The linear elastic properties of microcellular foams

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The mechanical behaviour of a new type of open-cell foam made by a thermally induced phase separation (TIPS) process was investigated. Foams made by the TIPS process are characterized by cell sizes which are 10–100 times smaller than conventional foam materials. In this work, the linear elastic modulus of these foams in dynamic tension/compression was measured. A comparison was made with the theoretical predictions and experimental data for conventional large-cell foams. Foams studied include polystyrene, poly(4-methyl-1-pentene), polyacrylonitrile and poly(γ-benzyl-L-glutamate) in the density range 0.04–0.13 g cm^{-3}.

(Keywords: foam; microcellular; modulus; mechanical properties; polystyrene; poly(4-methyl-1-pentene); polyacrylonitrile; poly(γ-benzyl-L-glutamate)

INTRODUCTION

A new class of solid, cellular materials has emerged based on the thermally induced phase separation (TIPS) of polymer solutions[1–8]. In this method, a polymer is dissolved in a solvent above the critical solution temperature, the temperature is lowered to induce phase separation, and the solvent is removed to isolate a foam. The removal of the solvent may be by extraction if a gel forms, or by vacuum sublimation when a suitable solvent is used. These foam materials are termed microcellular or microporous because of their small pore diameters (0.1–20 μm) relative to conventional closed-cell foams made by thermoplastic foam extrusion using a blowing agent (100–200 μm)[9].

The open-celled foams formed by the TIPS process have expanded the use of cellular materials in the areas of high energy physics[3] and biomedical applications[6]. They also have potential as filters, controlled release media, catalytic substrates and three-dimensional reinforcements for composites. The emphasis has been on very low density materials (<0.05 g cm^{-3} or 3.1 lb ft^{-3}) made from dilute solutions. Polymers such as atactic polystyrene (a-PS)[1], isotactic PS[2], poly(4-methyl-1-pentene) (TPX)[3,4], polyacrylonitrile (PAN)[5], polymethylmethacrylate[1], dextran[3], and polyurethane[6] have been used to make microcellular foams by this method. A foam based on a lyotropic liquid crystal polymer (LCP), poly(γ-benzyl-L-glutamate) (PBLG)[7], has also been recently prepared.

In contrast to the relatively new microcellular foams discussed above, the mechanical properties of conventional foam materials have been extensively studied[9]. Experimental results have shown that the successful prediction of Young's modulus for an open-cell foam, E_f, in the linear elastic region requires an assumption that cell strut bending is the primary mode of deformation[9,10]. This assumption is based on experimentally observed behaviour. For an open cell foam

$$E_f/E_s = C_1(\rho_f/\rho_s)^2 \qquad (1)$$

where E_s and ρ_s are Young's modulus and the density of the solid polymer, ρ_f is the density of the foam and C_1 is a constant which depends on the cell geometry. Closed-cell foams require more complicated expressions due to membrane stresses and internal gas pressure in the cells[9].

Gibson and Ashby[9,10] evaluated C_1 on the basis of extensive experimental data for open-celled foams; the intercept of their plot of log E_f/E_s *versus* log ρ_f/ρ_s yielded a value of $C_1 \approx 1$. A theoretical model based on a tetrahedral unit cell was subsequently developed by Warren and Kraynik[11]. For low density foams, the foam modulus is also given by equation (1) using this model; however, the constant C_1 is explicitly derived from the specific strut geometry (or morphology). For cross sections which are circular and uniform, $C_1 = 0.91$, very close to the value found experimentally by Gibson and Ashby. (Other strut geometries, such as triangular or plateau border, give values of C_1 in the range 1.10–1.53.)

The objective of this study was to characterize the linear elastic mechanical response of microcellular foams made by the TIPS process from various polymers and to compare the response to the theoretical prediction given in equation (1). The morphologies of foams studied in this work are compared in *Figures 1a–f*, and include a-PS, TPX, PAN and PBLG in the density range 0.04–0.13 g cm^{-3}. In *Figure 1g*, a conventional, closed-cell expanded polystyrene foam is shown to illustrate the difference in scale and morphology between the two types of foam.

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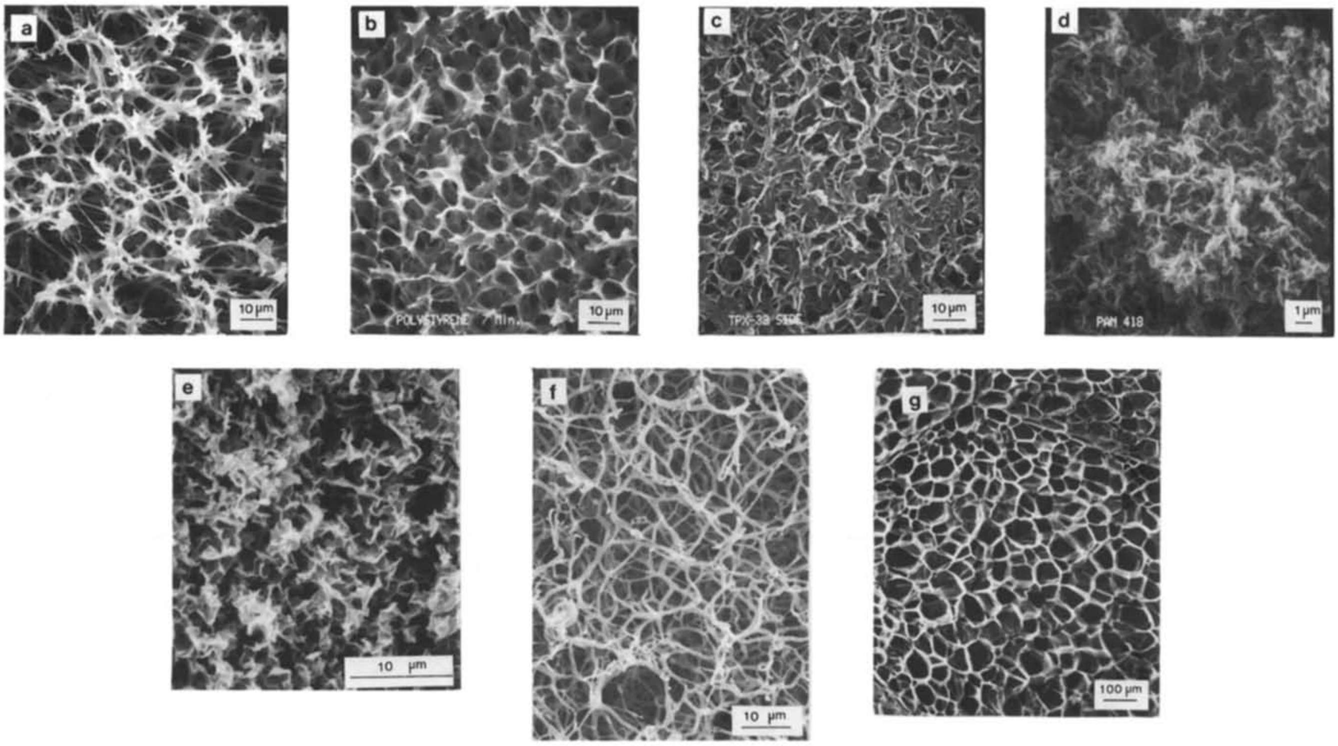

Figure 1 Scanning electron micrographs of foam morphology: (a) a-polystyrene (PS), $\rho_f = 0.040\ \mathrm{g\,cm^{-3}}$; (b) a-PS, $\rho_f = 0.127\ \mathrm{g\,cm^{-3}}$; (c) poly(4-methyl-1-pentene) (TPX), $\rho_f = 0.038\ \mathrm{g\,cm^{-3}}$; (d) polyacrylonitrile (PAN), $\rho_f = 0.047\ \mathrm{g\,cm^{-3}}$; (e) PAN, $\rho_f = 0.073\ \mathrm{g\,cm^{-3}}$; (f) poly($\gamma$-benzyl-L-glutamate) (PBLG), $\rho_f = 0.040\ \mathrm{g\,cm^{-3}}$; (g) expanded PS, $\rho_f = 0.059\ \mathrm{g\,cm^{-3}}$

Table 1 Solid polymer properties

Polymer	ρ_s (g cm^{-3})	E_s (GPa)	Temperature (°C)	E_s[a] (GPa)	M_w (g mol^{-1})
PS	1.04	2.8–4.1[12] 1.4–3.0[9,13]	Below T_g	2.0	2230000
TPX	0.83	1.1–1.4[12] 0.9[13]	Below T_g	1.25	879000
PAN	1.18	3.1–3.8[14]	Below T_g	3.4	150000
PBLG	1.30	1.4[b]	13	–	190000
		3.1[c]	13	3.1	
		2.6[c]	18	2.6	
		1.8[c]	20	1.8	
		1.3[c]	22	1.3	
		0.78[c]	28	0.78	

[a] Value of E_s we used in calculation with equation (1)

[b] Calculated from the shear modulus data of a cast film of PBLG from reference 15 using $E = 2(1 + \mu)G$, where Poisson's ratio, μ, is assumed to equal 0.3 for PBLG

[c] Calculated from the shear modulus data of a compression-moulded sample from reference 16 using the same method as in note *b* above

EXPERIMENTAL

Materials

Foams were prepared by phase separation methods from the polymers listed in *Table 1*. The foams were machined carefully to produce flat, parallel surfaces for the mechanical tests. The PS, TPX and PAN foams were cut with a dovetailed blade on a milling machine; the PBLG was cut with a rapidly vibrating horizontal blade.

Modulus measurements

The modulus of the foam was measured in tension/compression using the linear motor on the Rheometrics System IV with the parallel plate fixtures (25 mm diameter). In this experiment, the foam is placed between the upper and lower plates, and the upper plate moves up and down at a specified frequency. The vertical displacement is determined by the percentage strain input to the computer, calculated based on the gap. The transducer, attached to the lower plate, measures the normal force response of the material. The value measured for the dynamic modulus, E', at 1 Hz will be referred to as E_f.

The machined foam samples were cut into rectangular pieces and glued to the plates to correct for slight defects or non-parallel surfaces of the sample. A number of different glues were compared, including Duco cement, 5 min Epoxy and Elmer's white glue. Although the water-based Elmer's glue took the longest to dry (1.5–2 h), it was chosen for these tests because it was most easily spread into a thin layer, and polymer foam dissolution at the interface was not a concern. Most samples analysed were ≈2 mm thick, although sample thickness did not significantly affect the moduli in the range 1–4 mm investigated. Various rectangular sizes were also tested to check for the 'constrained cylinder' effect, which occurs in solids when the diameter to height ratio is large and the ends of the specimen are constrained[17]. Such effects were not observed for the foams, which were fairly low-density and compressible.

Samples were first analysed at very low strain ($<1.0\%$) as a function of strain and frequency. The symmetry of the normal force signal was monitored as an indication of the secure attachment of the sample to the plate and the continued integrity of the sample. The range of normal forces measured was 10–500*g*, well within the 2–2000*g* range of the transducer. Some studies were conducted at lower temperature using the control provided by the System IV oven attachment.

A frequency of 1 Hz was used for the strain sweeps. The strain was gradually increased to 1.0, 2.0 and 5.0% to obtain reliable data on undamaged samples. The strain response was linear up to a strain of approximately 1–2%. At higher strains (2–5%), the normal force signal became asymmetric and the moduli data originally obtained at low strains were irreversibly decreased.

The modulus of an expanded PS conventional closed-cell foam was measured by this method as a control. A value of 7 MPa was obtained for E_f in the linear elastic region (0.1–0.5% strain and a frequency of 1 Hz). This is consistent with the experimental values given elsewhere[9].

RESULTS AND DISCUSSION

The linear elastic response of microcellular foams prepared by the TIPS process was measured for four different polymers. *Table 2* summarizes the polymer–solvent systems studied, the method of solvent removal, the experimentally measured foam densities, ρ_f, and the foam moduli, E_f. Each value of E_f represents a separate specimen loading, and all data were obtained at room temperature (≈22°C). In general, the temperature does not affect the foam modulus significantly for polymers well below their glass transition temperature, T_g (ref. 9). This is the case for PS and PAN, with T_gs of 100 and 97°C, respectively[12]. TPX is a semi-crystalline polymer which would be much less affected by the T_g, reported to be ≈30°C (ref. 12). A temperature dependence was noted for PBLG, to be discussed in detail later.

As expected in the linear elastic (low strain) region, the Young's moduli of the foams were found to be independent of strain and frequency, as shown in *Figures 2* and *3*, respectively. The values of E_f listed in *Table 2* were obtained from averaged data of the type shown in *Figure 2*, in the 0.1–0.5% strain region. The low strain moduli were used for quantitative measurements because they were reproducible during strain-sweep cycles. At higher strains ($>2\%$), an irreversible decrease in the modulus occurred; both irreversible damage and detachment of the specimen from the plates are possible explanations. An example of an scanning electron microscopy (SEM) photomicrograph for the PBLG040 foam subjected to 5% strain is shown in *Figure 4*; the foam is bent into folds at the edge.

The effect of frequency on the foam modulus (*Figure 3*) was minimal for the PS, TPX and PAN foams in the linear elastic region. The data for PBLG at two different temperatures are also shown in *Figure 3*, illustrating the temperature dependence alluded to earlier. This temperature dependence is shown more clearly in *Figure 5*, along with similar data on the PS040 foam, used as a control.

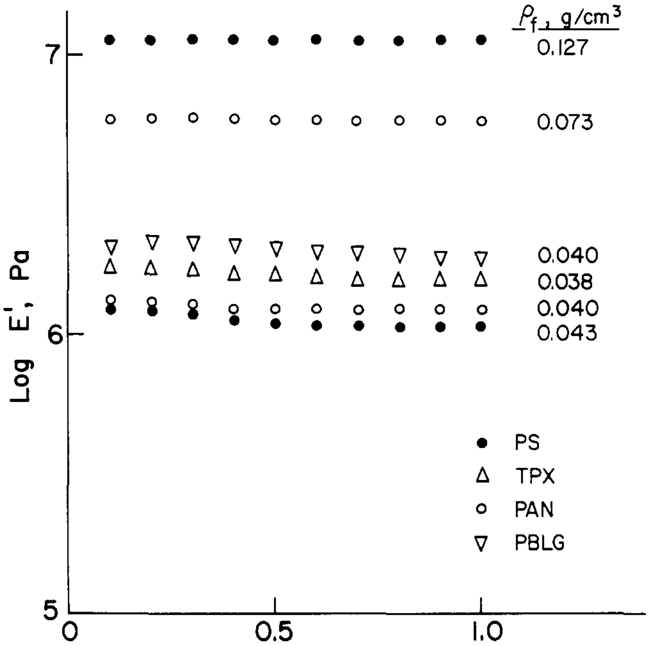

Figure 2 Effect of strain on foam modulus (1 Hz)

Table 2 Foam properties

Polymer	ρ_f (g cm^{-3})	E_f[a] (MPa)	Solvent	Method[b]
PS040	0.040	1.26, 0.98, 1.09	Cyclohexane	Subl.
PS127	0.127	11.3, 12.6, 14.2	Cyclohexane	Subl.
TPX038	0.038	1.62, 3.00, 1.25	50:50 Dioxane/cyclohexane	Ext.
TPX047	0.047	4.86, 4.69, 3.62	50:50 Dioxane/cyclohexane	Subl.
PAN047	0.047	1.26, 1.36	78:22 DMF[c]/ethylene glycol	Ext.
PAN073	0.073	5.89, 4.40	Maleic anhydride	Subl.
PBLG040	0.040	1.91, 1.99, 2.25	93:7 Dioxane/water	Subl.

[a] E_f at 0.1–0.5% strain, 1 Hz, ≈22°C
[b] Ext., extraction; subl., sublimation
[c] DMF, dimethylformamide

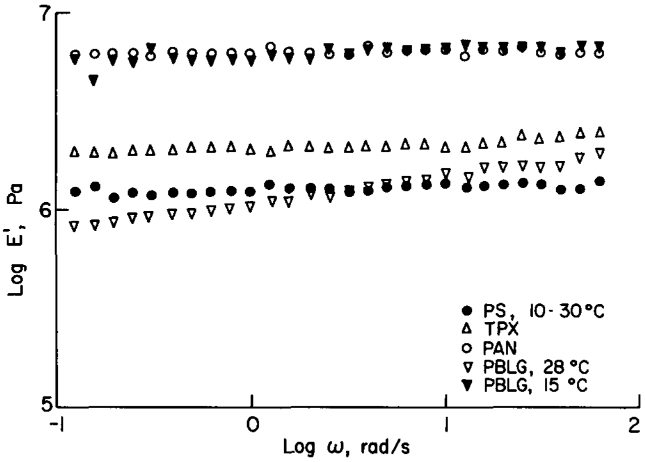

Figure 3 Effect of frequency on foam storage modulus (0.1% strain)

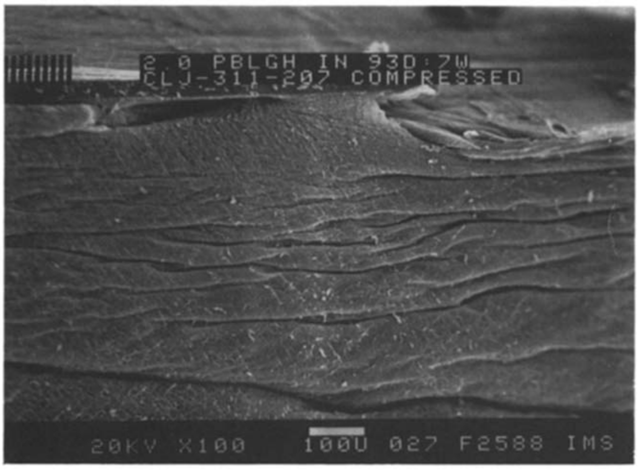

Figure 4 Scanning electron micrograph of PBLG040 foam showing buckling near edge at high strain (5%)

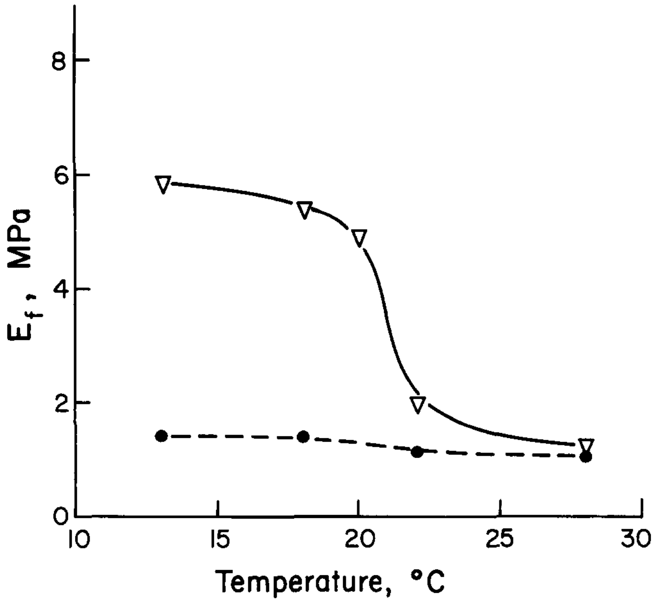

Figure 5 Effect of temperature on PBLG040 (▽) and PS040 (●) foam moduli (0.5% strain, 1 Hz)

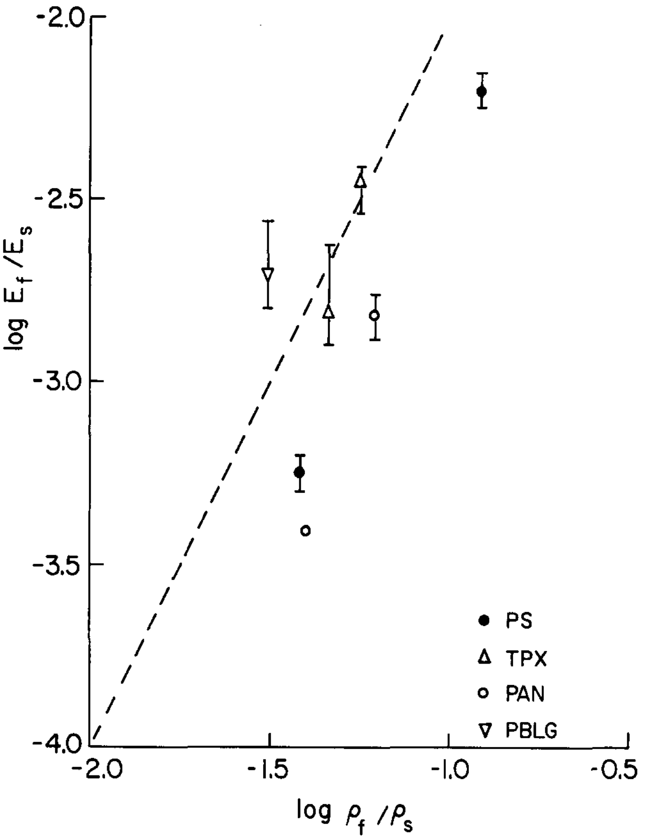

Figure 6 Comparison of experimental values of the relative Young's modulus, E_f/E_s *versus* relative density, ρ_f/ρ_s with the theoretical prediction of a slope of 2 (---) given by equation (1). The error bars represent the range of the experimental data

Although PBLG is a highly crystalline material in the solid state and melts with decomposition above 300°C, a solid-state transition has been reported around 15–20°C and has been attributed to both motion of the benzyl side chains[16] and a glass transition temperature[12]. It is believed that this transition is the cause of the abrupt decrease in modulus at ≈18–22°C for the PBLG foam.

In *Figure 6*, the experimental foam moduli of various polymers are compared in a universal plot[18] according to equation (1), using the solid polymer properties indicated in *Table 1*. A reference line gives the theoretical prediction[10,11] for $C_1 = 1$ and a slope of two. The vertical bars indicate the range of the experimental data, obtained from *Table 2*. (For PBLG, the data in *Table 2* were combined with the moduli measured as a function of temperature using the appropriate value of E_s. The vertical bar in *Figure 6* indicates the range of the data.)

The data for microcellular foams made by the TIPS process, shown in *Figure 6*, are consistent with the extensive experimental data of Gibson and Ashby[10] for conventional open-cell foams. The amount of scatter in our experimental data is also similar and can be attributed to both experimental error and inherent difficulties in the comparison. For example, the agreement between theory and experiment for the data in *Figure 6* depends markedly on the value of E_s used. The higher the value of E_s, the lower the value of E_f/E_s is relative to the theoretical prediction. This makes the calculation of the experimental slope for the collective data inherently subjective. For this reason and because of the limited amount of data presented, no quantitative calculation of the experimental slope will be made.

We prepared *Figure 6* using average values of E_s available from the range of values reported in *Table 2*. (The exception to this is the value for PS, for which a large amount of published data of the solid polymer properties of the foamed polymer[9] is available, and a typical value of 2.0 GPa is believed to be more accurate.) Even if the lowest value of E_s is used, however, some of the data still fall slightly below the theoretical curve, with the exception of the PBLG and TPX foams. Reasons for the low moduli may include an imperfect cell geometry compared with the theory as well as the inefficient use of the polymer in making up the cell microstructure. The PAN moduli data, which fall the furthest below the theoretical curve, may be explained by the rather inefficient cluster-like appearance of the microstructure, shown in *Figures 1d* and *e*. Another possible explanation, however, is that the friable PAN foams may have been damaged during cutting and mounting. In contrast, the foams from the more crystalline polymers, TPX and PBLG, have the highest relative modulus to density value. This may be related to the more efficient cell microstructure shown in *Figures 1c* and *1f* and, for PBLG, the additional property of molecular orientation within the fibre-like struts[7].

Williams[13] reported the only other known moduli data for microcellular foams, specifically TPX made by two different processes in the density range $0.02 \leqslant \rho_f \leqslant 0.09$ g cm^{-3}. A penetrometer method was used to determine Young's modulus, which is quite different from the dynamic tension/compression method used in this work. Using a low value of 900 MPa for E_s, the TPX data still fall well below the theoretical curve predicted by equation (1). In an attempt to explain the low modulus data, Williams developed an expression which accounts for a non-contributing mass fraction of material. Our results for TPX, shown in *Figure 6*, actually follow the theoretical prediction quite well, even after normalizing with a higher value of E_s. This suggests that an inherent difference is present in the TPX foams studied or the method used to test the modulus. The microstructure of the TPX foams studied in this work (*Figure 1c*) does appear to be more finely interconnected than the TPX foams studied by Williams.

CONCLUSION

Microcellular foams made from various polymer/solvent systems by the TIPS process have similar linear elastic mechanical properties. In this respect, they also are comparable to larger cell size, open-celled foams made by conventional foaming processes. The linear elastic properties are described satisfactorily by the theoretical prediction[10,11] of the dependence of the modulus on the square of the polymer volume fraction in the foam.

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REFERENCES

1 Aubert, J. H. and Clough, R. L. *Polymer* 1985, **26**, 2047

2 Aubert, J. H. *Macromolecules* 1988, **29**, 3468

3 Coudeville, A., Eyharts, P., Perrine, J. P., Rey, L. and Rouillard, R. *J. Vac. Sci. Technol.* 1981, **18**, 1227

4 Williams, J. P. and Moore, J. E. *Polymer* 1987, **28**, 1950

5 Sylwester, A. P., Aubert, J. H., Rand, P. B., Arnold, C. and Clough, R. L. *PSME Prepr.* 1987, **57**, 113

6 Aubert, J. H., Sylwester, A. P. and Rand, P. *Polym. Prepr.* 1989, **30**, 447

7 Jackson, C. L. and Shaw, M. T. *Polymer* 1990, **31**, 1070

8 Young, A. T. *J. Cell. Plast.* 1987, **23**, 55

9 Gibson, L. J. and Ashby, M. F. 'Cellular Solids, Structure and Properties', Pergamon Press, Oxford, UK, 1988

10 Gibson, L. J. and Ashby, M. F. *Proc. R. Soc. Lond.* 1982, **A382**, 43

11 Warren, W. E. and Kraynik, A. M. *J. Appl. Mech.* 1988, **55**, 341

12 Brandrup, J. and Immergut, E. H. (Eds.) 'Polymer Handbook', 2nd Edn., 1975

13 Williams, J. M. *J. Mat. Sci.* 1988, **23**, 900

14 Agranoff, J. (Ed.) 'Modern Plastics Encyclopedia', 1985, **62** (10A), 25

15 Saba, R., Sauer, J. A. and Woodward, A. E. *J. Polym. Sci. A* 1963, **1**, 1483

16 Hiltner, A., Anderson, J. M., and Borkowski, E. *Macromolecules* 1972, **5**, 446

17 Gent, A. N. and Lindley, P. B. *Proc. Inst. Mech. Eng.* 1959, **173**, 111

18 Jackson, C. L. *Ph.D. Dissertation*, The University of Connecticut, Storrs, CT, USA, 1988. (The plot given in Figure 66 of the thesis was found to have a units error (factor of 10) which shifts the polystyrene data above the curve)