Simulation of liquid physical blowing agents for forming rigid urethane foams

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ABSTRACT: A computer-based simulation for rigid polyurethane foam-forming reactions was compared with experimental data for six blowing agents including methyl formate and C5-C6 hydrocarbons. Evaporation of blowing agent was modeled as an overall mass transfer coefficient times the difference in activity of the blowing agent in the gas foam cells versus the resin walls of the cells. Successful modeling hinged upon use of a mass transfer coefficient that decreased to near zero as the foam resin approached its gel point. Modeling on density agreed with experimental measurements. The fitted parameters allowed for interpretations of the final disposition of the blowing agent, especially, if the blowing agent successfully led to larger foam cells versus being entrapped in the resin. The only component-specific fitted parameters used in the modeling was the activity coefficient that was lower for methyl formate than the value used for hydrocarbons. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42454.

INTRODUCTION

The market demand of polyurethane (PU) is growing every year due to its versatile application. Average annual growth rates reach 5% with over 12 million metric tons of its raw material consumed globally.[1] The applications of polyurethane range from rigid insulation in buildings and refrigerators, cushions for furniture, and elastomeric wheels and tires.[2]
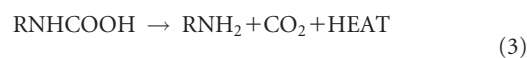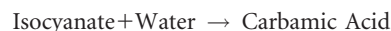
Polyurethane foams are produced from the reaction of polyol(s) and isocyanate (eq. 1) in the presence of, catalysts, surfactants, fire retardants, and physical and/or chemical blowing agent.[3]

$$RNCO + R'CH_2OH \rightarrow RNHCOOCH_2R'$$
$$\text{Isocyanate} + \text{Alcohol} \rightarrow \text{PU} \tag{1}$$
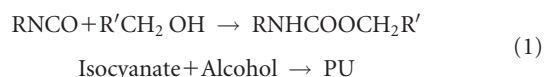
Foam is generated by using blowing agent that is able to yield a cellular gas-filled structure. Liquid blowing agents are typically mixed with the liquid polyol monomers prior to mixing with the isocyanate monomer. The blowing agent is what transforms a solid plastic or elastomer to a foam. For physical blowing agents the heat generated by exothermic reactions evaporates the blowing agent. Successful foam formation requires the successful synchronizing of temperature increase, which causes the blowing agent to evaporate, with the increase viscosity, which is

key to stabilizing the gas cells. The blowing agent controls the density, the cellular microstructure, and morphology of the foam which are critical to the end use and performance.[4,5]

Commonly, water is used as a chemical blowing agent since it reacts with isocyanate to form carbon dioxide (eqs. 2 and 3). The heat generated from this exothermic reaction and the exothermic polymerization reaction are used to evaporate another added physical blowing agent (PBA) to provide more gas for foaming and some desired properties to the foam.[6,7]

$$RNCO + H_2O \rightarrow RNHCOOH$$
$$\text{Isocyanate} + \text{Water} \rightarrow \text{Carbamic Acid} \tag{2}$$

$$RNHCOOH \rightarrow RNH_2 + CO_2 + HEAT$$
$$\text{Carbamic Acid} \rightarrow \text{Amine} + \text{Carbon Dioxide} \tag{3}$$

Physical blowing agents can be defined as low boiling point inert liquids.[8] Heat and temperature increases from exothermic reactions cause the physical blowing agents to evaporate *in-situ*.[9] Amount and type of the physical blowing agent impacts foam density by creating and expanding gas cells. More blowing agent tends to create a lower-density foam with impact on foam properties such as compressive strength and thermal conductivity.[10]

Modeling foam height and temperature profiles have attracted the attention of many research workers. Baser and Khakhar.[11,12]

Table I. Gel and Foaming Recipes of Rigid Polyurethane Gel and Foam

	Weight, g	
Ingredients	Gel Formulation	Foaming Formulation
B-side materials		
Voranol 360	43.5	43.5
Dimethylcyclohexylamine (Cat8)	0.44	0.44
Momentive L6900	0.6	0.6
TCPP	2	2
Physical blowing agent	0	see Table III
A-side material		
PMDI	41.7	41.7

predicted both temperature and density of polyurethane foams blown by chemical and physical blowing agents (water and R-11) based on mass and energy balance, rate of viscosity increase, kinetic parameters, and thermodynamic relations.

Cell size distributions in foams blown with either water or Freon were correlated with energy balance equations and the rate of evaporation of the blowing agent by Niyogi et al.[13] After that, Niyogi et al.[14] developed a model that combined equations of energy balance, kinetics of the reactions of isocyanate with water and polyol, and nucleation and growth of CO2 bubbles to predict bubble size and distribution of polyurethanes foams blown by water as a chemical blowing agent.

Later, Tesser et al.[15] developed the mathematical modeling of Rojas et al.[16] by improving the vapor-liquid phase equilibrium of the blowing agent and the polymer mixture and using the kinetic parameters of the polyol and isocyanate and different amounts of blowing agent. Modesti et al.[17] develop a theoretical model to predict temperature profile, foam density, and other physical–mechanical properties using oligomeric isocyanate and a mixture of polyether polyols blown by either water, methyl formate, or n-pentane.

This work differs from previous because the simulation is based, to a first approximation, only on pure component parameters and dozens of differential equations capable of simulating performances of mixtures and able to predict performance based on pure component parameters. Shen et al.[18] expanded the code of simulation code of Zhao et al.[19] to predict foam density

of polyurethane foams blown by different concentrations of water and methyl formate.

Shen's code was based on an assumption of equilibrium between blowing agent in the resin walls of the gas cells with the gas in the cells. Equation (4) summarizes the modified Raoult's law which is a practical estimate of the equilibrium condition that sets the activity of the blowing agent in the vapor phase equal to the activity in the liquid phase.

$$x_{Ri} \cdot \gamma \cdot P^{sat} = y_i \cdot P \tag{4}$$

where x_{Ri} and y_i are mole fractions of blowing agent in the liquid and gas phases respectively, P is the total pressure (assumed to be equals to 1 atm.), γ is the activity coefficient. The activity coefficient is set to the same value for the hydrocarbons; a lower value is used for methyl formate. The activity coefficient is a fitted parameter, but methods are available to predict the activity coefficient.

In the work presented by this paper, an approach using a mass transfer driving force is used which includes the rapid decrease in the mass transfer coefficient as the gel point is approached. The driving force of evaporation of the physical blowing agent is expressed as a differential equation that has been solved with other differential equations of polyol-isocyanate reactions in the computer code.

$$\frac{dC_{PBA}}{dt} = -K\, C_{PBA}(\gamma \cdot X_{liq} - X_{Ri}) \tag{5}$$

Where C_{PBA} is the concentration of the physical blowing agent, K is the overall mass transfer coefficient, X_{liq} is the molar concentration and the equilibrium molar concentration of the physical blowing agent in the liquid phase. The overall mass transfer coefficient includes the impact of surface area. At the onset of the reaction, the value of K increases both due to increasing surface area and increasing temperature. As polymerization proceeds, crosslinking has an increasing impact on viscosity leading to a decrease in polymer concentration and rapid increase in viscosity. Noting that the concentration of polymer in the system qualitatively followings these important trends, the mass transfer coefficient was estimated as being equal to a fitted constant, k_1, times the polymer concentration ($C_{Polymer}$).

$$K = k_1 C_{Polymer} \tag{6}$$

Also, the polymer concentration can be used to estimate the polymer degree of polymerization (PDP) according to the following equation:

$$PDP = \frac{\text{Moles of isocyanate and polyols initially present} - \text{moles of isocyanate and polyols at time (t)}}{\text{Moles of Polymer}} \tag{7}$$

The work presented here can be distinguished from previous work due to the ability to estimate the rapid decrease in the overall mass transfer coefficient as the concentration of polymer goes to zero. The models for both the activity coefficients and mass transfer coefficients would be characterized as semi-fundamental since the models follow known fundamental trends. Model performances versus

experimental data are compared for six different blowing agents.

METHODOLOGY

Materials and Recipes

Gel and Foaming Formulation. Table I summarizes gel and foaming formulations at an isocyanate index of 110. Amounts

Table II. Specifications of Voranol 360 and Isocyanate

Property	V360	PMDI
Density, g cm^{-3}	1.081	1.23
Average molecular weight	728	340
Functionality	4.5	2.7
Hydroxyl number, mg KOH g^{-1}	360	–
Equivalent weight	155.55	134
Viscosity, mPa s at 25°C	3500	150–220
NCO content by weight, %	–	31.4
Vapor pressure, mm Hg at 25°C	–	<10^{-5}
Specific heat, g.cal/g.at 25°C	–	0.43

Table III. Amount of Each Blowing Agents Used in the Foaming Formulation

Physical blowing agent	Weight, g
Methyl Formate	5.856
n-Pentane	7.042
iso-Pentane	7.042
cyclo-Pentane	6.842
n-Hexane	8.411
cyclo-Hexane	8.214

of polyol, catalyst, surfactant, fire retardant, and isocyanate were kept constant for all the rigid polyurethane foams. RUBINATE M isocyanate and Voranol 360 were manufactured by Huntsman Company and Dow Chemical, respectively. N, N-dimethylcyclohexylamine is a gelling catalyst, Momentive L6900 is the surfactant, and Tris (1-chloro-2-propyl) Phosphate (TCPP) was used as a fire retardant.

Experiments were performed to evaluate the performance of different blowing agents with the moles of each blowing agent kept constant. Table II shows the specifications of Voranol 360 and Rubinate M isocyanate (thereafter referred as PMDI) used in the gel and foaming formulation. Voranol 360 (V360) is identified as having 5% secondary and 95% hindered secondary moiety fraction according to the previous study.[19]

Physical Blowing Agents. Equal moles of six different physical blowing agents was tested with recording of height profiles. Experiments were performed with 0.0975 moles of blowing agent with Table III summarizing the respective mass loadings.

A modified Antoine equation was used to estimate vapor pressure of each blowing agent as a function of reaction temperature according to eq. 8.

$$\ln\left(\frac{P^{sat}}{P_c}\right) = (1-x)^{-1}\left[Ax + Bx^{1.5} + Cx^3 + Dx^6\right] \qquad (8)$$

where $x = (1 - T/T_c)$, T_c is the critical temperature in Kelvins, P^{sat} is the vapor pressure in bars, and P_c is the critical pressure in bars. This equation provides a wide temperature range of 220–487 K which covers the foaming reaction temperature change. Values of A, B, C, and D constants and critical temperature and pressure of the physical blowing agents are provided in Table IV. For simulation purposes, the latent heat of evaporation of the physical blowing agents is calculated using Giacalone equation.[20]

Table V summarizes the physical properties of the blowing agents along with their ozone depletion potential and global worming potential. Researchers are actively pursuing blends and new blowing agents[21–24] to both improve rigid polyurethane foam properties like thermal conductivity, compressive strength, and fire resistance and to decrease environmental impact. A key aspect of the present work is to establish the accuracy of simulation to predict the performance of blowing agents so that simulation can play a role in faster and better evolution of blowing agents in urethane foams.

EXPERIMENTAL

Gel and foaming experiments were performed using the recipes shown in Table I to prepare polyurethane gels and foams using different physical blowing agents. Experiments consisted of the following steps:

– The B-side components are weighted and added together as a B-side into a closed 150 ml glass beaker and mixed until the mixture mixed well.
– The beaker is left open for two minute for degasing and then weighted to measure the weight of physical blowing agent lost during mixing.
– The B-side mixture is poured into a plastic cap and the A-side component is added.
– The mixture mixed with a 2000 rpm mixer for 10 seconds.
– For gel, the mixture is left in the cup and reaction temperature is recorded.
– For rigid polyurethane foam, the mixture is quickly poured into a wooden box with aluminum foil lining to measure temperature and height profiles.

Table IV. Antoine Constants, Critical Pressure, and Critical Temperature for the Physical Blowing Agents[20]

Component	A	B	C	D	Tmin	Tmax	Pc	Tc
Methyl Formate	−6.99601	0.89328	−2.52294	−3.16636	220	487.2	60	487.2
n-Pentane	−7.28936	1.53679	−3.08367	−1.02456	195	469.7	33.7	469.7
iso-Pentane	−7.12727	1.38996	−2.54302	−2.45657	220	460.4	33.9	460.4
cyclo-Pentane	−6.51809	0.38442	−1.11706	−4.50275	289	511.7	45.1	511.7
n-Hexane	−7.46765	1.44211	−3.28222	−2.50941	220	507.5	30.1	507.5
cyclo-Hexane	−6.96009	1.31328	−2.75683	−2.45491	288	553.5	40.7	553.5

Table V. Physical Properties, Ozone Depletion Potential, and Global Worming Potential of the Blowing Agents

Physical blowing agent	Boiling Point, °C	Molecular weight	ΔH_{vap}, J mol-1	Vapor Pressure, Kpa, 20°C	Surface tension, 20°C (mN m^{-1})	ODP	GWP
Methyl Formate	31.8	60.05	27648.65	63.51	21.384	0	0
n-Pentane	36.1	72.15	26363.35	57.9	15.82	0	11
iso-Pentane	27.85	72.15	25372.42	76.99	16.05	0	11
cyclo-Pentane	49.26	70.15	26378.72	35.3	23	0	11
n-Hexane	68	86.18	29543.3	17.3	18.43	0	0
cyclo-Hexane	80.7	84.16	30108.86	12.9	24.95	0	0

– The foaming mixture is allowed to expand until foam temperature started to cool down.

LabView soft-ware was used to measure gel and foam reaction temperature and foam height using type-K thermocouple and ultrasound device attached through a national instruments SCB-68 box to a national PCI 6024E data acquisition card. The LabView soft-ware is recording the time-temperature and time-height data in the computer as x-y axis.

A high-speed mixer blade attached to a floor-model drill press was used to mix the chemicals.

The tack-free time is measured for the rigid polyurethane foams prepared using the different physical blowing agents. It can be defined as the span time between pouring the A- and B- side mixture in the foaming box and the time when the surface of the foam does not show stickiness when touched with a spatula.[8]

As a test to determine if blowing agent remained in the resin phase after formation of foam, foams were crashed and the resulting resin was placed in an oven for three hours at a temperature of 150°C. The reduction in mass that occurred as a result of this was attributed to entrapped resin that evaporated as a result of the higher temperatures, time of exposure, and exposed surface areas.

RESULTS AND DISCUSSION

Gel Reaction
Gel reaction temperature profiles were measured and used as a control (benchmark) to assist in interpreting the data for the
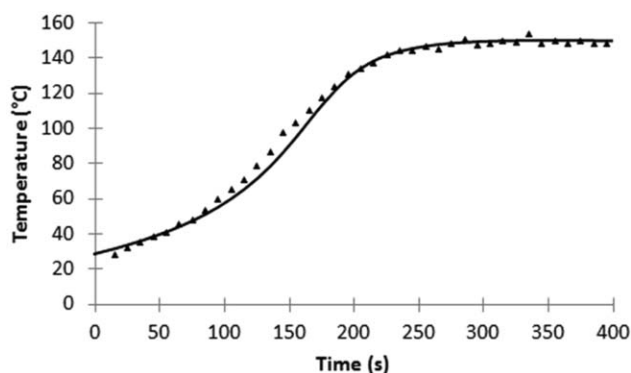
foam reactions; the gel reaction is the polymerization without blowing agent. Figure 1 shows a good fit of the model to the data using previously published kinetic and thermodynamic parameters for V360.[19]

Figure 2 shows how the simulation can generate profiles for alcohol moiety, isocyanate moiety, isocyanate monomer, and polymer concentrations. Those concentrations were used to calculate reaction temperature and polymer concentration by solving the kinetic reaction equations. Polymer concentration increases at the beginning of the reaction and then reduces to a very low number due to the polymer-polymer crosslinking as is prevalent when polyols of high functionality are used in formulations.

Crosslinking of polymers to a concentration that approaches zero is the indication of the gel point. For foam systems this gel point should occur at a time similar to the tack-free time.

Foam Reaction
Figures 3 compares temperature and height profiles for the six different blowing agents. As compared to the gel reaction, the foam reactions are slower due to the evaporative cooling caused by the blowing agents.

The simulation results show good agreement with both the temperature and height profiles. The tack-free times are indicated by vertical lines that correlate well with the increase in degree of polymerization. The height of the foam is essentially constant after the tack-free time is reached.
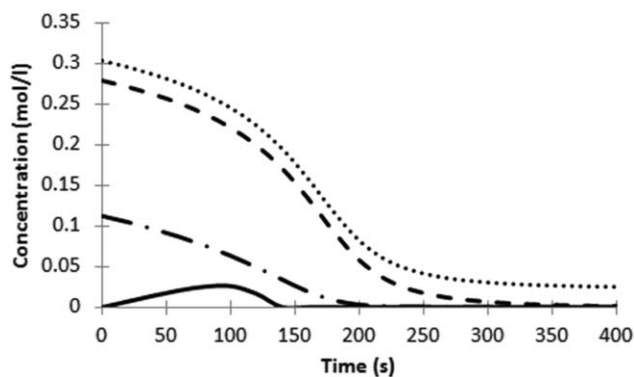
Figure 1. Temperature profile of polyurethane gel reaction. Symbol "▲" represent experimental data and solid line represents simulation.

Figure 2. Concentration profile of isocyanate and alcohol moieties, isocyanate monomer, and polymer. Lines from top to bottom represent concentration profile of isocyanate moieties, alcohol moieties, isocyanate monomer, and polymer.
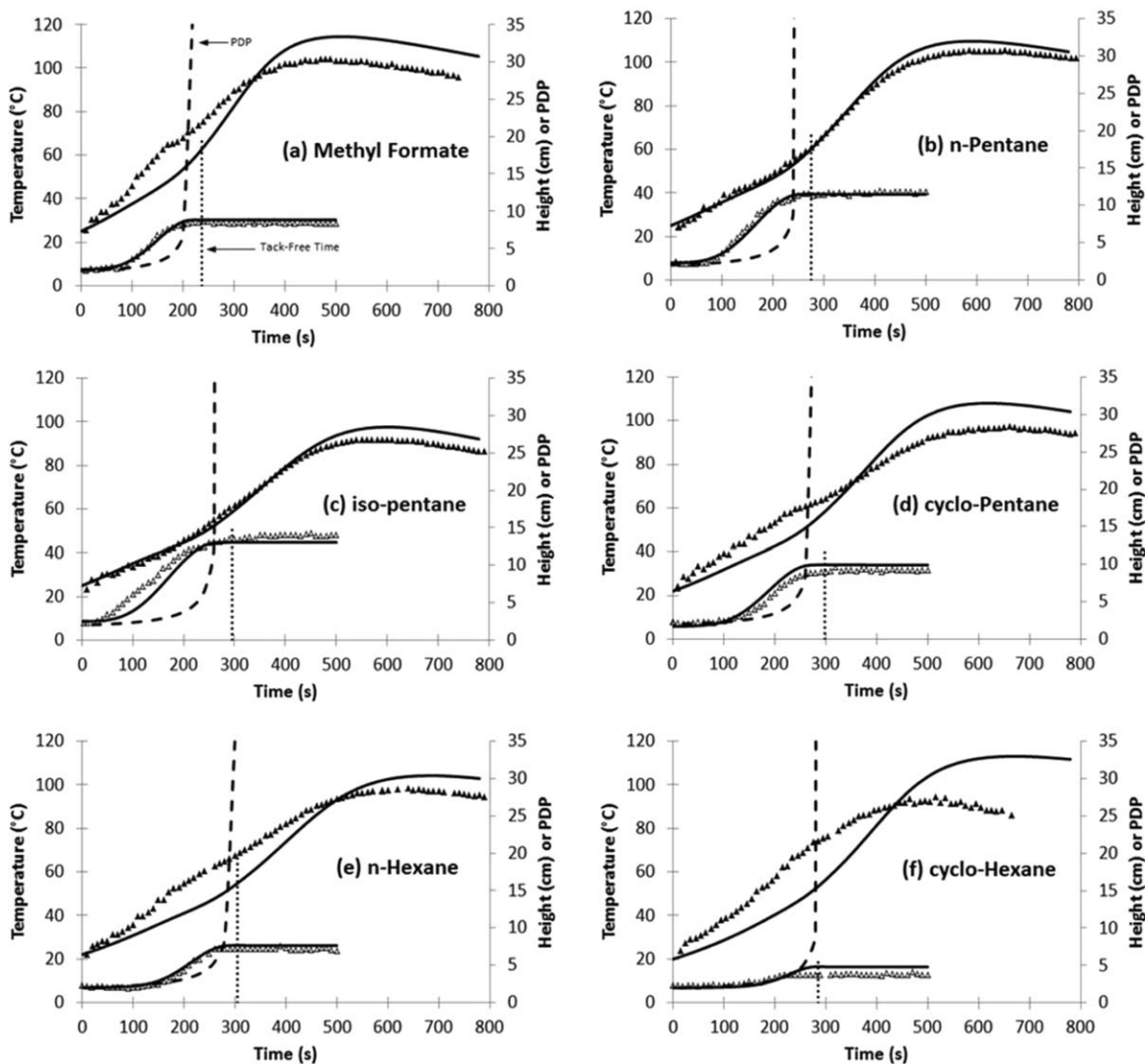
Figure 3. Experimental and simulation results of temperature profile, PDP, and tack-free time of rigid polyurethane foams blown by (a) Methyl Formate, (b) n-Pentane, (c) iso-Pentane, (d) cyclo-Pentane, (e) n-Hexane, (f) cyclo-Hexane. Symbols "▲" and "Δ" represent experimental data of temperature and height profiles, respectively. Solid lines represent simulation results for temperature and height. Dashed line and dot line represent PDP and tack-free time.
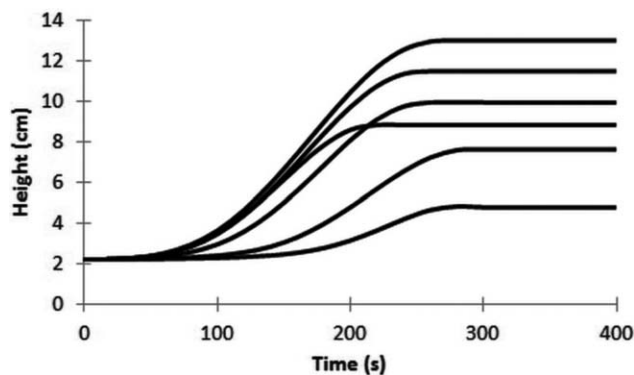

Figure 4. Comparison of simulated foam heights blown by different blowing agents. Lines from high height to low height represent height profiles of foams blown by iso-Pentane, n-Pentane, cyclo-Pentane, Methyl Formate, n-Hexane, and cyclo-Hexane respectively.
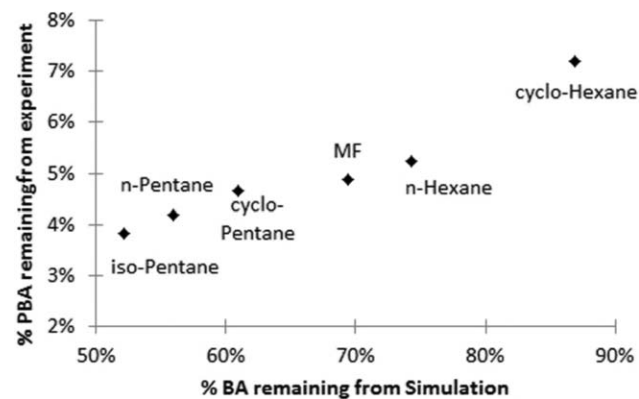

Figure 5. Experimental and simulation percentage and of blowing agent remaining in the foam resin.
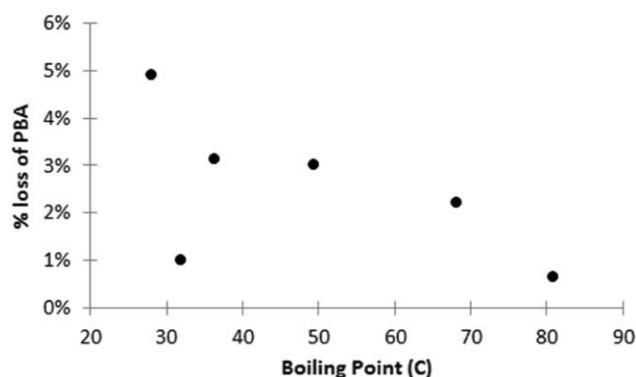
Figure 6. % losses of blowing agents during mixing.

As the polymer degree of polymerization increases and the polymer become more viscous, the foam stops expanding and the remaining amount of the physical blowing agent is entrapped in the resin phase walls of the foam cells (versus the gas phase in the cells).

For the cyclohexane solvent (3f), the simulation's temperature profile deviates from experimental data. This is attributed to the large amount of cyclohexane used in the foaming formulation that quenched the reactions and the high heat of evaporation, which are both attributed to the higher molecular weight of cyclohexane. Despite the issues with the temperature profile, the simulation's height profile is accurate.

Figure 4 shows a comparison of the simulated height profile for the different physical blowing agents to allow a better direct comparison of the performances. The following observations can be noted for the hydrocarbon blowing agents:

– Foam height increased with decreasing boiling point.
– Foam height increases with decreasing latent heat of vaporization of the blowing agent.

The blowing agents evaporate as a result of the heat of reaction. As the temperature of the reaction mixture increases, the blowing agents with lower boiling points evaporate first while many highly reactive alcohol moieties are available to keep the exotherm going. Lower heats of vaporization result in lower impacts on the temperature profiles.

There are a compounding of effects that lead to lower heights for the higher boiling point blowing agents, including: (a)

higher heats of evaporation result in greater impacts on temperature, (b) the resin is more viscous at the later times which resists expansion for blowing agents that evaporate at later times, and (c) at the later reaction times the ability of the reaction to continue is hindered both by the absence of the more-reactive alcohol moieties, viscosity hindering mobility of moieties, and a greater fraction of the moieties are attached to polymer chains which further exasperates the impact of viscosity on the mobility of reactive moieties.

Methyl formate tends to be less efficient toward cell expansion than hydrocarbons of similar volatility. This is attributed to the lower activity coefficient of methyl formate in the resin phase.

One of the factors not taken into account is mass transfer rate. For the methyl formate system, uncertainty in the mass transfer rate creates an uncertainty in the activity coefficient; which when combined, explain the deviation in the fit to methyl formate data. Future work is focusing on modeling and understanding the impact of mass transfer rates and how increasing viscosities and temperatures cause huge changes in mass transfer rates.

The simulation code predicts that substantial amounts of blowing agent remain in the foam. The weight loss of crushed foam samples is compared to the fraction remaining in the foam by Figure 5. Higher mass losses from the resin correlate with higher residual amounts of the higher boiling point blowing agents. Less evaporates in the crushed samples than anticipated based on simulation primarily due to (a) some blowing agent will remain in the crushed foam even after evaporation in the oven and (b) some blowing agent is lost during mixing of monomers (mixing is open to atmosphere, blowing agent is added to the B-side before mixing). The loss of blowing agent during mixing was independently measured as summarized by Figure 6.

Figure 6 summarizes the effect of the boiling point of the physical blowing agent on the percent loss during monomer mixing with the other components of the B-side components. As the boiling point temperature increases, the losses during mixing decrease for all the C5 and C6 hydrocarbons. Methyl formate has lower losses due to evaporation which can be attributed to a lower activity coefficient for methyl formate.

The experimental measurements in combination with simulation results enable an estimate of the ultimate fate of the

Table VI. Material Balance of the Physical Blowing Agents

PBA	Amount of PBA evaporated during mixing	Amount that remained in resin phase	Amount that escaped to surrounding air	Amount that went into cells to form a foam	Amount that remained entrapped in the resin phase
Methyl Formate	0.061	0.199	0.123	1.811	3.696
N-Pentane	0.223	0.149	0.117	3.014	3.567
iso-Pentane	0.347	0.126	0.115	3.457	3.015
cyclo-Pentane	0.208	0.162	0.10	2.627	3.760
n-Hexane	0.190	0.172	0.220	2.210	5.639
cyclo-Hexane	0.054	0.536	0.213	1.065	6.362

blowing agents. Table VI shows the material balance of the physical blowing agents. The results indicate that appreciable amounts of blowing agent are entrapped in the resin and do not contribute to expansion.

These amounts are not indicative of commercial foams since commercial foams have been optimized for performance rather than formulated for fundamental insight. None-the-less, the data show that entrapment in the resin phase can lead to substantial losses in efficacy of the blowing agent. The data also show that this entrapment can be predicted; hence, simulation can be an important and effective tool in developing new blowing agents.

CONCLUSIONS

The simulation of foam-forming reactions was effective for providing insight into mechanisms of efficiency and lack of efficiency of physical blowing agents for forming foams. A blowing agent overall mass transfer coefficient that rapidly decreases as the reacting system approached its gel point (tack-free time) was the most critical aspect of the simulation that led to both insight and quantitative predication of performance.

For the hydrocarbon blowing agents, a single fitted parameter was able to transfer prediction from one system to another. That single fitted parameter accounted for both the activity coefficient and a constant used in an equation for the overall mass transfer coefficient. This validates the fundamentally-correct nature of the simulation which validates the ability of the simulation to be extrapolated to other systems including mixtures of blowing agents.

A major source of inefficiency of blowing agents was identified as the entrapment of blowing agent in the resin phase. Future work will include the use of established methods for estimating activity coefficients and mass transfer in liquids to improve the accuracy of the simulation and to gain further insight in many chemical and physical processes occurring during foam-forming reactions.

ACKNOWLEDGMENTS

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