Article
Limits of Performance of Polyurethane Blowing Agents

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Abstract: A MATLAB program was developed to simulate urethane-forming reactions by solving over a dozen differential equations, energy balance, mass balance, and constitutive equations simultaneously. The simulation program was developed for half a decade to simulate the basic kinetics of polyurethane reactions and more complex phenomena that cannot be obtained in laboratories. In the current investigation, the simulation is applied to determine the limits of the performance of polyurethane foam formation. n-pentane, cyclohexane, and methyl formate were used as physical blowing agents, and water was used as a chemical blowing agent. The simulation code increases the accuracy of the results and makes the foam performance process less time- and money-consuming. Specifically, the MATLAB code was developed to study the impact of physical and chemical blowing agents at different loadings on the performance of rigid polyurethane foams. Experimental data were used to validate the simulation results, including temperature profiles, height profiles, and the tack-free time of urethane foam reactions. The simulation results provide a window for the proper type and the optimum amount range of different physical and chemical blowing agents.

Keywords: polyurethane; foam; blowing agent; simulation; viscosity

1. Introduction

In many areas of engineering systems that involve chemical reaction, developing a model and performing a computation are tremendously useful in investigating the role of dependent parameters and optimizing them [1,2]. This in turn helps chemical engineers to determine the reaction rates [3], the best design and size of chemical systems [3], and the relation between the reactions and other physics that may interact with them, such as mass transfer limitations [4,5]. Perhaps the simulation of polymerization reactions is viewed as a unique challenge, since they are complicated and need a combination of different computational methodologies. The urethane reaction (whether formation of rigid or flexible foam) is the best example of complicated polymerization reactions, and it is important to be understood, as it has many applications [6–8].

Rigid polyurethane foam (PU) is produced by the reaction of the alcohol moiety in polyols and the isocyanate moiety in the presence of chosen catalysts, surfactants, fire retardants, and physical and/or chemical blowing agents, as shown in the below equation [9,10]. PU is a polymer made up of organic units connected by carbamate (urethane) linkages [11].

$$RNCO + R'CH_2OH \rightarrow RNHCOOCH_2R' \tag{1}$$

Foam formation may be brought about either physically or chemically, or by combining the two. The bubbles' cellular structure is filled with the gas created when the blowing agents evaporate. Because of its reactivity with the isocyanate moieties, water is utilized in

the chemical industry as a blowing agent. This allows for the production of carbon dioxide gas, which is necessary for the blowing processes [12].

$$RNCO + H_2O \rightarrow RNHCOOH \tag{2}$$

$$RNHCOOH \rightarrow RHN_2 + CO_2 + heat \tag{3}$$
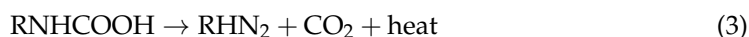
In general, a blowing agent is a crucial material for the foaming process and the properties of the produced foam. The quality, quantity, and nature of a blowing agent control the final characteristics and properties of the produced foam. The optimum blowing agent should have the following characteristics: it should be harmonious with the base resin, produce a sleek foam surface, have a uniform foam core transition, and achieve the best blowing performance (minimum concentration).

Most foaming material is derived from the blowing agent during the process of foaming, produced from the liquid phase, or produced from the reaction or decomposition of chemical material under heat or catalyst effect. Blowing agents can be classified in many ways. However, according to the mechanism by which gas is liberated during the foaming process, it can be classified as physical and chemical blowing agents. In addition to the two types, we can add gases directly added to the liquid polymer to make foam a third type [13,14].

Blowing or foaming agents are chemicals that quickly evaporate at certain temperatures, producing enormous amounts of gases or vapors. Chemical and physical blowing agents may be distinguished as a result. Polyurethane formulation often employs physical blowing agents (PBAs) such as n-pentane, methyl formate, and cyclohexane. Compounds that undergo a rapid expansion due to a phase change, such as the evaporation of liquids or the compression of liquefied gases at the foaming temperature, are categorized as physical blowing agents [15]. The foamed result will be less dense if the physical blowing agent evaporates faster. Water and other chemical blowing agents are examples of inorganic and organic substances that undergo heat decomposition into gases without interacting with the polymer matrix. This process is often exothermic and irreversible, resulting in improved final foam qualities [16,17].

Physical blowing agents can provide additional gas during foaming, adding desired properties to the foam [18,19]. Once the gas(es) liberates from the chemical blowing agent, it acts as a physical blowing agent. Because they are too expensive, chemical blowing agents are mostly used when high or medium polymer foams are required. The produced foam is 400 to 800 kg/m^3 (i.e., a 20 to 45% reduction from the original liquid polymer density) [20].

Using chemical blowing agents has many advantages. It is easy to add to the liquid polymer to be formed, and the forming process needs little modification in the process line of an existing thermoplastic polymer. However, it is not easy to recycle results from unreached materials. On the other hand, the blowing agent may affect foam properties, such as density, cellular structure, and cooling time [21].

The vapor–liquid equilibrium governs the evaporation of the blowing agent with a volatile component between the polymer matrix and vapor phase. Commercial foams' most important physical properties are density, compressive strength, and thermal conductivity [22].

Many research workers have extensively studied polyurethane-blowing agents' performance. Baser and Khakhar [23] devised theoretical models for making rigid polyurethane foam from water and a physical blowing agent. They conducted an in-depth experimental investigation to assess temperature and density variations throughout the foam production process. However, they did not investigate how thermocouples affect temperature profiles or how heat moves to the environment around them.

Tesser et al. [24] modified the formulation of the vapor–liquid equilibrium of the blowing agent and the polymeric phase by using an extended Flory–Huggins equation. This equation explains the non-ideal behavior of these reacting mixtures. The model was adjusted to incorporate heat transfer.

Rigid polyurethane foams (RPUFs) were simulated. Ordinary differential equations (ODEs) were solved to account for elementary reactions, the energy balance of the reactor, and physical processes like the mass transfer of blowing agents. In their prior research, Al-Moameri et al. [25] developed a modification in the blowing agent function of the previous versions of the MATLAB program to model the effects of several blowing agents. This code also specified methyl formate, n-pentane, and cyclohexane, in addition to water. However, it is only confined to simulating the blowing performance of these blowing agents without considering the loading limiting.

The current research developed the simulation code of the previous study. It focuses on the ability to simulate chemical and physical blowing agent performance limits and their mixture at different blowing agent loadings. Temperature profile, height profile, and tack-free time data acquired experimentally from urethane foam reactions supported the simulation results.

Formulation development was first aided by urethane-forming reaction modeling by obtaining temperature, concentration [26], and foam height [27] profiles as functions of time. Most urethane formulations require the adjustment of more than a dozen variables (including reagents, catalysts, initial temperature, blowing agents, and additives), so the design process begins with the construction of a base case simulation program that is subsequently (and continues to be) iteratively enhanced to increase accuracy and versatility. The reactive moieties in the polyol were assumed to be primary, secondary, and hindered-secondary [28]. The last was representative of the mass transfer limitations. Changes to the simulation fall into one of the six areas listed below:

- Accuracy enhancement;
- Enhancing the basic form of the governing equations (and the associated physical constants) to expand their applicability (extrapolation to other conditions and reagents);
- Increasing versatility via the use of group contribution methods (such as heat capacity, viscosity, and reaction rate constants);
- Usage as an alternate strategy for studying and comprehending polymer science;
- Developing it to be used in predicting polymer physical characteristics (e.g., thermal conductivity, compressive strength);
- Increase its use as an analytical technique.

The second phase of the research project relied on using different blowing agents, including water, and examining the simulation's accuracy when using blowing agent mixtures [29]. In addition, it included the successful prediction of the thermoset polymerization mechanism [30,31], gelling and blowing catalysts [32,33], foam shrinkage [34], cell morphology [25], resin viscosity [35], isocyanate reactivities [36], the surfactant rule [37], and heat capacity [38] during thermoset reactions.

The last phase focused on eliminating the early assumed hindered secondary moieties and considering the mass transfer limitation base on the viscosity increase [39,40]. This was accompanied by reducing the degree of freedom for the simulation program. Furthermore, this phase included the production of the physical and chemical properties of the final rigid urethane foam in addition to the current research on the limit of performance of blowing agents. The current research is expected to attract the PU industry, with the goal of simulating the limits of using industrial (commercial) blowing agents.

The FoamSim MATLAB program can successfully predict many failure modes of polyurethane foam. Table 1 lists these failures regarding the blowing agents, polyols, and isocyanates. However, some visual forms of failure cannot be predicted by the code, and Table 2 lists these visual modes.

Table 1. Indications of failure based on foaming process simulation.

Feature	Failure Mode
Blowing agent concentration	The blowing agent does not evaporate completely during foaming.
Temperature	The temperature of the reaction is either too low or too high.
Recipes concentration	Not all the isocyanate, polyol, and/or blowing agents reacted.
Height	The height of the foam is very short.
Degree of polymerization	Low degree of polymerization.

Table 2. Visual failure modes of foams.

Feature	Failure Mode
Surface	Rough and stiff.
	Not rigid enough.
Bubbles at the surface	No bubbles at the surface.
	Too many bubbles at the surface.
Failure to form a cell network	At the start of foaming, bubbles rupture without preservation of the cell.
	The gooey surface persists all the way to the end of the foaming process.
Failure to retain cell structure	When foam cools (0.05–4 h), the sides of foam collapse in.
	Too high an open cell content.
Cell morphology problems	Smaller than normal.
	Larger than normal.
Foam has inadequate compressive strength	Easy to smash.

2. Experimental Procedure

2.1. Materials

The research used Dow Chemical Co.'s PMDI (standard polymeric MDI) as the isocyanate (A-side) and Voranol 360 (45 g) as the polyol (B-side); their respective technical details are shown in Table 3. N, N, N′, N″, N″-pentamethyldiethylene-triamine (PMDETA) from FSI (catalyst 5) and N, N-dimethylcyclohexyl-amine (DMCHA) from Sigma-Aldrich (catalyst 8) were used as amine-based catalysts. Surfactant Momentive L6900 and flame retardant Tris (1-chloro-2-propyl) Phosphate (TCPP) were utilized. The blowing agents utilized were n-pentane, cyclohexane, and methyl formate from Sigma-Aldrich, and water. In order to compare the efficacy of various blowing agents, the quantities of polyol, catalysts 8 and 5, surfactants, and fire retardants used in each foaming experiment were kept constant. All reactions maintained a constant isocyanate index of 1.1.

Table 3. Specifications of PMDI and Voranol 360.

Property	V360	PMDI
Density, $g \cdot cm^{-3}$	1.081	1.23
Viscosity, mPa.s @25 °C	3500	150–220
Average molecular weight	728	369.9
Vapor pressure, mmHg @25 °C	-	$<10^{-5}$
Functionality	4.5	2.7
Equivalent weight	155.55	137
Hydroxyl number, mg KOH g^{-1}	360	-
NCO content by weight, %	-	31.4
Specific heat at 25 °C (gcal/g)	-	0.43

Table 3 displays the formulations for rigid polyurethane foam catalytic reaction. Table 4 summarizes the mass loading condition of every blowing agent together with the matching quantities of PMDI and catalysts. The reaction temperature, as well as the height of the foam, were acquired using temperature- and height-time profiles.

Table 4. Amounts of blowing agents, PMDI, and catalysts.

Exp no.	Blowing Agent	Weight (g)	PMDI (1.1 Index)	Catalyst 8	Catalyst 5
1	n-pentane	2	43	0.5	0
2	n-pentane	4	43	0.5	0
3	n-pentane	8	43	0.5	0
4	n-pentane	12	43	0.5	0
5	methyl formate	2	43	0.5	0
6	methyl formate	6	43	0.5	0
7	methyl formate	10	43	0.5	0
8	methyl formate	14	43	0.5	0
9	water	0.2	46.26	0.12	0.32
10	water	0.5	51.2	0.12	0.32
11	water	1	59.46	0.12	0.32
12	water	2	75.96	0.12	0.32
13	cyclohexane	1	43	0.5	0
14	cyclohexane	2	43	0.5	0
15	water/cyclohexane	0.5/2	51.2	0.12	0.32
16	water/cyclohexane	0.5/4	51.2	0.12	0.32
17	water/cyclohexane	0.5/6	51.2	0.12	0.32
18	water/cyclohexane	0.5/12	51.2	0.12	0.32
19	water/n-pentane	0.5/4	51.2	0.12	0.32
20	n-pentane/methyl formate	3/3	43	0.5	0

2.2. Preparation of PU Foam

The components for the B-side, which included catalysts, polyols, surfactants, blowing agents, and fire retardants, were measured out, weighed, and then placed in a closed beaker containing 250 mL. The components for the B-side were manually shaken for a total of five minutes. The beaker was covered for five minutes to prevent the loss of any physical blowing agent. After that, the contents of the mixture were transferred into a plastic cup. The necessary quantity of isocyanate (A-side components) was determined by using a syringe. Using the syringe would help minimize the amount of isocyanate lost due to weight loss in the cup. After pouring the B-side components into a plastic cup, they were mixed with the isocyanate for ten seconds at a speed of 2000 revolutions per minute. In each of the studies, the mixing rate and time were maintained at the same level of consistency. Finally, the mixture was transferred into a wooden box with a 12.7 by 12.7 cm base size. It was lined with aluminum foil in the walls to avoid the foam sticking in the box. The foam was permitted to grow vertically. All experiments were conducted at ambient temperature to ensure uniformity in reaction kinetics and polymer molecular weight [41]. A drill press with a high-speed mixer blade was utilized to combine the ingredients. LabView software and a type-K thermocouple, with an ultrasound device wired up to a National Instruments SCB-68 box and a National Instruments PCI 6024E data acquisition card were employed to track the temperature and height patterns of the foam reactions. The tack-free time for every foam was determined by the amount of time it took to show no evidence of sickness after handling it with a spatula.

3. Results and Discussion

3.1. Gel Reaction

Figure 1 shows the simulation results for the gel reaction temperature and density. It is calculated based on solving the partial differential equations of polyurethane reactions, reaction temperature, and height change rate when the blowing agent is present. The simulation of the gel reaction verifies the assumption of no changes in foam height parameters. The simulation considers the volume of the nucleation sites generated from mixing the monomer prior to the reaction.
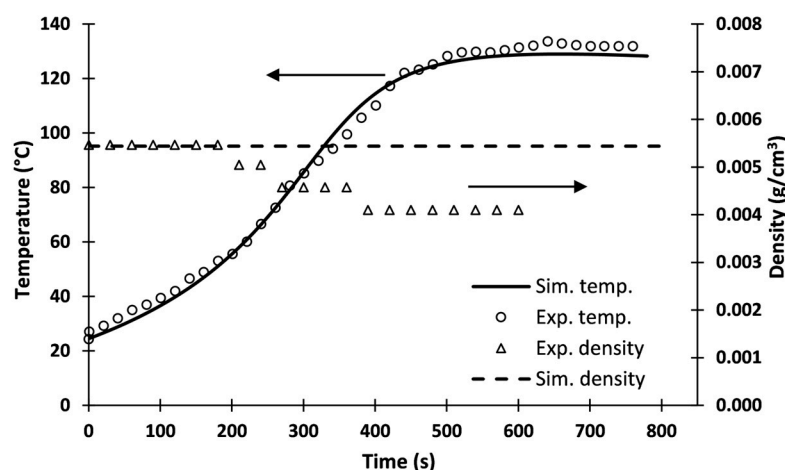
Figure 1. Experimental data and simulation results of reaction temperature and resin density using PMDI with V360 gel system at 1.1 isocyanate index.

The gel density experimental results show a weight decrease compared to the gel recipes. This decrease is due to an increase in gel height due to volume changes due to liquid-phase mixing. In addition, the decrease may be due to the fact that polyol may absorb some moisture that reacts with isocyanate and works as a chemical blowing agent. The total volume of gel equals the final mixture left in the paper cup plus the volume of nucleation sites that occurred during the mixing. The simulation of the gel reaction and density verifies the ability of the simulation program to be used for simulating the polyurethane foaming process.

3.2. n-Pentane

A series of experiments were performed to identify each blowing agent's performance limits. The same foam recipes were used with different loadings of blowing agents ranging from low to high concentrations. The reaction temperature and foam height were recorded experimentally and compared to the simulation results. The simulation code assumes ideal performance for the blowing agent, including no escaping from the foam's top during foam rising and no entrapment in the polymer matrix. Eight experiments were performed for each blowing agent, and four results were presented where the foam failure became evident.

Foaming experiments were performed using n-pentane (Figure 2) as a physical blowing agent. Loadings of 2, 4, 8, and 12 g were chosen where performance limits became obvious. In comparison to the simulation results, the experimental data of foams blown by the 2 g loading showed a lower foam height. This is attributed to some blowing agent entrapped in the resin matrix. This was obviously observed when the resulting foam had a high density and a dark color similar to the gel. Experimental data using 4 and 8 g of n-pentane showed good agreement with the simulation results. The 12 g loading of n-pentane showed failure. The foam showed bubbles on its top surface, indicating that the greatest part of the blowing agent escaped from the foam during the foaming reaction. The simulation code predicted a lower temperature profile as it assumed approximately 50% of the n-pentane was evaporated to form the foam cells. The n-pentane blowing agent's performance limits were identified as the window between 2 and approximately 10 g where 40% to 80% evaporates and diffuses to the cells to form foam.
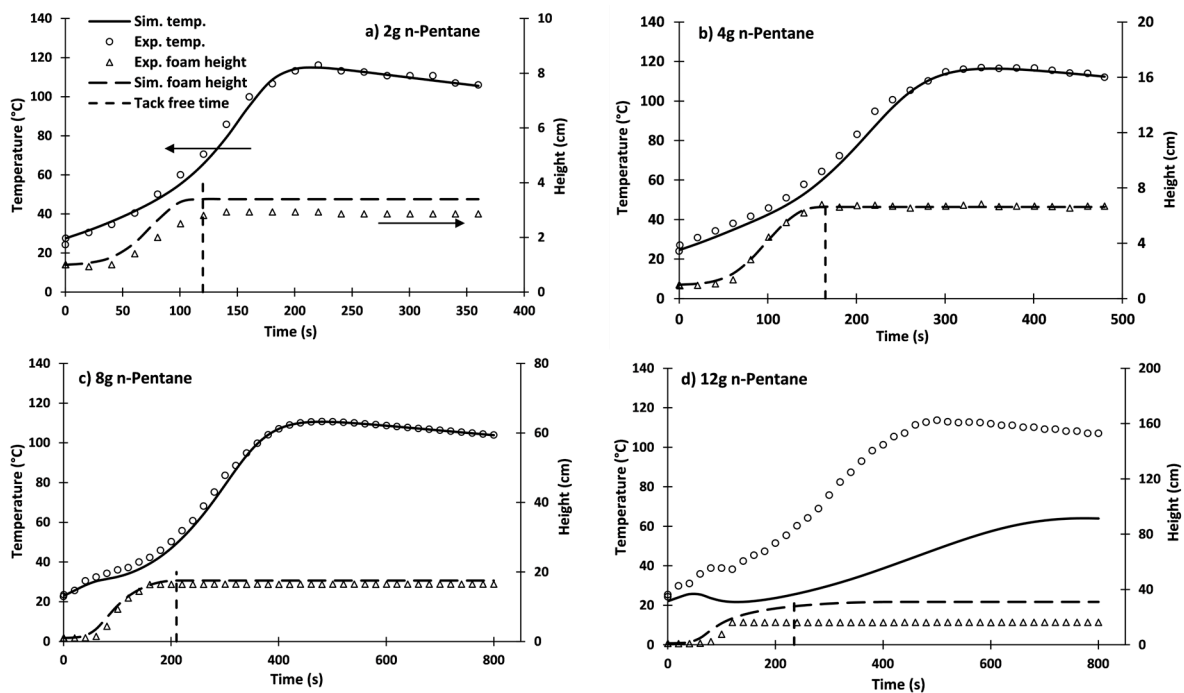
Figure 2. Simulation and experimental results of the temperature profile, height profile, and tack-free time of RPUF blown by n-pentane (legends are applied to all figures).

3.3. Methyl Formate

Figure 3 shows foaming experiments on a second blowing agent that were performed to identify the performance limits. Methyl formate loadings of 2, 6, 10, and 14 g were chosen. Foams of 2 and 14 g methyl formate showed failure where the height of the foam was lower than the simulation results. The resulting foam from the 6 g of methyl formate loading agreed well with the simulation results. The 10 g loading of methyl formate resulted in foams with little deviation in reaction temperature and foam height compared to the simulation results. This region was identified as the start of foam failure. The performance limits for methyl formate as a blowing agent were identified as the window between 6 and 10 g where 5% to 20% evaporates and diffuses into the cells to form the foam.

3.4. Water

The limits of performance were measured for water as a chemical blowing agent. Water reacts with isocyanate to generate carbon dioxide, which diffuses to the nucleation sites to form foam bubbles. The rate of reaction of isocyanate and water is much faster than the polymerization reaction; however, the heat generated by the water reaction increases the polymerization reaction rate based on the Arrhenius equation. In addition, the amount of the generated gas should be within a limit proportional to the amount of polymer blown. For that, optimizing the amount of water used in the polyurethane formulation is crucial.

A 0.2, 0.5, 1, and 2 g loading of water was used as a blowing agent, as shown in Figure 4. The 0.2 loading showed that foam height was lower than the predicted value from the simulation code. This was attributed to the low amount of water that generated a low amount of carbon dioxide, which entrapped the resin matrix. The 0.5 and 1 g loading showed good agreement with the simulation and produced good foams. The loading of 2 g also showed lower foam height compared to the simulation. This was attributed to the high amount of blowing agent generated at the initial reaction time before enough polymer formed to hold the gas in the cell. The foam showed bubbles on the top surface and showed bubbles escaping during the reaction. The water performance limits were in the region above 95%. Increasing the water loading led to increased carbon dioxide gas, which escaped from the surface and led to density failure of the foam.
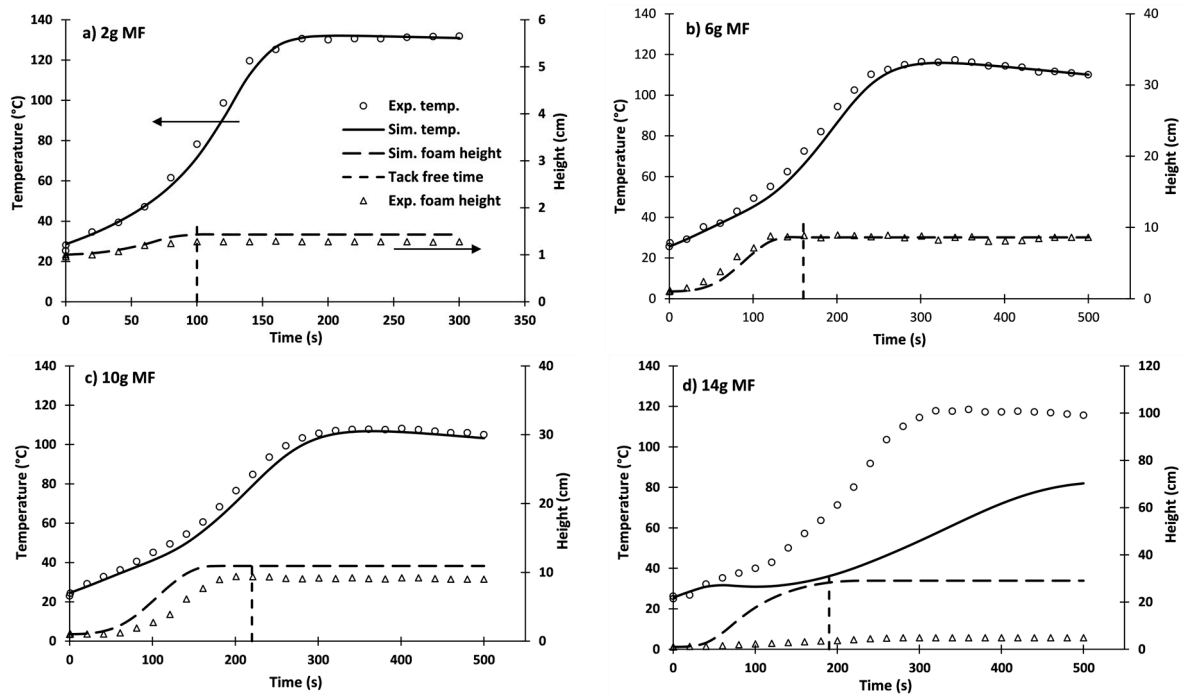
Figure 3. Simulation and experimental results of the temperature profile, height profile, and tack-free time of RPUF blown by methyl formate (legends are applied to all figures).
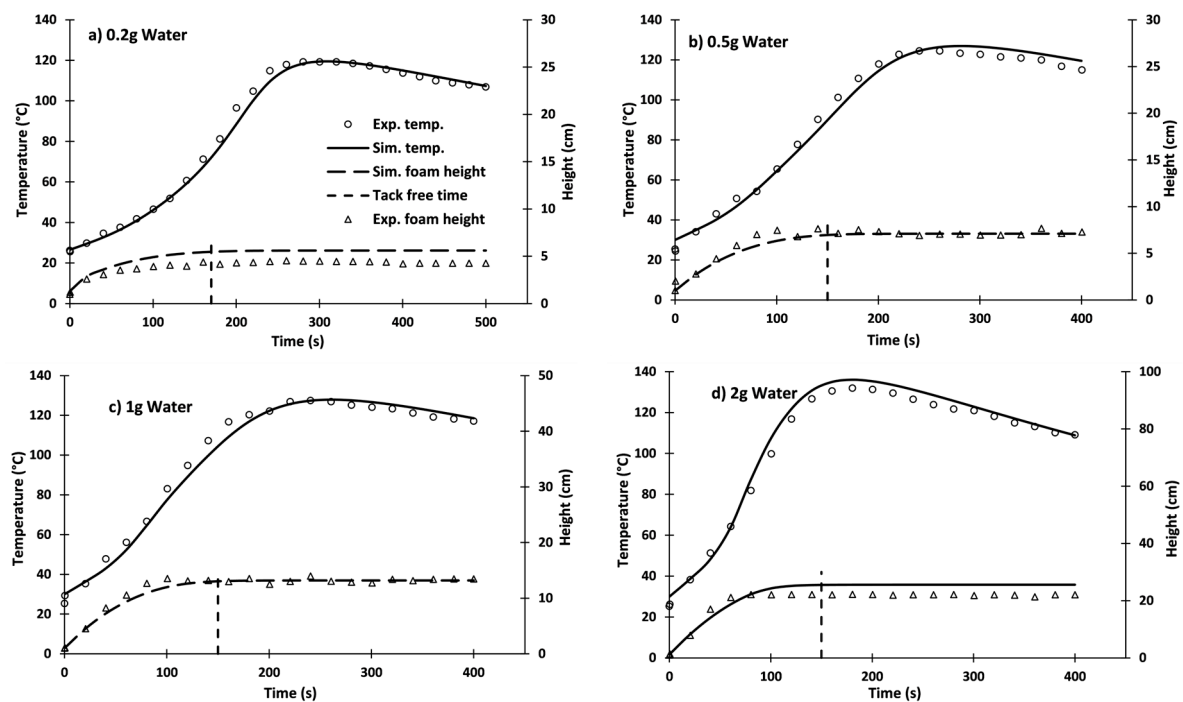

Figure 4. Simulation and experimental results of the temperature profile, height profile, and tack-free time of RPUF blown by water (legends are applied to all figures).

3.5. Cyclohexane

Experiments were performed using cyclohexane as a blowing agent. All foams blown by this blowing agent failed, as shown in Figure 5. The foam height did not rise even at low loadings. This failure can be attributed to the high heat of vaporization of cyclohexane and elevated boiling temperatures. It causes bubble formation and expansion at greater extents

of reaction, where the viscosity is higher, creating more resistance to bubble expansion and a slower diffusion of gases into the bubbles. This happens because the higher viscosity makes the bubbles push against each other more when they try to grow.
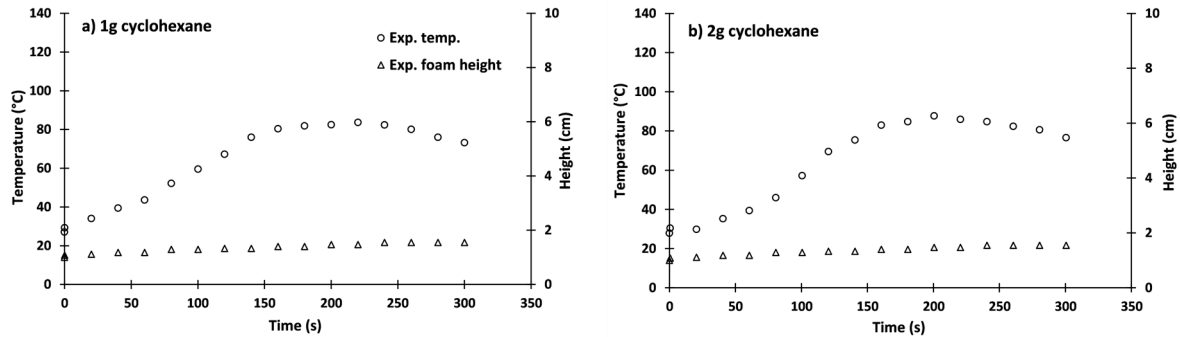

Figure 5. Experimental temperature and height profiles of RPUF blown by cyclohexane.

One way to avoid this foam failure was by increasing the heat of the reaction at the earlier stages by adding 0.5 g of water. Water reacts with isocyanate to generate heat, increasing the polymerization reaction rate. Experimental data and simulation results of 2, 4, 6, and 12 g loadings of cyclohexane (and 0.5 g water) are shown in Figure 6. The resulting foam from the 2 g loading showed good density and surface properties with good agreement of experimental data of temperature and foam height with the simulation results. Beyond the 2 g loading, the foams showed signs of failure in foam shape, foam surface, and the presence of some bubbles on the top surface. These signs became more obvious as the cyclohexane loading increased. Simulation results of reaction temperature and foam height showed good agreement for the 2 g loading, and the deviation increased as the loading increased. From these experiments, we identified that the performance limits were in the region below the 2 g loading, where less than 20% of the cyclohexane evaporates and diffuses into the cells.
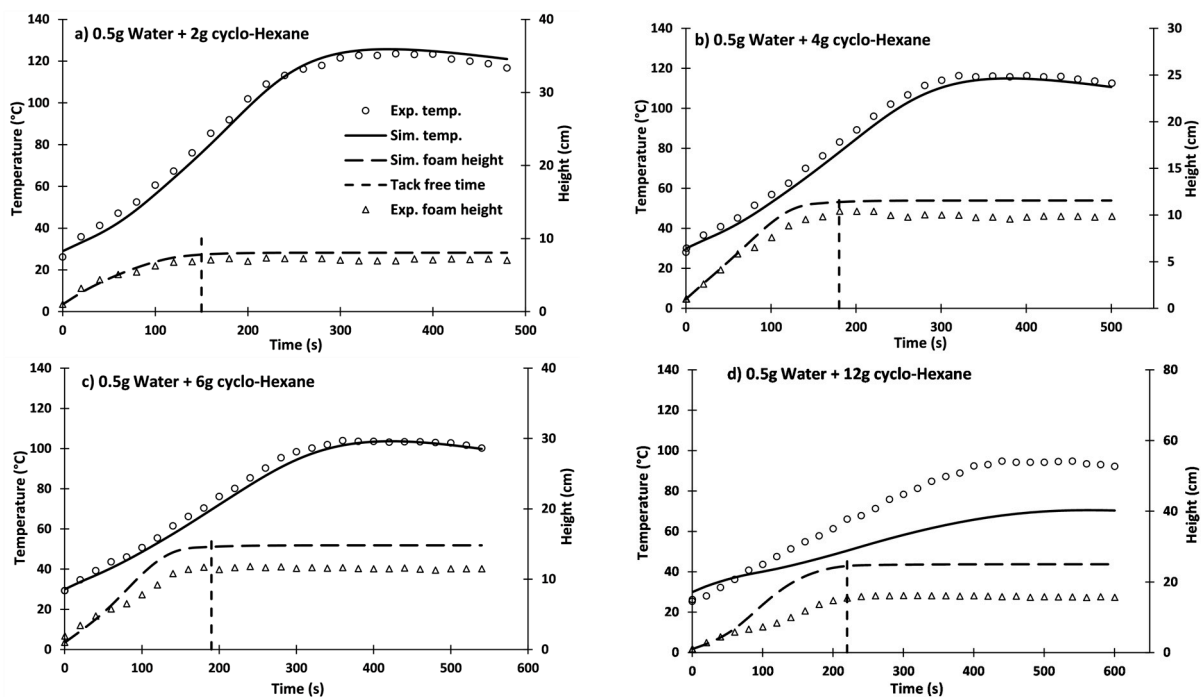

Figure 6. Simulation and experimental results of temperature profile, height profile, and tack-free time of RPUF blown cyclohexane and water (legends are applied to all figures).

4. Limits of Performance

The key aspect of the good blowing agent performance was synchronizing the viscosity of the polymer during foaming with the amount of blowing agent evaporated within the same period. Experimental data of viscosity were plotted versus the percent blowing agent evaporated obtained from the simulation to identify the limits of performance of each blowing agent discussed in this paper, as shown in Figure 7. This figure provides the advantage of predicting whether a specific loading of each blowing agent will return a good foam or foam failure, depending on whether it lies within or outside the window.
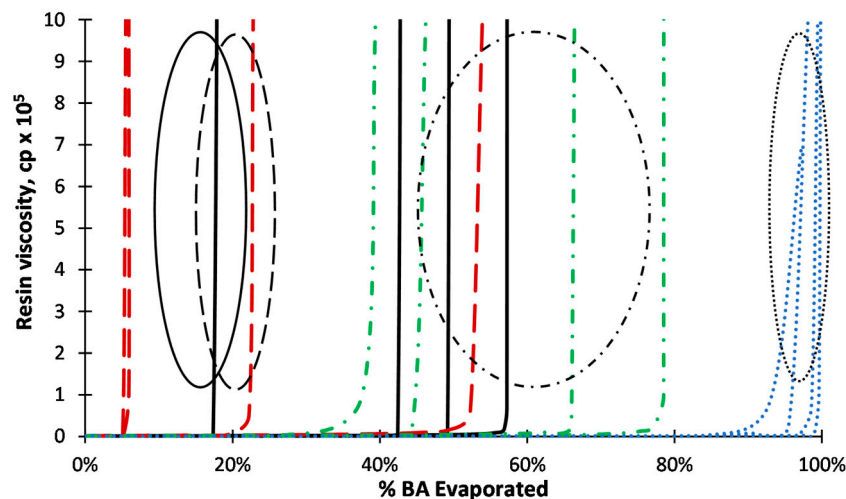

Figure 7. Limits of performance values of polyurethane blowing agents. Straight, long dash, dash-dot, and round dot refer to cyclohexane (black), methyl formate (red), n-pentane (green), and water (blue), respectively.

The above provides the advantage of predicting the limits of performance of any mixture of these blowing agents, as shown in Figure 8. A good foam blown by a mixture of these foams lies within the limits of the two blowing agents. Two different loadings of a mixture of blowing agents were tested. The first experiment used a 3 g n-pentane/3 g methyl formate blowing agent mixture, and the second used a 0.5 g water/4 g n-pentane blowing agent mixture. The limits of performance of the 3 g n-pentane/3 g methyl formate blowing agent mixture were identified within the limits of the two-blowing agent (5–80%), where 40% evaporates and diffuses to the cells to form a foam. The limits of performance of the 0.5 g water/4 g n-pentane blowing agent mixture were identified within the limits of the two-blowing agent (40–99%), where 65% evaporates and diffuses to the cells to form a foam.
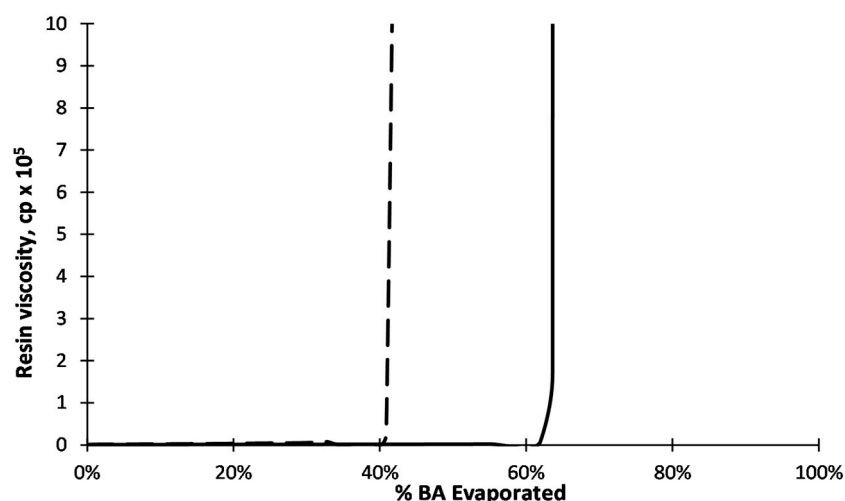
Figure 8. Limits of performance values of polyurethane blowing agents. Straight and long dash refer to (0.5 g water/4 g n-pentane) blowing agent mixture and (3 g n-pentane/3 g methyl formate) blowing agent mixture, respectively.

5. Conclusions

The MATLAB computer simulation code was developed to simulate the limits of performance of blowing agents based on temperature profiles, height profiles, and the tack-free time of rigid polyurethane foam reactions. The limits of performance were measured for water as a chemical blowing agent and n-pentane, methyl formate, and cyclohexane as physical blowing agents at different loadings. The loadings ranged from very low to high loadings to identify the limits where the blowing agent yields good foams in terms of foam density, form failure, and the simulation results where the foaming performance is ideal. The simulation results of % blowing agent evaporated to the cell and resin viscosity for each blowing agent gave the region where a blowing agent loading can produce good foam versus the regions where foams fail. The simulation presents a range of the optimal amount and type of blowing agent where foam failure can be avoided. The current study provides insight into the limits of performance of every blowing agent. It can predict the limits of performance of any mixture of these blowing agents.

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References

1. Field, M.J. Simulating chemical reactions in complex systems. In *Handbook of Numerical Analysis*; Elsevier: Amsterdam, The Netherlands, 2003; Volume 10, pp. 667–697.
2. Ayash, A.A. 2-D parametric analysis of Gas-Liquid Contacting in a Spinning Spiral Contactor. In Proceedings of the 6th International Conference of Fluid Flow, Heat and Mass Transfer (FFHMT′19), Ottawa, ON, Canada, 18–19 June 2019; p. FFHMT 144.
3. Higham, D.J. Modeling and Simulating Chemical Reactions. *SIAM Rev.* **2008**, *50*, 347–368. [CrossRef]
4. Ayash, A.A.; MacInnes, J.M. Mass transfer prediction of gas-liquid contacting in a rotating spiral channel. In Proceedings of the 4th International Conference of Fluid Flow, Heat and Mass Transfer (FFHMT′17), Toronto, ON, Canada, 21–23 August 2017; p. 132.

5.   Zhang, B.; Yi, C.; Wu, D.; Qiao, J.; Zhang, L. A High-Permeance Organic Solvent Nanofiltration Membrane via Polymerization of Ether Oxide-Based Polymeric Chains for Sustainable Dye Separation. *Sustainability* **2023**, *15*, 3446. [CrossRef]

6.   Al-Moameri, H.H.; Ayash, A.A.; Al-Najjar, S.Z.A.; Lubguban, A.A.; Malaluan, R.M. Simulation Study of the Liquid–Solid Multistage Adsorption Process. *Sustainability* **2023**, *15*, 3345. [CrossRef]

7.   Ayash, A.A.; Al-Moameri, H.H.; Salman, A.A.; Lubguban, A.A.; Malaluan, R.M. Analysis and Simulation of Blood Cells Separation in a Polymeric Serpentine Microchannel under Dielectrophoresis Effect. *Sustainability* **2023**, *15*, 3444. [CrossRef]

8.   D'Agostino, D.; Landolfi, R.; Nicolella, M.; Minichiello, F. Experimental Study on the Performance Decay of Thermal Insulation and Related Influence on Heating Energy Consumption in Buildings. *Sustainability* **2022**, *14*, 2947. [CrossRef]

9.   Król, P. Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers. *Prog. Mater. Sci.* **2007**, *52*, 915–1015. [CrossRef]

10. Ionescu, M. Chapter 2-Basic chemistry of polyurethanes. In *Chemistry and Technology of Polyols for Polyurethanes*; De Gruyter: Berlin/Heidelberg, Germany; Boston, MA, USA, 2019; Volume 1, pp. 11–26.

11. Ashida, K. *Polyurethane and Related Foams: Chemistry and Technology*, 1st ed.; CRC Press: Boca Raton, FL, USA, 2006; p. 154.

12. Szycher, M. *Szycher's Handbook of Polyurethanes*; CRC Press: Boca Raton, FL, USA, 2012; p. 1144.

13. Lee, S.-T.; Ramesh, N.S. *Polymeric Foams: Mechanisms and Materials*, 1st ed.; CRC Press: Boca Raton, FL, USA, 2004; p. 360.

14. Cavaco, L.I.; Melo, J.A. *Polyurethane: Properties, Structure and Applications*, 1st ed.; Nova Science Publishers, Incorporated: Hauppauge, NY, USA, 2012; p. 162.

15. Andersons, J.; Modniks, J.; Kirpluks, M. Estimation of the effective diffusivity of blowing agents in closed-cell low-density polyurethane foams based on thermal aging data. *J. Build. Eng.* **2021**, *44*, 103365. [CrossRef]

16. Reghunadhan, A.; Thomas, S. Chapter 1-Polyurethanes: Structure, Properties, Synthesis, Characterization, and Applications. In *Polyurethane Polymers*; Thomas, S., Datta, J., Haponiuk, J.T., Reghunadhan, A., Eds.; Elsevier: Amsterdam, The Netherlands, 2017; pp. 1–16.

17. Mohammed, M.M.; Al-Jarrah, M.M.; Lateef, A.A.A. Effect of NCO/OH on the Mechanical properties of Polyurethane Elastomers. *Al-Nahrain J. Eng. Sci.* **2008**, *11*, 485–493.

18. Brondi, C.; Di Maio, E.; Bertucelli, L.; Parenti, V.; Mosciatti, T. Competing bubble formation mechanisms in rigid polyurethane foaming. *Polymer* **2021**, *228*, 123877. [CrossRef]

19. Ferkl, P.; Kršková, I.; Kosek, J. Evolution of mass distribution in walls of rigid polyurethane foams. *Chem. Eng. Sci.* **2018**, *176*, 50–58. [CrossRef]

20. Eaves, D. *Handbook of Polymer Foams*; Rapra Technology Limited: Shrewsbury, UK, 2004; p. 304.

21. Andersons, J.; Modniks, J.; Kirpluks, M. Modelling the effect of morphology on thermal aging of low-density closed-cell PU foams. *Int. Commun. Heat Mass Transf.* **2022**, *139*, 106432. [CrossRef]

22. Mishra, M. *Encyclopedia of Polymer Applications*; CRC Press: Boca Raton, FL, USA, 2018; Volume 1, p. 2954.

23. Baser, S.A.; Khakhar, D.V. Modeling of the Dynamics of Water and R-11 blown polyurethane foam formation. *Polym. Eng. Sci.* **1994**, *34*, 642–649. [CrossRef]

24. Tesser, R.; Di Serio, M.; Sclafani, A.; Santacesaria, E. Modeling of polyurethane foam formation. *J. Appl. Polym. Sci.* **2004**, *92*, 1875–1886. [CrossRef]

25. Al-Moameri, H.; Zhao, Y.; Ghoreishi, R.; Suppes, G.J. Simulation Blowing Agent Performance, Cell Morphology, and Cell Pressure in Rigid Polyurethane Foams. *Ind. Eng. Chem. Res.* **2016**, *55*, 2336–2344. [CrossRef]

26. Zhao, Y.; Gordon, M.J.; Tekeei, A.; Hsieh, F.-H.; Suppes, G.J. Modeling reaction kinetics of rigid polyurethane foaming process. *J. Appl. Polym. Sci.* **2013**, *130*, 1131–1138. [CrossRef]

27. Shen, L.; Zhao, Y.; Tekeei, A.; Hsieh, F.-H.; Suppes, G.J. Density modeling of polyurethane box foam. *Polym. Eng. Sci.* **2014**, *54*, 1503–1511. [CrossRef]

28. Ghoreishi, R.; Zhao, Y.; Suppes, G.J. Reaction modeling of urethane polyols using fraction primary secondary and hindered-secondary hydroxyl content. *J. Appl. Polym. Sci.* **2014**, *131*, 40388. [CrossRef]

29. Al-Moameri, H.; Zhao, Y.; Ghoreishi, R.; Suppes, G.J. Simulation of liquid physical blowing agents for forming rigid urethane foams. *J. Appl. Polym. Sci.* **2015**, *132*, 42454. [CrossRef]

30. Al-Moameri, H.; Jaf, L.; Suppes, G.J. Simulation approaches for the mechanisms of thermoset polymerization reactions. *Mol. Cat.* **2021**, *504*, 111485. [CrossRef]

31. Ghoreishi, R.; Suppes, G.J. Chain growth polymerization mechanism in polyurethane-forming reactions. *RSC Adv.* **2015**, *5*, 68361–68368. [CrossRef]

32. Zhao, Y.; Zhong, F.; Tekeei, A.; Suppes, G.J. Modeling impact of catalyst loading on polyurethane foam polymerization. *Appl. Catal. A Gen.* **2014**, *469*, 229–238. [CrossRef]

33. Zhao, Y.; Suppes, G.J. Simulation of Catalyzed Urethane Polymerization: An Approach to Expedite Commercialization of Bio-based Materials. *Catal. Surv. Asia* **2014**, *18*, 89–98. [CrossRef]

34. Al-Moameri, H.; Ghoreishi, R.; Zhao, Y.; Suppes, G.J. Impact of the maximum foam reaction temperature on reducing foam shrinkage. *RSC Adv.* **2015**, *5*, 17171–17178. [CrossRef]

35. Fu, Z.; Suppes, G.J. Group contribution modeling of viscosity during urethane reaction. *J. Polym. Eng.* **2015**, *35*, 11–20. [CrossRef]

36. Jaf, L.; Al-Moameri, H.; Ghosh, T. Simulation approach for characterizing the isocyanates reactivity in polyurethane gel reactions. *J. Polym. Res.* **2022**, *29*, 92. [CrossRef]

37. Al-Moameri, H.H.; Jaf, L.A.; Suppes, G.J. Simulation Approach to Learning Polymer Science. *J. Chem. Educ.* **2018**, *95*, 1554–1561. [CrossRef]

38. An, S.; Shen, L.; Suppes, G.J. Group contribution modeling of heat capacities in urethane-forming reactions. *Fibers Polym.* **2017**, *18*, 1031–1039. [CrossRef]

39. Al-Moameri, H.; Ghoreishi, R.; Suppes, G. Impact of inter- and intra-molecular movements on thermoset polymerization reactions. *Chem. Eng. Sci.* **2017**, *161*, 14–23. [CrossRef]

40. Al-Moameri, H.; Jaf, L.; Suppes, G.J. Viscosity-dependent frequency factor for modeling polymerization kinetics. *RSC Adv.* **2017**, *7*, 26583–26592. [CrossRef]

41. Kolodziej, P.; Macosko, C.W.; Ranz, W.E. The influence of impingement mixing on striation thickness distribution and properties in fast polyurethane polymerization. *Polym. Eng. Sci.* **1982**, *22*, 388–392. [CrossRef]