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THE MICROSTRUCTURE OF CELLULAR SILICONE AS SHOWN BY THE
SCANNING ELECTRON MICROSCOPE

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THE MICROSTRUCTURE OF CELLULAR SILICONE AS SHOWN BY THE SCANNING ELECTRON MICROSCOPE

INTRODUCTION

Cellular Silicone^{*} was developed by Union Carbide Corporation in 1960 in response to LLL needs for an elastomeric stress cushion with controllable thickness and shape, reproducible load-deflection characteristics, and minimal temperature dependence in the military range.^{1,2} A patent was granted on the material and process in 1966.³ Detailed description of the composition and fabrication of the material will be found in other reports.⁴⁻⁹ It is sufficient for this note to state that the material is made from a poly (methyl, phenyl) siloxane, containing a small proportion of vinyl groups. The cellular structure is obtained by incorporating urea prills (tiny spheroids) as a temporary filler. Crosslinking is accomplished by adding a peroxide and molding to shape under heat and pressure. The temporary filler is subsequently washed out, and the material is given a post cure.

Union Carbide personnel have considered the material to be largely closed cell, and postulate that the urea solution permeates through the silicone rubber during the washing (leaching) process. The load-deflection behavior is not consistent with a closed cell structure; however, it is known that silicone rubbers have very high air permeability. Open cell content measurements made at LLL using the Remington-Pariser apparatus¹⁰ showed both Y-3260 (density about 0.53 g/cm³) and Y-3333 (density about 0.34 g/cm³) to be essentially open cell. This apparatus is operated with a procedure (formerly ASTM D 1940) using a ΔP of 20 Torr (2.7 kPa). The air pycnometer, more commonly in use for determining the open-cell content of cellular plastics (ASTM D 2856-70), uses a ΔP of 1 or 1/2 atmosphere (100 or 50 kPa), obviously unsuitable for soft, flexible cellular materials.

The shallow depth of field of an optical microscope, especially at high magnifications, makes it unsuitable for examining the microstructure of cellular silicone. The scanning electron microscope (SEM), on the other hand, is ideally suited for examining three-dimensional structures over a range of magnifications. At my request the Metallurgy Division at LLL examined specimens of cellular silicone with the SEM. The instrument was operated by Wayne Steele, who also took the photographs (Figs. 1-16).

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I am at a loss to explain why the second set of photographs of Y3260 (Figs. 11-14) shows a much more porous material than that shown in the second set taken of Y-3333 (Figs. 3-10), unless the specimens were accidentally interchanged. Steele feels this did not happen. At best, cellular silicone is not a highly uniform material on a microscopic scale, and it could simply be that a porous section of Y-3260, originally containing a high concentration of urea spheres, was selected for examination.

SUMMARY

Specimens of cellular silicone, Y-3260 and Y-3333 were examined at magnifications of 20X to 2000X by a scanning electron microscope. The spherical cell structure due to leaching of the temporary filler is readily apparent. Other voids due to broken urea particles are also seen and an irregular porosity is evident which interconnects cells and accounts for the measured open cell content. I welcome further interpretation.

DISCUSSION

For the first set of pictures, specimens of Y-3260 and Y-3333 cellular silicones were immersed in liquid nitrogen and then fractured. They were then examined in the SEM. The scanning lines on the photos are probably due to insufficient deposition of gold on the surface of the cellular silicone. (It is necessary to make the normally non-conducting surface of plastics conducting by depositing a thin metallic coating; otherwise electrons bounce from the surface with consequent loss of detail.)

At low magnification, 20X, the spherical depressions left by the prilled urea are readily visible. The urea particles were screened to 25-40 mesh (0.707 to 0.420 mm or 0.0276 to 0.0164 in.). In Fig. 1a (of Y-3260) the depressions appear randomly distributed, but in Fig. 2a (of Y-3333) the depressions appear to be almost close-packed. The torn surface of the fractured rubber is apparent in both figures and becomes more obvious at higher magnifications. Figures 1b and 2b, Y-3260 and Y-3333 respectively at 50X, show the surface of the depressions in more detail. Numerous voids are seen; these probably interconnect with adjacent cells to account for the open-cell structure. The fine structure is shown at magnifications of 100X and 200X in Figs. 1c-d and 2c-d. Figure 2d (Y-3333 at 200X) shows especially well the cell surface with voids penetrating to adjacent cells.

The next set of pictures was taken of Y-3333 specimens prepared by:

(1) fracturing after cooling in liquid nitrogen, (2) making a sharp knife cut across the specimen, and (3) the unmodified molded surface of the material. This time we examined specific areas or structures in detail by increasing the magnification. Figures 3-6 examine the fractured surface of Y-3333. Figure 3a shows a nearly close-packed structure, with many small voids penetrating the depressions left by the urea spheres. Arrow A points to a curious wedge-shaped depression that is further

magnified in Figs. 3b at 100X and 3c at 200X. The cause of the depression is unknown, but it is possibly due to a formation on the original urea particle, or to moisture associated with the urea particle which could have turned to steam at curing and molding temperature. Arrow B (Fig. 4a) points to a portion of the silicone rubber in between cells, and is further shown in Figs. 4b at 100X and 4c at 200X. It appears to contain irregular voids, substantially smaller than the spherical depressions; these voids may have been caused by a tearing action during fracture. In Fig. 5a the frame outlines two opposing cusps formed by fracturing the rubber between cells. Figure 5b shows this area at 500X. Note the depression just above the cusp points; it is shown at 2000X in Fig. 5c. Figures 6b and 6c show an area outlined by the small frame in Fig. 6a. It is a typical fracture surface and shows some small voids that may have been caused by broken urea particles. In all cases, we see many small irregular voids, some of which penetrate from one large spherical cell to the next. The cell surface appears glossy on high magnification, but has many irregularities.

Figures 7-9 examine the cut surface of Y-3333. The spherical cell enclosed by the box in Fig. 7a (50X) has a bulge that is shown in more detail in Figs. 7b and 7c, 100X and 200X. It would appear to be caused by a depression in the original urea prill. These prills are formed by dropping a concentrated urea solution from a tower; during evaporation, hollows can form in the prills. The arrow in Fig. 7a points to a relatively solid area, magnified at 100X, 200X, 500X, and 1000X in Figs. 8a, 8b, 8c, and 8d. Note the marks from the imperfections in the knife blade. Note also the numerous small irregular voids which do not appear to penetrate deeply. These may be caused by broken urea particles. In Fig. 9a the frame outlines an area in the spherical depression (cell) further magnified in Figs. 9b, 9c, and 9d. Again, we see the relatively smooth cell surface marred by numerous blemishes, possibly on the original urea prill, or possibly formed during curing and leaching.

Figure 10 shows the molded surface of Y-3333 at 50X to 1000X. The surface has many projections and some voids. The projections are one impediment to accurate thickness measurement of thin sheets or shaped parts of cellular silicone. Voids may be due to broken urea particles, leached out in processing. At high magnification, the surface appears relatively smooth.

A fractured specimen of Y-3260 is shown in Figs. 11-12. The spherical depressions left by the urea particles are well defined and appear to be almost close-packed in Fig. 11a. The frame indicates a cell and the area immediately below it that are further enlarged in Figs. 11b, 11c, and 11d at 100X, 200X, and 500X. The crack was probably formed when the specimen was fractured after being cooled in liquid nitrogen. The area to the left of the cell has numerous irregular pores which apparently penetrate adjacent cells as in Fig. 11d. Figures 12b and 12c show greater detail at 500X and 1000X of the areas indicated by arrows A and B in Fig. 12a. Figure 12d at 1000X shows an odd formation on the surface of a cell, which is indicated in Fig. 12a by arrow C.

A specimen prepared by a knife cut shows similar high porosity, Fig. 13. In Fig. 13a, 100X, the larger box indicates the cell surface shown in greater detail in Figs. 13b and 13c, 500X and 1000X. Again, intercellular porosity is apparent, but the peculiar roll and the line are hard to explain unless they are impressions from the original urea particle. Figure 13d, 1000X, shows a void probably due to a broken urea particle.

Figure 14 show a very rough and porous portion of the molded surface of Y3260. Circular openings were caused by urea spheres, and some irregular voids left by broken urea particles are apparent. The area indicated by the frame in Fig. 14 at 100X is magnified at 200X, 500X, and 1000X in Figs. 14b-d.

The urea prills are shown in Fig. 15. Figure 15a shows some screened prills at 25X. They are only roughly spherical, and have projections and hollows. The prill enclosed by the frame in Fig. 15a is shown at 100X in Fig. 15b, and at 1000X in Fig. 15c. Small crystals may be observed on the surface at high magnification. These may be dislodged during blending of the prills with the base silicone (Y-3219), and may account for some of the voids seen in the cellular silicone. Most of the surface shows evidence of rapid crystallization, and is not as smooth as might be expected from cell surfaces seen in the cellular silicone.

We wanted to see whether some of the voids might have been caused by the washing process. Figures 16a and 16b show the surface of a sheet of Y-3219 at 1000X; this is the same base as the cellular silicone, but was not mixed with urea prills prior to molding and curing. It shows a relatively smooth surface free from voids. Figures 16c and 16d show the surface of Y3219 at 1000X after washing and drying. Again it is void-free, although Fig. 16d shows some irregular particles on the surface. It is possible, but unlikely, that Y3219, washed after molding, but before post-curing, would show a more porous structure.

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a. (20X)

b. (50X)

c. (100X)

d. (200X)

Fig. 1. Torn surface of Y-3260 cellular silicone.

a. (20X)

b. (50X)

c. (100X)

d. (200X)

Fig. 2. Torn surface of Y-3333 cellular silicone.

a. (50X)

b. (100X)

c. (200X)

Fig. 3. Fractured surface of Y-3333; note wedge shaped depression.

a. (50X)

b. (100X)

c. (200X)

Fig. 4. Fractured surface of Y-3333; detail of web between cells.

a. (50X)

b. (500X)

c. (2000X)

Fig. 5. Fractured surface of Y-3333; detail of cusp with depression.

a. (50X)

b. (500X)

c. (1000X)

Fig. 6. Fractured surface of Y-3333; detail of small voids.

a. (50X)

b. (100X)

c. (200X)

Fig. 7. Cut surface of Y-3333; detail of cell with a bulge.

a. (100X)

b. (200X)

c. (500X)

d. (1000X)

Fig. 8. Cut surface of Y-3333; note numerous shallow irregular voids.

a. (50X)

b. (200X)

c. (500X)

d. (1000X)

Fig. 9. Detail of cell wall of Y-3333; note relative smoothness.

a. (50X)

b. (200X)

c. (500X)

d. (1000X)

Fig. 10. Molded surface of Y-3333.

a. (50X)

b. (100X)

c. (200X)

d. (500X)

Fig. 11. Fractured surface of Y-3260; detail of cracked cell.

a. (50X)

b. (500X)

c. (1000X)

d. Odd formation (1000X)

Fig. 12. Fractured surface of Y-3260; details of cell wall and odd formation.

a. (100X)

b. (500X)

c. (1000X)

d. (1000X)

Fig. 13. Cut surface of Y-3260; details of cell surface and irregular voids.

a. (100X)

b. (200X)

c. (500X)

d. (1000X)

Fig. 14. Molded surface of Y-3260; details of rough porous area.

a. (25X)

b. (100X)

c. (1000X)

Fig. 15. Urea prills; details showing irregularities and small crystals.

a. (1000X)

b. (1000X)

c. (1000X)

d. (1000X)

Fig. 16. Y-3219 non-cellular silicone; a and b—before washing, c and d—after washing.

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