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)$^9$, isotactic PS$^2$, poly(4-methyl-1-pentene) (TPX)$^3$–$^4$, polyacrylonitrile (PAN)$^5$, polymethylmethacrylate$^6$, 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

$$E_f/E_s = C_1 (ρ_f/ρ_s)^2$$

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.

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 $C_1 ≈ 1$. 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–j, and include a-PS, TPX, PAN and PBLG in the density range 0.04–0.13 g cm$^{-3}$. In Figure 1q, a conventional, closed-cell expanded polystyrene foam is shown to illustrate the difference in scale and morphology between the two types of foam.
Microcellular foams: C. L. Jackson et al.

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

Table 1 Solid polymer properties

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\rho_s$ (g cm$^{-3}$)</th>
<th>$E_s$ (GPa)</th>
<th>Temperature (°C)</th>
<th>$E_s$ (GPa)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>1.04</td>
<td>2.8-4.1$^{12}$</td>
<td>Below $T_g$</td>
<td>2.0</td>
<td>2230000</td>
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<tr>
<td>TPX</td>
<td>0.83</td>
<td>1.1-1.4$^{12}$</td>
<td>Below $T_g$</td>
<td>1.25</td>
<td>879000</td>
</tr>
<tr>
<td>PAN</td>
<td>1.18</td>
<td>3.1-3.8$^{14}$</td>
<td>Below $T_g$</td>
<td>3.4</td>
<td>150000</td>
</tr>
<tr>
<td>PBLG</td>
<td>1.30</td>
<td>1.4$^b$</td>
<td>13</td>
<td></td>
<td>190000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.1$^c$</td>
<td>13</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.6$^c$</td>
<td>18</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.8$^c$</td>
<td>20</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.3$^c$</td>
<td>22</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.78$^c$</td>
<td>28</td>
<td>0.78</td>
<td></td>
</tr>
</tbody>
</table>

*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, $\mu$, 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. 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 \( E_t \) 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.

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, \( \rho_f \), and the foam moduli, \( E_t \). Each value of \( E_t \) represents a separate specimen loading, and all data were obtained at room temperature (\( \approx 22^\circ \)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 \( T_g \)s of 100 and 97°C, respectively. TPX is a semi-crystalline polymer which would be much less affected by the \( T_g \) reported to be \( \approx 30^\circ \)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 \( E_t \) 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 PO40 foam, used as a control.

![Figure 3](image)

**Figure 3** Effect of frequency on the foam modulus

![Figure 4](image)

**Figure 4** SEM photomicrograph of the PBLG040 foam subjected to 5% strain

### Table 2 Foam properties

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \rho_f ) (g cm(^{-3}))</th>
<th>( E_t ) (MPa)</th>
<th>Solvent</th>
<th>Method(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS040</td>
<td>0.040</td>
<td>1.26, 0.98, 1.09</td>
<td>Cyclohexane</td>
<td>Subl.</td>
</tr>
<tr>
<td>PS127</td>
<td>0.127</td>
<td>11.3, 12.6, 14.2</td>
<td>Cyclohexane</td>
<td>Subl.</td>
</tr>
<tr>
<td>TPX038</td>
<td>0.038</td>
<td>1.62, 3.00, 1.25</td>
<td>50:50 Dioxane/cyclohexane</td>
<td>Ext.</td>
</tr>
<tr>
<td>TPX047</td>
<td>0.047</td>
<td>4.86, 4.69, 3.62</td>
<td>50:50 Dioxane/cyclohexane</td>
<td>Subl.</td>
</tr>
<tr>
<td>PAN047</td>
<td>0.047</td>
<td>1.26, 1.36</td>
<td>78:22 DMF/ethylene glycol</td>
<td>Ext.</td>
</tr>
<tr>
<td>PAN073</td>
<td>0.073</td>
<td>5.89, 4.40</td>
<td>Maleic anhydride</td>
<td>Subl.</td>
</tr>
<tr>
<td>PBLG040</td>
<td>0.040</td>
<td>1.91, 1.99, 2.25</td>
<td>93:7 Dioxane/water</td>
<td>Subl.</td>
</tr>
</tbody>
</table>

\(^a\)\( E_t \) at 0.1–0.5% strain, 1 Hz, \( \approx 22^\circ \)C

\(^b\)Ext., extraction; subl., sublimation

\(^c\)DMF, dimethylformamide
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 and a glass transition temperature. 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 according to equation (1), using the solid polymer properties indicated in Table 1. A reference line gives the theoretical prediction 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 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/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 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.

Williams reported the only other known moduli data for microcellular foams, specifically TPX made by two different processes in the density range $0.02 \leq \rho_f \leq 0.09$ 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 of the dependence of the modulus on the square of the polymer volume fraction in the foam.

ACKNOWLEDGEMENTS

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