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THE MECHANICAL BEHAVIOR OF MICROCELLULAR FOAMS

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ABSTRACT

The mechanical behavior of microcellular open-cell foams prepared by a thermally induced phase separation process are investigated. The foams studied were prepared from isotactic polystyrene, polyacrylonitrile, and poly(4-methyl-1-pentene) (rigid foams), and polyurethane and Lycra (elastomeric foams). Their densities were in the range 0.04-0.27 g/cm3. Conventional polystyrene foams were used for comparison. The moduli and collapse stresses of these foams were measured in compression and compared with the current constitutive laws which relate mechanical properties to densities. A reinforcement technique based on the in-situ precipitation of silica was used to improve the mechanical properties.

INTRODUCTION

Microcellular foams have primarily been developed for their use in inertial confinement fusion in high energy physics laboratories [1]. Recently, however, the possibility of using these foams in biomedical and drug release applications has also been discussed [2]. The preparation technique and pore structure of microcellular foams are different than those of conventional foams. These differences are a result of using a thermally-induced phase separation technique. First, the polymer and solvent are heated above their critical point to form a homogenous solution, then phase separation is induced by lowering the temperature, and finally the solvent is removed by either extraction or by vacuum sublimation, to produce a foam. The cells thus formed are open and have dimensions of 0.1 to 20 μm which are 10 to 100 times smaller than that of conventional foams having the same density.

The constitutive laws for conventional foams have been previously formulated [3,4] and are well understood. Under small strains, the wall elements perpendicular to the applied force bend and the relative modulus depends on the relative density according to the following equation for open-cell foams:

$$\frac{E_f}{E_s} = C_1 \left(\frac{\rho_f}{\rho_s}\right)^2 \qquad (1)$$

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where E_f and E_S are the Young's moduli and ρ_f and ρ_s are the densities of the foam and cell wall polymer, respectively. Here C_1 is a constant which was found experimentally to be nearly equal to 1 [4]. A theoretical model [5] predicted C_1=0.91. When the applied force increases, the walls parallel to the force begin to buckle reversibly in the case of the elastomeric foams. The collapse mechanism and the

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resulting collapse stress are different for the rigid polymers; plastic hinges are formed at the adjoining points of vertical and horizontal wall elements and the collapse stress σ_{pl} is given by;

$$\frac{\sigma_{pl}}{\sigma_{ys}} = C_2\left(\frac{\rho_f}{\rho_s}\right)^{3/2} \tag{2}$$

where σ_{ys} is the yielding strength of the polymer and C_2 is a constant which was found experimentally to be 0.30 [4]. For the closed-cell foams the membrane forces and the pressure of the gas in the cells should also be considered.

The elastic mechanical properties of microcellular foams have been previously studied [6,7] by the models given above, and the constant C_1 in eq.(1) was found to be smaller than the predicted value. In this study, an attempt was made to understand the discrepancy between the theoretical and experimental results by introducing defects into the structure of the foams by compressing the rigid conventional ones in the plastic region. Large decreases in the modulus were observed during the reloading experiment.

The polymers used to make the foams are isotactic polystyrene (IPS), polyacrylonitrile (PAN), and poly(4-methyl-1-pentene) (TPX) (rigid foams), and polyurethane (PU) and Lycra (elastomeric foams). The densities of foams are in the range 0.04-0.27 g/cm^3.

A technique based on the in-situ precipitation of silica, which has been widely used for the reinforcement of elastomers [8], was applied and the effect of the reinforcement on the mechanical properties was also investigated.

EXPERIMENTAL

The foams were prepared by using the solvents listed in Table I. The test samples were prepared by putting them between two parallel plates and cutting the part of the sample protruding with a blade perpendicular to the plates. The irregularities on the surface were removed by rubbing the sample between similar plates where each surface of the plates were covered with sand paper. The dimensions of samples were approximetly 10X10X8mm.

Compression testing of foams was carried out using an Instron Testing Machine (1122 model) with a 1000 lb load cell. The crosshead speed was 0.02 inch/min, and the strain was calculated from the displacement of cross-head. The tests were made at a temperature of 20°C ±1°C.

The effect of sample height/lateral dimension ratio on the results was tested and none was observed. The samples were also tested in different directions and no obvious difference was obtained, indicating that the foams are isotropic. Although the samples showed long term relaxation, the effect of strain rate on the modulus over a range of an order of magnitude was not seen.

Extruded closed-cell polystyrene foams (provided by the E and C Company, Cardena CA) were compressed to produce defects in the structure. For each compression ratio a different sample was used, and after preloading the sample was left for recovery, and then reloaded. The moduli and collapse stresses were determined from the loading and reloading experiments.

Silica Reinforcement

The TPX, PU, and Lycra samples were held immersed in tetraethoxysilane (TEOS) for 24 hours. The other samples were placed in TEOS vapor for the same period of time. The hydrolysis of TEOS (with diethyl-amine as catalyst) was carried out according to the reaction

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \tag{3}$$

which results in the precipitation of silica particles into and onto the polymer. The amount of silica precipitated was calculated from the difference between the densities before and after the treatment.

Table.I Foam and polymer properties

Foam	Foam			Polymer		
	ρ_f(g/cm^3)	Solvent	Method	ρ_s(g/cm^3)	E_s (MPa)	σ_{ys} (MPa)
IPS 350	0.162	1-chlorodecane	Gelation/with extraction	1.11 [9]	5600 [10]	148 [11]
IPS 351	0.155					
IPS 352	0.168					
IPS 353	0.094					
IPS 354	0.099					
IPS 444	0.137	1-chlorodecane	Gelation/extrac.			
PAN 221A	0.040	Maleic anhyride	Sublimation	1.18 [7]	3400 [7]	83 [12]
PAN 247	0.092					
PAN 389	0.081	Dimethylformamide and ethylene slyrol	Gelation/ extraction			
PAN 391	0.058					
PAN 444	0.052					
TPX 101	0.046	Decalin and 1-dodecanol	Gelation/ extraction	0.83 [7]	1250 [7]	
Lycra-23	0.225	Dimethylacetamide /H_2O	Gelation/ extraction	1.20 [13,4]	45 [13,4]	
PU	0.234			1.20 [4]	45 [4]	
PU	0.274					

TEST RESULTS and DISCUSSION

A double logarithmic plot of relative modulus versus relative density for the microcellular foams is given in Fig.1, together with the prediction of the theory (eq.1) for conventional foams. A least squares linear regression analysis gives a slope of 2.29 and the constant C_1=0.38, which are predicted by the theory to be 2 and 1, respectively.The similar plot of the relative collapse stress versus relative density for rigid foams is given in Fig.2. Linear regression gives a slope of 1.85 and C_2=0.15. The theoretical curve of eq.(2), which has slope of 1.5 and C_2=0.3, is also given in this figure.

The experimental data lie well below the theoretical curves in both Figures 1 and 2. The E_s and σ_s values given in Table II were taken from the literature. The importance of the value of E_s chosen has been previously mentioned [7], where the higher the value of E_s, the lower the

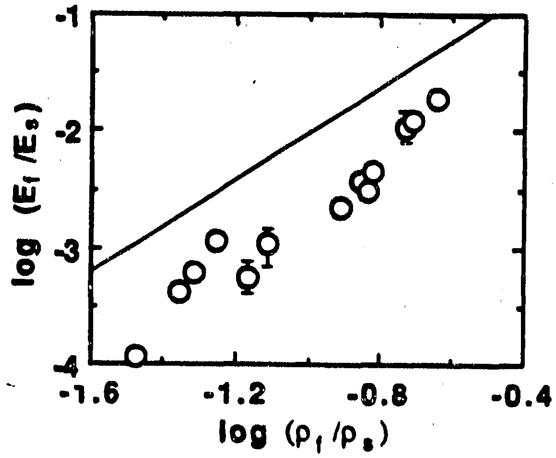

Fig.1.Variation of relative modulus with relative density. The solid line is eq.(1).

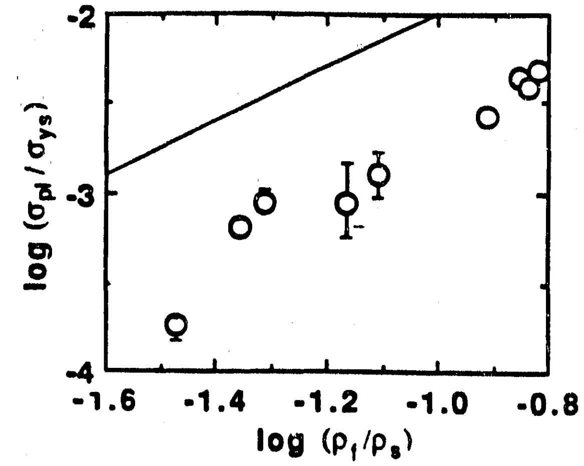

Fig.2.Variation of relative collapse stress with relative density.The solid line is eq.(2).

also true for the σ_S values, but it appears that choosing even the lowest values for E_S and σ_S is not enough to approach the predicted curves. Williams [6] measured the moduli of microcellular TPX foams by using the penetration method, and he explained the lower values of the modulus by a fraction of non-contributing material, and the ineffiency of the contributing mass. He also observed that the foams having a loose and randomly distributed structure have lower values of the modulus than those which have an orderly distributed polymer structure. Jackson et al. [7], using the dynamic tension-compression measurements, found the constant C_1 to be 0.16 in eq.(1). They concluded that the imperfect cell geometry and the inefficient use of polymer in making up the cell microstructure were responsible for the discrepancy from the theory. They also added that the friable foams might have been damaged during the cutting and mounting process.

The moduli and collapse stresses of preloaded extruded polystyrene foams are given in Table II, together with the prestrain values and permanent strains obtained after the preloading. Permanent strains appear to be small enough not to cause a significant densification. When the amount of prestrain increases, so does the number of defects produced in the structure, which results in a decrease in the modulus . For a prestrain of 65%, the modulus drops to 13% of its original value. The initial linear portion of the stress-strain curve shows a break before reaching the collapse stress, indicating a kind of buckling, and under large prestrains, the collapse stress disappears. Under moderate prestrains, the collapse stresses were not influenced very much by this process.

In Fig. 3 the stress-strain curves for the microcellular foams are given. For both rigid and elastomeric foams, the plateau regions of the curves show no horizontal or flat portion. Instead, they increase continuously with the strain. Similar behavior has been observed for the highly preloaded extruded polystyrene foams described in Fig. 4. The length of the horizontal portions of the curves decrease when the applied prestrain increases, and finally for higher values of prestrain it disappears entirely.

The dramatic decrease in the modulus of preloaded conventional foams and the similarity between the stress-strain curves of these foams and the microcellular ones

Table II. The Change of Modulus and Collapse Stress with Prestrain

Prestrain(%) :	11.0	15.2	20.2	30.1	39.9	51.4	65.0
Permanent strain(%) :	5.0	7.4	9.1	9.8	15.3	16.1	16.8
$E_{final}/E_{initial}$:	0.86	0.60	0.49	0.22	0.19	0.16	0.13
$\sigma_{final}/\sigma_{initial}$:	0.99	1.00	0.98	1.03	1.03	1.13	-

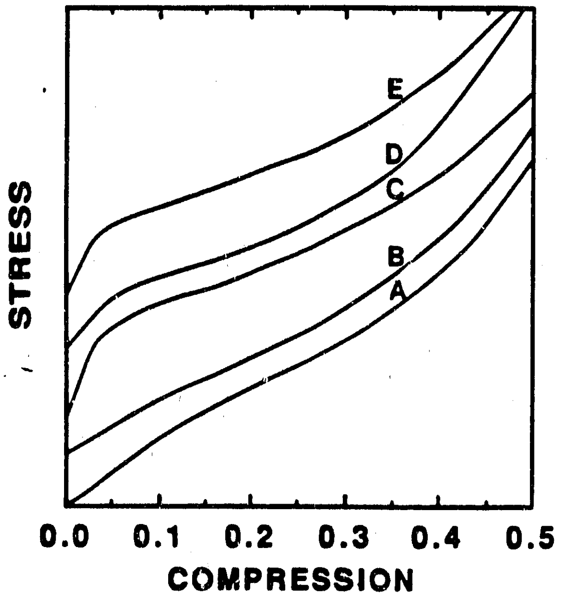

Fig.3. The stress- strain curves of microcellular foams. A:PU; B:Lycra; C:TPX 101; D:PAN 391; E:IPS 351.The scale of the vertical axis is arbitrary

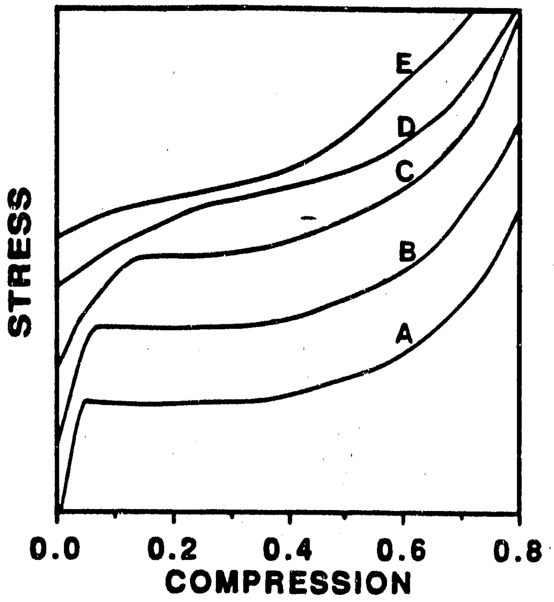

Fig.4. The stress-strain curves of preloaded extruded polystyrene foam Prestrain(%): A;0; B:11; C:20.2; D:30.1; E:65.0

indicate that the lower values obtained in the mechanical response of microcellular foams might be due to the defects produced in the structure during production. These defects might appear as nonuniform wall elements, cracked and broken elements, or plasticaly deformed elements which are formed because of the non-uniform temperature distribution present in the foam during the cooling process. Also any shrinkage that occurred during the removal of the solvent might be another reason. The explanation based on the damage occurring during the shaping of samples might be true for only the lower density and friable foams, but it is not the case for the elastomeric or high density rigid ones which are tough enough to be shaped without causing any damage.

The modulus and collapse stresses of the microcellular foams which are reinforced by the in-situ silica precipitation method are given in Table III. It appears that both moduli and collapse stresses increase by the treatment, indicating that the modulus and yield strength of rigid polymers, and the modulus of elastomeric ones are increased by this method. However, the ratio of the increase in the mechanical properties with the increase in the densities is greater for the elastomers than for the rigid ones. The samples showed shrinkage in different extents during the treatment process, and the increase in the densities after the treatment is partially due to this shrinkage.

CONCLUSIONS

The moduli and collapse stresses of microcellular foams were compared with the current constitutive laws of conventional foams. Although the square dependence of the modulus and the 1.5 power dependence of the collapse stress on relative densities predicted by the theory appear satisfactory, the experimental data lie well below the predicted curves. It is concluded that the defects formed during the production are responsible for the discrepancies from theory. In-situ silica reinforcement is a convenient method to increase both the moduli and collapse stresses of microcellular foams.

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11. The ratio of yield stress/modulus is calculated for the polystyrenes given in Modern Plastics Encyclopedia, edited by J.Agranoff, (McGraw-Hill Inc., 61, NewYork, NY 1984-1985) p.453 , and an average ratio of 0.0265 is obtained; by using this ratio, and the modulus given in Ref.10, the yield stress of IPS is calculated to be 148 MPa.
12. Ref.11, p.353.
13. The Lycra has been mentioned as a polyurethane in W.M. Phillips, W.S. Pierce, G. Rosenberg and J.H.Donachy in Synthetic Biomedical Polymers, Concepts and Application, edited by M. Szychen and W.J.Robinson (Technomic Publishing Co. Company, Inc.,Westport, CT 1980) p.41, therefore, the values given in Ref.4 for the polyurethane are also used for the Lycra.

Table III. Properties of Silica Reinforced Foams

Foam	Density (g/cm3)	Shrinkage (vol.%)	SiO2 (wt.%)	E_t^*/E_f	σ_{ct}^*/σ_c
IPS350	0.296	43.0	5.2	4.2	4.9
	0.271	36.4	5.2	3.7	4.6
IPS351	0.244	34.3	4.9	1.9	2.5
	0.175	7.7	5.1	1.5	1.5
IPS352	0.284	31.0	13.0	3.3	-
IPS353	0.120	20.1	2.3	1.5	1.5
	0.119	17.4	2.9	1.8	2.5
IPS354	0.145	24.3	15.2	4.4	3.6
PAN 389	0.257	60.0	26.7	9.9	17.0
	0.142	31.0	23.3	3.1	3.1
	0.113	13.8	11.0	1.9	1.7
	0.107	8.0	7.5	2.0	1.9
PAN391	0.122	45.0	19.1	2.4	2.2
TPX101	0.267	57.0	174.0	12.6	13.3
PU	0.474	33.6	13.9	5.4	6.4
	0.345	17.7	16.3	3.6	4.0
	0.332	23.3	4.3	2.6	2.6
	0.270	10.0	2.2	1.9	1.5
LYCRA	0.344	21.0	29.2	6.1	5.3
	0.330	8.0	43.5	5.7	
	0.303	10.4	25.0	2.8	3.2
	0.269	11.1	7.0	2.6	2.7

* Substcript "t"shows the treated foam properties and σ_c shows the collapse stress.

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