Rapid Development of Rigid Foam Systems thru Use of Computer-Aided Simulation

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ABSTRACT

In today's slow economy, one particular market that is hard hit is the construction industry. With the down turn in construction start ups went the demand for insulation, of which polyurethane foams have a significant market share. Despite the stimulative efforts by the federal government to encourage energy conservation, insulation seems low in demand. Thus, lean staffed R&D organizations must find ways to develop new foam products in anticipation of an economic upturn. In this regard, a recent development from Principle Product Development Group is a polyurethane simulation tool, which allows formulating chemists to make pre-calculations and evaluate polyurethane systems quickly to a targeted isocyanate index and component ratio. This paper focuses on the use of the recently commercialized web-based simulation software called GoFormulate™ for designing, developing, and commercializing polyurethane systems with emphasis on the foam simulation module component.

INTRODUCTION

In a recent survey conducted online by SpecialChem4coatings.com, over two-thirds of responders indicated that they are willing to outsource their formulation work for one reason or another. For over 40% of responders, the main reason is to help with innovation. In order for understaffed R&D organizations to have higher throughput, it becomes necessary to have efficiency tools and/or embrace a culture of open innovation to leverage expertise across other organizations.

Principle PDG specializes in partnering with other organizations as well as in developing knowledge-based efficiency tools for use in product development. GoFormulate™ was developed with the idea in mind of not only pre-calculating composition as a function of targeted isocyanate index and component ratios in isocyanate-reactive systems, but to also pre-calculate free-rise density in case of foams as a function of a hypothesized exotherm temperature. By having this ability, rapid development of foam systems has become possible.

In order to effectively use the GoFormulate™ software, it requires the user have a working knowledge of structure-property relationships. However, with mentoring from a seasoned formulator who has a full grasp of structure-property relationships, a raw chemist can quickly become a proficient formulator.

In this paper, case studies are presented on the simulation of several polyurethane rigid foam systems and how they impacted the project development timeline. The foam systems were first simulated, tested, and surprisingly, in some instances, fit for immediate commercialization.

OBJECTIVE

The objective of this paper is to demonstrate that simulation can reduce product development time and bring foam products to market quicker. Five foam systems, which are all water-blown, with different free rise densities were simulated on the GoFormulate™ software. While targeting certain free rise densities, the goal was also to achieve whole number, process friendly ratios such as 1:1 or 1:2 by volume at a pre-determined isocyanate index.

EXPERIMENTAL

The GoFormulate™ simulator raw materials database was pre-populated with commercially available components that are used or potentially useful in foam formulations. The simulation begins with identifying and selecting key raw materials with the application in mind. Thus, for rigid foam system, high hydroxyl- number polyols and polymeric MDI are necessary.

Where fire rating is required, flame retardants are added. Other components such as catalysts, surfactants, and blowing agents are also included.

The data for each raw material that are used for the calculations are milliequivalents per gram (calculated from equivalent weight, hydroxyl number or percent NCO for the isocyanates), specific gravity, and price. They are part of the raw material database that is automatically used in the pre-calculation when the raw material is entered for the simulation.

After identifying and selecting key raw materials, they are entered and given hypothetical amounts in the formulation page. The amounts can later be changed in an iterative process as the changes are used to balance the system to achieve a certain isocyanate index, free rise density, and volume ratio.

Alternatively, starting point formulations, which are ubiquitous in the open literature, could be used and modified to achieve the targeted index, free rise density and volume ratio.

Table 1 below summarizes the list of the targeted foam systems. The systems are all water blown and targeted to a round number volume ratio, such as 1:1 or 2:1 with the idea that these ratios can be processed in lower cost application equipment. With the exception of the 0.5 lb/ft^3 foam, all the polyurethane systems were targeted to 110 isocyanate index while the polyisocyanurate system was targeted to greater than 200.

Table 1. Summary of Targeted Foam Systems.

Target Free-rise Density (lb/ft^3)	System Type	Iso Index	Primary Blowing agent	Application
0.5	Spray PUR 1:1 v/v	--*	Water	Spray Insulation
1.7	Pour PIR 2:1 v/v	>200	Water	Panel Insulation
2.0	Spray PUR 1:1 v/v	110	Water	Spray Insulation
3.5	Pour PUR 1:1 v/v	110	Water	Concrete lift
10.0	Pour PUR 1:1 v/v	110	Water	Composite Panel

*Not targeted.

Once the target densities, indexes and volume ratios are met in the simulation, the systems are prepared in the lab and evaluated. For fast reacting systems, the B-sides were prepared with exclusion of the catalyst. This allows the A side to be pre-mixed with the B-side in a cup, followed by the addition of the required amount of catalyst with a syringe. The reactivity profiles of each system were noted and the foams tested for density and compressive properties. Density was measured by cutting foam into a cuboid with a band saw, weighing and measuring the dimensions to obtain the volume. Compressive strength was measured according to ASTM D1621.

RESULTS AND DISCUSSIONS

The simulation is a user driven iterative process which relies on the user's experience to develop new formulas or to modify existing ones that may closely resemble the target foam system. Table 2 summarizes the final compositions that were obtained after the simulation. When the densities of the foams obtained were plotted versus the water content in the B-side of the systems, the graph shown in Figure 1 is obtained. The R^2=0.99 indicates a high degree correlation which allows a high level of confidence in predicting foam density based on the amount of water used for blowing.

Half Pound Foam Formulation

The simulations indicate that water-blown, half pound foam formulation could not have an index greater than 100 where isocyanate equivalents exceed that of active hydrogens. This is because the B-side has so much water that there is more than enough to convert all the isocyanate into CO_2 and amines, which could otherwise prevent formation of urethane or urea linkages. In reality, this low density foam system has a very fast reactivity profile and the exotherm temperature reaches the point where water becomes steam. Because steam formation is necessary for the blowing process, low density systems where low reactivity are required such as in pour foam applications, may be difficult to achieve if the exotherm temperatures do not reach the boiling point of water.

Another discovery in the simulation and experimentation cycle for the half pound foam is that the theoretical and actual foam densities are not equal. This is because the foam is open-celled. In the process of blowing, some of the water vented out and was not used to its full potential for expanding the foam. Thus, the foam resulted in a higher density. In order to achieve the actual 0.5 lb/ft^3 density, the system needed to be targeted to a theoretical density of 0.4 lb/ft^3. When simulated to a theoretical density of 0.5 lb/ft^3, the experimental density obtained was 0.66 lb/ft^3.

Table 2. Summary of Final Compositions from Simulation.					
Ref. #	4-046	4-045	4-044	4-033	4-028
Target Free Rise Density (lb/ft^3)	0.4	1.7	2.0	3.5	10.0
Hypothesized Exotherm Temp (ºC)	110	140	170	150	120
Polyol 1 (OHv=94)	29.67%	15.00%	--	--	--
Polyol 2 (OHv=240)	--	--	--	17.00%	--
Polyol 3 (OHv=280)	--	10.65%	32.17%	58.79%	--
Polyol 4 (OHv=490)	4.35%	--	18.80%	17.06%	31.27%
Glycerin	--	--	--	--	6.32%
Flame Retardant 1	39.57%	60.00%	40.00%	--	--
Flame Retardant 2	--	--	--	--	20.08%
Flame Retardant 3	--	--	--	--	20.08%
Flame Retardant 4	--	--	--	--	20.08%
Dispersant	--	--	--	--	0.12%
Catalyst 1	4.95%	--	--	--	--
Catalyst 2	--	0.87%	--	--	0.30%
Catalyst 3	--	2.14%	--	--	--
Catalyst 4	--	1.17%	--	--	0.45%
Catalyst 5	--	--	4.50%	4.50%	--
Silicone Surfactant 1	1.09%	3.30%	1.98%	0.75%	0.60%
Silicone Surfactant 2	--	1.00%	--	--	--
Non-silicone surfactant	1.09%	--	0.70%	--	--
Water	19.29%	5.87%	3.72%	1.90%	0.70%
Polymeric MDI Index	39	207	110	110	110
REACTIVITY PROFILE					
Cream Time (min:sec)	0:05	0:22	0:06	0:09	0:40
String Gel Time (min:sec)	0:15	1:15	0:20	0:22	1:20
Free Rise Time (min:sec)	0:22	1:44	0:35	0:35	1:51
Tack Free Time (min:sec)	0:22	1:35	0:28	0:28	1:33
PROPERTIES					
Appearance	Clear	Clear	Clear	Clear	White viscous
B-side viscosity(cP @ 25 ºC)	64	80	592	1,856	12,170
Free Rise Density,lb/ft^3	0.56	1.72	2.08	3.49	10.1
Compressive Strength, psi (parallel to rise) @ 10% deflection	ND	24	22	83	253
Compressive Strength, psi (perpendicular to rise) @ 10% deflection	ND	11	15	43	148

1.7 lb/ft^3 Pour Polyisocyanurate Foam Formulation

The rationale for all water-blown PIR system was the high thermal resistance of PIR foams and the avoidance of the use of flammable hydrocarbon blowing agents. However, the simulator indicated that it was not possible to have indices near 300 where thermally resistant PIR systems are typically formulated. The high water amount increased demand for isocyanate, which made it impossible to simultaneously meet both the volume ratio requirement and the high index. Thus, a compromise must be made.

The simulation made it possible to determine what is achievable. It indicated that when the constraints were set to 1:1 or 2:1 (A:B) volume ratio and the index was targeted to greater than 200, there is a limit in the density of water-blown PIR systems that could be achieved. At a 1:1 volume ratio and a minimum index of 200, the minimum theoretical density that can be achieved is 2.0 lb/ft^3, while a 2:1 volume ratio can afford the sought after 1.7 lb/ft^3 density foam. The 2.0 lb/ft^3 was not sought because it would lead to higher density panels because of the compression required in the production.

In the process of simulation-experimentation cycle, it was discovered that the simulator indicates a need for low hydroxyl polyols in order for the calculations to work out to meet the constraints. The low hydroxyl polyols are not typically used or even considered for use in rigid foam systems. However, upon preparing the foams as the simulator prescribed, good quality rigid foams with low friability were obtained. Increasing the amount of none reactive components can also help meet the constraints, but it cannot circumvent the need for low hydroxyl polyols.

The next round of experimentation revolved around identification and optimization of catalyst package in order to have a reactivity profile that can be processed in the lamination equipment. In this case the foam is fabricated into panels without facers. This offers an advantage to custom laminators who prefer to bond facings onto smooth surfaced panels instead of those derived from slicing of slab stock. They find the bond strength is better when the facings are adhered to a smooth surface rather than to a porous foam surface.

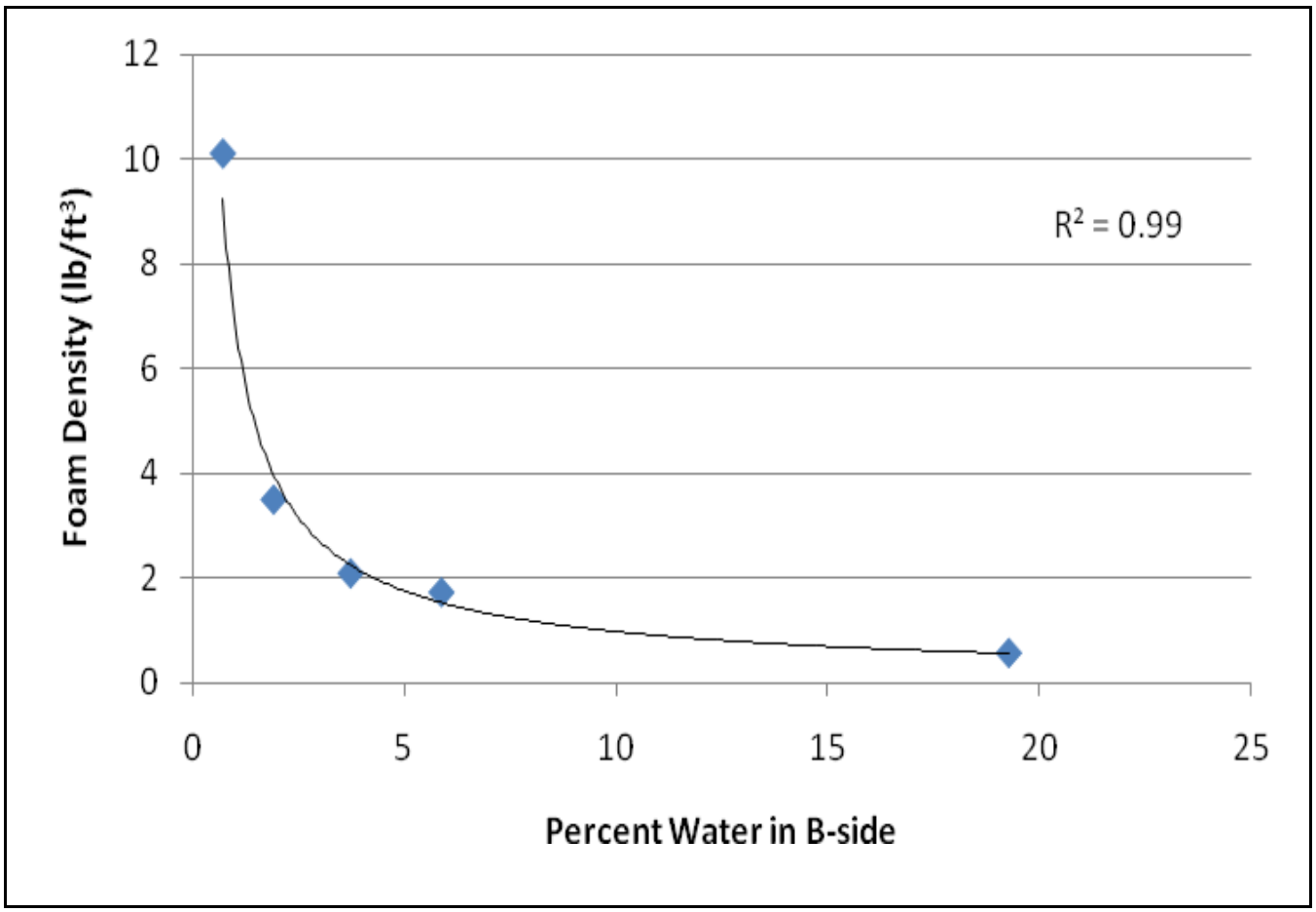

Figure 1. *Foam Density as a function of Water Content in the B-side.*

Two-Pound Spray Polyurethane Foam Formulation

Although they have low Ozone Depleting Potential (ODP), HFC blowing agents such as 245fa are presently scrutinized for their Global Warming Potential (GWP) and are targets for eventual phase out as mandated by the Kyoto Protocol. Though the United States is not a signatory to the protocol, the political climate appears to make that favorable to happen.

Until cost effective blowing agents with low ODP and GWP are developed, water and hydrocarbons are front-running alternatives. Due to the flammability of hydrocarbons, the development of a 2-pound water-blown spray foam for insulation was the alternative chosen.

The use of water as blowing agent poses some interesting challenges. Under high pH conditions that come from the combination of water and amine catalysts, polyester polyols in the B-sides of foam systems are susceptible to hydrolysis under storage conditions. This negatively impacts the reactivity profile and quality of the foam. Thus, polyether polyols are the preferred polyols.

Simulation of a two-pound water-blown spray foam was easily achieved with the GoFormulate™ simulator. There were many possible variations using combinations of polyether polyols with different hydroxyl values. When this is the case, other screening criteria come into consideration such as flame retardant properties, dimensional stability, compressive strength, reactivity profile, and raw material viscosities, but these are beyond the capabilities of the simulator. Thus, formulating chemists will have to rely on their understanding of structure-property relationships in order to recognize the preferred raw materials and the best candidates to use as starting points. If there are several good candidates, design of experiments can be implemented whereby all the candidates are included in the design space.

Alternatively, rather than addressing all the target properties in a large design of experiments, the properties that are most easily derived were addressed first. Typically these are the reactivity profile and dimensional stability, which are modulated by catalysts and surfactants. These constitute less than 5% by weight of the overall system formula. Use of a master batch process is the most effective way to screen, identify and determine the proper loading of the catalyst and surfactants. This accelerated the development process in that many variations of catalysts and surfactants were quickly evaluated. The same process was used to home in on the other desirable properties.

3.5 lb/ft^3 Polyurethane Pour Foam Formulation

The 3.5 lb/ft^3 polyurethane pour foam formulation was another easily simulated system. Like the 2-pound foam and others at higher densities, many formula variations can be derived thru simulation. Because the intended application is for concrete lifting, a foam system with superior compressive strength is necessary. This is coupled with the need for low viscosity components so that they can flow easily to fill the voids underneath the structure to be elevated.

This application does not require flame retardant properties which made the development more expedient. The simulation allowed the rapid development of a starter formulation from which to refine for the appropriate reactivity profile and foam cell structure. Using the master batch process as discussed in the previous section, the catalyst and surfactant packages were quickly identified and the formula was scaled up for evaluation in the application process equipment. Based on feedback from the application, the formula was adjusted slightly to accelerate the reactivity profile and it was ready for field trial. The field trial was successful and the product is now commercial.

Ten-Pound Polyurethane Pour Foam Formulation

The ten-pound polyurethane pour foam is a filled system that is designed to be processed thru a laminator for producing structural composite panels. The10 lb/ft^3 free rise system is processed to a density of 16 lb/ft^3. It is a flame-retarded system for use in the sub-flooring of buses, trains, buildings and homes. A starter formulation was already available, but it had short comings with high viscosity and insufficient flexural strength. The starter formulation was too viscous because of the large amount of fillers used in the B-side to achieve the level of flame retardants needed to pass certain fire tests. The high viscosity affected the wetting of the fiberglass webbing, which directly impacted the flexural strength.

In order to improve the wetting, it was necessary lower the B-side viscosity. Because the combination of filler loading and high polyol viscosity are the primary causes of the high viscosity, the obvious remedies to decrease the viscosity were to either decrease the filler loading, adjust the change the polyol, or a combination of both. Each potential solution was its own drawback.

By using a combination of synergistic solid flame retardants, the filler loading was decreased. However, with the decreased filler loading, the B-side density decreased, but the hydroxyl number increased. The decrease in B-side density means more A-side (isocyanate) is needed to maintain the 1:1 volume. Although the reduction of fillers increases the hydroxyl number of the B-side and therefore also increases isocyanate demand, the simulation indicated that it was not sufficient to offset the increased index. Thus, it was necessary to find a lower equivalent weight (higher hydroxyl number) polyol which does not greatly impact the total volume of the B-side.

Glycerol was found to fit this requirement because it is also low cost and trifunctional, which did not negatively impact the flexural properties. The reduction of filler content was sufficient to lower the viscosity and improved the flexural properties of the sandwich panel. This made it no longer necessary to explore the adjustment of the polyol blend as a means of lowering the viscosity.

Today the 10-pound foam system is being used to manufacture 4'x8'x0.7" skin-core-skin composite panels for various assembly applications.

CONCLUSIONS

The GoFormulate™ simulation software is a very powerful tool for use in developing isocyanate reactive foam systems. It helps the formulator to intuitively identify raw materials that are needed to achieve the desired result. It also allows the formulator to determine if it is possible to achieve a certain foam system. The ability to electronically archive formulations allows ease of retrieval and modification into another product. Overall, the simulator speeds up the product development process and helps bring products to market quicker. All the products discussed were developed within a period of a few months and are either commercial or on the verge of being commercial. Another benefit of the simulation software allows for consolidation of raw materials so that a wide variety of products can be prepared from a narrow set of raw materials. This gives leverage in pricing by allowing purchasing in volume.

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BIOGRAPHY

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Augusto (Gus) is a Senior Scientist at Principle Product Development Group. He holds a Doctorate of Philosophy degree in Organic Chemistry from the University of South Florida. He has worked with polyurethanes for over 20 years and recently joined Principle PDG. He is responsible for product development with special emphasis on isocyanate reactive systems such as PUR and PIR foams and CASE applications. He developed the pre-cursor working models that were converted into the GoFormulate™ simulation software. Principle PDG is an open innovation organization that seeks to partner with companies having similar technological interests for mutual benefit.