

Modeling Reaction Kinetics of Rigid Polyurethane Foaming Process

Yusheng Zhao,¹ Michael J. Gordon,¹ Ali Tekeei,¹ Fu-Hung Hsieh,² Galen J. Suppes¹

¹Department of Chemical Engineering, University of Missouri-Columbia, Columbia, Missouri 65211

²Department of Biological Engineering, University of Missouri-Columbia, Columbia, Missouri 65211

Correspondence to: Y. Zhao (E-mail: yzpk2@mail.missouri.edu)

ABSTRACT: A theoretical model was developed to simulate the polyurethane foaming process for a rigid foam. In the model, multiple ordinary differential equations were solved by MATLAB and the model was able to predict temperature profiles by inputting foam recipe information. This initial study on foam modeling focusses on reaction kinetic parameters that were fitted to experimental temperature data as a function of time. The modeling was able to accurately model temperature profiles of single-polyol polyurethane formulations and was able to accurately predict temperature profiles of mixtures based on pure component kinetic parameters. A primary goal of this work is to expedite the ability to develop new foam formulations by simulation—especially for incorporation of new bio-based polyols into formulations. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1131–1138, 2013

KEYWORDS: polyurethane foams; kinetics; theory and modeling

Received 1 October 2012; accepted 14 March 2013; Published online 17 April 2013

DOI: 10.1002/app.39287

INTRODUCTION

Polyurethanes are used in a range of applications, including the manufacture of flexible, high-resilience foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting compounds, high performance adhesives, and surface coating. For the manufacture of polyurethane polymers, two bifunctional groups are needed as the reactants. Isocyanate groups and compounds with active hydrogen atoms have been used.¹ The structure and molecular size of these compounds influence the polymerization. In addition, additives such as catalysts,² surfactants, blowing agents,³ cross linkers, flame retardants, light stabilizers, and fillers⁴ are used to control and modify the reaction process and performance characteristics of the polymer.

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

Ni has performed kinetic study with a titration method to determine the concentration of the isocyanate group as a function of time and estimated the rate constants of the reaction of

isocyanate with water by linear regression.² Others have worked on modeling to predict material properties in order to reduce time on performance tests. Conor Briody¹⁰ has developed a visco-hyperelastic numerical material model for simulating the uni-axial and shear behavior of polymer foams. H. Jmal et al.¹¹ used a memory integer model and the difference-forces method to identify the Quasi-static behavior of polyurethane foam. Their model was able to identify the viscoelastic and global elastic parameters of the macroscopic integer model. While the modeling of some specified properties of polyurethane foam has been widely studied, the modeling studies on the reaction process have been scarce.

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

The purpose of this article is to provide a simplified engineering model for modeling complex polyurethane foaming reaction. Previous works were not able to solve multiple ordinary differential equations^{12–16} simultaneously by hand calculation. Therefore, a MATLAB program was developed to solve these equations to model temperature profiles as a function of time during the foaming process and compare that to experimental data during the first 15 min of the foaming reaction. This program was able to easily predict temperature profiles of any foam recipes. In general, the dynamics of the foaming process has been studied using two approaches: (i) assuming the foam to be made up of many microscopic unit cells, and (ii) assuming the foam to be a single pseudo-homogeneous phase.

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

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

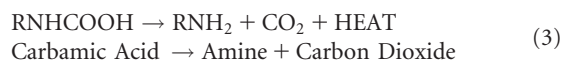
MODELING

The polyurethane foaming process involves two competing reactions (gel reaction and blow reaction). The gel reaction, also sometimes called the polymerization reaction, involves the reaction of an isocyanate group with an alcohol group to give a urethane linkage as shown in eq. (1). As polyurethane foams usually utilize polyfunctional reactants (typically difunctional isocyanate and trifunctional polyols), this reaction leads to the formation of a cross-linked polymer.



The reaction of a urethane group with an isocyanate group to form an allophanate group is another possible way to further crosslink the polymer. However, compared with gelation reaction this side reaction can be neglected.^{12–14,17}

The blow reaction is a two-step reaction described by eqs. (2) and (3). An isocyanate group reacts with water to yield a thermally unstable carbamic acid which decomposes to give an amine functionality, carbon dioxide, and heat.



The newly formed amine group reacts with another isocyanate group to give a disubstituted urea. There are other secondary reactions, involving the formation of biuret and allophanate linkages which could lead to the formation of covalent cross-linking points. A common practice in literatures is to neglect these side reactions.^{12–14,17} This current work provided a base case simulation where the impact of these side reactions was neglected and where the impact can be further evaluated in subsequent studies.

For the reactions above, relationships between main variables are listed below. Equations (4) and (5) represent the rates of gel and blow reaction;

$$r_{\text{gel}} = \sum_i k_{\text{gel}i} \times c_{\text{catgel}} \times c_{\text{iso}} \times c_{\text{OH}i} = \sum_i r_{\text{gel}i} \quad (4)$$

$$r_{\text{blow}} = k_{\text{blow}} \times c_{\text{catblow}} \times c_{\text{iso}} \times c_{\text{water}} \quad (5)$$

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

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

Equations (6–10) relates the concentrations of isocyanate, polyol, water, urethane, and carbon dioxide to the fundamental rate equations.

$$\frac{dc_{\text{iso}}}{dt} = -r_{\text{gel}} - r_{\text{blow}} \quad (6)$$

$$\frac{dc_{\text{OH}i}}{dt} = -r_{\text{gel}i} \quad (7)$$

$$\frac{dc_{\text{water}}}{dt} = -r_{\text{blow}} \quad (8)$$

$$\frac{dc_{\text{ure}}}{dt} = r_{\text{gel}} \quad (9)$$

$$\frac{dc_{\text{CO}_2}}{dt} = r_{\text{blow}} \quad (10)$$

where c_{ure} is the concentration of urethane, and c_{CO_2} is the concentration of carbon dioxide. Equation (11) shows the

Table I. Material Properties

Component	Isocyanate	Polyol	Polyurethane	Water	Carbon dioxide	Amine
Heat capacity (J/g-K)	1.799	1.57~1.89	1.4-1.5	4.19	0.846-0.939 (300-400 K)	1.55-1.64
Heat capacity (J/equiv-K)	242.86	264.86	362.5	75.42	39.6	128
Product	Fn	Sp. Gravity @25°C	% NCO	Eq. wt.	Viscosity cps@25°C	
RUBINATE M	2.70	1.23	31.2	135	190	
Product	Poly G76-635	Voranol 360	Jeffol R315x			
OH number	635	360	315			
Equivalent weight (g/mol OH)	88.3	155.8	178			
Product	MW	Physical state	Boiling point (°C)	Flash point (°C)		
Methyl formate	60	Liquid	31.5	-19		

relationships of internal temperature versus time. As the volume changes, polymer chains stretch and the elastic energy stored in the chains during this deformation will contribute to the total internal energy. However in this case, we neglect this contribution to internal energy and assume that the heat of reaction is a constant. The energy balance is given by

$$\frac{dT}{dt} = \frac{\sum_i \Delta H_{gel_i} \times r_{gel_i} + \Delta H_{blow} \times r_{blow} - \Delta H_{vap} \times \left(-\frac{dn_{MFL}}{dt}\right) + UA \Delta T}{\sum (n \times C_p)} \quad (11)$$

where U is the overall heat transfer coefficient from the surroundings. A is the surface area of the foam related to different foam height¹⁸ which is the summation of base area and lateral area. ΔH_{gel_i} is the heat of gel reaction respect to polyol i , ΔH_{blow} is the heat of blowing reaction, ΔH_{vap} (27,920 J/mol) is the enthalpy of vaporization of methyl formate,¹⁹ for sake of simplicity it was assumed as a constant under different temperature. $-\frac{dn_{MFL}}{dt}$ is the evaporation rate of methyl formate, and $\sum (n \times C_p)$ is the summation of heat capacities of all the chemicals used. Based on the heat capacity values under different temperatures,^{20,21} we assume that heat capacity is a linear function of temperature and it increases 0.1% as temperature rises 1 K in the study temperature range.

Equation (12), based on the ideal gas law, predicts foam height according to the volume of foam at different temperatures. Both carbon dioxide and methyl formate make a contribution to foam volume rise. The model allows for dynamic heat transfer primarily from the exposed top surface of the foam.

$$\frac{dh}{dt} = \frac{dV}{dt} \times \frac{1}{A} = \left(\frac{22.4 \times T}{273.15}\right) \times \left(\frac{dn_{CO_2}}{dt} + \frac{dn_{MFL}}{dt}\right) \times \frac{1}{A} \quad (12)$$

where the bases of boxes had an area, A , which is 1.02 dm². Equivalent volume of ideal gas at standard condition is 22.4 L/mol. Raoult's Law Equation was used in combination with heat and energy balances to solve the equilibrium between vapor and

liquid phases of methyl formate. Details about methyl formate, foam height modeling, and study on efficiencies of water and methyl formate will be discussed in future work.

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

MATERIALS AND METHODS

Materials

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

Experimental Design and Formulation

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

Table II lists the regular control recipe used in foam reaction and Table III lists the recipes used in gel reactions for gathering kinetic parameters.

Table II. Foaming Formulation of Rigid Polyurethane Foam

B-side materials	Weight/g	Moles of functional groups
Poly G76-635	13.84	0.1567
Voranol 360	15.68	0.1006
Jeffol R315x	4	0.0225
Dimethylcyclohexylamine (Cat8 gelling catalyst)	0.12	
Pentamethyldiethylenetriamine (Cat5 blowing catalyst)	0.32	
Momentive L6900	0.6	
TCP	2	
Distilled water (Blowing agent)	1.04	0.1156
Methyl formate	2.4	
<i>A-side material</i>		
RUBINATE M	61.548	0.4559
Isocyanate index	1.15	

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

Experimental Procedures and Data Collection

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

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

Table III. Gel reaction Recipes

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

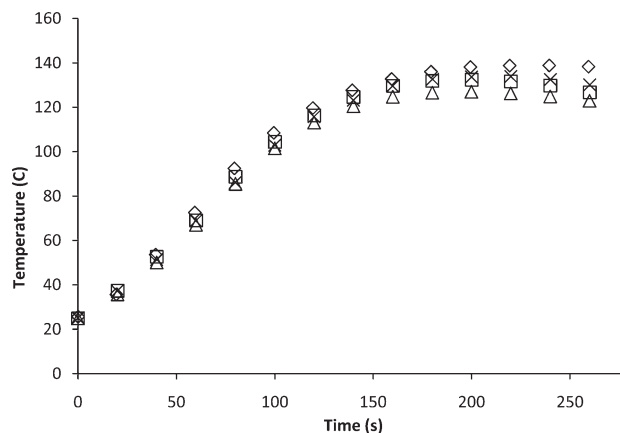


Figure 1. Internal temperature during the foaming process of four times repeated test. Four different symbols respectively represent four groups of data.

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

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

A high speed mixer blade (540 rpm) attached to a floor-model drill press was used to mix the chemicals. LabVIEW software was used to monitor the temperature of the gel or foam reactions for the first 15 min with a type-k thermocouple attached through a National Instruments SCB-68 box to a National Instruments PCI 6024E data acquisition card.

RESULTS AND DISCUSSION

Data on Repeatability

Figure 1 shows the experimental data of internal temperature in the foaming process and the experiment was repeated four times under the same condition.

Experimental deviation is attributed to a number of factors including minor variations in measuring/transfer of chemicals and the imperfect mixing. However, temperature profiles are substantially repeatable. The highest temperature and the corresponding time needed to reach the temperature were about 130–140°C and 200 s. The reduction in temperature toward the end is at least in part attributed to heat transfer from the sample to the surroundings.

Single-polyol Gel-reaction Modeling and Kinetic Parameter Estimations

The internal temperature was measured during the gel reactions for each of three polyols. Recipes listed in Table III were used to

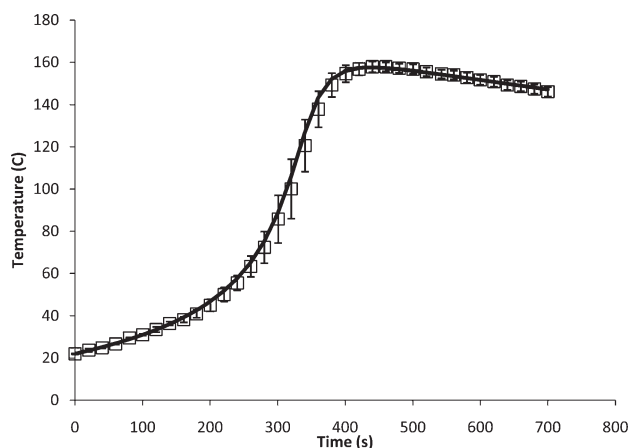


Figure 2. Internal temperature of gel reaction in Poly G76–635 case. Symbol “□” represents the experimental data and solid line represents the modeling result.

perform each test. There was a slight difference between isocyanate indices for each test. Kinetic parameters in the model were manually adjusted to provide good fits to experimental data. The comparison of experimental data and modeling results for Poly G76–635 is shown in Figure 2, and the results of Voranol 360 and Jeffol R315x are shown by Figures 3 and 4.

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

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

The highest temperature in the gel reaction of Poly Jeffol R315x case was about 130°C in about 350 s. The R315x polyol has a

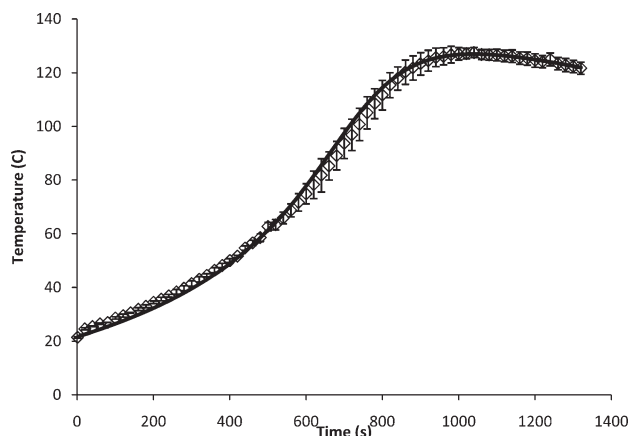


Figure 3. Internal temperature of gel reaction in Voranol 360 case. Symbol “□” represents the experimental data and solid line represents the modeling result.

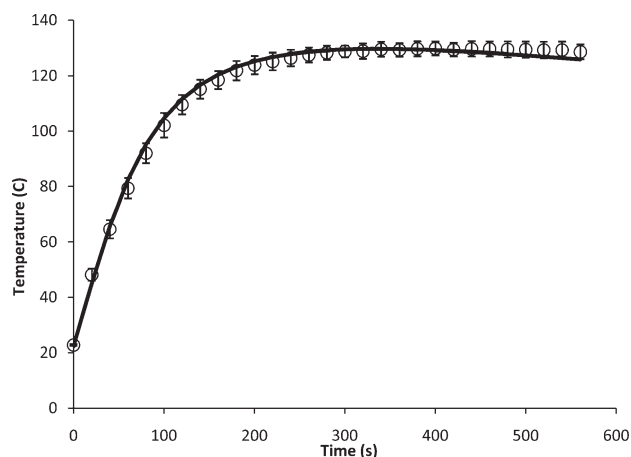


Figure 4. Internal temperature of gel reaction in Jeffol R315x case. Symbol “○” represents the experimental data and solid line represents the modeling result.

higher reactivity than V360 which can be attributed to a variety of factors including the nature of the hydroxyl groups and the presence of other functional groups or catalysts in the polyol. A hydroxyl number similar to that of V360 leads to a similar peak temperature.

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

Table IV summarizes the reaction parameters used to fit the model to the data. For comparison purposes, previously reported values for similar polyols are reported. The reaction conditions and chemicals used in this project were different from theirs in the references¹³ so that the values in the model were adjusted based on experimental data in this study. The kinetic parameters for these three polyols are comparable to what has been previously reported. When reported on an alcohol equivalent basis, the heats of reaction are similar, which reflects that heat release is directly related to the amount of alcohol groups reacting with isocyanate groups.

The activation energy and the pre-exponential factor for the R315x polyol were different than that of the others. This difference is reflected by the fundamentally different behavior summarized by Figure 4 where the temperature profile does not have an inflection point. One explanation is the possible presence of a built-in catalytic capacity of R315x which has a much higher reactivity at lower temperatures and the decrease in reagent concentration counters any increased reactivity with increasing temperatures.

Based on a comparison to previously reported values (see Table IV), previously reported kinetic parameters are within the range of the values reported for the three polyols of this study. The heats of reaction observed in these studies are similar to values previously reported. A greater variation was observed with the blow reaction parameters. This may be due to the fact that the

Table IV. Kinetic Parameters

		Current work results	Reference values
Pre-exponential factor K_{10} (25°C)	Poly 76-635	59 ml/(mol s g catalyst)	1734.8 ml/(equiv s) ¹³
	Poly V360	65 ml/(mol s g catalyst)	
	Poly R315x	1900 ml/(mol s g catalyst)	
Activation energy E_1	Poly 76-635	50,000 J/mol	40,400 J/mol ¹³
	Poly V360	40,000 J/mol	
	Poly R315x	10,000 J/mol	
Heat of reaction ΔH_1	Poly 76-635	71,000 J/mol	70,750 J/mol ¹³
	Poly V360	62,000 J/mol	
	Poly R315x	59,000 J/mol	
Pre-exponential factor k_{20} (25°C)		800 ml/(mol s g catalyst)	1385/s ¹³
Activation energy E_2		40,000 J/mol	32,660 J/mol ¹³
Heat of reaction ΔH_2		65,000 J/mol	86,000 J/mol ¹³

program does not account for the impact from side reactions, especially the reaction between isocyanate and amine.

By plotting $\ln(T - T_0)$ as a function of time, a straight line is obtained from which the slope of heat transfer coefficient can be evaluated. For all the runs, average values of $U = 3$ (W/m²-K) for gel reactions in plastic cups and $U_f = 1$ (W/m²-K) for foam reactions in wood box were used in the modeling.

Model Prediction of Mixture Performance

The MATLAB model implicitly accounts for chemical mixtures by including the appropriate rate equation for each polyol that is present. The primary modes of interaction between the different polyols are their cumulative releases of heat of reactions and cumulative consumption of isocyanate—both of these are implicitly accounted for in the model.

Figure 5 shows a good agreement between experimental data and the predicted performance based only on pure component properties. The data are well within the standard deviations.

These data validate the accuracy of this modeling approach as well as the utility of the modeling method. Here, as is the

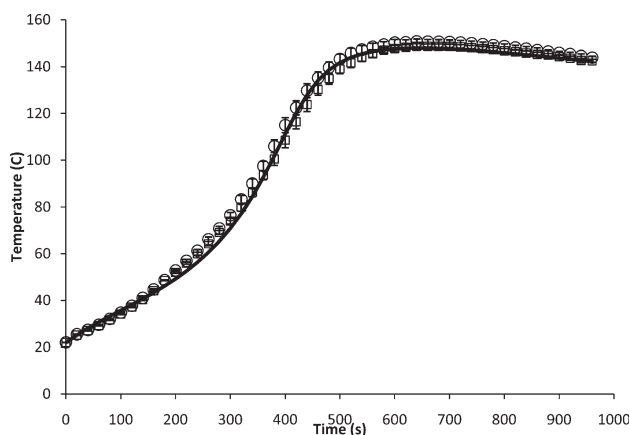


Figure 5. Internal temperature of gel reaction in three polyols mixture case. Symbol “□” and symbol “○” represent two different groups of experimental data and solid line represents the modeling result.

general case, the value of fundamentally based models is that they allow a limited amount of pure component data to be used to predict the performance of an infinite number of possible mixtures of the pure reagents.

Blowing catalyst and blowing agent (water and methyl formate) were added to the gel formation to create rigid foams and monitor the foaming processing. The isocyanate reacts with water to generate carbon dioxide which is a blowing agent.²² In addition, methyl formate is a blowing agent due to its high volatility (32°C). Internal temperature and foam height were measured during the experimental process and compared with the modeling results to correct the kinetic parameters of blow reaction. Figure 6 shows the component concentrations estimated by the model during the foaming reaction.

Excess isocyanate was used in the experiment to ensure that polyols and water react completely. Water was consumed in about 80 s and polyols were consumed at about 150 s. Fourier

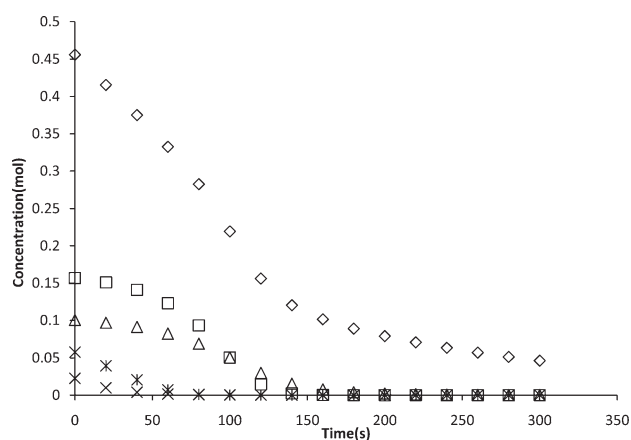


Figure 6. Component concentrations of foam reaction in three polyols mixture case. Symbol “♦” represents the concentration of Isocyanate Rubinate M, symbol “□” represents Poly G76-635, symbol “△” represents Poly V360, symbol “×” represents Poly Jeffol R315x, and symbol “*” represents water.

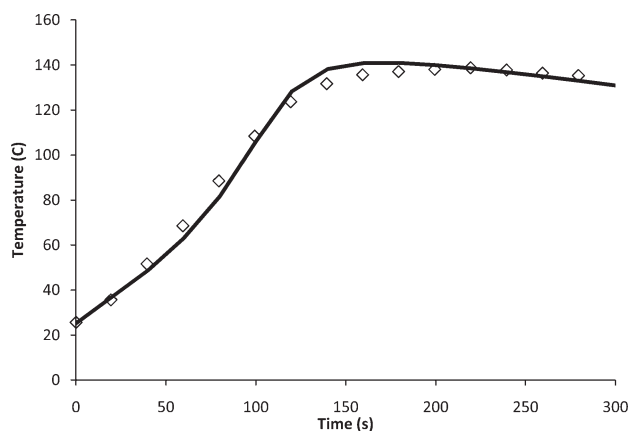


Figure 7. Internal temperature of foam reaction in three polyols mixture case. Symbol “ \blacklozenge ” represents the experimental data and solid line represents the modeling result.

transform infrared spectroscopy (FTIR) analyses of foams reveal that they contain no free isocyanate even when excess isocyanate is used in the formulation. However, the analyses were performed several days after the synthesis process, the excess isocyanate could react with moisture in air and, therefore, the isocyanate band will not appear in FTIR. The concentration profiles of Figure 6 show unreacted isocyanate present after reaction—this is a discrepancy between the model and observed phenomena.

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

Figures 7 and 8 summarize the internal temperature and foam height profiles. As summarized by Figure 7, the peak foam temperature of 140°C was attained at about 200 s. After this, convective cooling of the foam led to reductions in temperature. The rates of temperature rise were greater for the foaming reactions both because of the highly exothermic nature and would be accounted for in the model.

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

CONCLUSIONS

This work represents a modeling effort for the thermoset polyurethane reaction that goes beyond what have previously been achieved, including: effective modeling of single-polyol gel-reaction temperature profiles including estimation of pre-exponential factors, Arrhenius activation energy, and heat of reaction

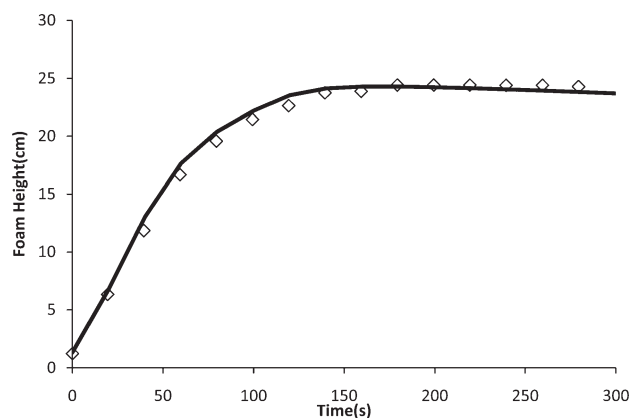


Figure 8. Foam height of foam reaction in three polyols mixture case. Symbol “ \blacklozenge ” represents the experimental data and solid line represents the modeling result.

with confirmation of accepted convective heat transfer coefficients for cooling. Based on pure component kinetic parameters, the modeling can be used to predict the performance of mixtures of polyols and to estimate component concentration profiles. Furthermore, it can be used to estimate the foam density as a function of time with blowing agent efficiency less than 100% effective.

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

ACKNOWLEDGMENTS

The authors thank the United Soybean Board for financial support of the experimental studies used to validate the modeling work. The authors thank the students Siyuan Yang and Joongsub Lee from the University of Missouri Columbia for their help in performing experiments and collecting data. They also thank FSI Company for providing foam formulas and technology support. None of the authors has conflicts of interest with companies producing RUBINATE M isocyanate, Poly G76–635, Voranol 360, Jef-fol R315x, and Momentive L6900.

REFERENCES

- Huo, S. P.; Nie, M. C.; Kong, Z. W.; Wu, G. M.; Chen, J. J. *Appl. Polym. Sci.* **2012**, *125*, 152.
- Ni, H.; Nash, H. A.; Worden, J. G.; Soucek, M. D. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 1677.
- Modesti, M.; Adriani, V.; Simioni, F. *Polym. Eng. Sci.* **2000**, *40*, 2046.

4. Paciorek-Sadowska, J.; Czuprynski, B.; Liszkowska, J.; Piszczek, K. *J. Polym. Eng.* **2012**, *32*, 71.
5. Hongyu Fan, A. T.; Suppes, G. J.; Hsieh, F.-H. *Int. J. Polym. Sci.* **2012**, 2012, doi: 10.1155/2012/474803.
6. Yang, L. T.; Zhao, C. S.; Dai, C. L.; Fu, L. Y.; Lin, S. Q. *J. Polym. Environ.* **2012**, *20*, 230.
7. Tay, G.S.; Ong, L. N.; Rozman, H. D. *J. Appl. Polym. Sci.* **2012**, *125*, 158.
8. Thirumal, M.; Khastgir, D.; Singha, N. K.; Manjunath, B. S.; Naik, Y. P. *Cell. Polym.* **2009**, *28*, 145.
9. Draye, A.C.; Tondeur, J. *J. React. Kinet. Catal. Lett.* **1999**, *66*, 319.
10. Briody, C.; Duignan, B.; Jerrams, S.; Tiernan, J. *Comput. Mater. Sci.* **2012**, doi: 10.1016/j.commatsci.2012.04.012.
11. Jmal, H.; Dupuis, R.; Aubry, E. *J. Cell. Plast.* **2011**, *47*, 447.
12. Baser, S. A.; Khakhar, D. V. *Polym. Eng. Sci.* **1994**, *34*, 632.
13. Baser, S. A.; Khakhar, D. V. *Polym. Eng. Sci.* **1994**, *34*, 642.
14. Tesser, R.; Di Serio, M.; Sclafani, A.; Santacesaria, E. *J. Appl. Polym. Sci.* **2004**, *92*, 1875.
15. Albu, P.; Bolcu, C.; Vlase, G.; Doca, N.; Vlase, T. *J. Therm. Anal. Calorimetry* **2011**, *105*, 685.
16. Semsarzadeh, M. A.; Navarchian, A. H.; Morshedian, J. *Adv. Polym. Technol.* **2004**, *23*, 239.
17. Harikrishnan, G.; Khakhar, D. V. *AIChE J.* **2010**, *56*, 522.
18. Gong, Q.; Zhai, T.; Xia, H. Conductive rigid polyurethane foams with negative temperature coefficient. *Polym. Mater. Sci. Eng.* **2012**, *28*, 53.
19. Majer, V. S.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation*; Blackwell Scientific Publications: Oxford, **1985**.
20. Weast, R. C. *CRC Handbook of Chemistry and Physics*; CRC Press: Florida, **1990**.
21. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 71st ed.; CRC Press: Florida, 1990–1991.
22. Mu, Y.; Wan, X.; Han, Z.; Peng, Y.; Zhong, S. *J. Appl. Polym. Sci.* **2012**, *124*, 4331.