Microstructures and properties of some microcellular foams

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The microstructures of a variety of low-density (less than $0.1 \, g \, cm^{-3}$) polymeric foam materials are presented. Structures include the large, but well-defined, closed cells of commercially produced foams and a variety of finer, but often less well-defined, open cells of research foams produced from polymers, carbon, and silica. Other topics covered are the sizes and lowest densities of foams available, optical and X-ray opacity, and ease of handling.

1. Introduction

Broadly defined, a foam is a structure that consists of material domains separated by voids which may be filled with gases. An office building or home can be considered a foam with very large cells (rooms). Honeycombs in beehives are easier to visualize. In a one-dimensional sense, stacked films or sheets or material are foams. Soot can also be considered a foam, albeit, a very weak one. Cinder blocks are good examples of inorganic foams. Most practical, low-density foams (like the cushion you are probably sitting on) are based on organic polymers. Commercially available, organic, low-density foams consist mainly of the blown foam type with large (100 to $1000 \, \mu m$), closed cells and thick (10 to $100 \, \mu m$) cell walls.

A number of applications can benefit from materials with cells of $1 \, \mu m$ or less. The major one, to our knowledge, is the use of foams by physicists to simulate high-density gases [1]. Another potential application is their use as media to capture micrometre-size cosmic dust particles [2]. Materials with improved insulating efficiency could be made from microcellular foams [3]. A microcellular porous material may improve the biocompatibility of vascular replacements in coronary surgery [4]. This paper presents microstructures and properties for some small cell-size foam materials that are being produced either commercially or experimentally. The intention is to give the reader a quick survey and visual perception of the microstructures of some low-density, macro- and microcellular materials that exist.

2. Microcellular foam materials

Only materials with bulk densities less than or close to $0.1 \, g \, cm^3$ are considered in this report. Higher density materials are abundant: especially notable are the structural-type foams, porous filters, and porous membranes. The sources of the foams reviewed in this article can be found in Table I. Only general references are given for preparing the commercially available products. Specific references are cited for research materials under development at the US National Laboratories [Los Alamos, New Mexico, Lawrence, Liver-more, and Sandia (Albuquerque, New Mexico and Livermore, California)] and Martin Marietta (Oak Ridge, Tennessee).

All foam microstructures were determined by scanning electron microscopy (SEM) on representative samples and are shown in Fig. 1. Several features are immediately apparent. The commercial foams (those in the left two columns and the reticulated carbon foam in column 6) have large cell structures. Typically cells are 0.1 to 1 mm (100 to $1000 \, \mu m$) and are generally closed as a result of the common practice of using expanding gases to produce the foams. A notable exception in Fig. 1 is the reticulated carbon foam which has porous membranes over the cell windows. These membranes are the residues remaining after the original closed-cell structure has been subjected to carbonizing conditions. Commercial foams generally have fairly well-defined cells with a narrow size range and uniform mass distribution. The walls are relatively thick ($> 10 \, \mu m$) because commercial foams are generally prepared for maximal mechanical properties at a given density. These thick walls are particularly noticeable in the polyethylene blown foam shown in Fig. 1. The microstructure of polystyrene bead foam is a good example of a very non-uniform distribution of mass. Note the higher density at the outer regions of the beads. These gradient densities can be detected on X-ray films. Some mechanical strength is sacrificed for the moulding convenience offered by the expanding beads. The "Dow Special" polystyrene extruded material was made in an attempt to push commercial technology towards a smaller cell size. The foam has a very narrow size distribution of closed cells and good mechanical properties, but only cell sizes slightly less than $100 \, \mu m$ were achieved at the bulk density produced. Thus, expanding gas technology is limited in its ability to make small ($\ll 100 \, \mu m$) cells in low bulk density foams.

Unlike commercial foams where mechanical properties are of prime importance, research foams for physics applications have emphasized smallness of cell size ($< 10 \, \mu m$) and an open, interconnected structure to allow free movement of gases among the

TABLE I General information about the foams studied

| Material	Cellular structure	Source	Stage of develop.	Relative cost	Minimum Density ($g cm^{-3}$)	Maximum thickness (cm)	Ease of Handling	Cell size (μm)	Optical opacity	X-ray opacity (rel/cm)	Chemical composition	Impurities	Ref. for method of preparation
Polyethylene (blown)	Closed	Commercial	Final	Low	0.029	15	Easy	1200–1500	Opaque	2	C, H	Mg	[19]
Polyurethane (flexible)	Open/closed	Commercial	Final	Low	0.031	30	Easy	600–900	Opaque	3	C, H, N, O	Sn, Pb	[20]
Polyurethane (rigid)	Closed	Los Alamos Commercial	Final	Low	0.1	30	Easy to difficult	500–900	Opaque	10	C, H, N, O	Si	[20]
Polystyrene (bead)	Closed	Commercial	Final	Low	0.017	100+	Easy	30–300	Opaque	1	C, H		[21]
Polystyrene (extruded)	Closed	Commercial	Final	Low	0.016	15	Easy	250–300	Opaque	1	C, H	Br, Cl, F, Mg	[21]
Polystyrene (extruded)	Closed	Commercial (special Dow)	Final	Low	0.050	15	Easy	120–200	Opaque	3	C, H		[21]
Poly (4-methyl-1-pentene)	Open	Los Alamos	Final	High	0.020	2	Very difficult	35	Opaque	1	C, H		[1, 2, 22]
Polystyrene (atactic)	Open	Sandia (Abq. & Liverm.)	Middle	High	0.020	1	Difficult	5–20	Opaque	1	C, H		[5, 6]
Polystyrene (isotactic)	Open	Sandia (Abq.)	Early	High	0.080	2	Easy	1–3	Opaque	5	C, H	Cl	[23]
Polystyrene (emulsion)	Open	Los Alamos	Middle	Mod.	0.025	20	Easy	1–6	Opaque	2	C, H	K, S	[24, 25, 26]
Carbon (reticulated)	Open	Commercial (Union Carbide)	Final	Low	0.025	60	Difficult	10–40	Opaque	2	C	Ba, S, Fe, Na, Cl	[27]
Carbon (NaCl preform)	Open	Livermore National Lab.	Middle	High	0.068	2	Difficult	20–30	Opaque	3	C	Ca	[28]
Carbon (SiO$_2$ preform)	Open	Martin-Marietta	Early	High	0.068	2	Very difficult	0.06	Opaque	5	C	F, Al, Ti, Na, Cl	[29]
Silica Aerogel	Open	Commercial Airglass AB, Sweden	Middle/Final	Mod.	0.050	2	Very difficult	0.01	Transparent	31	Si, O	C, H, Na, Cl	[30]
Resorcinol	Open	Livermore National Lab.	Early	High	0.09	1	Difficult	0.01	Transparent	9	C, H, O	Na	[31]
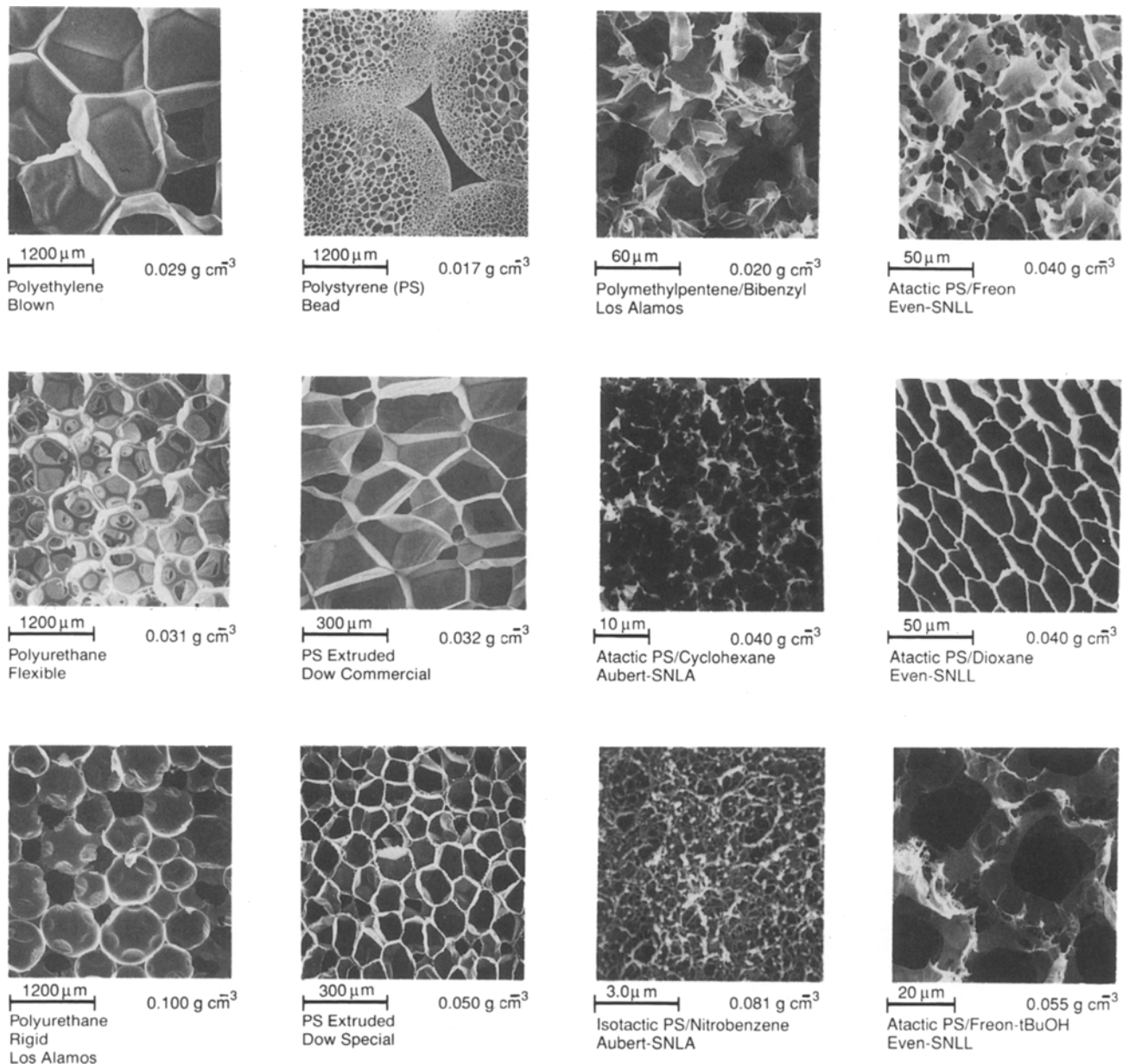
Figure 1 Scanning electron photomicrographs of assorted microcellular foams. Note the differing magnifications. The carbon-with-palladium photomicrograph contain two parts: the upper half is a standard SEM; the lower half is a backscattered image of the same area and emphasizes the high z-metal distribution.

interconnected cells. In some cases the foam structures do not have easily definable cells and the expression "cell size" takes on new meaning. In these cases, a cell is only an irregular void or gas volume surrounded by mass units whose physical character and connectivity are neither easily definable nor necessarily regular. Good examples of this situation are the PMP and PS foam structures shown in column 3 of Fig. 1. These foams result when solvents are removed from phase-separated polymer solutions without cell collapse. The foam structure is established during phase separation which is induced by thermally cooling the polymer solution. Ideally, the separating polymer will form well-defined cells around the separating solvent. This structure is analogous to those of the commercial blown foams, except that solvent, rather than gas, is utilized in the cell formation step. Such incidences of ideality are rare, but do exist as seen in column 4 of Fig. 1. In this series of foams (also consider the middle photo in column 3) prepared by workers at

Sandia National Laboratory (Albuquerque [5] and Livermore [6]), the phase-separation technique has been applied to atactic polystyrene dissolved in different solvents. In each case the entire phase-separated polymer/solvent mass was frozen before the solvent was removed. Changing the solvent from cyclohexane to freon (CF_2ClCCl_3) yielded a better connected and better defined, but still isotropic, cell structure. As a result of the interconnectivity, the foam formed from freon is much tougher at the same density. A solvent, such as dioxane, that forms elongated crystals on freezing, can force the polymer into an anisotropic structure. Such a structure is shown in column 4 of Fig. 1. (Note the trigonal intersections and their similarity to those in the isotropic polyethylene in column 1.) This foam exhibits little resistance to collapse when a force is applied perpendicular to the canal length, but possesses exceptional resistance to collapse along the length of the canals. (See Gibson and Ashby [7] and Williams [8] for discussions of foam
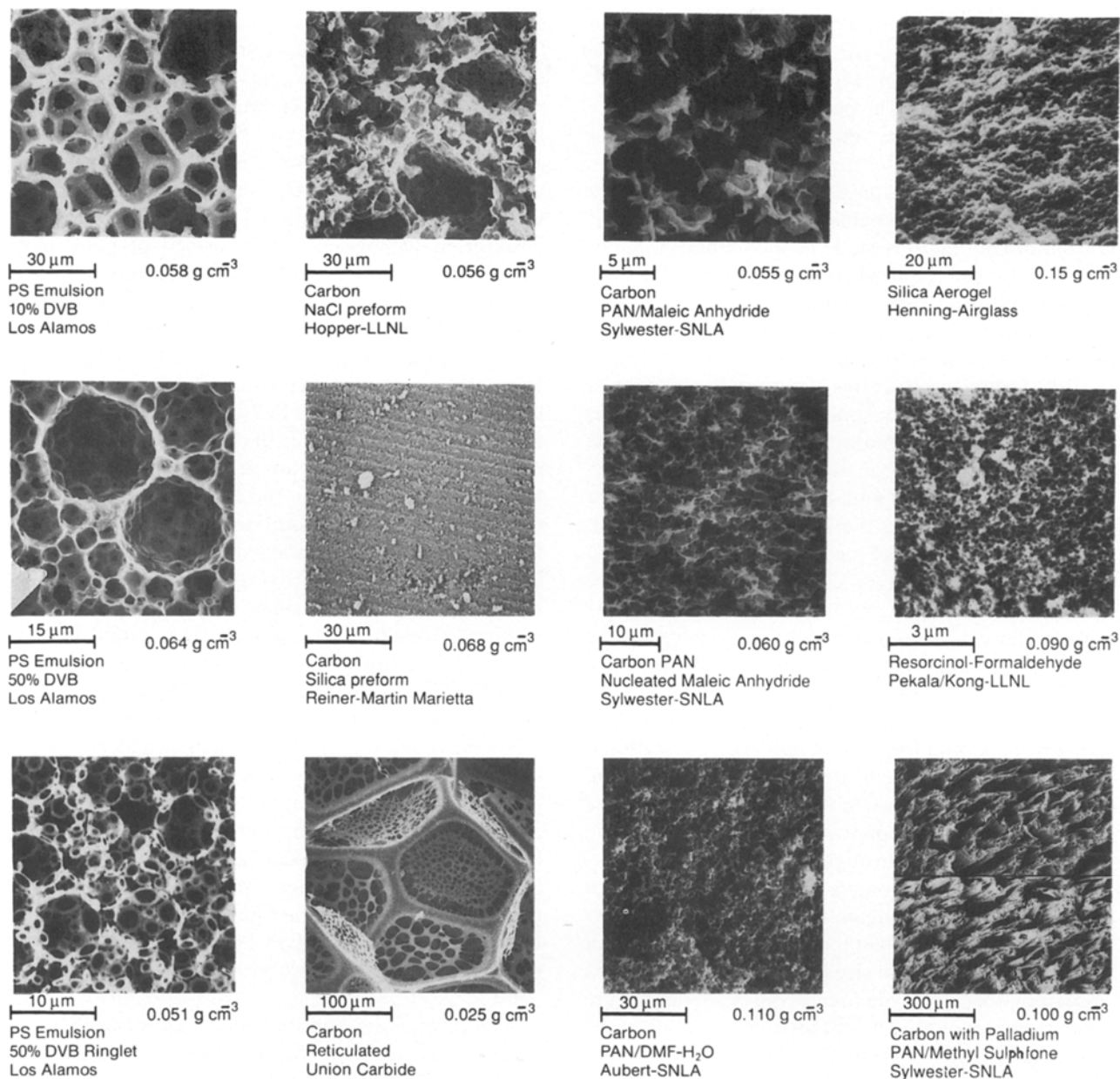
| 30 μm 0.058 g cm⁻³ | 30 μm 0.056 g cm⁻³ | 5 μm 0.055 g cm⁻³ | 20 μm 0.15 g cm⁻³ |

PS Emulsion 10% DVB Los Alamos — Carbon NaCl preform Hopper-LLNL — Carbon PAN/Maleic Anhydride Sylwester-SNLA — Silica Aerogel Henning-Airglass

PS Emulsion 50% DVB Los Alamos (15 μm, 0.064 g cm⁻³) — Carbon Silica preform Reiner-Martin Marietta (30 μm, 0.068 g cm⁻³) — Carbon PAN Nucleated Maleic Anhydride Sylwester-SNLA (10 μm, 0.060 g cm⁻³) — Resorcinol-Formaldehyde Pekala/Kong-LLNL (3 μm, 0.090 g cm⁻³)

PS Emulsion 50% DVB Ringlet Los Alamos (10 μm, 0.051 g cm⁻³) — Carbon Reticulated Union Carbide (100 μm, 0.025 g cm⁻³) — Carbon PAN/DMF-H₂O Aubert-SNLA (30 μm, 0.110 g cm⁻³) — Carbon with Palladium PAN/Methyl Sulphfone Sylwester-SNLA (300 μm, 0.100 g cm⁻³)

Figure 1 Continued

compression properties.) A combination of both isotropic and anisotropic structures can result when a dual solvent is used; as seen in Fig. 1 (bottom of column 4), 5% *t*-butyl alcohol (a *t*-BuOH) in freon (CF$_2$ClCCl$_3$) was effective in generating such a combination. Note the long well-defined tubes formed by the *t*-BuOH and the less well-defined accordion structure formed by the freon around the tubes. With the current level of understanding about phase separation behaviour [9], however, trial and error is still the methodology employed for making phase-separated foams and, hence, for achieving cellular structures by this technique.

More clearly defined cells can result when foams are made from emulsions. Monomers in the oil phase of a water-in-oil emulsion are polymerized and then the water is removed to yield a foam (see column 5, Fig. 1). In this case, nearly spherical water droplets serve the same function that the air and organic solvents did in the techniques described above; i.e. they act as preforms on which cell walls can be constructed. A broader distribution of cell sizes is observed in this case than with the commercial, blown foams. This occurs because the emulsion is structurally dynamic and is most stable when a range of smaller water droplets (cells-to-be) are created to fill in the interstices between the larger water droplets (also cells-to-be) [10]. In the blown foams, on the other hand, cells are generated fairly uniformly throughout the mass and each cell grows to approximately the same extent as every other.

Structures similar to those in the emulsion foams would result if tiny spheres were close-packed to form a preform around which polymer would be infiltrated. The preform would then be dissolved (leached) to give a foam. Easily dissolvable spherical preform materials in the micrometre size are difficult to find. Rectanguloid sodium choride particles in the 30 μm range have been used to make microcellular carbon foams of low density. Thus, rectanguloid shapes are left by the NaCl crystals when they are leached (Fig. 1, column 6). The ultimate extension of this concept is the use of

10 nm preform material. The fineness of the micro-structure in a carbon foam produced by using fine silica gel as the preform (Fig. 1, middle of column 6) illustrates this point. (The parallel lines on the surface are cut marks left by the vibrating razor blade used to prepare the surface.)

The thermal conversion of polymers to carbon is a common procedure. Reticulated carbon foam (Fig. 1, bottom of column 6) is made by a commercial application of this technique wherein the polymer structure is retained during carbonization. Workers at Sandia National Laboratory in Albuquerque have extended this scheme to prepare microcellular carbon foams [11, 12]. The microstructures of carbon foams derived from phase-separated polyacrylonitrile solutions (Fig. 1, column 7 and bottom of column 8) bear close resemblances to those of other phase-separated systems (Fig. 1, colums 3 and 4). Again the diversity of structures is related to the solvent–polymer system. The photomicrograph of the palladium-doped carbon foam (Fig. 1, bottom of column 8) illustrates the variety of features that can be combined into a single foam material. The anisotropic directionality of the large pores is readily apparent. The walls of these large pores are very porous. The photomicrograph is actually a composite of two images: the top half is a standard SEM and the bottom half is a backscattered image which shows the distribution of the palladium over the same area shown in the upper half. This is one of a variety of foam-supported metal arrays that have potential use in flow-through catalysis units.

Ultrafine microstructures are available through chemically reactive systems that produce gels. After extraction, these gels yield foams that appear to be an agglomeration of 10 nm size beads. Silica aerogel and resorcinol–formaldehyde foams (Fig. 1, column 8) are good examples of the fine microstructures that can be obtained by this technique. Unlike the concave void regions found in most foams, the void regions in these foams have convex surfaces.

General information (from [13–16]) about many of the foam materials for which microstructures were determined are summarized in Table I. Detailed characteristics, methods of preparation and elemental analyses for most of the foams are presented elsewhere [2]. The impurities listed are those present in greater than 0.03% (300 p.p.m.) and are based on neutron activation analysis (NAA) data collected on samples for which the microstructures were determined. In the case of the polystyrene emulsion foams, the potassium and sulphur levels can be practically eliminated by using 2,2′-azoisobutyronitrile (AIBN) polymerization initiator in the organic layer instead of potassium persulphate in the aqueous layer. The minimum density is based on typical commercial products or on the best experimental laboratory-scale foams. The latter are at various stages of development as indicated. Often the size of foam that can be produced is limited in at least one dimension. In Table I, this dimension is reported as the maximum thickness producible. The relative costs of production are quite subjective and have been evaluated from the ease of production and the labour required. Additional properties for the foams include optical opacity and X-ray opacity at the lowest density. The X-ray opacity value indicates whether X-radiography can be used to locate particles within the foam; only low values are useful in this regard. Interestingly, silica aerogel becomes cloudier as the density decreases and is nearly optically opaque at $0.020\,\mathrm{g\,cm^{-3}}$ because of the scattering of light. The following properties for the full-density materials used in making the foams tabulated in Table I are included in Table II: tensile strength, coefficient of thermal expansion (CTE), melting point and X-ray opacity. Equation of state (EOS) data are availabe for a number of full density polymeric materials [13]. Physicists use EOS data in computer simulations of materials behaviour. Only qualitative EOS data can currently be obtained for polymeric materials at less than full density.

At a given foam density, smaller cells can only be obtained by reducing the cell wall thickness. The theoretical limit to cell size is obviously the point just before the wall material becomes a gas; i.e. walls one molecule thick. The practical limit, however, occurs long before this state. For example, at $0.010\,\mathrm{g\,cm^{-3}}$ (seven times the density of air), the walls will be ultra-thin (3.4 nm, or just a few molecules thick) when the

TABLE II Information about full-density material comprising the foams studied

Material	Composition	Bulk density (g cm^{-3})	Melting point (°C)	Tensile strength* (p.s.i.)	CTE ($\times 10^6$)	Solvents to dissolve	Eqn of state
Polyethylene	C, H	0.92	115	4 000	(> 200)†	Yes	Yes
Polyurethane (crosslinked)	C, H, N, O	1.30	Decomp.	1 000		No	Yes (rigid)
Polystyrene (atactic)	C, H	1.05	237 105 (T_g)	7 500	80	Yes	Yes
Polystyrene (isotactic)	C, H	1.05	> 200	~ 7 500	(< 80)†	Yes	No
Polystyrene (crosslinked)	C, H	1.05	Decomp.	(> 7 500)†	(< 80)†	No	No
Poly (4-methyl-1-pentene)	C, H	0.83	235	4 000	120	Yes	No
Carbon	C	1.95	3650	29 000	4	No	No
Silica	Si, O	2.66	1713	7 000	55	No	Yes
Resorcinol	C, H, O	1.34	Decomp.	9 200	80	No	No

*103 p.s.i. = 6.89 N mm^{-2}.
†Estimates.

cells are only 1 μm in diameter. For flexible molecules, like polystyrene, this is hardly enough material to support even its own weight. A comparative study of the physical properties of all these foams has not been performed, although some data are available in [8]. In Table I, a qualitative evaluation of toughness is given in terms of the "ease of handling". In this scheme "easy" means that you can pick up a piece of the lowest density material without crushing it or having it fall apart when dropped from a height of several inches. In a very low-density material, connectivity of the mass is paramount for the material to withstand handling. The most fragile foams are those with poorly connected microstructures: for example, the PMP foam (like a crumbly marshmallow), the silica-preform carbon foam (like velvety black fluff), and the silica aerogel (like an anhydrous cube of clear gelatin).

The variety of microstructures may not be infinite for low-density foams, but many interesting and photogenic forms have already been observed. Other low-density microcellular foams are also currently being prepared in small, bench-top quantities. These include ultra-low density ($< 0.01\,\mathrm{g\,cm^{-3}}$) water-soluble polymer foams [17] and (0.01 to $0.2\,\mathrm{g\,cm^{-3}}$) agar foams [18].

Acknowledgements

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