\ i} + \Delta H_{blow} * r_{blow} - \Delta H_{vap} * \left(-\frac{dn_{MFL}}{dt}\right) + UA\Delta T}{\sum(n * C_p)} \quad (3.6)$$

where  $U$  is the overall heat transfer coefficient from the surroundings.  $A$  is the surface area of the foam related to different foam height [18] which is the summation of base area and lateral area.  $\Delta H_{gel\ i}$  is the heat of gel reaction respect to polyol  $i$ ,  $\Delta H_{blow}$  is the heat of blowing reaction,  $\Delta H_{vap}$  (27920 J/mol) is the enthalpy of vaporization of methyl formate [19], for sake of simplicity it was assumed as a constant under different temperature.  $-\frac{dn_{MFL}}{dt}$  is the evaporation rate of methyl formate, and  $\sum(n * C_p)$  is the summation of heat capacities of all the chemicals used. Based on the heat capacity values under different temperatures [20, 21] we assume that heat capacity is a linear function of temperature and it increases 0.1% as temperature rising 1K degree in the study temperature range.

However, based on more detailed experimental results it showed that the reactions could happen without the effect of catalysts. The modeling results could not fit experimental data perfectly under different catalyst loading conditions.



Therefore, a revised model needs to be developed to accurately simulate the effect of catalysts.

The initial gel reaction rate and blow reaction rate equations used in the original model were:

$$r_{gel} = k_{gel} * c_{catgel} * c_{iso} * c_{OH} \quad (3.7)$$

$$r_{blow} = k_{blow} * c_{blow} * c_{iso} * c_{water} \quad (3.8)$$

And the revised equations are expressed as:

$$r_{gel} = (k + k_{cat8} * c_{cat8} + k_{cat5} * c_{cat5}) * c_{iso} * c_{OH} \quad (3.9)$$

$$r_{blow} = (k'_{cat8} * c_{cat8} + k'_{cat5} * c_{cat5}) * c_{iso} * c_{water} \quad (3.10)$$

Where  $k$  represents the gel reaction rate under the condition without any catalysts,  $k_{cat8}$  is the gel reaction rate under the effect of catalyst8 (DMCHA),  $k_{cat5}$  is the gel reaction rate under the effect of catalyst 5 (PMDETA),  $k'_{cat8}$  is the blow reaction rate under the effect of catalyst8 and  $k'_{cat5}$  is the blow reaction rate under the effect of catalyst5. The revised reaction rates equations were expected to accurately model temperature profiles under multiple catalyst loading conditions (no catalysts, only DMCHA, only PMDETA, and both two catalysts).

In addition, the kinetics modeling was optimized to include side reactions. Equation 3.11 represents the reaction between isocyanate and amine. Equation 3.12 represents the reaction between isocyanate and urethane. These two side reactions provide a mechanism through which excess isocyanate continues to react after all alcohol is consumed.



Isocyanate + Amine  $\rightarrow$  Disubstituted Urea



Isocyanate + Urethane  $\rightarrow$  Allophanate

Based on the generalized rate equations 3.9 and 3.10, the concentration profiles and physical properties are estimated in the MATLAB program by solving a series of ten to twenty differential equations. The computer algorithm includes sequential solution of the following concentrations and properties:

- Alcohol, isocyanate, urethane, water, and carbon dioxide concentrations,
- Polyol monomer, isocyanate monomer, and urethane polymer concentrations,
- Temperature and height/density,
- Degree of polymerization and viscosity.

The mark-Houwink equation[35, 36] (Equation 3.13) gives a relation between intrinsic viscosity  $[\eta]$  and molecular weight  $M$ .

$$[\eta] = KM^a \quad (3.13)$$

From this equation the molecular weight of a polymer can be determined from data on the intrinsic viscosity and vice-versa. The values of the Mark-Houwink parameters,  $\alpha$  and  $K$ , depend on the particular polymer-solvent system. For solvents, a value of  $\alpha = 0.5$  is indicative of a theta solvent. The Grunberg-Nissan equation[37] (Equation 3.14) is used to calculate viscosity of liquid mixtures.

$$\ln \eta_{mix} = \sum_i x_i \ln \eta_i \quad (3.14)$$

where  $\eta_{mix}$  is the viscosity of liquid mixtures,  $x_i$  is the mole fraction of component

$i$  in mixtures and  $\eta_i$  is the viscosity of pure component  $i$ .

The formation of a quality foam hinges upon the proper balance of viscosity increase with gas generation so as to form cells with resin walls that are sufficiently elasticity to avoid foam collapse while sufficiently viscous to allow cell expansion (resulting from gas generation) until the foaming process is complete. Catalysts are used to control reactivity in the process of fine-tuning this balance. Here, the term “fine-tuning” of the balance reflects the fact that the inherent reactivities of the polyol and isocyanate monomers provide the primary impact on reactivities.

As elementary rate expressions, Equations 3.9 and 3.10 imply a mechanism on how the homogeneous catalysts function. The models assume that the reactivity is directly proportional to the catalyst concentration which is consistent with the homogenous catalysts providing “sites” for the reactions to occur; albeit the sites are catalyst molecules in solution rather than locations on a solid surface. The implementation (computer code) of the model assumes that the concentration of the catalysts do not change with reaction.

It should also be noted that this model would only tend to be valid over a limited range of catalyst concentration. At low concentration the model does not correctly converge on the inherent reactivities of the monomers in the absence of catalyst. At high concentrations the model does not take into account changes in activities of the catalysts—the model basically assumes a Henry’s constant type of activity (a constant activity coefficient reflective of minimal catalyst-catalyst interaction in the solution).

In this chapter the model has been developed in MATLAB code and compared to

experimental data. Agreement of the model and data would substantiate a validation of both the mechanisms of equations 3.9 and 3.10 as well as the programming code designed to simulate varying catalyst concentrations. A goal of this work is to improve the accuracy with which the rigid foaming reactions can be simulated, which in turn, can be used to expedite the development of new foam formulations.

### 3.3 Materials and methods

#### 3.3.1 Materials

RUBINATE M (Standard Polymeric MDI) was the isocyanate used in this study and the petroleum-based polyols were Poly G76-635, Voranol 360 and Jeffol R315x from Huntsman Company and Dow Chemical Co. The specifications are shown in Table 3.1 [20, 21]. N,N-dimethylcyclohexylamine (DMCHA) and N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA) were used as the gelling catalyst and the blowing catalyst respectively. However, PMDETA was found also having impact on gel reaction based on experimental results. The efficiency of PMDETA on catalyzing gel reaction was about 80% respect to DMCHA. Momentive L6900 was used as the surfactant for rigid foams, TCPP was used as the fire retardant, and distilled water and methyl formate were used as the blowing agents.

*Table 3.1 Raw material properties*

<b>Component</b>	<b>Isocyanate</b>	<b>Polyol</b>	<b>Polyurethane</b>	<b>Water</b>	<b>Carbon Dioxide</b>	<b>Amine</b>
Heat Capacity (J/g-K)	1.799	1.57 ~1.8 9	1.4~1.5	4.19	0.846~0.939 (300K~400K)	1.55~ 1.64

Heat Capacity (J/equiv-K)	242.86	264.86	362.5	75.42	39.6	128
<b>Product</b>	<b>Fn</b>	<b>Sp. Gravity @25°C</b>	<b>% NCO</b>	<b>Eq. Wt.</b>	<b>Viscosity cps@25°C</b>	
RUBINATE M	2.70	1.23	31.2	135	190	
<b>Product</b>		Poly G76-635	Voranol 360	Jeffol R315x		
<b>OH number</b>		635	360	315		
<b>Equivalent Weight(g/mol OH)</b>		88.3	155.8	178		
<b>Product</b>	<b>MW</b>	<b>Physical State</b>	<b>Boiling Point(°C)</b>	<b>Flash Point(°C)</b>	<b>LFL/UFL *</b>	
Methyl Formate	60	Liquid	31.5	-19	5/20	

### 3.3.2 Experimental design

Blowing agents (water and MF) are taken out from the recipe for the gel reaction. The experimental studies were comprised of two parts: one on Cat8 (DMCHA) and one on Cat5 (PMDETA). Single polyol gel reaction without any catalysts was performed to evaluate the rate constant  $k$ , gel reactions with only cat8 or only cat5 were performed to evaluate the values of  $k_{cat8}$  and  $k_{cat5}$ . Reagent mixture was prepared with an electronic balance with an accuracy of  $\pm 10^{-2}$  g in which the buoyancy effect was neglected, since errors in measuring mass fractions introduced by this work were much smaller than 0.1%. When weighting the mixture, all components were added at the same amounts throughout the experiments except for both catalysts, where one catalyst was set at a constant amount each run and a step

change was made to the other catalyst in order to control the impact of catalysts. The same approach was applied in the study on each polyol. The kinetics parameters of three single polyols were used to predict polyols mixture temperature profiles under different catalyst loading conditions and experimental data were gathered to verify the accuracy of this revised model. Moles of polyol and isocyanate were designed to lock in constant numbers in single polyol tests and recipe of mixture polyols was designed based on original foam recipe. Isocyanate indices in all runs were designed to lock in 1.15, however, there was deviation in actual numbers since it was uncontrollable when adding pre-weighted isocyanate.

Experiments with different catalyst loading conditions were performed to measure the viscosity of gel system. The amount of one catalyst was locked in and the other one was changed step by step to study on the impact of single catalyst on gel system viscosity. A Cole-Parmer® Basic Viscometer is used to measure the viscosity of the gel system during the reaction.

### **3.3.3 Foam preparation and data collection**

The following steps were used in the foam experiments:

1. Polyols, water, blowing catalyst, gelling catalysts, and surfactant (B-side components) were added into a plastic cup successively.
2. The B-side components were mixed for 10-15 seconds.
3. The mixture was allowed to degas for 2 min.

4. Thereafter, pre-weighed isocyanate (A-side material) was added and mixed at the same speed for 7-10s.
5. The reacting mixture was then quickly poured into a box lined with aluminum, and the foam was allowed to rise and sit at ambient conditions (25 °C) during curing.

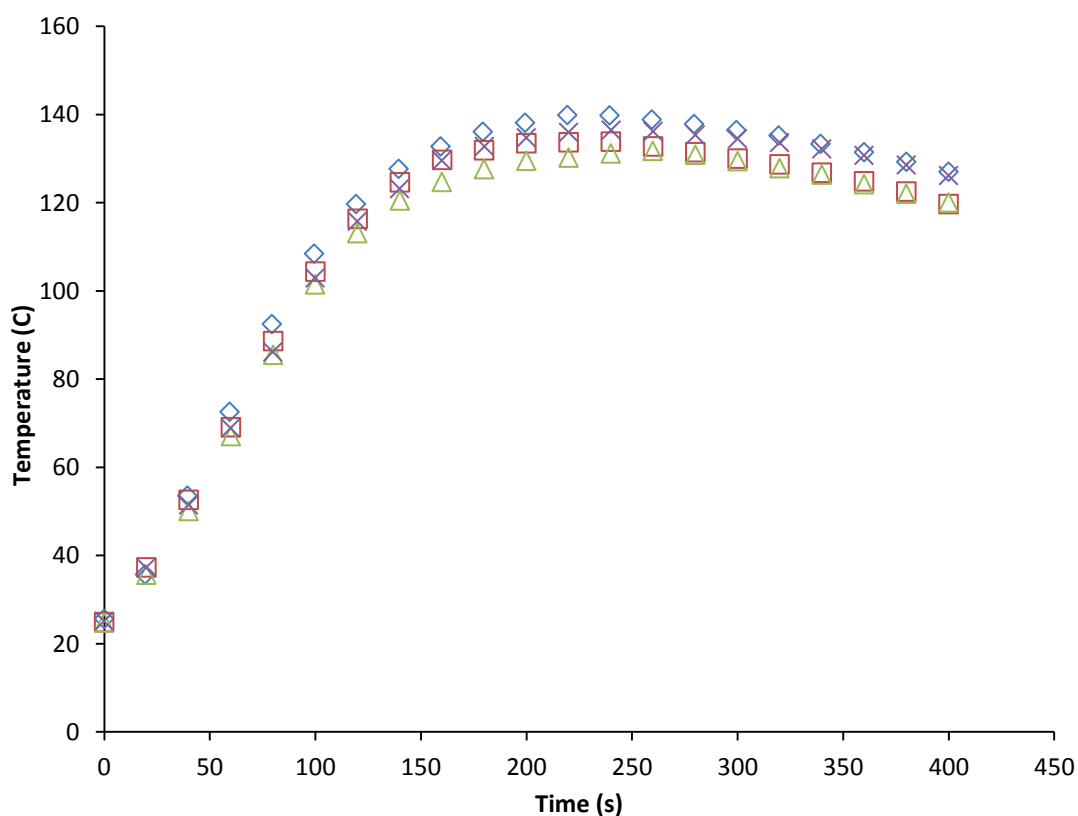
All the B-side chemicals were added in the foam reaction while blowing agents and blowing catalyst were not added in the gel reaction. Since the volume of gel mixture is much smaller than that of foam, the fluid level in wood box is too low to gather accurate data while performing gel reaction. Instead of using wood box for both reactions, step 5 was not performed in gel reactions and temperature was directly measured in plastic cups which could give a more accurate profile.

A high speed mixer blade (540 rpm) attached to a floor-model drill press was used to mix the chemicals. LabVIEW software was used to monitor the temperature of the gel or foam reactions for the first 10 minutes with a type-k thermocouple attached through a National Instruments SCB-68 box to a National Instruments PCI 6024E data acquisition card.

### 3.4 Results and discussion

#### 3.4.1 Data on repeatability

A control formulation was repeated four times to evaluate the repeatability of the experimental procedure. Figure 3.1 presents four groups of internal temperature experimental data. Experimental deviation is attributed to a number of factors including minor variations in measuring/transfer of chemicals and imperfect mixing. However, temperature profiles are substantially repeatable. The highest temperature and the corresponding time needed to reach the temperature were about 125-135 °C and 200-250 seconds.



**Figure 3.1 Internal temperature during the regular control foaming process of four times repeated test. Four different symbols respectively represent four groups of data.**



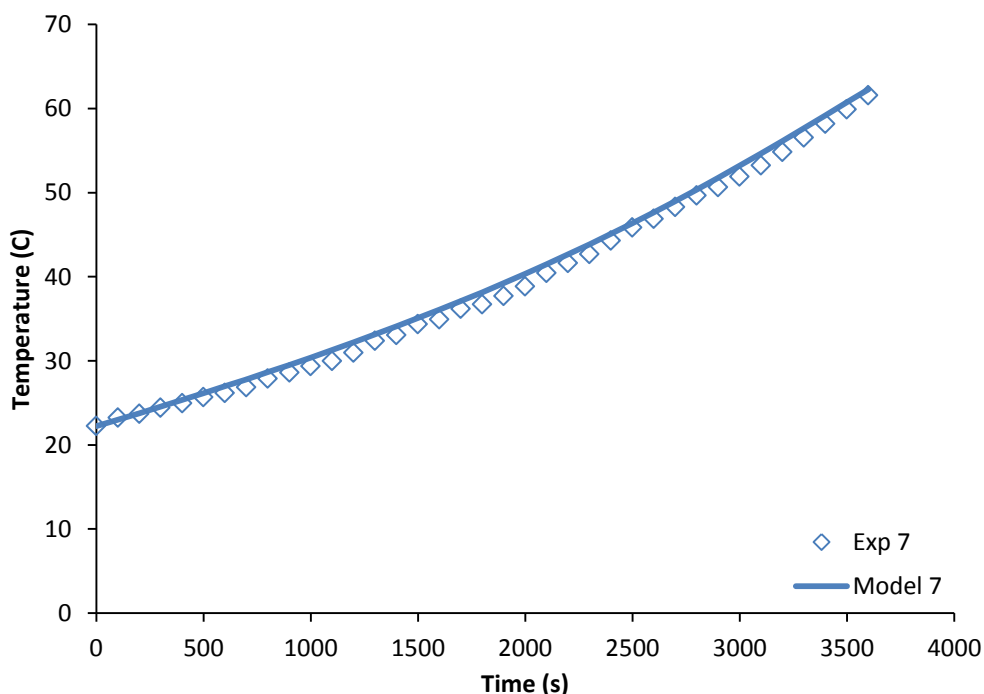
### 3.4.2 Evaluation on single polyol kinetics parameters

Recipes of Poly G76-635 gel reaction were listed in Table 3.2.

*Table 3.2 Recipes of single polyol gel reaction (poly G76-635)*

Mass (g)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9
G76-635	19.06	19.05	19	19.03	19.04	18.96	18.96	19.01	19.06
TCPP	2	2.02	2.02	2.02	2	2	2.01	2	2
L6900	0.6	0.61	0.6	0.6	0.6	0.6	0.61	0.6	0.6
Cat 8 (5)	0.12	0.12	0.12	0.12	0.179	0.181	0	(0.32)	(0.32)
Isocyanate	35.58	32.24	33.51	31.46	36.18	30.64	34.28	27.69	29.74
Moles									
G76-635	0.216	0.216	0.215	0.216	0.216	0.215	0.215	0.215	0.216
Isocyanate	0.264	0.239	0.248	0.233	0.268	0.227	0.254	0.205	0.220
Index	1.221	1.107	1.154	1.081	1.243	1.057	1.183	0.953	1.021
Total mass	57.36	54.04	55.25	53.23	58.00	52.38	55.86	49.3	51.4

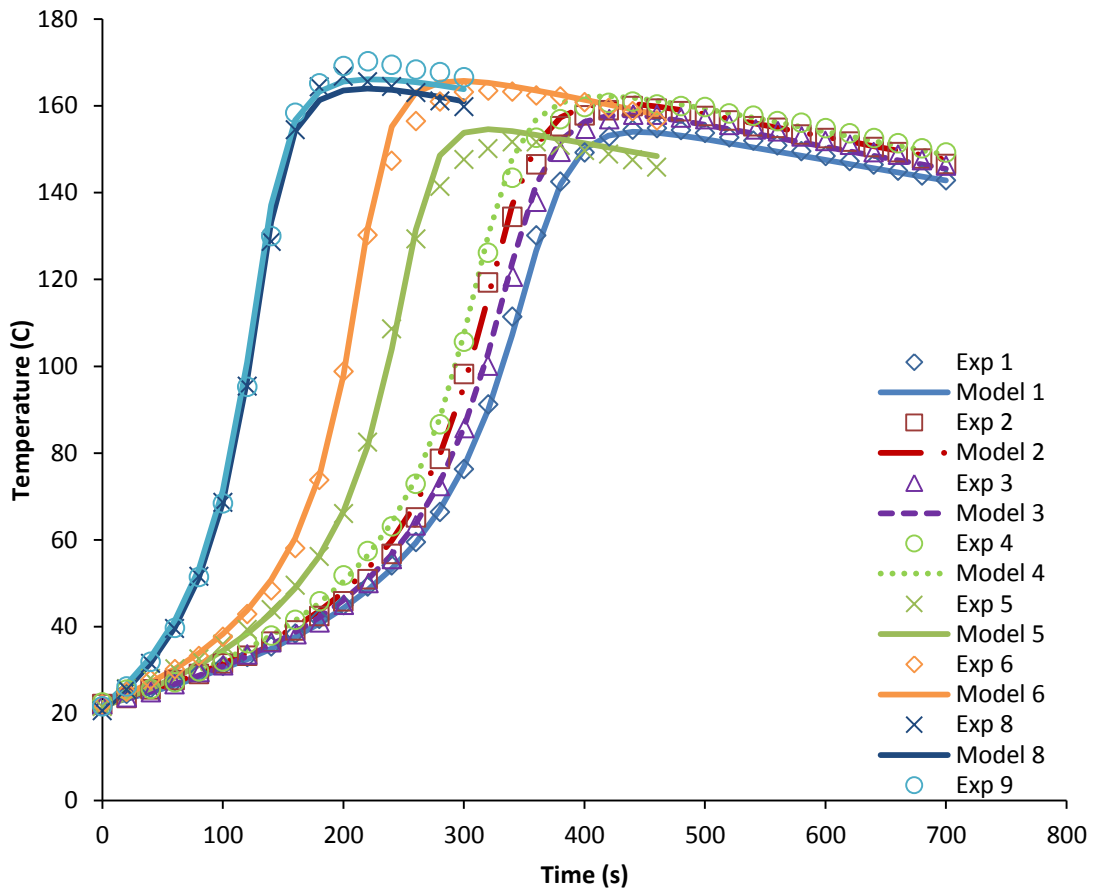
Figure 3.2 presents the average experimental data of internal temperature under no catalysts condition.



**Figure 3.2 Internal temperature of poly G76-635 gel reaction with no catalysts. The symbol represents average number of experimental data and the solid line represents modeling result.**

Based on the experimental results under no catalysts condition the value of  $k_0$  was found to be 0.7125 and  $E_0$  was 50000.

Figure 3.3 presents the experimental data of poly G76-635 gel reaction internal temperature under different catalyst loading conditions.



**Figure 3.3 Internal temperature of poly G76-635 gel reaction under different catalyst loading conditions. The symbols represent average numbers of experimental data and the solid lines represent modeling results.**

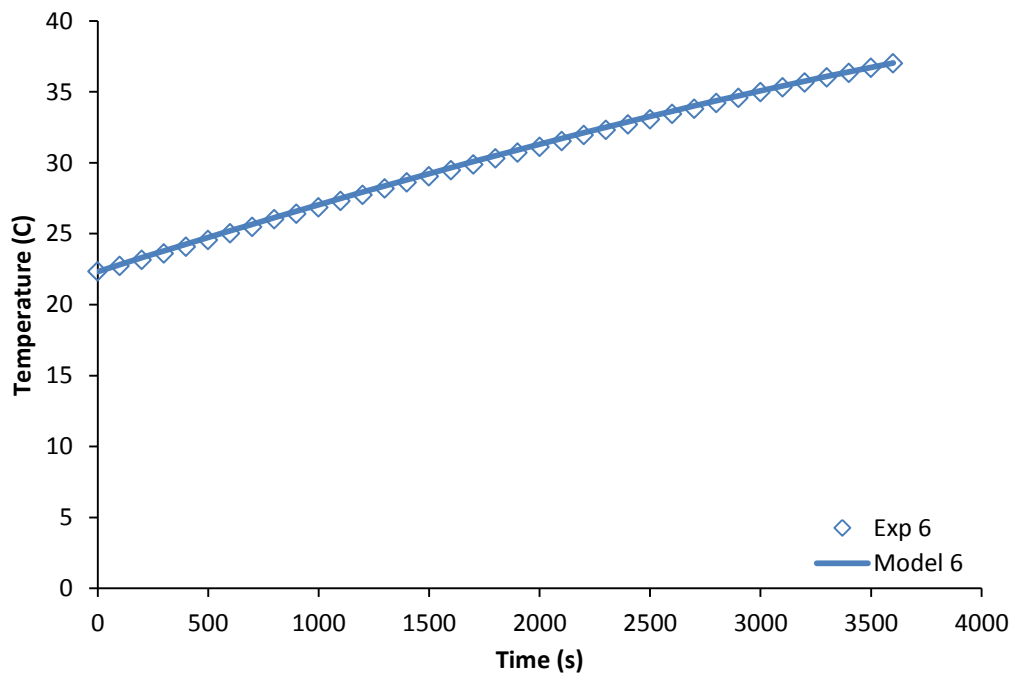
Based on the experimental results with only cat8 loading conditions the value of  $k_{cat8}$  was found to be 51 and  $E_0$  was 50000. Based on the experimental results with only cat5 loading conditions the value of  $k_{cat5}$  was found to be 54 and  $E_0$  was 43000.

Recipes of Poly V360 gel reaction were listed in Table 3.3.

**Table 3.3 Recipes of single polyol gel reaction (poly V360)**

Mass (g)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
polyolV-360	33.55	33.6	33.58	33.5	33.51	33.62	33.54
TCP	2	2	2	2	2	2.01	2
L6900	0.6	0.6	0.6	0.61	0.61	0.6	0.61
Cat 8 (5)	0.116	0.12	0.12	0.184	0.182	0	(0.32)
Isocyanate	34.92	38.76	33.14	40.45	38.32	34.12	30.21
Moles							
polyol V-360	0.21534	0.21566 1	0.21553 3	0.21501 9	0.21508 3	0.21578 9	0.21527 6
Isocyanate	0.25867	0.28711	0.24548	0.29963	0.28385	0.25274	0.22378
Index	1.2012	1.33131	1.13895	1.39350	1.31973	1.17124	1.03949
Total mass	71.186	75.08	69.44	76.744	74.622	70.35	66.36

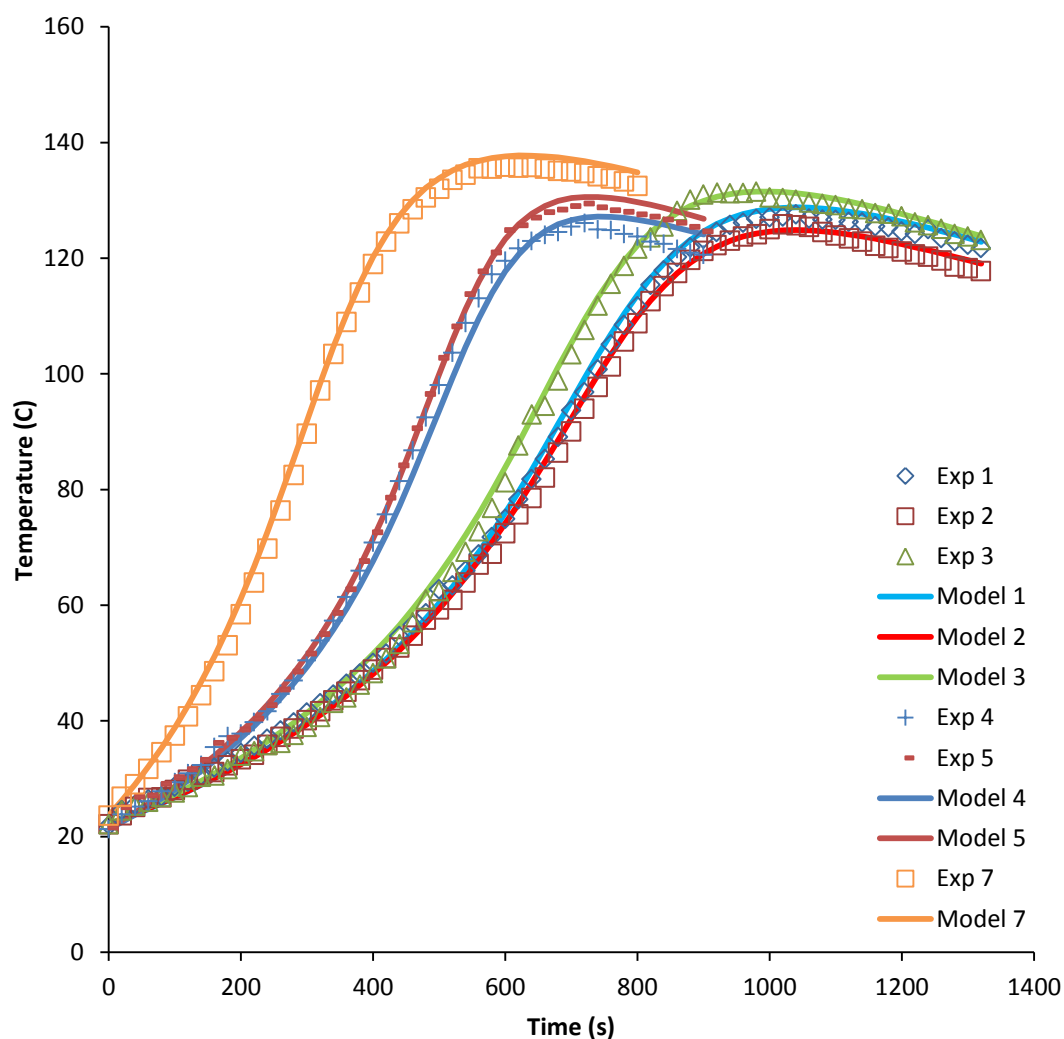
Figure 3.4 presents the average experimental data of internal temperature under no catalysts condition.



**Figure 3.4 Internal temperature of poly V360 gel reaction with no catalysts. The symbol represents average number of experimental data and the solid line represents modeling result.**

Based on the experimental results under no catalysts condition the value of  $k_0$  was found to be 0.75 and  $E_0$  was 39000.

Figure 3.5 presents the experimental data of poly V360 gel reaction internal temperature under different catalyst loading conditions.



**Figure 3.5 Internal temperature of poly V360 gel reaction under different catalyst loading conditions. The symbols represent average numbers of experimental data and the solid lines represent modeling results.**

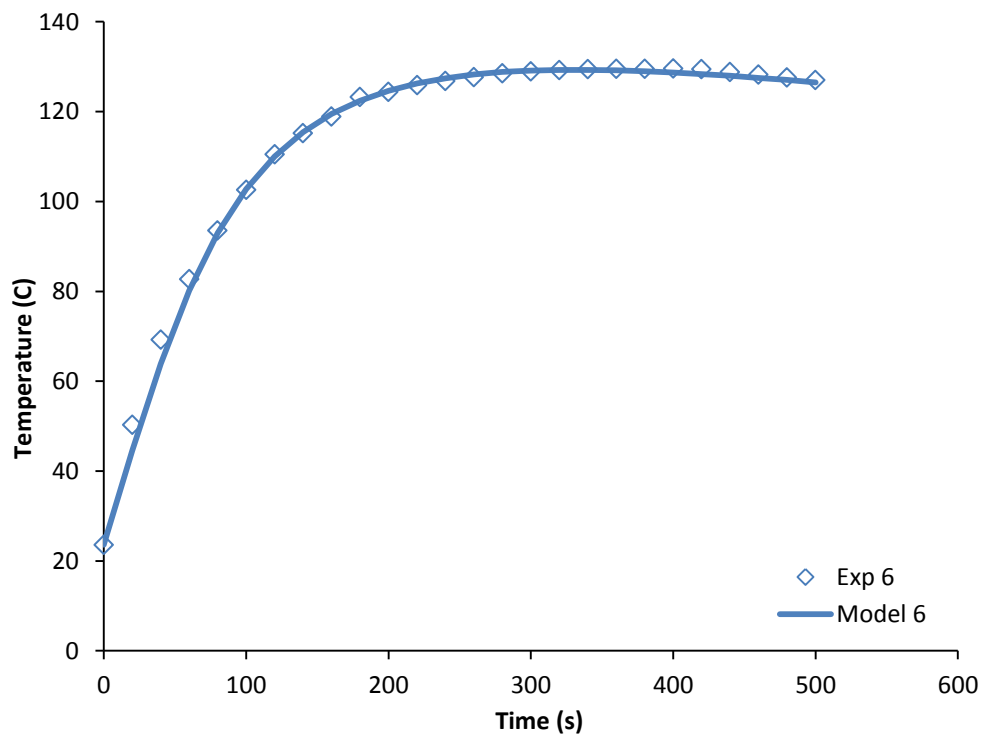
Based on the experimental results under only cat8 loading conditions the value of  $k_{cat8}$  was found to be 54 and  $E_0$  was 39000. Based on the experimental results under only cat5 loading conditions the value of  $k_{cat5}$  was found to be 51 and  $E_0$  was 30000.

Recipes of Poly R315x gel reaction were listed in Table 3.4.

*Table 3.4 Recipes of single polyol gel reaction (poly R315x)*

Mass (g)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
R315x	42	38.44	38.4	38.38	38.36	38.57	38.43	38.35
TCCP	2	2	2	2	2	2	2	2
L6900	0.61	0.61	0.61	0.6	0.63	0.6	0.6	0.61
Cat 8 (5)	0.12	0.126	0.12	0.177	0.18	0	(0.32)	(0.32)
Isocyanate	31.92	32.9	33.9	31.1	33.61	32.54	30.6	33.42
Moles								
R315x	0.2360	0.2160	0.2157	0.2156	0.2155	0.2167	0.2159	0.2154
Isocyanate	0.2364	0.2437	0.2511	0.2304	0.2490	0.2410	0.2267	0.2476
Index	1.0021	1.1285	1.1640	1.0684	1.1553	1.1124	1.0499	1.1490
Total mass	76.65	74.076	75.04	72.264	74.782	73.71	71.63	74.38

Figure 3.6 presents the average experimental data of internal temperature under no catalysts condition.

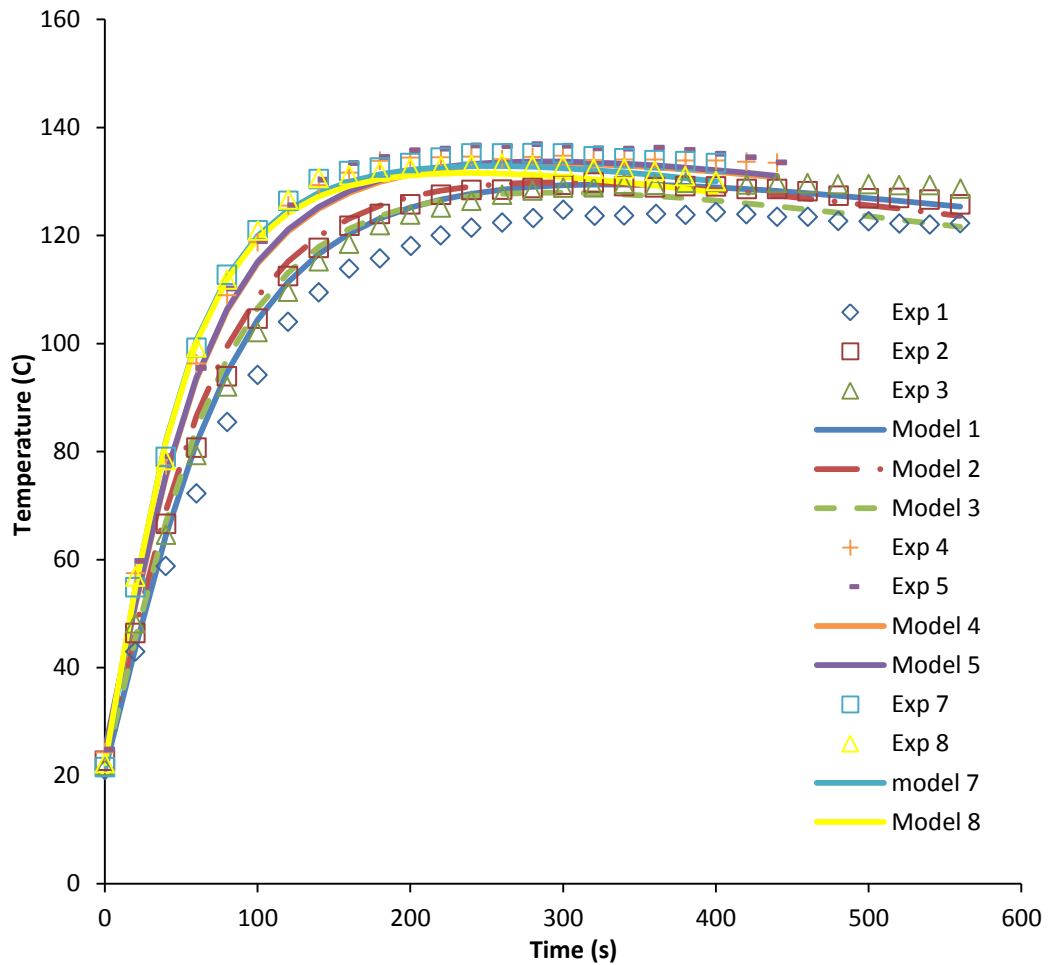


**Figure 3.6 Internal temperature of poly R315x gel reaction with no catalysts. The symbol represents average number of experimental data and the solid line represents modeling result.**

Based on the experimental results under no catalysts condition the value of  $k_0$  was found to be 200 and  $E_0$  was 10000. The gel reaction of poly R315x was much

faster than the other two polyols under no catalysts condition since it had a much higher activity.

Figure 3.7 presents the experimental data of poly R315x gel reaction internal temperature under different catalyst loading conditions.



**Figure 3.7 Internal temperature of poly R315x gel reaction under different catalyst loading conditions. The symbols represent average numbers of experimental data and the solid lines represent modeling results.**

Based on the experimental results under only cat8 loading conditions the value of  $k_{cat8}$  was found to be 300 and  $E_0$  was 10000. Based on the experimental results under only cat5 loading conditions the value of  $k_{cat5}$  was found to be 400 and  $E_0$  was 10000.

All single polyol kinetics parameters under different catalyst loadings were fitted based on experimental data. All detailed values were listed in Table 3.5. By plotting  $\ln(T-T_0)$  as a function of time, a straight line is obtained from which the slope of heat transfer coefficient can be evaluated. For all the runs, average values of  $U=4$  ( $W/m^2-K$ ) for gel reactions in plastic cups and  $U_f=1$  ( $W/m^2-K$ ) for foam reactions in wood box were used in the modeling.

*Table 3.5 Single polyol gel reaction kinetic parameters under different catalyst loadings*

<b>Poly G76-635</b>	<b>Without Catalyst</b>	<b>Catalyst 8</b>	<b>Catalyst 5</b>
k ml/(mol*s*g catalyst)	0.7125	51	60
E (J/mol)	50000	50000	43000
H (J/mol)	72500	72500	72500
<b>Poly V360</b>	<b>Without Catalyst</b>	<b>Catalyst 8</b>	<b>Catalyst 5</b>
k ml/(mol*s*g catalyst)	0.75	54	51
E (J/mol)	39000	39000	30000
H (J/mol)	67000	67000	67000
<b>Poly R315x</b>	<b>Without Catalyst</b>	<b>Catalyst 8</b>	<b>Catalyst 5</b>
k ml/(mol*s*g catalyst)	200	300	400
E (J/mol)	10000	10000	10000
H (J/mol)	60000	60000	60000

Both Cat8 and Cat5 have significant impact on gel reaction internal temperature. Increasing amount of catalyst accelerates gelling reaction, leading to an earlier and higher temperature rise. However, there is a slight difference between these two catalysts due to their specific structures and properties, which leads to different values of rate constant pre-exponential factor and activation energy respect to different catalyst. Heat of reaction does not change based on the type of catalyst since it is only dependent on the type of functional groups.

### 3.4.3 Prediction of polyols mixture temperature profiles

Temperature profiles of polyols mixture were predicted just based on the kinetics parameters provided above. Experiments were run to verify the modeling results.

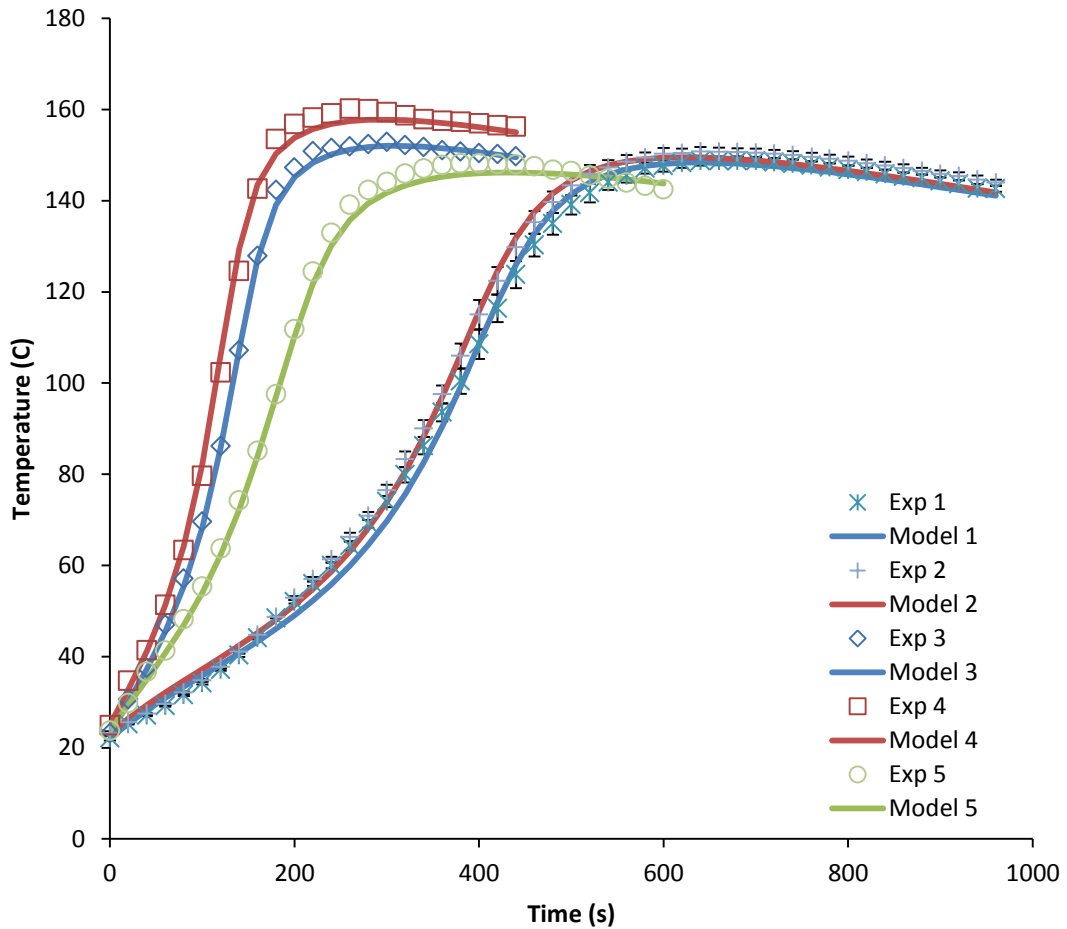
Recipes of polyols mixture gel reaction were listed in Table 3.6.

*Table 3.6 Recipes of polyols mixture gel reactions*

Mass (g)	Run 1	Run 2	Run 3	Run 4	Run 5
poly G76-635	13.86	13.87	13.85	13.85	13.87
polyolV-360	15.72	15.72	15.66	15.76	15.71
poly R315x	3.99	4.02	4	4.03	4.01
TCPP	2	2	2	2	2.01
L6900	0.6	0.62	0.61	0.6	0.61
Poly cat 8	0.123	0.12	0.12	0.122	0
Poly cat 5	0	0	0.32	0.321	0.322
Isocyanate	39.73	39.49	47.42	39.69	44.12
Moles (g-mol)					
poly G76-635	0.156965	0.157078	0.156852	0.156852	0.157078
polyolV-360	0.100899	0.100899	0.100513	0.101155	0.100834
poly R315x	0.022416	0.022584	0.022472	0.02264	0.022528
Isocyanate	0.294296	0.292519	0.351259	0.294	0.326815
Index	1.050011	1.04262	1.255228	1.047578	1.165362
Total mass	76.023	75.84	83.98	76.373	80.652

Figure 3.8 presents the experimental data of polyols mixture gel reaction internal temperature under different catalyst loading conditions. The polyols mixture modeling results were obtained by using the same kinetics parameters fitted only based on single polyol gel reaction results. These data validate the accuracy of this modeling approach as well as the utility of the modeling method. Here, as is the general case, the value of fundamentally based models is that they allow a limited amount of pure component data to be used to predict the performance of an infinite number of possible mixtures of the pure reagents with different catalyst loading.





**Figure 3.8 Internal temperature of polyols mixture gel reaction under different catalyst loading conditions. The symbols represent average numbers of experimental data and the solid lines represent modeling results.**

### 3.4.4 Evaluation on foam reaction kinetics parameters

Blowing catalysts and blowing agents (water and methyl formate) were added to the gel formation to create rigid foams and monitor the foaming processing. The isocyanate reacts with water to generate carbon dioxide which is blowing agent [22]. In addition, methyl formate is a blowing agent due to its high volatility (32 °C). Internal temperature was measured during the experimental process and compared with the modeling result to correct the kinetic parameters of blow reaction. Table 3.7 provides the blow reaction kinetics parameters respect to catalyst8 and catalyst5

based on experimental data under pure catalyst conditions.

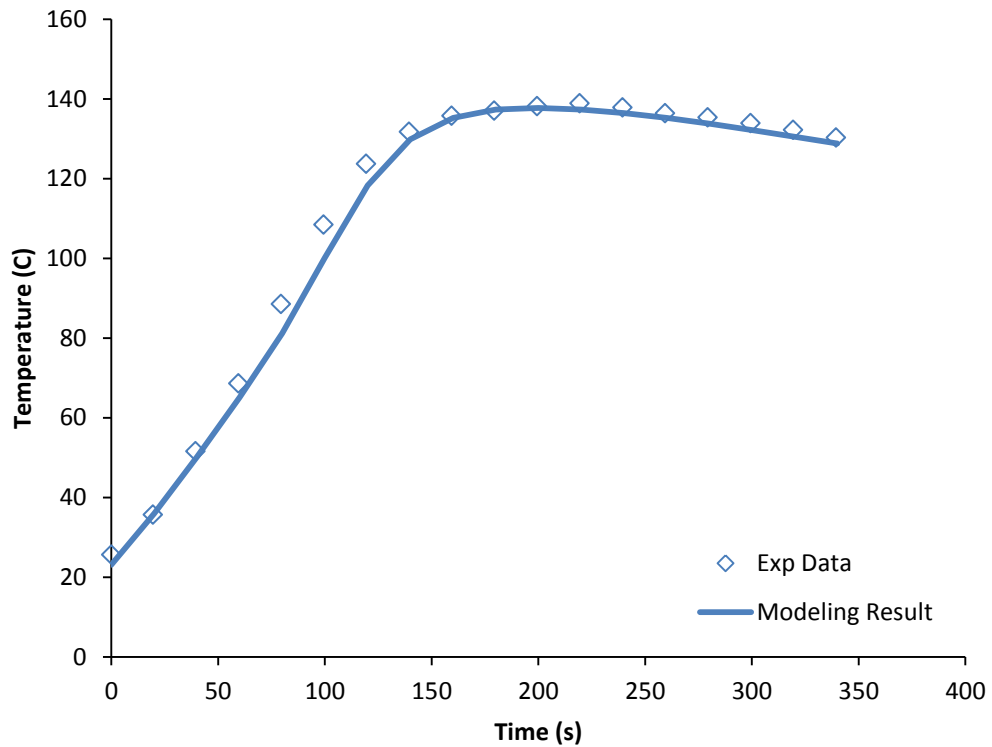
*Table 3.7 Blow reaction kinetic parameters under different catalyst loadings*

Iso -Water	Catalyst 8	Catalyst 5
k ml/(mol*s*g catalyst)	200	1000
E (J/mol)	35000	45000
H (J/mol)	75000	75000
Iso - Amine	Catalyst 8	Catalyst 5
k ml/(mol*s*g catalyst)	20	100
E (J/mol)	10000	10000
H (J/mol)	30000	30000

Catalyst5 (PMDETA) has major impact on blow reaction rather than catalyst8 (DMCHA) since it is regarded as a popular blowing catalyst in several works. Table 3.8 lists the regular control recipe used in foam reactions. Figure 3.9 presents the temperature profile of regular control foam reaction.

*Table 3.8 Foaming formulation of rigid polyurethane foam*

<b>B-side Materials</b>	Weight/g	Moles of functional groups
Poly G76-635	13.84	0.1567
Voranol 360	15.68	0.1006
Jeffol R315x	4	0.0225
Dimethylcyclohexylamine(Cat8)	0.12	
Pentamethyldiethylenetriamine(Cat5)	0.32	
Momentive L6900	0.6	
TCP	2	
Distilled Water (Blowing Agent)	1.04	0.1156
Methyl Formate (Blowing Agent)	2.4	
<b>A-side Material</b>		
RUBINATE M	61.548	0.4559
<b>Isocyanate Index</b>		1.15

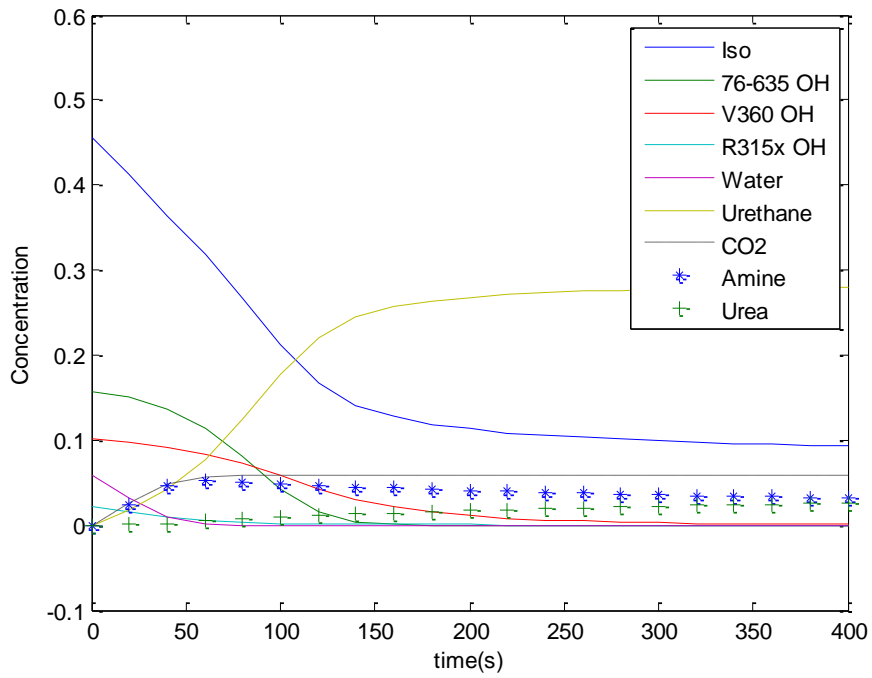


**Figure 3.9 Internal temperature of regular control blow reaction. The symbol represents average number of experimental data and the solid line represents modeling result.**

As summarized by Figure 3.9, the peak foam temperature of 140 °C was attained at about 200 seconds. After this, convective cooling of the foam led to reductions in temperature.

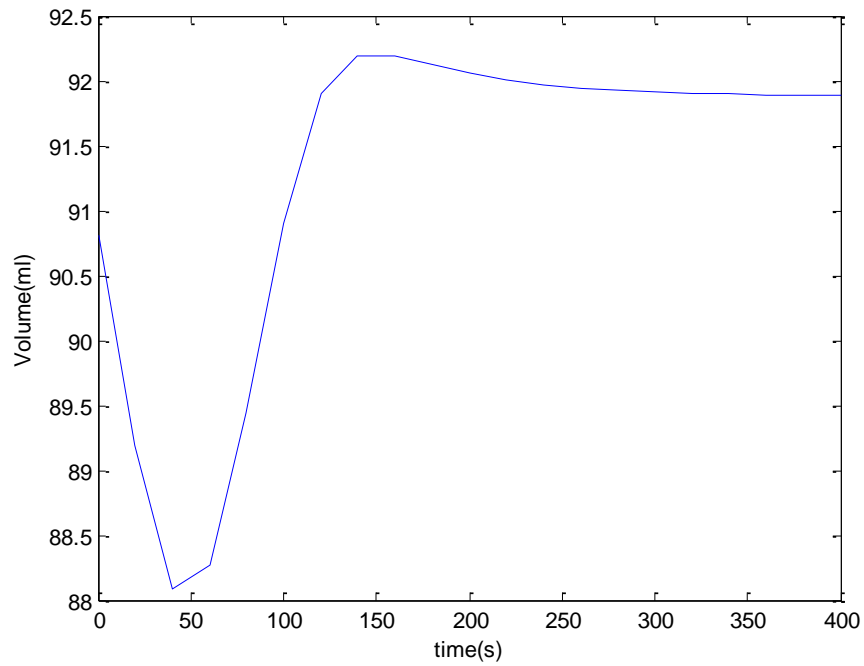
### 3.4.5 Checking the consistency of the program

Figure 3.10 shows the component concentrations estimated by the model during the foaming reaction. The concentration of amine increases first and then decreases because newly formed amine group from water blow reaction reacts with another isocyanate group to give a disubstituted urea.

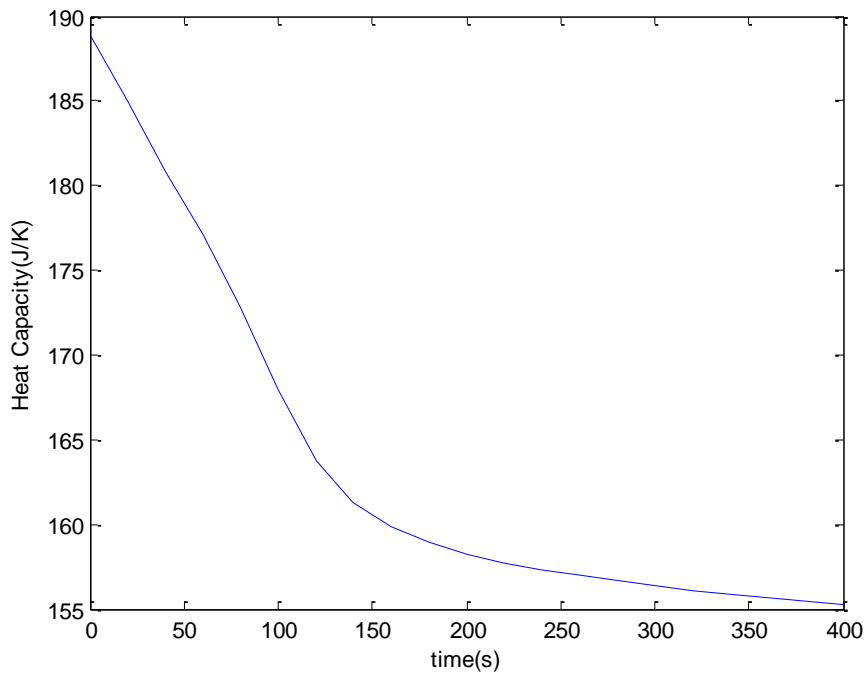


**Figure 3.10** Number of moles of components during polyols mixture foaming process

Figure 3.11 and Figure 3.12 shows the components total volume change and total heat capacity change during foaming process.



**Figure 3.11** Components total volume change during polyols mixture foaming process

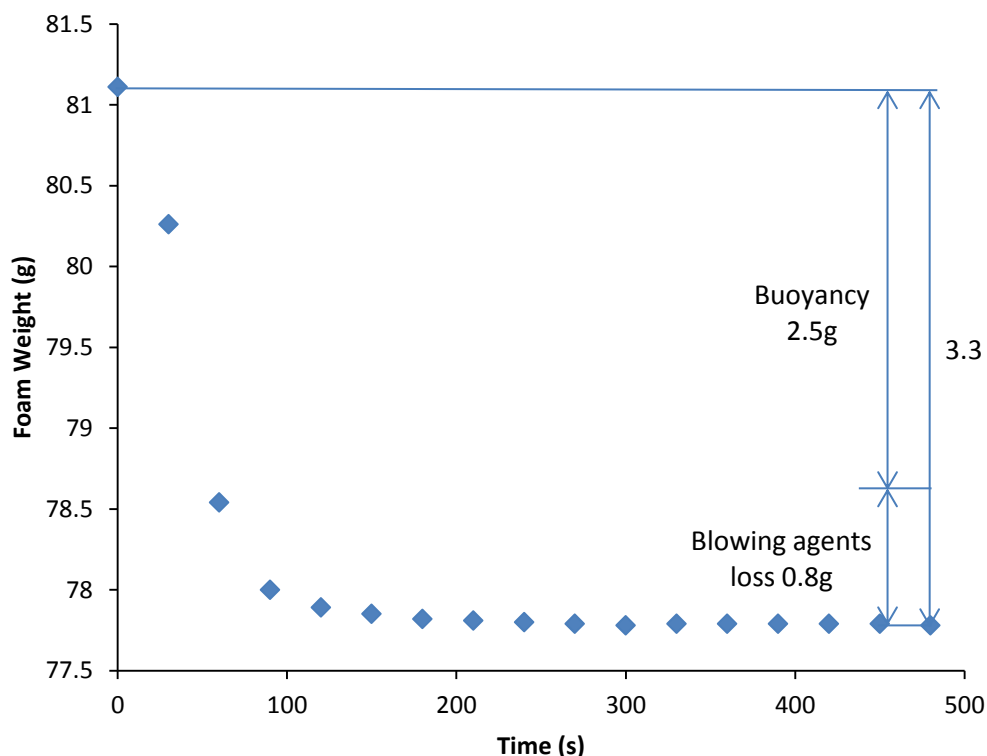


**Figure 3.12 Components total heat capacity change during polyols mixture foaming process**

The components total volume almost did not change during foaming process which provided a stable condition for reaction. The total heat capacity decreased because the heat capacity of one mole urethane was smaller than the sum of heat capacities of one mole isocyanate and one mole polyol. When isocyanate reacted with polyol and generated urethane, the total heat capacity of components therefore decreased.

A significant reduction in the measured weight of the foam with time was observed in all experiments. Due to increase in the volume of the foaming mixture with time there is an increase in the buoyant force acting on the foam. However, when the weight versus time data for the rising foam was corrected for the buoyancy effect of air, it was found that the weight loss recorded during foaming was just partially due to the buoyancy effect of air on the expanding foam and the contribution of blowing agents loss could not be neglected within the accuracy of the measurement.

Figure 3.13 shows foam weight loss result.



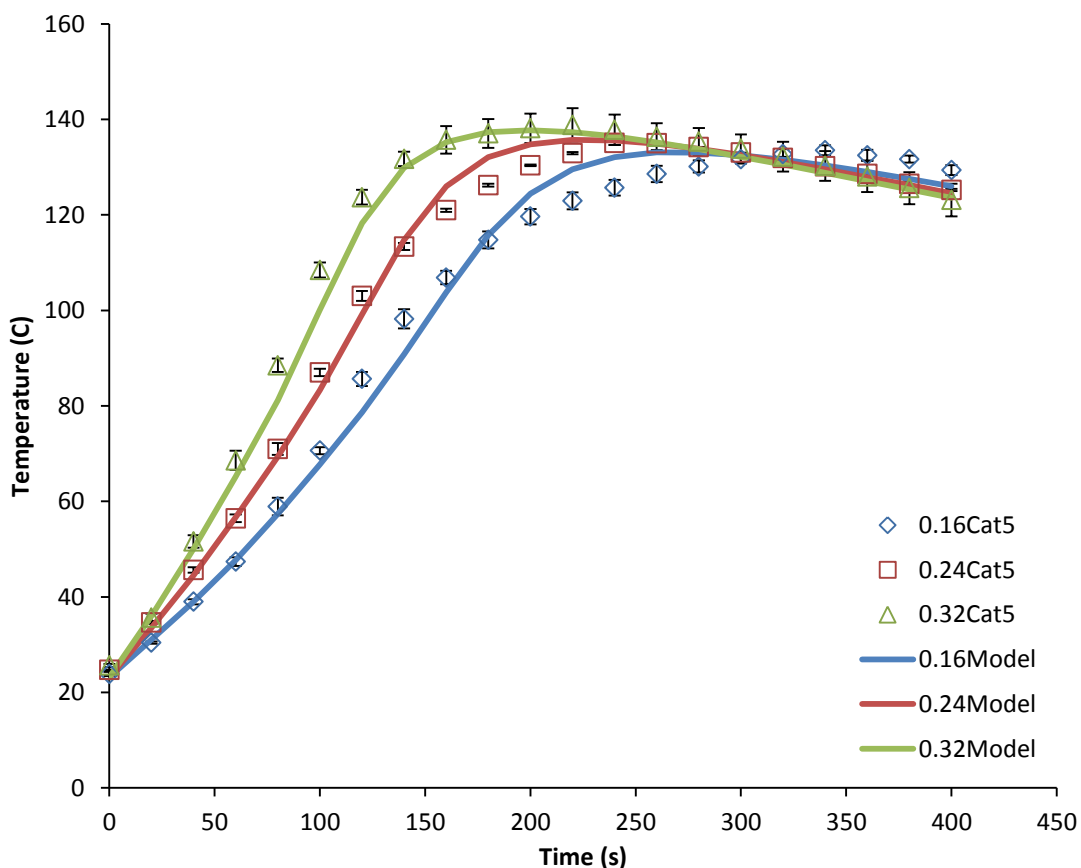
**Figure 3.13 Foam weight loss result during foaming process**

There was about 3.3g foam weight loss during foaming process and 25% of which was due to MF and carbon dioxide leaking. The foam tended to be stable at about 200 seconds when the reactions ended.

### 3.4.6 Impact of catalysts on foam reaction temperature

Figure 3.14 shows a comparison between modeling results and experimental data under various catalyst5 loading conditions where amounts of catalyst5 were adjusted on the basis of regular control recipe. Increasing the amount of catalyst5 makes the reaction faster which gives a higher temperature. The modeling results agree with the experimental data precisely under low concentration conditions. In higher catalyst concentration cases, the reaction was too fast to measure the internal

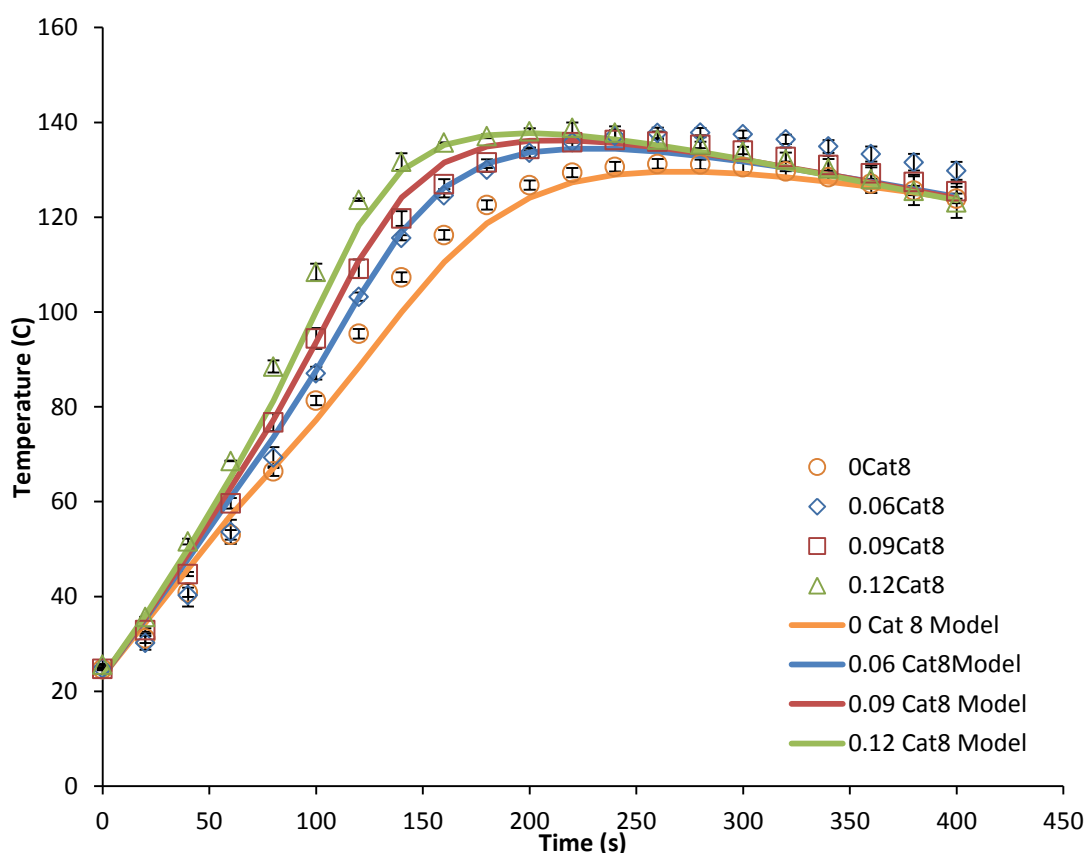
temperature over time accurately. A 0.32g loading of catalyst5 provides quality foams in a time frame where the reaction profiles can be easily followed.



**Figure 3.14 Internal temperature of foam reaction under different catalyst5 loading conditions. The symbols represent average numbers of experimental data and the solid lines represent modeling results.**

Figure 3.15 shows a comparison between modeling results and experimental data under various catalyst8 loading conditions where amounts of catalyst8 were adjusted on the basis of regular control recipe. The figure shows that increasing the amount of catalyst8 makes the reaction faster which gives a higher temperature. The slight deviation between modeling results and experimental data was caused by experimental deviations. The initial results show that catalyst8 has little impact on reaction temperature so that a trial experiment without catalyst8 was performed. It gives the same conclusion with highest temperature locating at 130 °C and 250

seconds.

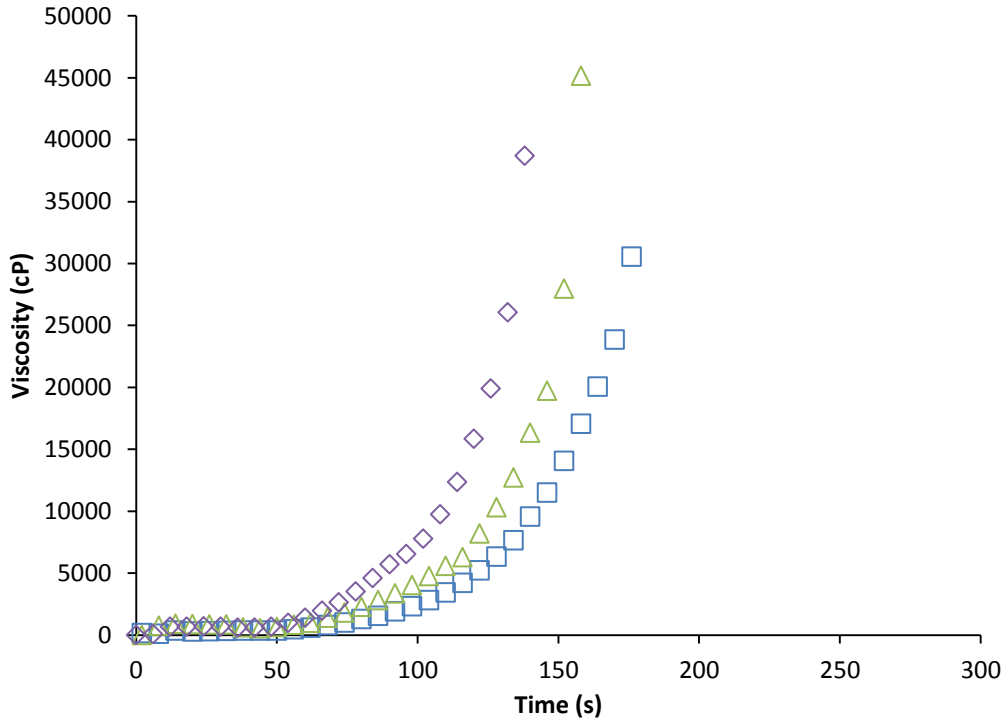


**Figure 3.15 Internal temperature of foam reaction under different catalyst8 loading conditions. The symbols represent average numbers of experimental data and the solid lines represent modeling results.**

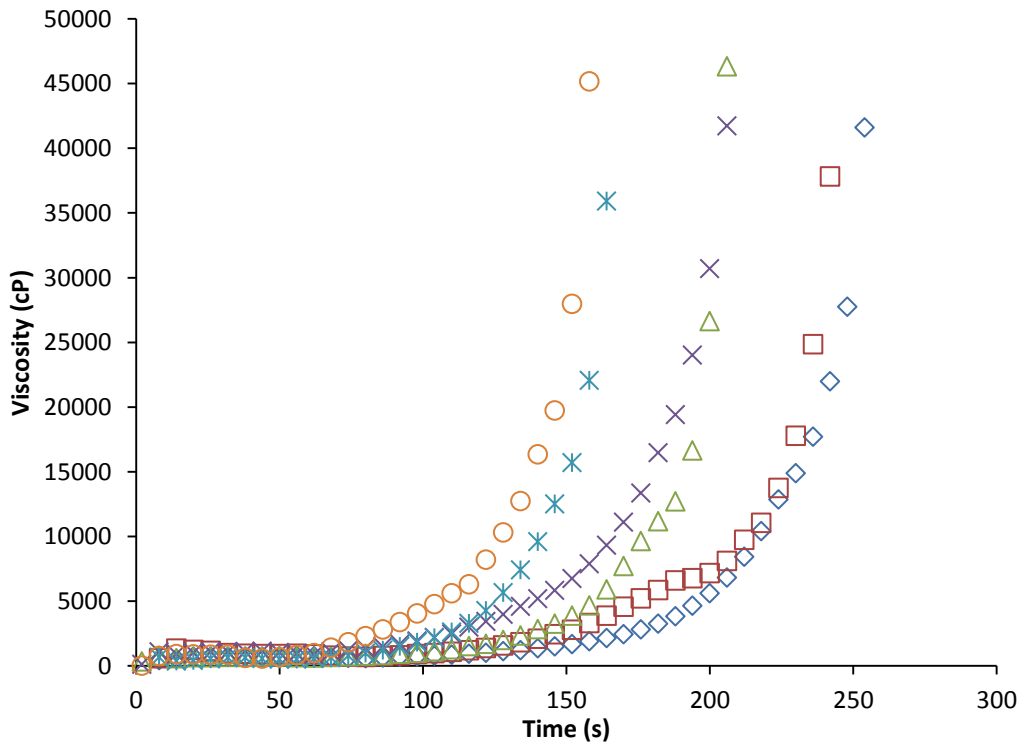
### 3.4.7 Impact of catalysts on gel reaction viscosity

Figures 3.16 and 3.17 provide experimental data of the gel system viscosity at different catalyst loadings. 0.32g catalyst5 is present in Figure 3.16 and 0.12g catalyst8 is present in Figure 3.17. Viscosities going to infinity indicate the forming of a solid highly-crosslinked final product. On temperature increase, both catalysts have similar impacts. These data indicate that Cat8 tends to have a better selectivity for cross-linking than Cat5.





**Figure 3.16 Gel system viscosity data over time under three different catalyst8 loading conditions. Symbol “□” represents 0.06g Cat8 case, symbol “△” represents 0.12g Cat8 case, and symbol “◇” represents 0.18g Cat8 case.**



**Figure 3.17 Gel system viscosity data over time under three different catalyst5 loading conditions. Symbol “□” and symbol “◇” represent 0.16g Cat5 cases, symbol “△” and symbol “X” represent 0.24g Cat5 cases, symbol “○” and symbol “+” represent 0.32g Cat5 cases.**

### 3.5 Conclusion

Temperature profiles of urethane gel and foam formulations were simulated using single-polyol and single-catalyst system parameters and the simultaneous solution of several ordinary differential equations that describe reactions and physical properties.

This work goes beyond what has been previously attained, including:

- Accurate simulation of mixtures of polyols based on performance of single polyols,
- Simulation of both water reaction and physical processes for gas formation,
- Accurate simulation of the impact of catalysts including the impact of catalyst concentration.

These studies validate the elementary reaction mechanism where, for a limited range of catalyst, the reaction rate is proportional to the catalyst concentration and where the non-catalytic and catalytic reactions are assumed to occur in parallel. This validated mechanism and the modeling method provided good agreement with experimental data.

Based on pure component kinetic parameters this model can be used to predict the performance of foams which have multiple combinations of isocyanate, polyols, catalysts, chemical blowing agents (such as water), and physical blowing agents (such as methyl formate) in recipes when parameters on pure component (e.g. single polyol) performance are obtained. This advantage can expedite the ability to develop new foam formulations by simulation – especially for incorporation of new bio-based

polyols into formulations.

A next and vital step to both simulate urethane foam formation and the foam's physical properties is to model and simulate the viscosity profiles. Preliminary data indicate that catalysts can have different selectivities for cross-linking reactions versus random reactions of monomers (as characterized by temperature); this will need to be considered as the simulation capabilities are extended.

# **CHAPTER 4. EVALUATE REACTIONS WITH EXCESS ISOCYANATE IN POLYURETHANE FOAMING PROCESS**

## **4.1 Introduction**

The theoretical modeling for polyurethane rigid foams was developed by several research groups [2, 9, 12-14, 17, 34] in the world. Although a common practice in literatures is to neglect the side reactions with excess isocyanate, in which the reaction between isocyanate and urethane to generate allophanate is the most well-known, becoming knowledge on the impact of side reactions on the foaming process will help us have better understanding on the control of reaction conditions and produce higher quality foams. Therefore studying on likely fates of unreacted isocyanate and developing experimental plan to evaluate reactions with excess isocyanate in solvents are significant. ASTM isocyanate titration is applied to measure isocyanate content in system during foaming process. Experiments with different amount of catalyst will be carried out to verify accuracy of the model. Kinetics parameters relate to side reaction will be obtained by fitting modeling results to experimental data. The goal of this project is to include impact of side reactions with excess isocyanate to improve accuracy of the model.

## **4.2 Background**

The polyurethane foaming process involves two competing reactions (gel reaction and blow reaction). It's important to note that both reaction schemes described

above occur simultaneously, and therefore it is critical to control the relative rates of these reactions in order to obtain a foam with a stable cellular structure and good physical properties. If the blow reaction takes place too fast in comparison to the gelation reaction, it would result in the cells opening before there is sufficient viscosity build-up to provide the foam struts with enough strength to uphold the foam, leading to the collapse of the foam. On the other hand, if the gelation reaction is faster than the blow reaction, it may result in foam with closed cells [32], which is not desirable.

To improve accuracy of kinetics modeling in polyurethane foaming process more detailed side reactions are taken into consideration. The optimization included the reaction between isocyanate and amine, and the reaction between isocyanate and urethane. As the existence of these two side reactions, excess isocyanate will not left in the end.

## **4.3 Materials and methods**

### **4.3.1 Materials**

RUBINATE M (Standard Polymeric MDI) was the isocyanate used in this study and the petroleum-based polyols were Poly G76-635, Voranol 360 and Jeffol R315x from Huntsman Company and Dow Chemical Co. The specifications are shown in Table 4.1 [20, 21]. N,N-dimethylcyclohexylamine (DMCHA) and N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA) were used as the gelling catalyst and the blowing catalyst respectively. However, PMDETA was found also

having impact on gel reaction based on experimental results. The efficiency of PMDETA on catalyzing gel reaction was about 80% respect to DMCHA. Momentive L6900 was used as the surfactant for rigid foams, TCPP was used as the fire retardant, and distilled water and methyl formate were used as the blowing agents.

*Table 4.1 Raw material properties*

<b>Component</b>	<b>Isocyanate</b>	<b>Polyol</b>	<b>Polyurethane</b>	<b>Water</b>	<b>Carbon Dioxide</b>	<b>Amine</b>
Heat Capacity (J/g-K)	1.799	1.57 ~1.89	1.4~1.5	4.19	0.846~0.939 (300K~400K)	1.55~1.64
Heat Capacity (J/equiv-K)	242.86	264.86	362.5	75.42	39.6	128
<b>Product</b>	<b>Fn</b>	<b>Sp. Gravity @25°C</b>	<b>% NCO</b>	<b>Eq. Wt.</b>	<b>Viscosity cps@25°C</b>	
RUBINATE M	2.70	1.23	31.2	135	190	
<b>Product</b>	<b>Poly G76-635</b>		<b>Voranol 360</b>		<b>Jeffol R315x</b>	
<b>OH number</b>	635		360		315	
<b>Equivalent Weight(g/mol OH)</b>	88.3		155.8		178	
<b>Product</b>	<b>MW</b>	<b>Physical State</b>	<b>Boiling Point(°C)</b>	<b>Flash Point(°C)</b>	<b>LFL/UFL *</b>	
Methyl Formate	60	Liquid	31.5	-19	5/20	

#### 4.3.2 Experimental design and foaming formulation

The formula of foaming reaction is listed in Table 4.2. Blowing agents (water and MF) are taken out from the recipe for the gel reaction. The experiment study

included using ASTM(D2572-97) isocyanate titration to obtain CNO function groups concentration during reaction process, and evaluating kinetics parameters relate to side reactions to fit modeling results to experimental data. The revised constants will be used to improve accuracy of predicting gel system viscosity. Experiments with different amount of catalyst loadings will be carried out to verify the accuracy of the optimized modeling.

*Table 4.2 Foaming formulation of rigid polyurethane foam*

<b>B-side Materials</b>	Weight/g	Moles of functional groups
Poly G76-635	13.84	0.1567
Voranol 360	15.68	0.1006
Jeffol R315x	4	0.0225
Dimethylcyclohexylamine(Cat8)	0.12	
Pentamethyldiethylenetriamine(Cat5)	0.32	
Momentive L6900	0.6	
TCP	2	
Distilled Water (Blowing Agent)	1.04	0.1156
Methyl Formate (Blowing Agent)	2.4	
<b>A-side Material</b>		
RUBINATE M	61.548	0.4559
<b>Isocyanate Index</b>	1.15	

#### 4.3.3 Foam preparation and data collection

The following steps were used in the foam experiments.

1. Polyols, water, blowing catalyst, gelling catalysts, and surfactant (B-side components) were added into a plastic cup successively.
2. The B-side components were mixed for 10-15 seconds.

3. The mixture was allowed to degas for 2 min.
4. Thereafter, pre-weighed isocyanate (A-side material) was added and mixed at the same speed for 7-10s.
5. The reacting mixture was then quickly poured into a box lined with aluminum, and the foam was allowed to rise and sit at ambient conditions (25 °C) during curing.

All the B-side chemicals were added in the foam reaction while water and blowing catalyst were not added in the gel reaction. A high speed mixer blade (540 rpm) attached to a floor-model drill press was used to mix the chemicals. Gel reactions with different catalyst loadings were performed to measure gel system viscosity. Cole-Parmer® Basic Viscometer is used to measure the viscosity of the gel system during the reaction.

#### **4.3.4 Standard test method for isocyanate groups in urethane materials or prepolymers**

ASTM D2572-97(2010) is the standard test method for isocyanate groups in urethane materials or prepolymers. The urethane prepolymer is allowed to react with an excess of di-*n*-butylamine in toluene. After the reaction is complete, the excess of di-*n*-butylamine is determined by back titration with standard hydrochloric acid.

The following procedures were used in the isocyanate titration:



1. Weigh to 0.1 g a specimen containing approximately 1.1 milliequivalents of NCO (for example, 1.0 g of prepolymer containing approximately 5% NCO) in a 250-mL Erlenmeyer flask.
2. Add 25 mL of dry toluene (If the polymer is insoluble, add 10mL of dry, analytical grade acetone to the toluene.), place a stopper in the flask, and swirl by hand or on a mechanical agitator to dissolve the prepolymer. Solution may be aided by warming on a hot plate.
3. Using a pipet, add 25.00 mL of 0.1 *N* di-*n*-butylamine solution and continue swirling for 15 min with stopper in place.
4. Add 100 mL of isopropyl alcohol and 4 to 6 drops of bromphenol blue indicator solution. Titrate with 0.1 *N* hydro-chloric acid to a yellow end point.
5. Run a blank titration including all reagents above but omitting the specimen.

Calculate the NCO content as follows (Equation 4.1):

$$NCO, \% = \frac{[(B - V) * N * 0.0420]}{W} * 100 \quad (4.1)$$

where:

B = volume of HCl for titration of the blank, ml,

V = volume of HCl for titration of the specimen, ml,

N = normality of HCl,

0.0420 = milliequivalent weight of the NCO group, and

W = grams of specimen weight, g.

## 4.4 Results and discussion

### 4.4.1 Preliminary simulation

Preliminary simulation result of isocyanate concentration during polyurethane foaming process was obtained from revised kinetics modeling. Excess isocyanate reacts with urethane so that their concentration both decrease until one of them tends to zero. Modeling result (Figure 4.1) shows that NCO functional groups are used up at about 350 seconds. Rate constant of the reaction between isocyanate and urethane will be adjusted based on experimental data.

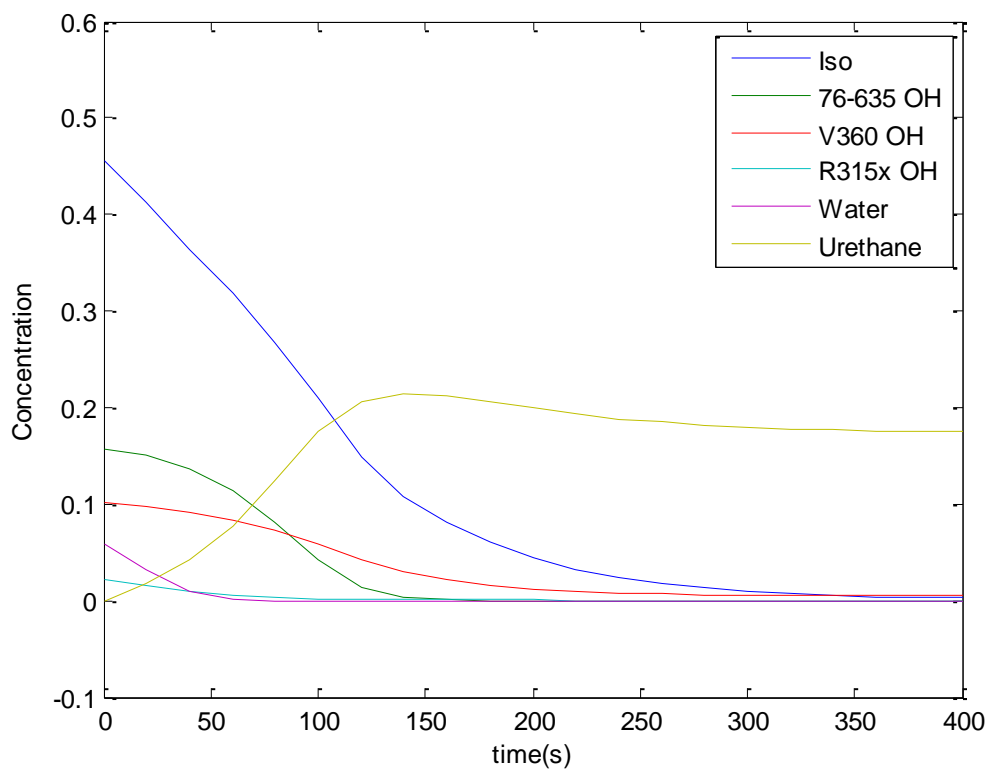


Figure 4.1 Preliminary simulation result of isocyanate concentration during foaming process

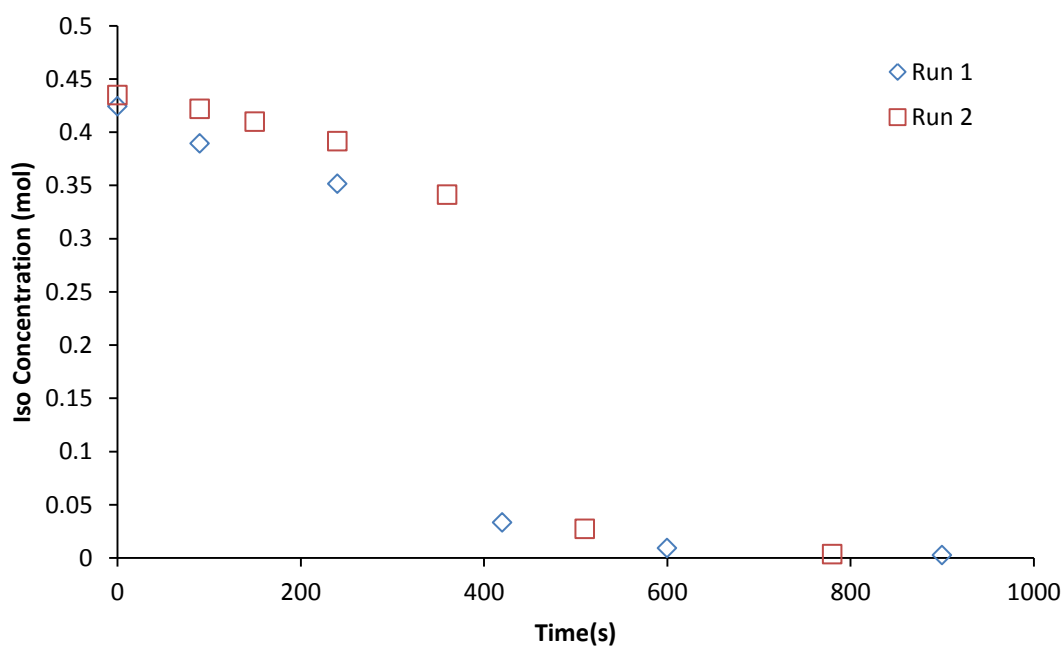
#### 4.4.2 Isocyanate titration results

Isocyanate titration was performed during gel reaction since it was difficult to pick up titration samples as foam built up. In the first step, single polyol and single catalyst were chosen to react with isocyanate to study the fundamentals of side reactions. Isocyanate index was set to be 1.5 to allow enough excess isocyanate reacted with urethane. Table 4.3 provides the recipe used for isocyanate titration.

*Table 4.3 Recipe used for isocyanate titration (poly G76-635)*

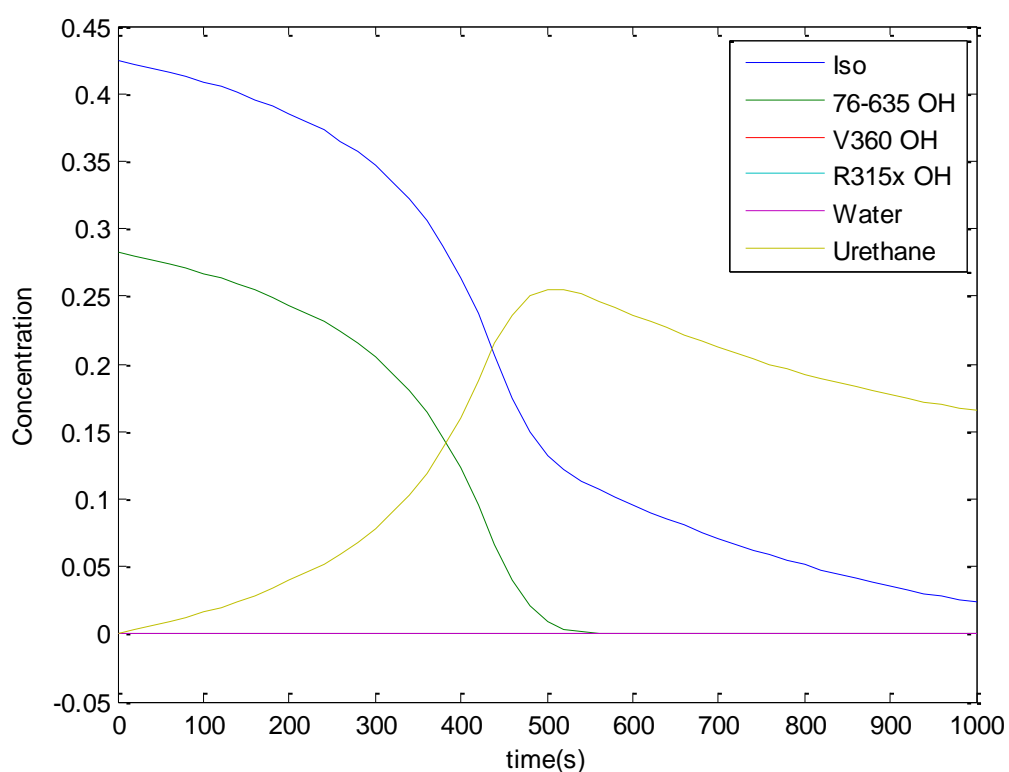
<b>B-side Materials</b>	Weight/g	Moles of functional groups
Poly G76-635	25.00	0.2831
Dimethylcyclohexylamine(Cat8)	0.12	
Momentive L6900	0.6	
TCP	2	
<b>A-side Material</b>		
RUBINATE M	57.33	0.4247
<b>Isocyanate Index</b>	1.5	

Figure 4.2 shows isocyanate titration results with poly G76-635.



**Figure 4.2 Isocyanate titration results during gel reaction process**

Based on the recipe in Table 4.3, modeling result is shown in Figure 4.3. Isocyanate titration results (Figure 4.2) show the concentration of isocyanate had a quick drop at 400 seconds since at this time the system temperature reached about 100°C and the reaction between isocyanate and urethane happened. The isocyanate concentration tended to zero at later time stage which agreed with our preliminary simulation (Figure 4.3).



**Figure 4.3 Preliminary simulation result of isocyanate titration during gel reaction process**

However the viscosity of system kept increasing during gel reaction process which led the reactants changed from liquid phase to solid phase. Hence, the titration samples picked up in the later time stage did not completely dissolve in the toluene solvent which may cause the titration results not reliable enough. A better choice is to use a linear structure alcohol (Pentanol) to react with isocyanate which

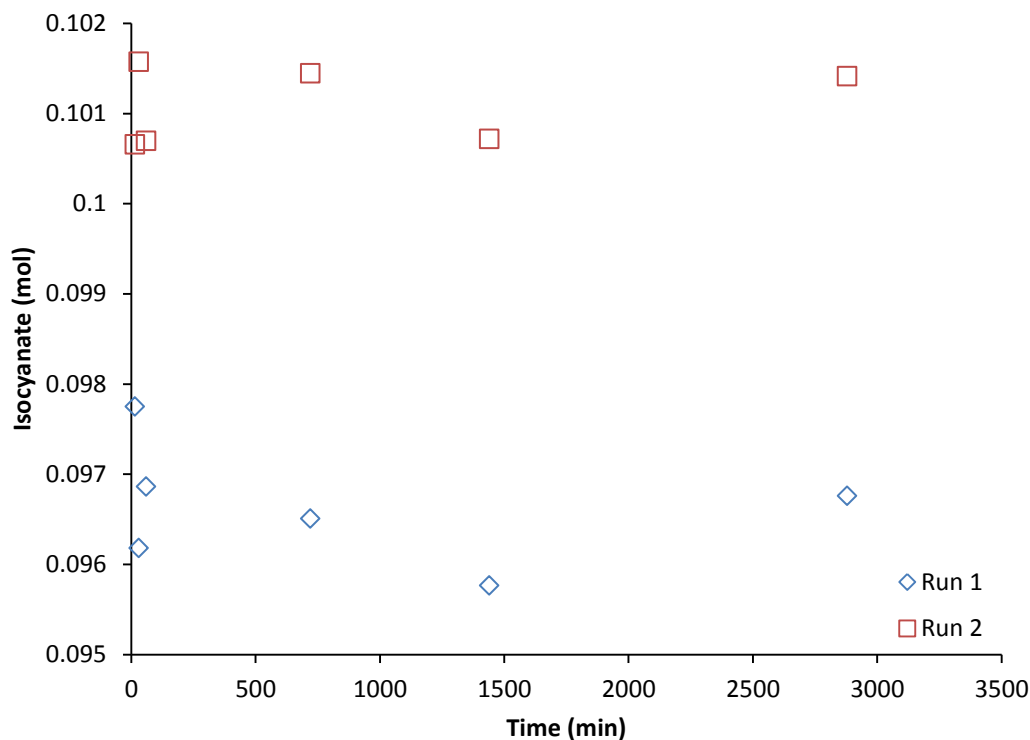
can ensure the reactants are liquid phase in the entire reaction process and all the titration samples can dissolve in the toluene solvent. Extra toluene (20% in volume) was added into the reactants to avoid overheat by increasing total heat capacity.

Table 4.4 lists the recipe with pentanol for isocyanate titration.

*Table 4.4 Recipes with pentanol for isocyanate titration*

	Run 1	Run 2
Pentanol	12.1	11.9
T CPP	2	2
L 6900	0.6	0.6
Poly cat8	0.12	0.12
Isocyanate	35.06	35.28
Toluene	10.3	10.2
Total	60.18	60.1
moles		
Pentanol	0.137266	0.134997
Isocyanate	0.259704	0.261333
Isocyanate Index	1.891974	1.935843
Volume	61.0625	60.89738

To focus on the reaction between excess isocyanate and urethane, isocyanate index was set to be 1.9-2.0 and titration was performed in the later time stage. During reaction process the container was kept warm in the oven (50°C) to reduce heat transfer to surroundings which could extend time for isocyanate to react with urethane. In theory, if the reaction between isocyanate and urethane does not exist, there should be about 0.125 g-mol isocyanate left in the system. Figure 4.4 shows isocyanate titration results in 48 hours period.



**Figure 4.4 Isocyanate titration results (pentanol) during gel reaction process**

The concentration of isocyanate tended to a constant value after 15 minutes. The deviations in the figure were within experimental error since the concentration differences were quite small ( $<0.5\%$ ) compare to the initial concentration of isocyanate. It indicated that there was no reaction related to isocyanate happened at later time period. However, in fact the excess isocyanate reacted with urethane before 15 minutes since the isocyanate concentration was lower than what it was supposed to be if there was no additional side reaction. Based on two groups of isocyanate titration results it is believed that the reaction between excess isocyanate and urethane does exist as long as the temperature reaches a certain degree. Details about the reaction conditions requirement and values of kinetics parameters will be evaluated in the future work.

## 4.5 Conclusion

This work represents an experimental effort to verify the existence of the side reaction between isocyanate and urethane which goes beyond what have previously been achieved. Although it is a common practice to neglect this reaction in polyurethane foams modeling, the reaction really exists and has a non-negligible impact on isocyanate concentration in system as long as the reaction temperature reaches a certain value.

Preliminary data in isocyanate titration with pentanol indicate that the reaction between isocyanate and urethane ends before 15 minutes. Therefore a next and vital step is to perform isocyanate titration in the time range between 0 to 15 minutes. Accurate experimental data can be used to fit kinetics parameters of isocyanate-urethane reaction in the revised modeling. Running reaction under different surrounding temperatures (setting different oven temperatures) can help figure out the temperature requirement for this side reaction to happen.

This revised model including all significant impacts will be more accurate and provide better insight into fundamental processes for polyurethane foaming reaction, have the potential to predict foam performance and ultimately expedite the ability to develop new foam formulations by simulation, especially for incorporation of new bio-based polyols into formulations. This work can save a lot of time for performing experiments, bring considerable economic benefits and most important make a valuable contribution to environmental protection by combining bio-based chemicals.

## BIBLIOGRAPHY

1. Huo, S.P., et al., *Crosslinking kinetics of the formation of lignin-aminated polyol-based polyurethane foam*. Journal of Applied Polymer Science, 2012. **125**(1): p. 152-157.
2. Ni, H., et al., *Effect of catalysts on the reaction of an aliphatic isocyanate and water*. Journal of Polymer Science, Part A: Polymer Chemistry, 2002. **40**(11): p. 1677-1688.
3. Modesti, M., V. Adriani, and F. Simioni, *Chemical and physical blowing agents in structural polyurethane foams: Simulation and characterization*. Polymer Engineering and Science, 2000. **40**(9): p. 2046-2057.
4. Paciorek-Sadowska, J., et al., *Preparation of rigid polyurethane foams with powder filler*. Journal of Polymer Engineering, 2012. **32**(2): p. 71-80.
5. Hongyu Fan, A.T., Galen J. Suppes, and Fu-Hung Hsieh, *Properties of Biobased Rigid Polyurethane Foams Reinforced with Fillers: Microspheres and Nanoclay*. International Journal of Polymer Science, 2012. **2012**.
6. Yang, L.T., et al., *Thermal and Mechanical Properties of Polyurethane Rigid Foam Based on Epoxidized Soybean Oil*. Journal of Polymers and the Environment, 2012. **20**(1): p. 230-236.
7. Tay, G.S., L.N. Ong, and H.D. Rozman, *Mechanical properties and fire retardant behavior of polyurethane foam reinforced with oil palm empty fruit bunch*. Journal of Applied Polymer Science, 2012. **125**(1): p. 158-164.
8. Thirumal, M., et al., *Mechanical, morphological and thermal properties of rigid polyurethane Foam: Effect of chain extender, polyol and blowing agent*. Cellular Polymers, 2009. **28**(2): p. 145-158.
9. Draye, A.C. and J.J. Tondeur, *Temperature effect on alcohol-isocyanate kinetics*. Reaction Kinetics and Catalysis Letters, 1999. **66**(2): p. 319-324.
10. Briody, C., et al., *The implementation of a visco-hyperelastic numerical material model for simulating the behaviour of polymer foam materials*. Computational Materials Science, 2012.
11. Jmal, H., R. Dupuis, and E. Aubry, *Quasi-static behavior identification of polyurethane foam using a memory integer model and the difference-forces method*. Journal of Cellular Plastics, 2011. **47**(5): p. 447-465.
12. Baser, S.A. and D.V. Khakhar, *Modeling of the dynamics of R-11 blown polyurethane foam formation*. Polymer Engineering and Science, 1994. **34**(8): p. 632-641.
13. Baser, S.A. and D.V. Khakhar, *Modeling of the dynamics of water and R-11 blown polyurethane foam formation*. Polymer Engineering and Science, 1994. **34**(8): p. 642-649.
14. Tesser, R., et al., *Modeling of polyurethane foam formation*. Journal of Applied Polymer Science, 2004. **92**(3): p. 1875-1886.
15. Albu, P., et al., *Kinetics of degradation under non-isothermal conditions of a thermooxidative stabilized polyurethane*. Journal of Thermal Analysis and Calorimetry, 2011. **105**(2): p. 685-689.
16. Semsarzadeh, M.A., A.H. Navarchian, and J. Morshedian, *Reactive extrusion of poly(urethane-isocyanurate)*. Advances in Polymer Technology, 2004. **23**(3): p. 239-255.
17. Harikrishnan, G. and D.V. Khakhar, *Modeling the dynamics of reactive foaming and film thinning in polyurethane foams*. AIChE Journal, 2010. **56**(2): p. 522-530.
18. Gong, Q., T. Zhai, and H. Xia, *Conductive rigid polyurethane foams with negative temperature coefficient*. Gaofenzi Cailiao Kexue Yu Gongcheng/Polymeric Materials Science and



- Engineering, 2012. **28**(2): p. 53-56.
19. Majer, V.S., V., *Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation*. Blackwell Scientific Publications, Oxford, 1985.
  20. R. C. Weast, e., *CRC Handbook of Chemistry and Physics*. CRC Press Inc. Florida, 1990.
  21. D. R. Lide, e., *CRC Handbook of Chemistry and Physics. 71st Edition*. CRC Press Inc. Florida, 1990-91.
  22. Mu, Y., et al., *Rigid polyurethane foams based on activated soybean meal*. Journal of Applied Polymer Science, 2012. **124**(5): p. 4331-4338.
  23. Pengjam, W., et al., *Copper-amine complexes as new catalysts for rigid polyurethane foam preparations*. Journal of Applied Polymer Science, 2012. **123**(6): p. 3520-3526.
  24. Listemann, M.L., A.C. Savoca, and A.L. Wressell, *Amine catalyst characterization by a foam model reaction*. Journal of Cellular Plastics, 1992. **28**(4): p. 360-398.
  25. Strachota, A., B. Strachotová, and M. Špírková, *Comparison of environmentally friendly, selective polyurethane catalysts*. Materials and Manufacturing Processes, 2008. **23**(6): p. 566-570.
  26. Ristić, I.S., et al., *Thermal stability of polyurethane materials based on castor oil as polyol component*. Journal of Thermal Analysis and Calorimetry, 2012: p. 1-9.
  27. Cakić, S., G. Nikolić, and J. Stamenković, *The thermal degradation of waterborne polyurethanes with catalysts of different selectivity*. Polymer - Plastics Technology and Engineering, 2007. **46**(3): p. 299-304.
  28. Fan, H., et al., *Rigid polyurethane foams made from high viscosity soy-polyols*. Journal of Applied Polymer Science, 2013. **127**(3): p. 1623-1629.
  29. Inoue, S.I., Y. Nagai, and H. Okamoto, *Amine-manganese complex as an efficient catalyst for polyurethane syntheses*. Polymer Journal, 2002. **34**(4): p. 298-301.
  30. Wu, Z., et al., *Study on structure and property of rigid polyurethane foam*. Jianzhu Cailiao Xuebao/Journal of Building Materials, 2009. **12**(4): p. 453-457.
  31. Monteavaro, L.L., et al., *Polyurethane networks from formiated soy polyols: Synthesis and mechanical characterization*. JAOCS, Journal of the American Oil Chemists' Society, 2005. **82**(5): p. 365-371.
  32. Guo, A., I. Javni, and Z. Petrovic, *Rigid polyurethane foams based on soybean oil*. Journal of Applied Polymer Science, 2000. **77**(2): p. 467-473.
  33. Van Maris, R., et al., *Polyurethane catalysis by tertiary amines*. Journal of Cellular Plastics, 2005. **41**(4): p. 305-322.
  34. Yusheng Zhao, M.J.G., Ali Tekeei, Fu-Hung Hsieh, and Galen J. Suppes, *Modeling Reaction Kinetics of Rigid Polyurethane Foaming Process*. Journal of Applied Polymer Science, 2013.
  35. Paul. Hiemenz C, L.P.T., *Polymer Chemistry. Second ed.* 2007: p. 336, 338-339.
  36. University, C.P.S., *Gel Permeation Chromatography*. 2007.
  37. Dabir S. Viswanath, T.K.G., Dasika H.L. Prasad, Nidamarty V.K. Dutt, Kalipatnapu Y.Rani, *Viscosity of Liquids: Theory, Estimation, Experiment, and Data*. 2006: p. 421.