Negative Poisson's Ratio Polymeric and Metallic Foams

adapted from

Friis, E. A., Lakes, R. S., and Park, J. B., "Negative Poisson's ratio polymeric and metallic materials", *Journal of Materials Science,* 23, 4406-4414 (1988).

ABSTRACT

Foam materials based on metal and several polymers were transformed so that their cellular architectures became re-entrant, ie. with inwardly protruding cell ribs. Foams with re-entrant structures exhibited negative Poisson's ratios as well as greater resilience than conventional foams. Foams with negative Poisson's ratios were prepared using different techniques and materials and their mechanical behavior and structure evaluated.

1. INTRODUCTION

1.1 Conventional Foams

Cellular solids, or structural foams, constitute a class of composite materials in which one phase is gaseous. Such foams are manufactured for a wide variety of applications; moreover, cellular solids occur in nature, eg. wood and bone. Foam materials may be classified as open cell, in which the interior of each cell communicates with the outside atmosphere; closed cell, in which each cell is sealed by cell walls; and mixed, in which both open and closed cells are present. The mechanical properties of foams are determined by the properties of the parent solid material; the volume fraction of solid material, equivalent to the relative density ρ_{foam}/ρ_{solid}; and the cell structure. As for the cell structure, the cells of most man-made polymer foams have a shape which can be modelled by the Kelvin minimum area tetrakaidecahedron [1]. This polyhedron, depicted in Fig. 1, is convex and has eight curved hexagonal faces and six curved square faces. The mechanical properties of foams can, however, be modelled using simple structural arguments in which the dominant deformation mode is assumed to be the bending of the cell ribs, combined with empirical determination of scaling constants [2,3]. Many mechanical properties can be successfully predicted by such an approach. In this article we are concerned principally with Young's modulus and Poisson's ratio. The modulus of elasticity E of open cell foams is given in terms of the density of the solid phase ρ_{solid} and the density of the foam ρ_{foam}, by

$$E_{foam}/E_{solid} = [\rho_{foam}/\rho_{solid}]^2 \; . \qquad (1)$$

Many closed cell foams have very thin cell walls and most of the material is in the ribs. Such foams also follow Eq. 1. Poisson's ratio based on this foam theory is given, for all densities, by

$$\nu = 0.33. \qquad (2)$$

The plastic collapse stress σ_{pl} for a foam in which the cell ribs yield (at a stress $ß_y$), is given, for relative density less than 0.3, by

$$\sigma_{pl}/\ \sigma_y = 0.3\ [\rho_{foam}/\rho_{solid}]^{3/2}. \qquad (3)$$

This article deals with foam materials with cell structure which differs considerably from that of the conventional foams considered in [2,3].

1.2 Re-entrant Foams

Nearly all ordinary materials, including foams, exhibit a positive Poisson's ratio, that is, they become smaller in cross section when stretched and larger when compressed.

Theoretically, however, negative Poisson's ratios are permissible. In particular, the allowable range of Poisson's ratio for an isotropic material is -1.0 to +0.5 [4]. Recently, one of the authors reported a new class of foam materials which exhibits a negative Poisson's ratio as well as other characteristics such as enhanced resilience [5,6]. These materials were produced by transformation of a conventional foam so that the cell ribs protrude inward rather than outward: a 're-entrant' structure. Fig. 2 displays an idealized re-entrant unit cell. To visualize the relationship between structure and Poisson's ratio, imagine tension to be applied to the vertically protruding ribs. The ribs in the lateral directions will tend to move out, causing lateral expansion. When compression is applied, the ribs, which are already curved inward, will bend inward further, thus resulting in lateral contraction in response to axial compression.

The technique for creating the re-entrant structure is to apply, by some method, permanent compression in three orthogonal directions. A foam with relatively low volume fraction of material must be used such that buckling of ribs may occur. Two methods were found suitable for creating re-entrant cell structures [5,6]. For thermoplastic polymer foams, the procedure entails triaxial compression by a factor of 1.4 to 4 in volume, followed by heating to a temperature above the softening point, followed by cooling under the volumetric constraint. For metallic foams made of ductile metal, the procedure consists of applying uniaxial compression at room temperature until the foam yields. Additional compressions are applied sequentially in each of three orthogonal directions until the desired volume change is achieved. The thermal transformation technique used on thermoplastic foams would, in principle, be applicable for metal foams. However, difficulty may be experienced due to the high, sharp melting point of such materials.

Re-entrant foams were found to be more resilient than conventional foams. Conventional foams typically exhibit an approximately linear compressive stress-strain curve up to about 5% strain [2,3]. Re-entrant foams exhibit a nearly linear relationship between stress and strain up to about 40% strain, depending on the amount of permanent compression applied in transformation [5,6]. A similar improvement in resiliency has been reported in foams with permanent uniaxial compression [7], but these foams do not exhibit a negative Poisson's ratio [5,6].

No restriction is imposed on the size of the cell structure since the theory of elasticity has no length scale. In principle, low density foams with microstructure on a scale smaller than one micron [1 µm] could be transformed to re-entrant structures with a negative Poisson's ratio [5].

Several other examples of materials exhibiting a negative Poisson's ratio are known. A "single crystal", possibly a twinned crystal, of pyrite with a Poisson's ratio of -0.14 was recognized by Love [8]. Other examples of a negative Poisson's ratio are in anisotropic single crystal cadmium in some directions [9] and in anisotropic, macroscopic two-dimensional flexible models of certain honeycomb structures (not materials) in some directions [3]. These examples, however, all exhibit a high degree of anisotropy; the negative Poisson effect only occurs in certain directions and then may be dominated by coupling between stretching force and shear deformation. An additional example of a structure with a negative Poisson's ratio is a framework of rods, hinges, and springs [10].

The objectives of this study were to develop and evaluate techniques transforming polymer and metal foams into materials with re-entrant microstructures.

2. MATERIALS AND METHODS

2.1. Sample Preparation

2.1.1 Thermoplastic Foam Transformation

Polyester urethane foam of solid volume fraction 0.043 was used for this segment. The method used was to pack the foam into a square cross section aluminum tube 22 mm by 22 mm in interior dimensions, such that an approximately equal compression in each of three orthogonal directions was applied to the sample. This tube was heated at 200^{o}C in a tubular furnace for approximately seven minutes and cooled to ambient temperature. Several such specimens were prepared. The permanent volumetric compression ratio in the material reported here was 3.4.

2.1.2 Thermosetting Foam Formation and Transformation

In this study, a RTV (room temperature vulcanizing) elastomeric silicone foam was chosen as a representative sample of a thermosetting polymeric foam. It was obtained from the manufacturer [11] as a two part mixture. Specific mixing instructions of the ingredients (silanol-terminated polymers, a cross-linking agent, a catalyst, and a foaming agent) were followed as recommended by the manufacturer. A 10:1 ratio of elastomer base to catalyst and a mixing time of 30 seconds were used. According to the manufacturer, foaming is completed in about 3 minutes and the material is fully cured in about 24 hours. In order to provide adequate mixing, a common paint stirrer inserted in a 3/8 inch hand held electric drill was used to stir the preparation during the initial foaming process. Following the initial 30 seconds of mixing, the foaming mixture was poured into a container and allowed to continue to foam and expand freely. Foaming continued for approximately 2 minutes. This conventional foam had a solid volume fraction of 0.14.

A method was developed in which the foam was mixed as usual and allowed to completely foam and set for anywhere from 15 to 30 minutes before triaxial compression was applied. Triaxial compression was accomplished using a custom made device. Plexiglas® plates coated with petroleum jelly were used to reduce the constraining force along the plates parallel to the direction of the applied compression. Compressions ranging from 10% to 40% strain in each direction were applied to various samples. The re-entrant foam reported here had a permanent volumetric compression ratio of 2.0.

2.1.3 Metal Foam Preparation

A 4x4x2 inch block of copper foam with a pore size of about 1 mm and solid volume fraction 0.053 was obtained from a manufacturer [12]. The copper foam was transformed into re-entrant foam by successive applications of small increments of plastic deformation in three orthogonal directions. A vise was used to apply the deformation. Plexiglas® sheets with coarse sandpaper covers were used to make an even surface on the faces of the vise. Several samples of compressed foam were prepared with strains of 20-35% in each of three orthogonal directions. The material reported here had a permanent volumetric compression ratio of 1.73.

2.2 Testing Methods

2.2.1 Mechanical Tests

Tensile tests were performed on polymeric foam samples on a servo-hydraulic materials testing machine (MTS Model 812, MTS Systems Corp., Minneapolis, MN). Special end attachments were devised in accordance with ASTM Standards [13]. These attachments allowed for elimination of bending moment through the universal joint such that pure tension was applied. Specimens were cemented onto the surfaces of the testing devices. A cyanoacrylate adhesive was used for the polyester foams and Duco® cement was used for the silicone foams. Special care was taken to ensure that the specimens were centered directly with the line of action of the ram of the machine. A strain rate of 0.008 /second was used. The specimens were made geometrically similar so that changes in strain with time would be similar for all samples. Load versus displacement curves, as plotted by the MTS x-y recorder, were obtained for all samples. Engineering stress strain curves were derived from these data.

Uniaxial compression tests were performed using the MTS materials testing machine on various samples of re-entrant and conventional copper foam. Specimens were cut into geometrically similar pieces using a diamond saw (Low Speed Isomet, Model 11-1180, Buehler LTD, Lake Bluff, IL) under water irrigation. Short, stubby samples were cut for compression tests. In compression testing, a special tilting compensation plate and end lubrication were used in accordance with ASTM Standards [14]. An initial strain rate of .010/min was utilized for both compression tests.

Load-displacement curves for were recorded for all mechanical tests and high magnification video tapings of the tests were taken for future use in measuring Poisson's ratios.

2.2.2 Data Reduction and Measuring Poisson's Ratio

For all samples tested, engineering stress-strain graphs were made from load displacement data. The graphs generally exhibited a bilinear form, therefore, elastic moduli for the Silastic® foam samples were measured for different regions of strain. E_1, which corresponds to a Young's modulus, was measured as the slope of the stress-strain curve in the region of just above zero to 1.5% strain and E_2, corresponding to a tangent modulus, was measured as the slope in the region of 3.5% to the final strain.

The Poisson's ratios of all samples tested was determined by viewing the high magnification video tapes of the tensile tests and measuring the displacements in both axial and transverse directions simultaneously. Other methods of measuring Poisson's ratio which comply with ASTM Standards [15] were tried and found unsuitable due to the inherently rough, porous surface of the foams.

2.3 SEM Evaluation of Foams

Scanning electron micrographs of re-entrant and conventional foams were taken at low magnifications to display the coarse cell structure. Accelerating beam voltages were 15 kV for the polyester and copper foams and 8 kV for the silicone rubber foams. The polyester and silicone rubber foams were sputter- coated with AuPd; the copper foams, being electrically conductive, did not require coating. Micrographs of polyester foam were taken of a re-entrant sample, a re-entrant sample in a state of tensile strain of approximately 40%, and the conventional foam. Micrographs of re-entrant and conventional copper and silicone rubber foams were also taken.

3. RESULTS AND DISCUSSION

3.1 Mechanical Tests

Figures 3-6 show that typical stress-strain curves for the thermosetting, thermoplastic, and copper foams. Table 1 contains a summary of the tensile tests of the Silastic® foam shown in Figure 3, as well as results dealing with the anisotropy of Poisson's ratio measured in different directions. Observe that the elastic moduli (E_1 and E_2) for the re-entrant foams are much lower than for the conventional foam control. It was found that 25% permanent axial strain (which corresponds to about a factor of 2 permanentvolumetric compression ratio) yielded the best results for silicone rubber foams. Both re-entrant samples had a substantial negative Poisson's ratio and the difference between the values can be accounted for by the nonuniformity of the original foam structure. The conventional control sample had a Poisson's ratio of around +0.5. Typical foams have a Poisson's ratio of $+0.3 \pm 0.1$. The anisotropy of the foam would account for the abnormally high Poisson's ratio.

Figure 4 is a tensile stress-strain graph of conventional and re-entrant polyester polyurethane (thermoplastic) foams. The conventional foam had a solid volume fraction of 0.043 and exhibited a Poisson's ratio of about +0.4. The re-entrant foam had a permanent volumetric compression ratio of 3.4 and a Poisson's ratio of -0.4. The increased resilience of the re-entrant foam is evident from the curves shown in Fig. 4.

Analysis of compressive tests on re-entrant and conventional copper foams yielded the stress-strain curves given in Figure 5. The conventional foam had a solid volume fraction of 0.053. The re-entrant sample had a permanent volumetric compression ratio of 1.7. As can be seen from Figure 6, a graph of the small strain region of the stress-strain curve, the re-entrant foam was less stiff than the conventional foam. The conventional copper foam exhibited a Poisson's ratio of about +0.42, typical for a foam material. In contrast, the re-entrant copper foam exhibited a Poisson's ratio of -0.39 in the initial stages of compression with progressively increasing values as the magnitude of axial strain increased.

The mode of deformation in the copper foam may be elucidated by evaluation of the plastic collapse stress of the conventional foam and comparison of this value with values predicted from the theory of cellular solids for different deformation modes. By use of Equation 3, which predicts the plastic collapse stress of foams which yield, it was found that the predicted plastic collapse stress differed from the observed plastic collapse stress of copper foam by only a factor of 1.2. The ideal foam theory predicts the major mode of deformation in the copper foams to be by plastic hinge formation. Microscopic examination of re-entrant foam structures, however, suggests that plastic buckling of the ribs also occurs.

3.2 SEM Results

Figure 7 shows the micrograph of the conventional polyester foam sample. The cells in this foam are rather round and symmetrical, similar to the ideal cell structure shown previously in Figure 1. In contrast, the cells of the re-entrant foam, shown in Figure 8, are convoluted and buckled, depicting the typical re-entrant structure. Figure 9 displays re-entrant foam under tension. The underlying kinematics responsible for the negative Poisson's ratio may be visualized from this micrograph. In comparison to the ribs of the cells in the unstrained re-entrant foam of Figure 8, the cell ribs of the strained re-entrant foam are straightened outward and the resulting cell structure is more similar to that of the conventional foam.

It can also be seen from Figures 7-9 that the polyester foam is actually a part closed, part open cell structure. The cell walls, however, appeared to be nearly translucent under optical microscopic examination and were very thin. This finding confirms the supposition [2,3] that man-made foams, even if closed cell in nature, often behave as an open-cell foam. Figure 9 shows a sample in a strained state: many of the cell walls have been torn or ruptured yet the ribs were intact. This observation supports the idea that the ribs are of greater mechanical importance than the walls in such foams.

SEM micrographs of a typical conventional and re-entrant Silastic® foam are shown in Figures 10 and 11, respectively. In the micrograph of the conventional foam in Figure 10, one can see from the relative thickness of the ribs that the Silastic® foam has a much higher solid volume fraction in comparison with the polyester foam shown in Figure 9, in agreement with the quantitative measurements of density described above. Also illustrated in Figure 10 is the nonuniformity in pore size. These two observations would indicate that this Silastic® foam might not respond to the transformation technique as well as some other lower density, more uniform foams such as the polyester foam. Figure 11 shows the re-entrant Silastic® foam after a permanent triaxial compression of approximately 25%. As one can see from Figure 11, the Silastic® re-entrant foam does exhibit a re-entrant type structure, however, this structure is not as clear and defined as with the lower density polyester re-entrant foams. This finding corresponds to the previous observation that the higher relative density Silastic® re-entrant foams do not exhibit as negative a Poisson's ratio as the lower density polyester re-entrant foams.

Figures 12 and 13 show micrographs of the conventional and re-entrant copper foam, respectively. From these pictures, one can see the typical strut-buckled re-entrant structure illustrated in the re-entrant copper foam. Also seen in this foam, however, are the deformations of the 'hinges' between the ribs. The SEM photographs thus provide verification of the predictions of foam theory.

4. CONCLUSIONS

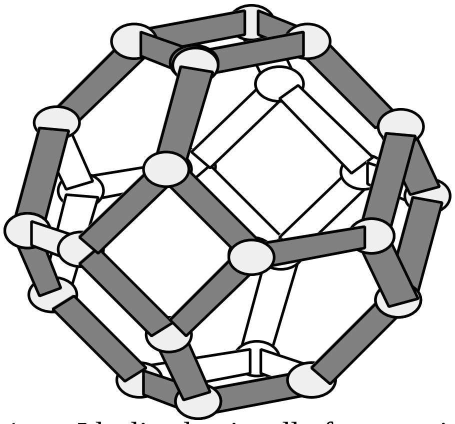
We draw the following conclusions.

1. Three methods are successful in transforming conventional foams to re-entrant foams. These methods are: triaxial compression followed by heat treatment for thermoplastic polymer foams; triaxial compression during the foaming process for thermosetting polymer foams; and sequential plastic compression in three directions for metal foams.
2. Re-entrant foams exhibited negative Poisson's ratios and had Young's moduli which were smaller than those of conventional foams.
3. Re-entrant polymer foams were more resilient than the corresponding conventional foams.
4. Re-entrant transformation of metal foam involves both plastic hinge formation and plastic buckling of the cell ribs.

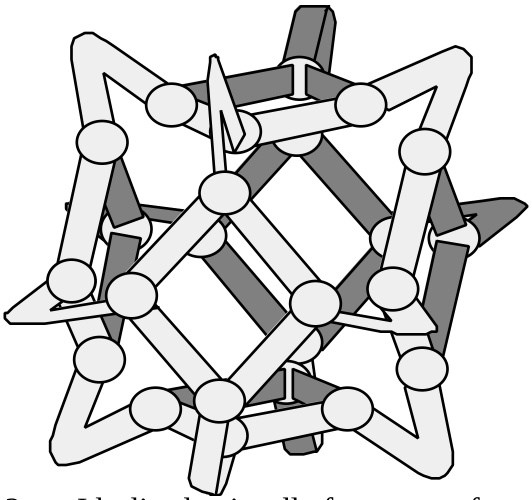
REFERENCES

1. H. A. Lanceley, J. Mann, G. Pogany, "Thermoplastic systems", pp. 221-289 in "Composite Materials", ed, L. Holliday, Elsevier, Amsterdam, (1966).
2. M.F. Ashby, *Metallurgical Transactions,* **14A** (1983) 1755.
3. L.J. Gibson, M.F. Ashby, G.S. Schajer, and C.I. Robertson. *Proc. R. Soc. Lond.* **A382** (1982) 25.
4. Y.C. Fung, "Foundations of Solid Mechanics" p. 353, Prentice-Hall, Englewood Cliffs, NJ, (1968).
5. R.S. Lakes, *Science* **235** (1987) 1038.
6. R.S. Lakes, U. S. Patent # 4,668,557, (1987).
7. W.R. Powers, U.S. Patent 3,025,200 (1962).
8. A.E.H. Love, "A Treatise on the Mathematical Theory of Elasticity" p. 163, 4th Ed.(Dover, New York, 1944).
9. Y. Li, *Phys. Status Solidi.* **38** (1976) 171.
10. R. F. Almgren, *J. Elasticity* **15** (1985) 427.
11. Dow Corning Corp. Midland, MI.
12. Astro Met Associates, Inc. Cincinnati, OH.
13. Annual Book of ASTM Standards."Standard Test Method for Rubber Properties in Tension" (1984) Designation: D412-83.
14. Annual Book of ASTM Standards."Standard Methods of Compression Testing of Metallic Materials at Room Temperature" (1984) Designation: E9-81.
15. Annual Book of ASTM Standards."Standard Test Method for Poisson's Ratio at Room Temperature", (1984) Designation: E132-61.

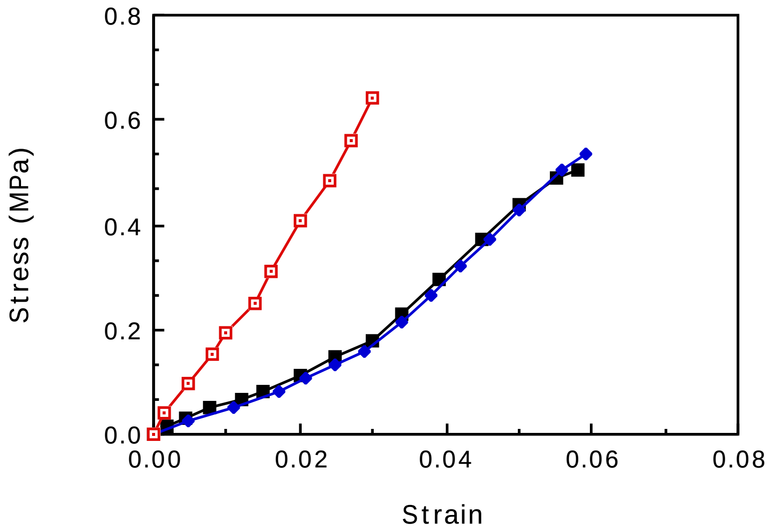
FIGURES



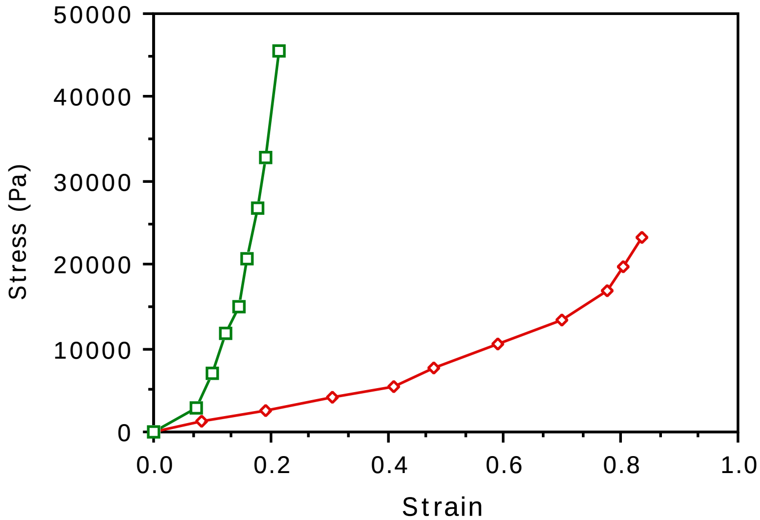
1. Idealized unit cell of conventional foam.



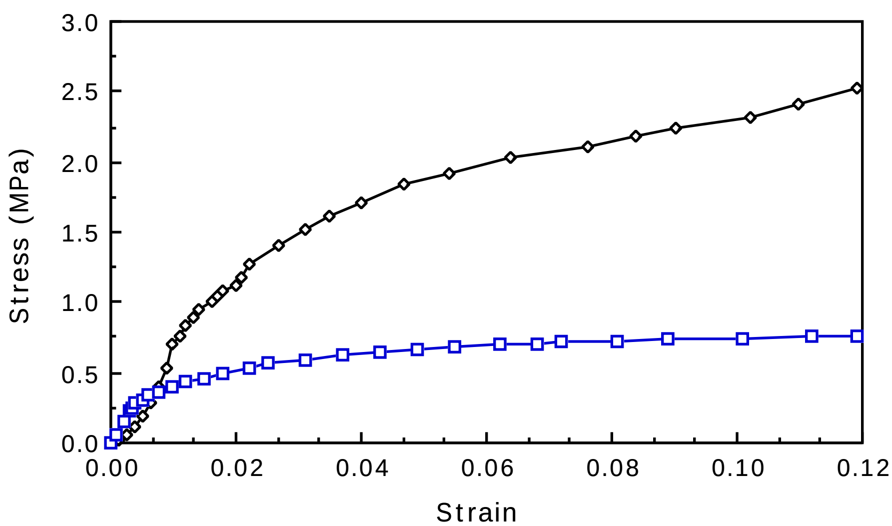
2. Idealized unit cell of re-entrant foam.



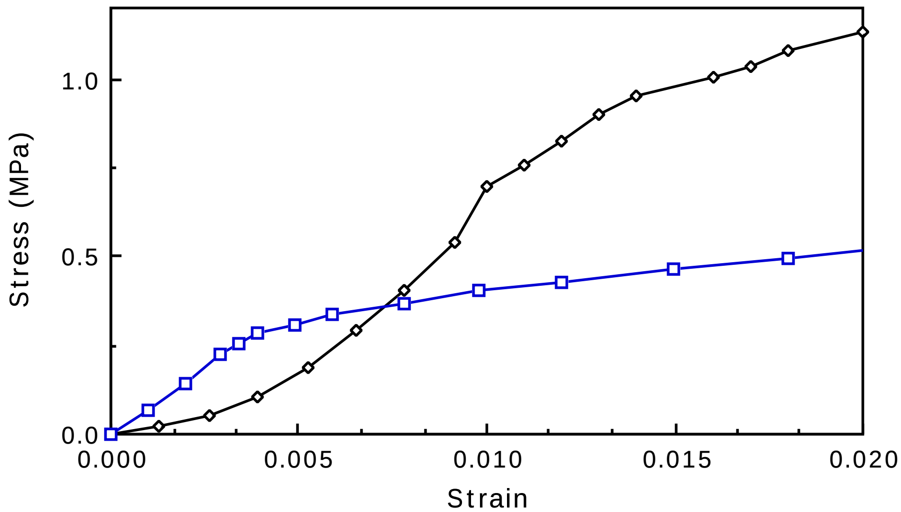
3. Tensile stress-strain curves for conventional and re-entrant silicone rubber foams.
Squares: conventional foam. Solid volume fraction: 0.14.
Solid symbols: two specimens of re-entrant foam.
Permanent volumetric compression ratio: 2.0



4. Tensile stress-strain curves for conventional and re-entrant polyurethane foams.
Squares : conventional foam. Solid volume fraction: 0.043.
◊: re-entrant foam. Permanent volumetric compression ratio: 3.4.



5. Compressive stress-strain curves for copper foams.
squares: conventional foam. Solid volume fraction: 0.053.
◊: re-entrant foam. Permanent volumetric compression ratio: 1.7.



6. Initial region of compressive stress-strain curves for copper foams.
squares: conventional foam. Solid volume fraction: 0.053.
◊: re-entrant foam. Permanent volumetric compression ratio: 1.7.

7. Scanning electron micrograph of conventional polyester foam.
Solid volume fraction: 0.043. For these see the original article.
8. Scanning electron micrograph of re-entrant polyester foam.
9. Scanning electron micrograph of re-entrant polyester foam stretched vertically.
10. Scanning electron micrograph of conventional silicone rubber foam. Solid volume fraction: 0.14.
11. Scanning electron micrograph of re-entrant silicone rubber foam.
12. Scanning electron micrograph of conventional copper foam.
Solid volume fraction: 0.053.
13. Scanning electron micrograph of re-entrant copper foam.

ACKNOWLEDGMENT

The help of Art Pudgil, Sang Hyun Park, Doug Henrich, and Tanya Shipkowitz is gratefully acknowledged.

Table 1. Tensile test results for re-entrant and control Silastic® foams.

Specimen	Permanent Strain(%)			Modulus of Elasticity (MPa)		Poisson's Ratio			Density (g/cm^3)
	ε_x	ε_y	ε_z	E_1	E_2	ν_1	ν_2	ν_3	ρ
Control	0	0	0	17.38	26.00	0.58	0.43	0.47	0.15
Re-entrant	28.6	24.4	25.6	4.78	11.83	-0.19	-0.25	-0.15	0.30
Re-entrant	28.6	24.4	25.6	4.33	13.30	-0.09	-0.05	-0.03	0.25