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Elastic modulus dependence on density for polymeric foams with systematically changing microstructures

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Several series of foams were prepared by filling an open-cellular foam preform with varying amounts of polymer. The foams had systematically changing cellular structures and their compressive moduli were found to vary as the square of the density. A change from plastic to elastic-plastic behaviour occurred as the density increased. Current mathematical models did not adequately handle the observed relationship between yield strength and density.

1. Introduction

Organic cellular materials (such as wood, honeycomb, sponges, etc.) are common in nature and abound in man-made articles (e.g. anything styrofoam, polyurethane cushions, porous membranes, corrugated cardboard, etc.). As such, these cellular materials play important roles in our daily lives. Practically speaking, anything, whether it is metal, glass, rock, polymer, etc., that is less than full density and has its void volume more or less uniformly distributed throughout can be classified as a cellular material. Gibson and Ashby [1] have presented an excellent treatise on the structure and properties of cellular solids. One of the difficulties in applying generalized treatments to cellular solids is the narrow range over which the density can be varied without significantly changing the gross structure of the material. In efforts to prepare foams with densities from 0.1 to 1.0 g cm^{-3}, we were able to produce a series of foams that possess only minor changes in their overall structure [2]. In this paper, we report the dependence of elastic compressive modulus and crush strength on density for several series of open-cellular polystyrene foams backfilled with varying amounts of polymer.

2. Experimental details

Right-cylindrical foam preforms 2.5 cm diameter by 2.5 cm high were cut from a 0.074 g cm^{-3} emulsion foam prepared from styrene/divinylbenzene (90/10 wt %) by an emulsion polymerization technique [3]. Monomer solutions were prepared from styrene, divinylbenzene, heptane, and azobisisobutyronitrile (AIBN, an initiator). Details of the amounts of each and the resulting phase behaviour, densities, volume changes, etc, are discussed elsewhere [2]. A foam preform was placed in a 125 ml jar, covered with 100 ml of the appropriate solution, and held beneath the surface with a stainless steel rod. A vacuum was applied at room temperature to remove the air entrapped in the foam. The vacuum/release cycle was repeated several times and then the jar was capped and heated overnight in a 60° C oven. The polymerized solid masses were removed from the jars by cracking the glass and carefully removing the glass fragments. Each sample was set on a piece of plate glass and dried in a 60 to 80° C forced-air convection oven and dried for several days or weeks, as was necessary for the very dense, gel-type samples. The largest crack-free right cylinder possible was machined from the preform portion of each dried mass.

Foam densities were determined from weight and volume measurements on the machined pieces. Compression analyses were determined on the right cylinders using an Instron with a 454 kg (1000 lb) or a 4540 kg (10 000 lb) load-cell and a platen speed of 0.127 cm min^{-1}). Elastic modulus was determined from the slope of the "linear" elastic portion of the stress–strain curve. Yield strength was determined from the first maximum on the stress–strain curve or, if there was no maximum, from the intersection of a line of minimum slope with the line used to determine the elastic modulus. The numerical listing of the test data is given elsewhere [2]. The scanning electron microscopy was determined as previously described [3].

3. Discussion

Bulk physical properties are a measure of the general usefulness of a material. Compression properties are measured on foams because foams have poor tensile properties and are difficult to grip for tensile testing. For practical use, elastic modulus and crush strength are recognized as figures of merit for comparing materials in compression. Gibson and Ashby [1] have described three general classes of foams: *elastomeric*, *elastic–plastic*, and *elastic–brittle*. (For consistency we will use these designations throughout this paper.) The stress–strain curve of each class begins with a

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linear elastic region in which cell wall bending occurs*. In the case of *elastomeric* foams, this is followed by a plateau region associated with elastic collapse as the cell walls buckle, and finally by a steep rise during material densification. No maximum is observed. The stress–strain curve of *elastic–plastic* foams is similar, except that a maximum is observed between the linear elastic and plateau regions. For this case, the plateau region is attributed to plastic yielding in the walls rather than buckling. For *elastic–brittle* foams, the linear elastic region is followed by a sharp decrease in stress with a plateau region comprising sharp oscillations in the stress as brittle crushing continues. The first two stress–strain types were prominent in our foams, although functionally they are more like *elastic–plastic* foams since the strain in the long horizontal plateau portion can seldom be recovered.

For open-celled foams, Gibson and Ashby [1] determined that Young's modulus (E) in the linear elastic region is related to density (ρ) for all three foam types by

$$E = E_s C_1 (\rho/\rho_s)^2,$$

where the s subscripts refer to full density solid and C_x is some constant. For *elastomeric* foams, they determined that the yield strength σ_e at initial crushing is also related to $(\rho/\rho_s)^2$, but at high densities is more correctly given as

$$\sigma_e = C_2(\rho/\rho_s)^2[1 + (\rho/\rho_s)^{1/2}]^2$$

For *elastic–plastic* foams, they determined that the yield strength σ_{pl} on crushing is approximately proportional to $(\rho/\rho_s)^{3/2}$; the density corrected form is

$$\sigma_{pl} = C_3 (\rho/\rho_s)^{3/2} [1 + (\rho/\rho_s)^{1/2}].$$

At high relative densities ($\rho/\rho_s > 0.3$), the beam-bending concept is noted to break down and the foam is best thought of as a solid with holes in it; at very low relative densities ($\rho/\rho_s < 0.04$), elastic collapse may precede and trigger plastic collapse. In spite of these restrictions, Gibson and Ashby [1] have included full and nearly full density solids as well as low density materials in their analyses of experimental data, especially elastic modulus.

To apply these mathematical equations to our back-filled foams, we have divided the foams into three groups according to filler type. The crosslinking and monomer concentrations needed to generate each filler type are show in Fig. 1. The appearances of representative filled-foams are seen in the scanning electron micrographs (SEM) of Fig. 2. The SEM of an unfilled preform is shown in the upper right corner for comparisons. The foams across the bottom of Fig. 2 have increasing amounts of pure (uncrosslinked) polystyrene which coat the walls of the foam preforms. The foams in the centre row have walls which are also coated; but this time, the coating is a gel-type crosslinked polystyrene. The foams at the top are filled with increasing amounts of macroporous-type, crosslinked polystyrene. At low filler levels, this filler coats the walls. As the filler levels increase, the filler also permeates the cell voids. Eventually the void regions are filled, but the filler is not in intimate contact with the walls. In each of these series, the filler material is chemically equivalent to the foam preform, but the degree of crosslinking may be different and, hence, the physical properties may be, too. However, the polystyrene homopolymer and gel series with their systematically thickening walls as their densities increase seem appropriate for testing the equations set forth by Gibson and Ashby [1].

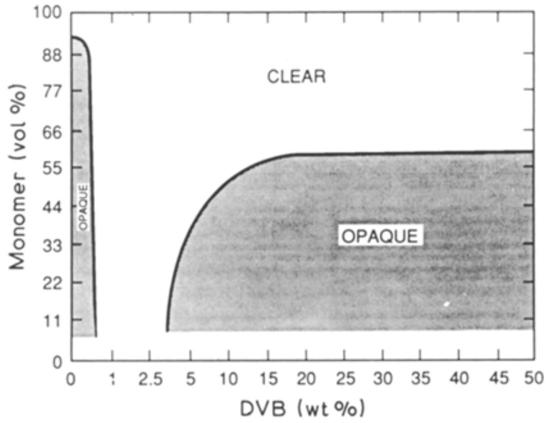

Figure 1 Physical appearance of bulk polymer after drying and exterior to the foam preform. The clear region denotes gel (G) polymer conditions. The large opaque region denotes macroporous (MP) polymer conditions. The small opaque region denotes polystyrene (PS) without crosslinking.

If E_s and ρ_s are assumed constant for a given series of foams, the data can be treated with the equation

$$\log (E) = 2 \log (\rho) + C$$

The compression moduli for foams filled with several filler materials are plotted as a logarithmic function of density in Fig. 3. The solid lines are curves through the data points. The dashed curves have slopes of 2 (as predicted by the equation) and are set arbitrarily above and below the experimental data for reference. The elastic modulus – density relationship for the polystyrene-filled foams (Fig. 3c) follows the theoretical prediction very well. In fact, the extrapolated E_s value (1800 MPa) is in reasonably good agreement with the published value (1400 MPa) [6] for extruded polystyrene. The reason for the slight (~ 30%) change in the curve around $0.25\,\mathrm{g\,cm^{-3}}$ is not clear. Similar changes around this density are also noted for the gel-filled foams (Fig. 3b). A possible reason for the discontinuity may be found in the fact that the structure of the cells in the foams change from very round to somewhat distorted cells in this region (see Fig. 2). The cell sizes are also somewhat larger. These structural changes result from the swelling of the preform followed by some contraction. Around a filled-foam

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*Warren and Kraynik [4, 5] have several papers that provide a more rigorous micromechanical analysis of low density (well below 10%), open-celled foams. They confirm that the bending of struts dominates in the linear elastic region, but show that stretching of the microstructure becomes important and may even dominate at high deformations. Bending and stretching have different dependencies on density. They also demonstrated that the constants in the Gibson–Ashby equations are not arbitrary, but are fixed and microstructure related.

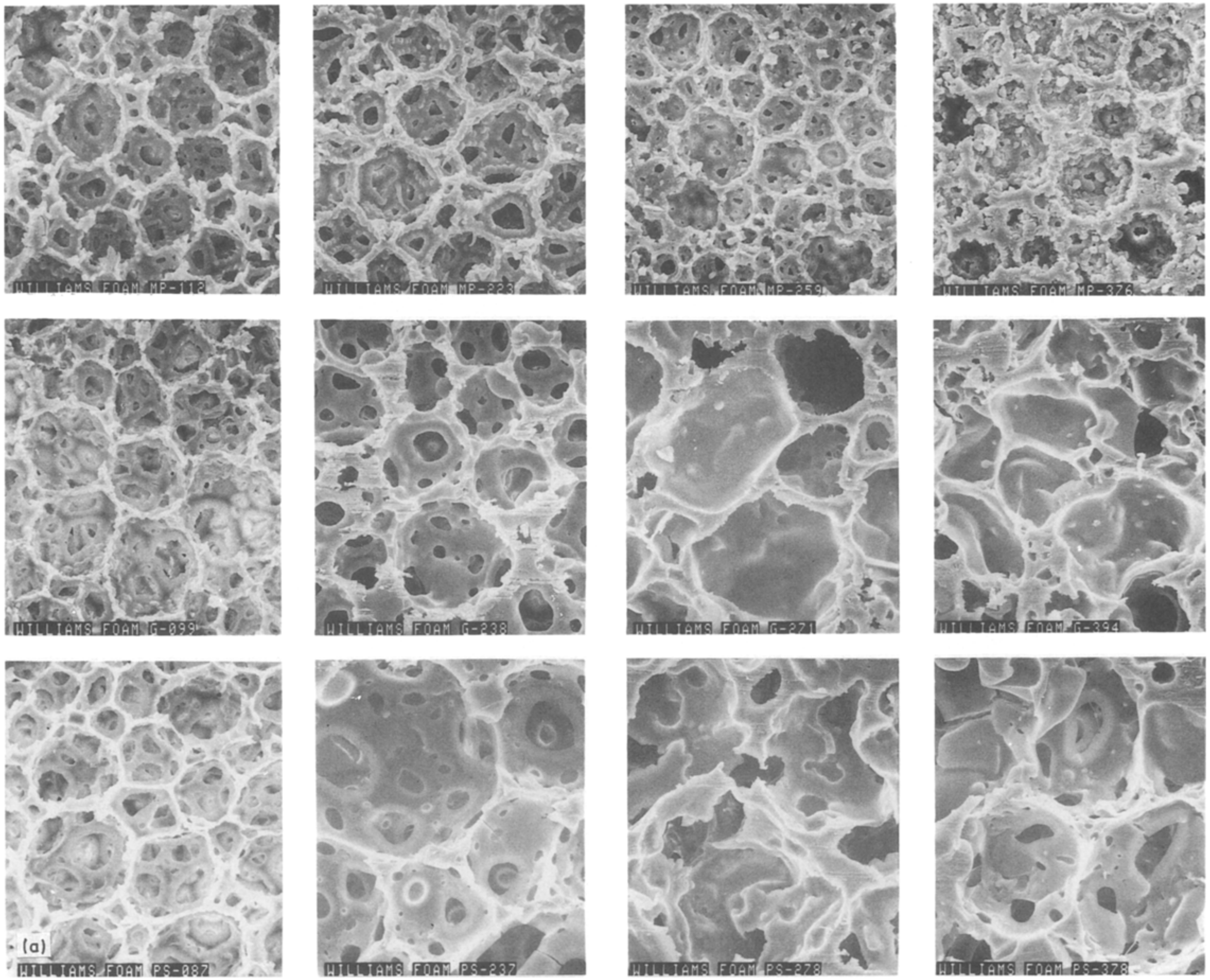


Figure 2 Scanning electron micrographs showing the microstructures of foams backfilled with various types of polystyrene polymers. The letters on each photo identify the polymer type (MP = macroporous, G = gel, and PS = polystyrene) and the subsequent number indicates the same density in mg cm^{-3}.

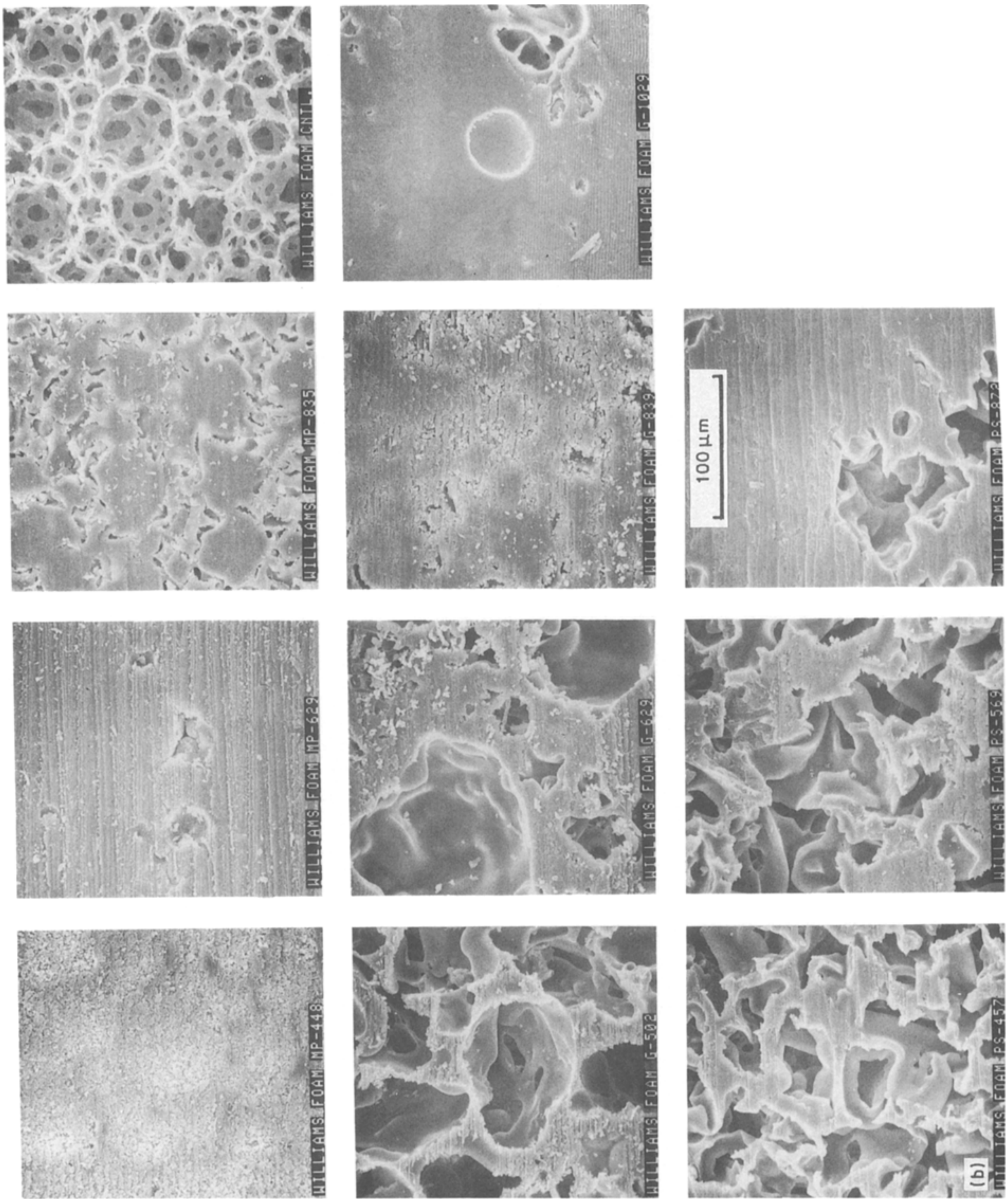
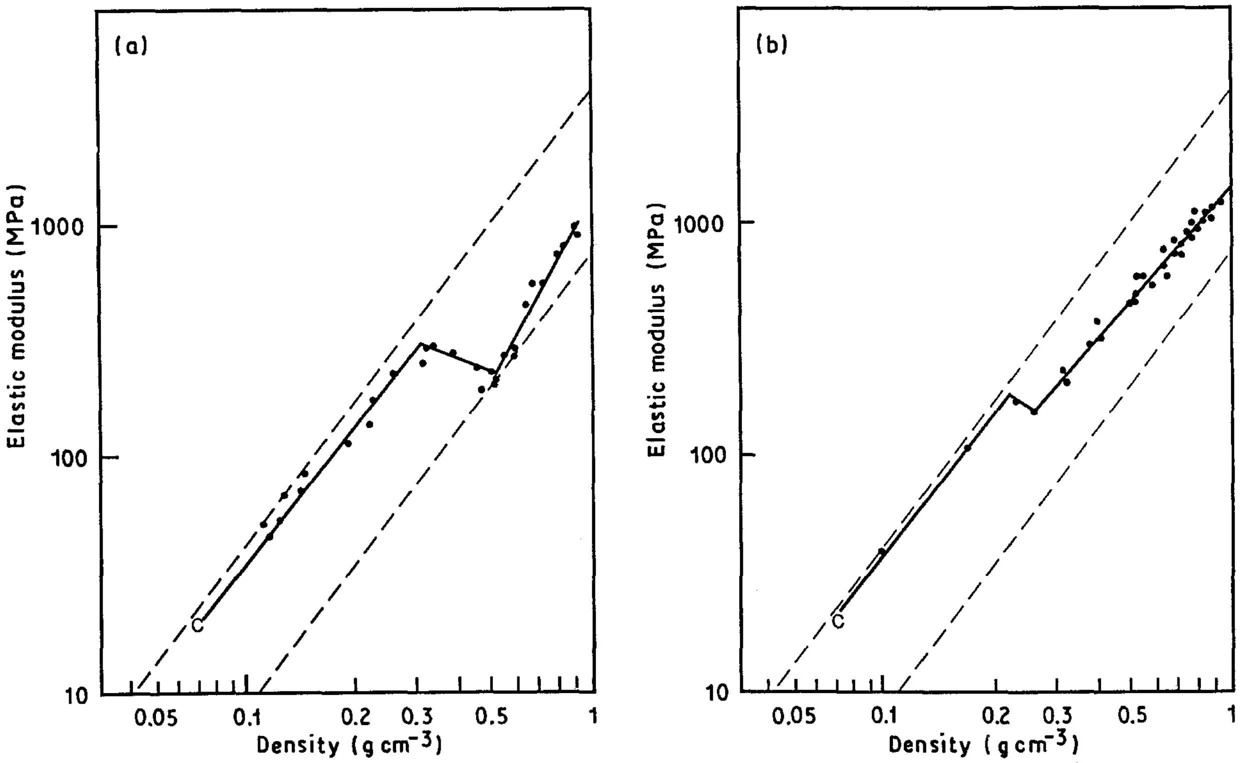

WILLIAMS FOAM CNTL
WILLIAMS FOAM G-1029
WILLIAMS FOAM MP-835
WILLIAMS FOAM G-839
WILLIAMS FOAM PS-872
100 µm
WILLIAMS FOAM MP-629
WILLIAMS FOAM G-629
WILLIAMS FOAM PS-569
WILLIAMS FOAM MP-448
WILLIAMS FOAM G-502
(b)
WILLIAMS FOAM PS-457

Figure 2b



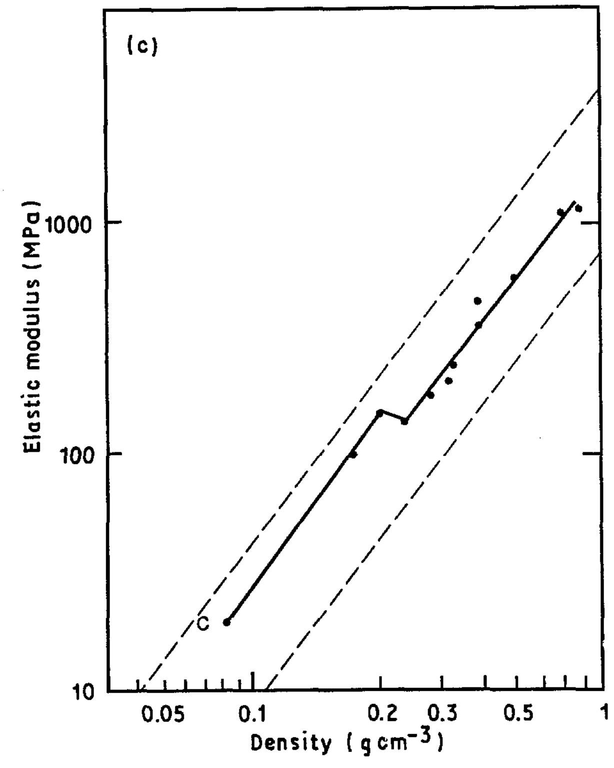


Figure 3 Elastic modulus dependence of filled foams on foam density. Foams are filled with (a) macroporous- or (b) gel-type styrene/divinylbenzene copolymer or (c) polystyrene. The "C" on each graph is the position of the unfilled preform.

density of 0.25 g cm^{-3}, the retraction strength of the filler material is sufficient to cause distortions of this type [2].

The elastic modulus – density relationship for the gel-type filled foams also agrees fairly well with theory (Fig. 3b). The small discontinuity around 0.25 g cm^{-3} can again be seen. At higher densities, our data for the gel-type filler deviates from the mathematical model. We attribute the poorer performance (see Fig. 4 for an overlay comparison) to an increase in microcracking levels [2]. This is consistent with the fact that the highest moduli recorded are for samples that are near full density (note the sharp upswing in Fig. 3) and yet only have 2.5 to 5% crosslinking agent present [2].

The macroporous-filled foams do not follow the elastic modulus – density relationship as well as do the gel and homopolymer-filled foams (Figs 3a and 4). Up to a density of about 0.32 g cm^{-3}, the data fit the theoretical, 2nd power equation very well as the structure of the foams does not change much since the filler is primarily associated with the walls (Fig. 2). Around 0.32 g cm^{-3}, however, the foam structure begins to change dramatically as the filler begins to fill the void space in the cell (Fig. 2). Between densities of 0.32 and 0.52 g cm^{-3}, the elastic modulus actually decreases with increases in density! We attribute this to a phenomenon that occurs during the preparation of the filled foams [2]. Thus, at low filler levels, all of the filler monomer goes into the walls to help solvate the newly formed polymer and to finally become part of that polymer. At higher filler levels, polymer forms in the cell voids as well as in the walls and this void-filling polymer competes for the monomer. The macroporous material forming in the cells does not possess significant modulus at low concentrations because the beads do not bond strongly to one another. Consequently, the modulus of the filled foams drop as less cell wall material is generated. Around 0.52 g cm^{-3}, the material forming in the cells begins to contribute to the modulus which begins to rise more rapidly than would be predicted. The extrapolated E_s of the macroporous-filled foams is comparable to the values for gel and homopolymer-filled foams.

Part of the abrupt change in the elastic modulus against density (Figs 3 and 4) is due to the logarithmic scaling of density. When a linear density scale is used, the curves flow more smoothly through the data

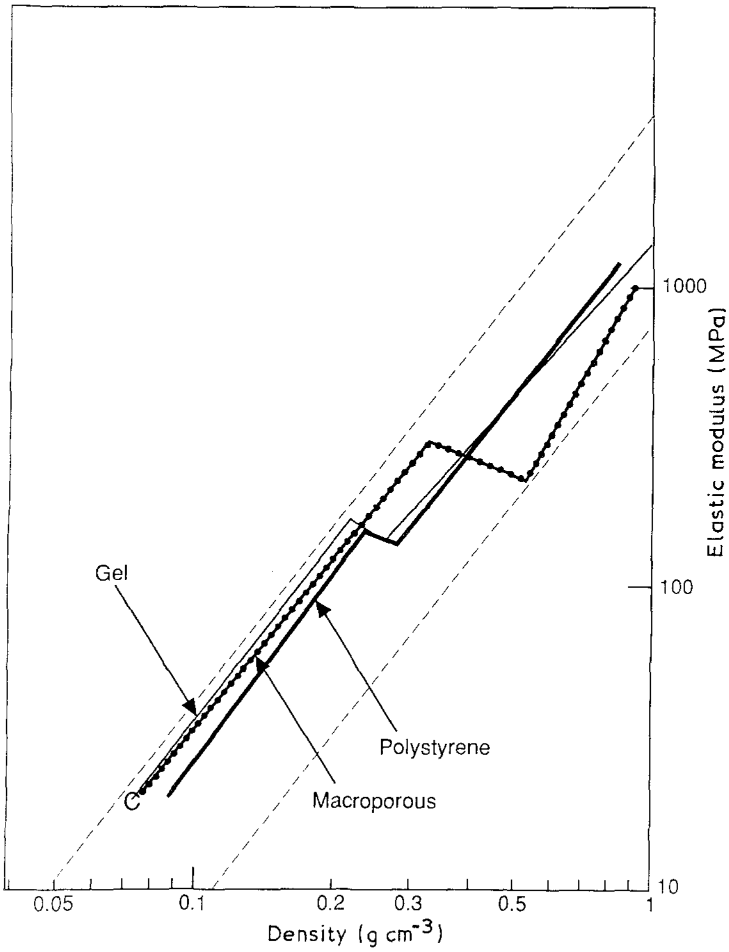


Figure 4 Elastic modulus dependence on foam density and filler type.

(Fig. 5) while the main features are still prevalent. In addition, a general tendency towards higher than predicted modulus stands out. This may be due in part to the increasing contribution of the preform foam as the filler level is reduced. Indeed, the unfilled preform is right in line with the extrapolated filled-foam curves. Figure 5 also shows just how rapidly modulus (and, by implication, other properties, too) drop off as the density falls below 10% full density.

While the modulus dependence on density is straightforward, the yield strength dependency is not (Fig. 6). Two prominent behaviours appear: one for densities above 0.4 g cm^{-3} and one for densities below 0.2 g cm^{-3}. Above 0.4 g cm^{-3}, the gel and homopolymer-filled foams conform nicely to

$$\sigma = C_4(\rho/\rho_s)^{5/2}$$

The agreement between the experimental data and the equation for *elastomeric* foams is quite good since the density-corrected form [1]

$$\sigma_e = C_2(\rho/\rho_s)^2 [1 + (\rho/\rho_s)^{1/2}]^2$$

is approximately $\sigma_e = C_5(\rho/\rho_s)^{5/2}$ above 0.3 g cm^{-3}. The negative deviation of the macroporous-filled foams is reasonably understood in terms of the factors discussed above for the modulus behaviour. Above 0.6 g cm^{-3}, even these foams converge to the theoretical line. At densities below 0.2 g cm^{-3}, the gel and

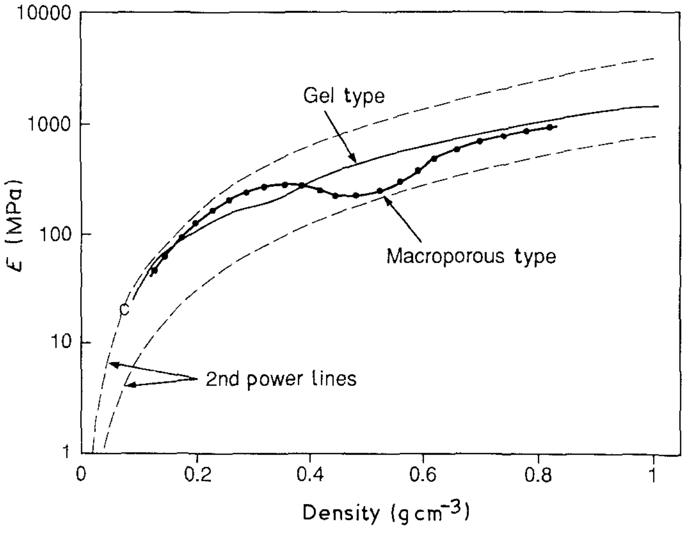


Figure 5 Elastic modulus dependence on foam density and filler type.

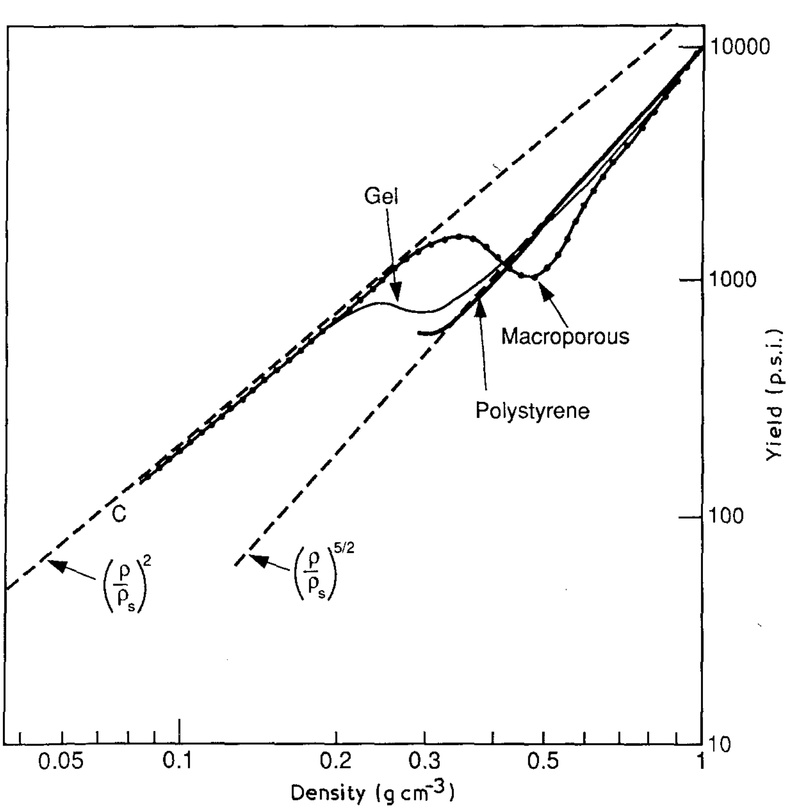


Figure 6 Yield strength dependence on foam density.

macroporous-filled foams again follow a second power relationship with density, but with a different constant term. Since there are only a few points for the homopolymer-filled foams below 0.3 g cm^{-3}, a line through them would be erratic; therefore, we have omitted it. A general downward trend, however, is also obtained. The behaviour of the filled foams below 0.2 g cm^{-3}, like that above 0.4 g cm^{-3}, is similar to that expected [1] for *elastomeric* foams [$\sigma_e = C_6(\rho/\rho_s)^2$] rather than that for *elastic-plastic* foams [$\sigma_{pl} = C_3(\rho/\rho_s)^{3/2}$]. The dramatic discontinuity between the experimental results and the theory for foams with densities from 0.2 to 0.4 g cm^{-3} is problematic.

Two types of stress–strain responses are observed for these filled foams at yield: (1) *elastic–plastic behaviour* with a stress–strain maximum and sharp cracking of the foam; and (2) *elastomeric behaviour* with no stress–strain maximum and smooth crushing of the foam (Fig. 7). (*Elastomeric*, in this context, is not the same as one finds for rubber since these foams do not recoil to their original shape when the load is removed. Elastic–plastic would be a better designation, as will be seen further on.) The macroporous-filled foams have a sharper boundary between crack and smooth crush behaviour with respect to density than do the gel-filled foams (Fig. 8). This sharper boundary corresponds to the dramatic changes in the macroporous-filled foam structure (compare MP-259 to MP-448 in Fig. 2), whereas no such change occurs for the gel and polystyrene-homopolymer-filled foams. The discontinuity in the yield strength against density relationship corresponds very well with the change in the crush behaviour from *plastic* to *elastic*.

The yield behaviour is not entirely consistent with the assertion by Gibson and Ashby [1] that "at very low relative densities ($\rho/\rho_s < 0.04$), elastic collapse may precede plastic collapse". Our data implies that, at least in these filled foams, plastic yield occurs at low

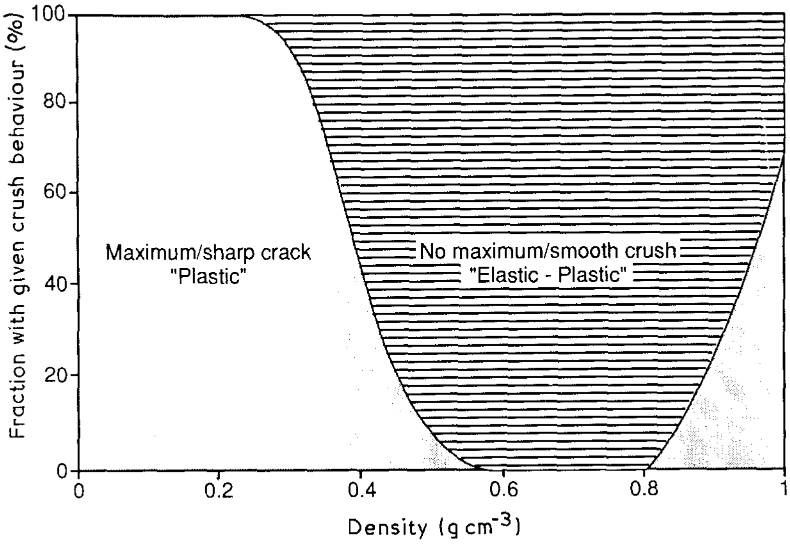


Figure 7 Yield behaviour of filled foams.

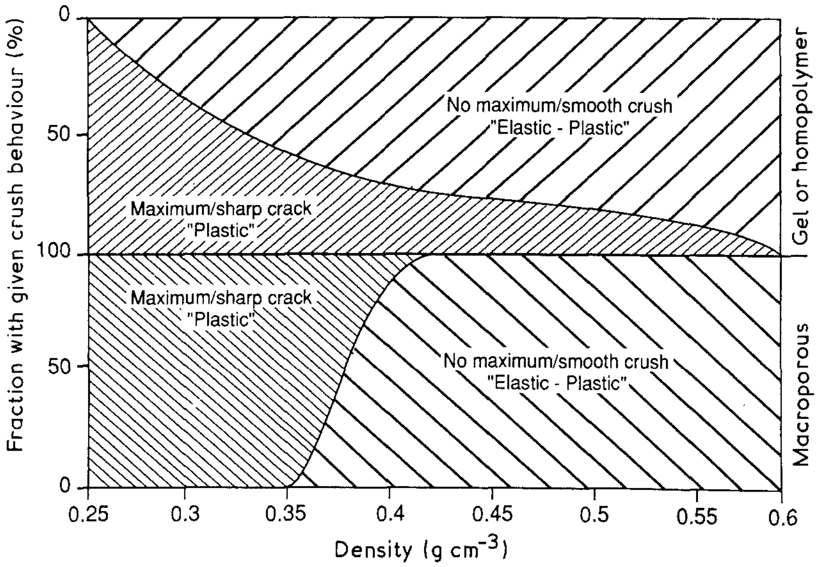


Figure 8 Influence of filler type on the yield behaviour of foams. The upper half represents foams filled with gel or homopolymer; the lower half represents foams filled with macroporous material.

densities ($0.07 < \rho/\rho_s < 0.3$) and very high densities ($\rho/\rho_s > 0.9$) and that elastic yield occurs at intermediate densities. Crosslinked polystyrene emulsion foams, such as the preform used here, demonstrate plastic yield behaviour [3] down to $\rho/\rho_s = 0.03$. In diffidence to Gibson and Ashby, one such foam at $\rho/\rho_s = 0.03$ has shown nearly true *elastomeric* behaviour, i.e., recoverable strain [3]. The change from *elastomeric* to plastic behaviour as density decreases is not reflected in a change from a $(\rho/\rho_s)^2$ to $(\rho/\rho_s)^{3/2}$ dependence of yield as expected [1]. Indeed, the yield strength against density relationship on both sides of the discontinuity is the same $[(\rho/\rho_s)^2]$. Dominance by the preform component below 0.3 g cm^{-3} and by the filler above 0.4–0.5 g cm^{-3} may provide a partial explanation about the discontinuity, but not the failure of the *plastic* behaviour to conform to the correct mathematical equation. The whole matter is rather perplexing. The filled foams behave much more like plastics than elastomers since they have poor strain recovery in the stress–strain plateau region, show *plastic* and *elastomeric* character in their yield behaviour, and yet conform mainly to the mathematical models derived for *elastomers*.

In conclusion, the compressive moduli of foams with a systematically changing cellular structure conform very well to a $(\rho/\rho_s)^2$ dependence. Systematic changes in microstructure are difficult to maintain experimentally and is probably the cause of the small discontinuities we found in the elastic moduli response of the homopolymer and gel filled foams. The dramatic discontinuity in the elastic moduli response of the macroporous filled foams emphasizes the importance of microstructure, however. The models proposed by Gibson and Ashby [1] did not fit our yield strength data. We found that the same relationship with density held experimentally for both *elastic–plastic* and *elastomeric* behaviour, although the two behaviours have been shown to be theoretically different [1]. Change from *elastic–plastic* to *elastomeric* behaviour occurred with a loss in yield strength at the same density. For us, this change in behaviour occurred over a 0.1 to 0.2 g cm^{-3} interval in the density vicinity of 0.2 to 0.5 g cm^{-3}. A slight change in stiffness (modulus) occurred at the same time. Although a change in stress–strain response is clearly obtained, the terms *elastic–plastic* and *elastomeric*, as designated by Gibson and Ashby [1], do not adequately represent our foam materials; **plastic** and **elastic–plastic** do, in spite of the failure of the yield strength models [1] to fit the data property.

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