

# Hydraulic Resistance of Rigid Polyurethane Foams. I. Effect of Different Surfactants on Foam Structure and Properties

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Received 18 December 2003; accepted 5 April 2004

DOI 10.1002/app.20764

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Foams used in buoyancy applications must resist penetration by water at significant depths of immersion. The behavior of water blown rigid polyurethane foam at different water pressures from 0 to 3 MPa are studied in this work. The effects of different surfactants on the cell structure and hydraulic resistance of the foams are examined. The foams have densities in the range of 145 to 160 kg/m<sup>3</sup>. With increasing applied hydraulic pressure, it is found that the foams have very small buoyancy losses at low pressures but beyond a threshold pressure, buoyancy losses increase rapidly. The threshold pressures of the foams increase with decrease in cell window area. A cell window is

the lamella of the foam material that separates two adjacent cells. The cell sizes of the foam are found to correlate with the size of the air bubbles entrained during initial mixing. Surfactants, which reduce the surface tension of the polyol to the greatest extent, are found to give the finest initial bubbles, smaller cells, and foams with the highest hydraulic resistance. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2821–2829, 2004

**Key words:** polyurethanes; rigid foam; surfactants; hydraulic resistance; structure–property relations

## INTRODUCTION

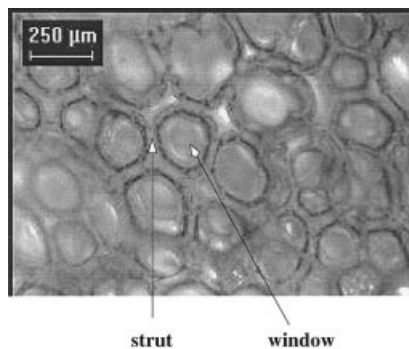
Syntactic foams are used deep inside water for offshore exploration and production, to support electronics and instrumentation, to provide buoyancy for remotely operated subsea vehicles, and to float flexible risers, hoses, and pipelines in deepwater, besides some other specific applications. They comprise micro-size hollow glass spheres with composites of polymers. Generally, epoxy resins are used as the matrix polymer, as well as interpenetrating network of PVC and polyurea, polyesters, polyurethane, and silicone rubber. Sometimes larger macro-sized spheres made from fiberglass are also used as fillers.<sup>1–3</sup> The basic requirement of the foam for this application is that the foam should not lose its buoyancy due to high water pressure. If rigid polyurethane foam is placed deep inside water, due to high water pressure cell windows may get ruptured, causing water to penetrate into the foam. This reduces buoyancy of the foam. Thus, a high hydraulic resistance of the foam is necessary for buoyancy applications. We consider here the possibility of using rigid polyurethane foams for buoyancy applications.

In water blown rigid polyurethane foam, the ingredients are polyol, water, catalyst, surfactant, and isocyanate. Initially the polyol is mixed with water, catalyst, and surfactant, and then the polyol mixture is mixed with isocyanate to react. During mixing a large number of fine air bubbles are entrained into the mixture. They serve as bubble nuclei for foam cells.<sup>4</sup> Water reacts with isocyanate and initially produces carbamic acid, which decomposes to an amine and carbon dioxide. The carbon dioxide diffuses into the already present air bubbles and hence the foam rises due to increase in bubble size. At the same time, the viscosity of the medium increases due to the reactions of isocyanate with hydroxyl group of the polyol and with the amine. The viscosity build up arrests the foam rise, producing a solid foam at gelation.

Silicone surfactants are commonly used in the manufacture of polyurethane foams. Common surfactants are polydimethyl siloxanes on which random or block copolymers of ethylene and propylene oxide are grafted.<sup>4–8</sup> The surface tension lowering ability of these silicone surfactants mainly depends on the silicone/polyether ratio of the surfactants.<sup>4,7</sup> Silicone surfactants reduce the polyol surface tension and thereby facilitate generation of a large number of small bubbles during initial mixing. During foam formation they stabilize these gas bubbles and prevent coalescence.<sup>4</sup>

When the gas volume fraction exceeds 74%, dispersed spherical bubbles deform into multisided poly-

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**Figure 1** Figure showing a cell window and cell strut in a typical rigid polyurethane foam.

hedra.<sup>4,9</sup> 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. Cell windows and cell struts of a typical rigid polyurethane foam are shown in Figure 1. The micrograph shows only two of three windows meeting at a strut since the top cells are cut during sample preparation. Due to capillary pressure fluid drainage occurs from cell windows to the struts and thereby the cell windows become gradually thinner. Surfactants play an important role to reduce cell window drainage by creating a surface tension gradient along the surface and by reducing the surface tension. Also, the enhanced viscosity of the medium slows cell window drainage. For a fixed foam density, increase in the number of cells per unit volume implies smaller cells. Cell sizes correlate well with the size of cell windows and thickness of struts. Since cell sizes are difficult to infer from sectioned foam micrographs as shown in Figure 1, we characterize the foam structure by measuring cell window areas and strut widths.

There is only one reported work available in the literature on the hydraulic resistance of rigid polyurethane foam. Swaminathan and Khakhar<sup>10</sup> studied the hydraulic resistance of rigid polyurethane foam within the pressure range 0 to 0.3 MPa. They found that amount of water absorbed by the foams, decreased with increase in density. Low density foams absorbed lesser amount of water when the isocyanate index was increased from 125 to 150. However, there was little effect of isocyanate index on the water absorbed by the higher density foams. It was also observed that with decrease in window area, foams absorbed a lesser amount of water. The maximum use pressure for less than 20% buoyancy losses was reported to be 0.3 MPa for the foams studied.

In a series of three papers we report on studies of the effect of formulation parameters on foam properties with special emphasis on "hydraulic resistance" of rigid polyurethane foams. Foams in these three papers

are hand mixed and made at identical conditions, that is, with same mixing speed and mixing time. This paper is Part 1 and describes the effect of different surfactants on foam structure and properties. In Part 2, the effect of variation of concentrations of surfactant, water, and nucleating agent on foam structure and properties is given.<sup>11</sup> Part 3 contains the effect of variation of the concentration of catalysts to alter relative rates of gas generation and curing.<sup>12</sup>

In this work eight formulations are used to make water blown rigid polyurethane foams, with densities of 145 to 160 kg/m<sup>3</sup>. One of the foams is without any surfactant, and the remaining seven are with seven different commercially available surfactants. Out of seven surfactants used, three are silicone surfactants and the remaining four are polyether surfactants. The objective of this work is to study the hydraulic resistance behavior of rigid polyurethane foam for possible use in buoyancy applications. The effect of different surfactants on cell structure and hence on foam properties, especially on hydraulic resistance, is examined.

## 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, 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) (SU-PRASEC 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, Tegostab B8406, and Tegostab B8407, silicone surfactants, were donated by Goldschmidt AG (Essen, Germany). Atsurf 3315, Atsurf 3800, Cresmer 3845, and Cresmer B246M were donated by ICI (Mumbai, 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 with required amounts of water, catalysts, and surfactant for half an hour. The details of the formulations used are given in Table I. The polyol mixture was mixed thoroughly with a predetermined amount of isocyanate for 15 s using a high-speed stirrer at 2800 rpm. The same speed and mixing time was maintained for all formulations. The mixing time was the maximum

**TABLE I**  
**Formulation Used for Making the Foams. Different**  
**Surfactants Were Used to Make Different Foams**

| Ingredients          | pphp* |
|----------------------|-------|
| polyol               | 100   |
| water                | 1.0   |
| DBTDL                | 0.5   |
| TEA                  | 0.5   |
| surfactant           | 3     |
| Isocyanate index 105 |       |

\* parts per hundred g of polyol

time possible that still left adequate time for pouring into the mold before the foam started rising. The mixture was immediately poured into a stainless steel mold. The mold was closed and kept at room temperature for 15 min. The foam was then removed from the mold. The mold had the dimensions of 127 × 127 × 317.5 mm and was coated with a mold-release agent (wax). 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. Mixing using a high pressure impingement mixing is known to give smaller final cell sizes as compared to hand mixing.<sup>13</sup> However, studies using machine mixing were not used in view of the excessive material requirement for each run.

### Characterization

#### Surface tension

Surface tensions of the polyol and solutions of the surfactants (3 weight percent) in polyol were measured at room temperature by a Du Nouy Ring Tensiometer (Fisher Surface Tensiometer, Model 21; Fisher Scientific International, Inc., 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 the one-hour equilibration period, the pressure was found to decrease due to water absorption by the foam samples. Thus the pressure was checked at intervals of 5 to 10 min, and if there was any decrease, the pressure was raised to the specified

value using the hand pump. The buoyancy loss was calculated by using the following formula,

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

where  $\rho_f$ ,  $\rho_f'$ , and  $\rho_w$  are the initial foam density, density of the foam after water absorption, and density of the water, respectively. The buoyancy loss was measured for different hydraulic pressures in the range 0 to 3 MPa. It was assumed that the 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 were corrected to a density of 150 kg/m<sup>3</sup> using the following relationship,<sup>13</sup>

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

where  $E_{\rho=150}$  is the corrected compressive modulus for density 150 kg/m<sup>3</sup>, and  $E_{ob}$  and  $\rho_{ob}$  are the observed compressive modulus and density, respectively.

#### Closed cell content

The closed cell content of each foam was measured according to ASTM D2856. The test specimen dimensions were 51 × 51 × 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.<sup>14</sup>

TABLE II  
Different Properties of Polyol Solution and Cured Foam

| Surfactant         | In polyol solution     |   | In cured foam            |                         |                                       |
|--------------------|------------------------|---|--------------------------|-------------------------|---------------------------------------|
|                    | Surface tension (mN/m) | Average bubble diameter ( $\mu\text{m}$ ) | Threshold pressure (MPa) | Closed cell content (%) | Percentage buoyancy loss at 0.068 MPa |
| Without surfactant | 36.2                   | 57 $\pm$ 24                               | 0.0                      | 87.8 $\pm$ 1.4          | 2.47 $\pm$ 0.63                       |
| Atsurf 3315        | 37.9                   | 54 $\pm$ 21                               | 0.0                      | 90.3 $\pm$ 1.1          | 1.43 $\pm$ 0.34                       |
| Atsurf 3800        | 37.9                   | 54 $\pm$ 23                               | 0.0                      | 81.1 $\pm$ 4.8          | 3.07 $\pm$ 0.48                       |
| Cresmer 3845       | 36.1                   | 54 $\pm$ 24                               | 0.0                      | 81.8 $\pm$ 4.3          | 4.54 $\pm$ 0.81                       |
| Cresmer B246M      | 29.9                   | 44 $\pm$ 17                               | 1.12                     | 95.4 $\pm$ 2.0          | 0.38 $\pm$ 0.07                       |
| Tegostab B8404     | 22.5                   | 27 $\pm$ 9                                | 1.31                     | 96.3 $\pm$ 1.6          | 0.59 $\pm$ 0.08                       |
| Tegostab B8406     | 22.5                   | 30 $\pm$ 9                                | 1.42                     | 96.0 $\pm$ 0.7          | 0.50 $\pm$ 0.09                       |
| Tegostab B8407     | 21.7                   | 26 $\pm$ 11                               | 1.25                     | 95.7 $\pm$ 1.4          | 0.55 $\pm$ 0.04                       |

#### Bubble size, cell window, and strut width measurement

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, 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 Cybernetics, 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 was taken. Seventy measurements were made for each foam.

## RESULTS AND DISCUSSION

The surface tension values and average bubble diameter using different surfactants are given in Table II. The polyol had a low surface tension of 36.2 mN/m. This value was further reduced by the silicone surfactants (Tegostab series) to a lowest value of about 22 mN/m. Cresmer B246M reduced the polyol surface tension to around 30 mN/m. The rest of the polyether surfactants (Atsurf series and Cresmer 3845) did not reduce the surface tension of the polyol. The initial bubble size in the polyol mixture depends on the surface tension of the solution and results in Table II

indicate that the bubble size decreases with decrease in surface tension of the polyol solution.

The effect of different surfactants on the hydraulic resistance of the foams is shown in Figure 2. The error bars represent standard deviation for four samples. A lower buoyancy loss corresponds to a higher hydraulic resistance. Foams with no surfactant and with Atsurf 3800, Atsurf 3315, and Cresmer 3845 have very high buoyancy losses even at low pressures. These foams thus have very poor hydraulic resistance. However, foams with silicone surfactants (Tegostab B8404, B8406, and B8407) have very low buoyancy losses (less than 10%) up to water pressures of around 1.3 MPa (equivalent to 133 m water depth). Beyond this pressure, the buoyancy losses of these foams are large for a small increase in water pressure. Foams made with Cresmer B246M behave like foams made with silicone surfactants; however, the buoyancy loss of these foams is slightly higher than that of the foams with silicone surfactants, for a given applied pressure.

Figure 2 shows that at low pressures the portions of the curves for the foams made with the three silicone surfactants and Cresmer B246M are almost parallel to the pressure axis. However, at high pressures, the portions are very steep. A threshold pressure was defined as the point of intersection of the two straight lines, representing the best straight lines for the data at low pressures and at high pressures. In Figure 3 a typical calculation of threshold pressure is shown. The threshold pressures for the different foams are given in Table II. The threshold pressure of the foam with Cresmer B246M is lower than that of the foams with silicone surfactants. Tegostab B8406 had the highest threshold pressure.

Two of the foams, with Cresmer B246M and Tegostab B8404, were made for a second time using identical formulations to check the reproducibility of the experiments. The buoyancy loss-pressure profile for the initial foams and the repeats are compared in Figure 4. The results show good reproducibility.

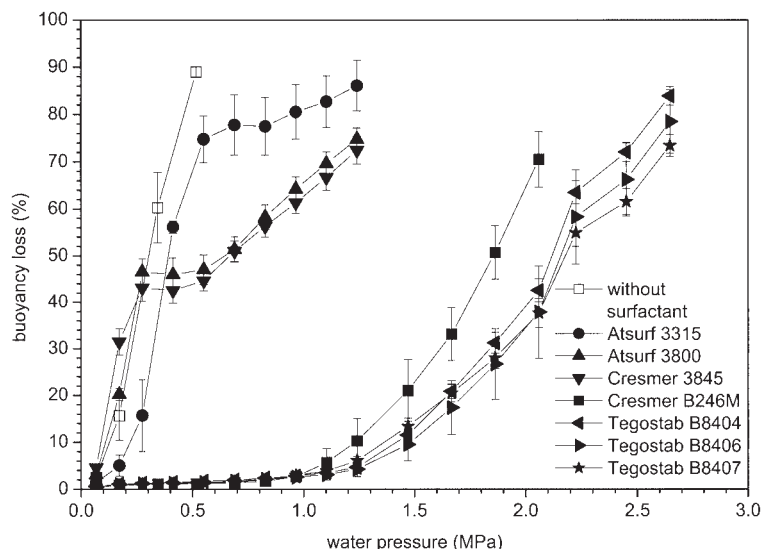


Figure 2 Effect of different surfactants on the hydraulic resistance of the foams.

Typical images of the different foams are compared in Figure 5. All images given in the figure are at a magnification of 40×. Figure 5 shows that cell windows and strut widths of the foams are significantly smaller for the foams made with polyols with low surface tension. These results are consistent with the measurements given in the Figures 6 and 7. We note that in the measurements, 100× magnification was used for the analysis of the foams with the smaller cells for greater accuracy.

The distributions for the cell window area and the strut width of different foams are shown in Figures 6 and 7, respectively. The average values with standard deviation are also given in the figures. Note that the scales in the Figure 6 along the x-axis for the different foams are different. The cell window areas of the foams with no surfactant, with Atsurf 3315, Atsurf

3800, and Cresmer 3845, are very large and they are very widely distributed. In comparison to these foams, the remaining four foams, with Cresmer B246M, Tegostab B8404, B8406, and B8407, 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 those in the foams with Tegostab surfactants. The strut width distribution pattern is similar to that of cell window area distribution patterns. The struts in the foams with no surfactant, with Atsurf 3315, Atsurf 3800, and Cresmer 3845, are very thick and they are very widely distributed in comparison to the foams with Cresmer B246M and with Tegostab surfactants.

The “closed cell content” of different foams is given in Table II. The closed cell content of the foams with

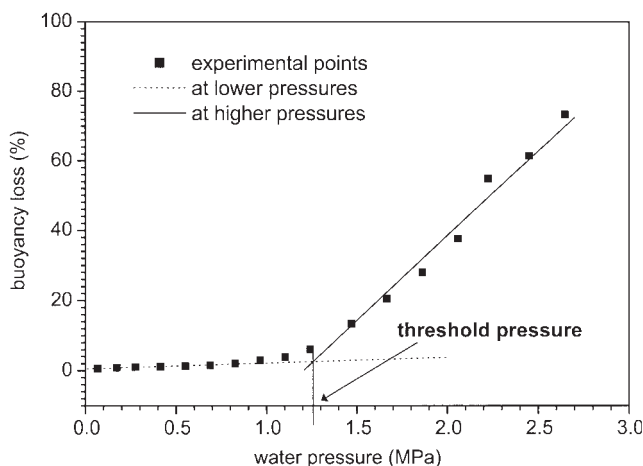


Figure 3 A typical calculation of threshold pressure.

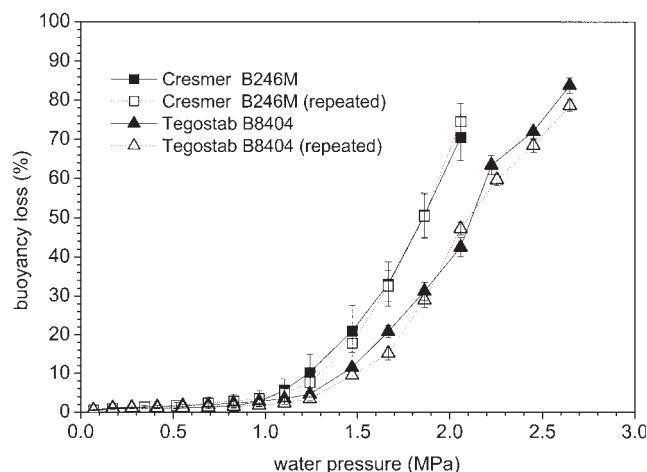
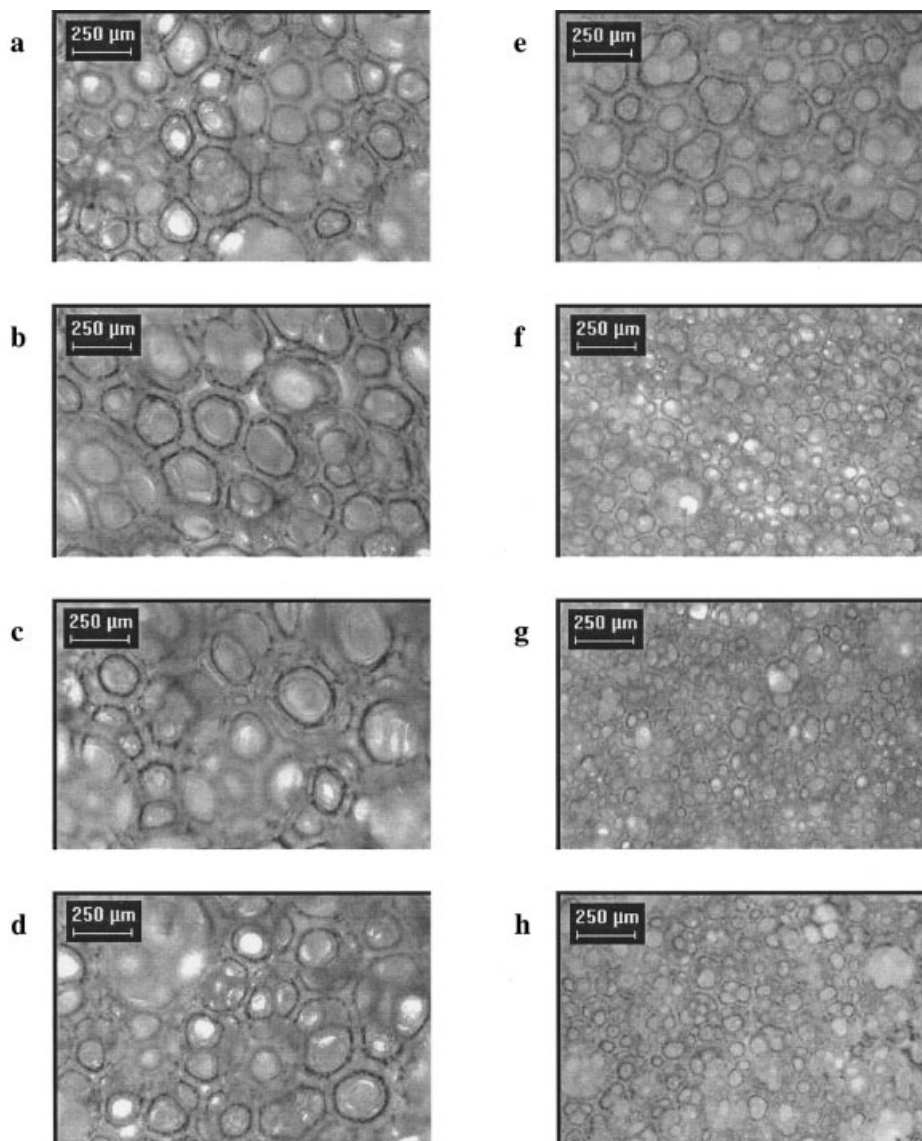


Figure 4 Comparison of results for two foams made with identical formulation for each surfactant.



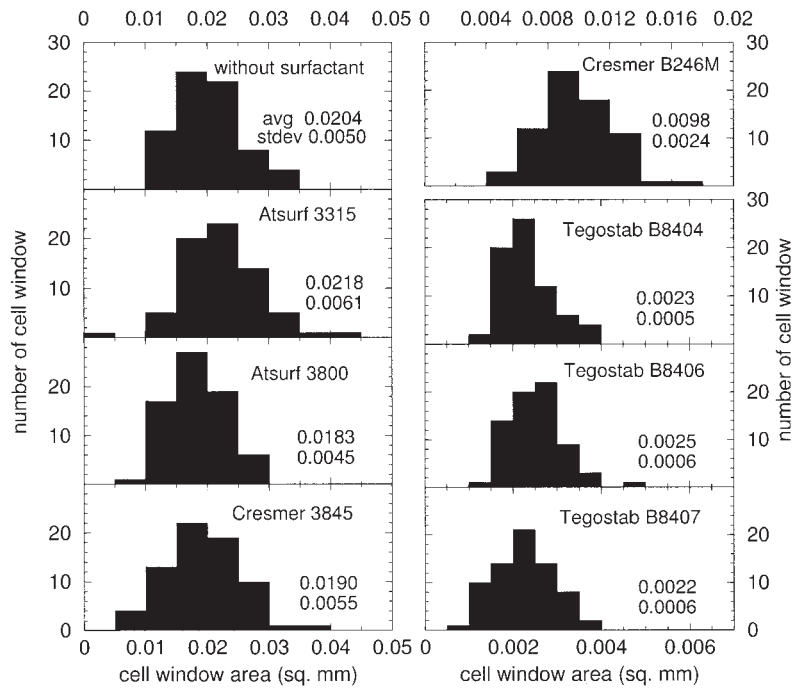
**Figure 5** Sample images of different foams: (a) without surfactant, (b) Atsurf 3315, (c) Atsurf 3800, (d) Cresmer 3845, (e) Cresmer B246M, (f) Tegostab B8404, (g) Tegostab B8406, (h) Tegostab B8407.

Cresmer B246M and with Tegostab surfactants are nearly 95%. However, the closed cell content of the foams with Atsurf 3800 and Cresmer 3845 are around 81%. The closed cell content of the foam with no surfactant is 87%. These values are in agreement with the percentage buoyancy loss at 0.068 MPa water pressure (Table II). This pressure is equivalent to the pressure at a depth of nearly 7 m under water. At this low pressure, the buoyancy loss of the foam is due to the water absorption by the cells on the surface of the foam sample, which are damaged during sample preparation, and by the open cells, which are adjacent to those damaged cells. A negligible fraction of the cell windows are ruptured at this pressure.

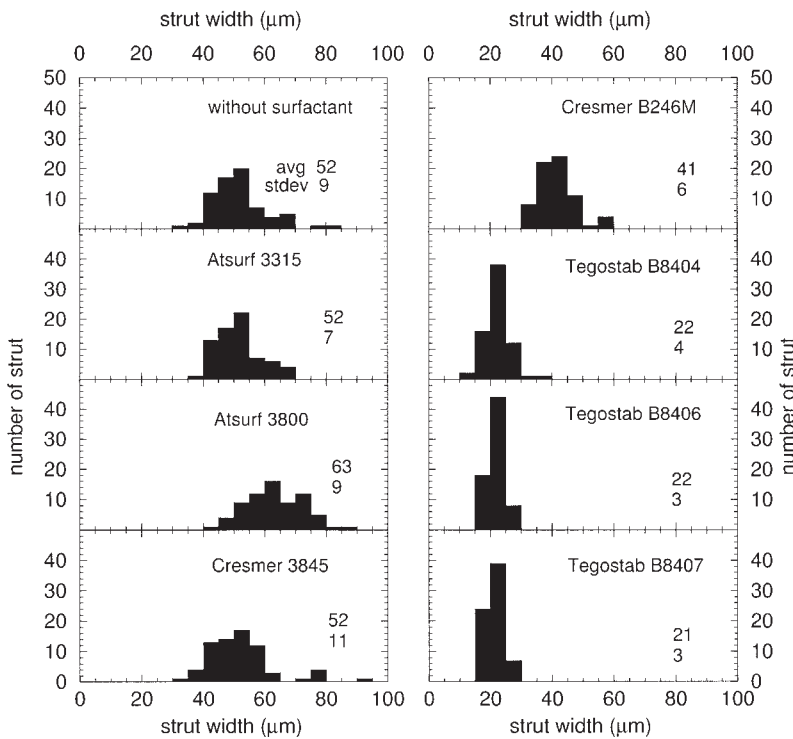
The compressive modulus of different foams is shown in Figure 8. The error bars represent standard deviation over five samples. There are no significant

differences in the compressive modulus among different foams made with different surfactants, although the cell structures of these foams are very different. This can be attributed to the fact that the relatively high density of the foams would mask the effect of cell structure. However, it is interesting to note that foams with Tegostab surfactants are anisotropic. Another interesting result is that the foam with no surfactant has slightly higher compressive modulus along the direction perpendicular to the foam rise than that parallel to the rise direction. These variations are a consequence of the anisotropy in foam structure, which is related to the rate of foam rise.

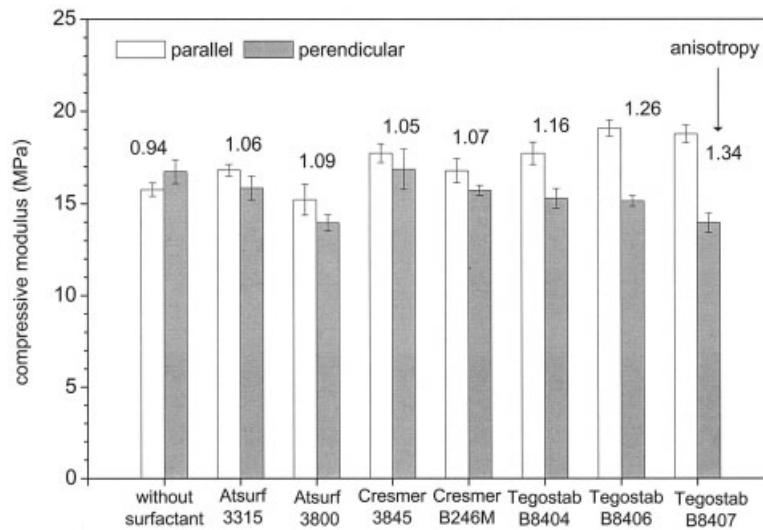
Small compression of the foams was observed at high hydraulic pressures. The foams with Tegostab B8406 and Tegostab B8407 surfactants got slightly compressed for pressure higher than 1.47 MPa. Com-



**Figure 6** Effect of different surfactants on the distribution of cell window area of foams. The average cell window area (avg) and the standard deviation (stdev) are indicated in each graph.



**Figure 7** Effect of different surfactants on the distribution of cell strut width of foams. The average strut width (avg) and the standard deviation (stdev) are given in each graph.



**Figure 8** Effect of different surfactants on the compressive modulus of foams. The measurements 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.

pression was noticed for foams with Tegostab B8404 for pressures higher than 1.66 MPa water pressure. For the foams with Cresmer B246M, the compression was noticed for the pressures greater than 2.05 MPa. Due to this compression, the buoyancy loss is slightly higher than the reported values, calculated assuming volume remained constant. The compression was not uniform; the surfaces parallel to the foam rise direction were deformed to become concave, and thus precise measurement of volume was difficult.

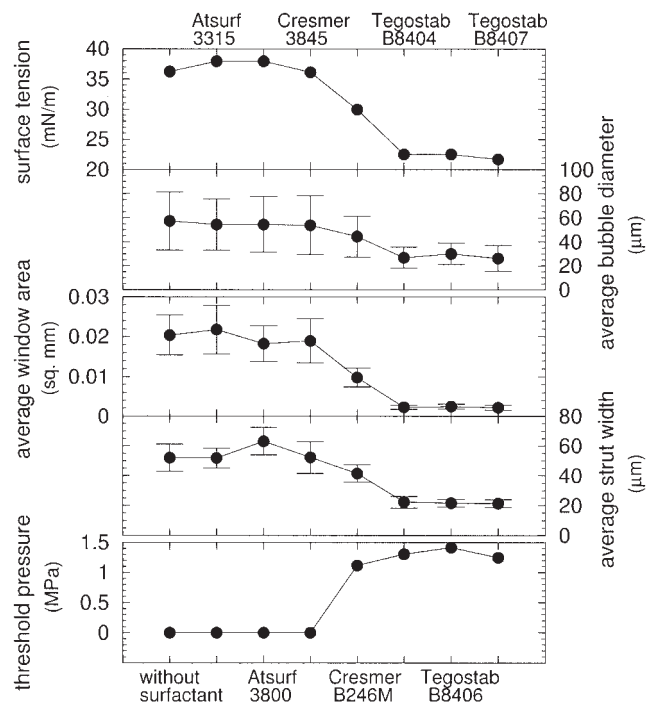
A summary of the results obtained is shown in Figure 9. Low surface tension of the polyol solution facilitates generation of tiny bubbles during mixing and this ultimately leads to foam with very small cell window area and thus increased threshold pressure.

## CONCLUSION

Rigid polyurethane foams for buoyancy applications were prepared using different surfactants. The effect of different surfactants on polyol surface tension and hence on initial bubble sizes were studied. In the cured foams, the effects of different surfactants on hydraulic resistance, cell structure, closed cell content, and compressive modulus were examined. Surfactants, which lowered the polyol surface tension to the greatest extent, facilitated generation of a large number of tiny bubbles in the initial mixing step and stabilized them during foam formation. As a result, in the cured foam, cell windows were very small and narrowly distributed. Hydraulic resistance and hence threshold pressure of the foam increased with decrease in cell window area. Foams made with Tegostab surfactants were anisotropic and above threshold pressure they were com-

pressed along the direction perpendicular to the foam rise direction.

The best performing foam gave a threshold pressure of 1.42 MPa, corresponding to 145 m of water depth. The loss in buoyancy at this pressure was around 8%. The results indicate that rigid polyurethane foams are indeed promising candidates for underwater buoyancy applications. Several im-



**Figure 9** Effect of different surfactants on surface tension of the polyol and initial bubble sizes in polyol, on cell window area and strut width, and on threshold pressures.



provements are possible to increase the depth of use. Mixing using a high-pressure mixing-head as opposed to a stirrer gives finer and more uniform cells,<sup>13</sup> which should give higher threshold pressures. Higher compressive strengths would also contribute to higher hydraulic resistance. This can be achieved by use of appropriate polyols, as well as by the use of reinforcing fillers.

The authors gratefully acknowledge the support of Goldschmidt AG Germany and ICI India in providing the surfactants used in this study.

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