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The microstructure of rigid polyurethane foams

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A study has been made of the microstructure of rigid closed-cell polyurethane foams in the density range 35 to 420 kg m^{-3}. Existing models for the structure of foams of this type have been evaluated using optical and scanning electron microscope techniques. Foams with a density of the order of 35 kg m^{-3} are shown to be best represented as a pentagonal dodecahedron. Medium density foams from 70 to 300 kg m^{-3} have a structure described as rounded polyhedra and high-density foams from 300 to 420 kg m^{-3} have an isolated spherical structure. A relationship between average cell size and density is given.

1. Introduction

The mechanical behaviour of polymer foams is governed by the properties of the bulk polymer, the volume-fraction of polymer present (i.e., the density of the foam) and the geometry of the cell structure. Usually polymer foams are produced by the introduction of a gaseous phase into the liquid-state polymer which is then solidified by thermal or chemical means.

This foaming process can be divided into three stages [1]:

(a) the nucleation of small cells in the liquid polymer;

(b) the growth of the cells to a desired volume; and

(c) stabilization of the structure.

Cells are nucleated as spherical bubbles which grow rapidly as gas from the blowing agent diffuses into them and which continue to expand as the volume-fraction of gas increases. Since spherical cells can only occupy 76% of the volume [2, 3] the spherical shape is lost as the volume-fraction of gas exceeds this limit. Where the growing cells impinge the liquid drains away to leave a thin, flat membrane, or window, of material between the cells. At the junction between windows, comparatively thick, straight struts of material are left. Thus, a structure is formed consisting of irregular polyhedral cells bounded by the polygonal windows with thick struts at their edges [4]. Constrictions to the expansion of the foam usually lead to a preferred "rise direction" which causes elongation of the cells in that direction [3].

Several models of cell structure have been proposed and used to characterize the properties of foams. Gent and Thomas [5] used a simple cubic lattice of struts which Kanakkanatt [6] modified to include anisotropy. Doherty *et al.* [7] described a tetrakaidodecahedron, i.e., a polyhedron with six square and eight hexagonal faces. Ko [8] described the polyhedral structures produced from different packings of spherical cells: hexagon close packing producing a trapezo-rhombic dodecahedron (i.e., six equilateral trapezoids and six congruent rhombic faces) and face-centred cubic packing transforming each sphere into a rhombic dodecahedron (i.e., with twelve congruent rhombic faces). In a real foam most of the cells were pentagonal dodecahedra (i.e., twelve pentagonal faces) which were formed by packing five spheres around the hollow between two adjacent spheres. Jones and Fesman [9] made a study of a series of urethane foams in which cells were observed to be pentagonal dodecahedra, but not all of the pentagons were regular. A model was proposed which was an elongated pentagonal dodecahedron with its axis of symmetry parallel to the foam rise direction. The cell height-to-width ratio varied from 1.5 to 2.0 and the cross-sectional shape of the strut tended to be triangular but was better described as a hypocycloid of three cusps. Harding

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[3] favoured the pentagonal dodecahedron model. This model optimizes wet-foam stability because of its equiangular structure. The tetrakaidodecahedron minimizes surface area but its non-equiangular configuration imbalances capillary pressure to produce unstable wet foams. Cell elongation destroys equiangularity of the structure without disrupting its equilateral character. Patel and Finnie [10] decided that the requirements of a model were that the windows should meet at an angle of 120° and that the struts should meet at an angle of 109.47°. Whilst no regular polyhedron met these requirements the tetrakaidodecahedron and pentagonal dodecahedron were the best models, with the latter being preferred. Chan and Nakamura [11] and Menges and Knipschild [12] used the regular pentagonal dodecahedron as a model for the mechanical behaviour of foams. Smith [13] compared the structure of foams, metal grains and animal and plant cells. By considering topological and surface-tension requirements, he concluded the average number of sides per window was $5\frac{1}{7}$. Experimental observations showed that most windows were pentagonal with relatively few four- and six-sided windows present. Waterman and Phillips [14] stated that the structure of foams of density higher than about 200 kg m^{-3} was one of isolated spherical holes in a polymer matrix, low-density foams had a polyhedral structure foams and foams of density 100 kg m^{-3} had a structure intermediate between the two extremes.

The aim of the present work was to examine the microstructure of rigid closed-cell polyurethane foams in the density range 35 to 420 kg m^{-3}, and to evaluate the most suitable model for predicting the mechanical properties of the foams.

2. Experimental procedure

2.1. Materials

The material used for this investigation was the "Caradol–Caradate" system of rigid closed-cell polyester–polyurethane foams marketed by Shell Chemicals Ltd. Water is used to produce CO_2 as the primary blowing agent. The final density of the foam is controlled by the secondary blowing agent, trichlorofluoromethane.

Foams were produced by two methods, a conventional spray technique using an air-assisted spray-gun to spray the material on to a vertical hardboard substrate and by moulding of specimens in a demountable wooden mould in the laboratory.

2.2. Microscopy

Limitations of depth-of-field in optical microscopy mean that, for the three-dimensional structure of foams, only low magnifications are useful. Optical microscopy, however, has the advantage that for semi-transparent materials, such as the foam being studied here, it is possible to focus on structure beneath the surface and thus avoid surface damage caused in cutting the specimen. Sections of very low density foams (< 50 kg m^{-3}) for microscopy could be satisfactorily cut with a scalpel. Foams of higher density were cut with a diamond wafering blade, running in iso-pentane, on a low-speed "Isomet" saw. These specimens were then ultrasonically cleaned in iso-pentane.

Because of the small cell size of high-density foams, the high magnification required and consequent lack of depth-of-field made optical examination unsatisfactory. Very high density foams (> 400 kg m^{-3}) could be ground and polished by conventional metallographic techniques for high-power optical microscopy.

Scanning electron microscopy provides the required depth-of-field for examination of foams but transparency of the specimen is lost so that surface damage could obscure the undamaged structure. Fracture surfaces were found to provide good specimens for scanning electron microscopy. Cell-size measurements were made from scanning electron micrographs; measurements were made both parallel with and perpendicular to the "rise" direction.

3. Results and discussion

3.1. Low-density foams

Optical photomicrographs of low-density foams clearly show their characteristic polyhedral structure. Fig. 1 is a photomicrograph of a foam of density 35 kg m^{-3} and shows the network of struts forming the edges of the cell faces. Each polygonal cell-face is covered by a thin membranous window. The windows are considerably thinner than the struts, as shown in Fig. 2, a SEM micrograph of a cross-section of a broken strut. The cross-sectional shape of the strut is approximately triangular and has been described as a hypocycloid of three cusps [9]. The following observations were made of the structure of low-density foams:

(a) The vast majority of windows were pentagonal, as seen in Figs 1, 3 and 4. A number of four- and six-sided windows were observed but

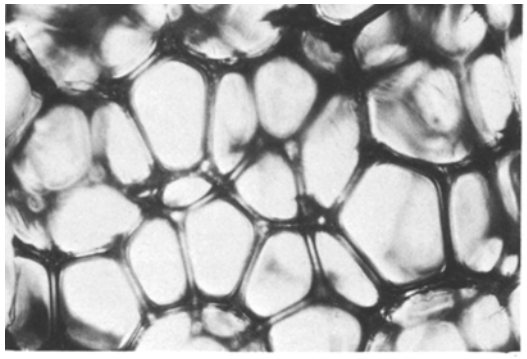

Figure 1 Photomicrograph of foam of density of 35 kg m^{-3} showing characteristic polyhedral cellular structure (× 60).

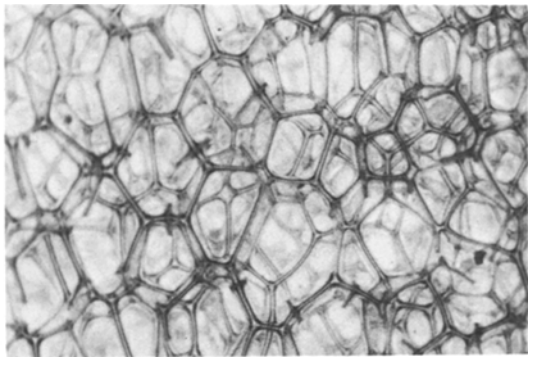

Figure 3 Photomicrograph of section of foam of density 29 kg m^{-3} taken parallel to rise direction (× 20).

their number was insignificant compared with the number of pentagonal windows.

(b) Struts were always formed at the junction of three windows, as seen in Fig. 2. The angle between the windows was approximately 120° C.

(c) Nodes, i.e., the junction of struts, were always formed by four struts. The three struts seen at each node in Fig. 1 are accompanied by a strut out of the plane of the micrograph.

(d) The pentagonal windows tended to be equilateral, the struts meeting at an angle of 108°, as seen in Fig. 1, rather than equilateral as suggested by Harding [3].

From these observations it is concluded that the best model to represent the structure of low-density foams is the pentagonal dodecahedron. Although regular pentagonal dodecahedra do not pack together to fill space, this can be accounted for by local distortions and the presence of occasional four- and six-sided windows. The angle between the faces of a regular pentagonal dodecahedron is 116.56°, which is quite close to the 120° observed in foams. The angle between the struts in the model is 108° which is very close to the tetrahedral angle of 109.47° required for four struts to meet at a point.

The anisotropy of low-density foams is apparent from the shape of the pentagonal windows, which are not regular pentagons but are elongated in the rise direction. A comparison of photomicrographs of sections of a foam cut parallel with and perpendicular to the rise direction, Figs 3 and 4, respectively, demonstrates this elongation.

3.2. Medium and high-density foams

The characteristic polyhedral structure of low-density foams is caused by distortion of spherical bubbles as they impinge and continue to grow. In high-density foams where the volume-fraction of gas is much less than 76% very little distortion would be expected and the bubbles should remain spherical. This can be seen from Fig. 5, a micrograph of a polished section of a foam of density

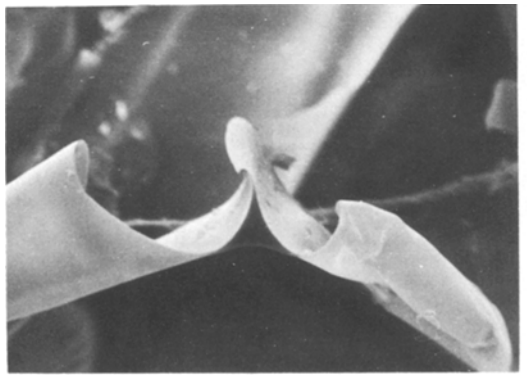

Figure 2 Scanning electron micrograph of cross-section of broken struts in foam of 35 kg m^{-3} density (× 320).

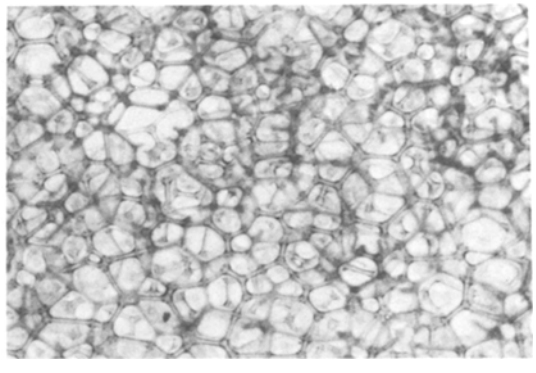

Figure 4 Photomicrograph of section of foam of density 29 kg m^{-3} taken perpendicular to rise direction (× 20).

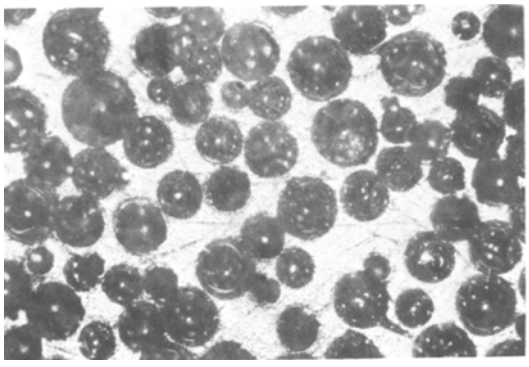

Figure 5 Photomicrograph of polished section of foam of density 420 kg m^{-3} (× 60).

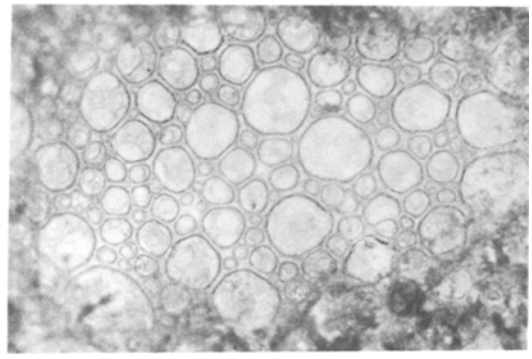

Figure 7 Photomicrograph of foam of density 70 kg m^{-3} showing slightly distorted cells (× 40).

420 kg m^{-3}. The cells appear to be essentially spherical but are not entirely isolated as impingement is frequent; where this occurs a circular window is formed. Circular windows can be seen in some of the cells of Fig. 6, a SEM micrograph of a moulded foam of density of 420 kg m^{-3}.

Medium density foams have a structure intermediate between the two extremes. The growing bubbles of gas impinge and distort but not to the same extent as in the lower densities. The windows tend to remain circular or form polygons with rounded corners. Fig. 7 shows a foam where the windows are slightly distorted from their circular shape and are beginning to form polygons. The SEM micrograph in Fig. 8 shows cells with rounded windows. The struts still have their triangular cross-section. The cells in these intermediate-density foams, shown in Figs 7 and 8, could be described as "rounded polyhedra". Thus, foams can be classed as of low, medium or high density on the basis of their cell structure. The pentagonal dodecahedra of low-density foams are found at densities of up to about 70 kg m^{-3}. The intermediate structure, medium-density foams occur in the density range from 70 to about 300 kg m^{-3}. At densities greater than about 300 kg m^{-3} the isolated spherical structure of high-density foams is found.

A feature of sprayed polyurethane foam not mentioned in the literature is the presence of "weld lines" between the layers. Sprayed foams are built up of several layers, each formed by a single pass of the spray-gun. The surface of each layer is, until the next layer is deposited, in contact with the air. This causes the polyurethane to cure more quickly, preventing the expansion of the cells nearest the surface and creates a surface of very small cells at the junction of the layers; this can be seen in Fig. 9 as a distinct "weld line" when the foam is sectioned. In high-density foams where the layers are quite thin (2 to 3 mm) many weld lines are present.

3.3. Cell size

The density of the foams is controlled by the amount of gas released by the blowing agent. This

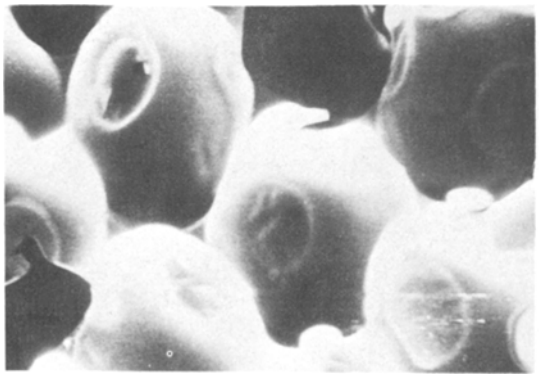

Figure 6 Scanning electron micrograph showing structure of foam of density 420 kg m^{-3} (× 100).

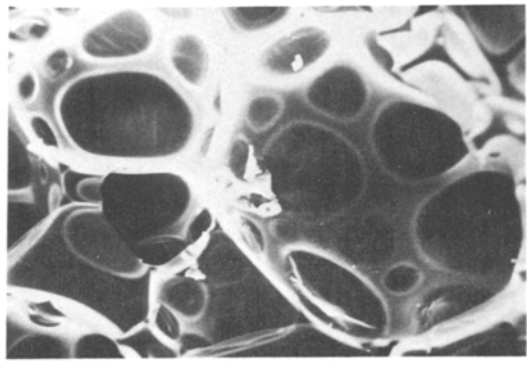

Figure 8 Scanning electron micrograph showing structure of foam of density 70 kg m^{-3} (× 140).

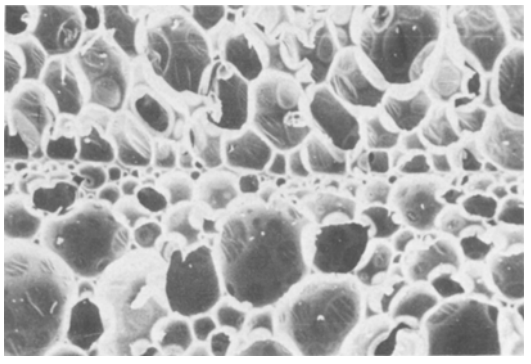

Figure 9 Scanning electron micrograph of foam of density 106 kg m^{-3} showing internal skin structure (× 140).

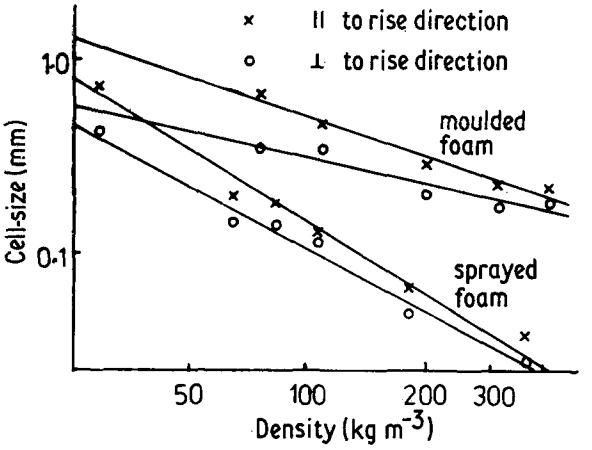

Figure 10 Plot showing variation of cell size with density.

also affects the average cell-size, d, and the following general relation is found to hold:

$$d = a\rho^{-b}, \qquad (1)$$

where ρ is foam density in kg m^{-3}, a and b are constants and the average cell-size, d, is in mm. The following relationships were derived from cell-size measurements from a number of foams:

(i) for moulded foams parallel to the rise direction, $d = 10.84\rho^{-0.66}$;

(ii) for moulded foams perpendicular to the rise direction, $d = 2.41\rho^{-0.44}$;

(iii) for sprayed foam parallel to the rise direction, $d = 34.67\rho^{-1.19}$; and

(iv) for sprayed foams perpendicular to the rise direction, $d = 15.28\rho^{-1.08}$.

The above relationships are shown in a logarithmic plot of cell size against density shown in Fig. 10. This illustrates anisotropy of cell size which is greatest at lowest densities. As the density increases the anisotropy becomes less marked. At the highest densities, however, where the cells appear to be almost spherical (as in Fig. 5), anisotropy is still evident as shown by the measurements of cell dimensions. The average cell-size of the sprayed and moulded foams differs considerably. The sprayed foams have a smaller average cell-size than the moulded foams, particularly at higher densities. This means that the sprayed foams must have a larger number of cells nucleated per unit volume, in the initial stage of foaming.

4. Conclusion

The most suitable model for the structure of low-density foams is the elongated pentagonal dodecahedron with edges formed of struts of triangular cross-section and with faces covered by thin, membranous windows. At medium densities the dodecahedra are "rounded" and less elongated whilst at high densities the cells tend to be spherical although anisotropy is still evident. Average cell-size, d, is found to vary with density, ρ, according to an expression of the form

$$d = a\rho^{-b}.$$

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