ABSTRACT
Obtaining low density (less than 30Kg/m$^3$) foams in all water blown MDI based foams without compromising mechanical performance (Tensile strength and Tear Strength) and compression sets has been a significant challenge for Polyurethane foamers. While it is straightforward to make such foams with TDI, with MDI it becomes very difficult. In this paper we present low density MDI based foams with Dow’s proprietary technology.

INTRODUCTION
MDI based polyurethane foams offer some distinct advantages over TDI based systems. These advantages include superior flame retardance, ability to obtain harder grades without the usage of copolymer polyols, lower density and hardness variation across a bun, faster cure times and lower EH&S risks [1-4]. However, a big challenge with MDI based systems is to obtain durable foams at low densities (less than 30Kg/m$^3$) in all water blown formulations. It might still be possible to obtain lower densities in MDI based systems using auxiliary blowing agents [5] or through the use of variable pressure foaming systems [6, 7]. These technologies may require additional capital investments and may be proprietary technologies. For all water blown polyurethane foams the usage of very high ortho para monomeric MDI containing MDIs maybe a good proposition as can be noted from a few patents in the area [8, 9]. Here we showcase an approach to create MDI foams of low densities using lower amounts of op MDI content with just water as a chemical blowing agent.

Low density MDI based systems could provide significant benefits over a TDI based system in manufacture of tall (> 2 meters tall) cylindrical foams for laminated foam applications. The quick through put times due to faster MDI cure and low hardness and density distribution can help develop cheaper and uniform foams for such applications.

HARD PHASE OF MDI BASED SYSTEMS:

One of the significant reasons why it is so difficult to create the MDI based foams of low density is the large increase in the amount of water that is required to get to low densities in such foams. After approximately four parts of water per hundred parts of polyol of the formulation it becomes increasingly difficult to reduce density by further increases in water. Furthermore, the amount of hard segments approximately increases linearly with the amount of water. This causes the urea content to rise rapidly with very little gains in reduction of density. Hence it becomes a case of diminishing returns when high amounts of water are used to reduce the density of MDI based foams. Figure 1 below shows the theoretical variation of density of TDI and MDI based foam as a function of water of the formulation. In making the graph a best case scenario is assumed that all the water of the formulation converts into carbon dioxide which is completely used to blow the foam to get to a low density. This is the assumption of perfect blowing efficiency. In reality the blowing efficiency of polyurethane foams formulations is less than perfect. This causes the actual density of foams to be higher (in some cases significantly higher) than what is predicted to be theoretical minimum.

As can be noticed from Figure 1 to theoretically obtain a 20 Kg/m$^3$ MDI based foam approximately 5 parts of water per hundred parts of polyol have to be used as compared to approximately 4 parts per hundred parts of polyol in case of TDI based foams. It should also be noted that the molecular weight per molecule of urea for a MDI based foam is higher.
than TDI based urea. This is due to the higher molecular weight of a MDI molecule compared to TDI. These factors cause the amount of urea hard phase in MDI based foams to be significantly higher than TDI based foams. Theoretically the weight fraction of urea hard phase increases from around 22% in case of TDI based foams to about 35% in case of MDI based foams. As these are theoretical numbers the actual numbers will be even higher due poorer than perfect blowing efficiencies of polyurethane formulations.

The higher weight fraction of urea hard phase in MDI based foams will cause the foams to be harder than corresponding TDI based formulations, they will have poorer resiliencies and very poor compression sets.

Figure 1: Theoretical variation of density and mass fraction of urea as a function of water in the formulation.

Another set of challenges that MDI based formulations have over TDI based systems is due to the presence of higher oligomers which can cause poor hard phase organization in MDI based systems. The higher oligomers also increase the functionality of the isocyanate to greater than two. Higher functionality of the isocyanate may cause faster reactivity and gelling kinetics. MDI based systems have in general faster reactivity than TDI based systems. With increased amounts of water in the formulation, problems may arise such as too fast a reactivity profile to obtain good processing characteristics.

DOW’S PROPRIETARY SYSTEM:

We have been able to develop a patent pending all water blown MDI based formulation that allows us to make low density (< 30Kg/m³) foams with good foam properties. In

Figure 2 below the control represents a standard MDI formulation where attempt has been made to reduce the density in all water blown formulations to below 25Kgs/m³. As can be noticed the compression sets, resiliency, tear strength and tensile strength are all severely compromised at this low density. Furthermore the reactivity rates are too fast to allow for good processibility. It should be noted that density of a polyurethane foam may depend upon the altitude above sea level where it is made due to the changes in atmospheric pressure with altitude. For reference the experiments of Figure 2 were performed at a lab with altitude of around 750 meters above sea level where the atmospheric pressure is approximately 8% lower than at sea level.

With our new formulations we have been able to significantly improve compression sets (90%) to below 10%. We have been able to substantially increase Tear and Tensile strength (in some cases greater than 100%). Significant improvements are also made in resiliency where improvements as high as 45% have been made. Refer
CONCLUSION:

MDI based polyurethane foams offer some distinct advantages in performance compared to TDI based formulations. These advantages include superior flame retardance, ability to obtain harder grades of foams without the usage of copolymer polyols, lower density and hardness variation across a bun, faster cure times and lower EH&S risks. However, a great challenge with MDI systems has been to create durable low density foams. To obtain low density MDI based foams one must overcome the challenge of diminishing returns of using water for blowing above four parts of water per hundred parts of polyol, high hard phase content, reduced blowing efficiencies, poor compression sets and poor mechanical strength. With Dow’s patent pending technology based on unique formulations we have been able to overcome some of these significant challenges.

REFERENCES:


BIOGRAPHIES

Venkat Minnikanti

Venkat Minnikanti got his Bachelor's in Technology in Chemical Engineering from Indian Institute of Technology, Kharagpur, India (1999). He obtained his Ph.D. in Chemical Engineering from Cornell University (2006). He has been working with Dow Chemicals since 2007. He is currently working in Polyurethane R&D.

Bruno Motta

Bruno Motta has a chemical engineering degree at Universidade de Sao Paulo (2006) and a master in chemical engineering in the polyurethanes area (2011). Bruno has worked in Dow Brazil for 5 years doing technical services and development of new products in the polyurethanes business, his work was mostly concentrated in flexible foam applications.

Rogelio Gamboa

Mr. Rogelio R. Gamboa completed 2 years of Chemical Technologist program at Brazosport College. He joined The Dow Chemical Company in 1989. He has had various assignments as a technologist in both the process and product R&D and manufacturing. He is currently working in flex foams technology development for the PU TS&D/R&D groups.