Simulation Physical and Chemical Blowing Agents for Polyurethane Foam Production

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Abstract. Use of computer simulation to quantify the effectiveness of blowing agents can be an effective tool for optimizing formulations and for the adopting of new blowing agents. This paper focuses on a mass balance on blowing agent during foaming including the quantification of the amount that stays in the resin, the amount that ends up in the foam cells, and the pressure of the blowing agent in the foam cells. Experimental data is presented both in the sense of developing the simulation capabilities and the validating of simulation results.

Abbreviations

| Symbol | Description |
|--------|-------------|
| A_f    | Total mass-transfer area (cm²) |
| K      | The overall mass-transfer coeff. (cm/s) |
| n_o    | Initial number of moles of BA in the resin, mole |
| n_cells| Moles of BA in the cells, mole |
| n_PBA  | Moles of PBA in the resin, mole |
| P_0    | Atm. Pressure, 1 atm |
| P_cell | Pressure in foam cell (atm) |
| P_max  | Maximum pressure inside foam cells, atm |
| T_0    | Initial temperature (295 K) |
| T_max  | Maximum reaction temperature, K |
| V_oBA  | Volume of foam when 100% BA evaporation , cm³ |
| V_f    | Final volume of the foam, cm³ |
| V_Resin| Volume of urethane resin, cm³ |
| x      | Mole-fraction of PBA in liquid-phase |
| x*     | Equilibrium mole-fraction of PBA in the liquid-phase |
| γ      | Activity coefficient |

1. Introduction

A key raw material in the production of high performance, rigid polyurethane (PUR) foam is the blowing agent (BA) since it can have a great impact on the final properties of the polyurethane foams like density and thermal conductivity [1, 2]. Global warming potential, ozone depletion potential, insulation performance, molecular weight, and vapor pressure have been adopted as the main factors of choosing a blowing agent[3].

Chemical and physical blowing agents (BA) are used in PU formulation[4, 5]. Liquid physical blowing agents are inert liquids that evaporate by the heat generated by exothermic reactions of the polyol-isocyanate (Eq. 1), and the generated vapor forms bubbles that become gas cells in the urethane foam as the resin cures[6, 7]. The rate of evaporation is determined by the vapor pressure of the
blowing agent, which is the driving force for gas formation, and the mass transfer rate from the resin to the gas bubble/cell. The overall mass transfer coefficient of the blowing agent vapor decreases as the viscosity of the resin increases [8-10].

Water is used as a chemical blowing agent [11]. Unlike the liquid physical blowing agents, water reacts with isocyanate to generate carbon dioxide (Eq. 2 and 3) that expands the urethane foam [12, 13]. The rate of water-isocyanate reaction is faster than polyol-isocyanate reaction. Because the water–isocyanate reaction is an exothermic reaction, the water-blowing reaction indirectly impacts the rate of alcohol-isocyanate reactions by increasing the resin temperature. As the polymerization in the resin phase progresses, the viscosity increases [14]. This increase in viscosity decreases the rate of diffusion of CO₂ from the resin phase to the gas phase inside the bubbles and part of the CO₂ entrapped in the resin matrix [15, 16].

\[
\begin{align*}
\text{RNCO+R'CH}_2\text{OH} & \rightarrow \text{RNHCOOCH}_2\text{R'} \\
\text{RNCO + H}_2\text{O} & \rightarrow \text{RNHCOOH} \\
\text{RNHCOOH} & \rightarrow \text{RNH}_2 + \text{CO}_2 + \text{HEAT}
\end{align*}
\]

Simulation of blowing agent performance helps to quantify of the amount that ends up in the foam cells versus the amount that stays in the resin matrix (entrapped). This information can be used to optimize of effectively the blowing agent is utilized, and ultimately, help formulators provide more cost-effective formulations [17].

While the vapor/gas pressure inside cells is initially near atmospheric pressure, as viscosity increases pressure increase inside cells increases above atmospheric pressure. The simulation allows the pressure in the cells to be estimated applying the ideal gas law to the simulated quantities of BA that went to the cells, volume of cells, and reaction temperature [18].

2. Simulation Code and System Assumptions

This paper uses a MatLab simulation code for the urethane foaming process to better understand blowing agent mass balance in rigid foams [19]. The simulation code is based on fitting parameters of kinetic and physical properties as previously published. Figure 1 shows an algorithm of the simulation code. The recipe, initial conditions, and the database parameters are input to the FoamSim code, after which, the ODE45 function solves the differential equations of the rate of change in reaction temperature, concentrations, foam height, the rate of evaporation of the physical blowing agent (equation 2), and mass transfer rates of blowing agents from the resin to the cells. Viscosity of the resin is calculated using group contribution method [20]. The rate of CO₂ diffusion and the overall mass-transfer coefficient of the physical blowing agent are functions of viscosity and described using Einstein equation.

\[
\frac{dn_{\text{cell}}}{dt} = -\frac{n_{\text{PBA}}}{v_{\text{Resin}}} A_f \cdot K \cdot (x - x^*)
\]

Initial conditions in the simulation include the specification of the concentration of nucleation sites for cell formation which is used to calculate the initial radius based on an assumed, and very low, initial amount of gas in the cell. Ultimately, as long as the number of nucleation sites is accurate and the initial radius is very low, these initial conditions do not impact calculation results. This number is back-calculated from typical final foam properties. The rate of increasing cell radius is calculated using Equation 5 which derived from hydrodynamic force balance of the foam cell.

\[
\frac{dr}{dt} = \left( P_{\text{cell}} - P_0 \right) / \left[ 4\eta \left( \frac{1}{r} \right) \right]
\]
The partial pressure of the blowing agent in the gas phase is calculated using a mass balance on the blowing agent (Eq. 4), the temperature of the foam, the radius of the bubble/cell, and the ideal gas law. The vapor pressure of the liquid is calculated by modified Raoult’s law. By neglecting the volume of the resin, the effectiveness of blowing agent can be defined as:

\[
\% \text{Effectiveness} = \frac{V_f \times \left( \frac{P_{\text{max}}}{T_{\text{max}}} \right)}{V_{\text{OBA}} \times \left( \frac{P_0}{T_0} \right)} \times 100 = \frac{\text{Moles of BA in the cells}}{\text{Initial moles in the recipe}} \times 100 = \frac{n_{\text{cells}}}{n_0} \times 100
\]  

(6)

The effectiveness of BAs was calculated from density data of many literatures using different PU raw recipes. An effectiveness of 33-40% was reported using different loadings of Methyl Formate (MF), 80-83% using different loadings of water, and 50-67% using blends of MF/water[21]. Approximately 83-86% effectiveness of water was reported using biobased polyol. For the current PU recipes, and effectiveness of >85% for water and 16-30% for n-Pentane was observed.

The following assumptions were adopted in the code:

- Foam cells are assumed to have spherical shape all times and the gravitational forces are neglected.
- Neglecting the interaction of the growing bubble with each other since the posteriori that the growing cells is influenced is almost exclusively by diffusion form a thin shell surrounding it [18].
- The gas phase inside the cells is assumed to be ideal-gas.
- Nucleations is assumed to be homogeneous.
- No blowing agent losses during foaming.
- The foam is assumed to be of uniform temperature throughout at a temperature close to the adiabatic condition. Accordingly, all foam conditions are uniform, and the gelation occurs at the same instant. Hence, the cells stop growing in the entire mold at the same time.
• No cells collapse of collision.

3. Materials and Recipes
Tables 1 and 2 summarize the amount and function of the B-side recipes. An isocyanate index of 1.1 is used in all the experiments. Polymeric isocyanate (thereafter referred as PMDI) (average molecular weight 340 and 2.7 functionality) and Polyol 360 (thereafter referred as P360) (Hydroxyl number 360, average molecular weight 728, and 4.5 functionality) were used. P360 is identified as having 10% secondary and 90% hindered secondary fractional group according to the previous studies [22].

Table 1. Foaming recipes.

| Ingredients                     | Function   | Weight, g |
|---------------------------------|------------|-----------|
| P360                            | Polyol     | 45        |
| Dimethylcyclohexylamine (Cat8)  | Gelling catalyst | see Table 2 |
| Pentamethyldiethylenetriamine (Cat5) | Foaming catalyst | see Table 2 |
| Surfactant 69                   | Surfactant | 0.6       |
| TCPP                            | Fire retardant | 2         |
| n-Pentane                       | Physical Blowing agent | see Table 2 |
| Water                           | Chemical Blowing agent | see Table 2 |

Table 3 shows the specifications of P360 and the PMDI used. The amounts of the polyol, catalysts, fire retardant, and surfactant are kept the same to get clear observation of the efficiency of the physical and chemical blowing agents.

Table 2. Blowing agent loading.

| Blowing Agent | Weight, g | Cat5 | Cat8 | PMDI |
|---------------|-----------|------|------|------|
| n-Pentane     | 6         | 0    | 0.5  | 43   |
| n-Pentane     | 7         | 0    | 0.5  | 43   |
| n-Pentane     | 8         | 0    | 0.5  | 43   |
| Water         | 0.5       | 0.12 | 0.32 | 51.2 |
| Water         | 0.75      | 0.12 | 0.32 | 55.3 |
| Water         | 1         | 0.12 | 0.32 | 59.5 |

Table 3. Specifications of P360 and PMDI

| Properties                  | P360   | PMDI  |
|-----------------------------|--------|-------|
| Density (g/cm³)             | 1.08   | 1.23  |
| Avg. mol. wt.               | 728    | 340   |
| Functionality(f)            | 4.5    | 2.7   |
| OH-number (mg KOH/g⁻¹)      | 360    |       |
| Equivalent weight(Eq. wt.)  | 155.5  | 134   |
| Viscosity (mPa.s @25°C)     | 3500   | 150 - 220 |
| NCO content(weight%)        | 31.42  |       |
| Vap. pressure(mmHg at 25°C) | < 10 - 5 |       |
| Specific heat(gcal/g at 25°C)| 0.431 |       |

4. Experimental Work
Experiments of polyurethane foams were performed for the foaming recipes shown Tables 1 and 2 in the following steps:
• The components of B-side in Tables 1 and 2 were weighted in a closed 200-ml beaker. The beaker was allowed to degas for two minutes. The amount of blowing agent lost by mixing was measured.
The mixture of B side materials was poured in a plastic-cup and mix after adding the A side materials in a 2000-rpm mixer blade for 10 seconds.

The mixture was poured into a wooden-box that has an aluminium foil lining. Foam was allowed to expand during the polymerization reaction until the temperature start decreases.

Reaction temperature and foaming height profiles were measured via LabView software connected to type-K thermocouple and ultrasound device attached via a National Instruments SCB 68 box to a National PCI-6024E data acquisition card. The LabView software records the time vs temperature and time vs height data in the computer.

5. Results and Discussion

Figures 2 and 3 show the temperature and height profiles of polyurethane foams blown by a physical blowing agent (PBA) (n-Pentane) and water respectively. The runs are based on total moles of physical blowing agents of 0.083, 0.097, and 0.11 and total moles of water of 0.028, 0.0412, and 0.055 respectively. This translates to about a density of 0.028, 0.0244, and 0.021 g/cm³ if the physical blowing agent were 100% effective and 0.072, 0.048, and 0.036 g/cm³ if the water was 100% effective.

The heat of vaporization of the physical blowing agent, heat generated from water-isocyanate reaction, and the amount of gas generated on reaction temperature during foaming are the key for blowing agent simulation. The results show that the lower maximum reaction temperature and higher foam height obtained as more PBA present in the formulation. The heat of reaction reduces as more PBA present in the formulation. This lead to slower attaining the gel point of the resin (slower viscosity increase) that allows more BA to diffuse frim the resin phase to the cells and higher foam height.

![Figure 2. Temperature profile of polyurethane foam blown by different loadings of n-Pentane and water. Symbols and lines refer to experimental data and simulation respectively. Green, red, and blue refer to 8, 7, and 6 g n-Pentane loading (A) and 1, 0.75, and 0.5 g water loading (B) respectively.](image1)

![Figure 3. Height profile of polyurethane foam blown by different loadings of n-Pentane and water. Symbols and lines refer to experimental data and simulation respectively. Green, red, and blue refer to 8, 7, and 6 g n-Pentane loading (A) and 1, 0.75, and 0.5 g water loading (B) respectively. Vertical lines indicate tack-free time of the corresponding foams.](image2)
Also the results show higher reaction temperature and higher foam height obtained when increasing water loading in the formulation. As more water present in the formulation, the heat of reaction increases and this lead to faster attaining to the gel point (faster viscosity increase); however, because water/isocyanate reaction is faster than polyl/isocyanate reactions, more CO$_2$ diffuses to the cells as more water added. The experimental results of the tack-free time shows that the gel point happened as the foam stops growing for both n-Pentane and water.

The superimposed simulation profiles for the temperature and height in these figures is used to empower the verification of the concentration profile of the blowing agents and pressure profile. Figures 4 and 5 show how the simulation code can successfully predict the concentration profile of the PBA and CO$_2$ gas. The results of BA concentration profile is verified by foam height and viscosity profiles.

Figure 4 shows that the foam starts growing when the PBAs starts diffusing form the resin phase to the cells and foam height stops increasing when the PBAs stops diffusing. In addition, the results show more PBA present in the formulation leads to less PBA entrapped and this can be attributed to the impact of the PBA to the heat of reaction. In the case of water (Figure 4B), the results show fast increasing in CO$_2$ and height profiles and this attributed to the fact that water started reaction with isocyanate directly after adding the isocyanate to the B-side recipes.

Figure 5 shows that as the viscosity of the resin reach high values, the diffusion rate of the BA decreases rapidly, and the remaining amount of the BAs entrapped inside the resin-phase.

Figures 6 and 7 show the simulation of the pressure in the cells using n-Pentane and water respectively. The results provide the following information:

- More PBAs leads to lower gas-pressure in the cells.
The pressure in the cell start increase when the height of the foam stops increasing and the viscosity of the resin phase reaches higher value.

The pressure inside cells is increasing due to increase in temperature of the reaction form the reactive alcohol-moieties that still available to keep the exothermic-reaction going.

The pressure starts to decrease when the reactions end and the foam cools down. In addition, the trend of the pressure profile provides valuable information on foam shrinkage when the foam cannot withstands the vacuum forces inside the cells.

Figure 6. Simulation results of n-Pentane and CO₂ pressure profiles and foam height profiles. Green, red, and blue lines refer to simulation using 8, 7, and 6 g n-Pentane loading (A) and 1, 0.75, and 0.5 g water loading (B) respectively. Solid lines refer to pressure profile and dash lines refer to foam height.

Figure 7. Simulation results of n-Pentane and CO₂ pressure profiles and resin viscosity profiles. Green, red, and blue lines refer to simulation using 8, 7, and 6 g n-Pentane loading (A) and 1, 0.75, and 0.5 g water loading (B) respectively. Solid lines refer to pressure profile and dash lines refer to resin viscosity.

Viscosity data in Figure 7 shows good agreement with the trends of pressure profile for both n-Pentane and water.

6. Conclusions
Simulating of polyurethane foaming reaction provides insight in the effectiveness of physical and chemical blowing agents. The results allow for conclusions based on agreements of dynamic temperature profiles, foam height, and mass balances.

A primary mechanism of loss of effectiveness of blowing agents can be entrapment in the resin phase. As the reaction system reaches its gel point, the rate of diffusion of the blowing agent decreased rapidly and part of the blowing agent entrapped in the resin matrix and this is the main reason for lack of effectiveness of the blowing agents.

The carbon dioxide produced from water reactions tends to have high efficiencies relative to physical blowing agents with lower fractions entrapped in the resin.
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