

# Hydraulic Resistance of Rigid Polyurethane Foams. III. Effect of Variation of the Concentration of Catalysts on Foam Structure and Properties

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**ABSTRACT:** Water blown rigid polyurethane foams are made using dibutyltin dilaurate and triethanol amine as catalysts. The rate of carbon dioxide generation due to the reaction of isocyanate with water and the rate of polymerization are varied by changing the relative proportion of the catalysts keeping the total catalyst concentration fixed. The foams have densities in the range of 134 to 164 kg/m<sup>3</sup>. Foams are characterized for hydraulic resistance, "closed cell content," and compressive modulus. 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. The cell window area and strut width of the foam cells are measured by optical microscopy. It is

found that cell window area and strut width decrease and the respective distribution becomes narrower as the proportion of dibutyltin dilaurate in the total amount of the catalysts is increased. The hydraulic resistance and hence threshold pressure of the foams increases with increase in the proportion of dibutyltin dilaurate. The maximum threshold pressure of 1.81 MPa is observed for the foam made with dibutyltin dilaurate alone. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2838–2843, 2004

**Key words:** polyurethanes; rigid foam; catalyst concentration; hydraulic resistance; structure-property relations

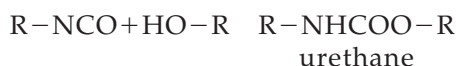
## INTRODUCTION

Rigid polyurethane foams are widely used as insulating materials besides other applications such as in construction, transportation, etc.<sup>1,2</sup> There are two types of chemical reactions that occur during foam formation. One is the blowing reaction, which is the reaction of isocyanate with water. Initially, unstable carbamic acid is formed. This decomposes to an amine and carbon dioxide, which blows the foam. The other type of reaction is network formation, resulting from the reaction of isocyanate with the hydroxyl groups of the polyol. The amine, which is generated due to the decomposition of carbamic acid, also reacts with isocyanate and forms disubstituted urea. Both types of reaction are exothermic. The reactions are shown below.

### Blowing Reaction



### Network Formation



The above-mentioned reactions are slow, and catalysts are added to accelerate them according to the requirement and to establish a balance between the network formation and the blowing reaction. The catalysts most commonly used are tertiary amines and organometallic catalysts, especially organotin catalysts. Tertiary amines are catalysts for both the blowing and network formation, whereas organometallic catalysts catalyze mainly isocyanate-hydroxyl reaction.<sup>3–5</sup> The viscosity of the medium is gradually increased due to the network formation. Due to capillary pressure fluid drainage occurs from cell windows to the struts and thereby cell windows become gradually thinner. The enhanced viscosity of the medium prevents cell window drainage and bubble coalescence.

We consider here rigid polyurethane foams for buoyancy applications. Such 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.<sup>6–8</sup>

When rigid polyurethane foam is placed deep inside water, due to high hydraulic pressure, the foam's cell windows may get ruptured, causing water to pen-

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erate inside the foam. This lowers the buoyancy of the foam. The rupture of the cell windows can be prevented if the areas of the cell windows are small and they are thick. In this paper we consider the effect of changing the relative rates of the foaming and gas generation by changing catalyst concentration. 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.<sup>9</sup> The possibility of using rigid polyurethane foam for buoyancy applications is examined in a series of three papers with an emphasis on "hydraulic resistance" of the foams. Part 1 describes the effect of different surfactants on foam structure and properties.<sup>10</sup> In Part 2, effect of variation of surfactant, water, and nucleating agent concentration on foam structure and properties is given.<sup>11</sup>

The objective of this work is to enhance the rate of network formation so that viscosity build up is slightly faster than the blowing reaction. This would prevent bubble coalescence and slow down cell window drainage. In the final foam, cells would be smaller with thicker cell windows, and thus have a higher hydraulic resistance. In this study foams with densities in the range of 134 to 164 kg/m<sup>3</sup> are made with variation of the concentration of the catalysts, keeping total concentration of the catalysts constant. The effect of variation of the concentration of the catalysts on cell structure and foam properties, especially buoyancy loss at high pressures, is studied.

## 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 was used as surfactant. This silicone surfactant was donated by Goldschmidt AG (Essen, Germany). 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

**TABLE I**  
Formulation Used for Making Different Foams

Ingredients	Formulations (pphp <sup>1</sup> )				
	P_00	P_25	P_50	P_75	P_100
polyol	100	100	100	100	100
water	1.0	1.0	1.0	1.0	1.0
surfactant	3.0	3.0	3.0	3.0	3.0
DBTDL <sup>2</sup>	0.0	0.63	1.26	1.89	2.53
TEA <sup>3</sup>	0.60	0.45	0.30	0.15	0.0
	isocyanate index 105				

<sup>1</sup> parts per hundred g of polyol.

<sup>2</sup> molecular weight 631.11.

<sup>3</sup> molecular weight 149.

containing 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 predetermined amount of isocyanate for 15 s using a high-speed stirrer. The same speed (2800 rpm) was maintained for all formulations. 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.

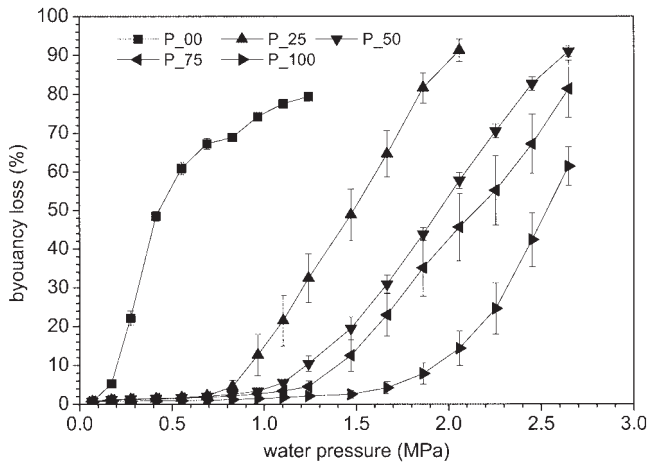
### Characterization

#### 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,

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

where  $\rho_f$ ,  $\rho_f'$ , and  $\rho_w$  are the initial foam density, density of the foam after water absorption, and den-



**Figure 1** Effect of variation of the concentration of the catalysts on the hydraulic resistance of the foams. The error bars represent the standard deviation for four samples.

sity 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  $51 \times 51 \times 30$  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  $150 \text{ kg/m}^3$  using the following relationship,<sup>12</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  $150 \text{ kg/m}^3$ , 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  $51 \times 51 \times 30$  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  $32^\circ\text{C}$ ) and low pressures would behave ideally. The details of experimental set up are given elsewhere.<sup>13</sup>

#### Cell window and strut width measurement

The cell window area and the strut width distributions were measured using an optical microscope (Model BX60 Olympus; Tokyo, Japan). Thin slices, less than 1 mm, were cut from each foam sample. Images were captured by an on-line CCD video camera (Model XC 77CE Sony; Tokyo, Japan) and frame grabber (Model Oculus MX, Coreco; Quebec, Canada). The captured images were analyzed to measure cell window area and strut width by manually selecting the window area and strut width using an image analysis software (Image Pro Plus version 4.1; Media Cybernetics, Inc., Silver Spring, MD). Only those cell windows for which the entire window came into focus was taken. Seventy measurements were made for each foam.

#### Gel time measurement

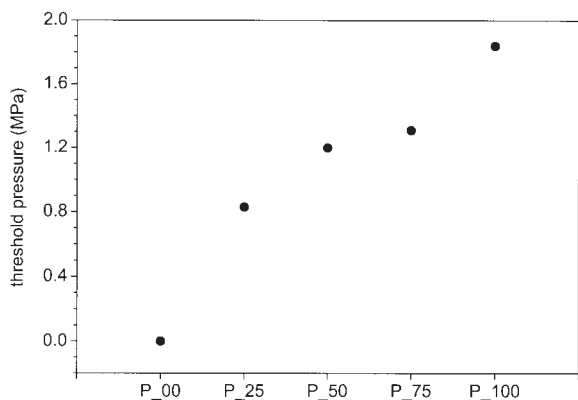
Initially the polyol mixture was prepared and then that was mixed with isocyanate for 15 s. A glass rod was vibrated in the reacting mixture. The point at which the mixture became stiff was considered as gel point. The gel time is the time between the start of mixing and the gel point.

## RESULTS AND DISCUSSION

The buoyancy losses of the foams at different water pressures are shown in Figure 1. The error bars represent the standard deviation for four samples. At any particular water pressure, the buoyancy loss gradually

**TABLE II**  
Gel Time, Closed Cell Content, and Percentage Buoyancy Loss at 0.068 MPa Water Pressure for Different Foams

Foams	Gel time (seconds)	Closed cell content (%)	Buoyancy loss (%) at 0.068 MPa water pressure
P_00	362	$94.8 \pm 1.9$	$0.65 \pm 0.07$
P_25	45	$95.0 \pm 3.8$	$0.66 \pm 0.09$
P_50	37	$96.3 \pm 2.9$	$0.77 \pm 0.14$
P_75	32	$96.0 \pm 1.6$	$0.72 \pm 0.06$
P_100	29	$93.4 \pm 4.1$	$0.55 \pm 0.07$



**Figure 2** Effect of variation of the concentration of the catalysts on threshold pressure of the foams.

decreases with increase in DBTDL proportion. The gel time for different foams is given in Table II. The gel time decreases as the proportion of DBTDL increases. The gel time was maximum (362 s) for foam P\_00 and minimum (29 s) for foam P\_100. When triethanol amine was replaced by DABCO (1,4-diazabicyclo[2,2,2]octane) the gel time reduced from nearly 6 min to 86 s. This value of gel time is still much higher than any foams made with DBTDL.

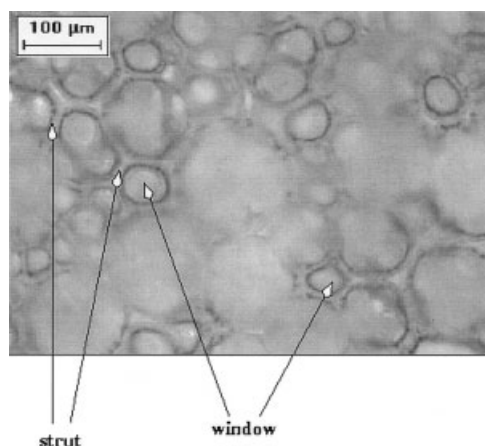
Figure 1 shows that at lower pressures all curves, except that for foam P\_00, are almost parallel to the pressure axis. However, at higher pressures the curves are very steep. A threshold pressure is defined as the point of intersection of the two straight lines, representing the best fitted straight lines of the points at low pressures and at high pressures. A typical calculation of threshold pressure has been shown in part 1.<sup>10</sup> The threshold pressure for different foams is shown in Figure 2. The threshold pressure gradually increases with increase in DBTDL proportion. Foam P\_100, which was made with DBTDL catalyst alone, has the maximum threshold pressure of 1.81 MPa and the corresponding percentage of buoyancy loss is less than 8% (Fig. 1).

Figure 3 shows a typical optical micrograph of the section of the foam. Window and strut are marked in the micrograph. Figure 4 shows the distributions of cell window area and the strut width. Note that in Figure 4 the scales along the x-axis in both window area and strut width distributions for foam P\_00 are different from the rest of the distributions. The average and standard deviation of the measured quantity are given in each graph. The cells in foam P\_00 are very coarse even observed by the naked eye. The cell window area and strut width of this foam are the 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. With increasing mole fraction of DBTDL from 0.25 to 0.75,

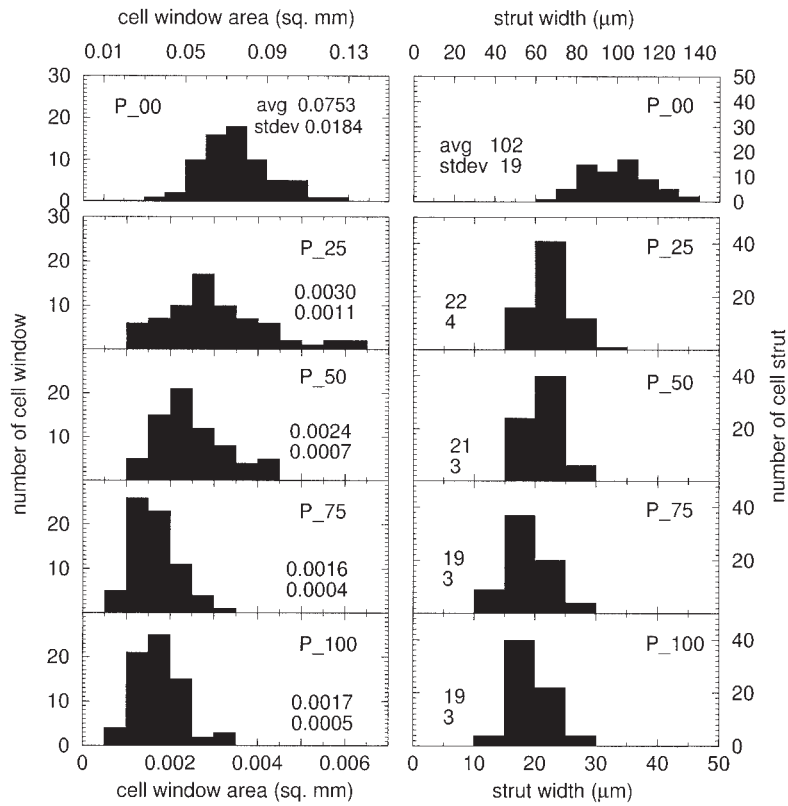
both cell window area and strut width distributions become narrower. However, there are no appreciable differences in the distributions or in the average values between foams P\_75 and P\_100.

The closed cell content of the foams is shown in Table II. There is no change in the closed cell content due to variation of catalyst concentration, and this is further supported by the fact that at 0.068 MPa water pressure, the percentage buoyancy loss of all foams is nearly the same (Table II). 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.<sup>10</sup>

The compressive modulus values of the foams are shown in Figure 5. The error bars represent the standard deviation for five samples. Anisotropy, which is the ratio of parallel to perpendicular compressive modulus, is also mentioned in the figure for each foam. For all the foams, the anisotropy is greater than one. This is usual for rigid polyurethane foam.<sup>12,14–16</sup> However, the anisotropies of foams P\_00 and P\_100 are comparatively higher than the other foams. In the case of P\_100, the anisotropy is 1.23. Baser and Khakhar<sup>12</sup> studied the effect of DBTDL concentration on the compressive strength of the castor oil based rigid polyurethane foams. They found that foams became more anisotropic with increase in the concentration of the DBTDL. Jin et al.<sup>14</sup> attributed this anisotropy to the build up of crosslinked structure in the polymer matrix at an early stage in the foam expansion process. Table II shows that foam P\_100 had the lowest gel time. Thus faster network build up makes foam P\_100 more anisotropic than foams P\_25, P\_50, and P\_75. However, the reason behind the anisotropic nature of the cells in foam P\_00 is not clear to us. Table II shows much longer gel time for this foam and during foam formation it was observed that this foam rose very slowly. Jin et al.<sup>14</sup> measured the compressive strength



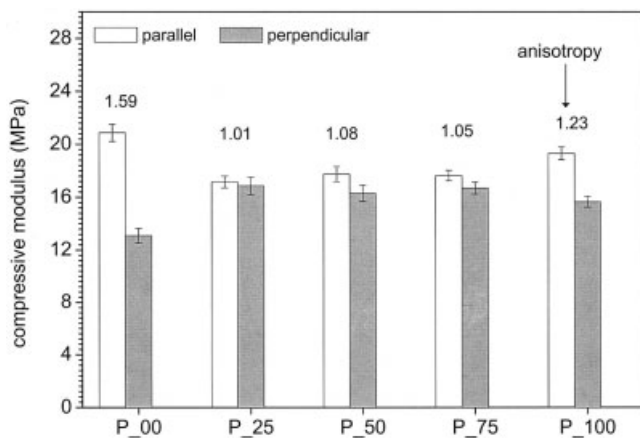
**Figure 3** Typical optical micrograph showing cell windows and struts in rigid polyurethane foam.



**Figure 4** Effect of variation of the concentration of the catalysts on the distributions of cell window areas and strut widths of different foams. The average cell window area (avg) and the standard deviation (stdev) are given in each graph.

in both directions and also measured cell dimensions in scanning electron micrographs (taking cross sections both perpendicular and parallel to the foam rise direction) for the foams studied. For one of the foams, the calculated anisotropy from compressive strength

data was much higher than that obtained from the scanning electron micrographs. Therefore, anisotropy, measured from compressive strength, is not always related to an anisotropic cell geometry. The most important information that comes from Figure 5 is that foam is isotropic if both the reactions are well balanced.



**Figure 5** Effect of variation of the concentration of the catalysts on the compressive modulus of the foams. Compressive modulus both parallel and perpendicular to the foam rise directions are shown. The error bars represent the standard deviation for five samples. Anisotropy is the ratio of parallel to perpendicular compressive modulus.

We present the following qualitative discussion to explain the variation of hydraulic resistance of the foams based on the above supporting measurements. The catalytic efficiencies of the different catalysts are different. For foam P\_00, the rate of network formation is much slower than any other foam, so the viscosity build up is very slow resulting in coalescence of the bubbles. For this reason the cell windows of 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 P\_00 are very large even at low pressures. As the proportion of DBTDL is increased, the rate of network formation is accelerated and so there is lesser coalescence of the bubbles. Consequently, in the final foams there are more numerous cells of smaller size and thus the cell windows are smaller. Figure 4 shows that the cell window areas and strut widths of foams P\_75 and P\_100 are almost the same. But the hydraulic resis-

tance of P<sub>100</sub> is more than that of P<sub>75</sub>. This indicates the windows of P<sub>100</sub> are stronger, and hence thicker than the windows of P<sub>75</sub>. The gel time of P<sub>100</sub> is less than P<sub>75</sub>, so the viscosity built up is faster for P<sub>100</sub> and thus there is less time for cell window drainage. This would lead to thicker windows for P<sub>100</sub>.

### CONCLUSION

Rigid polyurethane foams for buoyancy applications were prepared with variation of the concentration of the catalysts. The effect of this variation on hydraulic resistance, cell structure, closed cell content, and compressive modulus were examined. With increase in the proportion of DBTDL, the gel time decreased and so the viscosity build up was faster. The enhanced viscosity prevented the gas bubbles from coalescence and reduced the cell window drainage. The window areas of the foams decreased with increase in the proportion of the DBTDL, and therefore the hydraulic resistance of the foams increased. Foams became anisotropic when the reactions for foaming and gelling were not well balanced.

The maximum threshold pressure of 1.81 MPa (equivalent to pressure at 185 m under water) was observed for the foam made with dibutyltin dilaurate alone. The loss in buoyancy at this pressure was less than 8%. These results are useful to improve the hydraulic resistance of the foam, and that is essential for buoyancy applications. Reinforcing the cell windows to make them stronger can increase the hydraulic resistance of the foam further and this needs to be explored.

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