

MODELING AND EXPERIMENTAL STUDY OF POLYURETHANE FOAMING
AND GELLING REACTIONS

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Doctor of Philosophy

by

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

MODELING AND EXPERIMENTAL STUDY OF POLYURETHANE FOAMING
AND GELLING REACTIONS

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Luay Jaf

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ABSTRACT

Numerous reactions take place within a polyurethane polymerization process. Homogeneous and catalytic reactions occur at the same time and intermediate compounds are formed. As the reaction proceeds, long chains of polymer are formed which drastically affect the kinetics of the reaction. Temperature and viscosity profiles of the reacting mixture are two strong indicators of the extent of reaction and the way the reactions are carried out. Therefore, simulating polyurethane gel and foam systems helps interpret temperature and viscosity profiles and gain insight into the kinetics of the system.

Using MATLAB program, a model was introduced which simultaneously solves over 80 ordinary differential equations and provide temperature and viscosity profiles as well as concentration profiles, degrees of polymerization, gel point and foam height for individual formulations.

Experimental data were used to validate the code showing the model is fundamentally correct. Simulation results showed good fits to the experimental data providing reaction kinetics of the system. The model was modified to simulate reaction systems with minimal change in kinetic parameters.

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

CHAPTER 1. INTRODUCTION

Polyurethanes are influential polymers that help human beings live a greener and more efficient life. From insulation to coatings to adhesives to elastomers to mattresses, polyurethanes have a wide range of applications. Hence, studying urethane reactions is of paramount importance. Deeper knowledge into urethane reactions helps optimizing urethane polymerization process as well as its monomers and final products.

Innumerable efforts on studying polyurethanes have led to significant findings. Nevertheless, they all intersect in the method used: laboratory experiments specific to one or few monomers or processes. In other words, they all lack compatibility to further materials or procedures. This results in the need for even more experiments and subsequently countless hours spent in labs.

Simulation is a fundamental and substantially effective method to overcome this obstacle. Simulation provides means to investigate complex reaction systems. Huge matrices and numerous lines of code might seem confusing, but simulation makes analyzing polyurethane polymerization astonishingly simple. Using simulation, determining key properties of a particular foam will not take more than a few minutes, needless of performing time consuming and resource intensive laboratory experiments.

Obviously, simulation has its own limitations and cannot answer all the questions that arise while analyzing a polymerization system. However, it is the most effective and organized method in gaining fundamental insight into polyurethanes. Various types of monomers, constant code updates and introducing alternative polymerization mechanisms help modify the code and gain more accurate simulation results.

The polyol Group at University of Missouri, Columbia have simulated temperature, height, density and viscosity profiles of a polyurethane system using MATLAB. This dissertation focuses on four major implications of the simulation including effect of reactivity of isocyanate moieties on urethane simulation, impacts of temperature and viscosity profiles for urethane gelling reactions, polymer engineering as part of the chemical reaction engineering course and limits of performance of polyurethane foaming blowing agents.

The model used for simulating the reaction system was simultaneously solved over a dozen differential equations.

CHAPTER 2. A CHAPTER ON POLYMER ENGINEERING AS PART OF THE CHEMICAL REACTION ENGINEERING CORE COURSE

2.1 Abstract

The polymer industry is debatably the largest employer of chemical engineers, and polymer-forming reactors are debatably the most prevalent chemical reactors aside from fermenters. Yet, typical chemical engineering curriculum only cover the basics of polymer chemistry or engineering in elective courses. It is now possible to go from polymer basics to some of the most advanced topics in polymer science as a continuation of reaction engineering topics due to recent advances in the simulation of polymer-forming reactions.

This paper can be used to supplement textbooks on reaction engineering or as the source of content for writing a chapter in a textbook. The topic is a natural continuation of the most common core material of reaction engineering courses and is based around MATLAB programming code that solves the multiple ordinary differential equations resulting from elementary chemical reactions and associated physical processes. In addition to reinforcing key concepts of reaction engineering courses, this simulation approach will strengthen student's capabilities in important ODE-solving, programming, and chemistry skills.

2.2 Introduction

Reaction Engineering Courses - Based on the 2010 survey, more than 90% of core-curriculum chemical reaction engineering courses cover the topics listed in Table 2-1 [1]. Table 2-2 lists additional topics that are covered by 70% (catalysis and catalytic reactors) to 10% (models for non-ideal reactors) of the courses. The alternative topics often consumer about 35% of the course time, or about five weeks.

Table 2-1. Topics covered by 90% of chemical reaction engineering courses as part of core curriculum in chemical engineering.

Common topics	
1	Mole balances.
2	Conversion & Reactor Sizing.
3	Rate Laws & Stoichiometry.
4	Isothermal Reactor Design.
5	Collection & Analysis of Rate Data.
6	Multiple Reactions.
7	Steady-State Nonisothermal Reactor Design.

Table 2-2. Additional topics, some of which are included in courses in reaction engineering.

Alternative topics	
1	Catalysis and Catalytic Reactors
2	Reaction Mechanisms, Pathways, Bioreactions, & Bioreactors.
3	External Diffusion Effects of Heterogeneous Reactions.
4	Diffusion & Reaction.
5	Distributions of Residence Times for Chemical Reactors.
6	Models for Non-Ideal Reactors

Silverstein and Vigeant [1] also cite the most common challenges in reaction engineering courses as a) ODE solving skills, b) mathematical software skills, and c) chemistry

preparation. The approach to learning about polymers in this paper is based on MATLAB programming to solve ODEs where the ODEs are derived from chemistry basics.

Suppes et al. [2–6] developed an approach to simulate thermoset polymerization. The approach is established on the solution of the ordinary differential equations (ODEs) resulting from a series of elementary reactions, the reactor's energy balance, and physical processes such as mass transfer for blowing agents. The most-basic simulation can be performed by solving three reactions; the more-complex involves the solution of over 50 ODEs.

The approach directly applies topics 1, 2, 3, 6, and 7 of the Table 1 topics as presented in this paper. Topics 4, and 5 can be applied to the polymer systems with short paragraphs of introduction on how reactors are specified.

Advanced topics are discussed in several articles [7,8] and provide enlightening extensions on topics of catalysis, the impact of diffusion on reaction, molecular simulation estimate of reaction parameters, and a variation of the Arrhenius equation.

Two to four weeks of covering polymer materials and polymer-formation simulation is a worthy expenditure of time in an undergraduate course on reaction engineering with discussion on how they can use simulation used [9] because the polymer industry is one of largest employers of chemical engineers, polymer batch reactions are debatably the most common in industry (aside from bio-reactors...e.g. beer and wine), and students are able to readily associate with the topic because of the prevalence of polymer products in the classroom or home.

In industry, the design of new reactors is not a routine event. Normally, it is a specialty of process design performed by design firms or researchers who work closely with design

firms. However, the batch reactors used to mold items from surfboards to car seat foams are regularly reformulated. Because of this nature of the polymer industry, applications of the methods developed in this paper can be immediately useful to graduates and provide competitive advantages in the industry.

The outcomes, concepts, and methods of this paper include: simulating/understanding homo-polymerization and hetro-polymerization, writing MATLAB code for multiple reactions to perform the simulation, understanding methods of near adiabatic reaction simulation, and understanding terminology and characterizations used in the polymer industry.

2.3 Homo-Polymerization Reaction

2.3.1 Isothermal Homo-Polymerization Reaction

Polymers are large molecules formed when many (poly) monomer chemical units (mers) combined in chain-like and/or branched structures. Figure 2-1 is an example overall homo-polymerization reaction, each styrene monomer's double bond remedy as a single bond addition a bond to another styrene monomer to produce polystyrene.

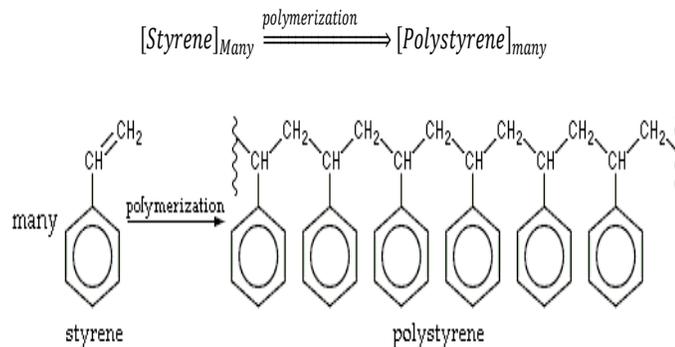


Figure 2-1 Polystyrene, an example of homo-polymerization reaction [10].

Simulation of the reaction is possible if all polymers of different degrees of polymerization (DP) are referred to as a polymer characterized as a single, average DP. Fortunately, an average DP is all that is needed to specify the most important of the polymer properties and the process to make that polymer.

Table 2-3 lists the main reactions and rate of reactions of isothermal homo-polymerization Homogenous reactions describing polystyrene polymerization. A, P, k, C, and f_A represent isocyanate monomer, polymer, reaction rate coefficient, concentration, and functionality of A.

Table 2-3. Isothermal homo-polymerization main reactions and rate expressions

Rxn. #	Reaction	Rate Expression
1	$A + A \rightarrow P$	$r_1 = k_1 f_A C_A f_A C_A$
2	$A + P_A \rightarrow P$	$r_2 = k_2 f_A C_A P_A$
3	$P_A + P_A \rightarrow P$	$r_3 = k_3 P_A P_A$

The reactions of Table 2-3 are elementary; however, unlike simple molecular reactions, the rate expressions are based on the reaction of functional groups rather than molecules. For example, the concentration of styrene is C_A , and each styrene monomer has two functional groups ($f_A=2$); the non-aromatic pi-bonds has the ability to react to form two new covalent bonds. Hence, the concentration of functional groups is $f_A C_A$.

Table 2-4 provides program code for simulating this isothermal homo-polymerization reaction. MATLAB's ODE45 function is used to solve the ordinary differential of

component concentration. The reactions rates r_1 , r_2 , and r_3 , are defined by lines 4, 5, and 6 of the floryrxn function. Lines 7, 8, and 9 of the floryrxn define how the reaction rates are combined to specify the rates of change of monomer A, polymer, and A-moieties.

Table 2-4. MATLAB code for simulating isothermal homo-polymerization reaction.

line #	Script
1	<code>global fa k;</code>
2	<code>fa=2;</code> %functionality of Amon
3	<code>k=[5E-3 5E-3 5E-3];</code> %Rate constants (l/mol/s)
4	<code>c0=[1 0 fa*1];</code> %Initial concentration of Amonomer, polymer, and A moieties, all in mol/l.
5	<code>[t,ct]=ode45('floryrxn', [0:0.1:500],c0)</code> %Solves the ODEs
6	<code>figure;plot(t,ct)</code> %Plotting concentrations.
line #	Function
1	<code>function ydot=floryrxn(tt,c);</code>
2	<code>global fa k ;</code>
3	<code>CPA=c(3)-fa*c(1);</code> %Amoi in polymer
4	<code>r1=k(1)*fa*c(1)*fa*c(1);</code> % monomer + monomer rxn
5	<code>r2=k(2)*fa*c(1)*CPA;</code> % monomer A + polymer rxn
6	<code>r3=k(3)*CPA*CPA;</code> %polymer + polymer rxn
7	<code>ydot(1)=-2*r1-r2;</code> %rate of change of Amon
8	<code>ydot(2)=r1-r3;</code> %rate of change of polymer
9	<code>ydot(3)=-2*r1-2*r2-2*r3;</code> % moiety A accumulation
10	<code>ydot=ydot';</code>

Initial conditions and reactions rate constants are set in the script file. Line 2 specifies the functionality of the styrene monomer (A_{mon}), line 3 specifies the rate constants of the three elementary reactions of Table 2-1, and line 4 specifies the initial concentrations of the formulation/recipe (mol/l). The concentration vector, c_0 , use the comment feature to specify the order in which initial concentrations are provided and the units of A monomer, polymer, and A moiety. Line 5 uses the ODE45 function to solve the ordinary differential equation (ODE) initial condition problem as a function of time in the time span of 0 to 500 seconds as defined in line 5.

An important aspect of the program is that the specification of the units for the rate constants, the units of the concentrations, and their direct use in the setting the reactions rates; implicitly; specifies the units of the ODEs as mol/l/s. The rate constants are assumed the same for all three reactions, and the specification of constant values indicates that the reaction is isothermal.

The simulation results of Figure 2-2 show the concentration profiles of the A monomer, polymer, and A moiety. A monomer and A moiety concentrations are decreasing gradually from their initial conditions.

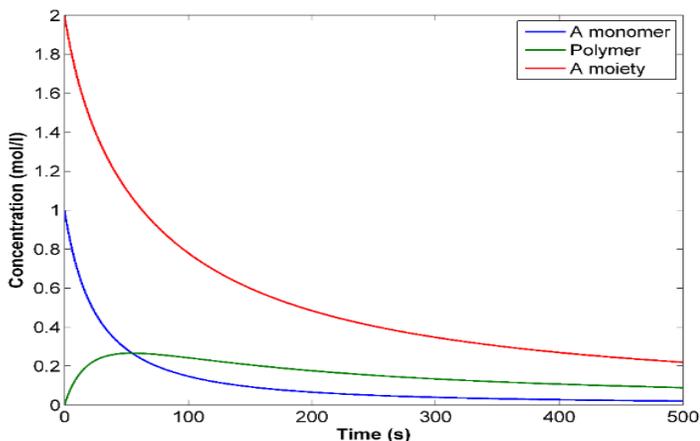


Figure 2-2 Concentration Profile of isothermal homo-polymerization reaction. The graph is specifically generated from the code of Table 2-4

Initial student exercises on polymerization would consist of copying the code into MATLAB and performing the simulation toward solving questions such as those posed in Table 2-5 one problem provides the MATLAB code as a starting point; the other question specifies the reactions and provides the parameters. For this problem, it is possible to prepare analytical solutions; however, even minor variations of the problem statements would require numerical solutions such as presented by the code.

Table 2-5. Example online questions for simulating isothermal homo-polymerization reactions.

Question 1

A k vector (k) has the quantities 1, 2, and 3 in the vector for reaction rate constants of the reactions $A + A \rightarrow P$, $A + P \rightarrow P$, and $P + P \rightarrow P$. A concentration (c) has the values 0.2 (A monomer), 0.01 (polymer) and 0.5 (A moiety). Select the equation number that has the proper Matlab code for calculating the reaction rate of a monomer with another monomer and add to it the value for this reaction rate (use $f_a = 2.0$, report the sum of the two): 1) $k_1 c_1$, 2) $2 * k_1 * c_1^2$, 3) $2 * k_1 * c(1) * c(1)$, or 4) $4 * k(1) * c(1) * c(1)$.

Question 2

A polymer-forming reaction network includes the following reactions: (1) $A+A \rightarrow P$, (2) $A+P \rightarrow P$, and (3) $P+P \rightarrow P$. The script file of the simulation program is: `global fa k; fa=2; k=[5E-3 5E-3 5E-3]; [t,ct]=ode45('floryrxn', (0:0.1: 500),(1 0 fa*1)); . and corresponding function: function ydot=floryrxn(tt,c); global fa k ; CPA=c(3)-fa*c(1); r1=k(1)*fa*c(1)*fa*c(1); r2=k(2)*fa*c(1)*CPA; r3=k(3)*CPA*CPA; ydot(1)=-2*r1-r2; ydot(2)= r1-r3; ydot(3)=-2*r1-2*r2-2*r3; ydot=ydot. What is the degree of polymerization (DP) after [X] seconds? HINT: Assume that all monomers that react are on the polymer products where the average number of monomers per polymer is the DP.`

The questions are designed to be self-contained to allow rapid solution in online quiz environments. Variations in the parameters have been introduced to create formula-type questions in Blackboard that create ten or more versions of each question.

The Figure 2-2 isothermal simulation code is not an accurate representation of homo-polymerization due to a long time it would take for the reaction to proceed to commercially

viable degrees of polymerization. Lower initial rate constants are necessary to prevent the polymer from plugging the inlet ports to the reactor, while higher final reactions are necessary to complete reaction towards high degrees of polymerization. Simulation of adiabatic or near-adiabatic is more-representative of commercial processing.

2.3.2 Near – Adiabatic Homo-Polymerization Reaction

Table 2-6 presents version of the Table 2-4 code. Reactions rate constant of the three reactions in Table 2-3 are calculated based on the Arrhenius equation, and the pre-exponential factors were assumed constant. The Arrhenius equation (Equation 2-1) is used to account for the temperature dependence of the reaction rate constants.

$$k = A^{\circ} * e^{\frac{-E^{\circ}}{RT}} \quad \text{Equation 2-1}$$

The rate of change of temperature is added based on the heat balance (Equation 2-2). The mass basis of the calculation times the heat capacity (mCp) is assumed constant, and heat loss is introduced through the incorporation of an overall mass transfer coefficient times a representative area for this heat loss (UAr).

$$\frac{dT}{dt} = \frac{\sum(\Delta H_i r_i) + U A r (T_s - T)}{m C_p} \quad \text{Equation 2-2}$$

Table 2-6 provides the MATLAB program coding for simulating near-adiabatic homo-polymerization. Initial conditions are the input to the script file. The heat of reaction, Hrxn, of A moiety is assumed constant and independent of whether this moiety is attached to a monomer or a polymer, the ambient temperature, Ts, is added for heat loss calculation and specified separately from the initial temperature, T0.

Table 2-6. MATLAB code for simulating near-adiabatic homo-polymerization reaction.

line #	Script
1	<code>global fa Hrxn T0 A0 E0 mCp UA ;</code>
2	<code>fa=2;</code> %functionality of Amon
3	<code>mCp=1.5;</code> %Total mass*Heat Capacity
4	<code>Hrxn=-70;</code> %Heat of reactions
5	<code>UA=0.0025;</code> %Over all heat transfer*Area
6	<code>T0=295.15;</code> %Initial temperature
7	<code>E0=[40 40 40];</code> %Activation energy
8	<code>A0=[1E4 1E4 1E4];</code> %Pre-exponential factor
9	<code>c0=[1 0 fa*1 T0];</code> %Initial conditions
10	<code>[t,ct]=ode45('floryrxn',[0:1: 500],c0);</code>
11	<code>figure;plot(t,ct(:,1),t,ct(:,2),t,ct(:,3))</code>
12	<code>figure;plot(t,ct(:,4))</code>
line #	Function
1	<code>function ydot=floryrxn(tt,c);</code>
2	<code>global fa k Hrxn A0 E0 mCp UA ;</code>
3	<code>for i=1:3;k(i)=A0(i)*exp(-E0(i)/(0.008314*c(4)));end;</code>
4	<code>CPA=c(3)-fa*c(1);</code> %Amoi in polymer
5	<code>r1=k(1)*fa*c(1)*fa*c(1);</code> % monomer + monomer rxn
6	<code>r2=k(2)*fa*c(1)*CPA;</code> % monomer A + polymer rxn
7	<code>r3=k(3)*CPA*CPA;</code> % polymer + polymer rxn
8	<code>ydot(1)=-2*r1-r2;</code> %rate of change of Amon
9	<code>ydot(2)=r1-r3;</code> %rate of change of polymer
10	<code>ydot(3)=-2*r1-2*r2-2*r3;</code> % moiety A accumulation
11	<code>ydot(4)=(Hrxn*(-2*r1-2*r2-2*r3))/(mCp) +((UA)*(295.15-c(4)))/(mCp);</code>
12	<code>ydot=ydot';</code>

The concentration and temperature profiles of this simulation code are provided in Figure 2-3 A monomer, and A moiety is decreasing gradually from their initial conditions as they consumed with the reactions proceed and polymer concentration. Figure 2-3 (right) provides the reaction temperature profile; temperature starts from the initial value of 295.15k and increases as a heat generated from exothermic reactions, the initial slope of temperature profile is highly impacted by the assumed value of pre-exponential factor “k0” of Arrhenius equation. The slope of the temperature profile (Figure 2-3, right) after the peak temperature depends primarily on the overall heat transfer coefficient.

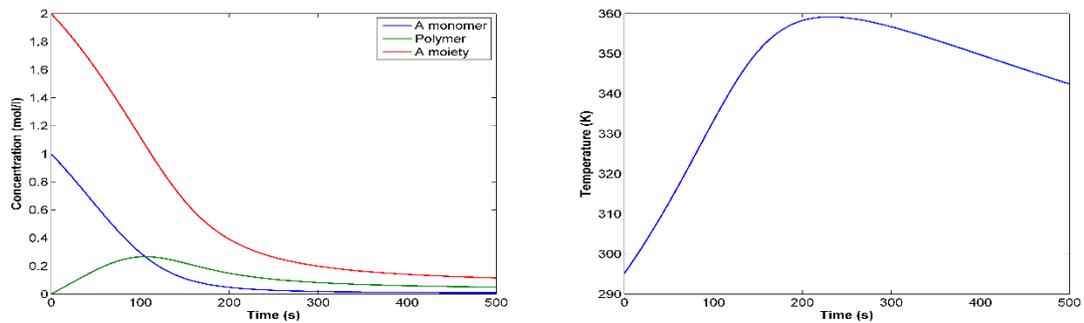


Figure 2-3 Simulation results of concentration profile (left) and reaction temperature profile (right) for the near-adiabatic homo-polymerization reaction. The graphs are generated from the code of Table 2-6.

Table 2-7 provides example questions based on the use of the near-adiabatic reaction code. The primary variation from the previous questions is the introduction of questions related to temperature output.

Table 2-7. An example online questions for simulating adiabatic homo-polymerization reactions.

Question 3

A polymer-forming reaction network includes the following reactions: (1) $A+A \rightarrow P$, (2) $A+P \rightarrow P$, and (3) $P+P \rightarrow P$. The script file of the simulation program is: `global fa Hrxn T0 A0 E0 mCp UA; fa=2; mCp=1.5; Hrxn=-70; UA=0.0025; T0= 295.15; E0= [40 40 40]; A0= [1E4 1E4 1E4]; [t,ct]=ode45('floryrxn', [0:1: 500],[1 0 fa*1 T0]);`, and corresponding function: `function ydot=floryrxn(tt,c);global fa k Hrxn A0 E0 mCp UA ;for i=1:3;k(i)= A0(i)*exp(-E0(i)/(0.008314*c(4)));end;CPA=c(3)-fa*c(1);r1=k(1)*fa*c(1)* fa*c(1); r2=k(2)*fa*c(1)*CPA; r3=k(3)*CPA*CPA; ydot(1)=-2*r1-r2; ydot(2)=r1-r3;ydot(3)=-2*r1-2*r2-2*r3;ydot(4)=(Hrxn*(-2*r1-2*r2-2*r3))/(mCp)+((UA)*(295.15-c(4)))/(mCp);ydot=ydot';`

- a. What is the maximum reaction temperature if the functionality of A monomer is [X]?
- b. What is the concentration of A monomer after [X] seconds?

The simulation code of Table 2-6 better approximates commercial processes resulting in higher degrees of polymerization. Most homo-polymerization processes result in

thermoplastic polymers that are pelletized at commercial facilities and extruded into consumer products by commercial partners who manufacture devices or consumer products from the thermoplastic. Example products produced in this way include polyethylene trash bags and polystyrene plexiglass. Thermoplastic polymers are made from monomers having functionalities of 2.

2.4 Hetro-Polymerization Reaction

2.4.1 Isothermal Hetro-Polymerization Reaction

When monomer functionalities exceed 2, polymers that initially form as separate molecules are able to crosslink. Cross-linking expedites the rate of polymer growth, eventually leading to a polymer "device" that is essentially one large molecule. Unlike a thermoplastic where heating reduces the viscosity and allows molding, heating that is sufficiently hot to break the cross-link bonds will destroy the polymer.

Monomers forming thermoset polymers are reacted to either form the final device or to form a polymer block that can be cut into a final product. An example of a thermoset polymer reacted to a final product is a car seat exhibiting a complex final geometry. An example of a thermoset polymer cut to a final shape is a mattress foam. Polyurethane spray foam insulation is an example of a thermoset polymer that is sprayed on a surface in a manner to provide the desired thickness.

Thermoset polymers tend to be used in "high performance" polymers which are put in applications intended for years of use.

Thermoplastic polymers may be homo-polymers or hetro-polymers. Thermoset polymers are primarily hetro-polymers. The rapid polymer growth possible with crosslinking allows thermoset polymers to be produced in a matter of a few dozen seconds which is critical for commercial manufacturing where the cost-effectiveness of manufacturing often depends on how many polymer devices can be made from one mold per hour of operation.

Polyurethane thermoset polymerization reaction is an example of hetro-polymerization reaction. Urethanes are often the most prevalent high-performance polymer found in homes with global production values at tens of billions of dollars per year. Most polyurethanes are produced in near-adiabatic molds forming final devices or conveyor belts producing foam that is cut into foam pads or panels

Polyurethane produces from the exothermic step-growth polymeric reaction of an isocyanate and a polyol as shown in Figure 2-4. For example purposes, di-functional monomers are used for this example, while in practice average functionalities of the isocyanate are from 2.0 to 2.7 and the polyol are from 3 to 6.

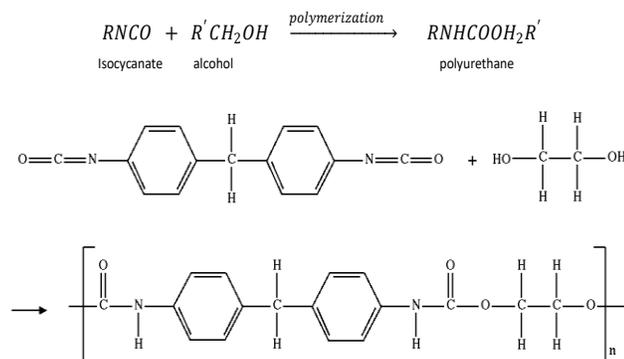


Figure 2-4 Polyurethane, an example of hetro-polymerization reaction [11].

Table 2-8 lists the smallest set of reactions to represent hetro-polymerization. Paul J. Flory, an American chemist and Nobel laureate in the field of polymers, provided the following series of assumptions that allowed analytical methods (simple integration) to be used to characterize the polymerization process during the mid-twentieth century:

- All reactions occur between A and B
- All functional groups on a branch unit are equally reactive

There are no intramolecular reactions

Table 2-8. Isothermal hetro-polymerization main reactions and rate expressions. A, B, P, k, C, f_A, and f_B represent isocyanate monomer, polyol monomer, polymer, reaction rate coefficient, concentration, functionality of A. and functionality of B.

Rxn. #	Reaction	Rate Expression
1	$A + B \rightarrow P$	$r_1 = k_1 f_A C_A f_B C_B$
2	$A + P_B \rightarrow P$	$r_2 = k_2 f_A C_A P_B$
3	$B + P_A \rightarrow P$	$r_3 = k_3 P_A f_B C_B$
4	$P_A + P_B \rightarrow P$	$r_4 = k_4 P_A P_B$

These assumptions provide a starting point for preparing code to simulate polymerization. The simulation code will allow incremental/progressive variation from these assumptions both evaluate the validity of the assumptions and to better-approximate commercial reactions.

Table 2-9 provides the coding of the program for simulating isothermal hetro-polymerization reaction. And this code showing:

- Recipes input.
- Initial conditions

- ODE45 function setting
- Material balance of moieties
- Rate of reactions
- The rate of change of components.

Table 2-9. MATLAB code for simulating isothermal hetro-polymerization reaction.

line #	Script
1	<code>global fa fb k;</code>
2	<code>fa=3;</code> %functionality of Amon
3	<code>fb=3;</code> %functionality of Bmon
4	<code>k=[5E-3 5E-3 5E-3 5E-3];</code> %Rate constants
5	<code>c0=[1.1 1 0 fa*1.1 fb*1];</code> %Initial conditions
6	<code>[t,ct]=ode45('floryrxn',[0:1:250],c0)</code> %Solves the ODEs
7	<code>figure;plot(t,ct)</code> %Plotting Concentration
line #	Function
1	<code>function ydot=floryrxn(tt,c);</code>
2	<code>global fa fb k intra;</code>
3	<code>CPA=c(4)-fa*c(1);</code> %Amoi in polymer
4	<code>CPB=c(5)-fb*c(2);</code> %Bmoi in polymer
5	<code>r1=k(1)*fa*c(1)*fb*c(2);</code> %monomer + monomer rxn
6	<code>r2=k(2)*fa*c(1)*CPB;</code> %monomer A + polymer rxn
7	<code>r3=k(3)*CPA*fb*c(2);</code> % polymer + monomer B rxn
8	<code>r4=k(4)*CPA*CPB;</code> %polymer + polymer rxn
9	<code>ydot(1)=-r1-r2;</code> %rate of change of Amon
10	<code>ydot(2)=-r1-r3;</code> %rate of change of Bmon
11	<code>ydot(3)=r1-r4;</code> %rate of change of polymer
12	<code>ydot(4)=-r1-r2-r3-r4;</code> % moiety A accumulation
13	<code>ydot(5)=-r1-r2-r3-r4;</code> % moiety B accumulation
14	<code>ydot=ydot';</code>

The simulation results of Figure 2-5 show the concentration profiles of the A monomer, B monomer, polymer, A moiety and B moiety. Monomer and moiety concentrations decrease from their initial conditions. The polymer concentration increases to a maximum concentration due to the formation of a new polymer from the monomers; eventually, polymer cross-linking causes polymer concentration to decrease. For this graph, the

concentration becomes negative at a time of about 100 seconds. Negative values of concentration are not realistic, but the simulation is realistic until the polymer concentration approaches zero. MATLAB's odeset function is introduced in the next section to prevent the generation of simulated negative concentrations.

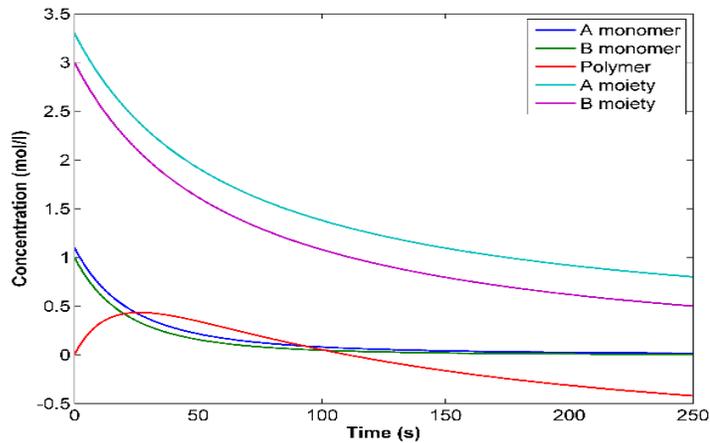


Figure 2-5 Concentration Profile of isothermal hetero-polymerization reaction. The graph is specifically generated from the code of Table 2-9

Table 2-10 provides example questions of a simulating code for isothermal hetero-polymerization reaction.

Table 2-10. An example online questions for simulating isothermal hetero-polymerization reactions.

Question 4

A program set up to simulate a polymerization under Flory's assumptions includes the following conditions: f_a (3), f_b (3), k (0.01 0.01 0.01 0.01; l/mol/s), and initial concentrations (1 1 0 $f_a \cdot 1$ $f_b \cdot 1$).

- a) What is the time at which critical conversion is reached if the fraction of intra (intra/(intra+inter)) polymer reaction is 0.09?

- b) What is the A-moiety concentration at the critical conversion (gel point) if the polymer-polymer reaction rate constant is 0.0081?
- c) What is the A-moiety concentration at which critical conversion is reached if the functionality of both monomers is 3.28?

Question 5

A polymer-forming reaction network includes the following reactions: (1) $A+B \rightarrow P$, (2) $A+P \rightarrow P$, (3) $B+P \rightarrow P$, and (4) $P+P \rightarrow P$. The respective rate constants are 1.1, 1.0, 1.0, and 0.5 all in L/mol/s where the mol units are in terms of functional groups (not molecules). The functionalities of A and B are 3 and 3.1. The concentrations (and initial concentrations) of A, B, and P are 0.8 (1.0), 0.4 (1.0), and 0.0067 (0); respectively.

- a) What is the average degree of polymerization of the mixture (DP)?
- b) What is the average degree of polymerization of the polymer (PDP)?
- c) What is the average MW of the polymers that have formed in this system?

The questions of Table 2-10 were used in a reaction engineering course that included about two weeks of content on simulating polymerization reactions as the last topic of the semester. Students took the online quizzes in groups of three under a hybrid course format with two 50-minute lectures per week (3 credit hour course, two-semester year) and the expectation that students would work in their groups for 1.2 to 2.5 hours per week. The course also included individual online quizzes, homework, three exams, and a final. The exams and final had questions very similar to the online quiz questions which did not require the use of a computer--the exams and final were performed in the absence of any electronics except a basic calculator provided by the department for the exam.

Figure 2-6 summarizes the performances of students as evaluated using online quiz versions of these Table 2-10 questions. The online quizzes included re-take options to convert the evaluation into a better learning experience. Students were allowed to take the quiz up to three times with random generation of questions having different parameters with the final grade being the average of all attempts.

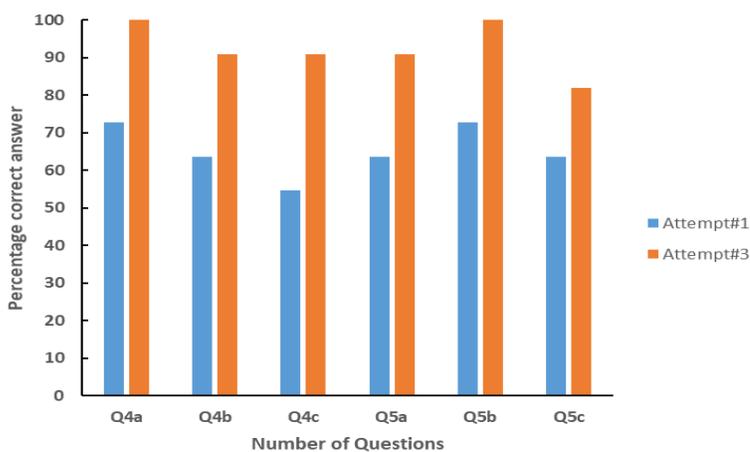


Figure 2-6 Student performances on Questions 4 & 5 in Table 2-10.

The student performances of Figure 2-6 show a good initial understanding of the polymer course material with excellent performance after the group learning experience including the option to retake the online quizzes.

2.4.2 Near – Adiabatic Hetro-Polymerization Reaction

The coding simulation of Table 2-11 simulates near-adiabatic hetro-polymerization. The Arrhenius equation (equation 1) accounts for the temperature dependence of reaction rates, including the assumption of constant pre-exponential terms. An energy balance of the polymer (equation 2) estimates the rate of change of reaction temperature as directly

proportional to the reaction rates. Line 19 of the script file estimates viscosity as a function of the degree of polymerization, DP, and temperature.

Table 2-11. MATLAB code for simulating near-adiabatic hetro-polymerization reaction.

line #	Script
1	<code>global fa fb mCp Hrxn T0 A0 E0 Ts U Ar intra;</code>
2	<code>fa=3.5;</code> %functionality of Amon
3	<code>fb=3.5;</code> %functionality of Bmon
4	<code>mCp=1.5;</code> %Total mass*Heat capacity
5	<code>Hrxn=-70;</code> %Heat of reactions
6	<code>U=1;</code> %Overall heat transfer coefficient
7	<code>T0=295.15;</code> %Initial temperature
8	<code>Ts=295.15;</code> %Ambient temperature
9	<code>A=0.0025;</code> %Surface area of the gel
10	<code>E0=[40 40 40 40];</code> %Activation energy
11	<code>A0=[1E4 1E4 1E4 1E4];</code> %Pre-exponential factor
12	<code>MW=500;</code> %Molecular weight
13	<code>intra=0;</code> % percent intra reactions
14	<code>c0=[1.1 1 0 fa*1.1 fb*1 T0];</code> %Initial conditions
15	<code>tspan=[0:5: 150];</code> %Time span for ODE solutions
16	<code>options=odeset('NonNegative',1:5);</code>
17	<code>[t,ct]=ode45('floryrxn',tspan,c0,options);</code>
18	<code>dp=(c0(1)+c0(2))./(ct(:,1)+ct(:,2)+ct(:,3))</code>
19	<code>viscosity= MW*dp.*exp(0.0005*dp + 2.13*dp./ct(:,6) + 0.32);</code>
20	<code>figure;plot(t,ct(:,1),t,ct(:,2),t,ct(:,3),t,ct(:,4),t,ct(:,5))</code>
21	<code>figure;plot(t,dp)</code> %Plotting dp
22	<code>figure;plot(t,ct(:,6))</code> %Plotting Temperature
23	<code>figure;plot(t,viscosity)</code> %Plotting Viscosity
line #	Function
1	<code>function ydot=floryrxn(tt,c);</code>
2	<code>global fa fb k mCp Hrxn A0 E0 Ts U Ar intra;</code>
3	<code>for i=1:4;k(i)=k0(i)*exp(-E0(i)/(0.008314*c(6)));end;</code>
4	<code>CPA=c(4)-fa*c(1);</code> %Amoi in polymer
5	<code>CPB=c(5)-fb*c(2);</code> %Bmoi in polymer
6	<code>r1=k(1)*fa*c(1)*fb*c(2);</code> % monomer + monomer rxn
7	<code>r2=k(2)*fa*c(1)*CPB;</code> % monomer A + polymer rxn
8	<code>r3=k(3)*CPA*fb*c(2);</code> % polymer + monomer B rxn
9	<code>r4=k(4)*CPA*CPB;</code> % polymer + polymer rxn
10	<code>ydot(1)=-r1-r2;</code> %rate of change of Amon
11	<code>ydot(2)=-r1-r3;</code> %rate of change of Bmon
12	<code>ydot(3)=r1-r4*(1-intra);</code> %rate of change of polymer
13	<code>ydot(4)=-r1-r2-r3-r4;</code> % moiety A accumulation
14	<code>ydot(5)=-r1-r2-r3-r4;</code> % moiety B accumulation
15	<code>ydot(6)=(Hrxn*(-r1-r2-r3-r4) +U*Ar*(Ts-c(6)))/(mCp);</code>

The output from the simulation includes concentration profiles, degree of polymerization profile, reaction temperature profile and viscosity profile. Figure 2-7 (a, b, c and d) presents these profiles.

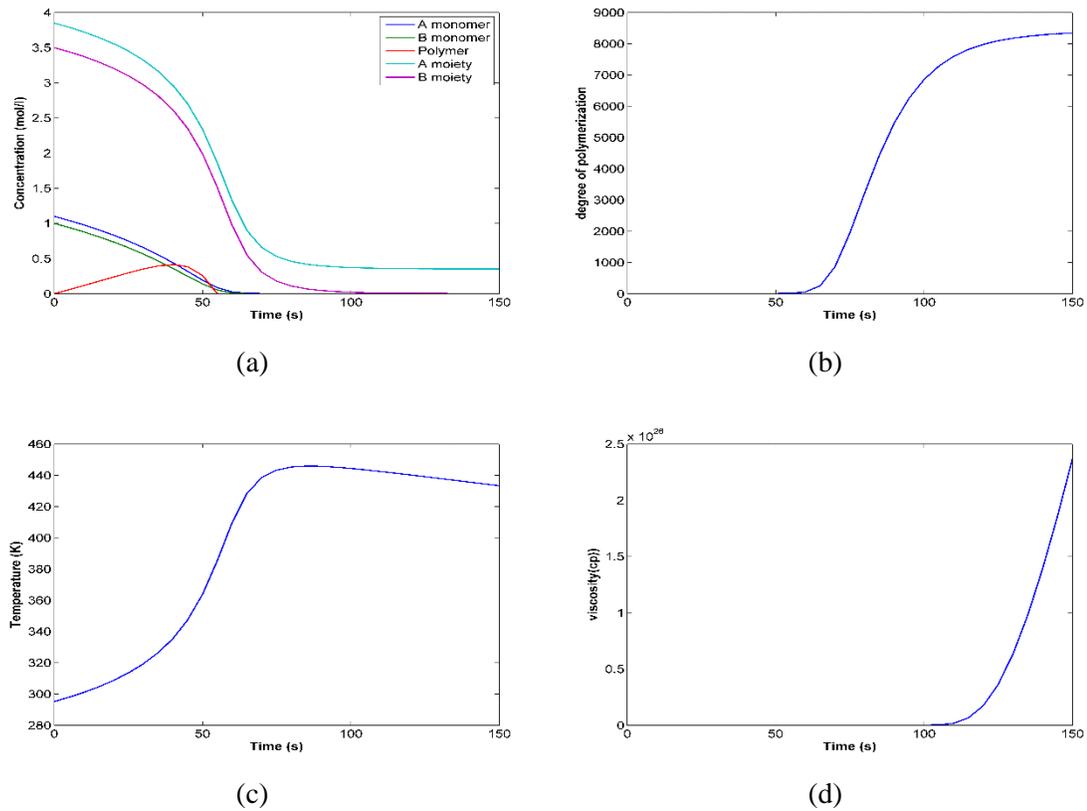


Figure 2-7 Simulation results of concentration profile (a), degree of polymerization (b), reaction temperature profile (c) and (d) Viscosity profile for the near-adiabatic hetero-polymerization. The graph is specifically generated from the code of Table 2-11.

MATLAB's `odeset` function (script code 16) prevents the generation of negative values of concentration. The resulting simulation profiles contain an abundance of information that

allows for study, interpretation, and understanding of the complexities of polymerization. From a commercial perspective, the most important of these outputs is the gel point time (identified as the critical conversion) where the polymer concentration reaches about 0.1% of its maximum value. This is the time where the polymer device shape is set and can be removed from the mold.

Table 2-12 provides example questions of a simulating code for near-adiabatic hetro-polymerization reaction.

Table 2-12. An example online questions for simulating isothermal hetro-polymerization reactions.

Question 6

An adiabatic simulation program of 1-liter basis set up to simulate a polymerization under Flory's assumptions includes the following script file: global fa fb m Cp Hrxn T0 k0 E0 Ts U A; fa=3.5; fb=3.5; m=1; Cp=1.5; Hrxn=-70; U=1; A=0.0025; E0=[40 40 40 40]; k0=[1E4 1E4 1E4 1E4];[t,ct]=ode45('floryrxn',[0:5: 150],[1.1 1 0 fa*1.1 fb*1 295.15],options) ; and their function : function ydot=floryrxn(tt,c); global fa fb k m Cp Hrxn k0 E0 Ts U A; for i=1:4; k(i)=k0(i)*exp(-E0(i)/(0.008314*c(6))); end; CPA=c(4)-fa*c(1); CPB=c(5)-fb*c(2); r1=k(1)*fa*c(1)*fb*c(2); r2=k(2)*fa*c(1)*CPB; r3=k(3)*CPA*fb*c(2) ; r4=k(4)*CPA*CPB; ydot(1)=-r1-r2; ydot(2)=-r1-r3; ydot(3)=r1-r4*(1-intra); ydot(4)=-r1-r2-r3-r4; ydot(5)=-r1-r2-r3-r4; ydot(6)=(Hrxn*(-r1-r2-r3-r4) +U*A*(295.15-c(6)))/(m*Cp); ydot=ydot';

- a) What is the time at which critical conversion is reached if the fraction of polymer-polymer reactions which are intramolecular is [X]?
- b) What is the time at which critical conversion is reached if the functionality of both monomers is 2.96?

An exam question on interpreting simulation results and as designed to be performed without access to a computer is provided in Table 2-13. A version of this question is repeated for two courses with over 30 students in each class. Figure 2-8 summarizes the performances on these questions.

Table 2-13. Final exam question is requiring interpretation of polymer-reaction simulation results.

Question 7

A liquid phase polymer-forming reaction network includes the following reactions: (1) $A+B \rightarrow P$, (2) $A+P \rightarrow P$, (3) $B+P \rightarrow P$, and (4) $P+P \rightarrow P$. The respective rate constants are 1.0, 1.0, 1.0, and 0.5, all in L/mol/s where the mol units are in terms of functional groups (not molecules). The functionalities of A and B are 3 and 2. The concentrations of A, B, and functional groups (moieties) of type A are 1, 1, and 4.0; respectively. Initially, the concentrations of A and B were 2 and 3 with no polymer present.

- a) What is the total concentration of functional groups of type B (mol/L) (at the indicated concentrations, NOT the initial condition)?
- b) What is the concentration of functional groups of type B (mol/L) not on monomer B (at the indicated concentrations, NOT the initial condition)?
- c) What is the rate of change of the B-monomer (mol/L/s)?

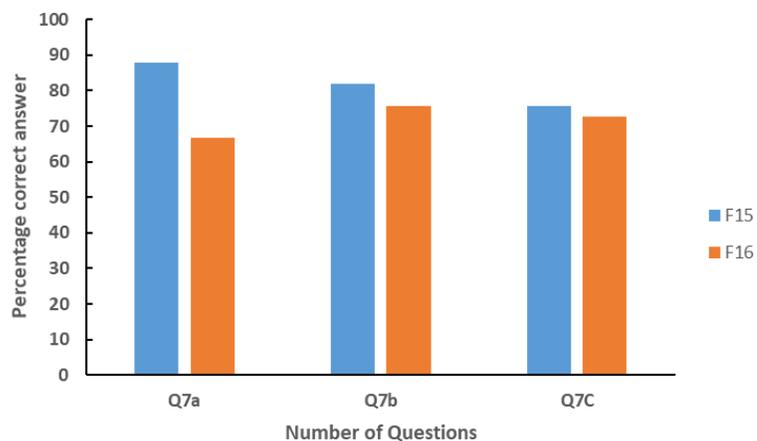


Figure 2-8 Exam performance results from for Table 2-13 questions on the final exam of chemical reaction engineering courses.

The questions are graded all-or-nothing, based only on having correct answers; and based on this, the performances of Figure 2-8 indicate a good mastery of the subject matter. In addition to requiring an understanding of the fundamentals of polymerization, these questions reinforce the application of balance equations and conversion of elementary reactions to reaction rates.

2.5 Advanced Topics

In practice, essentially all polyurethane production incorporates multiple catalysts to control a variety of properties. Simple approximations to the catalytic reactions are possible [12]; however, the complexity actual catalytic mechanisms are important to accurately describe the mechanisms which do have an impact on polymer properties [13]. Catalysis of these homogeneous reaction systems is one of several advanced topics related to polymerization. Table 2-14 lists advance topics that have been studied and published (or are in progress) using simulation. The simulation approach to understanding

polymerization has value both as an educational tool and a platform on which to build the future of this important industry.

Table 2-14. List of advanced topics.

Advanced topics	Outcomes
Critical analysis of the number of parameters needed to simulate industrially-important polymerization reactions topics	<ul style="list-style-type: none"> • Density • Molecular weight • Hydroxyl number • Heat capacity • The overall heat transfer coefficient • Viscosity • Fraction alcohol moieties • Heat of reaction • The activation energy of non-catalytic & catalytic reaction of the moieties • Frequency factor of the non-catalytic & catalytic reaction of the moieties
Summary of group contribution approaches [14]	<ul style="list-style-type: none"> • Count the types and number (n_k) of molecular groups that make the molecule. • Sum the values of $n_k \cdot A_k$ and $n_k \cdot B_k$ to obtain A and B. • Calculate pure viscosity (η) by substituting A and B into Orrick and Erbar equation. • Determine the mass fraction of each component in the mixture • Using the Grunberg-Nissan model of the equation to calculate mixture viscosity (η_m) from molecules
How viscosity impact polymerization processes	<p>Polymerization course of homogenous systems, the viscosity of the reaction mass increases by several orders of extent, viscosity increase is affected by</p> <ul style="list-style-type: none"> • Reaction conditions, concentration, and properties of the formed polymer. • Polymerization kinetics as well as heat, mass and momentum balances of the polymerization reactor.
How diffusion rate impact thermoset reactions	<ul style="list-style-type: none"> • high viscosity materials are reacting • The reaction leads to large increase in resin viscosity • The reactions after gel point continue

2.6 Conclusion

A meaningful coverage of polymer-forming reactions is possible in about 0.5 credit hours of coverage of a three-credit hour core-curriculum course on chemical reaction engineering. The polymer-forming simulation topic as provided in this paper is a natural extension of the standard content of this course.

Unique aspects of the approach include a) moiety reaction versus molecule reaction, b) use of visible learning re-enforcement from the generation of concentration/temperature profiles, and c) incrementally extension of the number and complexity of reactions. These can combine to improve the understanding and retention of the core concepts while simultaneously providing for the learning of important concepts of polymer engineering. Since the topic of polymers is introduced by building upon the class's core knowledge on reactions; the learning of polymer science can also be enhanced with improved retention.

Immediately useful topics to new engineers entering the work force include: a) an understanding of gel point time which is the critical reaction time in thermoset polymer molds, b) an understanding of the impact of monomer functionality and purity monomers on polymerization, and c) extended use of mole balances (extent of reaction) as applied to polymer systems.

2.7 Nomenclature

Symbols	Meaning
A°	Pre-exponential factor of Arrhenius equation
Ar	Based and lateral area of the gel (m^2)
A	"A" moiety in isocyanate monomer
A _{mon}	Monomer concentration of component "A" (mol/l)
A _{moi}	Moiety concentration of component "A" (mol/l)
B	"B" moiety in polyol monomer
B _{mon}	Monomer concentration of component "B" (mol/l)
B _{moi}	Moiety concentration of component "B" (mol/l)
C	Concentration (mol/l)
C _p	Heat capacity(J/K)
E°	Activation Energy(KJ/mol)
f _a	Functionality of "A" monomer
f _b	Functionality of "B" monomer
H _{rxn}	Heat of reactions
P	Polymer concentration (mol/l)
P _A	"A" moieties attached to polymer
P _B	"B" moieties attached to polymer
P	Polymer concentration (mol/l)
R	Gas constant(KJ/K.mol)
r	Rate of reaction
T°	Initial temperature(k)
T _s	Ambient temperature(k)
U	Overall heat transfer coefficient (KJ/K.mol)
f _a	Functionality of "A" monomer
f _b	Functionality of "B" monomer
Y _{dot}	Rate of change of component concentration of temperature
n _k	Number of groups of chemical structure
A _k	Group contribution to A
B _k	Group contribution to B
η	Liquid viscosity (cp)
η_m	Viscosity of mixture (cp)

2.8 References

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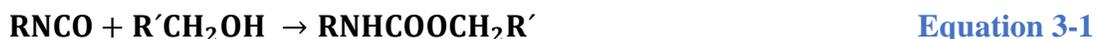
CHAPTER 3. SIMULATION APPROACH FOR CHARACTERIZING THE ISOCYANATES REACTIVITY IN POLYURETHANE GEL REACTIONS

3.1 Abstract

Applying simulation for determining the reactivities of an isocyanate minimizes the number of experimental needed for prediction reaction temperature of polyurethane gel reactions. Isocyanates reactivity characterization, along with polyol characterization done earlier, increases the accuracy of the results of reaction temperature which makes the processing of polyurethane less time and money consuming. In this paper, a MatLab code was improved to characterize the reactivates of different isocyanates based on para versus ortho isocyanate moieties. This approach also assists in predicting the fractional content of isocyanate moieties of in unknown polymeric isocyanates. Experimental data including temperature profiles and viscosity profiles of urethane gel reactions were used to validate the simulation results.

3.2 Introduction

Polyurethane (PU) is a polymer composed of organic units joined by carbamate (urethane) joins and are shaped by the reaction of polyols and isocyanate groups [1–3]. The common gelling reaction of polyurethane can be composed as:



Where R and R' are long organic chains that contain extra isocyanate and/or alcohol moieties. By the proper selection of the types of polyols, isocyanate components, and the

reaction conditions, a wide range of products spanning from elastomers to flexible and rigid foams can be obtained that are used in many areas. One of the crucial parameters in these synthesis is the reactivity of the isocyanate moieties with the alcohol moieties.

Large efforts have been made so far to study the reaction kinetics of the isocyanate and alcohol moieties to form polyurethane. Al-Moameri, Zhao, and Ghoreishi et al.[4–8] developed an approach to simulate thermoset polymerization. The approach is based on the solution of the ordinary differential equations (ODEs) resulting from a series of elementary reactions, the reactor's energy balance, and physical processes such as mass transfer for blowing agents.

The simulation of polyurethane reactions of Ghoreishi et al.[7] was based on the characterization polyols as primary, secondary, and hindered secondary alcohol moieties. The temperature profile of the reaction of different alcohol moieties with polymeric isocyanate was used to empower the simulation results. Follow-Up research on this topic shows that the hindered secondary alcohol moiety was not a separate kind of moieties, but it is an artifact of the slow reaction due to mass transfer limitation which decreases reaction rates [4–9]. The current research of this paper was built on the simulation code of those studies.

The isocyanate provides the source of NCO groups to react with functional from the polyol. The substance group of isocyanates could make partitioned into mono-, di- and polyisocyanates depend on the number of isocyanate groups. Diisocyanates, which have two reactive isocyanate groups, is the most broadly utilized, and the most common are diphenylmethane diisocyanate, toluene diisocyanate, hexamethylene diisocyanate and

isophorone diisocyanate, the polymeric MDI are also differentiated by viscosity, functionality, and reactivity and have lower vapor pressure than MDI.

In this paper, isocyanates were characterized based on the content of para and ortho isocyanates moieties using a MatLab simulation program based on the possible reaction of these moieties with alcohol moieties in the polyol. The simulation program provides a fast method of characterizing the fractional content of para and ortho isocyanate group of unknown polymeric isocyanates. The results of characterizing isocyanates were empowered by reaction temperature profile and viscosity profile during the reaction to polyurethane.

The reaction rate expressions in this code would identify the concentration of the reactants and also their functionalities. Inside the MatLab code, one matrix represents reaction rates, and another matrix represents stoichiometric coefficients of all moieties and components. Duplication of these two materials results in a set of ordinary differential equations that are at the same time illuminated by ODE45 function. The code simulates temperature profiles and viscosity profiles of all components.

Isocyanates characterization kinetics was the subject of interest of many researchers [10,11] including diphenylmethane -diisocyanate (MDI) [12], toluene-diisocyanate (TDI) [13] with various alcohols using different reaction conditions and monitoring methods such as titration [14], UV-vis photometry combined with high-performance liquid chromatography (HPLC) [15], fluorescence spectroscopy [16], and mass spectrometry [13,14]. According to the kinetic results of Nagy et al. [17] of uncatalyzed reactions of MDI isocyanate with primary and secondary alcohols, the reactivity of the isocyanate

moiety in the para-position is about four to six times higher than that the ortho-positioned isocyanate moiety, depending on the reacting alcohol. Also, large efforts have been devoted so far to study reaction kinetics of industrially important isocyanates including MDI, TDI, and HDI with various alcohols using different reaction conditions and monitoring methods.

Ferstandig and Scherrer [18] measured and compared the rate of reaction between a group of phenyl-substituted isocyanates and a group of benzyl-substituted isocyanates, and the energies of activation were figured out by utilizing Arrhenius equation. The benzyl isocyanates react more slowly than the Phenyl isocyanates type by first-order reaction mechanism in isocyanate and alcohol concentration.

Barbâlată et al.[19] compared the influence of different aromatic diisocyanate on the preparation and properties of polyurethanes that prepared from ethylene glycol and different diisocyanate using the spectrophotometric method, and they proved that thermal dissociation and discoloration in polyurethane rely on upon that reactivity of the diisocyanates.

Fred H. Brock [20] broke down the kinetics of the 2,4-tolylene diisocyanate alcohol reaction as far as a parallel and series reaction scheme comprising for two synchronous reaction paths as opposed to the regular strategy considering essentially one reaction path just , those outcomes that the last rate plot got from this hypothetical treatment is comparable to the one gotten from experimental data however that contrary to current assumptions, the rate constant values got from the two linear portions of this rate plot are not the devalues of the para and ortho isocyanate groups.

Sun and Sung [15] established a correlation between the intrinsic fluorescence intensity technique throughout the reactions between methylene 4,4-diphenyl diisocyanate (MDI) with alcohol and the degree of the reaction founded by IR. The rate constants and the activation energies for this reaction model and polyurethane formation got from the fluorescence comes about compared with the IR outcomes.

Nage et al. [13] studied the kinetics of uncatalyzed reactions of 2,4-TDI (2,4-toluene diisocyanate) and MDI (4,4-diphenylmethane-diisocyanate) with alcohol at different temperatures by applying high-performance liquid chromatography (HPLC) and off-line electrospray ionization mass spectrometry (ESI-MS) technique for observing the reaction products of diisocyanate-alcohol reactions and it might have been demonstrated that the para-isocyanate group in the 2,4-TDI reacts quicker with alcohols over the first group of MDI.

Huang and Sung [16] are used UV absorption, and fluorescence spectroscopy similarly as the principle apparatus to characterize the kinetics of the reaction between MDI diisocyanate and NDI diisocyanate with alcohol through polyurethane reactions and the comes about are investigated on getting the reactivity ration between the first isocyanate and the second one.

These studies were limited to specific recipes, non-catalyzed reactions and did not consider the mass transfer limitation on reaction kinetics.

This article simulates the reactivates of different isocyanate moieties using a MatLab code of polyurethane reaction and the results were empowered by the experimental results of temperature and viscosity profile obtained for urethane gel reactions. The simulation code

includes the reactions of Para and Ortho isocyanate moieties with primary and secondary alcohol moieties. However, the code is written so that it contains additional reactions from foaming urethane. The main reactions included in the code are presented in Table 3-1, in which A is an isocyanate, B is alcohol, and P is polymer respectively.

Table 3-1 The main reactions occurring in urethane polymerization Process

Reaction No.	Reaction
1	$A_{\text{para}} + B_{\text{Primary}} \rightarrow P$
2	$A_{\text{para}} + B_{\text{secondary}} \rightarrow P$
3	$A_{\text{ortho}} + B_{\text{Primary}} \rightarrow P$
4	$A_{\text{ortho}} + B_{\text{secondary}} \rightarrow P$

The kinetic parameters of alcohol were obtained from previous research of Al-Moameri *et al.* [9] for simulating temperature and viscosity profiles of polyurethane gel systems.

The values of E (activation energy) in Arrhenius equation (Equation 4-2) which used through the four reactions of Table 3-1 were also adopted from a previous study [7,9].

$$k = A^{\circ} * e^{\frac{-E^{\circ}}{RT}} \quad \text{Equation 3-2}$$

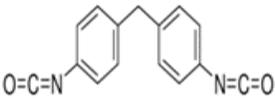
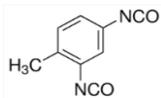
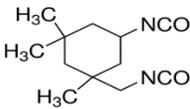
Where the pre-exponential factor of Arrhenius equation considered as a frequency factor, then the revised form of Equation 4-2 included the impact of inter-molecular diffusion and was assumed to be proportional to the reaction viscosity, the impact of intra -molecular diffusion and was assumed to be proportional to the reaction temperature to provides better simulation results [4,9].

$$k = \left(A'_1 \frac{T}{\mu} + A'_2 T \right) e^{\frac{-E^\circ}{RT}}$$

Equation 3-3

Table 3-2 shown the fractional content of para and ortho isocyanates moieties with the chemical structure for the most isocyanates used in polyurethane reactions, where diisocyanate structure have a tremendous effect on the preparation and properties of polyurethane depending on the NCO group content reactivity of diisocyanate.

Table 3-2 Structure of different isocyanate groups

Name	Linear Formula	Fractional isocyanate moieties ($X_{para} + X_{ortho} = 1$)	Structure
Methylene diphenyl diisocyanate (4,4'-MDI)	$CH_2(C_6H_4NCO)_2$	$X_{para} = 100\%$ $X_{ortho} = 0$	
Tolylene-2,4-diisocyanate (TDI)	$CH_3C_6H_3(NCO)_2$	$X_{para} = 50\%$ $X_{ortho} = 50\%$	
Hexamethylene diisocyanate (HDI)	$OCN(CH_2)_6NCO$	$X_{para} = 100\%$ $X_{ortho} = 0$	
Isophorone diisocyanate (IPDI)	$OCNC_6H_7(CH_3)_3$ CH_2NCO	$X_{para} = 50\%$ $X_{ortho} = 50\%$	

The goal of this paper is to specify kinetic parameters of different isocyanate and alcohol reactions toward specifying the fractional content of isocyanate moieties of in unknown polymeric isocyanate. This simulation allows prediction the performance of different polymeric isocyanate-based on the content of the location of the isocyanate moieties.

The novelty of this work relative to previous publications on this topic are: This work illustrates the validity of the approach and the potential for it to provide very useful analytical methods by using MatLab simulation code and we consider mass transfer limitation in getting the kinetic parameter of different reactions.

3.3 Experimental Procedure

Polyurethane gels were produced at different indices to verify simulation results using MDI from Sigma-Aldrich and TDI from Fisher as isocyanates (A side) used in this study, DEG from Sigma-Aldrich and Voranol 490 from Dow Chemical Co. were the two Polyols (B side) used in this study, and the specifications of each one appear in Table 3-3 .Amine catalyst, N,N-Dimethylcyclohexyl-amine(DMCHA) referred to as Cat8,was used as a gelling catalyst. Momentive L6900 is the surfactant, Tris (1-chloro-2-propyl) Phosphate (TCPP) is a fire retardant, and the amount of the surfactant and fire retardant was kept at 0.15% (mass fraction).

Table 3-4 shows the recipes of the catalytic reactions. The reaction temperature and viscosity change were obtained as temperature -time and viscosity-time profiles.

Recipes were mixed in a paper cup covered by a polyurethane foam to reduce the heat loss during the reaction. 2000 rpm mixing blade attached to a floor-model drill press was used to mix the recipes. The same mixing time for all experiment of 10 seconds was used to avoid any variation in viscosity profiles measurement [21]. A type-k thermocouple

attached to a national instruments SCB-68 box to a national PCI 6024E data acquisition was used to measure temperature profile using LabView software. The LabView software provides an instant reading of the reaction temperature versus reaction time. Viscosity profile of the resin was measured by a Cole-Parmer basic viscometer. All reaction temperature and viscosity experiments were carried out at room temperature to avoid deviations in reaction kinetics and molecular weights of the polymer [22].

Table 3-3 Specifications of (MDI and TDI) as isocyanates and (DEG and V490) as polyols

Property	MDI	TDI	DEG	V490
Density, g cm ⁻³	1.230	1.214	1.118	1.11
Average molecular weight	250.25	174.16	106.12	460
Functionality	2	2	2	4.3
Equivalent weight	125.15	87.08	53.06	115
Hydroxyl number, mg KOH g ⁻¹	-	-	1057	484.8
Vapor pressure, mm Hg at 25°C	0.000005	0.01	-	-

Table 3-4 Recipes for the Catalytic reaction of (MDI and TDI) as isocyanates and (DEG and V490) as polyols

Weight, g				
Ingredient	Experiment1	Experiment2	Experiment3	Experiment4
B-side Side materials	DEG	V490	DEG	V490
Polyol	20	20	20	20
TCCP	0.07	0.07	0.04	0.06
L6900	0.07	0.07	0.04	0.06
Catalyst 8	0.1	0.1	0.1	0.1
A-side materials	MDI	MDI	TDI	TDI
Isocyanate	25.93	24.55	18.05	17.08

3.4 Results and Discussion

The previous research of Al-Moameri et al. [9] gotten the kinetic parameters of the fraction content of primary and secondary alcohol moieties from the reaction of DEG and

V490 with polymeric MDI, where DEG might have been utilized as reference for getting the kinetic parameters of the fraction content of primary alcohol moieties, and V490 might have been utilized to getting the kinetic parameters of the fraction content of secondary alcohol moieties. The simulation of this approach gave great concurrence with experimental data for both reaction temperature and resin viscosity.

The shortcoming of this research was it did not characterize the polymeric isocyanate-based of the content and reactivates of para and ortho isocyanate groups.

The current research modified the simulation code of the previous study of Al-Moameri et al. [9], kinetic parameters of the reaction of para and ortho isocyanate moieties with primary and secondary alcohol moieties were obtained from temperature and viscosity profiles of the reactions of MDI and TDI as isocyanate with DEG and V490 as alcohol/polyol.

The kinetic parameter of the reaction of para isocyanate moieties and primary alcohol moieties (Reaction #1, Table 3-1) was obtained from simulating temperature, and viscosity profiles of the reaction of MDI and DEG where MDI has 100%, para isocyanate moiety and DEG have 100% primary alcohol moiety.

Due to the symmetrical structure of MDI, it tends to easily crystallize with a melting point of 38°C. Toluene was used as a solvent to dissolve the MDI and to cool the reaction.

The value of the kinetic parameter was tested at different indices. Figure 3-1 shows good agreement of the experimental data with simulation results.

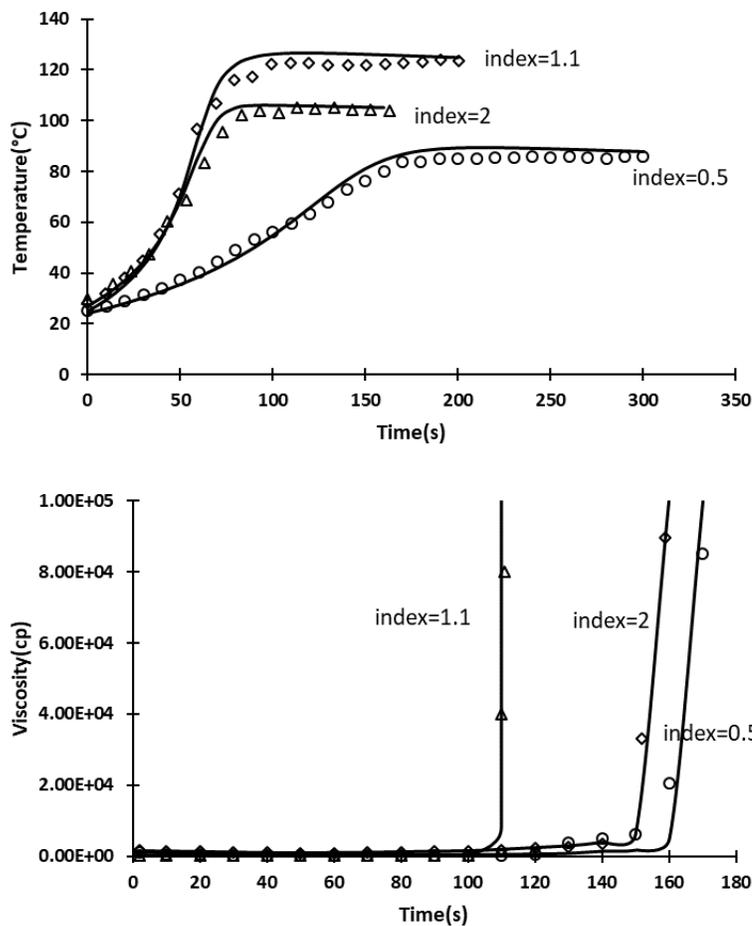


Figure 3-1 Experimental data and simulation results for (a) temperature profiles & (b) viscosity profile using MDI (A-side) with DEG (B-side) gel system at (0.5, 1.1 & 2) isocyanate index. Symbols and solid lines represent experimental and simulation results simultaneously.

The kinetic parameter of the reaction of para isocyanate moieties and secondary alcohol moieties (Reaction #2, Table 3-1) was obtained from the reaction of MDI and V490 where V490 was characterized to having a high content of secondary alcohol moieties based on previous studies [7,9]. Figure 3-2 shows the experimental data and simulation results of the reaction. The monomers were preheated to 50°C before the reaction to melt the isocyanate.

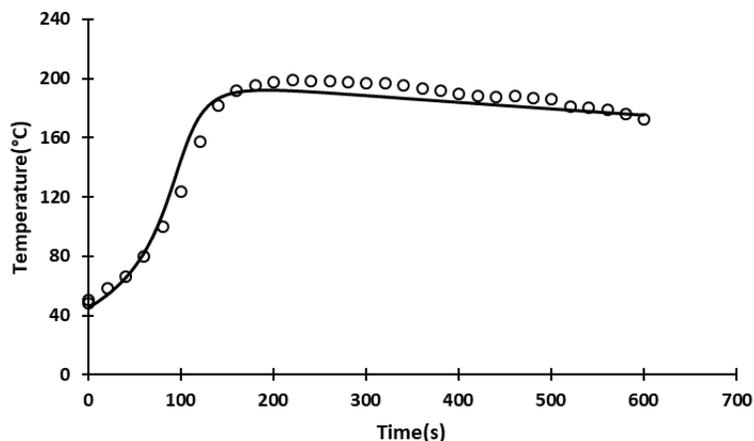


Figure 3-2 Experimental data and simulation results for temperature profiles using MDI (A-side) with V490 (B-side) gel system at 1.1 isocyanate index. Symbols and solid lines represent experimental and simulation results simultaneously.

In the same way, the kinetic parameter of the reaction of ortho isocyanate moiety and primary alcohol moiety (Reaction#3, Table 3-1) was obtained from the reaction of TDI and DEG where TDI was characterized as having 50/50 para/ortho isocyanate moieties. The kinetic parameter of the reaction of para isocyanate moieties and primary alcohol moieties was obtained previously from the simulation results of Figure 3-1. The obtained temperature profile at ambient temperature Figure 3-3 shows no reaction occurs. One way to increase the reaction rate of this reaction was to pre-heat the monomers to 50°C and increase the amount of catalyst. Under these conditions, simulation results show good agreement with a temperature profile as shown in Figure 3-3. It looks that the reaction temperature profile of TDI with DEG faster than that the reaction temperature profile of MDI with DEG, for the following reasons: a) MDI with DEG reaction, Toluene was used as solvent leads to cool the reaction, b) TDI with DEG reaction, increased the amount of catalyst leads to the reaction become faster.

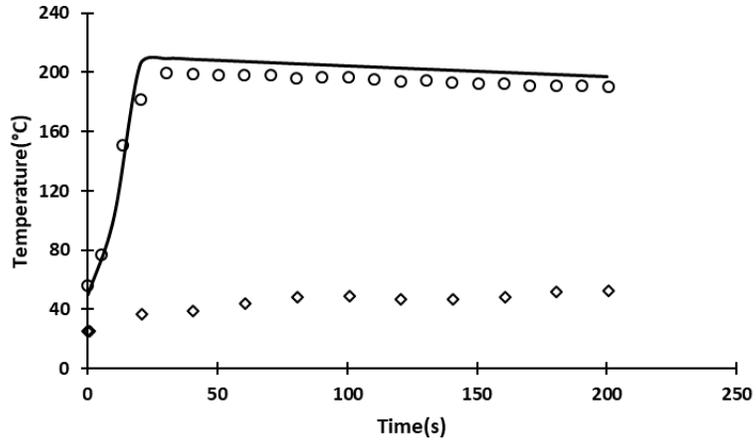


Figure 3-3 Experimental data and simulation results for temperature profiles using TDI (A-side) with DEG (B-side) gel system at 1.1 isocyanate index at ambient temperature and after pre-heat the monomers to 50°C. Symbols and solid lines represent experimental and simulation results simultaneously.

The kinetic parameter of the last reaction (Reaction# 4, Table 3-1) was obtained from the reaction of TDI and V490. The simulation results show good agreement with the experimental data as shown in Figure 3-4.

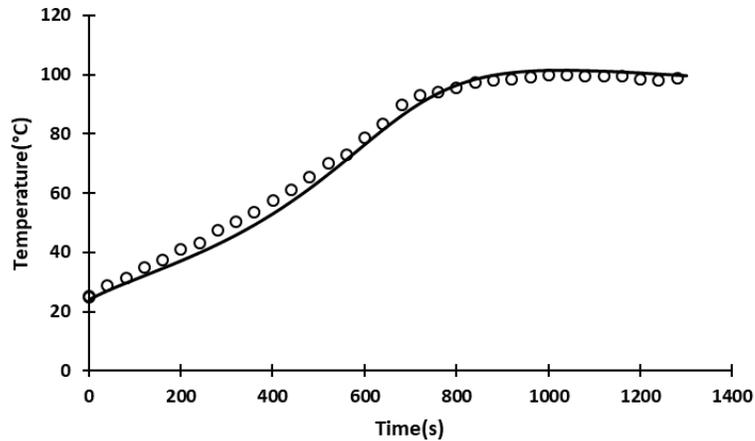


Figure 3-4 Experimental data and simulation results for temperature profiles using TDI (A-side) with V490 (B-side) gel system at 1.1 isocyanate index. Symbols and solid lines represent experimental and simulation results simultaneously.

A° (reaction rate constant at 25°C) in equation 2, were obtained based on visual fits of model parameters to the data.

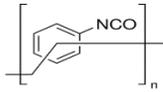
Table 3-5 summarizes the kinetic parameters (the pre-exponential value of Arrhenius equation) of the four reactions of Table 3-1. The kinetic parameter of the reaction of para-isocyanate moieties and primary alcohol moieties was found to have the highest value while the kinetic parameter of the reaction of ortho-isocyanate moieties and secondary alcohol moieties was found to have the lowest value.

Table 3-5 New kinetic parameters bases of PARA/ORTHO for Isocyanate and PRIMARY/SECONDARY for Polyol

Reaction No.	Parameter	A° ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)
1	Para-Primary	0.41
2	Para-Secondary	0.2
3	Ortho-Primary	0.22
4	Ortho-Secondary	0.11

Polymeric MDI where characterized according to the fraction of para- and ortho-isocyanate moieties. The different fraction was applied to a good fit to the reaction with DEG, and it is found that a fraction of 79% para and 21% ortho-isocyanate moieties gives the best results as summarizes in Table 3-6. This ratio was tested on the reaction of polymeric MDI and V490, and good fitting to the experimental data was obtained. The current simulation was improved the fitting as compared to the previous study [9] as shown in Figure 3-5. The polymeric MDI was found to have a small fraction of ortho-isocyanate moieties that may result from some side reaction during polymerization of MDI.

Table 3-6 summary of fitted parameter for polymeric MDI

Name	Linear Formula	Structure	Fractional isocyanate moieties ($X_{para}+X_{ortho}=1$)
Polymethylene polyphenyl isocyanate (Polymeric MDI)	$[C_6H_3(NCO)CH_2]_n$		$X_{para} = 79\%$ $X_{ortho} = 21\%$

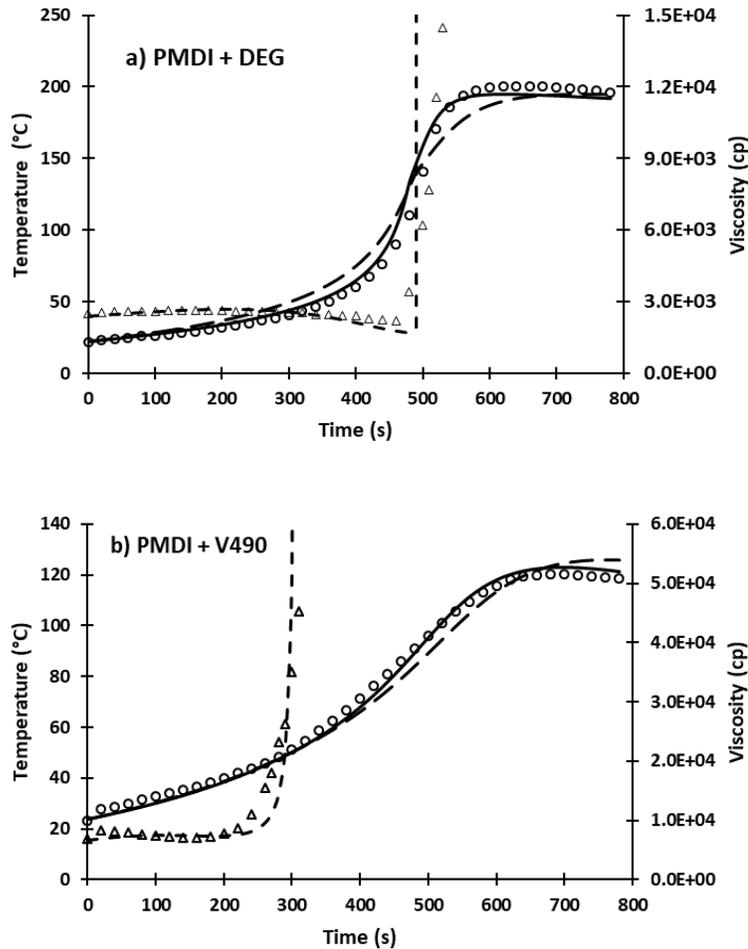


Figure 3-5 Experimental data and simulation results for temperature profiles using (a) PMDI (A-side) with DEG (B-side), (b) PMDI (A-side) with V490 (B-side) gel system at 1.1 isocyanate index. Symbols and solid lines represent experimental and simulation results simultaneously of current research. Long dash line represents the previous model simulation.

3.5 Conclusion

MatLab, computer simulation code, was modified to characterize unknown polymeric isocyanate based on the fractional content of para and ortho isocyanate moieties that based on the temperature and viscosity profiles of polyurethane gel reactions.

The current study shows that polymeric isocyanate (PMDI) has a fractional content of 79% para isocyanate moieties and 21% ortho-isocyanate moieties. The ortho-isocyanate moieties may result from side reactions during the polymerization process of MDI.

Characterizing polymeric isocyanate based on the reactivity of the isocyanate group improves the fitting of the simulation results as compared to the old simulation studies.

The current simulation provides insight of how the simulation package of polyurethane reaction can be used to characterize any unknown isocyanate-based of the fractional content of ortho- and para-isocyanate moieties and this approach is the starting point for a simulation methodology having a great potential

3.6 Nomenclature

Symbols	Meaning
A°	Pre-exponential factor of Arrhenius equation
A	“A” moiety in isocyanate monomer
B	“B” moiety in polyol monomer
C	Concentration (mol/l)
E°	Activation Energy(KJ/mol)
fa	Functionality of “A” monomer
fb	Functionality of “B” monomer
Hrxn	Heat of reactions
P	Polymer concentration (mol/l)
R	Gas constant(KJ/K.mol)
r	Rate of reaction
U	Overall heat transfer coefficient (KJ/K.mol)
fa	Functionality of “A” monomer
fb	Functionality of “B” monomer

3.7 References

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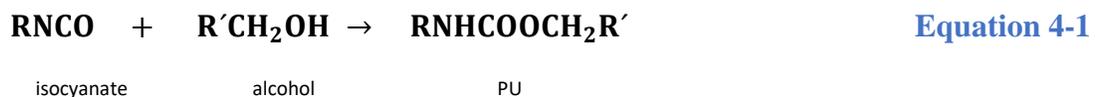
CHAPTER 4. LIMITS OF PERFORMANCE OF POLYURETHANE BLOWING AGENTS

4.1 Abstract

Applying simulation in determining the limits of performance of polyurethane foam formation. N-pentane, Cyclo-hexane, and Methyl formate were used as physical blowing agents, and water was used as a chemical blowing agent. Hence, simulation increases the accuracy of the results and also makes the foam performance process less time and money consuming. In this paper, a MatLab code was developed to study the impact of physical and chemical blowing agents at different loadings on the performance of rigid polyurethane foams. Experimental data including temperature profiles, height profile and a tack-free time of urethane foam reactions were used to validate the simulation results.

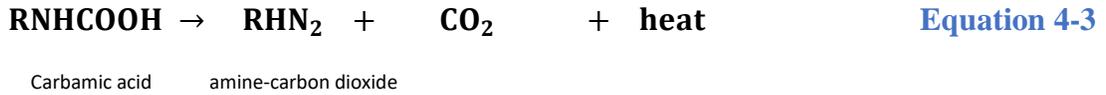
4.2 Introduction

Rigid polyurethane foam (PU) is a polymer composed of organic units joined by carbamate (urethane) links and are formed by the reaction of the isocyanate group and alcohol group in polyols [1–3] in the presence of selected catalysts, surfactants, fire retardants, and physical and /or chemical blowing agents [4], as described by the Equation 5-1.



Foaming is caused physically or chemically or by a combination of the two. The gas produced from the blowing agents fills the cellular structure of the bubbles. Water is used

as a chemical blowing agent because it reacts with the isocyanate group to generate carbon dioxide gas according to the reactions [5].



In general, a blowing agent is a key material for the foaming process and the quality, quantity, and nature of a blowing agent control the final characteristics and properties of the produced foam. The optimum blowing agent should have the following characteristics: harmonious with the base resin, produces sleek foam's surface, uniform foam core transition, and achieve the best blowing performance (minimum concentration and price).

Most foaming material is derived from the blowing agent during the process of foaming process, produced from the liquid phase, or produce from the reaction or decomposition of chemical material under heat or catalyst effect. Blowing agents can be classified in many ways. However, according to the mechanism by which gas is liberated during the foaming process, it can be classified to physical and chemical blowing agents. In addition to the two types, we can add gases that directly added to the liquid polymer to make foam as a third type[6].

Blowing or foaming agents are substances that decompose or vaporize easily at given temperatures to produce large quantities of gases or vapors. Accordingly, they may be divided into chemical and physical blowing agents.

Physical blowing agents (PBAs) such as n-pentane, methyl formate, and cyclo-hexane are widely used in polyurethane formulation. In general, physical blowing agents are compounds that expand quickly because of a phase change such as vaporization of liquids or of compressed liquefied gases at the foaming temperature. The lightness (or density) of the foamed product is affected by the rate of vaporization of the physical blowing agent; a higher rate produces a lighter foam. Chemical blowing agents such as water which are organic and inorganic compounds that decompose thermally into gases while not reacting with the polymer matrix are usually exothermic and irreversible [7] which in turn, provides better final foam properties [8–10].

Additional gas can be provided from physical blowing agents during foaming, which leads to adding some desired properties to the foam[6,11]. Once the gas(es) liberates from the chemical blowing agent, it acts as a physical blowing agent. Because they are too expensive, chemical blowing agents are mostly used when high or medium polymer foams are required. The produced foam is in range of 400 to 800 kg/m³ (i.e. 20 to 45% reduction from the original liquid polymer density)[12].

Using chemical blowing agents has many advantages, it is easy to add to the liquid polymer to be formed and the forming process needs little modification in the process line of an existing thermoplastic polymer. However, it is difficult for recycling. On the other hand, the blowing agent may affect on the properties of foam such as density, cellular structure and cooling time[13].

The evaporation of the blowing agent is governed by the vapor-liquid equilibrium with volatile components between the polymer matrix and vapor phase. For commercial foams,

the most physical properties concerned are density, compressive strength and thermal conductivity [14].

Large efforts have been made so far by many research workers to study the performance of polyurethane blowing agents. Baser and Khakhar developed theoretical modes for physical blowing agent rigid polyurethane foam formation [15] and water-blown polyurethane foams [16]. They carried out a detailed experimental study to measure both temperature density change during foam formation. However, they did not consider heat transfer to surroundings and the impact of thermocouples on temperature profiles.

Tesser et al. [17] 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 mixture.

Al-Moameri and Zhao et al. [5,8,18,19] developed an approach to simulate rigid polyurethane foams. The approach is based on the solution of the ordinary differential equations (ODEs) resulting from a series of elementary reactions, the reactor's energy balance, and physical processes such as mass transfer for blowing agents.

The previous study of Al-Moameri et al [5] used a MatLab code to simulate how different blowing agents can be used. In addition, to water, Methyl formate, n-Pentane, and cyclo-Hexane were defined in this code.

The current research further develops the simulation code of the previous study, focusing on the ability to simulate the limits of performance of chemical and physical blowing agent and their mixture at different blowing agents loading and the results were empowered by

the experimental results of temperature profile, height profile, and tack free time obtained from urethane foam reactions.

FoamSim MatLab program can successfully predict many failure modes of polyurethane foam. Table 4-1 lists these failures regarding the blowing agents, polyols, and isocyanates. However, some visual forms of failure cannot predict by the code and Table 4-2 list these visual modes.

Table 4-1 indications of failure based on foaming process simulation

Feature	Failure mode
Blowing agent concentration	The blowing agent does not evaporate completely during foaming.
Temperature	The temperature of reaction either too low or too high.
Recipes concentration	Not all the isocyanate, polyol, and/ or blowing agent is reacted.
Height	The height of the foam is very short.
Degree of polymerization	Low degree of polymerization.

Table 4-2 visual failure modes of foams

Feature	Failure mode
Surface	Rough and stiff.
	Not rigid enough.
Bubbles at the surface	No bubbles at the surface.
	Too many bubbles at the surface.
Failure to form cell network	At the start of foam, bubbles rupture without preservation of cell.

	Gooney surface persists all the way to the end of the foaming process.
Failure to retain cell structure	When foam cools (0.05-4 hrs.), the sides of foam collapse in.
Cell morphology problems	To high an open cell content. Smaller than normal. Larger than normal.
Foam has the inadequate compressive strength	Easy to smash.

4.3 Experimental Procedure

4.3.1 Materials

PMDI (standard polymeric MDI) from Dow Chemical Co. was the isocyanate (A side) used in this study, Voranol 360 from Dow Chemical Co. was the Polyol (B side) used in this study, and the specifications of each one is shown in Table 4-3. N,N-Dimethylcyclohexyl-amine(DMCHA) as catalyst 8 from Sigma-Aldrich, N,N,N',N'',N''-Pentamethyldiethylene-triamine (PMDETA) as catalyst 5 from FSI were used as amine based catalysts . Momentive L6900 was used as a surfactant, Tris (1-chloro-2-propyl) Phosphate (TCPP) was used as fire retardant. n-pentane, cyclo-Hexane, methyl formate from Sigma-Aldrich, and water were used as blowing agent. The amounts of polyol, catalyst 8, catalyst 5, surfactant and fire retardant were kept constant in all foam experiments

to evaluate the performance of blowing agents, the isocyanate index was kept at 1.1 for all reactions.

Table 4-3 Specifications of PMDI and Voranol 360

Property	PMDI	V360
Density, g cm ³	1.23	1.081
Average molecular weight	369.9	728
Functionality	2.7	4.5
Equivalent weight	137	155.55
Hydroxyl number, mg KOH g ⁻¹	-	360
Viscosity, mPa s at 25°C	150-220	3500
NCO content by weight, %	31.4	-
Vapor pressure, mm Hg at 25°C	<10 ⁻⁵	-
Specific heat at 25°C (g.cal/g)	0.43	-

Table 4-4 shows the foaming recipes for rigid polyurethane foam catalytic reaction and Table 4-5 summarizes the mass loadings of each blowing agent with the corresponding amounts of PMDI and catalysts. The reaction temperature and foam height were obtained as temperature -time and foam height-time profiles.

Table 4-4 Foaming Recipes for Rigid Polyurethane Foam

ingredient	weight (g)
A-side material	
PMDI (1.1 index)	see Table3
B-side materials	
Voranol 360	45
Dimethylcyclohexylamine (Catalyst8)	see Table3
Pentamethyldiethyleneamine (Catalyst5)	see Table3
Momentive L6900	0.4
TCPP	2
Blowing agent	see Table 3

4.3.2 Foam preparation and data collection

The following steps were used in the Foam experiments:

1. Polyols (B-side components), blowing agents, catalysts, surfactant and fire retardant were weighed and added in a closed 250 mL beaker, then the B-side components were mixed for 5 min.
2. After that, pre-weighed isocyanate (A-side material) by syringe to reduce weight loss, then (B-side components) poured into a plastic cup and mixed with (A-side material) at the same speed for 10s
3. Finally, the mixture poured into a wooden box (base area of 12.7 X 12.7 cm²) with an aluminum-foil lining.

All experiments were carried out at room temperature in order to avoid deviations in reaction kinetics and molecular weight of the polymer [20]. A high-speed mixer blade (2,000 rpm) attached to a floor-model drill press was used to mix the chemicals, LabView software with a type-K thermocouple and an ultrasound device attached through a National Instruments SCB-68 box to a National Instruments PCI 6024E data acquisition card was used to monitor the temperature and height profiles of foam reactions.

The tack-free time was measured for all the foams by measuring the time when the surface of the foam did not show sickness when touched with a spatula [21].

Table 4-5 Amounts of Blowing Agents, PMDI, and Catalysts.

Exp no.	Blowing agent	Weight (g)	PMDI (1.1 index)	Catalyst8	Catalyst5
1	n-pentane	2	43	0.5	0
2	n-pentane	4	43	0.5	0
3	n-pentane	8	43	0.5	0
4	n-pentane	12	43	0.5	0
5	methyl formate	2	43	0.5	0
6	methyl formate	6	43	0.5	0
7	methyl formate	10	43	0.5	0
8	methyl formate	14	43	0.5	0
9	water	0.2	46.26	0.12	0.32
10	water	0.5	51.2	0.12	0.32
11	water	1	59.46	0.12	0.32
12	water	2	75.96	0.12	0.32
13	cyclohexane	1	43	0.5	0
14	cyclohexane	2	43	0.5	0
15	water/ cyclohexane	0.5/2	51.2	0.12	0.32
16	water/ cyclohexane	0.5/4	51.2	0.12	0.32
17	water/ cyclohexane	0.5/6	51.2	0.12	0.32
18	water/ cyclohexane	0.5/12	51.2	0.12	0.32
19	water/ n-pentane	0.5/4	51.2	0.12	0.32
20	n-pentane/ methyl formate	3/3	43	0.5	0

4.4 Results and Discussion

Figure 4-1 shows simulation results of density which were calculated based on solving the partial differential equations of polyurethane reactions, reaction temperature, and rate of change of height when blowing agent present. Simulation gel density is correct assuming no changes in gel height. Simulation considers the volume of the nucleation sites generated formed by the mixing of the monomer prior to the reaction. Experimental results of gel reaction show no change in weight. Experimental results of gel density show decrease due to increase in gel height which is due to:

1. Any volume change due to liquid-phase mixing.
2. The polyol may be absorbed some moisture that reacts with isocyanate and works as a blowing agent.

The total volume of gel reaction equals the volume of final mixture left in the paper cup plus the volume of nucleation sites occurred during the mixing.

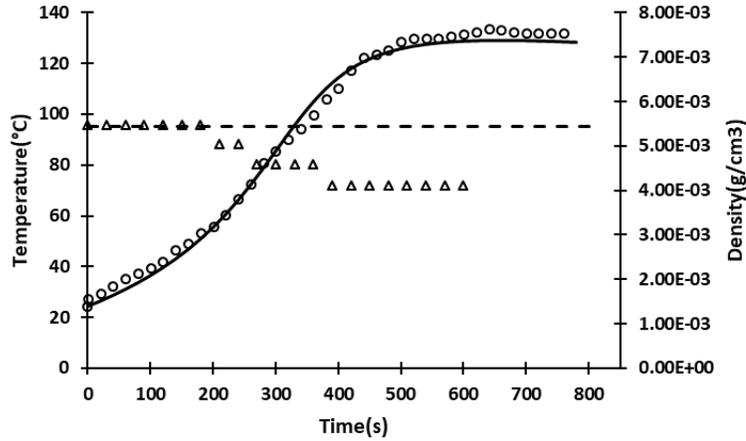


Figure 4-1 Experimental data and simulation results of reaction temperature (blue) and resin density (red) using PMDI (A-side) with V360 (B-side) gel system at 1.1 isocyanate index. Circles and Triangles refer to the experimental data of reaction temperature and resin density. Straight and dash lines refer to simulation results.

A series of experiments (as shown in Table 4-5) were performed toward identifying the limits of performance of each blowing agent. The same foam recipes were used with different loadings of blowing agents ranging from low to a high concentration. The reaction temperature and foam height were recorded experimentally and compared to the simulation results where the simulation code assumes ideal performance for the blowing agent including no escaping from the top of the foam during foam rising and no entrapment in the polymer matrix.

Eight experiments were performed for each blowing agent and four results were presented where the foam failure became obvious. Foaming experiments were performed using n-Pentane (Figure 4-2) as a physical blowing agent. Loadings of 2, 4, 8, and 12g were chosen where the limits of performance became obvious.

Experimental data of foams blown by 2g loading shows lower foam height compared to the simulation results. This was attributed to some of the blowing agent entrapped in the resin matrix. This was obviously observed where the resulting foam has high density and dark color similar to the gel.

Experimental data using 4 and 8g of n-Pentane shows good agreement with the simulation results. The 12g loading of n-Pentane show failure. The foam shows bubbles on the top surface of the foam indicating that the greatest part of the blowing agent was escaped from the foam during the foaming reaction. The simulation code predicts lower temperature profile as it assumes about 50% of the n-Pentane was evaporated to form the foam cells.

The limits of performance of n-Pentane blowing agent was identified as the window between the 2 and about 10g where 40% to 80% is evaporating and diffuses to the cells to form foam.

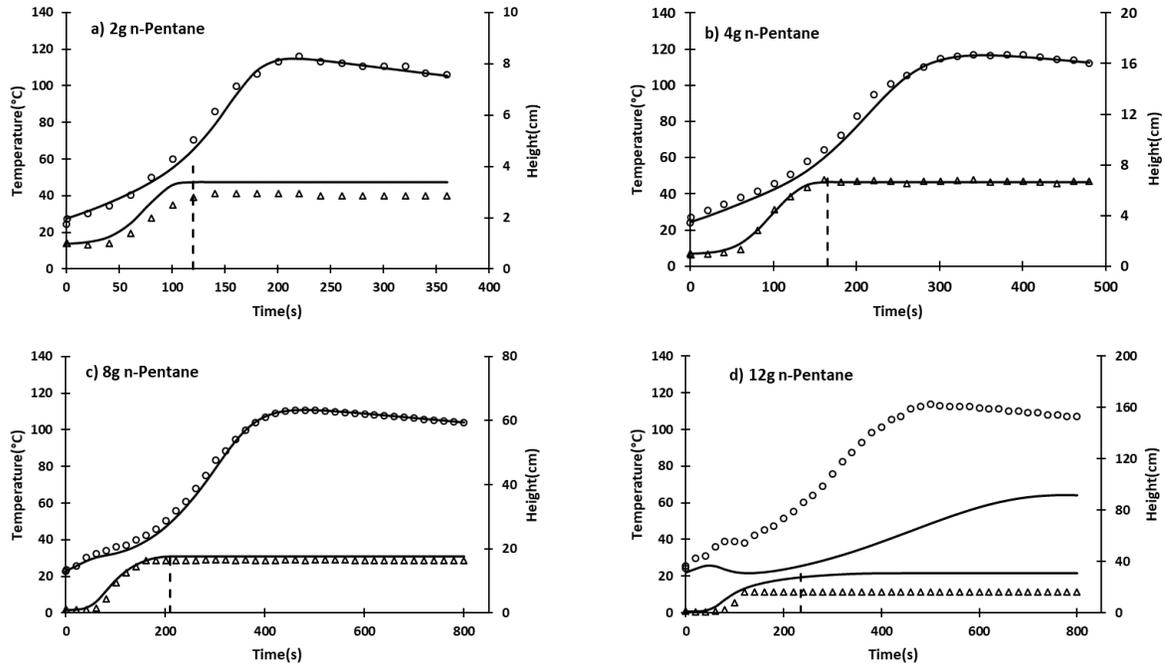


Figure 4-2 Experimental and simulation results of temperature profile, height profile, and tack-free time of rigid polyurethane foams blown by (2,4,8 and 12) g physical blowing agents n-Pentane. Symbols “o” and “Δ” represent experimental data of temperature and height profiles respectively. Solid lines represent simulation results for temperature and height. Dashed line represents tack-free time.

Figure 4-3 shows foaming experiments on a second blowing agent were performed to identify the limits of performance. Methyl formate loadings of 2, 6, 10, and 14g were chosen. Foams of 2 and 14g methyl formate show failure where foams height was lower the simulation results.

The resulting foam from the 6g methyl formate loading shows good agreement with the simulation results. The 10g loading of methyl formate results in foams with little deviation in reaction temperature and foam height compared to the simulation results. This region was identified as the start of foam failure.

The limits of performance for Methyl formate blowing agent was identified as the window between 6 and 10g where 5% to 20% is evaporating and diffuses into the cells to form the foam.

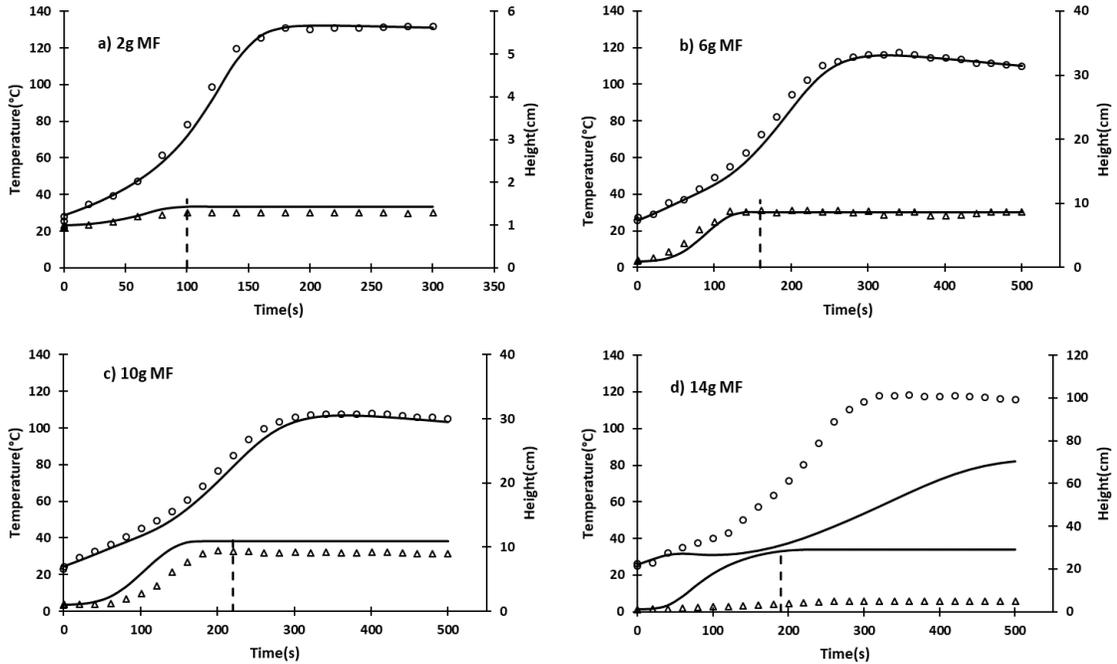


Figure 4-3 Experimental and simulation results of temperature profile, height profile, and tack-free time of rigid polyurethane foams blown by (2,6,10 and 14) g physical blowing agents Methylformate. Symbols “o” and “Δ” represent experimental data of temperature and height profiles respectively. Solid lines represent simulation results for temperature and height. Dashed line represents tack-free time.

The limits of performance were measured for water as chemical blowing agent. Water reacts with isocyanate to generate carbon dioxide which diffused to the nucleation sites to form the foam bubbles.

The rate reaction of isocyanate and water is much faster than the polymerization reaction; however, the heat generated by the water reaction increases the rate of polymerization

reaction based on Arrhenius equation. In addition, the amount of the generated gas should be within a limit that proportional to the amount of polymer blown.

For that, it is important to optimize the amount of water that should be used in the polyurethane formulation. A 0.2, 0.5, 1, and 2g loading of water was used as blowing agent as shown in Figure 4-4. The 0.2 loading shows that foam height is lower the predicted value from the simulation code. this was attributed to the low amount of water that generated a low amount of carbon dioxide which in turn entrapped in the resin matrix. The 0.5 and 1g loading shows good agreement with simulation and produces good foams.

The loading of 2g was also shown lower foam height compared to the simulation. This was attributed to the high amount of blowing agent generated at the initial time of the reaction before enough amount of polymer formed to hold the gas in the cell. The foam shows bubbles of the top surface that shows bubble escaping during the reaction.

The limits of performance of water were in the region above 95%. Increasing water loading leads to increase carbon dioxide gas which in turn escapes from the surface and lead to density failure of the foam.

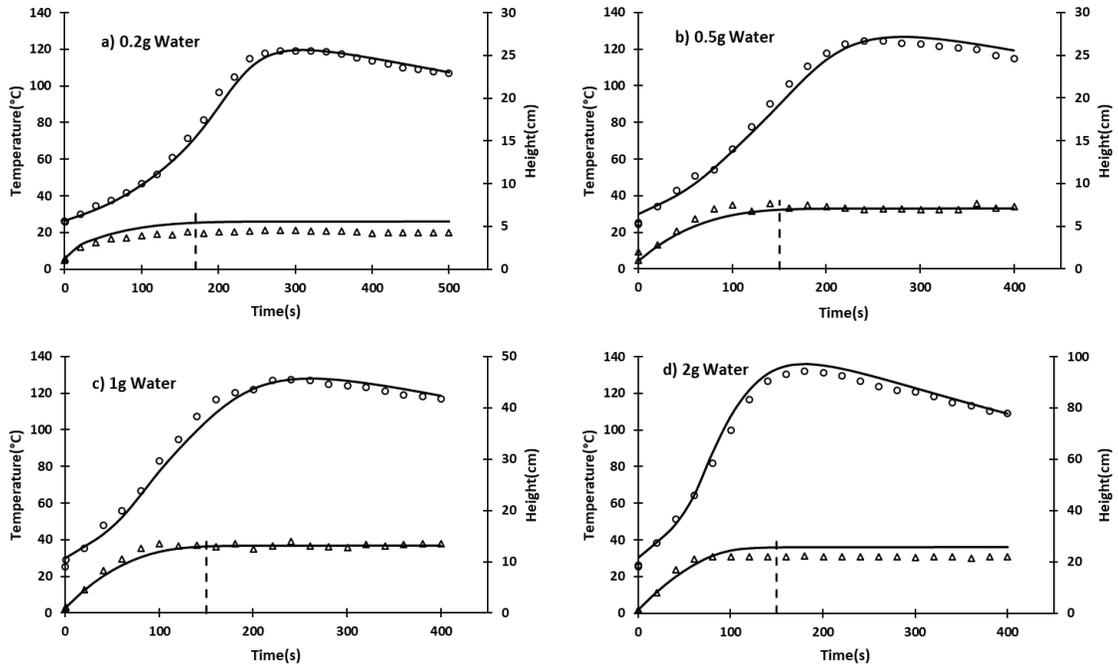


Figure 4-4 Experimental and simulation results of temperature profile, height profile, and tack-free time of rigid polyurethane foams blown by (0.2,0.5,1 and 2) g chemical blowing agents Water Symbols “o” and “Δ” represent experimental data of temperature and height profiles respectively. Solid lines represent simulation results for temperature and height. Dashed line represents tack-free time.

Experiments were performed using cyclo-Hexane as blowing agent. All foams blown by this blowing agent were failed as shown in Figure 4-5. Foam height was not rising even at low loadings. This failure can be attributed to the high heat of vaporization of cyclo-Hexane higher boiling temperatures lead to bubble formation and expansion at greater extents of reaction where the viscosity is higher, causing more resistance to bubble expansion and slower diffusion of gases into the bubbles.

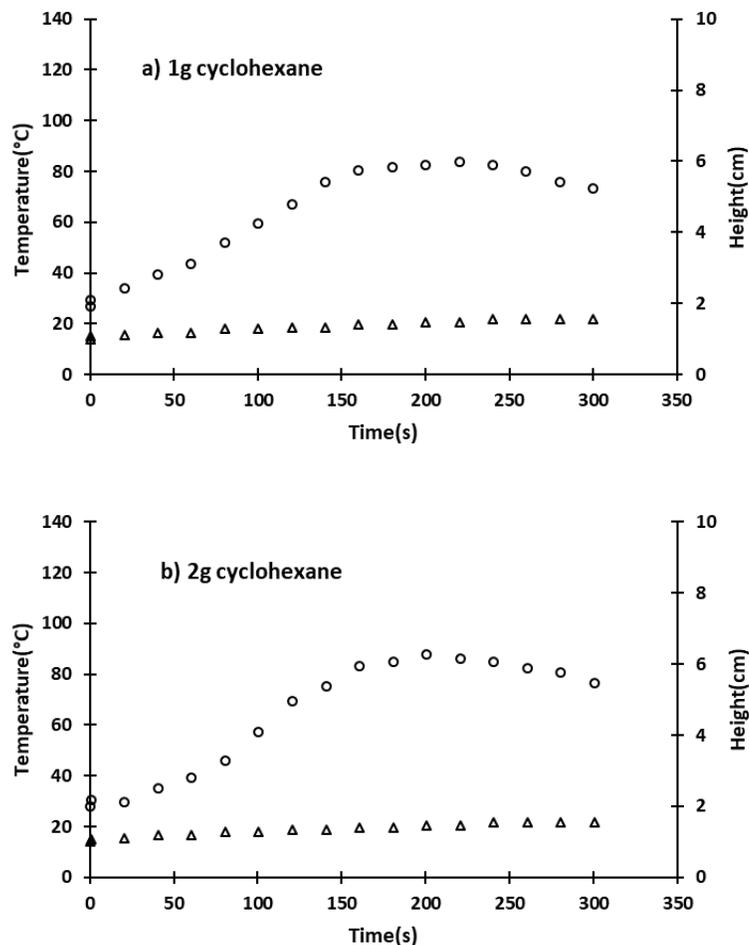


Figure 4-5 Experimental of temperature profile, height profile of rigid polyurethane foams blown by (1 and 2) g physical blowing agents cyclohexane.

One way to avoid this foam failure was by increasing the heat of reaction at the earlier stages of reaction by adding 0.5g of water. Water reacts with isocyanate to generate heat which in turn increases the rate of polymerization reactions.

Experimental data and simulation results of 2, 4, 6, and 12g loadings of cyclo-Hexane (and 0.5g water) are shown in Figure 4-6. The resulting foam forms the 2g loading show good density and surface properties with the good agreement of experimental data of temperature and foam height with the simulation results.

Beyond the 2g loading, the foams show signs of failure in foam shape, foam surface, and some bubbles on the top surface. These signs became more obvious as the cyclo-Hexane loading increases. Simulation results of reaction temperature and foam height show good agreement for the 2g loading and the deviation increases as the loading increases.

Form these experiments, we identified that the limits of performance were in the region below the 2g loading where less than 20% of the cyclo-Hexane is evaporating and diffuses into the cells.

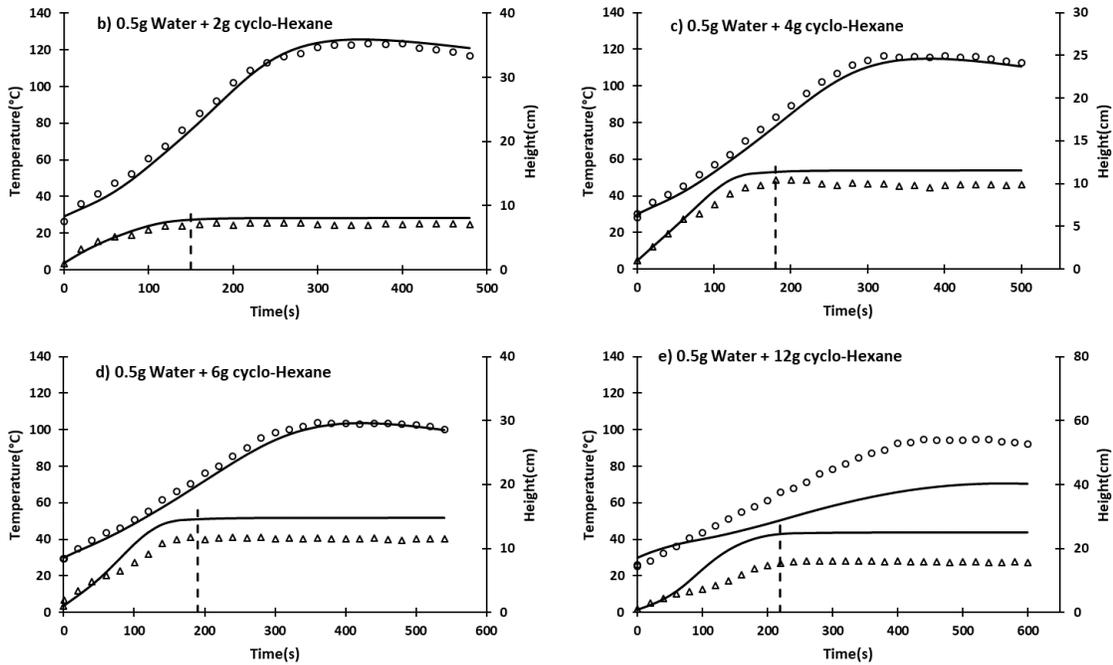


Figure 4-6 Experimental and simulation results of temperature profile, height profile, and tack-free time of rigid polyurethane foams blown by 1g physical blowing agents cyclo-Hexane, (2,4,6and12) g cyclo-Hexane with 0.5g Water respectively. Symbols “o” and “Δ” represent experimental data of temperature and height profiles respectively. Solid lines represent simulation results for temperature and height. Dashed line represents tack-free time.

The key aspect of the good blowing agent performance was synchronizing the viscosity of the polymer during foaming with the amount of blowing agent evaporated within the same time period.

Experimental data of viscosity were plotted versus percent blowing agent evaporated obtained from simulation toward the goal of identifying the limits of performance of each blowing agent discussed in this paper as shown in Figure 4-7.

We identified that the limits of performance were in the region less than 20% of the cyclo-Hexane, the limits of performance were in the region between 5% to 20% of the Methyl formate, the limits of performance were in the region between 40% to 80% of the n-pentane and the limits of performance were in the region above 95% of water.

This figure provides the advantage of predicting whether a specific loading of each blowing agent will return a good foam or foam failure depending on whether it lies within or outside the window.

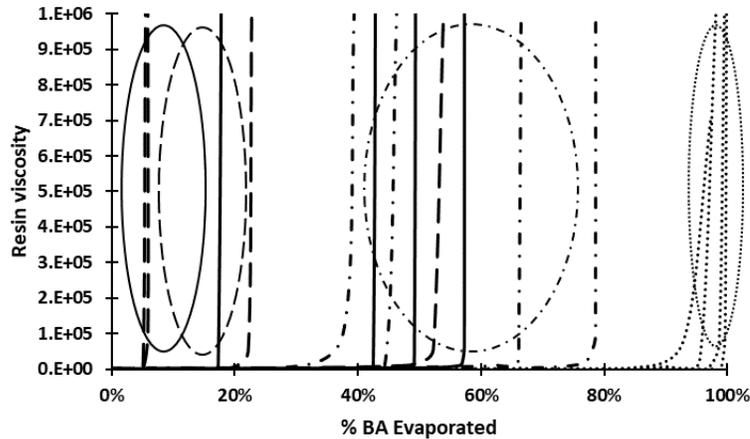


Figure 4-7 limits of performance values of polyurethane blowing agents. Straight, long dash, dash dot, and round dot refer to cyclo-Hexane, Methyl formate, n-pentane, and water respectively.

The above shows the advantage of predicting the limits of performance of any mixture of these polyurethane blowing agent as shown in Figure 4-8 limits of performance values of polyurethane blowing agents. Straight and long dash refer to (0.5g water / 4g n-pentane) blowing agent mixture and (3g n-pentane / 3g methyl formate) blowing agent mixture respectively.

. A good foam blown by a mixture of these foams is lying within the limits of the two blowing agents.

Two different loadings of a mixture of blowing agents were tested. The first experiment was performed using (3g n-pentane / 3g methyl formate) blowing agent mixture and the second experiment was performed using (0.5g water / 4g n-pentane) blowing agent mixture.

The limits of performance of (3g n-pentane / 3g methyl formate) blowing agent mixture were identified within the limits of the two-blowing agent (5% - 80%) where 40% is evaporating and diffuses to the cells to form a foam.

The limits of performance of (0.5g water / 4g n-pentane) blowing agent mixture were identified within the limits of the two-blowing agent (40% - 99%) where 65% is evaporating and diffuses to the cells to form a foam.

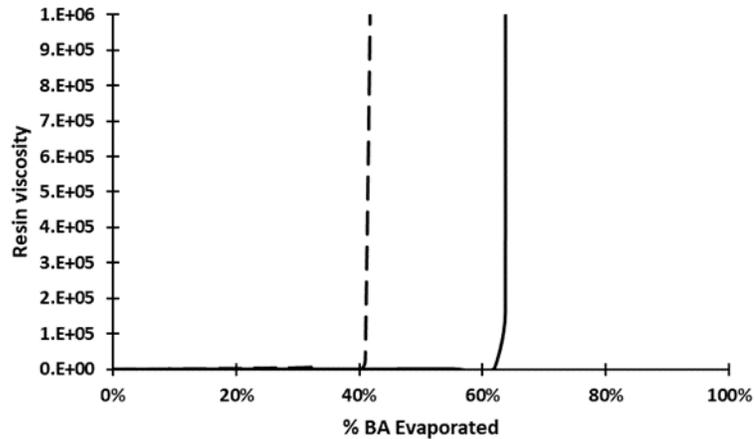


Figure 4-8 limits of performance values of polyurethane blowing agents. Straight and long dash refer to (0.5g water / 4g n-pentane) blowing agent mixture and (3g n-pentane / 3g methyl formate) blowing agent mixture respectively.

4.5 Conclusions

MatLab computer simulation code was developed to simulate the limits of performance of blowing agents based on temperature profiles, height profiles and tack free time of rigid polyurethane foam reactions.

The limits of performance were measured for water as chemical blowing agent; n-Pentane, Methyl formate, and cyclo-Hexane as physical blowing agent at different loadings.

The loadings were ranged from very low loadings to high loading to identify the limits where the blowing agent yield good foams in terms of foam density, form failure, and the results of the simulation where the foaming performance is ideal.

The simulating results of % blowing agent evaporated to the cell and resin viscosity for each blowing agent gave the region where a blowing agent loading can produce good foam versus the regions where foams fail.

The current study provides insight into limits of performance of each single blowing agent and the advantage of predicting the limits of performance of any mixture of these blowing agents.

4.6 References

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CHAPTER 5. CONCLUSIONS AND FUTURE WORK

5.1 Conclusions of Current Research

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

The first approach of chapter two, a meaningful coverage of polymer-forming reactions is possible in about 0.5 credit hours of coverage of a three-credit hour core-curriculum course on chemical reaction engineering. The polymer-forming simulation topic as provided in this paper is a natural extension of the standard content of this course.

Unique aspects of the approach include a) moiety reaction versus molecule reaction, b) use of visible learning re-enforcement from the generation of concentration/temperature profiles, and c) incrementally extension of the number and complexity of reactions. These can combine to improve the understanding and retention of the core concepts while simultaneously providing for the learning of important concepts of polymer engineering. Since the topic of polymers is introduced by building upon the class's core knowledge on reactions; the learning of polymer science can also be enhanced with improved retention.

Immediately useful topics to new engineers entering the work force include: a) an understanding of gel point time which is the critical reaction time in thermoset polymer molds, b) an understanding of the impact of monomer functionality and purity monomers on polymerization, and c) extended use of mole balances (extent of reaction) as applied to polymer systems.

MATLAB, computer simulation code, the second approach of chapter three was modified to characterize unknown polymeric isocyanate based on the fractional content of para and ortho isocyanate moieties that based on the temperature and viscosity profiles of polyurethane gel reactions.

The current study shows that polymeric isocyanate (PMDI) has a fractional content of 79% para isocyanate moieties and 21% ortho-isocyanate moieties. The ortho-isocyanate moieties may result from side reactions during the polymerization process of MDI.

Characterizing polymeric isocyanate based on the reactivity of the isocyanate group improves the fitting of the simulation results as compared to the old simulation studies.

The current simulation provides insight of how the simulation package of polyurethane reaction can be used to characterize any unknown isocyanate-based of the fractional content of ortho- and para-isocyanate moieties and this approach is the starting point for a simulation methodology having a great potential.

MATLAB computer simulation code, the third approach of chapter four was developed to simulate the limits of performance of blowing agents based on temperature profiles, height profiles and tack free time of rigid polyurethane foam reactions.

The limits of performance were measured for water as chemical blowing agent; n-Pentane, Methyl formate, and cyclo-Hexane as physical blowing agent at different loadings.

The loadings were ranged from very low loadings to high loading to identify the limits where the blowing agent yield good foams in terms of foam density, form failure, and the results of the simulation where the foaming performance is ideal.

The simulating results of % blowing agent evaporated to the cell and resin viscosity for each blowing agent gave the region where a blowing agent loading can produce good foam versus the regions where foams fail.

The current study provides insight into limits of performance of each single blowing agent and the advantage of predicting the limits of performance of any mixture of these blowing agents.

5.2 Recommendations for Further Research

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

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

- Studying the impact of surfactants and fire retardants.
- Identifying the mechanism of different catalyst attachments based on simulation where catalyst may interact with alcohol moieties or with both alcohol and isocyanate moieties.
- Modelling epoxy group fate in urethane formulation.
- Prediction/Correlation of glass transition temperature.
- Increasingly accurate prediction of foam failure and improved insight into modes of foam failure.
- Simulation of Bubble/cell bursting and closed cell content.

VITA

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