Hydraulic Resistance of Rigid Polyurethane Foams. II. Effect of Variation of Surfactant, Water, and Nucleating Agent Concentrations on Foam Structure and Properties

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ABSTRACT: Hydraulic resistance of rigid polyurethane foams to penetration by water at high pressures is studied in this work in the context of buoyancy applications. Micron sized silica particles are used as nucleating agents. The effect of the variation of the concentrations of the surfactant, water, and nucleating agent on cell structure, closed cell content, and compressive modulus, is examined. Foams have densities in the range of 145 to 165 kg/m^3. At a particular water concentration, with increase in the concentration of the surfactant, the window area of the cells becomes smaller and the hydraulic resistance of the foam increases. A cell window is the lamella of the foam material that separates two adjacent cells. With increase in the concentration of water keeping surfactant concentration constant, the average window area remains almost the same but the cell window area distribution becomes wider and the hydraulic resistance of the foams decreases. Foams made with silica have smaller cell windows but lower hydraulic resistance than that of the foams made without silica. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2830–2837, 2004

Key words: polyurethanes; rigid foam; surfactant concentration; hydraulic resistance; structure–property relations

INTRODUCTION

Polyurethane is an important synthetic polymer used as flexible foam, rigid foam, elastomer, sealant, and coatings. In water blown rigid polyurethane foams, the blowing agent is carbon dioxide, which is generated *in situ*. There are two parallel processes in water blown rigid polyurethane foam. One is the blowing by carbon dioxide. The gas is generated by the reaction of isocyanate with water. The other is network formation due to the reaction of isocyanate with polyol. During mixing tiny air bubbles are introduced in the reaction mixture. Bubble size gradually increases due to the blowing reaction and coalescence of the bubbles. Surfactants are added into the reaction mixture to stabilize the growing bubbles. Added surfactants are responsible for final cell structure of the foam.[1–4]

We consider rigid polyurethane foams as candidates for buoyancy applications. Such foams must be resistant to the penetration of water when immersed deep into water, so as to maintain their buoyancy. Typical applications include offshore exploration and production, to support electronics and instrumentation, to provide buoyancy for remotely operated subsea vehicles, and to float flexible risers, hoses, and pipelines in deepwater, besides some other specific applications.[5–7]

There is only one reported work available in the literature on the hydraulic resistance of the rigid polyurethane foam in the pressure range 0.0 to 0.3 MPa.[8] The variation of structures and properties of rigid polyurethane foam with formulation parameters is studied in the context of buoyancy applications in a series of three works. This work is part 2. Part 1 describes the effect of different surfactants on foam structure and properties.[9] Part 3 contains the effect of variation of the concentration of the catalysts on foam structure and properties.[10] The emphasis in each work is on the "hydraulic resistance" of the foams.

The main objective of this work is to study the effect of variation of surfactant and water concentration on foam structure and hence on foam properties, especially on hydraulic resistance. The effect of nucleating agent is also studied using micron sized silica particles. Experimental details are given next, followed by results and discussion and conclusions.

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,

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TABLE I
Formulation Used for Making Different Foams

Ingredients	For foams XwYs (pphp[1])	For foams ZsiYs (pphp[1])
polyol	100	100
DBTDL	0.5	0.5
TEA	0.5	0.5
water	X	1
surfactant[2]	Y	Y
silica	0.0	Z
isocyanate index 105		

[1] parts per hundred g of polyol.
[2] Tegostab B8404.

Mumbai, India). The polyol had a hydroxyl number of 440 mg of KOH per gram of the polyol and an equivalent weight of 128 g/mol. The isocyanate was a polymeric diphenyl methane diisocyanate (MDI) (SUPRASEC 5005, Huntsman International). The isocyanate had an equivalent weight of 132 g/mol. The catalysts used were dibutyltin dilaurate (DBTDL) (Lancaster Synthesis, Lancashire, UK) and triethanolamine (TEA) (Spectrochem, Mumbai, India). Tegostab B8404, silicone surfactant, used in this study was donated by Goldschmidt AG (Essen, Germany). Silica was procured from Spectrochem, India. All materials were used as received without further purification.

Foam formation

Initially polyol mixtures were prepared by stirring 250 g of the polyol in a one-liter plastic container containing water, catalysts, and surfactant for half an hour. The polyol mixture was mixed thoroughly with predetermined amount of isocyanate for 15 s using a high-speed stirrer at 2800 rpm. The same speed was maintained for all formulations. The mixture was immediately poured into a mold. The mold was closed and kept at room temperature for 15 min. The foam was then removed from the mold. The formulations used for making different foams are shown in Table I. Foams with 3% water were prepared in a cylindrical mild-steel mold with diameter 100 mm and height 200 mm. All other foams were prepared in a stainless steel mold having dimensions of 127 × 127 × 317.5 mm. All characterizations were done after curing the foams at room temperature for at least one day. All foams were uniform in color according to visual observation, indicating uniform mixing of the reactants.

Characterization

Surface tension

Surface tension of the pure polyol and the polyol containing different weight percent of surfactant were

measured at room temperature by Du Nouy Ring Tensiometer (Fisher Surface Tensiomat; Model 21; Fisher Scientific Co., Pittsburgh, PA).

Hydraulic resistance

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 intervals of 5 to 10 min, the pressure was checked and if there was any drop, the pressure was raised to the specified value. The buoyancy loss was calculated by using the following formula,

$$\text{percentage buoyancy loss} = \frac{\rho_f' - \rho_f}{\rho_w - \rho_f} \times 100$$
(1)

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

Compressive modulus

The compressive modulus of the foam samples was determined according to ASTM D 1621 73 using a Universal Tensile Testing Machine (UT 2000 series, R and D Electronics, Mumbai, India), using a compression cage. Test specimen dimensions were 51 × 51 × 30 mm. The crosshead speed was 3 mm/min. The compressive modulus was measured for compression in both parallel and perpendicular directions to the foam rise. A total of five samples were used for each measurement. Anisotropy, which is the ratio of parallel to perpendicular compressive modulus, was calculated from the compressive modulus data. For all samples the compressive modulus was corrected to a density of 150 kg/m³ using the following relationship,[11]

$$E_{\rho=150} = E_{ob}\left(\frac{150}{\rho_{ob}}\right)^{1.57}$$
(2)

where $E_{\rho=150}$ is the corrected compressive modulus for density 150 kg/m³, and E_{ob} and ρ_{ob} are the ob-

Closed cell content

The closed cell content of the foams was measured according to ASTM D2856. The test specimen dimensions were $51 \times 51 \times 30$ mm. A total of five samples were used for each measurement. Due to cellular structure of the foam, the true volume of a foam sample is lower than that of its dimensional volume. The closed cell content is the ratio of true volume to dimensional volume multiplied by 100. The true volumes of the foam samples were measured by applying Boyle's law. It was assumed that air at room temperature (27 to 32°C) and low pressures would behave ideally. The details of experimental set up are given elsewhere.[12]

Bubble size, cell window, and strut width measurement

The average bubble sizes in the polyol containing different weight percent of water and surfactant were measured by using an optical microscope (Model BX60 Olympus; Tokyo, Japan). A drop of the polyol mixture after stirring for 20 min 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, Tokyo, Japan) and frame grabber (Model Occulus MX, Coreco; Quebec, Canada). 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; Media Cybernatics, Inc., Silver Spring, MD). 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 were taken. Seventy measurements were made for each foam.

Silica particles size measurement

A small quantity of the powder sample was taken in a large quantity of water and sonicated for two minutes. The dispersion was taken in a cuvette (1 cm ×1 cm cross section) containing a small magnetic stirrer, and the particle size distribution was measured by laser particle size analyzer (Galai CIS 1; Galai Production, Ltd., Migdal Haemek, Israel).
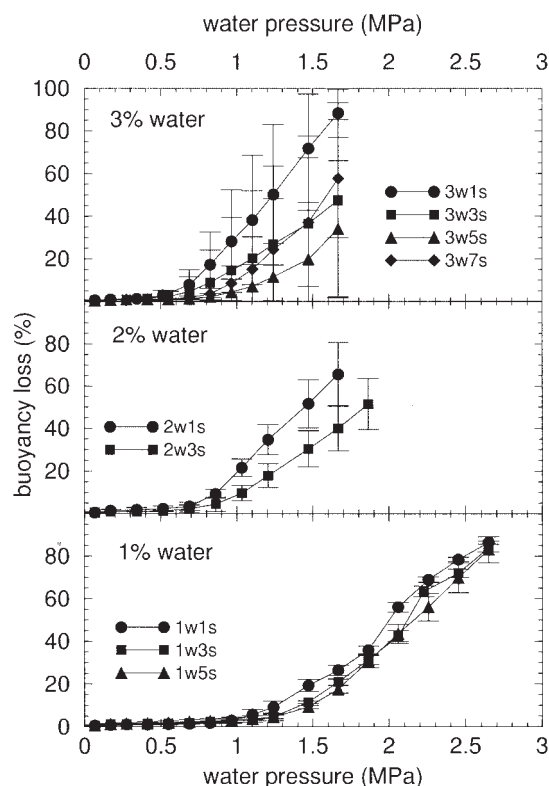

Figure 1 Effect of surfactant and water concentration on the hydraulic resistance of the foams. The error bars represent standard deviation for four samples.

RESULTS AND DISCUSSION

The effect of water and surfactant concentration on buoyancy loss is shown in Figure 1. The error bars represent standard deviation for four samples. A low buoyancy loss implies a high hydraulic resistance. For a constant surfactant concentration, the buoyancy loss increases with increase in the concentration of water; whereas for a constant water concentration, the buoyancy loss decreases with increase in the concentration of surfactant. The efficacy of the surfactant to lower the buoyancy loss increases with increase in the concentration of water. For the foams made with 1% water, the buoyancy loss decreases with increase in surfactant concentration from 1 to 3% (foams 1w1s and 1w3s). Further increase in the concentration of surfactant from 3 to 5% (foams 1w3s and 1w5s) does not further reduce the buoyancy loss. At 2% water, the decrease in the buoyancy loss due to increase in surfactant concentration from 1 to 3% (foams 2w1s and 2w3s) is more than that in the foams made with 1% water. For foams made with 3% water, the buoyancy loss decreases with increase in the concentration of surfactant from 1 to 5% (foams 3w1s, 3w3s, 3w5s). However, the buoyancy loss is increased with further increase in the concentration of surfactant from 5 to 7% (foam 3w7s). This indicates an optimal surfactant
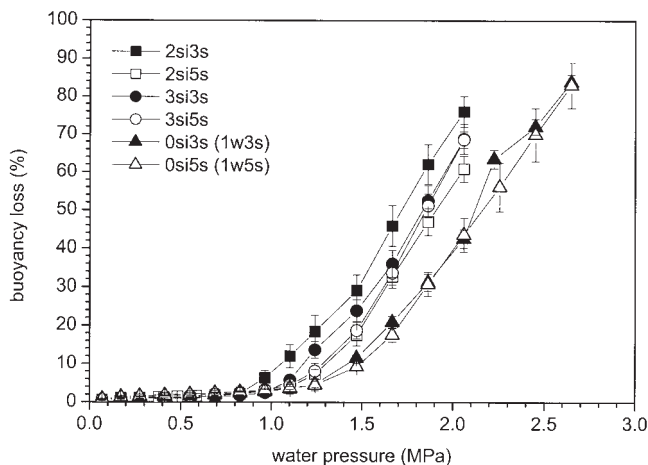
Figure 2 Effect of nucleating agent (silica particles) on the hydraulic resistance of the foams. The error bars represent standard deviation for four samples.

Figure 3 Effect of surfactant, water, and nucleating agent (silica particles) concentration on the threshold pressure of the foams.

concentration of around 5%, beyond which properties do not improve for this water concentration.

The effect of silica particles as nucleating agents on buoyancy loss is shown in Figure 2. The error bars represent standard deviation for four samples. The average particle diameter was $0.69 \pm 0.16 \ \mu$m. Note that 0si3s and 1w3s are the same foam as are 0si5s 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. At 2% silica, when the surfactant concentration is increased from 3 to 5% (2si3s to 2si5s) the buoyancy loss decreases slightly. However, there is no significant change in the buoyancy loss between foams 3si3s and 3si5s. The results indicate that silica does not improve the hydraulic resistance of the foams.

Figures 1 and 2 show that at lower pressures, the curves are almost parallel to the pressure axis; however, at higher pressures the curves are very steep. A threshold pressure is defined as the point of intersection of the two straight lines, representing the best fitted straight lines of the points at low pressures and at high pressures. A typical calculation of threshold pressure has been shown in part 1.[9] The threshold pressure of different foams is shown in Figure 3. At a particular surfactant concentration, the threshold pressure decreases with increase in water concentration, whereas, at a particular water concentration, the threshold pressure increases with increase in the concentration of surfactant. However the threshold pressure of the foam 3w7s is lower than that of the foam 3w5s. Beyond the threshold pressure the standard deviation of the buoyancy losses increases with increase in the concentration of water (Fig. 1).

The closed cell content of a few of the foams is given in Table II. The closed cell content for all measured foams is high and remains high even when the water
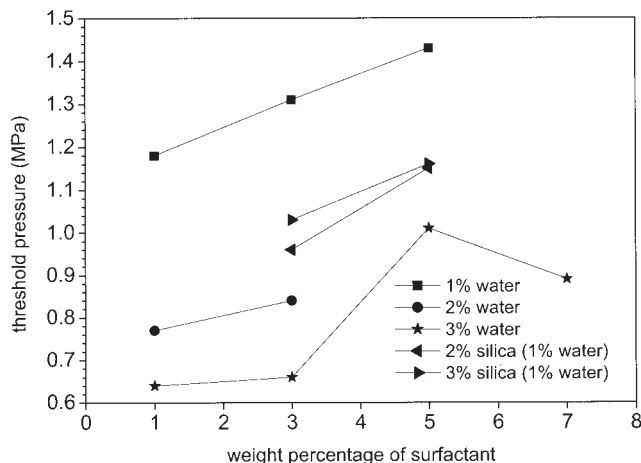
concentration is increased from 1 to 3%. The percentage buoyancy losses at 0.068 MPa (equivalent to pressure at nearly 7 m under water) for all foams are very small, from 0.45 to 0.75 (Figs. 1 and 2). At this low pressure the buoyancy loss is related to the closed cell content and would be high for a foam whose closed cell content is low.[9] Moreover, Figures 1 and 2 show that buoyancy loss of all foams is very low and nearly the same, at least up to water pressure of 0.50 MPa. This indicates closed cell content for all foams is high even for the foams for which the closed cell content was not measured (foams with 2% water and with silica). It is interesting to note that there was no rupture of cell windows due to increase in water content or use of silica in the foam formulations.

The typical structure of rigid polyurethane foam is shown in Figure 4 by means of an optical micrograph of a section of the foam. The cell windows and cell struts are marked in the figure. The measured distributions of the cell window area and the strut width are shown in Figures 5 and 6, respectively. The average and standard deviation are given in each graph (Figs. 5 and 6). At a particular water concentration, with increase in the surfactant concentration, both the cell window area and the cell strut width distributions

TABLE II
Closed Cell Content of Different Foams

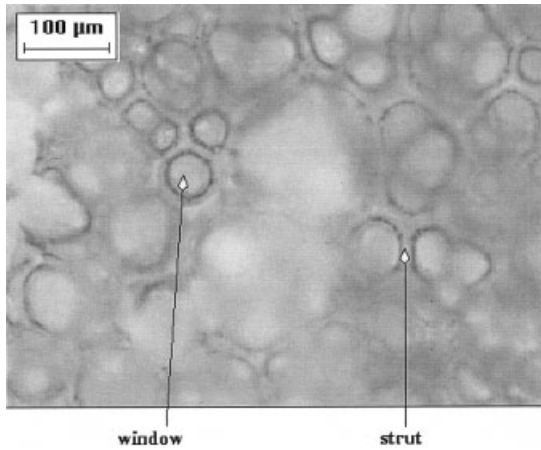| Foam	Closed cell content (%)
1w1s	93.3 ± 4.1
1w3s	94.7 ± 1.8
1w5s	96.7 ± 1.7
3w1s	92.4 ± 5.0
3w3s	95.7 ± 1.1
3w5s	92.1 ± 1.4
3w7s	95.7 ± 1.0

Figure 4 Sample optical micrograph showing cell windows and struts in rigid polyurethane foam.

become narrower and the average values become smaller. At 3% water, when surfactant concentration is increased from 5 to 7% (foams 3w5s and 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% (foams 1w1s and 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% (foams 2w1s and 3w1s).

The effect of nucleating agent on the distribution of cell window area and strut width is shown in Figure 7. The average values and standard deviation are given in each graph. The cell windows become smaller due 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 nucleating agent concentration and surfactant concentration.

The compressive modulus of different foams is shown in Figure 8. The error bars represent standard deviation for five samples. There is no significant change in compressive modulus values for different foams made with variation of surfactant and water concentrations. However, with increase in surfactant concentration, keeping water concentration constant, the foams become more isotropic. The foam cells become more isotropic with increase in water concentration from 1 to 3% at 1% surfactant concentration.
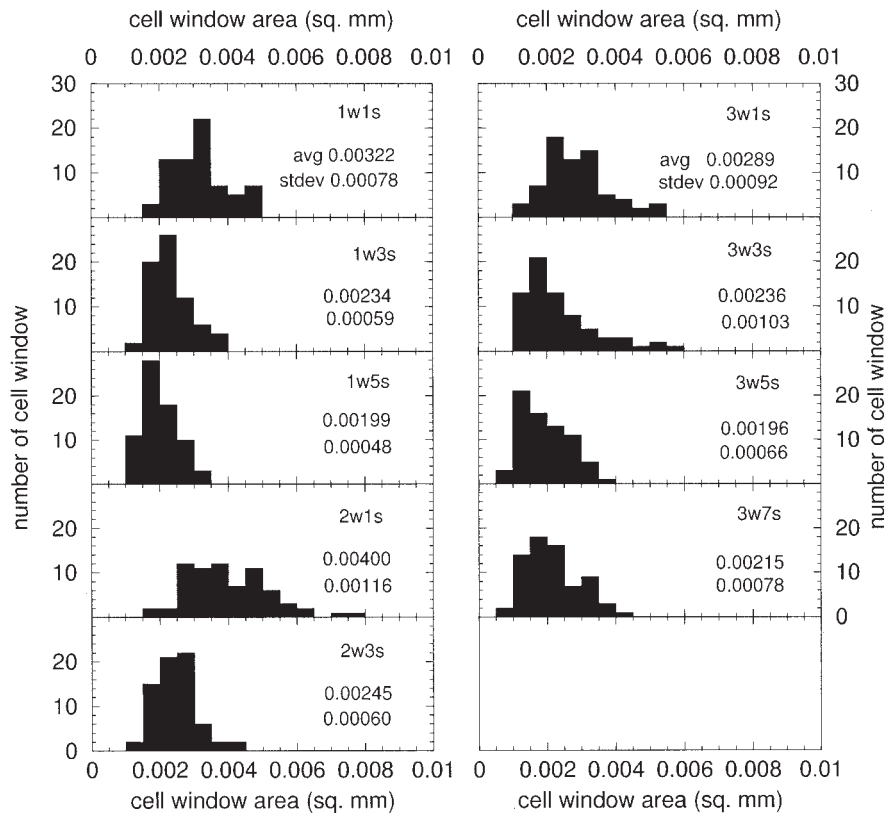

Figure 5 Effect of surfactant and water concentration on the distribution of cell window area. The average cell window area (avg) and the standard deviation (stdev) are given in each graph.
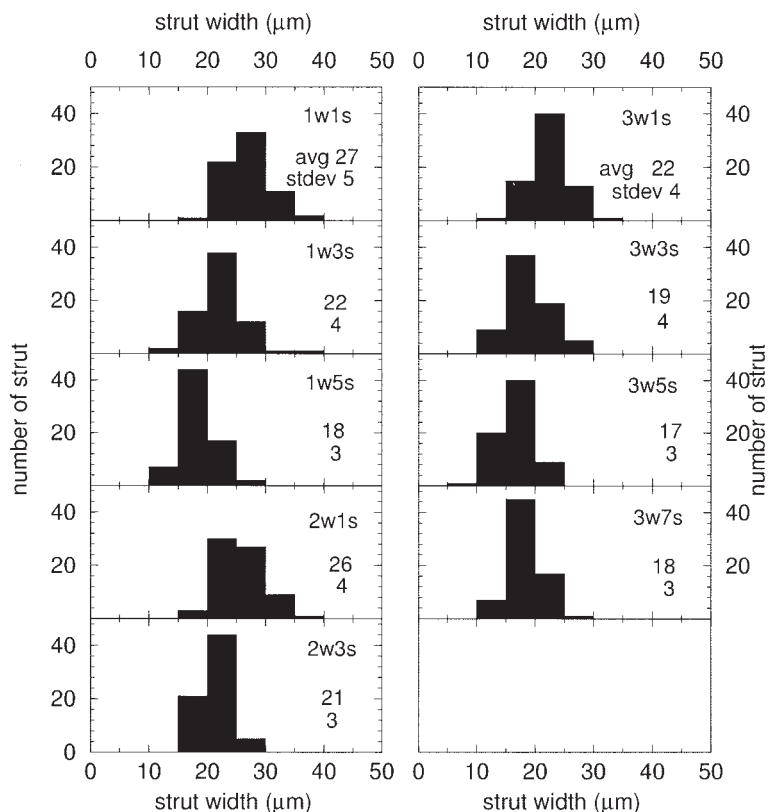
Figure 6 Effect of different surfactant and water concentration on the distribution of cell strut width. The average cell strut width (avg) and the standard deviation (stdev) are given in each graph.

The initial bubble size in the polyol mixtures and the average window area in the final foams are compared in Figure 9. The figure shows that initial bubble sizes in the polyol mixtures are nearly the same and there is no variation due to change in surfactant concentration. The polyol had surface tension of 36.2 mN/m. The surface tension of the surfactant solution in polyol remained constant at 22.5 mN/m for the change of surfactant concentration from 0.1 to 5.0 g/100 g of polyol.

We now discuss the above results in the context of the results obtained for hydraulic resistance. The penetration of water into the foam at high pressure essentially results from a sequential rupture of cell windows. The resistance to rupture of a cell window is higher for smaller and thicker windows, and thus cell structure should have a significant effect on the hydraulic resistance. Consider first the variation of hydraulic resistance with water concentration. The data show a monotonic increase in buoyancy loss with water concentration; however, the cell window size is nearly the same for the foams. This indicates that the cell window thickness decreases with 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 is increased, the rate of generation of carbon dioxide is higher. Thus, the foam films are formed at an earlier stage, providing for more time for the fluid to

drain from the films before the polymer gels. The windows consequently become thinner and require less force to rupture.

When the surfactant concentration is increased keeping water concentration constant, the initial bubble sizes in the polyol mixture remain nearly the same. However, in the final foams the windows are smaller and the hydraulic resistance of the foams increases. The higher amount of surfactant most likely prevents the coalescence of the gas bubbles at the initial stage of foam formation. Thus in the final foams, the cells are smaller and their windows are smaller. These windows need comparatively more force to rupture and the hydraulic resistance of the foams increases with increase in surfactant concentration.

When silica particles are used as nucleating agents, 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 thinner than the windows in the foams without silica. Independent measurements are not available to confirm this, however.

CONCLUSION

Water blown rigid polyurethane foams were prepared with different concentrations of surfactant, water, and
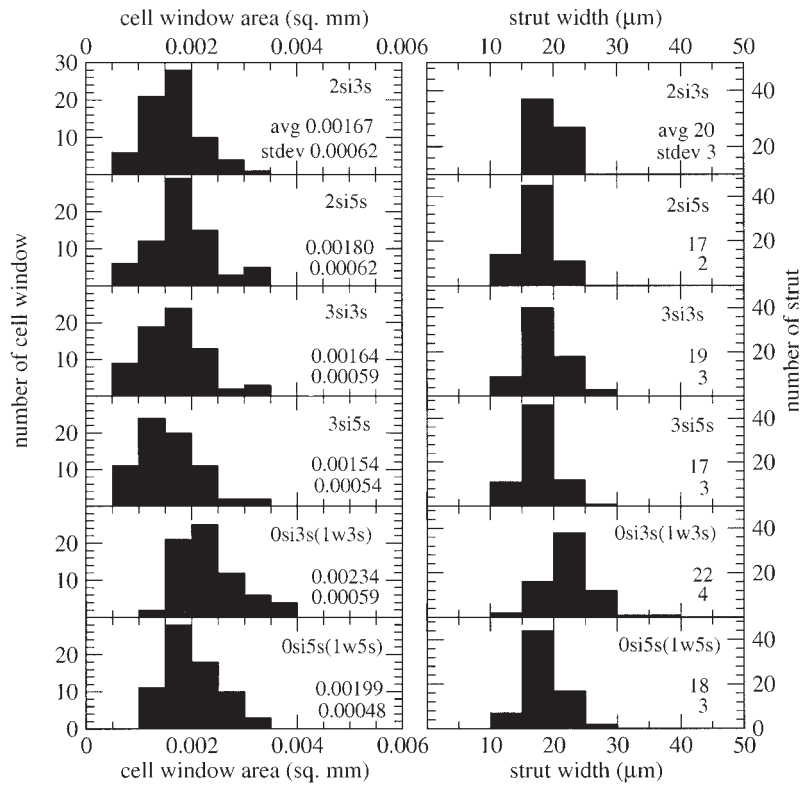
Figure 7 Effect of nucleating agent (silica particles) on the distribution of cell window area and strut width. The average values (avg) of cell window area and strut width and standard deviation (stdev) are given in each graph.

nucleating agent. The effect of variation of these ingredients on the buoyancy losses of the foams was studied. The effect of variation of the concentration of these ingredients on closed cell content, cell structure, and compressive modulus was also examined.

The initial bubble sizes in the different formulations were the same, but the cell structure was different
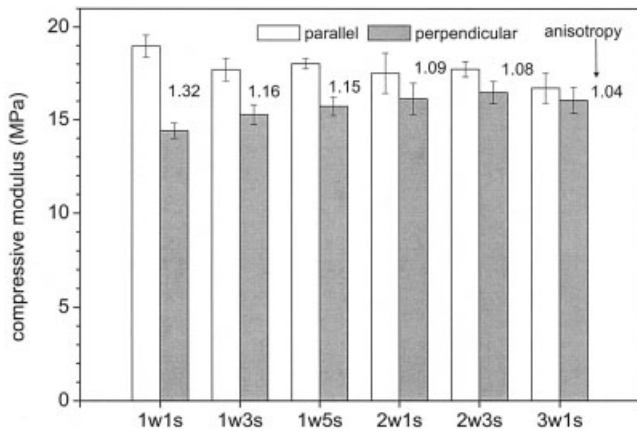

Figure 8 Effect of surfactant and water concentration on the compressive modulus of foams. Compressive modulus parallel and perpendicular to the direction of foam rise are shown. The error bars represent the standard deviation for five samples. Anisotropy is the ratio of parallel to perpendicular compressive modulus.
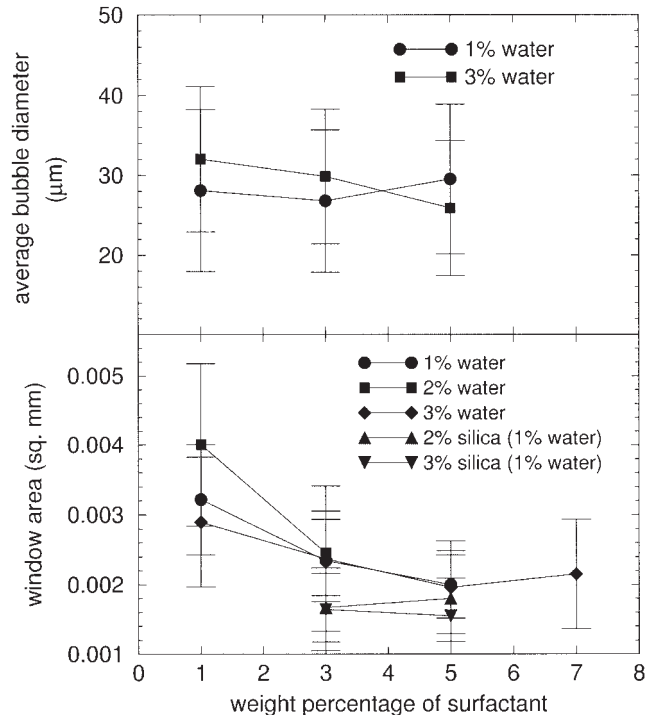

Figure 9 Effect of surfactant concentration at different water concentration on initial bubble size and cell window area.

from each other in the foams produced. When the surfactant concentration was increased keeping the concentration of the other ingredients constant, the cell window area became smaller and the hydraulic resistance of the foam increased. This was attributed to reduction of coalescence during foam formation by surfactant. In one case in which excess surfactant was used, the hydraulic resistance decreased with surfactant concentration. This seems to indicate an optimal surfactant concentration with respect to hydraulic resistance. When the water concentration was increased keeping concentration of other ingredients constant, the average window area remained almost the same but the cell window area distribution became wider and the hydraulic resistance of the foam decreased. The windows of the foams made with silica became smaller than those of the foams made without silica but the hydraulic resistance was lower. The closed cell content of the foams remained almost the same even after increase in the concentration of water. There was little effect of variation of system parameters on the compressive modulus of foams.

The maximum threshold pressure, 1.43 MPa, was observed for the foam 1w5s. This pressure is equivalent to pressure at 146 m under water. The buoyancy loss for that foam at this pressure was nearly 15%. The results presented show how system parameters affect the foam and are useful in regulating the cell structure of the foams that is necessary to improve the hydraulic resistance.

References

1. Oertel, G. Polyurethane Handbook; Hanser Publisher: Munich, 1985; Chap 6.
2. Szycher, M. Handbook of Polyurethanes; CRC Press LLC: New York, 1999; Chap 8.
3. Zhang, X. D.; Macosco, C. W.; Davis, H. T.; Nikolov, A. D.; Wasan, D. T. J Colloid Interface Sci 1999, 215, 270.
4. Kollmeier, H. J.; Schator, H. J. Cell Plast 1985, July–August, 239.
5. Cuming Corporation Flotation, Syntactic Foam Flotation Equipment for the Offshore Oil and Gas. http://www.cumingcorp.com/flotation.php (accessed October 2003).
6. CRP Group, Ltd., Subsea Bouyancy Products. http://www.crpgroup.com/downloads/subseapr.pdf (accessed October 2003).
7. Hyperlast, Offshore Insulation & Protection. http://www.hyperlast.co.uk/offshore1b.htm (accessed October 2003).
8. Swaminathan, A.; Khakhar, D. V. Cellular Polymers 2000, 19, 103.
9. Mondal, P.; Khakhar, D. V. J Appl Polym Sci, to appear.
10. Mondal, P.; Khakhar, D. V. J Appl Polym Sci, to appear.
11. Baser, S. A.; Khakhar, D. V. Cellular Polymers 1993, 12, 390.
12. Baser, S. A. PhD Thesis, IIT, Bombay 1993.