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Regulation of Cell Structure in Water Blown Rigid Polyurethane Foam

*Pravakar Mondal, D. V. Khakhar**

Department of Chemical Engineering, Indian Institute of Technology, Bombay,
Mumbai-400076, India
E-mail: khakhar@che.iitb.ac.in

Summary: Rigid polyurethane foams are generally "closed celled" with a gas entrapped in each cell. The properties of such foams are significantly affected by the cell size distribution and morphology of the cells. For example, in thermal insulation foams, small cells lead to lower thermal conductivity and in foams for buoyancy applications, stronger cell windows are resistant to ingress of water until higher hydraulic pressures. The effect of formulation parameters on the size and structure of rigid polyurethane foams was investigated. Foams were made with different surfactants, with variation of surfactant concentration at different blowing agent concentration, with variation of nucleating agent concentration and with variation of catalyst concentration. Micron sized silica particles were used as nucleating agent. The densities of the foams were in the range of 140 to 165 kg/m^3. The cell window areas of different foams have been measured. The bubble size in the polyol depends on the surface tension lowering ability of a surfactant, and the entrainment of a large number of small bubbles during mixing leads to a foam with a small cell size and a narrow cell size distribution. Increasing the concentration of the surfactant reduces the cell size and narrows the distribution. Increasing the proportion of organometallic catalyst in the amount of total catalyst used, results in smaller cell sizes, which are narrowly distributed. Hydraulic resistance of the foams was monitored by measuring buoyancy losses at different hydraulic pressures. Hydraulic resistance of the foams can be improved by decreasing the area and increasing the thickness of the cell windows.

Keywords: cell size; cell window area; polyurethanes; rigid foam; structure-property relations

Introduction

Polyurethane is an important synthetic polymer used as flexible foam, rigid foam, elastomer, sealant and coatings.[1, 2] For making water blown rigid polyurethane foam, initially the polyol is

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mixed with water, catalysts and surfactant. Then the polyol mixture is mixed with isocyanate to react. During each mixing step some air bubbles are introduced into the mixture and they serve as nuclei for foam cells. Water reacts with isocyanate and initially produces carbamic acid, which decomposes to an amine and carbon dioxide. This carbon dioxide diffuses to the already present air bubbles and hence foam rises due to the increase in bubble size. At the same time, viscosity of the medium increases with polymerization and gelation. The role of the surfactant is to stabilize gas bubbles. Silicone based surfactants are generally used for polyurethane foams. They are polydimethyl siloxanes on which random or block copolymers of ethylene or propylene oxide are grafted.[3, 4] The surface tension lowering ability of these silicone surfactants mainly depends on the silicone/polyether ratio of the surfactants.[5, 6] Catalysts are added to accelerate the reactions according to the requirement and to establish a balance between the network formation and the blowing reaction. Tertiary amines are catalysts for both the blowing and network formation, whereas organometallic catalysts catalyze mainly the isocyanate-hydroxyl reaction.[7-9] When the gas volume fraction exceeds 74%, dispersed spherical bubbles deform into multisided polyhedra.[5, 10] These individual polyhedra are called cells in the final foam. A cell window is the lamella of the foam material that separates two adjacent cells. A strut is generated where three windows of three different cells meet. Due to high gas pressure inside the cells, fluid drainage occurs and thereby the cell windows become gradually thinner. The enhanced viscosity of the medium slows the cell window drainage. Added surfactant also has an important role to reduce cell window drainage by reducing the surface tension and hence gas pressure inside the bubbles. Clearly formulation components could have a significant effect on the cell size distribution and other geometrical parameters of the foam. These in turn affect foam properties. For example, in thermal insulation foams, smaller cell sizes result in lower thermal conductivity.[11] Aging of these foams is related to the diffusion of entrapped gas through the cell windows and thus directly depends on the window thickness. Rigid foams used for buoyancy applications need to be resistant to uptake of water at high hydraulic pressures. The thickness and thus strength of the cell window determines the maximum pressure the foam can withstand.[12]

The basic objective of this work was to understand the effect of formulation parameters on the cell structure of the foam and how cell structure affect hydraulic resistance of the foam. Foams were made with different surfactants, with variation of surfactant concentration at different blowing agent concentration, with variation of nucleating agent concentration and with variation of catalyst concentration. Foams were characterized for cell window area, strut width and hydraulic resistance besides measurement of surface tension and bubble size in the polyol mixture.

Experimental

Raw Materials

The raw materials required to make water blown rigid polyurethane foam are polyol, isocyanate, catalysts, and surfactant. The polyol used was a sucrose based polyether polyol (DC 9911, Huntsman International, India). The polyol had a hydroxyl number 440 mg of KOH per gram of the polyol and an equivalent weight of 128 g/mole. The isocyanate was a polymeric diphenyl methane diisocyanate (MDI) (SUPRASEC 5005, Huntsman International). The isocyanate had an equivalent weight of 132 g/mole. The catalysts used were dibutyltin dilaurate (DBTDL) (Lancaster, England) and triethanolamine (TEA) (Spectrochem, India). Silica was procured from spectrochem, India. Tegostab B8404, silicone surfactant, was donated by Goldschmidt AG Germany. Atsurf 3315 and Cresmer B246M, polyether surfactants, were donated by ICI India. All materials were used as received without further purification.

Foam Formation

Polyol mixtures were prepared by stirring the 250 g of polyol containing different weight percentage (of the polyol) of water, catalysts and surfactant for half an hour. Then each polyol mixture was mixed thoroughly with predetermined amount of isocyanate for 15 seconds using a high-speed stirrer. The same speed was maintained for all formulations. Immediately the mixture was poured into a mould, which was kept at room temperature for 15 minutes. The foam was removed from the mould and all characterizations were done after curing the foams at room temperature for at least one day. All foams were made with an isocyanate index of 105. The densities of the foams were in the range of 140 to 165 kg/m^3.

Characterization

Surface tension of the polyol and solution of the surfactants (3 weight percent) in polyol were measured by Du Nouy Ring Tensiometer (Fisher Surface Tensiomat; Model 21). The average bubble size in the polyol containing one percent water and three percent surfactant was measured by using an optical microscope (Model BX60 Olympus). A drop of the polyol mixture after stirring for 20 minutes was taken over a glass slide and covered with a cover slip. Images were captured by an on-line CCD video camera (Model XC 77CE Sony) and frame grabber (Model Occulus MX, Coreco). All solutions were stirred at the same speed at which all foams were made. The average bubble diameter of the 400 bubbles was measured using an image analysis software (Image Pro Plus version 4.1). The cell window area and the strut width distributions were measured using the same transmission optical microscope. Thin slices, less than 1 mm, were cut from each foam sample and images were captured. The captured images were analyzed to measure cell window area and strut width by manually selecting the window area and strut width using the same image analysis software. Only those cell windows for which the whole window came into focus was taken. 70 measurements were made for each foam.

For hydraulic resistance measurement four samples of cubical shape with side 45 to 48 mm were cut from each foam. The weight of the samples was measured and then the samples were immersed in a sealed container filled with water. The container was connected to a pressure gauge. The pressure inside the container was raised to a specific value using a hydraulic hand pump. After one hour the foam samples were taken out and water from the surface of the samples was removed by a piece of cloth and again weighed. During this one hour the pressure was found to decrease due to water absorption by the foam samples. Thus at 5,10,15,20,25,30,40,50,55 minutes the pressure was checked and if there was any drop, the pressure was raised to the specified value. The percentage buoyancy loss was calculated by using the following formula,

$$percentage\ \ buoyancy\ loss = \frac{\rho_f' - \rho_f}{\rho_w - \rho_f} \times 100$$

where ρ_f, ρ_f' ρ_w are the initial foam density, density of the foam after water absorption and the density of water respectively. The percentage buoyancy loss was measured for different hydraulic pressures in the range of 0 to 3 MPa.

Gel time was measured as follows. Initially the polyol mixture was prepared and then that was mixed with isocyanate for 15 seconds. A glass rod was vibrated into the reacting mixture. The point at which the mixture became stiff was considered as gel point. The gel time is the time between the start of mixing and the gel point.

Results and Discussion

a) Effect of Different Surfactant

Four foams were made for this part of the work. One of them was without any surfactant and the remaining three were with three different commercially available surfactants. In the formulations, the polyol contained 0.5% DBTDL, 0.5% TEA, 1% water and 3% respective surfactant. The surface tension of the polyol was 36.2 mN/m and with Atsurf 3315 it was 37.8 mN/m. The surface tension of the polyol with Cresmer B246M was 30 mN/m. Tegostab B8404 further lowered this value to 22 mN/m. The bubble size decreased with decrease in surface tension of the polyol. The average bubble diameter in the polyol was 57±24 μm, in Atsurf 3315 54±21 μm, in Cresmer B246M 44±17 μm and in tegostab B8404 27±9 μm. The distribution of cell window area of different foams has been shown in figure 1. Note the scales along x-axis for different foams are different. The average and standard deviation are given in each graph. The cell window areas of the foams with no surfactant and with Atsurf 3315 are very large and they are very widely distributed. Compare to these foams, the foams with Cresmer B246M and Tegostab B8404 have very small cell windows and their cell windows are very narrowly distributed. The cell windows of the foam with Cresmer B246M are bigger and the distribution is wider than that in the foams with Tegostab B8404. The strut width distribution pattern is similar to the distribution of cell window area. The average strut width in the foams with no surfactant and with Atsurf 3315 are 52±9 and 52±7 μm respectively. Whereas in the foams with Cresmer B246M and with Tegostab B8404 the average strut width are 41±6 and 25±4 μm respectively.

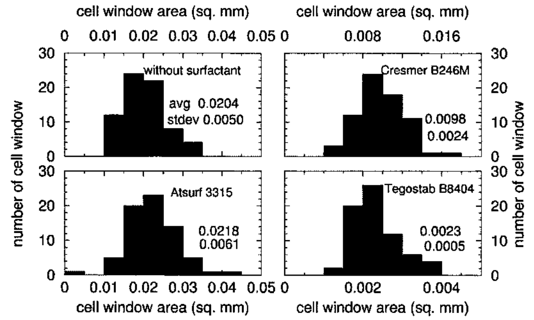

Figure 1. Effect of different surfactants on the distribution of cell window area. The average cell window area (avg) and the standard deviation (stdev) are indicated in each graph.

The above results indicate that a lower surface tension of the polyol mixture generates finer cells with a narrower distribution. The effect seems to be primarily due to a larger number of fine bubbles entrained during mixing. The effect of cell structure on hydraulic resistance of the foams is shown in figure 2. The error bars represent standard deviation for four samples. Lower

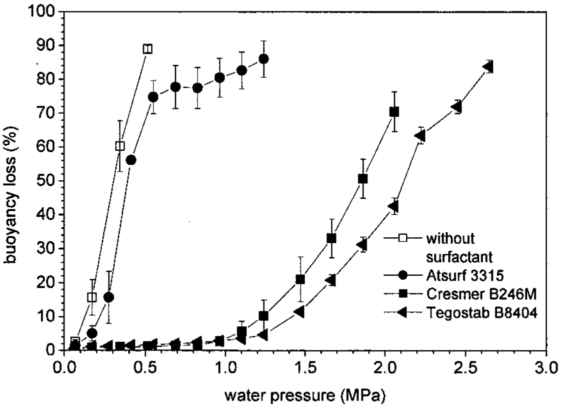

Figure 2. Effect of different surfactants on the hydraulic resistance of the foams. The error bar represents standard deviation for four samples.

the buoyancy loss higher is the foam's hydraulic resistance. The figure shows that foams with no surfactant and with Atsurf 3315 have very poor hydraulic resistance. The hydraulic resistance of the foams with Tegostab surfactant is more than that of the foam with Cresmer B246M. Thus hydraulic resistance of the foams increases with decrease in cell window area.

b) Effect of Surfactant Concentration at Different Water Concentration

For this part of the work nine foams were made. In the formulations, the polyol contained 0.5% DBTDL, 0.5% TEA. The amount of water and surfactant (Tegostab B804) are mentioned in the foam nomenclature. For example, foam XwYs was made with X% of water and Y% of surfactant.

The distribution of the cell window area is shown in figure 3. The average and standard deviation are given in each graph. At a particular water concentration, with increase in the surfactant concentration, the cell window area distributions become narrower and the average values become smaller. At 3% water, when surfactant concentration is increased from 5% to 7% (from foam 3w5s 3w7s) the cell windows become slightly bigger. At 3% and 5% surfactant concentrations, with increase in the concentration of water there is no appreciable change in the average values of cell window area. However the cell window area distributions become wider. At 1% surfactant concentration, when the water concentration is increased from 1% to 2% (from foam 1w1s to 2w1s), the average value of the cell window area increases. The distribution of cell window area also becomes wider. The cell windows become smaller and the distribution becomes narrower for further increase in water concentration from 2% to 3% (from foam 2w1s to 3w1s). The strut width distribution pattern is similar to that of the window area distribution pattern. The average strut width of the foams are in the range of 17±3 to 27±5 μm.

The effect of cell structure on hydraulic resistance of the foams is shown in figure 4. The error bars represent standard deviation for four samples. For constant surfactant concentration, the buoyancy loss increases with increase in the concentration of water, whereas for constant water concentration, the buoyancy loss decreases with increase in the concentration of surfactant. The efficiency of the surfactant concentration to lower the buoyancy loss increases with increase in the concentration of water. The penetration of water into the foam at high pressure essentially

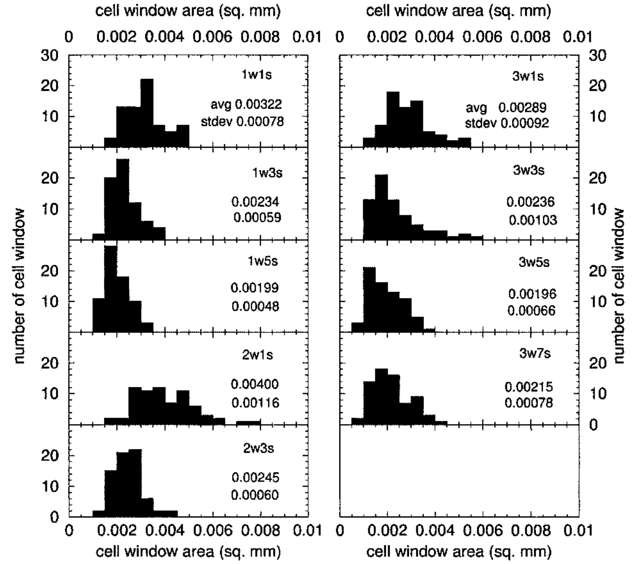

Figure 3. Effect of surfactant concentration at different water concentration on the distribution of cell window area. The average cell window area (avg) and the standard deviation (stdev) are given in each graph.

results from a sequential rupture of cell windows. The resistance to rupture of a cell window is higher for smaller and thicker windows. When the surfactant concentration is increased keeping water concentration constant, the windows are smaller and the hydraulic resistance of the foams increases. Higher amount of surfactant might have prevented the gas bubbles from coalescence at the initial stage of foam formation. When the water concentration is increased keeping surfactant concentration constant, the cell window area remains almost same however the hydraulic resistance decreases. This indicates that the cell window thickness decreases with increase in water concentration. This parameter was not measured in our experiments but a possible mechanism to explain why this should happen is as follows. When the water concentration was increased greater amount of carbon dioxide was generated, as the isocyanate index was kept constant. So the pressure inside the bubbles was higher. This higher pressure caused further drainage of the liquid. For this reason with increase in water concentration the windows become thinner and require less force to rupture.

c) Effect of Nucleating Agent Concentration

Micron sized silica particles were used as nucleating agent. The average particle diameter was 0.69 ± 0.16 μm. In the formulations the polyol contained 0.5% DBTDL, 0.5% TEA, 1% water. The amount of silica and surfactant (Tegostab B8404) are mentioned in the foam nomenclature. Foam ZsiYs was made with Z% of silica and Y% of surfactant.

The effect of nucleating agent on the distribution of cell window area and strut width is shown in figure 5. The average and standard deviation are mentioned in each graph. Note that 0si3s and 1w3s are the same foam as are 0si5s and 1w5s. The cell windows become smaller due

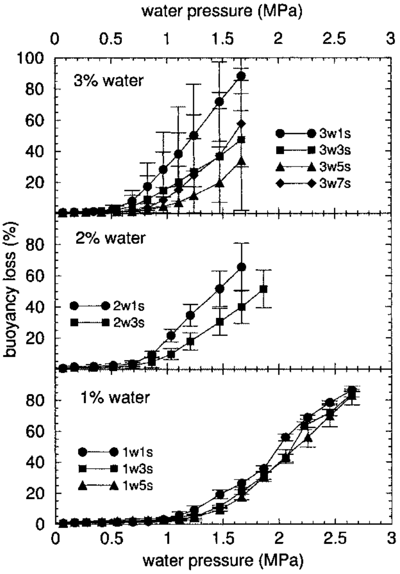

Figure 4. Effect of surfactant and water concentration on the hydraulic resistance of the foams. The error bar represents standard deviation for four samples.

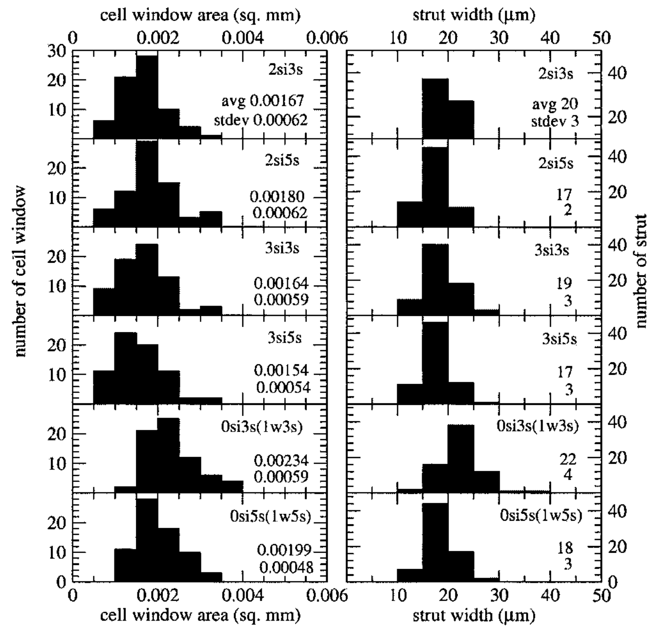

Figure 5. Effect of nucleating agent (silica particles) on the distribution of cell window area and strut width. The average values (avg) of cell window area and strut width and standard deviation (stdev) are given in each graph.

to addition of nucleating agent. However, there is no noticeable change either in the distribution or in the average values due to the variation of the concentration of nucleating agent and surfactant. The effect of silica particles as nucleating agent on buoyancy loss is shown in figure 6. The error bars represent standard deviation for four samples. Note that Osi3s and 1w3s are the same foam as are Osi5s and 1w5s. At higher pressures (0.80 MPa onwards) the buoyancy losses of the foams made with silica, are more than that of the foams made without silica. Thus, when silica particles are used as nucleating agent the cell windows are smaller but the buoyancy losses are more than that of the foams made without silica. This indicates cell windows in the foams with silica are much more thinner than the windows in the foams without silica. Independent measurements are not available to confirm this, however.

d) Effect of Variation of the Concentration the Catalysts

Foams for this part of the work were made with variation of the concentration of the catalysts, keeping total concentration (0.004 mole/100 gram of polyol) of the catalysts constant. In the formulations the polyol contained 1% water, 3% surfactant (Tegostab B8404). The proportion of DBTDL is mentioned in the foam nomenclature. For example, the proportion of DBTDL in the foam P_X is X.

Figure 7 shows the distributions of cell window area and the strut width. Note that the scales along x-axis in both window area and strut width distributions for the foam P_00 are different from rest of the distributions. The average and standard deviation of the measured quantity are mentioned in each graph. The cells in the foam P_00 are very coarse even observed by naked eye. The cell window area and strut width of this foam are most widely distributed and the average values of the cell window area and the strut width are also the largest. The distributions are much narrower and the average values are also smaller for the other foams. Increasing the mole fraction of DBTDL from 0.25 to 0.75 (from foam P_25 to P_75), both the cell window area and strut width distributions become narrower. However there are no appreciable differences both in the distributions and in the average values between foam P_75 and P_100.

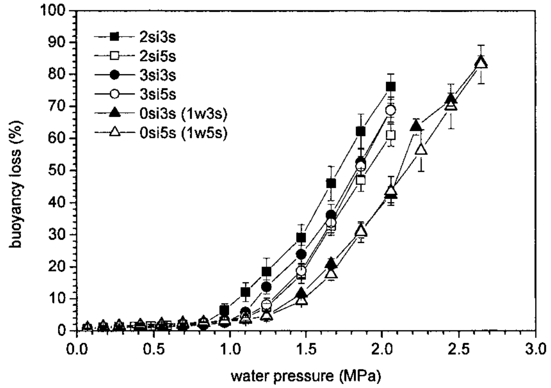

Figure 6. Effect of nucleating agent (silica particles) on the hydraulic resistance of the foams. The error bar represents standard deviation for four samples.

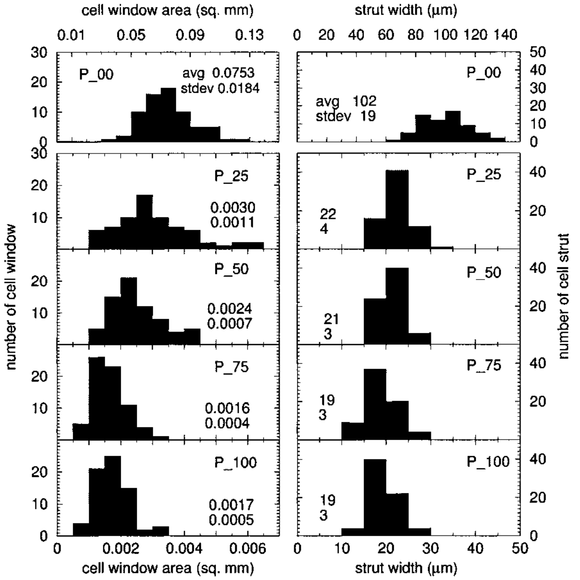

Figure 7. Effect of variation of catalysts concentration on the distribution of cell window area. The average cell window area (avg) and the standard deviation (stdev) are indicated in each graph.

The buoyancy losses of the foams at different water pressures are shown in figure 8. The error bars represent the standard deviation for four samples. At any particular water pressure, the buoyancy loss gradually decreases with increase in DBTDL proportion in the total concentration of the catalysts. The gel time was at a maximum for the foam P_00 (362 seconds) and minimum for the foam P_100 (29 seconds). The gel times of the other foams were as follows: 45 seconds for P_25, 37 seconds for P_50 and 32 seconds for P_75. The catalytic efficiencies of the different catalysts are different. For the foam P_00, the rate of network formation is much slower than any other foam, so the viscosity build up is not fast enough to withstand the pressure inside the bubbles, resulting in coalesence of the bubbles. For this reason the cell windows of the P_00 are very large. Due to low viscosity there is more cell window drainage and hence very thin cell windows. As a consequence the buoyancy losses of the P_00 are very large even at low pressures.

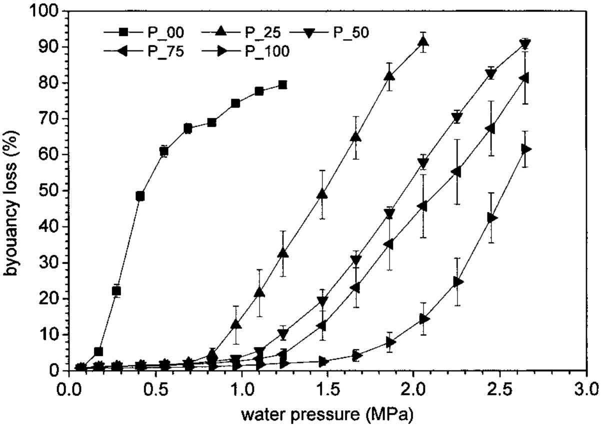

Figure 8. Effect of the variation of the concentration of the catalysts on the hydraulic resistance of the foams. The error bars represent the standard deviation for four samples.

As the proportion of DBTDL is increased the rate of network formation is accelerated and so there are lesser coalescence of the bubbles. In the final foams the cell windows are smaller. Figure 3 shows that the cell window areas and strut widths of the foams P_75 and P_100 are almost same. But the hydraulic resistance of the P_100 is more than that of P_75. This indicates the windows of P_100 are stronger, and hence thicker than the windows of P_75. The gel time of P_100 is less than P_75, so the viscosity built up is faster for P_100 and thus there is less time for cell windows drainage. This would lead to thicker windows for P_100.

Conclusion

Cell size in rigid polyurethane foam can be regulated according to the requirement. Proper selection of the surfactant that can lower the surface tension of the polyol and thereby facilitate generation of large number of small bubbles, giving foam with very small cell size. Cell sizes can be reduced with a narrow distribution by increasing the concentration of the surfactant. Using nucleating agent cell size can be reduced but the windows become thinner. Finally, by adjusting the rate of the blowing and network formation, foam can be made with narrowly distributed cells having thicker cell windows.

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