Reaction Modeling of Urethane Polyols Using Fraction Primary Secondary and Hindered-Secondary Hydroxyl Content

Rima Ghoreishi, Yusheng Zhao, Galen J. Suppes

Department of Chemical Engineering, University of Missouri-Columbia, W2033 Lafferre Hall, Columbia, Missouri 65211
Correspondence to: R. Ghoreishi (E-mail: rgwc7@mail.missouri.edu).

ABSTRACT: The effect of primary, secondary, and hindered-secondary hydroxyl groups on reactions and temperature profiles of polyurethane gels was investigated and modeled using a computer simulation that simultaneously solves over a dozen differential equations. Using urethane gel reaction temperature profiles of the reference compounds 1-pentanol, 2-pentanol, and Voranol 360 reactivity parameters were determined for reference primary, secondary, and hindered-secondary hydroxyl moieties. The reaction parameters, including Arrhenius constants and heats of reaction, were consistent with previous values reported in literature. The approach of using fractions primary, secondary, and hindered-secondary hydroxyl content to characterize reactivity sets the basis for a powerful approach to simulating/predicting urethane reaction performance with limited data on new polyols and catalysts. This code can be used for all polyols, as the kinetic parameters are based on the fraction primary, secondary, and hindered-secondary alcohol moieties, not the type of the polyol. Kinetic parameters are also specific to catalysts where at least one parameter specific to each catalyst is necessary to simulate the impact of that catalyst. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40388.

INTRODUCTION

Many researchers have noted that the performance of polyols is dominated by the fraction of primary, secondary, and hindered-secondary hydroxyl groups. Therefore, defining a polyol characterization and modeling/simulation method based on characterizing a polyol's fraction of primary, secondary, and hindered-secondary hydroxyl moieties is of high importance. Alternative to the simulation of performance and recognizing that primary, secondary, and hindered-secondary hydroxyl groups contribute differently to the gel's temperature profiles and polyol reaction rate; a robust model could be used to define the primary, secondary, and hindered-secondary content of an unknown polyol to characterize and understand that polyol.

Some researchers have used mathematical or computer models to determine polyurethane foam properties. Ni et al. have performed kinetic study with a titration method to determine the concentration of the isocyanate group as a function of time and has estimated the rate constants of the reaction of isocyanate with water by linear regression.[1] Conor Briody et al. have developed a visco-hyperelastic numerical material model for simulating the uniaxial and shear behavior of polymer foams.[2] Jmal et al. 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.[3]

Baser et al. developed theoretical models for physical blowing agent blown rigid polyurethane foam formation[4] and water-blown polyurethane foams.[5] While the modeling of some specified properties of polyurethane foam has been widely studied, the modeling studies on the reaction process have been scarce. In a review on the versatility of urethane/urea bonds, Delebecq et al. reported generally accepted relative reaction rates for reversible reactions.[6] Table I represents relative reactivity of active hydrogen compounds. The data in Table I are normalized according to water-isocyanate reaction.[7]

Kinetics of polyurethane reactions have been studied using experimental procedures as well. Parnell et al. studied polyurethane polymerization kinetics using Raman spectroscopy and reported factor and activation energy for a thermoset polyurethane.[8] Fernandez d'Arlas et al. applied DSC and Fourier transform spectroscopy for determining reaction rate of polycarbonate-*co*-esterdiol and diisocyanate.[9] Papadopoulos et al. reported reaction rates as well as factors for a diisocyanate polyurethane by calorimetric and rheological methods.[10]

No previous work has been located, which directly relates reaction behavior to reference primary, secondary, and hindered-

Table I. Relative Reactivity of Active Hydrogen Compounds Against Isocyanate

| Hydrogen active compound	Formula	Relative reaction rate (noncatalyzed, 25°C)
Primary aliphatic amine	$R-NH_2$	1000
Secondary aliphatic amine	R_2NH	200–500
Primary aromatic amine	$Ar-NH_2$	2–3
Primary hydroxyl	RCH_2-OH	1
Water	HOH	1
Secondary hydroxyl	R_2CH-OH	0.3
Urea	$R-NH-CO-NH-R$	0.15
Hindered-secondary hydroxyl	R_3C-OH	0.005
Phenolic hydroxyl	$Ar-OH$	0.001–0.005
Urethane	$R-NH-COOR$	0.001

secondary hydroxyl moieties for the purpose of characterizing reactivity and using that characterization to simulate the urethane reaction dynamics.

For a simulation package used to simulate foaming, it is possible to characterize a polyol by three parameters (of average): hydroxyl number, fraction primary, secondary, and hindered-secondary hydroxyl content, and functionality. This approach will reduce the number of parameters needed for simulation and fully characterize a polyol.

On the topic of the impact of catalysts, the impact is expected to be less dependent on the actual polyol and more dependent on the impact of primary, secondary, and hindered-secondary alcohols. Hence, this approach to urethane reaction simulation has possible utility for usefully extrapolating the performance of a catalyst from one polyol to another.

MODEL DESCRIPTION

Equation (1) is the main reaction occurring in a polyurethane gel formation process. The alcohol may contain primary, secondary, and hindered-secondary hydroxyl groups. For the approach in this article, the reactions of primary, secondary, and hindered-secondary hydroxyl moieties are considered separately with separate Arrhenius reaction parameters.

$$RNCO + R'CH_2OH \rightarrow RNHCOOCH_2R'$$

$$\text{Isocyanate} + \text{Alcohol} \rightarrow \text{Urethane} \qquad (1)$$
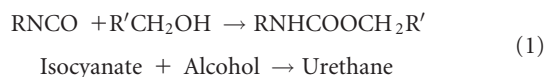
Several other reactions such as alcohol-polymer and isocyanate-urethane reactions take place in both gel and foam processes. Other than that, polyurethane foam is produced in the presence of water (blowing agent), which adds more reactions such as water-isocyanate and amine-isocyanate. Although only polyurethane gel process was investigated in this research, all possible reactions have been included in the code to make it multipurpose and ready to use for a foam process modeling. Table II presents the chemical reactions occurring in a polyurethane production process (gel or foam).

The initial gel reaction rate expression used in Zhao et al.'s model[11] is shown in eq. (2) in which k represents homogeneous gel reaction rate, k_{cat8} is the gel reaction rate in the presence of

catalyst8 (DMCHA), and c_{cat8}, c_{iso}, and c_{OH} are concentrations of catalyst 8, isocyanate and alcohol, respectively.

$$r_{gel} = (k + k_{cat8} * c_{cat8}) * c_{iso} * c_{OH} \qquad (2)$$

Reaction rate expressions for the pertinent reactions are presented in Table III. The code is written for three different polyols therefore numbers for k0, E, h, and r may not correlate to the numbers the reactions are presented with. For each reaction, the factor and activation energy values for homogeneous and catalyzed reactions are embedded in k0 and E, according to the rate constants of eq. (2).

Table II. Summary of Reactions

No.	Reaction
1	$A + B_P \rightarrow P$
2	$A + B_S \rightarrow P$
3	$A + B_{HS} \rightarrow P$
4	$A + P_{BP} \rightarrow P$
5	$A + P_{BS} \rightarrow P$
6	$A + P_{BHS} \rightarrow P$
7	$B_P + P_A \rightarrow P$
8	$B_S + P_A \rightarrow P$
9	$B_{HS} + P_A \rightarrow P$
10	$P_A + P_{BP} \rightarrow P$
11	$P_A + P_{BS} \rightarrow P$
12	$P_A + P_{BHS} \rightarrow P$
13	$A + Ur \rightarrow P$
14	$P_A + Ur \rightarrow P$
15	$A + W \rightarrow N + CO_2$
16	$P_A + W \rightarrow P + CO_2$
17	$N + A \rightarrow P$
18	$N + P_A \rightarrow P$

A is isocyanate monomer, B is polyol monomer, P is polymer, B_P is primary alcohol group on monomer B, B_S is secondary alcohol group on monomer B, B_{HS} is hindered-secondary alcohol group on monomer B, P_A is isocyanate group on polymer, P_{BP} is primary alcohol group on polymer, P_{BS} is secondary alcohol group on polymer, P_{BHS} is hindered-secondary alcohol group on polymer, N is amine, W is water, and Ur is urethane moiety.

Table III. Reaction Rate Expressions for the Reactions Presented in Table II

Rxn. No.	k0	E	h	Reaction Rate Expression
1	$k0\,(1)$	$E\,(1)$	$h\,(1)$	$r\,(1) = k\,(1)\ f_A C_A\ X_P f_B C_B$
2	$k0\,(2)$	$E\,(2)$	$h\,(2)$	$r\,(2) = k\,(2)\ f_A C_A\ X_S f_B C_B$
3	$k0\,(3)$	$E\,(3)$	$h\,(3)$	$r\,(3) = k\,(3)\ f_A C_A\ X_{HS} f_B C_B$
4	$k\,(10) = c_1\,k\,(1)$		$h\,(1)$	$r\,(10) = k\,(10)\ f_A C_A\ (M_{BP} - X_P f_B C_B)$
5	$k\,(11) = c_1\,k\,(2)$		$h\,(2)$	$r\,(11) = k\,(11)\ f_A C_A\ (M_{BS} - X_S f_B C_B)$
6	$k\,(12) = c_1\,k\,(3)$		$h\,(3)$	$r\,(12) = k\,(12)\ f_A C_A\ (M_{BHS} - X_{HS} f_B C_B)$
7	$k\,(13) = c_1\,k\,(1)$		$h\,(1)$	$r\,(13) = k\,(13)\ X_P f_B C_B\ (M_A - f_A C_A)$
8	$k\,(14) = c_1\,k\,(2)$		$h\,(2)$	$r\,(14) = k\,(14)\ X_S f_B C_B\ (M_A - f_A C_A)$
9	$k\,(15) = c_1\,k\,(3)$		$h\,(3)$	$r\,(15) = k\,(15)\ X_{HS} f_B C_B\ (M_A - f_A C_A)$
10	$k\,(22) = c_2\,k\,(1)$		$h\,(1)$	$r\,(22) = k\,(22)\ (M_A - f_A C_A)\ (M_{BP} - X_P f_B C_B)$
11	$k\,(23) = c_2\,k\,(2)$		$h\,(2)$	$r\,(23) = k\,(23)\ (M_A - f_A C_A)\ (M_{BS} - X_S f_B C_B)$
12	$k\,(24) = c_2\,k\,(3)$		$h\,(3)$	$r\,(24) = k\,(24)\ (M_A - f_A C_A)\ (M_{BHS} - X_{HS} f_B C_B)$
13	$k0\,(25)$	$E\,(25)$	$h\,(25)$	$r\,(25) = k\,(25)\ f_A C_A C_{Ur}$
14	$k\,(26) = c_3\,k\,(25)$		$h\,(25)$	$r\,(26) = k\,(26)\ C_{Ur}(M_A - f_A C_A)$
15	$k0\,(27)$	$E\,(27)$	$h\,(27)$	$r\,(27) = k\,(27)\ f_A C_A C_W$
16	$k\,(28) = c_4\,k\,(27)$		$h\,(27)$	$r\,(28) = k\,(28)\ C_W(M_A - f_A C_A)$
17	$k0\,(29)$	$E\,(29)$	$h\,(29)$	$r\,(29) = k\,(29)\ f_A C_A C_U$
18	$k\,(29) = c_4\,k\,(29)$		$h\,(29)$	$r\,(30) = k\,(30)\ C_U\,(M_A - f_A C_A)$

k0 and E are Arrhenius equation constants and h is the enthalpy of reaction. Subscripts are P (primary), S (secondary), HS (hindered-secondary), B (alcohol moiety), and A (isocyanate moiety). The term c_i indicate constants.

A variable X is introduced to help split the primary, secondary, and hindered-secondary reaction rates. Equation (3) shows the expression used for primary alcohol content.

$$X_p = \frac{\mathrm{OH}_{\mathrm{primary}}}{\mathrm{OH}_{\mathrm{total}}} \qquad (3)$$

Equations (4–6) show how the reaction rates have been separated for primary, secondary, and hindered-secondary alcohols.

$$c_{OH_P} = X_p * c_{OH} \qquad (4)$$
$$c_{OH_S} = X_s * c_{OH} \qquad (5)$$
$$c_{OH_t} = X_t * c_{OH} \qquad (6)$$

Temperature profiles were generated using eq. (7) in which U is the overall heat transfer coefficient from the surroundings. A is the surface area of the foam related to different foam height,[12] which is the summation of base area and lateral area. $\Delta H_{\mathrm{gel}\ i}$ is the heat of gel reaction with respect to polyol i, ΔH_{blow} is the heat of blowing reaction, and $\sum (n*C_P)$ is the summation of heat capacities of all the chemicals used. Based on the heat capacity values under different temperatures,[13,14] heat capacity is modeled as a linear function of temperature increasing 0.1% for a temperature rise of 1 Kelvin degree.

$$\frac{dT}{dt} = \frac{\sum_i \Delta H_{\mathrm{gel}\ i} * r_{gel\,i} + \Delta H_{\mathrm{blow}} * r_{blow} + UA\,\Delta T}{\sum (n*C_P)} \qquad (7)$$

Reaction rate constant at 25°C, activation energy and enthalpy of reaction for primary, secondary, and hindered-secondary alcohols were obtained using the temperature profiles of 1-pentanol, 2-pentanol, and Voranol 360. It is recognized that the selection of these compounds to determine reference perform-

ances is not absolute; however, it provides a starting point for evaluating the modeling process and possible optimal selection of reference compounds.

EXPERIMENTAL

Polyurethane gels were produced using RUBINATE M (Standard Polymeric MDI, PMDI) as isocyanate, 1-pentanol, 2-pentanol, Poly G76–635, Voranol 360, Voranol 490, and Jeffol R-315x (Huntsman Company and Dow Chemical) as alcohols/polyols, N,N-dimethylcyclohexylamine (DMCHA) as catalyst 8, Momentive L6900 (silicone-based) as surfactant, tris (1-chloro-2-propyl) phosphate as fire retardant and toluene as solvent.

Each gel was prepared using one polyol, PMDI, 0.16%(mass) catalyst, toluene, surfactant, and fire retardant. The isocyanate index was kept at 1.1–1.2 for all gels. Chemicals were mixed in a plastic cup with a drill press. Then the cup was put into a polyurethane foam box to insulate the gel system and reduce the heat loss. Temperature profiles were obtained by a type-k thermocouple attached through a National Instruments SCB-68 box to a National Instruments PCI 6024E data acquisition card (shown in Figure 1) synchronized with LabVIEW software.

RESULTS AND DISCUSSION

Results

Kinetic parameters as well as primary, secondary, and hindered-secondary content of polyols are obtained using temperature profiles of polyurethane gel reactions. Figure 2 summarizes the systems and temperature profiles used to obtain the kinetic parameters (Arrhenius constants and heat of reaction) for the

Figure 1. Experimental system used to obtain temperature profiles.
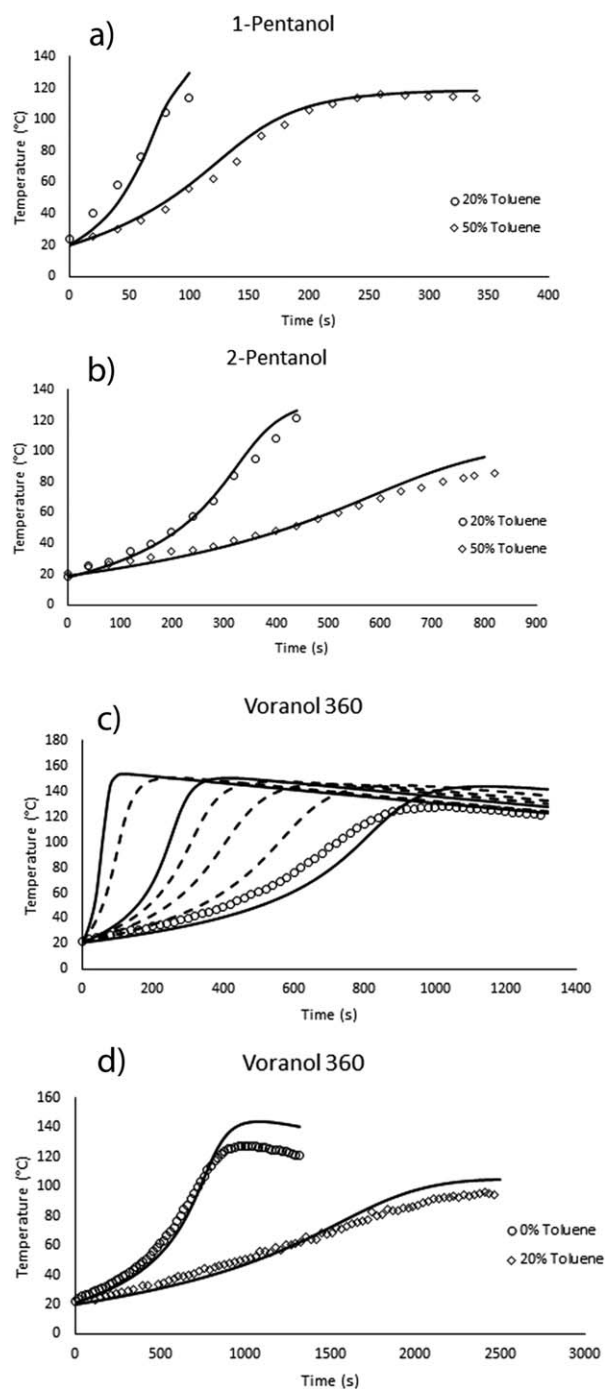
reference primary, secondary, and hindered-secondary hydroxyl moieties. 1-Pentanol is a 100% primary alcohol and was used to obtain parameters for primary moieties. A toluene solvent was used because this system is particularly hot without solvent. The model is able to take into account the amount of solvent as illustrated by the fits to both 20 and 50% solvent using the same kinetic parameters. When toluene was present in the system, data after reaching 110°C was discarded due to evaporative cooling created by toluene.

2-Pentanol was used to determine the secondary hydroxyl moiety reactivity. The model fits well for the majority of the temperature rise with a greater error at later times attributed to experimental measurement error. Using the computer simulation, a contour plot was made for Voranol 360 temperature profile to obtain hindered-secondary kinetic parameters where Voranol 360 was assumed to be 5% secondary and 95% hindered-secondary. Figure 2(c) shows the contour plots (unique to the isocyanate index, hydroxyl number, and catalyst content for this Voranol 360 formulation) for systematic variation of the hydroxyl moieties. The contour plot is a useful approach to observe how the performance of a polyol deviates from expected trends based on the simplifying assumptions used in the simulation.

k0 (reaction rate constant at 25°C), E (activation energy), h (heat of reaction), and U (heat transfer coefficient) for primary, secondary, and hindered-secondary hydroxyl groups were obtained based on visual fits of model parameters to the data and are presented in Table IV. A good fit was obtained with the same heat of reaction for each type of hydroxyl group. The heat transfer coefficient is characteristic of the experimental system with those characteristics kept relatively constant for all experiments. Similar activation energies were used for primary and secondary system. Higher activation energy was found to be appropriate for the hindered-secondary system.

Based on these performances of primary, secondary, and hindered-secondary functional groups as summarized by Table

II, other polyols can have reactivities characterized as fractions of primary, secondary, and hindered-secondary. Table V summarizes the fit of Voranol 360, Voranol 490, Poly G76–635, and Jeffol R315x based on this method. The fit of the model and parameters are summarized by Figures 3 through 5.

Figure 2. Gel temperature profiles used to obtain reaction rates for reference systems. The reference systems are (a) 1-pentanol for primary hydroxyl moieties, (b) 2-pentaol for secondary, and (c) Voranol 360 as 5% secondary and 95% hindered-secondary superimposed over contour plot of where from left to right are XP = 1.0, XP = 0.5, and XS = 0.5, XS = 1.0, XS = 0.75, and XHS = 0.25, XS = 0.5, and XHS = 0.5, XS = 0.25 and XHS = 0.75, XHS = 1.0, and (d) comparison of Voranol 360 data and simulations with 0 and 20% toluene.

Table IV. Primary, Secondary, and Hindered-Secondary Fitted Kinetic Parameters

	k0		E			
Parameter	No Cat	Cat8	No Cat	Cat8	h	U
Primary	28	500	39,000	37,000	68,000	2
Secondary	12	55	42,000	40,000	68,000	2
Hindered-secondary	0.85	42	54,000	40,000	68,000	2

Poly G76–635 fits well based on the contour plot superimposition. The system is a bit hotter than the model projects. This variation could come from a number of sources, including: (a) unique heat capacity, (b) experimental error, or (c) slight error in hydroxyl number. As with the systems presented by Figure 2, the model accurately models the dilution effect of toluene.

For Voranol 490, with and without toluene, the initial reaction rate follows the code output well, and the total heat is within 10% of an adjacent line. The problem appears to be with reactivity at higher temperatures, which could originate from a couple of sources: (a) this could be due to a lower activation energy possibly due to unique structures locations of the hydroxyl group or (b) it could be due to the prospect that polymer functional groups are more reactive than monomer functional groups for this polyol. For this second case, the polymer may lock in hydroxyl and isocyanate functional groups in proximity such that intrapolymer reaction is highly favored. Within the certainty of hydroxyl number, heat capacity, and experimental data, the model accurately represents Voranol 490.

The temperature profile for Jeffol R315x is faster than 1-pentanol, which was specified as 100% primary alcohol. This variation in performance is most likely due to either (a) the presence of a more-reactive group such as amine functionality rather than hydroxyl and/or (b) catalyst included with the R315x mix.

As summarized by Table II, the reactivities of the alcohol moieties are characterized for both the case of the homogeneous reaction and for the reaction in the presence of catalyst. For systems such as Jeffol R-315, a modeling option would include treating it as both a catalyst and as a polyol. The catalyst aspect of the polyol would have its own Arrhenius constants and would impact the reactivity of both Jeffol R-315 and other polyols present in the system. This extension of the modeling is beyond the present scope of work.

Table V. Summary of Fitted Parameters for Several Polyols

|	Voranol 360	Voranol 490	Poly G76–635	Jeffol R315x
Primary (X_P)	0	0	0	0.65
Secondary (X_S)	0.05	0.25	0.3	0
Hindered-secondary (X_T)	0.95	0.75	0.7	0.35
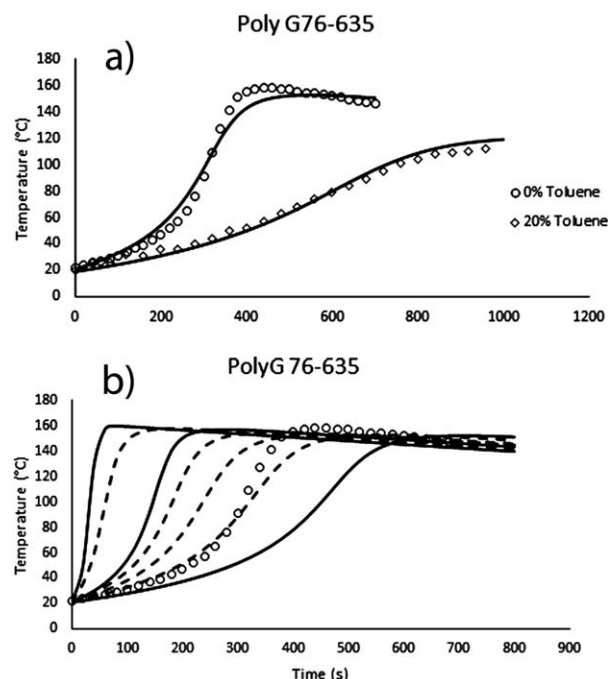
Figure 3. Modeling of Poly G76–635 gel for (a) 0 and 20% toluene systems and (b) as superimposed over the contour plots.

It is evident based on the contour plots that the characterization of a polyol by its gel temperature profile could be used to characterize both its hydroxyl number and reactivity. There are advantages of characterizing hydroxyl number in addition to fraction of primary, secondary, and hindered-secondary hydroxyl moieties in that the simultaneous characterization improves efficiency of characterizing a polyol and, possibly, would improve accuracy of performance extrapolation.

Coefficient of determination (R^2) has been calculated to evaluate the accuracy of the simulation. These values are presented in Table VI. It should be noted that the R^2 values represent the accumulation of all deviations (e.g., errors in hydroxyl number, errors in masses of each material put in the formulation), not just the accuracy of the model.

Discussion

The model presented here is a more rigorous hurdle than what would be applied in practice for most systems since actual foaming systems are formulated to substantially react in the first five, if not two, minutes. In principle, a model that is relatively
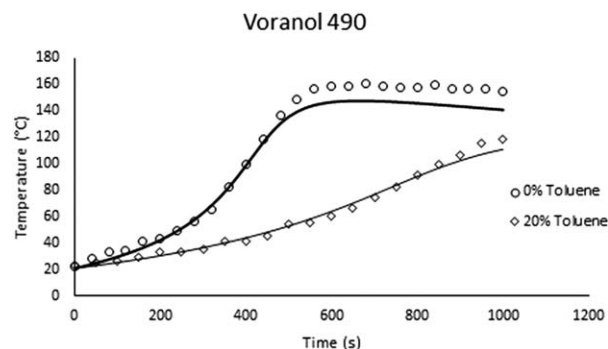
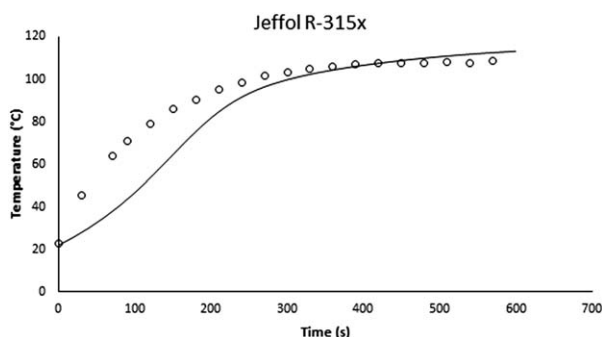**Figure 4.** Temperature profile for Voranol 490 gel.

Figure 5. Temperature profile for Jeffol R315× gel.

Table VI. Values of Objective Function for Gel Systems

	R^2 (%)		
Gel System	0% Toluene	20% Toluene	50% Toluene
1-Pentanol	NA	91.8	98.1
2-Pentanol	NA	97.5	93.9
Voranol 360	93.1	94.2	NA
Voranol 490	97.1	98.9	NA
PolyG 76–635	98.6	98.4	NA
Jeffol R315x	NA	61.5	NA

accurate for gels with peak temperatures occurring from 20 to 2000 s will tend to be able to be fine-tuned for even better performance for peak temperatures occurring (for real systems) between 20 and 600 s.

This simulation approach provides useful insight into the polyol properties—this insight can be used to better use existing polyols and to molecular engineer new and improved polyols. Based on the model, if both temperature and viscosity profiles are obtained, it should be possible to estimate polyol functionality in addition to hydroxyl number and reactivity (e.g., XS). This information could then be used to estimate both molecular weight and equivalent molecular weight. Due to uncertainties in estimating functionalities of current methods, this approach could be both efficient and more accurate than current methods.

A key next step in modeling is to evaluate the ability of modeling and simulation to predict the performance of a catalyst based on limited data such as the performance of a catalyst on a single polyol in a single formulation. In regards to characterization of polyols, expanding the approach to characterizing of functionality would be the next step—charactering total average molecular weight, and respective functionality, is currently prone with uncertainty when using methods like gel permeation chromatography.

Improving the accuracy of the kinetic parameters for the alcohol moieties, determining the best choice of reference kinetics, and better understanding of how to characterize deviations from standard performance is an ongoing effort. The primary factors needed to advance these important topics are time and experience from studies over a range of polyols.

CONCLUSION

A computer simulation has been developed that allows the operator to characterize a polyol's primary, secondary and hindered-secondary content based on the gel reaction temperature profile. The approach allows a polyol reactivity to be characterized by a single parameter (e.g., percent secondary versus hindered-secondary) and provides a starting point for projecting performance based on known performance patterns. Through the model, quantitative predictions are possible that can expedite the effective incorporation of polyols into formulations.

This approach is the starting point for a simulation methodology having a great potential. If the fraction of primary, secondary, and hindered-secondary alcohols were independently measured (e.g., HNMR) in the polyols, this information could improve the model and provide a prediction of performance based on these independent measurements. While the studies reported here are only for gel reactions, the extension of the results to foam systems is relatively straight forward.

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