Time and Temperature Dependence of the Mechanical Properties of Polystyrene Bead Foam

J. A. RINDE and K. G. HOGE, Lawrence Radiation Laboratory, University of California, Livermore, California 94550

Synopsis

Tensile and compressive properties of polystyrene bead (PSB) foams at room temperature for strain rates from 10^{-3} to 10^{5} min⁻¹ can be represented as nearly linearly increasing functions of modulus or stress versus the logarithm of the strain rate. The shear modulus and tensile data, including failure properties, on 0.054 g/cc PSB foam at various temperatures and strain rates can be represented by master curves of log (stress or modulus) versus log (reduced strain rate). These master curves are formed by a time and temperature superposition method, wherein data at one temperature are superposed on data at another temperature by a shift along the log (strain rate) axis. These time-temperature shift factors are calculated using a form of the Arrhenius equation.

INTRODUCTION

Plastic foams are being used in structural applications in many areas of modern technology where their unique properties give them advantages over other materials. Such diversified areas as military, aerospace, automotive, and packaging often require knowledge of foam properties at high rates of deformation and at temperatures other than normal room temperatures. Results found in the literature¹⁻⁶ generally show that the tensile and compressive strengths of both rigid and semirigid foams increase with an increase in strain rate and a decrease in temperature. Modulus values for rigid foams are reported to be independent of strain rate over a broad range of rates, while the modulus for semirigid foams increases with increasing strain rate. Modulus values for both rigid and semirigid foams decrease with increasing temperature.

Our results on PSB foams tested in tension, compression, or dynamic shear over a broad range of temperatures and testing rates substantially support the above findings; however, we did find the modulus to be slightly rate dependent. In tension, the modulus increased about 10% with a strain rate increase from 10^{-3} to 10^{+3} min⁻¹, while the compressive modulus showed little or no increase over this range of strain rates. The dynamic shear modulus increased with increasing test frequency at all temperatures from -20° C to 80° C and for all frequencies from 0.005 Hz to 0.5 Hz.

With PSB foam of 0.054 g/cc density at room temperature, strength properties such as compressive yield stress and tensile failure stress increase

© 1971 by John Wiley & Sons, Inc.

linearly with the logarithm of the strain rate for all strain rates from 10^{-3} to 10^{5} min⁻¹. These same properties with PSB foam at a higher nominal density (0.10 g/cc) increase linearly with the logarithm of the strain rate for rates up to 10^{+3} min⁻¹; then the properties increase at a higher rate up to 10^{+5} min⁻¹. The properties of 0.054 g/cc density PSB foam in tension at 49°C and 74°C show the same qualitative dependence on strain rate, as indicated by the room temperature data for rates from 10^{-3} to 10^{+1} min⁻¹.

It is shown that the dynamic shear modulus data and the tensile data of 0.054 g/cc PSB foam at various strain rates and temperatures can be represented by master curves of log (stress or modulus) versus log (reduced strain rate). These master curves were formed by shifting the data at one temperature along the log (strain rate) axis to achieve superposition upon data at the chosen reference temperature. It was found that the shift factors could be calculated from a form of the Arrhenius equation using a ΔH value of 39.0 kcal/mole. These master curves represent the mechanical properties of the foam over a broad range in temperature and testing rates.

EXPERIMENTAL

Molding of PSB Foam

PSB foam at nominal densities of 0.05 and 0.10 g/cc is produced for Lawrence Radiation Laboratory by the Bendix Corporation, Kansas City Division. The process differs from commercial practice in that hot nitrogen gas is used as the heat transfer medium instead of steam. This necessitates using long cycle times (up to 4 hr per block), but eliminates the need for drying cycles to remove trapped water. The properties required of the PSB foam blocks are good uniformity and high tensile and compressive strengths.

The PSB foam was produced using Dow Chemical Co. SD-505 (formerly Pelaspan 222L) polystyrene beads. The foam is produced in large cylinders which are 76 cm high and 124 cm in diameter. A typical molding cycle consists of loading the mold with preexpanded beads, placing the mold in an autoclave, starting gas flow through the mold, raising the temperature, and increasing the gas pressure. The temperature is raised in steps to the molding temperature, and the pressure is increased as necessary to maintain a specific gas flow rate through the mold. At 0.05 g/cc nominal density, the following molding cycle is typical: The temperature is raised to 71°C, 77°C, 82°C, 88°C, and finally 97°C. Each temperature is held for 45 min. The pressure starts at 20 psig and generally has to be increased to 35–45 psig to maintain gas flow. After the pressure is released, the block is allowed to "bake" at the molding temperature for 20 min before being removed from the autoclave.

Foam Properties

Some of the common physical and mechanical properties of the PSB foams and base polymer are shown in Table I. Figure 1 shows typical

1378

stress-strain curves in tension and compression obtained at low testing speeds at room temperature using ASTM Method D-1623 and D-1621. Figure 2 shows the density dependence of the 0.05 g/cc foam for densities near nominal and also shows the relative amounts of scatter in the data. (It should be pointed out that the general strength-density relationship for foams over a broad density range is of the form $\sigma = a\rho^b$. For small density ranges, a linear function plot of strength-density is generally quite satisfactory within the limits of normal scatter in the data.)

Nominal properties	Density 0.05 g/cm³	Density 0.10 g/cm ³	ASTM test method
Strength, psi ^a			
tension, at failure	80(5.5)	150(10.3)	D-1623
compression, at yield	40(2.7)	90(6.2)	D-1621
shear, at yield	$\sim \! 50(3.4)$	$\sim \! 105(7.2)$	
at failure	$\sim 69(4.7)$	$\sim 131(9.0)$	
Modulus, psi ^a			
tension	5,200(360)	11,000(760)	D-1623
compression	4,100(280)	7,000(480)	D-1621
shear	1,900(130)	4,200(290)	
Poisson's ratio			
tension	0.31	0.33	Ref. 22
compression	0.22	0.25	
Coefficient of expansion,			
$(\mathrm{cm/em/^{o}C}) imes 10^{-6}$	68	68	Ref. 1
Thermal conductivity, kcal-			
m/hr/sq. m/°C	0.33		C-177
Moisture content, %	< 0.05	< 0.05%	Ref. 1
Water vapor transmission, 23°C 50% R.H. (g/24 hr/m ²) 1.27			
cm thick	23.5		C-355
Heat distortion temperature,			
°C	85	85	Ref. 23
Molecular weight			
M_n	75,	Ref. 1	
M_w	210,		
Polymer vicat heat distort on			
temperature, °C		105	Ref. 23

TABLE I							
Properties of SD-505	Polystyrene	Read	Foam				

^a Values in parentheses are expressed in $(dynes/cm^2) \times 10^6$.

Figure 3 represents the temperature dependence of the 0.054 g/cc foam in tension at a low rate of testing. These values of foam stress and modulus show an almost linear dependence upon temperature for temperatures from 20° C to 75° C, and also show that dependence upon temperature is reduced at lower temperatures. Some previous data⁷ on PSB foams showed a maximum in the tensile failure stress at about 0° C, possible due to bond failures, while the compressive yield stress increased continuously with decreasing temperature.

Cell size has been determined for these PSB foams. For both foam densities, the cell size varies from 0.08 to 0.3 mm, while the cell wall thickness



Fig. 1. Representive stress-strain curves for polystyrene bead foam in tension and compression, strain rate of 0.01 min⁻¹ in compression and 0.02 min⁻¹ in tension.



Fig. 2. Variation in tensile failure stress and compressive yield stress with density.



Fig. 3. Temperature dependence of various properties of 0.054 g/cc polystyrene bead foam when tested in tension.

is about 0.003 mm for the 0.05 g/cc foam and 0.005 mm for the 0.1 g/cc foam. For these PSB foams, the variation in bead size is approximately $\pm 100\%$ from nominal, while the size of cells within a bead is quite uniform but varies from bead to bead depending on the degree of nucleation. Within the limits of this variation, no cell elongations are visible.

Our PSB foam was tested for total volatiles by the ASTM Method D-2362. The manufacturer reports the blowing agent to be a mixture of approximately 75% *n*-pentane and 25% pentane isomers. Results on the 0.1 g/cc foam showed 1.6% volatiles, while the 0.05 g/cc foam had 1.9% volatiles. Test specimens were prepared and tested within about one month's time, so that the pentane concentration remained essentially constant. The data by Fossey⁸ shows that the tensile strength for both 0.05 and 0.10 g/cc PSB foam increases by 25–30% when the pentane concentration is reduced from 2.0% to 0.2%. The amount of pentane loss during our test period should be about 0.2%, which would give a strength increase of approximately 3%.

Test Procedures

Uniaxial tests at strain rates of 20 min⁻¹ and less were conducted on a universal test machine. At strain rates of 0.1 min⁻¹ and below, the instrument's recorder was used to record the load-deformation curves. At rates greater than 0.1 min⁻¹, an oscillographic recorder was used to record the data. Tests at strain rates from 200 to 6000 min⁻¹ were run on a Dynapak metal-working machine modified for mechanical testing.^{1,9} Specimen deformation was measured with an Optron Model 680 optical extensometer. Load and deformation outputs were recorded as a function of time on a Tektronix Model 555 oscilloscope and as an X-Y plot on a Model 536 oscilloscope. Tests at very high strain rates were performed by the Hopkinson

split-bar technique. The technique was modified by placing quartz crystals between the specimen bar faces to sense specimen stress.¹ Since considerable deformation occurs prior to the time when stress and strain conditions reach equilibrium throughout the specimen, this test method does not provide valid modulus data; however, it does provide valid stress-strain data at higher strains.

Compression tests on PSB foam conform to ASTM-D-1621, with the exception of the Hopkinson bar tests. The test specimens are 5.08 ± 0.25 cm cubes with all sides perpendicular to within ± 0.013 cm and opposite sides parallel to within ± 0.003 cm. Density of the specimens is chosen to be within $\pm 5\%$ of nominal density. End plates, which are $7 \times 10 \times 0.317$ cm of ground-steel stock parallel to within ± 0.0003 cm, are bonded on the loaded surfaces. After bonding, the outside surfaces of the end plates are parallel to ± 0.003 cm. End plates were not used on tests at rates above 50 cm/min cross-head speed, since they tend to produce undesirable inertia forces.

Tensile tests, except for Hopkinson bar tests, conform to the ASTM D-1623 test method with type B specimens. Specimen geometry is a cube 2.540 ± 0.25 cm on a side, with all sides perpendicular to within ± 0.008 cm and opposite sides parallel to within ± 0.003 cm. The foam cubes are bonded to end tabs 2.54 cm high $\times 2.54$ cm wide $\times 3.81$ cm long, ± 0.025 cm on each dimension, using a gluing fixture to ensure alignment. An extensometer is attached to the end tabs 0.32 cm from the foam and measures the separation between these points. For high strain rate tests, hollow aluminum end fixtures were used to reduce weight (and hence inertia) effects. For Hopkinson bar tests, small disk-shaped specimens were used; these were 1.22 cm in diameter and 0.8 to 1.27 cm thick.

Complex-shear modulus data were obtained on a torsional oscillating machine.¹⁰ Tests were conducted in the frequency range from 5×10^{-3} Hz to 0.5 Hz and in the temperature range from -20° C to 82° C. The foam specimens were cylinders 2.54 cm in length and 2.54 cm in diameter. The solid polymer specimens were cylinders 4.06 cm in length and 1.01 cm in diameter.

RESULTS AND DISCUSSION

Strain Rate Dependence of Polystyrene Bead Foam

In this section, we show the rate dependence of the tensile and compressive properties of PSB foam at room temperature, for both 0.054 and 0.10 g/cc density PSB foam and strain rates from 10^{-3} to 10^{5} min⁻¹. We also show the variation in the time- and temperature-dependent properties of 0.054 g/cc foam (in tension only) for several temperatures from -7° C to 74°C, and for all strain rates below 20 min⁻¹. We then discuss the time and temperature dependences of the dynamic shear modulus of 0.054 g/cc foam. The two sets of time and temperature data are used to construct master plots using a time and temperature superposition technique. The effect of strain rate on the tensile and compressive properties of both 0.054 and 0.10 g/cc hot-gas-processed PSB foam have been determined over the strain rate range of 10^{-3} to 10^5 min⁻¹ at 23°C. Figures 4 and 5 present the average tensile data obtained from six test specimens tested at each cross-head speed. Density of these specimens was chosen to be $\pm 5\%$.



Fig. 4. Strain rate dependence of 0.054 g/cc polystyrene bead foam in tension.



Fig. 5. Strain rate dependence of nominal 0.10 g/cc polystyrene bead foam in tension.

At each cross-head speed, three test specimens were oriented to be parallel with the vertical axis of the foam block. The other three specimens were oriented to be 90 degrees fron the vertical axis. No differences due to orientation could be seen in the tensile properties within the limits of the density variations and material variability. The curves shown for tests at rates greater than 20 min^{-1} are single tests and are representative of results obtained at these high rates.

In all these tests, the tensile failure was propagated across the specimen through the beads and did not follow the bead boundaries. When this foam was well fused at 0.05 g/cc density, the tensile failure stress is about 100 psi at a strain rate of 0.05 cm/min, but drops to about 50 psi or less when fracture occurs at the bead interfaces.

As shown in the Figures 4 and 5, the tensile properties at low strains are not very dependent on strain rate. Modulus values and the stress at 1.0%strain show only small variations. However, the stresses at higher strains and the failure stress do show substantial dependence on strain rate. In all cases, the failure strain in tension is independent of strain rate.

The stress-strain curve for a test rate of $84,000 \text{ min}^{-1}$ in Figure 5 was obtained using the Hopkinson split-bar technique. Since this method does not provide valid data for these foams at low strains, this portion of the stress-strain curve is represented by a dashed line indicating its presumed shape. This is also true for test rates greater than 70,000 min⁻¹, as shown in Figures 6 and 7.

In trying to compare our tensile test results with other results from the literature, we were able to find only one other reference⁵ that reported data on polystyrene foam tested in tension at several strain rates. These results do not agree with ours, as they show no change in failure strength but an increase in modulus for a 1.1 lb/ft³ PSB foam. Since the range of strain rates covered is quite small, 2.5 to $26 \times 10^{-4} \text{ sec}^{-1}$, this may account for the different results. The strain rate dependence of solid polystyrene has been reported by Strella,¹¹ who found the tensile failure stress for amorphous polystyrene at 23°C to nearly double and the modulus to increase about 30% on a rate increase from 0.05 to 1800 in./min. Lohr¹² reports the tensile yield stress of polystyrene sheet to increase with reduced strain rate for strain rates from 0.003 to 300 min⁻¹ at all temperatures from $T_g + 15^{\circ}$ C to $T_g - 100^{\circ}$ C.

Rigid polyurethane foams in tension reportedly show² that the failure stress is independent of rate and that the modulus increases with strain rate up to 1.0 sec^{-1} and then increases more rapidly. For the semirigid foam reported,² the modulus and fracture stress are both nearly independent of strain rate up to 1.0 sec^{-1} , and then both increase rapidly.

The compressive properties of the two densities of PSB foams are presented in Figures 6 and 7. The six 0.10 g/cc specimens tested at each rate were oriented in the same way as the above tensile specimens. At the 0.054 g/cc density, ten specimens were tested at each cross-head speed. All the specimens were oriented in the same direction, except for a second

1384



Fig. 6. Strain rate dependence of 0.054 g/cc polystyrene bead foam in compression.

set tested at 0.05 cm/min. These tests show that this foam is anisotropic in compressive properties by about 10%, the strength being greater in the vertical direction of the molded block. Strains were calculated from the cross-head motion for all tests except for those done at 0.5 and 0.05 cm/min. At these rates, an extensometer was used to measure the strain. Modulus values calculated using extensometer-measured strains are higher by about 10% than those obtained from the cross-head motion. The latter are low primarily due to the lack of rigidity in the load-measuring system.

The curves in Figures 6 and 7 at rates of 10 min^{-1} and below are the average of six to ten tests, while curves at higher rates are single tests and represent only the average results. These curves show the almost total lack of rate dependence of the modulus in compression and also the properties up to the yield stress at 1.0% to 1.5% strain. These properties are very dependent on strain rate at higher strains.

Few literature reports concerning rate effects on polystyrene foams in compression are available. Results of Benjamin⁵ are again in disagreement with our results, showing a decrease in modulus and a slight increase in yield stress for 3.6 lb/ft³ PSB foam. Results of Hoge and Wasley¹ on conven-



Fig. 7. Strain rate dependence of nominal 0.10 g/cc polystyrene bead foam in compression.

tionally produced PSB foam at 0.05 and 0.10 g/cc nominal density are in substantial agreement with our results.

Since there is a large amount of published data on the strain rate dependence of polyurethane foams in compression, it is instructive to review these data. Foam properties vary owing to the different polymers involved, and also owing to cell size and cell shape. However, the rate dependence of those properties which depend on the cellular structure of materials should show much of the same behavior if the polymers properties are alike, i.e., rigid polyurethane foams and rigid polystyrene foams.

Results on various rigid polyurethane foams in compression show that the yield stress increases with rate for a 4.7 and 9.6 lb/ft³ foam,³ a 20 lb/ft³ foam,⁴ and a 3.5 and 15 lb/ft³ foam.² Other tests show little or no effect of strain rate on a 5 lb/ft³ foam; but at 9 and 12 lb/ft³ foam densities,⁶ the yield stress increases with rate. The compressive modulus for rigid polyurethane foams is reported to be independent of rate at 3.5 lb/ft^3 density, but increasing with increasing rate at 15 lb/ft^3 . Traeger⁶ finds the modulus to be independent of rate at low rates, and then increasing with rate after a critical strain rate is reached. These critical rates range from greater than 80 sec^{-1} for 5 lb/ft^3 foam to about 50 sec^{-1} for 40 lb/ft^3 foam. A semirigid polyurethane foam² is reported to increase in both molecules and compressive yield stress with increasing strain rate, while for a flexible polyurethane foam³ the stress increases with rate from static to 100 sec^{-1} and then remains constant to 300 sec^{-1} . Patel¹³ shows that the yield stress in compression follows a linear relationship with the log plot of the strain rate for polyurethanes of densities $3.1, 6.2, 12.3, 43, \text{ and } 77 \text{ lb/ft}^3$ at rates in the range from 4.5×10^{-5} to $4.5 \times 10^{-2} \text{ sec}^{-1}$.

In general, the above work shows that, for foams in tension or compression, the strain rate dependence of the foam properties depends upon the degree of flexibility of the foams. For most foams, the high strain properties are also rate dependent. However, for the modulus to be strain rate dependent, the foam must have some degree of flexibility, i.e., it must be nonfriable.

The rate dependence of our test data at 23°C is shown in Figures 8 and 9, plotted as modulus or stress versus the log plot of the strain rate. In Figure 8, the modulus values for the two foams are plotted in both tension and compression. The points at the lower rates with flags are the average values obtained. The flags give the estimated standard deviations for each set of values. The other points, primarily at the higher rates, are results from single tests at different strain rates. This figure shows that the tensile modulus is strain rate dependent at both densities and that the compressive modulus has little or no rate dependence within our limits of error. It also shows that the tensile modulus is greater than the compressive modulus for



Fig. 8. Strain rate dependence of the tangent modulus of polystyrene bead foams in tension and compression.



Fig. 9. Strain rate dependence of the tensile failure stress and compressive yield stres of polystyrene bead foams.

foams of both densities. Figure 9 shows the compressive yield stress and tensile failure stress plotted versus log (strain rate). In this figure, the curves have been separated for visual clarity by adding a factor A to the stress of some of the curves. For both densities of PSB foam in compression, the curves in Figure 9 show that the compressive yield stress is linear with log (strain rate) over the range covered in this investigation. Also, note that the scatter in the data is relatively small. Other compressive data such as the stress at 5% and 10% strain also plot linearly with log (strain rate) and form curves that are parallel to, but higher than, the yield stress curve. The tensile failure stress curves are linear to about 10^3 \min^{-1} and then increase at a higher rate. Other tensile properties such as the proportional-limit stress and the tensile stress at 2% strain also plot linearly with log (strain rate) for the rate range where we have data from 0.002 to 20 min⁻¹. The increase in modulus is 10% or less for a seven-decade increase in rate, while the value of the properties at strains greater than 1% increases about 50% over this same range.

Time and Temperature Superposition at Temperatures below T_{g}

For polymers above their glass transition temperatures, data obtained at various testing temperatures and rates can generally be superposed using shift factors calculated from the well-known WLF equation¹⁴. However, as the temperature decreases below T_{ϱ} , this equation becomes inapplicable. Below T_{ϱ} , the temperature dependence of a_T is expected to follow an equation of the Arrhenius form¹⁵ where log a_T is proportional to 1/T. Several reports^{12,16,19} have been published showing the dependence of log a_T on temperature for polymers below their T_{ϱ} values.

Takahashi et al.¹⁶ report master curves for stress relaxation for polysty-

rene, poly(methyl methacrylate), and poly(methyl acrylate). The curves were constructed using shift factors derived from a modified WLF equation with good agreement above T_g but substantial deviations at lower temperatures. Lohr¹² presents master curves for stress relaxation and yield stress of four polymers, including polystyrene, at temperatures below T_{a} . The yield stress master curves were plotted semilogarithmically as stress versus log ia_T , where i is the strain rate and a_T is the shift factor. Shift factors are presented plotted versus temperature. The shift factors for polystyrene tested in stress relaxation^{12,16} are about the same, but are greater than corresponding shift factors from yield stress data.¹² Sato¹⁷ presents a master curve for the poly(methyl methacrylate) in creep at temperatures below T_{q} . He found the shift factors to depend on 1/T and calculated an activation energy of 30 kcal/mole. Chang^{18,19} finds the temperature dependence of shift factors for polystyrene, ABS (acrylonitrile, butadiene, styrene), polyethylene, and poly(vinyl chloride) to be dependent on 1/T for modulus and tensile yield stress. The master curves of tensile yield stress are used to estimate long-term pipe-bursting stresses at various times and temperatures. His A-factor for ABS, which is equal to $\Delta H/2.3R$, yields a ΔH value of approximately 48 kcal/mole when read from the figure for temperatures above 100°F.

To understand the time and temperature dependence of PSB foam, the series of low strain rate tests described in a preceding section were repeated in tension at -7° C, 49° C, and 74° C on the 0.054 g/cc density foam. These data, when plotted in the same manner as in Figure 9, showed that the increases in the mechanical properties due to testing rate are greater at the higher temperatures. All the tensile data on 0.054 g/cc PSB foam are presented in Table II as the average properties of five tests at each strain rate. Tests at the two higher rates at 74° C did not yield accurate strain measurements, and therefore the strain-dependent properties are not included.

Data taken at various temperatures and testing rates can be presented in several forms. The data in Table II are presented in Figure 10 in the form of master curves of the various properties. In this figure, curves are presented for the modulus, proportional limit stress, and failure stress plotted at log (stress or modulus) versus log ϵa_T , where ϵ is the strain rate in min⁻¹ and a_T is the shift factor. Figure 10 represents the various properties of the foam at 23°C (the reference temperature chosen) over the strain rate range from about 10⁻⁷ to 10⁵ min⁻¹. The stress at 2% strain can also be plotted in this manner; however, for clarity these data are not shown. Figure 10 shows that the plot of these properties form smooth curves and that most data points are within 0.05 log units of the lines drawn through the points. Also shown is the good agreement between data taken at different temperatures and rates in regions where the data overlap.

Figure 10 was constructed by plotting the data obtained at each temperature on a separate piece of paper and visually shifting these curves along the log $\dot{\epsilon}$ axis to obtain superposition. The resulting shift factors for modulus,

Strain rate, min ⁻¹	Modulus, psi	Proportional limit		Stress at	Failure	
		Stress, psi	Strain, %	2% strain, psi	Stress, psi	Strain, %
			7°C			
0.02	5940	66.1	1.1	94.7	109.5	3.0
0.2	6000	80.0	1.3	102.1	117.5	3.0
			23°C			
0.002	5700	50	0.8	82	93	3.2
0.02	6020	55	0.9	90	97	2.8
0.2	5900	66	1.1	96	106	3.1
2.0	6200	65	1.1	102	112	2.8
20.0	6560	78	1.2	110	122	2.7
			49°C			
0.002	5280	43.4	0.8	70.6	78.5	3.4
0.02	5290	45.7	0.9	72.2	79.0	3.2
0.2	5360	52.6	1.0	80.1	88.5	3.3
2.0	5520	66.4	1.2	87.9	97.3	3.2
20.0	6130	82.1	1.3	101.1	114.0	3.3
			74°C			
0.002	4020	26.2	0.6	41.0	41.6	2.9
0.02	4590	35.5	0.8	56.2	58.8	4.3
0.2	4640	42.1	0.9	63.1	70.3	4.8
2.0		54.3			79.2	
20.0		56.9			83.2	

TABLE II

* Each point is the average value for five tests.

proportional limit stress, and failure stress are shown plotted versus $10^3/T$ in Figure 10. The straight line is the calculated line for $\Delta H = 39$ kcal/ mole and represents the data within about ± 8 kcal/mole. The precision of these data is obviously not very good; however, the G' data in Figures 12 and 13 give this same ΔH value with good precision. Therefore, in Figure 10, the log a_T values are obtained from

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

where $T_0 = 296^{\circ}$ K, log a_T is the shift factor (equal to zero at $T = T_0$), ΔH is the activation energy, R is the gas constant, and T_0 is the reference temperature.

Dynamic Shear Modulus Data on 0.054 g/cc PSB Foam

The complex shear modulus of 0.054 g/cc PSB foam has been obtained on a torsional shear tester. The complex modulus is defined by the equation

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



Fig. 10. Master curves for properties of 0.054 g/cc polystyrene bead foam in tension.

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. The tests were conducted at three to five frequencies from 0.005 to 0.5 Hz at temperatures from $+82^{\circ}$ C to -20° C. All the data were taken on a single specimen with a maximum shear strain of 0.02%. These data are very precise and were obtained to define the time and temperature dependence of the foam modulus. These data are plotted in Figure 11 as log G' versus log ω , where ω is in rad/sec. Figure 11 shows the foam storage modulus to be rate dependent, with the modulus increasing with frequency at all temperatures. The linear rate dependence is consistent with the data in Figure 8 and is equal to 1/4% to 1/2% increase per decade increase in frequency. Also note that the rate dependence increases at the higher temperatures.

The data from Figure 11 are replotted in Figure 12 as log G' versus log ωa_T , where log a_T is given by the Arrhenius equation and ω is the frequency



Fig. 11. Storage modulus of nominal 0.05 g/cc polystyrene bead foam.

in rad/sec. The ΔH value was obtained by shifting the log G' data along the log ω axis to obtain log a_T values that best fit the data and then plotting these versus 1/T as shown in the figures. The ΔH that gave the best fit for the log G' data was 39.0 kcal/mole; this seems reasonable compared to literature values (18-30 kcal/mole) obtained on various solid polymers^{17,20,21} at temperatures below T_{σ} . As the figure shows, the log G' data superpose well and yield a single curve. Values for the storage modulus were obtained at 93°C; however, these data did not superpose with the lower temperature data. This indicates that nonrecoverable deformations are taking place at this temperature. This behavior was also shown by some measurements on a solid polystyrene sample at this same temperature. Loss modulus values at all these temperatures for the foam were less than 2% of the storage modulus. Because of their small value, no accurate measurements of G' values could be made.

Figure 13 shows the master curve of storage modulus for a solid polystyrene sample made from the same polymer as the bead foam. This figure shows the storage modulus to superpose to form a smooth curve when plotted in the same way as Figure 12. Also the shift factors, $\log a_r$, were calculated using the same equation with $\Delta H = 39$ kcal/mole. This value is the same for both the foam data in Figures 10 and 12 and the solid polymer in Figure 13. Since the same ΔH value is found for both the foam and solid polymer samples, this infers that the time and temperature dependence of any structural deformations in the foam are the same as the time and temperature dependence of the solid polymer. Loss modulus values for the solid polymer are less than 2% of the storage modulus values and therefore could not be accurately measured.

Using data from Figures 12 and 13, one can calculate the density dependence of the storage modulus using the generally accepted linear relationship between log modulus and log density. In this case, $\log G' = a + b \log \rho$, where G' is in psi and ρ in g/cc. From these data, a = 5.213 and b =



Fig. 12. Master curves for shear modulus of 0.054 g/cc polystyrene bead foam.



Fig. 13. Master curve of storage modulus for solid polystyrene.

1.475. A value for G' was calculated for a density of 0.1 g/cc; this value is 5480 psi, which is somewhat high when compared with a measured value of 4300 psi. The *b* value can be compared to a value for polyurethane foams (the only data available), where b = 1.08 for the shear modulus.⁶ A theoretical value for the shear modulus *b* value is reported¹³ to be 1.03. However, to achieve a better correspondence between the above calculated and measured values, a higher *b* value would be required and not a lower value, as one would infer from the polyurethane data.

We wish to thank Mr. A. T. Buckner for preparing the test specimens and performing the low rate tests.

This work was performed under the auspices of the U.S. Atomic Energy Commission. Reference to a company or product name does not imply approval or recommenda-

tion of the product by the University of California or the U.S. Atomic Energy Commission to the exclusion of others that may be suitable.

References

1. K. G. Hoge and R. J. Wasley, J. Appl. Polym. Sci. (Appl. Polym. Symp.), 12, 97 (1969).

2. S. J. Green, F. L. Schierloh, R. D. Perkins, and S. G. Babcock, *Exper. Mechanics*, 103 (March 1969).

3. R. M. Lacey, High Speed Testing, 5, 99 (1965).

4. O. L. Burchett, High Speed Testing, 6, 139 (1967).

5. B. B. Benjamin, Civil Eng. Public Works Rev., 60 (172) 1646 (1965).

6. R. K. Traeger, J. Cell. Plast.. 3, 405 (1967).

7. The Bendix Corporation, Kansas City Division, unpublished report.

8. D. Fossey, The Bendix Corporation, unpublished report.

9. K. G. Hoge, High Speed Testing, 6, 19 (1967).

10. M. A. Hamstad, Complex Shear Modulus of a High Explosive. UCRL-50357, 1967.

11. S. Strella, High Speed Testing, 1, 27 (1960).

12. J. J. Lohr, Trans. Soc. Rheol., 9:1, 65 (1965).

13. M. R. Patel and I. Finnie, *The Deformation and Fracture of Rigid Cellular Plastics* Under Multiaxial Stress, Lawrence Radiation Laboratory, Rept. UCRL-13420, Livermore, Calif., 1969.

14. M. L. Williams, R. F. Landel, and J. D. Ferry, J. Am. Chem. Soc., 77, 3701 (1955).

15. J. G. Ferry, Viscoelastic Properties of Polymers, Wiley, New York, 1961, Chap. 11, p. 235.

16. M. Takahashi, M. C. Shen, R. B. Taylor, and A. V. Tobalsky, J. Appl. Polym. Sci., 8, 1549 (1964).

17. K. Sato, H. Nakane, T. Hideshima, and S. Iwayanagi, J. Phys. Soc. Japan, 9, 413 (1954).

18. F. S. C. Chang, J. Polym. Sci., 57, 949 (1962).

19. F. S. C. Chang, paper presented at 27th ANTEC of Society of Plastic Engineers, *Technical Papers*, 15, 154 (1969).

20. S. Iwayanagi, J. Sci. Res. Inst. (Japan), 49, 4 (March 1955).

21. N. G. McCrum and E. L. Morris, Proc. Roy. Soc. Ser. A, 281, 258 (1964).

22. J. A. Rinde, J. Appl. Polym. Sci., 14, 1913 (1970).

23. Pelaspan Product Information Sheet, The Dow Chemical Company, Midland, Mich.

Received September 4, 1970

Revised February 25, 1971