The Elastic and Plastic Mechanical Responses of Microcellular Foams

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SYNOPSIS

Microcellular foams were prepared by the thermally induced phase-separation technique, which yields materials having very small cell dimensions (0.1–20 μm). The polymers employed were isotactic polystyrene, polyacrylonitrile, poly(4-methyl-1-pentene), polyurethane, and Lycra® and the resulting foams all had densities in the range 0.04–0.27 g cm^{-3}. Values of Young's modulus and the collapse stress for these foams were measured and compared with predictions for conventional foams containing defects. Also investigated were plastic deformations, some time-dependent behavior, and Poisson's ratio. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Microcellular foams are those having open cells with dimensions of 0.1–20 μm, which makes these cells about 10–100 times smaller than those of conventional foams. Such foams can be prepared by a thermally induced phase-separation technique that is explained in detail elsewhere.[1] Such microcellular foams have been used, e.g., in physics laboratories for targets in inertial confinement fusion because of their small-pore dimensions.[2] However, more recent investigations have explored the possibility of using these foams in new areas such as biomedical applications, controlled release of drugs,[3] and preparation of composite materials.[4] In some parallel investigations, the mechanical behavior of these foams has also received considerable attention. Such investigations of mechanical properties[5-7] have generally compared the experimentally measured moduli with the predictions of current theory for conventional foams.[8] According to such theory, the relative mechanical property of a foam can be related to its relative density by the formula

$$\frac{P_f}{P_s} = C\left(\frac{\rho_f}{\rho_s}\right)^n \tag{1}$$

where P_f is some property of the foam and P_s is the same property for the bulk (unfoamed) polymer. The quantities ρ_f and ρ_s are the densities of foam and bulk polymer, respectively. C is a constant that is equal to 1.0 when the property is the modulus and to 0.3 when it is the collapse stress. The exponent n equals 2 and 3/2 for the modulus and collapse stress, respectively. More elaborate formulations are also available.[8]

It has been found that the experimental compression moduli of microcellular foams are much smaller than those predicted by eq. (1).[5-7] In an earlier study,[9] an attempt was made to explain this behavior in terms of structural defects, presumably formed during the production of the foam. Support for this suggestion was obtained by introducing defects into the structure of a conventional, closed-cell polystyrene foam by applying compressive strains and then comparing the stress–strain curves of the reloaded foam with those for microcellular foams.[9] This study documented the reductions in the moduli of these foams.

The present investigation involves similar experiments, primarily on conventional, open-cell,

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rigid foams of the polyurethane and phenolic type. In addition, an elastomeric foam was included, and some open-cell, semirigid polyurethane and phenolic foams were punctured with a large number of needles to produce defects in their structures. Comparisons were then made between the microcellular foams and the damaged conventional ones with regard to the shapes of their stress–strain curves, their moduli, and their collapse stresses. Other properties investigated were plastic deformations, time-dependent behavior by stress-relaxation experiments, and Poisson's ratio in both the elastic and plastic deformation regions.

EXPERIMENTAL

Materials

The rigid microcellular foams tested were isotactic polystyrene (IPS), polyacrylonitrile (PAN), poly(4-methyl-1-pentene) (TPX), and polyurethane (PU). The elastomeric foams were polyurethane and Lycra®. Their densities were in the range 0.04–0.27 g cm^{-3}.

The polymers and the solvents, listed in Table I, were mixed and the temperature was raised above the critical point to obtain a homogeneous solution. The temperature was then lowered to induce phase separation. Finally, the solvents were removed by the methods listed in Table I to obtain the desired foams.

The samples were cut into dimensions 10 × 10 mm, with a thickness of 8 mm, using sharp blades. The upper and lower surfaces were then smoothed with sandpaper so that they became parallel to one other. Strips having the dimensions 2 × 4 × 30 mm were cut from samples of the elastomeric foams, and epoxy was used to glue some of the rigid foams to aluminum plates for tension experiments.

The open-cell, conventional foams tested were a rigid polyurethane (density: 0.005 g cm^{-3}, provided by the Stepan Co.), a semirigid polyurethane (density: 0.057 g cm^{-3}, provided by the Wescorp Co.), and a rigid phenolic (density: 0.023 g cm^{-3}). These materials were cut into 14 × 14 × 12 mm prismatic samples. Two different methods were used to introduce defects into their structures: For the rigid polyurethane and phenolic foams, uniaxial compressive strains were applied in different amounts, and for the semirigid polyurethane and phenolic foams, a large number of needles (0.2 mm diameter) were penetrated into the specimens. In this latter approach, one sample was punctured more than the other, so that there would be a different number of defects in the two samples.

Mechanical Property Measurements

The mechanical testing was carried out on an Instron testing machine (Model 1120) with a 500 lb load cell, at a strain rate of 0.02 in. min^{-1}. A smaller-capacity load cell (2 kg) was used for the tension

Table I Preparative Conditions for the Microcellular Foams

Foam	ρ_f (g cm^{-3})	Solvent	Method
IPS 350	0.162	1-Chlorodecane	Gelation/extraction
IPS 351	0.155		
IPS 352	0.168		
IPS 353[a]	0.094		
IPS 354[a]	0.099		
IPS 444	0.137	1-Chlorodecane	Gelation/extraction
PAN 221A	0.040	Maleic anhydride	Sublimation
PAN 247	0.092		
PAN 389	0.081	Dimethyl formamide and	Gelation/extraction
PAN 391	0.058	ethylene glycol	
PAN 444	0.052		
TPX 101	0.046	Decalin and 1-dodecanol	Gelation/extraction
Lycra-23®	0.225	Dimethylacetamide/water	Gelation/extraction
PU	0.234		
PU	0.274		

[a] IPS 353 and 354 were prepared from gels formed at 30°C, and the other IPS foams, from gels at 0°C.

tests on the elastomeric foams. The strain was measured by the displacement of the upper crosshead of the machine.

Time-dependent behavior was investigated in a series of stress–relaxation experiments. At each step, a predetermined strain was applied using the highest strain rate (20 in. min^{-1}) available from the testing machine and then kept constant during the experiment. The longitudinal deformation was obtained from the displacement of the upper crosshead, and the lateral deformation was measured using an optical cathetometer. In this way, Poisson's ratio was determined. After each step, the specimen was permitted to recover for 1 day, and then the plastic (permanent) strain was obtained by measuring the longitudinal dimension of the specimen using a micrometer. The tests were carried out at a temperature of 20 ± 1°C.

RESULTS AND DISCUSSION

The moduli were calculated from the initial, linear regions of the stress–strain curves. The collapse stress was taken to be the intersection of the lines drawn tangent to the initial linear region and the following region of the curve with minimum slope. Double-logarithmic plots of the relative modulus against the relative density of the microcellular foams are shown in Figure 1. Included is the prediction of the theory given by eq. (1) for $C = 1$ and $n = 2$. A similar plot for the relative collapse stress with respect to the yield stress (σ_{ys}) of the polymer is given in Figure 2. The solid line corresponds to eq. (1) with $C = 0.30$ and $n = 3/2$. The moduli and yield stresses of the bulk polymers taken from the literature are given in Table II, together with the corresponding densities. The data points are seen to lie well below the theoretical curves in both Figures 1 and 2.

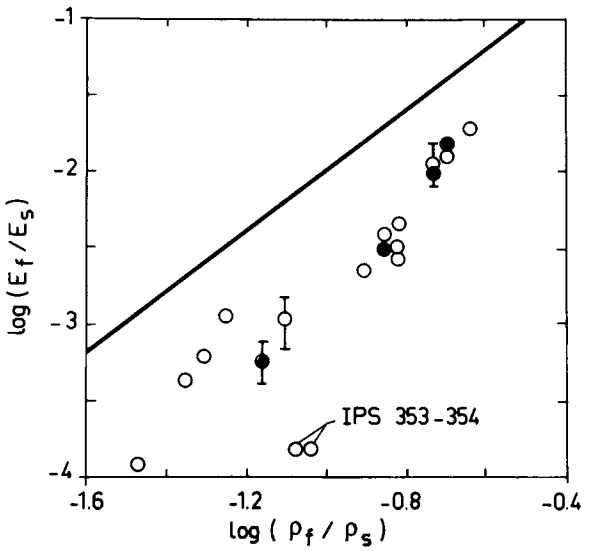

Figure 1 Variation of the relative modulus with relative density for the microcellular foams. The filled points were obtained from tensile tests, and the solid line is the prediction of the theory [eq. (1)].

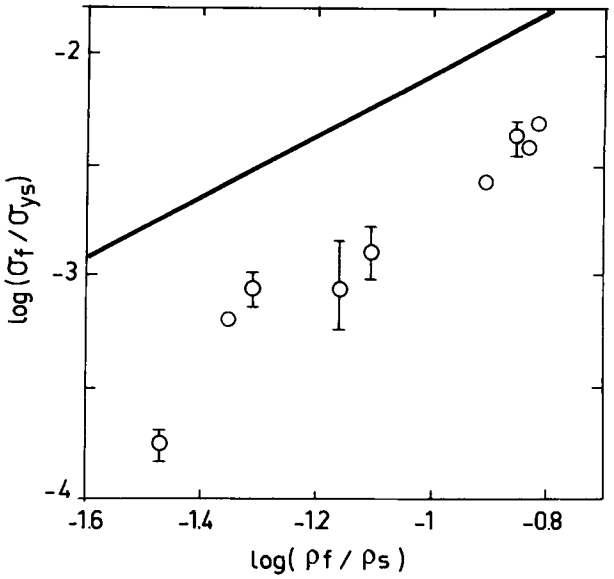

Figure 2 Variation of the relative collapse stress with relative density; see legend to Figure 1.

These unexpectedly low values were investigated using the conventional foams with defects, as described in the previous section. Table III gives the amounts of compression applied to the rigid polyurethane and phenolic foams and the permanent (plastic) strains obtained after recovery. The ratios of the moduli and the collapse stresses of the unloaded foams to the loaded ones are also shown in this table. Increase in prestrain increases the number of defects and decreases the modulus, as expected. Similar results were obtained on the samples in

Table II Properties of the Bulk Polymers

Polymer	ρ_s (g cm^{-3})	E_s (MPa)	σ_{ys} (MPa)
IPS	1.11[10]	5,600[11]	148[9]
PAN	1.18[6]	3,400[6]	83[12]
TPX	0.83[6]	1,250[6]	—
Lycra and PU	1.20[8,9]	45[8]	—

Table III Preparation and Properties of Preloaded Polyurethane and Phenolic Foams

Foams	Precompression (%)	Plastic Strain (%)	E_{load}/E_{unload}	$\sigma_{load}/\sigma_{unload}$
Rigid polyurethane	30.5	1.7	0.54	0.44
	40.0	7.5	0.43	0.43
	70.2	22.4	0.18	0.29
Phenolic	30.0	5.5	0.09	—
	55.0	12.9	0.07	—

which defects were introduced by the needles. Table IV presents the ratios of the moduli and collapse stresses of these punctured foams relative to the undamaged ones. In each group of two foams, the number of needles used (and thus the number of defects produced) was smaller in the case of the first sample. It is readily seen that the modulus and collapse stress both decrease significantly with increase in the amount of damage.

Another comparison made with the conventional foams involves the shape of the stress–strain curves. Figure 3 shows compression stress–strain curves for some of the microcellular foams. The common feature in all the curves is the complete absence of horizontal (plateau) regions. Instead, the compressive stress increases continuously with strain. The corresponding curves for the conventional foams are given in Figures 4–6. The lowest curve in each figure corresponds to the undamaged foam, and each such curve shows a long plateau region. In Figure 4, increase in prestrain decreases the length of the plateau region, which finally disappears for the largest prestrains. Analogous behavior is found for the prestrained, punctured foams; plateau regions are also absent at the highest prestrains. This behavior can be explained as follows: In conventional foams beyond the initial linear region of the stress–strain curve, the struts in the structures either buckle or yield depending on whether the polymer is elastomeric or rigid. This collapsing behavior takes place in a "rowlike" manner, as explained by Shaw and Sata,[13] starting from the weakest row and continuing until all the rows collapse. For the rigid preloaded foams (Figs. 4 and 5), the first rows to collapse are the ones previously deformed, because these struts are already damaged and have lower moduli. After that, the undamaged struts start collapsing, giving rise to at least some plateau region. For the foams

Table IV Properties of Punctured Semirigid Polyurethane and Phenolic Foams

Foam	Sample	E_{punct}/E	σ_{punct}/σ
Semirigid polyurethane	1	0.68	0.86
	2	0.33	0.42
Phenolic	1	0.70	0.66
	2	0.06	0.05

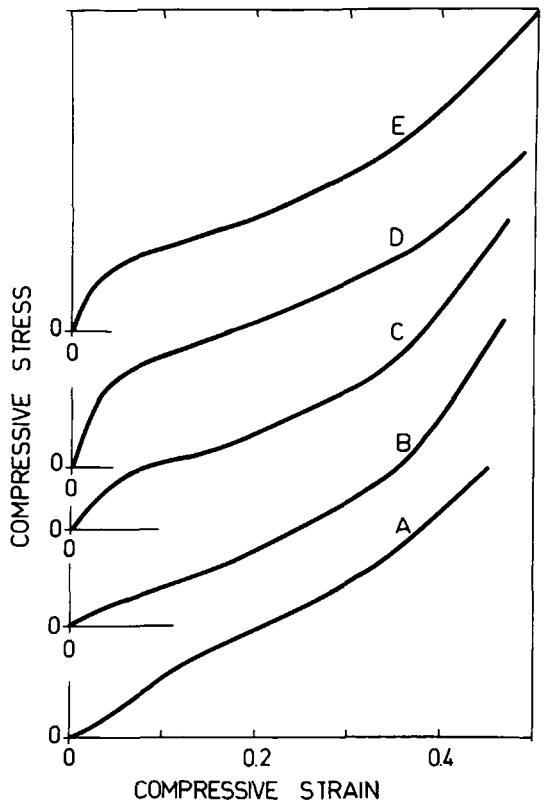

Figure 3 Stress–strain curves for microcellular foams in compression. (curve A) PU; (B) IPS 353; (C) PAN 391; (D) TPX 101; (E) IPS 351. The scale of the vertical axis is arbitrary.

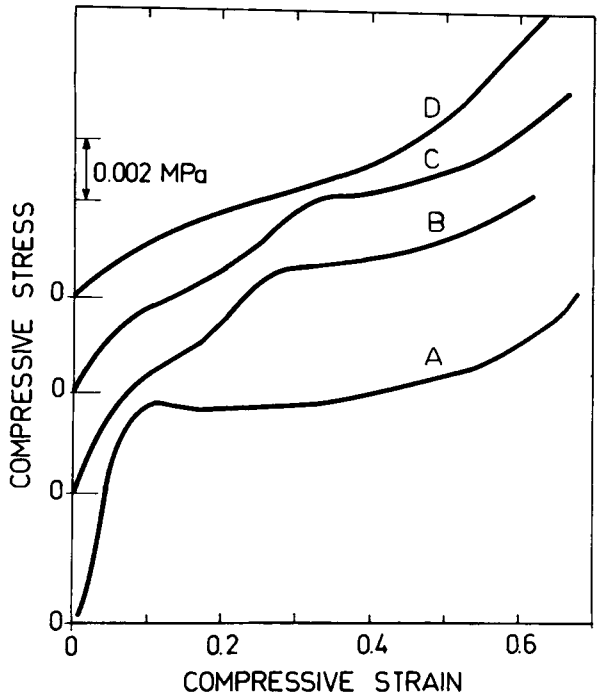

Figure 4 Stress–strain curves for preloaded open-cell, rigid polyurethane foams. Prestrains (%) were (A) 0, (B) 30.5, (C) 40.0, and (D) 70.0.

that had been preloaded until all the struts collapsed, there is no plateau region at all.

On the other hand, the foams that were punctured with needles contain defects distributed uniformly over their volumes. The collapsing in these cases occurs at the weakest struts of the structure in an individual manner, instead of row by row. This way the stress does not stay constant during collapse; instead, it rises continuously, and at each stress level some groups of the struts fail until all of them collapse. Densification follows the collapsing, as usual. It appears that the shape of the stress–strain curve is more sensitive to the defects in the structure than are the modulus and collapse stress. In Figures 5 and 6, the stress–strain curves show no plateau regions, even for the lightly punctured foams. The microcellular foams IPS 353 and 354 have much lower moduli and collapse stresses than do other IPS foams, as can be seen in Figures 1 and 2, although their densities are not much smaller.[†] In parallel with these lower values, the stress–strain curve of IPS 353 does not contain even a breaking point (as is also true for IPS 354, which is not described in Fig. 3). The same type of behavior has been observed for polystyrene[9] and polyethylene[15] foams.

Skochdopole and Rubens[16] performed similar experiments on closed-cell polyethylene foams. They punctured some of the foams with needles and also crushed one sample by applying compressions, as described in the present study. They also found that the stress–strain curves of these foams had no plateau regions and that the initial compressive modulus and compressive strength were lowered. Although they attributed this behavior to the conversion of some of the closed cells to open ones, it is known that open-cell foams generally do have plateau regions. Shaw and Sata[13] applied compressions to prismatic polystyrene foams in one direction and subsequently reloaded the same samples in the perpendicular directions. They reported lower values

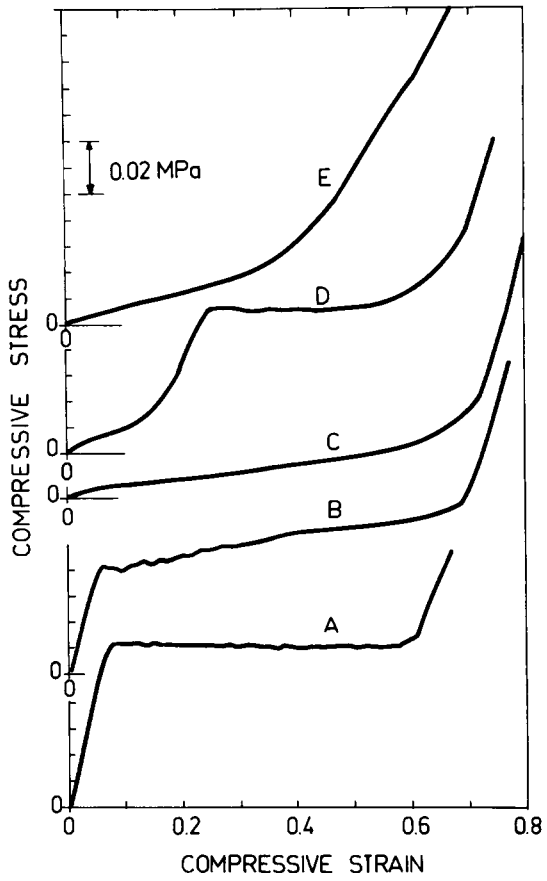

Figure 5 Stress–strain curves for preloaded or punctured open-cell, phenolic foams: (A) original; (B,C) punctured (with C more punctured than B); (D) prestrained 30%; (E) prestrained 55%.

[†] The low values of the moduli of IPS 353 and 354 relative to the other IPS foams have been attributed to differences in morphology of the foams in Ref. 14. IPS 353 and 354, which are from gels formed at 30°C, have "ball"-like morphology with the connectiveness of their gels arising from only surface contacts between the balls. On the other hand, the gels formed at 0°C have "strut"-like morphologies.

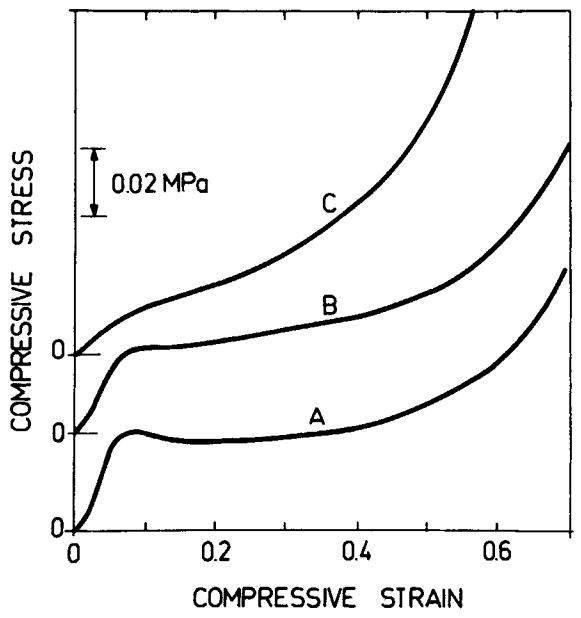

Figure 6 Stress–strain curves for punctured open-cell, semirigid polyurethane foams: (A) unpunctured; (B,C) punctured (with C more punctured than B).

of the modulus and collapse stress in the subsequent loadings, which they attributed to the damage formed in the structure during the first loading.

The plastic deformations of IPS 352 and PAN 389 were measured and compared with those of two conventional foams, namely, those of rigid polyurethane and rigid phenolic. The results are shown in Figure 7. There is a significant difference between the amounts of plastic deformation in microcellular and conventional foams, regardless of the type of polymer. The larger amounts of plastic deformation exhibited by the microcellular foams may indicate that these structures cannot recover as easily, because of reduced numbers of undamaged struts.

It seems likely that the defects formed during the production of these foams are responsible for the observed discrepancies from theory. Specific sources could be nonuniform temperature distribution in the foam during cooling or shrinkage occurring during removal of solvent. A similar conclusion was reached by Williams,[5] who suggested that the moduli were lowered by noncontributing material and reduced efficiencies in other parts of the foam. Jackson et al.[6] suggested imperfect cell geometry and inefficient use of polymer making up the cell microstructure. Finally, LeMay et al.[7] discussed the possibility of discontinuous structures in the microcells. All these explanations contain the common general conclusion that microcellular foams have structural defects that are responsible for the discrepancies from theory.

Time-dependent behavior was characterized by isochronal stress–strain curves at 10 s, 1 min, and 1 h. The results are given in Figures 8 and 9 for IPS 352 and PAN 389, respectively. Although the modulus did not change very much with time, the plastic

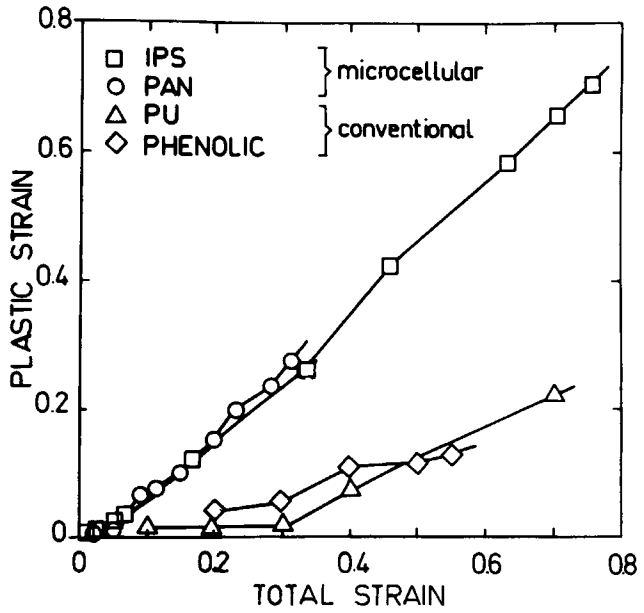

Figure 7 Comparison of plastic deformations for microcellular foams with those for conventional foams.

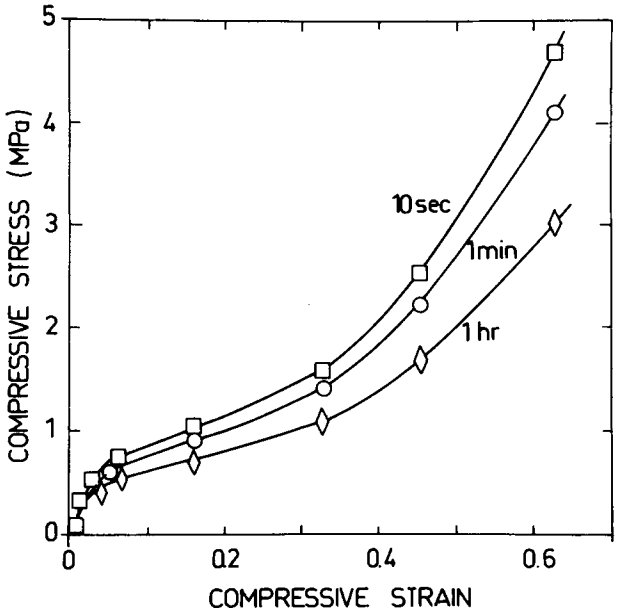

Figure 8 Isochronal stress–strain curves for IPS 352. The points were obtained from stress–relaxation data.

region of the curves moved to markedly lower values of the stress. The decreases were about 69% in 1 h for IPS and 61% in 1 h for PAN, indicating that this region is strongly time-dependent. Poisson's ratio (defined as the negative of the ratio of lateral to axial strains) was measured for IPS 352 and PAN 389 foams, and the results are given in Table V. At small deformations, the value of this ratio is about 0.32 for IPS, which is in good agreement with literature values and close to that of the solid polymer.[8,17] At higher strains (beyond the collapsing stress), it drops to 0.08 for IPS and to 0.07 for PAN. Shaw and Sata[13] reported 0.03 for polystyrene foam, and Rinde[17] reported 0.03–0.14 for different foams at large strains. It appears that values of Poisson's ratio for microcellular foams are not very different from those for conventional foams.

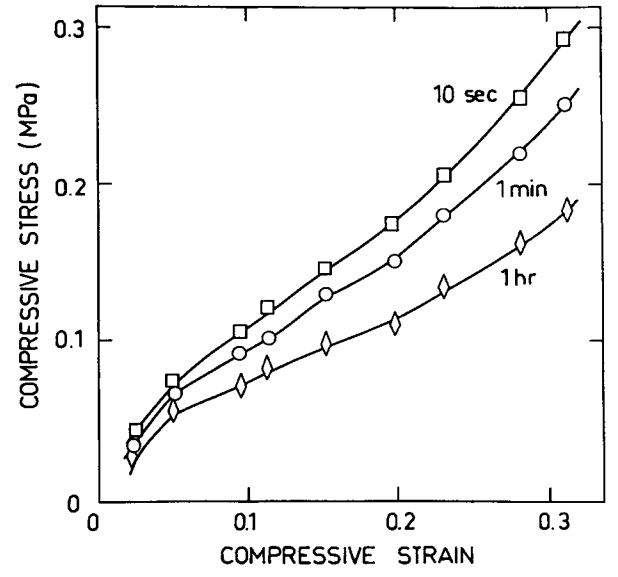

Figure 9 Isochronal stress–strain curves for PAN 389.

Table V Poisson's Ratio for Microcellular Foams

Foam	Strain Range	Poisson's Ratio	
		Mean Value	Range
IPS 352	< 0.01	0.32	0.31–0.33
IPS 352	0.03–0.13	0.08	0.07–0.10
PAN 389	0.05–0.30	0.07	0.06–0.09

CONCLUSIONS

The moduli and collapse stresses of microcellular foams are lower than those of conventional foams at the same densities. The shapes of the stress–strain curves for these foams are also different from those for conventional foams, particularly in that they have no plateau regions. Values of Poisson's ratio are found to lie within the range of values given in the literature for conventional foams. However, plastic (permanent) deformations are greater than those observed for conventional foams. The behavior of microcellular foams can be explained in terms of defects and, therefore, any new method that reduces the defects the foams contain should also significantly improve their mechanical properties.

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