

Modeling impact of catalyst loading on polyurethane foam polymerization



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ABSTRACT

A MATLAB model based on the simultaneous solution of several differential equations was developed to include the impact of catalyst loading for the reactions and physical processes of a urethane box foaming process. Experiments with different amounts of catalyst loading were conducted to fit the model parameters for this thermoset polymerization. Rate constants for the polyurethane foaming reaction were determined by polyol types, catalyst types and reaction temperatures. By combining these factors polyurethane reaction rates during whole foaming process can be calculated in this model and the model can be used to predict the performance of foams which have multiple combinations of isocyanate, polyols, catalysts, chemical blowing agents, and physical blowing agents in recipes when parameters on pure component (e.g. single polyol) performance are behavior.

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1. Introduction

Polyurethane (PU) is a polymer composed of a chain of organic units joined by carbamate (urethane) links. Polyurethane polymers are formed by reaction an isocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups per molecule. Polyurethanes are used in the manufacture of flexible, high-resilience foam seating; rigid foam insulation panels; durable elastomeric wheels and tires.

Sure enough, the chemistry of isocyanate is complex since it entails a variety of reactions with other simple functions, such as alcohol or amine, but also self-additions and trans-condensations. From the application point of view, the major parameter of the system is the temperature at which reactive functions are regenerated, in other words, the deblocking temperature of adduct. The rate and extent of regenerating isocyanate however depends on many factors: the chemical function containing the active hydrogen, the isocyanate and blocking molecule structures, the solvent properties, the presence of a catalyst, and the reaction temperature.

Catalysts have a most important role in making urethane foams. If the gas formation takes place too fast in comparison to the gelation reaction, it would result in the cells opening before there is sufficient viscosity build-up to provide the foam struts with enough strength to uphold the foam, leading to the collapse of the foam [1].

On the other hand, if the gelation reaction is faster than the gas formation, it may result in foam with closed cells [2] and hindered expansion, which is not desirable. Catalysts have the critical purpose of fine-tuning the kinetics so that gas formation and gelation are properly synchronized.

The impact of catalysts on polyurethane foaming reaction has been of great interest. Research results [3–5] show that the match between the gelatinizing rate and the foaming rate could be adjusted by specifying catalyst and changing catalyst amounts, thus the structure and properties of the polyurethane foam could be controlled. With a good selection of the catalyst, the desired profile in reaction, foaming, flow-ability, and foaming properties can be obtained [6]. Depending on concentration of catalysts in foaming recipe, the activity will be different [7,8]. This activity relates to the catalysis of the gel and blow reaction [9], which has a great impact on the properties and functions of the foam [10]. Chang [11] and Baker [12] measured rate constants for a model isocyanate-alcohol reaction catalyzed by tertiary amines and provided relative rate constants respect to different catalyzed conditions. Their relative reactivity data depending on catalyst concentration indicates that the reaction rate is in direct proportion to the amount of catalyst used.

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

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Table 1
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 ₂ NH	200–500
Primary aromatic amine	Ar-NH ₂	2–3
Primary hydroxyl	RCH ₂ -OH	1
Water	HOH	1
Secondary hydroxyl	R ₂ CH-OH	0.3
Urea	R-NH-CO-NH-R	0.15
Tertiary hydroxyl	R ₃ C-OH	0.005
Phenolic hydroxyl	Ar-OH	0.001–0.005
Urethane	R-NH-COOR	0.001

Basel developed theoretical models for physical blowing agent blown rigid polyurethane foam formation [13] and water-blown polyurethane foams [14]. They carried out detailed experimental study to measure both temperature and density change during foam formation. However, they did not consider heat transfer to surroundings and the impact of thermocouples on temperature profiles. Tesser [15] optimized a model to include heat transfer and modify the description of the vapor–liquid equilibrium of the blowing agent and the polymeric phase by means of an extended Flory–Huggins equation that well describes the nonideal behavior of these reacting mixtures. Tesser did not consider mixtures of polyols nor the prediction of mixtures based on single-polyol parameters. Also, the work did not consider water as a chemical blowing agent, and attributed basically all lack of inefficiency of foam height to Flory–Huggins non-idealities. Table 1 presents generally accepted relative reaction rate as a rule of thumb. All these reactions compete among each other and all are reversible. Data from Ref. [16] were normalized according to the rate of the water-isocyanate reaction. Combining reaction rates with respect to different pathways and the impact of catalysts can improve the simulation of reaction process.

Studying the system and above all kinetics from a fundamental prospect is significantly helpful to the isocyanate industry. The following advances are needed to make foam simulation more useful and are beyond what has previously been attained:

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

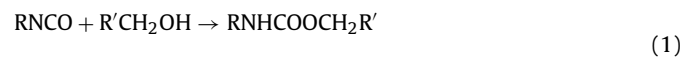
Zhao et al. [17] have initiated the first of several phases of modeling that will be necessary to attain these goals. Zhao et al.'s modeling work have included simulation of up to three polyols, a methyl formate physical blowing agent, and water reaction blowing agent. This work extends those initial studies to include modeling of homogeneous catalysts for these foam-forming reactions. In this modeling work the impact of temperature on process is important since temperatures will typically increase from 25 to in excess of 110 °C during foaming.

For urethane foams both physical blowing agents and gas-forming reactions are used for in situ formation of gases that lead to foam cells. In water-blown foams, gel reaction and blow reaction occur simultaneously [18], and so, catalysts have the added role of controlling the gas formation in addition to controlling

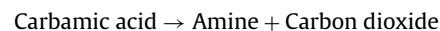
gelation rates. The goal of this work is to improve the versatility of simulation for predicting temperature profiles, viscosity profiles, and densities during urethane foam-forming processes and extend a newly developed thermoset polymerization model to include impact of catalyst concentration and combinations of catalysts.

2. Description of the model

This paper investigates a urethane rigid foam process that uses both physical (methyl formate) and blowing-reaction blowing agents. The initial model [17] was developed further to include the impact of catalyst on polyurethane foaming reaction. The blowing reaction competing with gel reaction was summarized by the following schemes. The gel reaction creates urethane as described in Eq. (1)



The blow reaction is a two-step reaction described by Eqs. (2) and (3)



The physical blowing process is based on the evaporation of a volatile compound that typically has a boiling point between 30 and 70 °C. The elementary rate expressions [17,19] for these reactions are summarized by Eqs. (4) and (5) along with the energy balance equation is expressed as Eq. (6). These rate expressions are based on functional group concentration rather than molecule concentration. Also, the model assumes that the reactivity of any functional group can be represented by a single rate constant—this is a simplifying assumption that can be improved-upon as the accuracy of the simulation is improved

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

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

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

$$\frac{dT}{dt} = \frac{\sum_i \Delta H_{gel\ i} * r_{gel\ i} + \Delta H_{blow} * r_{blow} - \Delta H_{vap} * \left(-\frac{dn_{MFL}}{dt}\right) + UA\Delta T}{\sum(n * c_p)} \quad (6)$$

where U is the overall heat transfer coefficient from the surroundings. A is the surface area of the foam related to different foam height [20] which is the summation of base area and lateral area. $\Delta H_{gel\ i}$ 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 [21], for sake of simplicity it was assumed as a constant under different temperature. $-\frac{dn_{MFL}}{dt}$ is the evaporation rate of methyl formate, and $\sum(n * c_p)$ is the summation of heat capacities of all the chemicals used. Based on the heat capacity values under different temperatures [22,23] we assume that

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