Dynamic Shear Modulus of Polystyrene Bead Foams

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Synopsis

The shear storage modulus has been determined for 0.05, 0.10, and 0.22 g/cc polystyrene bead foams and for the full density polymer at frequencies from 0.005 to 0.5 Hz at temperatures from $-5°$ to 84°C. These data are superposed to form master curves of log modulus versus log temperature-reduced frequency, using shift factors calculated by the Arrhenius equation. A plot of log modulus versus log density is linear for the three density foams; however, the modulus value for the solid polymer does not follow this relationship.

INTRODUCTION

In a previous paper[1] describing the mechanical properties of polystyrene bead (PSB) foams, the shear storage modulus of both 0.05 g/cc PSB foam and the solid polymer used to make the foam were reported. Because only one foam density was tested, it was not possible to determine whether the data followed the expected linear relationship between log modulus and log density. However, the data reported, as well as other shear modulus data, indicated that the relationship was not followed. In this paper, we present data for three PSB foam densities and the solid polymer. The polystyrene polymer and foams had a higher molecular weight and a broader distribution than the material reported in ref. 1.

Previous workers have reported the log shear modulus to be linear with log density for various polyurethane foams. Kujawa[2] shows that the shear modulus data fit the equation $SM = a\rho^b$, where a and b are constants and ρ is the density. The value for b computed from his shear modulus data is 1.7 for foams from 0.06 to 0.31 g/cc (4 to 20 pcf). Briscall and Thomas[3] report a b value of 1.8 for the shear modulus data on polyurethane foams that have densities of 0.1 g/cc and above. Earlier data published in Bender's book[4] for densities from 0.01 to 1.0 g/cc showed a value for b equal to 1.08. More recently, based on a structural analysis of a model foam cell geometry, Patel and Finnie[5] predicted a b value of 1.03 for the shear modulus. They also reported data on the compressive yield strength of polyurethane foams and showed that for densities from 0.05 to 0.2 g/cc (3 to 12 pcf) the log strength-versus-log density plot is nearly linear, although a 0.69 g/cc foam had a higher strength than the linear curve.

EXPERIMENTAL

The PSB foams of 0.05 and 0.10 g/cc density were made by the hot-gas molding process previously described.[1]   The 0.22 g/cc density foam was made by the same process; however, a small 12.5-cm-diam. by 25.4-cm-long laboratory mold was used.   All foams were made from the same bead batch of polystyrene beads (Pelaspan 500 GPM) produced by the Dow Chemical Co.   The solid polymer sample was machined from a block of compression-molded polystyrene.   The polystyrene was molded from beads, with the pentane removed, from the same bead batch as used to produce the foams.   This was done to ensure that the foam and solid polymer properties would be comparable.

Some of the properties of the polymer and the two lower-density foams are listed in Table I.   Comparable data on the other foam are not available.

TABLE I
Polymer and Foam Properties

Properties			Test method
Molecular weight	Polymer		
M_n	94,000 to 109,000		ref. 6
M_w	281,000 to 296,000		
Vicat softening point	107°C		ASTM D-1525
	Foam		
	0.05 g/cc	0.10 g/cc	
Strength, psi (10^6 dynes/cm^2)			
tension at failure	100(6.8)	185 (12.8)	ASTM D-1623
compression at yield	55 (3.8)	145(10.0)	ASTM D-1621
Modulus, psi			
tension	5600 (386)	12,600 (861)	ASTM D-1623
compression	4600 (317)	10,900 (751)	ASTM D-1621
Coefficient of expansion, (cm/cm/°C) $\times 10^{-6}$	63–71	63–71	ref. 6
Thermal conductivity, kcal-m/hr/m^2/°C	0.27	0.27	ASTM C-177
Heat distortion temperature, °C	85	85	ref. 7

The PSB foam tested was first given a thermal treatment at 77° to 80°C for one week in a forced-air circulating oven while in the form of 3.8-cm by 3.8-cm by 10-cm blocks.   This served the dual purpose of giving all foams a common thermal history and of relieving some stresses frozen in during molding.   It also reduced the pentane content slightly.   After the thermal treatment, cylinders 2.54 cm in diameter by 5.08 cm long were machined from the foam blocks.   These cylinders were stored at room temperature until tested.   After testing, total volatiles were determined by ASTM

Method D-2362. The blowing agent is approximately 100% n-pentane. Results are shown in Table II.

TABLE II
Foam Volatiles Content

Foam density, g/cc	Total volatiles, %
0.05	1.1
0.10	1.2
0.22	1.6

Since it is known[7] that the pentane concentration in PSB foam affects its tensile strength and modulus by increasing strength with decreasing pentane concentration, it can be assumed that it will also affect the shear modulus. No data exist to determine the magnitude of the effect of pentane on the shear modulus; but using the tensile data, one would expect the spread in our total volatiles content to result in no more than a 5% change in the shear modulus.

Dynamic shear modulus data were obtained on a torsional oscillating machine similar to that described by Gottenberg and Christensen.[8] Basically, the test apparatus consisted of placing a specimen in series with two spring–mass systems. The top surface of the specimen and the lower spring were fixed. The lower mass was driven by an electromagnetic shaker controlled by a Hewlett-Packard Model 3310A function generator. The storage and loss moduli were calculated from a plot of the torsional motion of the upper mass versus the difference in motion of the two masses. Tests were performed on solid polymer in the form of a cylinder 5.08 cm long by 1.27 cm in diameter; the foam samples were cylinders 5.08 cm long by 2.54 cm in diameter. The tests were conducted at five frequencies between 0.005 and 0.5 Hz at temperatures from $-5°$ to $84°C$. Tests were conducted in a Tenny Model TTUF-100250 environmental chamber to control the temperature. Specimens were allowed to soak at temperature for a minimum of 6 hr to ensure uniform temperature throughout the specimen. All tests were run at a maximum shear strain of 0.03%.

RESULTS AND DISCUSSION

The complex shear modulus is defined by the equation

$$G^* = G' + iG''$$

where G' is the storage modulus and a measure of the recoverable energy and G'' is the loss modulus and a measure of the energy dissipated into heat or nonrecoverable energy. In this series of tests, the loss modulus values at all temperatures were less than 2% of the storage modulus. These values are not reported because hysteresis of the recorder prevented accurate measurement of G''.
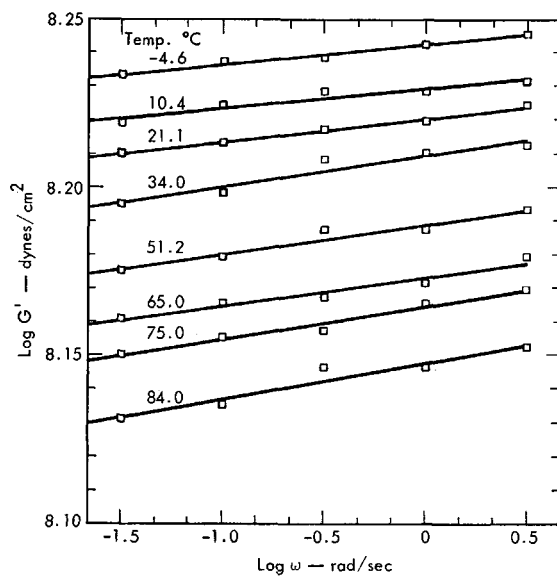
Fig. 1. Dynamic shear modulus of 0.05-g/cc density PSB foam at various temperatures and testing frequencies.

The shear storage modulus of the 0.05-g/cc PSB foam is shown plotted as log G' versus log ω in Figure 1. This figure represents the G' data obtained at the five testing frequencies at various temperatures from $-4.6°$ to 84.0°C. It is seen that data at these temperatures can be fit by a linear line over the frequency span covered. Also, note that the slope of the line increases with increasing temperature, with some scatter, as would be expected. The data in Figure 1 can be represented by a master curve of log G' versus log ωa_T, as described in ref. 1. The shift factor log a_T is given by the Arrhenius equation

$$\log a_T = \frac{\Delta H}{2.3R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

where ΔH is the activation energy, R is the gas constant, T is the test temperature, and T_0 is the reference temperature (296°K). In our analysis, the test data at each temperature were plotted on separate sheets of graph paper and shifted along the log a_T axis to achieve superposition. The log a_T values obtained in this manner were plotted versus $1/T$, and the slope of the best-fitting straight line was obtained by least squares. The ΔH values obtained from the slopes were then used in the above equation to calculate the log a_T values to construct Figure 2. In this work, we found the ΔH values to be slightly density dependent and about 10% higher than the 39.0 kcal/mole found previously. The values ranged from 42 to 47 kcal/mole; however, considering the errors in making the above shifts and the scatter in the log a_T versus $1/T$ plots, a single average value of 44 kcal/mole was used.
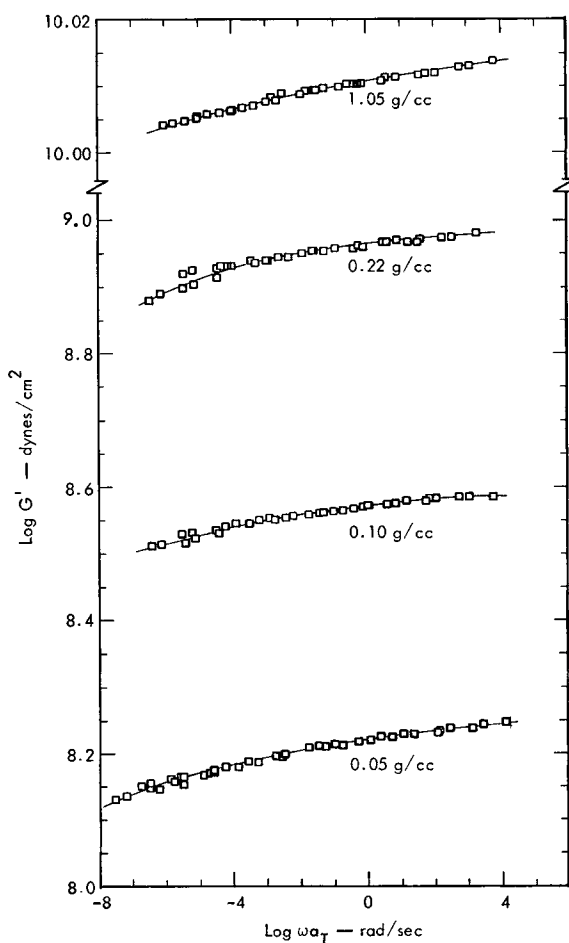
Fig. 2. Master curves of the dynamic shear modulus of three PSB foams and the solid polymer.

Figure 2 shows the master curves of log G' versus log ωa_T obtained for the three density foams and the solid polymer. The curves represent the shear storage modulus of these materials at 23°C. For all materials, the reduction in shear modulus going from room temperature to 75° to 85°C is 15% to 20% at constant frequency.

The shear modulus data at 23°C and 0.3 rad/sec for each density material is shown plotted in Figure 3. This figure shows the three foams of density below 0.22 g/cc to fall on a linear curve when plotted as log G' versus log ρ; however, it is seen that the solid polymer does not fit the linear curve. This is surprising in light of published data on polyurethane foams where a linear relationship has been reported up to the solid polymer density for shear modulus. That the PSB foams do not follow the poly-urethane foam data can be attributed to differences in the polymer and in
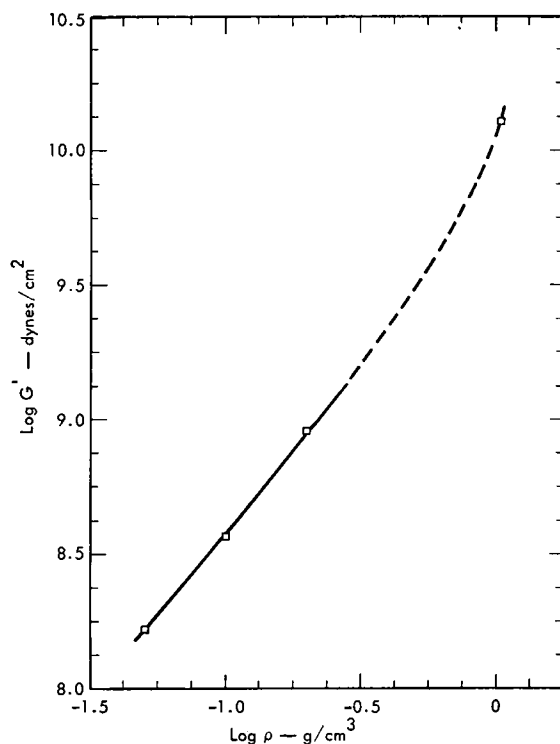
Fig. 3. Dynamic shear modulus of PSB foams and solid polymer as a function of density.

foam cell structure. It also may arise from scatter in the polyurethane data as a result of its anisotropic nature. The PSB foams are isotropic. The variation in pentane concentration observed in the three foam samples will affect the slope of the curve in Figure 3. However, the effect is estimated to be about 5%, while a greater than 50% increase in the G' values would be required to obtain a linear curve.

In Figure 3, the slope of the linear portion of the curve is 1.22 (or $G' = 6.38 \times 10^9 \rho^{1.22}$ dynes/cm² when ρ is in g/cc) and very close to the value of 1.03 predicted by Patel.[5] The difference is probably the result of simplifications required in the model he employed. Also, his model does not represent the actual foam structure as the foam density increases beyond about 0.5 g/cc. From the Patel model, there is no theoretical reason for the curve to be linear over the entire foam density range from low densities to the solid polymer density.

References

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