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Compression moduli of some PMP microcellular foams

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The elastic moduli of poly(4-methyl-1-pentene) foams made by several processes are measured. The results reveal that several terms need to be added to the currently accepted mathematical representation. Thus, the amount of noncontributing mass and the efficiency of the contributing mass must be considered along with the isotropic reduction in total mass. The mathematical equation derived gives new insight into the structure and properties of microcellular foams.

1. Introduction

Over the past few years, Los Alamos National Laboratory has been making microcellular foams for inertial confinement fusion (ICF) targets [1, 2]. The foams are prepared by phase separation of poly(4-methyl-1-pentene), or PMP, from a cooling solution followed by removal of the solvent [3]. In the 0.01 to 0.08 $\mathrm{g\,cm^{-3}}$ range, these foams are friable and difficult to handle. This is very much unlike the character of polystyrene blown foams. To quantify the difference, the compression moduli of two series of these PMP foams, ranging from 0.02 to 0.09 $\mathrm{g\,cm^{-3}}$ were measured and related to that for a 0.031 $\mathrm{g\,cm^{-3}}$ polystyrene insulation board foam. The dependency of the compression modulus on bulk density was then compared with a current model describing porous materials. This comparison has lead to several important considerations overlooked in treating these very low-density materials; namely, the possible presence of noncontributing material and the change in the effective modulus of the contributing material.

2. Experimental details

2.1. Foam preparation

Foams were made from poly(4-methyl-1-pentene) by the phase separation technique [1–3]. Series A was prepared with a solvent consisting of bibenzyl, diphenylmethane, biphenyl, and stearic acid. The solidified mass was extracted with methanol to produce an open microcellular foam. Series B was prepared with 1,2,4,5-tetramethylbenzene. The solid mass from each of these mixtures was also extracted with methanol to yield an open microcellular foam.

2.2. Compression testing

Cubes of foam approximately 1 cm × 1 cm × 1 cm were tested. The probe was a 6.35 mm (0.25 in.) diameter, stainless stain, dowel rod. Samples above 0.020 $\mathrm{g\,cm^{-3}}$ were tested (Method A) with a table model Instron using a 50 lb (~22.7 kg) compression load cell. The load was applied to a depth of 2.5 mm (0.10 in.) at a rate of 1.3 $\mathrm{mm\,sec^{-1}}$ (0.05 $\mathrm{in\,sec^{-1}}$). Those samples below 0.034 $\mathrm{g\,cm^{-3}}$ were also tested (Method B) with a 100 g load cell assembly developed at our laboratory by Hoover and Petrovic for testing silicon carbide whiskers. Because of the slight resistance of the cell, the recorded displacement was larger than the actual value. The correction was linear with load and easily eliminated. Load/deflection data (Table I) from each method were in very good agreement. Duplicate values were generally within 10% of one another. No sharp break in the load curve was observed up to 1.1 mm penetration.

The elastic modulus, E, was calculated by relating the stress, L_{sample}, at a given strain to the stress of a standard foam, L_{std}, measured at the same strain. Thus, the equation for the modulus is as

$$E = \left(\frac{L_{\text{sample}}}{L_{\text{std}}}\right) E_{\text{std}} \qquad (1)$$

The standard used was a 2.5 cm (1 in.) thick sheet of 0.031 $\mathrm{g\,cm^{-3}}$ extruded polystyrene insulation board (Classification D-369) made by Dow Chemical Co. The compression modulus was determined by ASTM Method D1621-73 using a 2.8 cm × 2.8 cm cross-section. The experimental E was 7.2 ± 0.2 MPa (1045 ± 25 p.s.i.). This compares favourably with the reported data [4]: 800 to 1000 p.s.i. (0.029 $\mathrm{g\,cm^{-3}}$) and 1200 p.s.i. (0.036 $\mathrm{g\,cm^{-3}}$).

Using Equation 1, the polystyrene standard and the 0.76 mm penetration data, the moduli of the tested examples (Table I) have been determined and plotted in Fig. 1.

3. Discussion

The compression moduli of the open microcellular poly(4-methyl-1-pentene) foams are indeed much less than that of a comparable density, closed cell, polystyrene blown foam. The moduli for the PMP foams are over an order of magnitude less although the modulus of bulk PMP polymer is only two to three times less than that of polystyrene (see Table II). Also the moduli of the PMP foams from the two processes are markedly different. The moduli of each foam type, however,

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TABLE I Stress data for foams

Sample	Density	Method	Load (g) for penetration depth* of			
			0.25 mm	0.37 mm	0.76 mm	1.13 mm
A-1	23.0	B A	6.5 ± 1.5 6.5 ± 0.5	9.5 ± 1.5 10 ± 2.0	18 ± 3 19 ± 3	26 ± 3 29 ± 4
A-2	30.0	B A	12.5 ± 0.5 12 ± 1	18.5 ± 1.5 17.5 ± 0.5	32.5 ± 1.5 30.5 ± 0.5	46.5 ± 1.5 45 ± 0
A-3	33.4	B A	29.5 ± 2.5 29.5 ± 2.5	41 ± 2 42.5 ± 2.5	– 74.5 ± 2.5	– 108.5 ± 1.5
A-4	34.2	A	35 ± 10	49 ± 13	85 ± 20	122 ± 26
A-5	43.2	A	28.5 ± 1.5	41.5 ± 1.5	77 ± 0	112.5 ± 0.5
A-6	49.1	A	59 ± 7	85.5 ± 7.5	158 ± 8	230 ± 10
A-7	87.0	A	470 ± 0	620 ± 0	1015 ± 5	1390 ± 10
A-8	90.4	A	390 ± 90	555 ± 95	995 ± 85	1410 ± 90
B-1	20.5	A	21 ± 1	28 ± 3	45 ± 5	67 ± 4
B-2	24.0	A	27 ± 2.5	37.5 ± 2.5	60 ± 5	82 ± 5
B-3	43.8	A	185 ± 40	250 ± 60	390 ± 90	500 ± 120
B-4	59.1	A	405 ± 35	630	1000 ± 40	1340 ± 40
B-5	71.4	A	615 ± 15	820 ± 0	1260 ± 20	1695 ± 15
B-6	75.0	A	940 ± 100	1170 ± 90	1680 ± 100	2040 ± 80
PS	30.3	A	390 ± 0	522 ± 3	860 ± 0	1170 ± 30

*Data for duplicate runs.

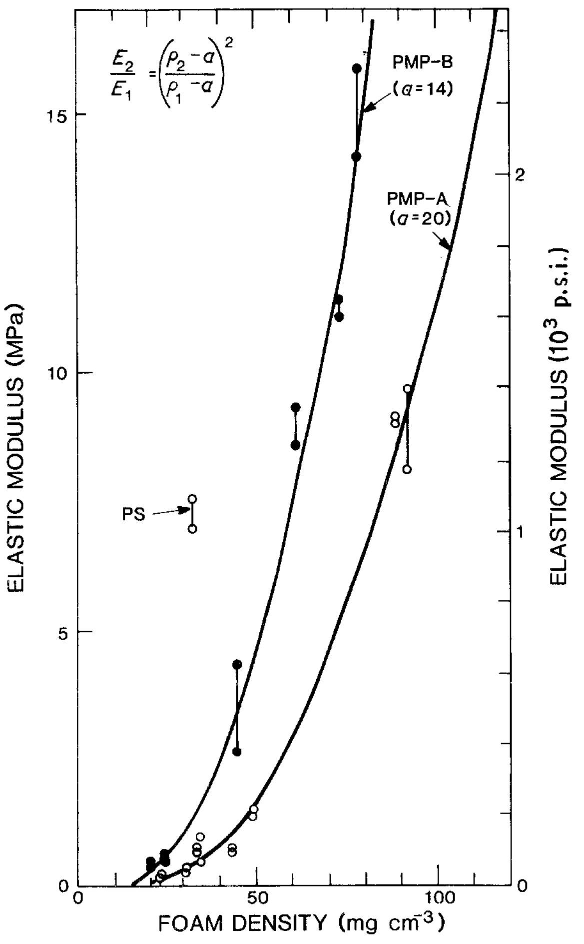

Figure 1 Elastic moduli of low-density foams. (Data at 0.76 mm penetration. Curves are based on Equation 2.)

conform to the same empirical representation

$$\frac{E_2}{E_1} = \left(\frac{\varrho_2 - a}{\varrho_1 - a}\right)^2 \qquad (2)$$

where ϱ_x is the density of sample x and a is a constant. For the foams prepared in Series A, $a = 0.020\,\mathrm{g\,cm^{-3}}$; in Series B, $a = 0.015\,\mathrm{g\,cm^{-3}}$. The implication appears to be that foams with densities below a in each series would have negative compression moduli. This does not rule out the making of foams with densities less than a, however, as we have, in fact, made a $0.012\,\mathrm{g\,cm^{-3}}$ foam in Series A. The cells must be large, however. The practical import of the modulus–density relationship is that these foams have a mass fraction that does not contribute to the compression modulus.

Several recent articles have addressed the elastic properties of porous materials [6–9]. The work by Gibson and Ashby [7] is directed at a wide variety of porous materials. The net result of the various studies

TABLE II Elastic moduli of polymers

Polymer	Modulus (MPa)	
	Source A [5]	Source B [6]
Polyethylene	680	200
Polypropylene	1200	
Polymethylpentene	1400	
Polystyrene	3400	1400* (2650†)
Polyvinylchloride	3400	3000

*Extruded.
†Expanded.

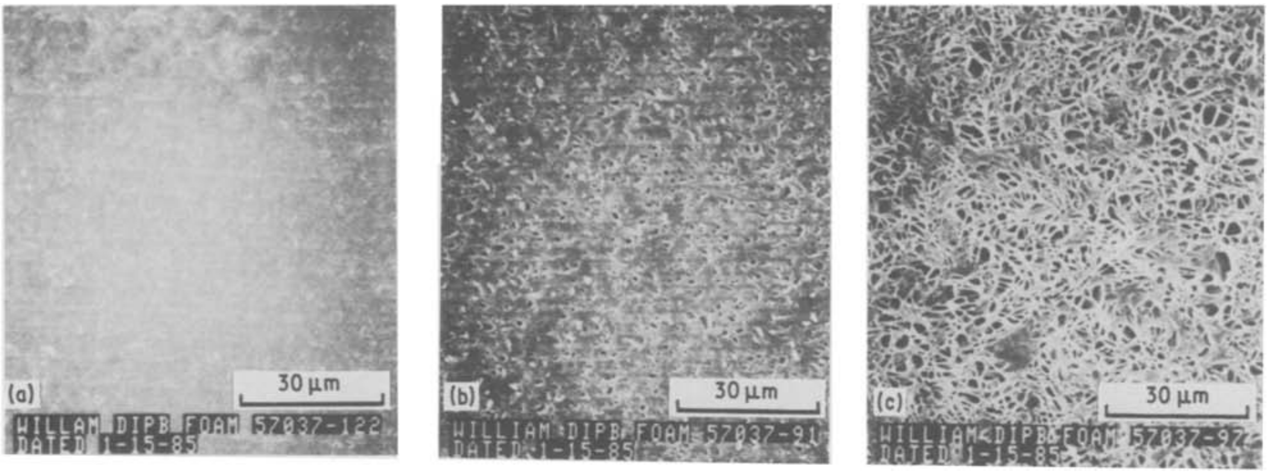

Figure 2 Scanning electron micrographs (SEM) of poly(4-methyl-1-pentene) foams. (a) 86% full density, (b) 46% fully density, (c) 18% full density.

is that the elastic modulus of a foam can be evaluated from the reduced density by the equation

$$\frac{E}{E_s} = \left(\frac{\varrho}{\varrho_s}\right)^2 \quad \text{or} \quad \frac{(1-c)^2}{1} \tag{3}$$

where the subscript s refers to the full density bulk material and c is the fraction of voids. Several features are notable about their correlation. (Fig. 6, in [6], shows this fit of Equation 3 to data for variety of foams.) First, little deviation from Equation 3 occurs until the bulk density has been halved. This is consistent with my finding that the unfilled space is submicrometre in size until more than half of the bulk material has been removed. Compare my Figs 2a to c. Second, a bulge to higher moduli occurs for closed cell foams. These materials possess pneumatically connected cell walls. The wall material may be stronger than the bulk material because of stretching (drawing). Open cell structures could also deviate in a positive fashion if, instead of a uniform dispersion of material occurring, the polymer formed thicker walls or interlocking structures. Third, the general trend of the data at low densities is strongly downward relative to the theoretical prediction. This trend has been overlooked by Gibson and Ashby [7]. A downward curve of E/E_s against relative density is to be expected. The curve should asymptotically approach some density line with the density of air (0.0015 $\mathrm{g\,cm^{-3}}$) being the lowest density possible. This deviation is simply a consequence of having only unconnected matter at some point and hence having a compression modulus of zero. To a first approximation, Equation 3 gives the right order of magnitude of E/E_s, but some refinement is needed.

The theoretical formula expressed in Equation 3 assumes uniform dispersion of support members whose efficiency remains constant and whose magnitude varies uniformly with total mass. More generally, however, there may be noncontributing mass and the efficiency of the contributing mass may vary. This can be represented by

$$\frac{E}{E_s} = \left[\frac{e(\varrho - \varrho^*)}{e_s\varrho_s}\right]^2 \quad \text{or} \quad \phi^2\left(\frac{\varrho - \varrho^*}{\varrho_s}\right)^2 \tag{4}$$

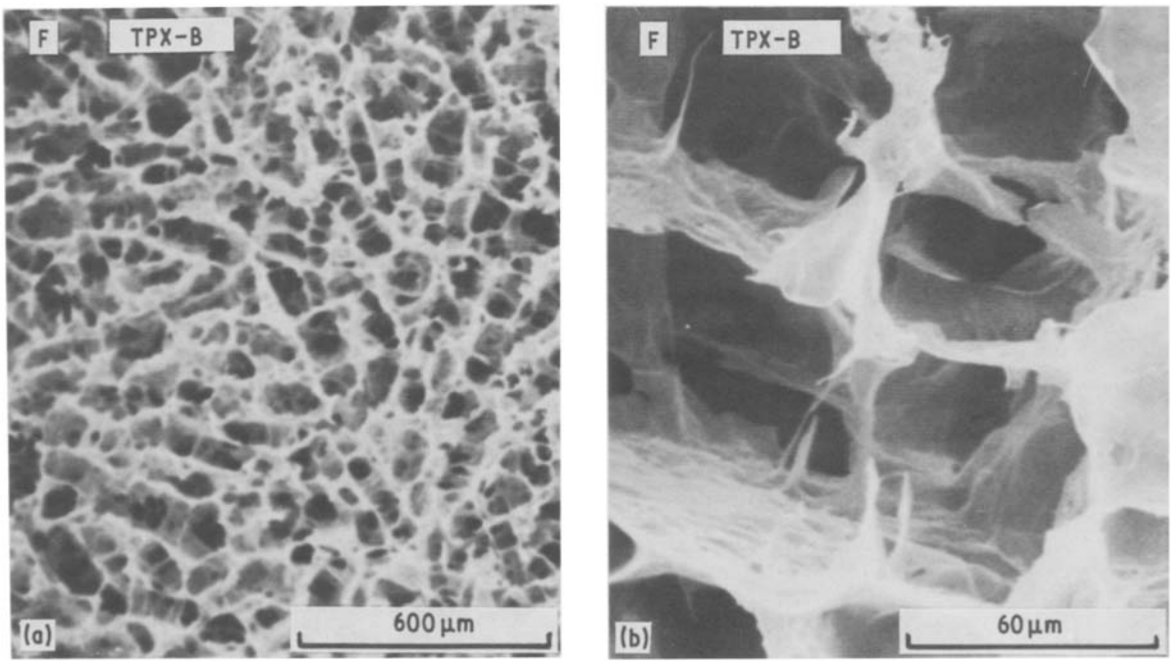

Figure 3 SEM of PMP foam prepared by Method A ($\varrho = 0.034\,\mathrm{g\,cm^{-3}}$).

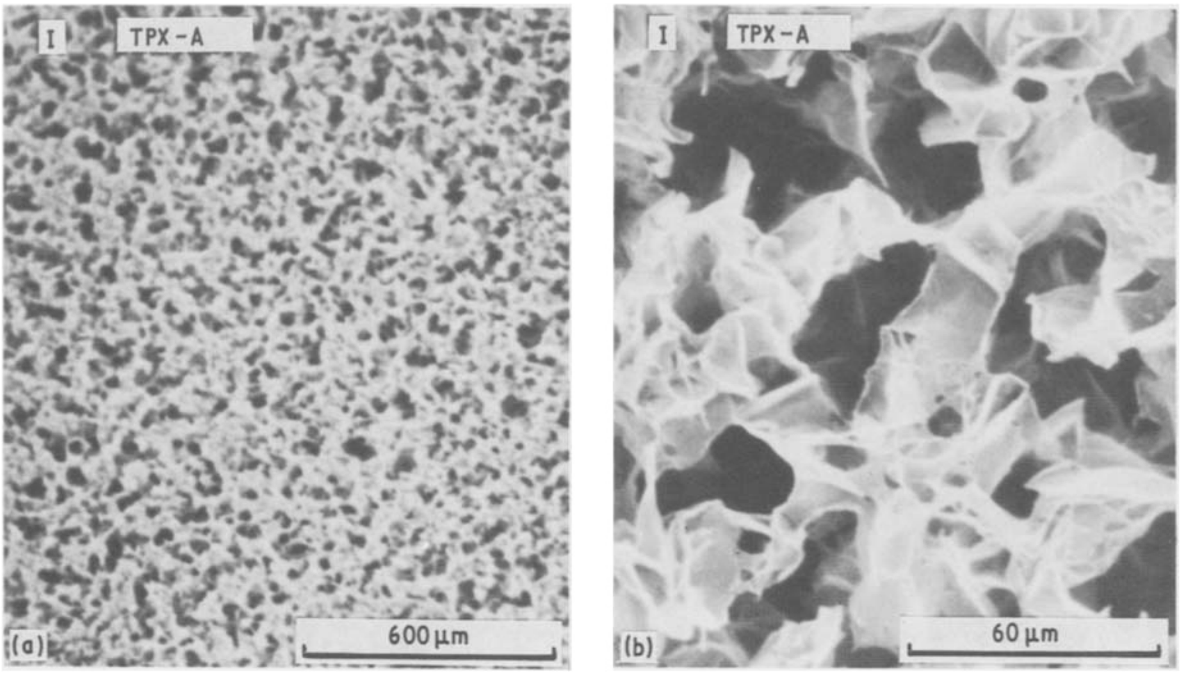

Figure 4 SEM of PMP foam prepared by Method B ($\varrho = 0.020\,\mathrm{g\,cm^{-3}}$).

where e is the efficiency of the contributing members and ϱ^* is the density of the noncontributing mass. For two foams of the same material (same E_s), the same contributing member efficiency, and the same amount of noncontributing material, Equation 4 becomes Equation 2 with $a = \varrho^*$. To handle the high mass end, Equation 4 must be modified to read

$$\frac{E}{E_s} = \phi^2 \left\{\left[\varrho - \varrho^*\left(1 - \frac{\varrho}{\varrho_s}\right)\right]\Big/\varrho_s\right\}^2 \qquad (5)$$

Equation 5 now allows the elastic modulus of the foam material to be addressed with regard to the amount of its material actually contributing to the modulus and the efficiency of that contributing material.

Several interesting items come to light when Equation 5 is applied to the data given in Fig. 1. At $0.030\,\mathrm{g\,cm^{-3}}$, Series A foam has 67% of its mass in a noncontributing role; Series B foam has only 47% noncontributing. This difference is visually supported by the structures shown in Figs 3 and 4. Furthermore, at $0.030\,\mathrm{g\,cm^{-3}}$ the Series B foam has a five-fold greater modulus than does the Series A foam. Part of this difference is due to the efficiency term, ϕ. At this density ($0.030\,\mathrm{g\,cm^{-3}}$), Series B foam has 60% more contributing material and that contributing material is 80% more efficient. The compact, orderly-distributed-polymer structure of the Series B foams (Fig. 4) is clearly more effective than the loose, randomly-distributed-polymer structure of the Series A foams (Fig. 3). Comparing Series B PMP foam with polystyrene (E(polystyrene)/E(Series B) = 5, at $\varrho = 0.035\,\mathrm{g\,cm^{-3}}$, $\varrho_s = 1.05$ (polystyrene) and 0.83 (PMP), and $E_s = 1400\,\mathrm{MPa}$ (polystyrene) [6] and 900 (PMP) [6] shows that the efficiency of the material in the polystyrene foam is 1.5 times greater than that in the Series B foam. As both are well-connected, a logical explanation is that the pneumatic effect in the polystyrene is considerable, that the polystyrene cell geometry (see Fig. 5) is more effective, and/or that the E_s of polystyrene is too low. The E_s for expanded polystyrene [6] ($E_s = 2650\,\mathrm{MPa}$) is probably more appropriate than the extruded value [6] ($E_s = 1400\,\mathrm{MPa}$) for blown foams. The more inclusive expression (Equation 5) thus provides significantly more knowledge about low-density foams than does the simpler version (Equation 3).

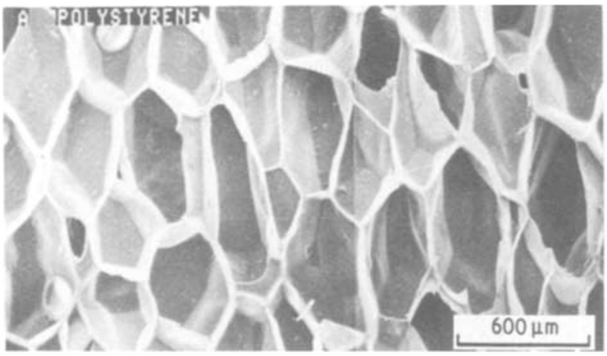

Figure 5 SEM of polystyrene foam board ($\varrho = 0.031\,\mathrm{g\,cm^{-3}}$).

The data generated herein for Series A PMP foams are plotted (Fig. 6) in the style set forth by Gibson and Ashby [7]. The E_s for PMP was taken at 900 MPa as this placed the $0.090\,\mathrm{g\,cm^{-3}}$ value in the appropriate location. This value is reasonable with respect to the published values reported in Table II. Curves calculated from Equations 3 and 5 are also plotted. The data are in good agreement with predictions based on Equation 5, but not Equation 3. The noncontributing component is seen to be considerable, although slightly less than predicted from Fig. 1. Series A PMP foams, in which the foam walls are not stretched during the formation of the foam, are not expected to show a positive deviation from the predicted compression modulus. Being open-cellular and having randomly distributed material, these foams have significant matter at low densities that does not contribute to their compression moduli.

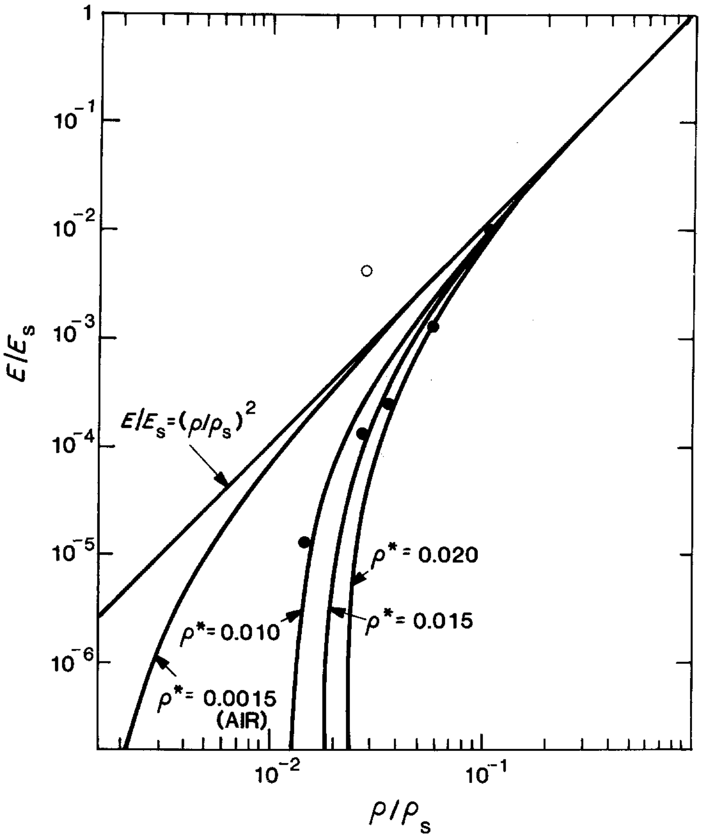

Figure 6 Influence of noncontributing material on the magnitude of the reduced elastic modulus at reduced material density. (Data at 0.25 mm penetration. Curves from Equation 3 or 5.) (○) PS (E_s = 1400 MPa), (●) PMP-A (E_s = 900 MPa).

In summary, low-density, open, microcellular foams can contain a substantial amount of material that does not contribute to the modulus of the foam. The amount of this noncontributing material and the efficiency of the contributing material can vary with processing conditions. The exact dependency of the modulus on the cellular structure must still be determined. This will influence the efficiency component (ϕ) of the refined Equation 5. The refined equation accounts for the reduced mass and the fraction of contributing material and its efficiency. The relationship derived herein thus provides a better view of foams than simply considering them as isotropically reduced masses.

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