Linear viscoelastic properties of epoxy resin polymers in dilatation and shear in the glass transition region.
1. Time-temperature superposition of creep data

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Measurements have been made of the creep compliance in dilatation and shear for an epoxy resin polymer, over a range of temperature spanning the glass transition region. Both compliances may be measured on the same specimen. The creep curves were superposed, and smooth composite curves were obtained both in dilatation and in shear. The WLF equation provides an adequate fit over the temperature range for which it is generally used. Shear creep data over a wide temperature range could be described by the Arrhenius equation, where the activation energy, ΔH, has a higher value above T_g than below T_g. For shear creep ΔH = 58 Kcal/mole for $T < T_g$, ΔH = 165 Kcal/mole for $T_g < T$. For creep in dilatation ΔH = 210 Kcal/mole.

INTRODUCTION

For a linear viscoelastic isotropic material the viscoelastic properties are completely defined by any two independent viscoelastic functions. Thus it is sufficient to measure for example the shear stress relaxation modulus $G(t,T)$, and the creep lateral contraction ratio $\nu(t,T)$. It is often more convenient to separate any general deformation into a change of shape combined with a change of volume, and to use as the basic viscoelastic functions the shear creep compliance $J(t,T)$ (which describes changes of shape only), and the bulk creep compliance $B(t,T)$ (which describes changes of volume only). The two functions $J(t,T)$ and $B(t,T)$ are very different, and many of the differences are obvious; for instance in a thermoplastic material $J(t,T)$ tends to infinity when the material melts, but $B(t,T)$ remains finite. Usually $J(t,T)$ has a wide distribution of relaxation times compared with $B(t,T)$ (Kono and coworkers[1,2]), and some workers have found that the glass transition regions may occur at different temperatures in different deformation modes[3–10]. Measurements of shear viscoelastic functions are fairly common in the literature, but volume viscoelastic data are much rarer, and for this reason it was decided to measure the bulk and shear creep compliances as functions of temperature in the main glass transition region and to make a comparison.

The methods used in this study allowed the bulk and shear creep compliances to be measured as functions of temperature on the same specimen. If necessary, tensile creep compliance and linear thermal expansion coefficient may also be measured as functions of temperature on the same specimen. Using these test methods it is possible to measure shear and bulk creep compliances simultaneously, but this was not done in the present study. The advantage of this method is that specimen to specimen variations are eliminated. An additional advantage is that strains may be kept well below 0.1%, thus eliminating the problem of non-linear viscoelasticity.

Various time–temperature superposition procedures were used, and for shear a very smooth 'master curve' could be produced.

The bulk data were obtained over a narrower range of temperature and creep times and a reasonable master curve has been produced. The data for bulk and shear were compared with the Arrhenius equation, and Williams Landel Ferry (*WLF*) equation[11], and apparent activation energies have been calculated using the Arrhenius equation.

MATERIALS AND SPECIMEN PREPARATION

The material used was an epoxy resin, diglycidyl ether of bisphenol A, (DGEBA), (CIBA-Geigy MY 750), cured by nadic methylanhydride, (NMA), (CIBA-Geigy HY 906). Small amounts of triethylamine were used as an accelerator. The material was composed of: 100 parts by weight, DGEBA; 90 parts by weight, NMA; 2 parts by weight, triethylamine, and the cure schedule adopted was 16 h at 100°C followed by 1 h at 150°C, and 0.5 h at 200°C.

Specimen preparation is described in detail by Crowson[12], and rather more briefly here. The test methods used in this paper employ circular cylindrical specimens which were cast in a split mould in which a circular steel rod was centrally positioned. The split mould surfaces shape the initial outside surface of the specimen, whilst the inside surface is shaped by the steel rod. The resin and curing agent were stirred continuously for about 30 min as the mixture was

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warmed to reduce its viscosity. The mixture was then allowed to stand to allow small air bubbles to escape. After another period of stirring the accelerator was added, the mixture stirred again, and transferred to the mould, which had been preheated to 100°C. The mould was then transferred to the curing oven, and the cure cycle was started. After curing, the outside surface of the specimen was machined to give an accurate and constant wall thickness of 1 mm. End plugs for the specimens were fashioned from material from the same batch, and given the same cure as the specimen.

CREEP IN SHEAR

Time–temperature superposition

The method of time–temperature superposition has been known at least since the work of Leaderman[13], and the first attempt to use the method to produce a 'master curve' appears to be that of Andrews and Tobolsky[14]. A summary of the history of time–temperature superposition has been given by Markovitz[15]. In more recent years the method has been used to produce smooth master curves for shear creep compliance[11], tensile stress relaxation modulus[16], creep lateral contraction ratio[17], and many other material properties, from plots of the time dependence of the property at different temperatures. Some authors have extended the method to include other variables such as pressure, molecular weight, degree of crystallinity, and so on, but in this paper 'superposition' will mean time–temperature superposition. In Leaderman's original work the tensile creep compliance $D(t)$ of several plastics was measured over a range of temperatures. Leaderman noticed that when $\log D(t)$ was plotted against $\log t$ the data obtained at different temperatures could be made to coincide by sliding by different amounts along the $\log t$ axis (horizontal shifting). Subsequently many modifications of the basic techniques have been used, and these are reviewed by McCrum and Morris[18], and McCrum and Pogany[19]. Andrews and Tobolsky[14,16] suggested that their stress relaxation data should be multiplied by T_0/T before attempting to match the curves by horizontal shifting. T_0 is the temperature to which the data are being shifted (the reference temperature), and T is the temperature at which measurements were made. T and T_0 are both measured on the Kelvin scale. The term T_0/T was included to allow for the temperature dependence of the relaxed tensile compliance, D_R. Ferry[20] suggested that the correction term should be $T_0\rho_0/T\rho$, where ρ and ρ_0 are the densities at T and T_0 respectively. The inclusion of a correction term corresponds to a vertical shift of the data. However, both of these two amendments of the basic Leaderman superposition technique make allowance only for the temperature dependence of the rubbery or relaxed compliance and for this reason they are not applicable to the glassy region. Ferry and FitzGerald[21] proposed a scheme whereby the unrelaxed shear compliance J_U was assumed to be temperature independent whilst the usual allowance was made for the temperature dependence of the relaxed shear compliance, J_R. Kê's technique quoted by McCrum and Morris[18] assumes that the temperature dependence of the relaxed compliance is identical to that of unrelaxed compliance, which is not the case for the glass transition of an amorphous polymer in shear. The McCrum and Morris technique[18] makes allowance for the temperature dependence of both J_U and J_R. In the work of McCrum and Pogany[19] $\log JU$ is assumed to be linear with temperature, and is obtained by extrapolating the curve for the 10 sec creep compliance, $\log J(10)$, against T in the glassy region. $J_R(T)$ is obtained by assuming that $1/J_R$ is linear with absolute temperature in accordance with the theory of rubber elasticity, and values are obtained by plotting $1/J(t)$ against T (K) for the rubbery region and extrapolating back through the origin.

The word 'normalized' has been used by McCrum and coworkers to refer to data which have been modified to take into account the temperature dependence of one or both of the limiting compliances, and this terminology is also used here.

Experimental

The experimental method used for measurement of shear compliance $J(t)$ has been described briefly by Crowson and Arridge[22], and in more detail by Crowson[12]. The specimen was in the form of a long thin-walled circular cylinder with closed ends. The dimensions were typically, length = 300 mm, radius = 9 mm, wall thickness = 1 mm. The upper end of the cylinder was clamped in a rigid support and a light disc was attached to the bottom of the specimen. Cords were passed around the disc, and over two fixed pulleys, and weights could be attached to the pans on the ends of the cords. Using this arrangement a constant torque could be applied to the specimen. A small mirror was attached to the bottom of the specimen, and a ray of light was beamed onto the mirror, and the reflected ray followed on a moving light cell chart recorder (Sefram Graphispot). This system allowed an accuracy of about 1% in the measurement of angle of twist, and the total error in the measured shear compliance was about 5%. The maximum shear strain used in this study was less than 0.1%.

Temperature was controlled using a cylindrical coil-wound heater, which enclosed the specimen. The heater was controlled by a Eurotherm temperature controller, which could maintain temperature to better than 0.1°C.

The experimental procedure adopted was as follows. Before commencing testing the specimen was heated to about 30°C above T_g and annealed for 10 min, then allowed to cool to room temperature. During testing the specimen was allowed to come to equilibrium at the required temperature for 30 min, the torque was applied for 30 min and the strain continuously recorded, and then the torque was removed, and the strain observed for a further 30 min. The procedure was repeated at 10°C intervals from 20° to 200°C and at 5°C intervals in the transition region. Measurements were taken mainly for ascending temperatures, since this has the advantage that in the transition region when the temperature is changed the compliance increases and any unrecovered strain can recover faster before the next loading cycle. The shortest time at which readings of strain could be made was one second and the longest time was 1800 sec, so the time scale covered by these experiments was 3¼ decades.

Results for shear creep

For each temperature one cycle of loading and unloading was used and from the chart recording produced the values of displacement of the recording pen were measured at regular intervals in logarithm of time for both creep and creep recovery. These data were converted to values of shear creep compliance $J(t)$, and then multiplied by $T\rho/T_0\rho_0$ (Ferry normalization). Graphs of $\log [J(t)(T\rho/T_0\rho_0)]$ versus $\log t$ were plotted for each temperature (*Figure 1*). Values of ρ were obtained from measurements of linear expansion coefficient of the same specimen by the method described in reference 22 in conjunction with a value of density at room

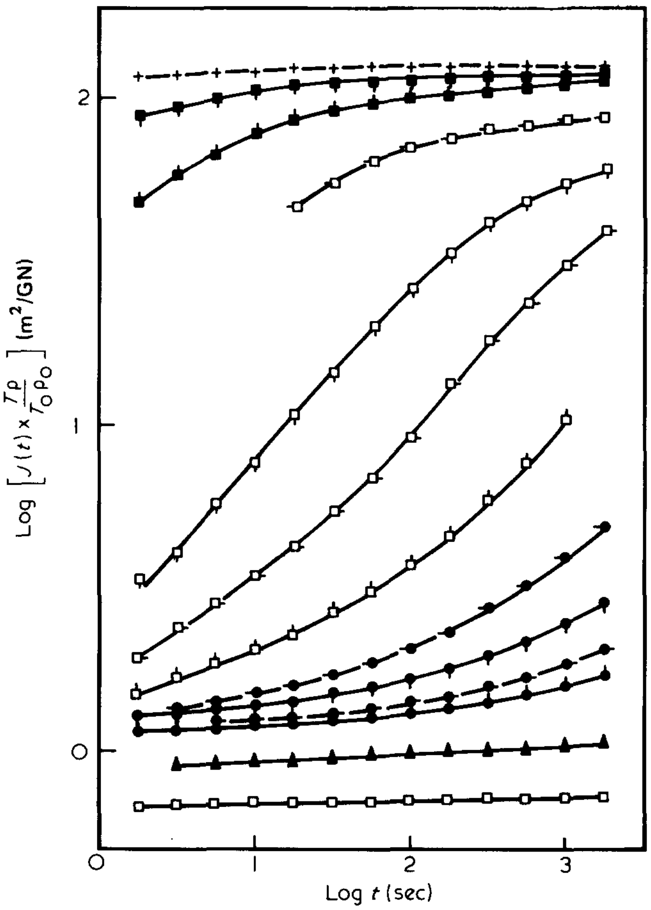

Figure 1 Log $J(t) \times T\rho/T_0\rho_0$ versus log t at different temperatures. An explanation of the symbols is given in Figure 3

temperature obtained by measuring the weight and volume of a parallelepiped of the material. The plots were made only for creep compliance (not for compliances measured in the recovery cycle) and transparent paper was used. The plots were then superposed using horizontal shifts only to give the smoothest possible master curve, and the shifting factor log a_T was recorded for each temperature. The curves were then separated and the matching procedure was repeated to see how subjective the judgement is, as to which is the best master curve. Each curve was obtained at a different temperature, and the temperatures in degrees absolute are noted in the caption. The curves at some of the temperatures in the plateau regions are omitted to avoid overcrowding the graph. The log a_T values obtained from the horizontal shifts are shown in *Figure 2* as a plot of log a_T versus 1000/T(K). The reference temperature has been chosen to be $T_0 = T_g$ = 427.4 K. (This is not the exact dilatometric T_g, but it is the nearest temperature at which data were obtained). Also shown in *Figure 2* are values of log a_T obtained from the WLF equation[11],

$$\log a_T = \frac{-17.44(T - T_g)}{51.6 + T - T_g}$$

where again a value of T_g = 427.4 K was used.

The composite curve produced by horizontal shifts is given in *Figure 3*. On this curve data are plotted from each of the experimental temperatures, but only data at integral values of log t are plotted to make the presentation clearer. Visual matching of the curves using only horizontal shifts was satisfactory throughout the temperature range employed, and a smooth composite curve was obtained. At lower temperatures in the glassy region the curves are all nearly flat, and whilst one can say that superposition is good, it is very difficult to estimate the horizontal shifts required, and therefore the values of log a_T at low temperatures are less reliable.

Examination of *Figure 2* shows that log a_T is clearly not linearly dependent on $1/T$, and we may thus conclude that the relaxation studied here may not be described by an Arrhenius relation with a single activation energy. The experimental data appear to follow the WLF equation[11] fairly closely above T_g. It may be possible to obtain better agreement by using different values for the constants in the WLF equation. If the transition region is interpreted as being due to Arrhenius type relaxation processes it would appear that two processes with different activation energies contribute. (This we deduce from the fact that *Figure 2* appears to consist of two straight lines of different slopes). If we assume that this is the case then we may fit the best straight lines to the two halves of the data and calculate the two values of activation energy from the Arrhenius equation

$$\log a_T = \frac{\Delta H}{2.303\,R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad (1)$$

where ΔH = activation energy, R = universal gas constant, and we find values of ΔH = 58 Kcal. mole^{-1} for the low

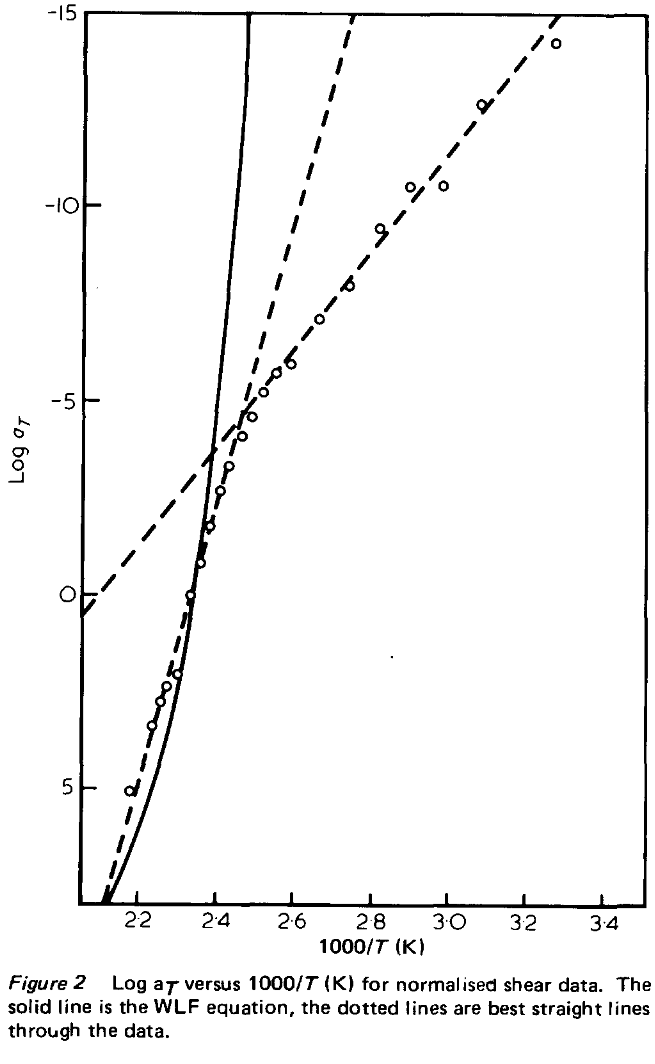

Figure 2 Log a_T versus 1000/T (K) for normalised shear data. The solid line is the WLF equation, the dotted lines are best straight lines through the data.

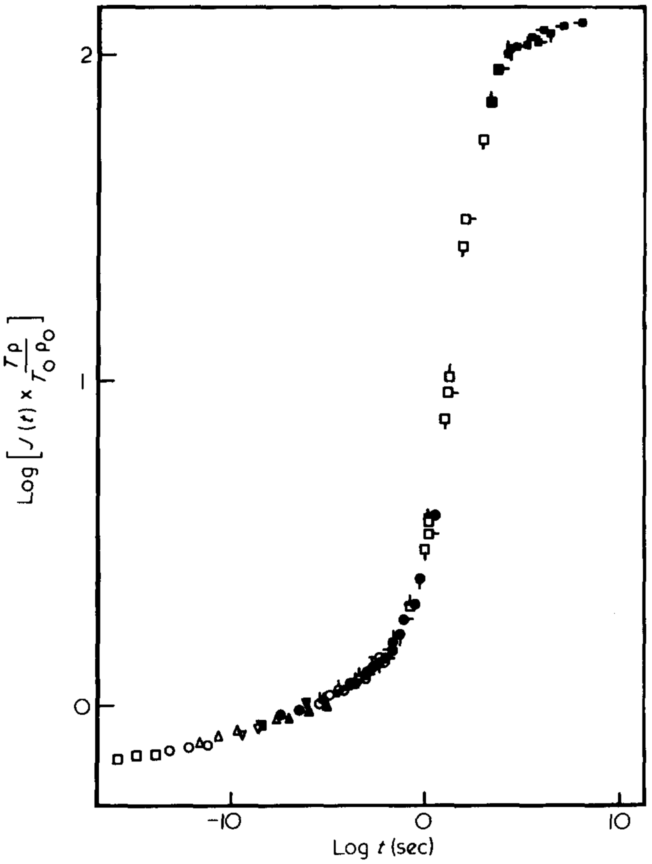

Figure 3 The composite curve reduced to T_g (= 427.4 degK) for normalised shear data. Temperatures: □, 294.3 degK; ○, 304.8 degK; △, 323.9 degK; ▽, 334.0 degK; ■, 344.1 degK; ●, 354.2 degK; ▲, 364.1 degK; ▼, 374.9 degK; ○, 381.1 degK; ○-, 385.2 degK; ○, 390.7 degK; -○, 395.7 degK; ●, 400.6 degK; ●-, 405.4 degK; ●, 410.2 degK; -●, 414.9 degK; □, 419.5 degK; □-, 422.6 degK; □, 427.4 degK -□, 434.3 degK; ■, 439.0 degK; ■-, 443.0 degK; ■, 447.0 degK; -□, 459.0 degK; +, 470.5 degK

temperature part of the relaxation and $\Delta H = 165$ Kcal. mole^{-1} for the high temperature part of the process. (1 cal = 4.186 8 J).

Because of the nature of the curves it is possible to have considerably more confidence in the value of ΔH obtained at the higher temperatures. At low temperatures the curves are too flat to be able to estimate accurately the shifting factors, but nevertheless there is sufficient accuracy to be able to say that if the temperature dependence of the shift factors is to be explained by an Arrhenius type equation, then there must be a large change in apparent activation energy at about 410K.

An alternative method of calculating an activation energy is the procedure outlined by Leaderman[13]. In this method the data are replotted as isochronous curves of $\log J(t)$ against T. The T_g for each curve is determined by some chosen procedure (in this case the T_g was chosen to be the temperature at which the curve passed through a $\log J(t)$ value equidistant from the glassy and rubbery plateau regions (a construction is given in *Figure 4*) and a graph of log t against $1/T_g$ is plotted. Since

$$\log a_T = \log\frac{\tau}{\tau_0} = \frac{\Delta H}{2.303R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad (1)$$

we may write

$$\log\left(\frac{t}{t_0}\right) = \frac{\Delta H}{2.303R}\left(\frac{1}{T_g} - \frac{1}{T_{g0}}\right) \qquad (2)$$

In equation (1) τ and τ_0 are characteristic relaxation times at temperatures T and T_0. In the equation (2) we choose two experimental time scales t and t_0, and then T_g and T_{g_0} are the glass transition temperatures corresponding to these time scales. Equation (2) may then be rewritten

$$\log t = \left(\frac{\Delta H}{2.303R}\right)\frac{1}{T_g} - \left(\frac{\Delta H}{2.303\,T_{g_0}} + \log t_0\right) \qquad (3)$$

and thus we may see that $\Delta H/2.303\,R$ is the slope of a graph of log t against $1/T_g$. This method, which has also been used by Kono[3], was attempted for the data already presented. The isochronous plots of $J(t)$ against T are shown in *Figure 5* and the T_g values obtained for different values of log t are shown as a plot of log t against $1000/T_g$ in *Figure 6*. This gives a value of ΔH of 145 Kcal/mole, which is in fair agreement with the values obtained for the high temperature end of the relaxation by time–temperature superposition. We expect the value obtained by this method to be valid over the range of temperature in which the glass transition manifests itself for the range of experimental time scales used, and this is roughly between 120 and 170°C.

Because of the compounding of errors in the collecting of the data, and the fairly elaborate treatment given to the data, the errors involved in calculation of the activation energy may be appreciable. If the time–temperature superposition

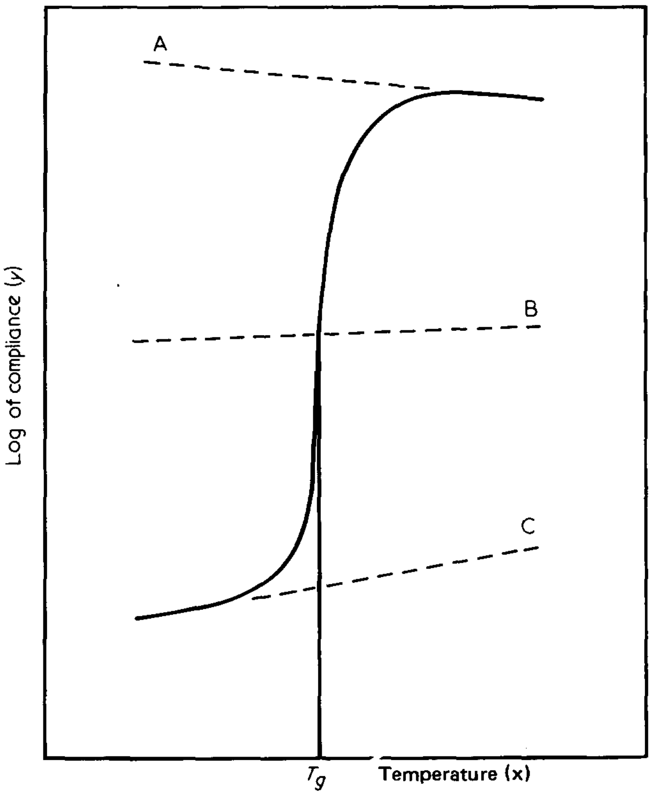

Figure 4 Schematic plot of log $J(t)$ versus T, showing the construction used to find T_g. A, $y = ax + b$; B, $y = [(a + c)x + (b + d)]/2$; C, $y = cx + d$

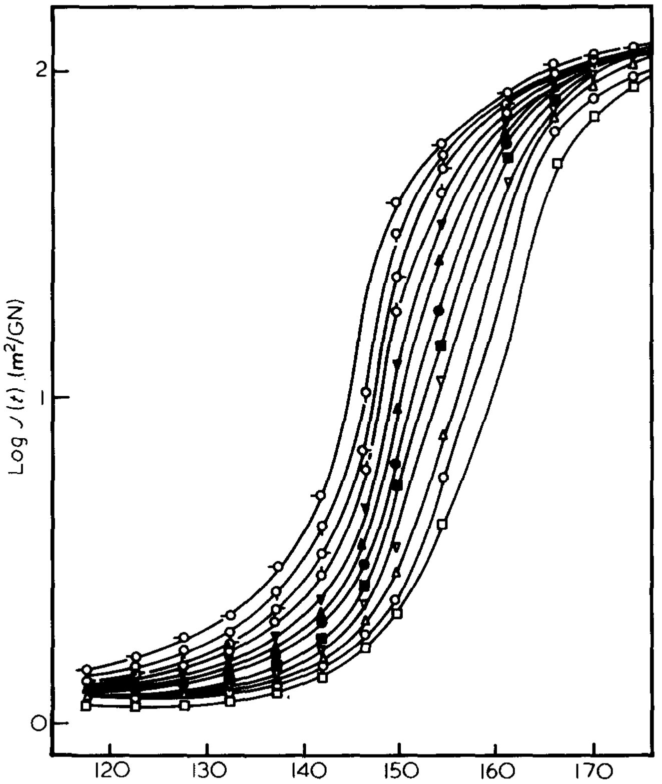

Figure 5 Isochronous plots of log $J(t)$ versus T. The values of log t are: □, 0.5; ○, 0.75; △, 1.0; ▽, 1.25; ■, 1.5; ●, 1.75; ▲, 2.0; ▼, 2.25; ό, 2.5; ○-, 2.75; ♀, 3.0; -○, 3.25

method is used the probable error in shear activation energy is estimated to be about 10%, compared with 15% if ΔH is obtained from the T_g shift method.

CREEP IN DILATATION

Time–temperature superposition

While the technique of time–temperature superposition is well accepted in shear, and has over recent years received considerable attention, the same cannot be said about time–temperature superposition for bulk deformations, and there are comparatively few papers in the literature which deal with this subject. Perhaps the most complete works are those of McKinney, Belcher, and Marvin[23], and McKinney and Belcher[24], who have modified the WLF equation[11] to include a pressure dependent term in order to reduce dynamic bulk compliance data obtained over a wide range of temperature, pressure, and frequency for polyvinylacetate, and a rubber sulphur vulcanisate. They suggest that bulk compliance data may be superposed by horizontal shifts after applying the following normalisation procedure (ignoring the pressure dependence)

$$B_1^{T_0}(\omega a_T) = \frac{B_1^T(\omega) - B_U^T}{B_R^T - B_U^T} \qquad (4)$$

$$B_2^{T_0}(\omega a_T) = \frac{B_2^T(\omega)}{B_R^T - B_U^T} \qquad (5)$$

where the subscript 1 denotes the real part of the complex compliance

subscript 2 denotes the imaginary part of the complex compliance

B_U^T is the unrelaxed bulk compliance at T

B_R^T is the relaxed bulk compliance at T

$B^T(\omega)$ and $B^{T_0}(\omega)$ are the measured dynamic bulk compliances as functions of frequency, ω, at temperatures T and T_0 respectively.

This procedure has also been used by Morita, Kono and Yoshizaki[1] to superpose data obtained on poly*i*butyl methacrylate, and has been found to produce smooth master curves. The data of Morita, Kono and Yoshizaki[1] were obtained by measurement of the ultrasonic longitudinal and shear wave velocities, and attenuation coefficients, and the complex bulk modulus K^* was calculated from the relation

$$K^* = K_1 + iK_2 = M^* - \frac{4}{3}G^*$$

where M^* = complex longitudinal modulus
G^* = complex shear modulus
K_1 = real part of the complex bulk modulus
K_2 = imaginary part of the complex bulk modulus.

Philipoff and Brodnyan[10] have used the Ferry[20] normalisation, and the simple Leaderman procedure[13] to superpose their bulk compliance data obtained on plasticised PVC and a commercial polyethylene, and were unable to decide which gives the best superposition. Theoretically there is no justification for applying this vertical shifting procedure to bulk data, since it is intended to correct for the temperature dependence of the relaxed compliance in shear. It is well known that J_R decreases with T whereas B_R appears

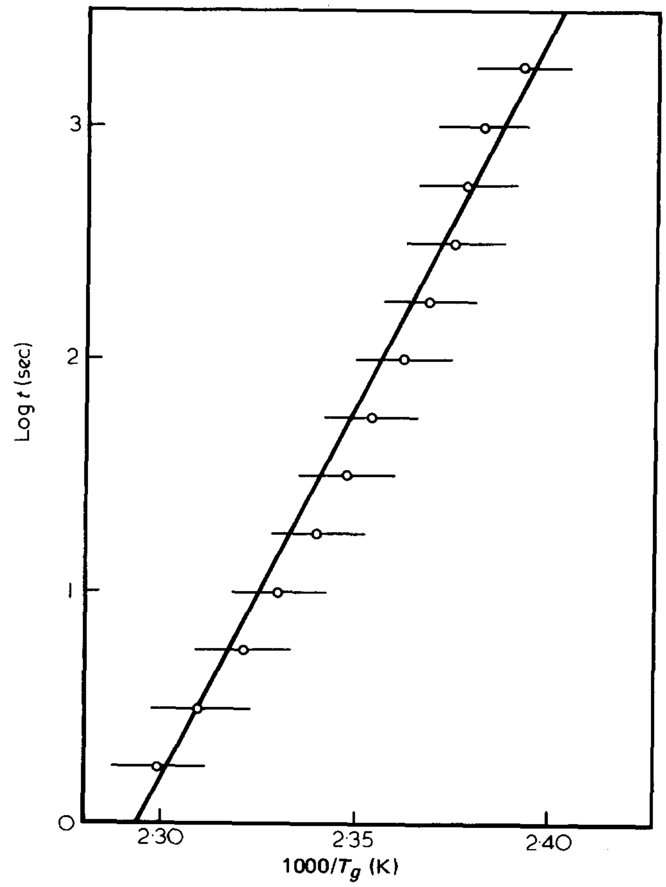

Figure 6 Log t versus 1000/T_g (K) for shear creep data

from our experiments to vary very little with T, and McKinney, Belcher and Marvin[23], and van der Wal *et al.*[25] find that B_R increases with T.

Theocaris[26] has devised a method to calculate the bulk creep compliance and bulk stress relaxation master curves from a knowledge of the tensile creep compliance and tensile stress relaxation modulus master curves, and has applied the technique to two epoxy polymers. The technique rests on the assumption that K and ν are only slowly varying functions of temperature and time. Thus if the values of K and ν are known at some starting point on the temperature or time scale it is possible to approximate either $\nu(t)$ or $K(t)$ in a small interval of time or temperature adjacent to this point by the value of ν or K at the starting point. Using the measured value of $E(t)$ and the assumed value of $\nu(t)$ or $K(t)$ a value of $K(t)$ or $\nu(t)$ in this time or temperature interval may be calculated from the usual equations of the elasticity theory. This value may then be used for the next time interval and values of $\nu(t)$ and $K(t)$ may be alternately calculated for the different time intervals. Thus from a knowledge of $E(t), D(t)$, and one single value of some other viscoelastic function at some arbitrary starting point, the complete set of viscoelastic functions may be calculated. Theocaris[26] has used the technique to find $\nu(t)$ for creep and stress relaxation, and also to find $K(t)$ and $B(t)$. The $\nu(t)$ values compared well with his experimental data on the same polymers. The derived bulk creep and stress relaxation values were found to superpose very well. The tensile data from which bulk data were calculated had been normalised by the Tobolsky[14,16] method before superposition by horizontal shifts.

Experimental

The bulk compliance was measured by a method based on that used for elastic materials by Mallock[27]. The method has been extended to cover the case of viscoelastic materials by Arridge[28], and the method has been described by Arridge[29], Crowson and Arridge[22], and Crowson[12]. The experimental arrangement is shown in *Figure 7*. When the tube is subjected to an internal pressure the bulk compliance may be expressed in terms of the axial strain by the equation

$$B(t) = 3\frac{dl}{l}\left(\frac{r_0^2 - r_i^2}{Pr_i^2}\right) \qquad (5)$$

where $B(t)$ = bulk compliance
dl/l = axial strain
r_0 = external radius of tube
r_i = internal radius of tube
P = internal pressure

A compressed nitrogen cylinder equipped with a reducing valve provided the pressure, and a precision Bourdon gauge (Budenberg Ltd) was used for pressure measurement. The axial strain was measured using a linear variable differential transformer (*LVDT*) (Electromechanisms Ltd), which is sensitive to 1 μm. Using this method $B(t)$ could be obtained for axial strains as low as 0.001%, but in general the axial strain level was kept below 0.05%, and an accuracy in B of about 5% could readily be achieved. Such small strain levels are particularly desirable for measurement of B, because in bulk deformation non-linearity of the stress–strain curve occurs at low strains.

The measurement of bulk creep was more difficult than shear creep because of the problem of 'noise' due to fluctuations in specimen temperature. This meant that although the initial strain is easily measurable, at long times after the specimen has been loaded the changes in length due to creep under the constant load reduce to the same order of magnitude as the changes in length due to fluctuations in temperature.

Another factor which complicates bulk creep measurements is the temperature drop which occurs when the tube is pressurised. This leads to a change in length which contributes to the observed transducer output. For measurements in the transition region, where only small pressures are needed to produce the required strain, the effect is negligible, but in the glassy region large pressures are necessary, and the immediate temperature drop of the air inside the tube may be as much as half a degree. The temperature drop of the specimen is much slower, and is at least an order of magnitude lower, but because the strains used in this method are so small, the error in the measured strain produced by this temperature drop was such that the accuracy of measurements of bulk creep in the glassy region was not satisfactory.

Because of the difficulties described above the measurements of bulk creep were confined to the transition region, where the bulk compliance is most strongly time dependent. Fairly large pressures were used, since by doing this the signal may be increased without simultaneously increasing the noise. The maximum axial strain used in these experiments was 0.05%. Creep tests were run for 2 min. The bulk creep data have thus been obtained for a narrower range of conditions than for shear.

RESULTS

The procedure for measurement of creep in dilatation was very similar to that already described for shear creep, and the

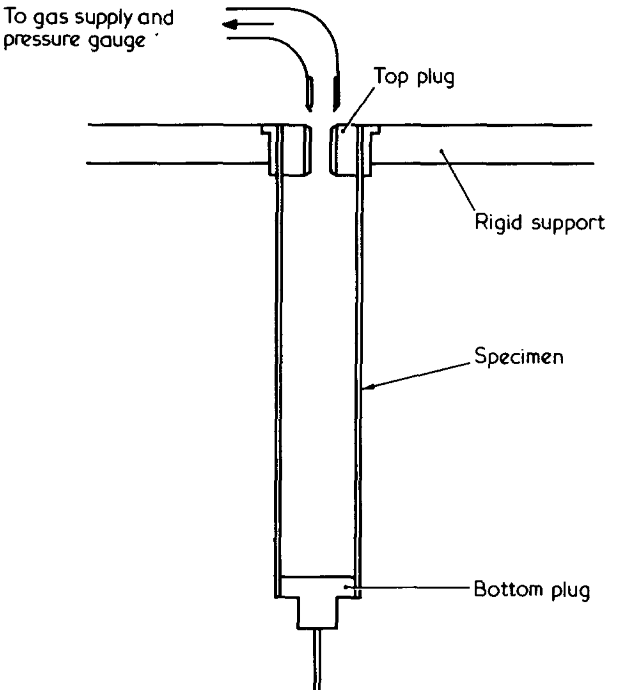

Figure 7 Apparatus for measurement of bulk compliance

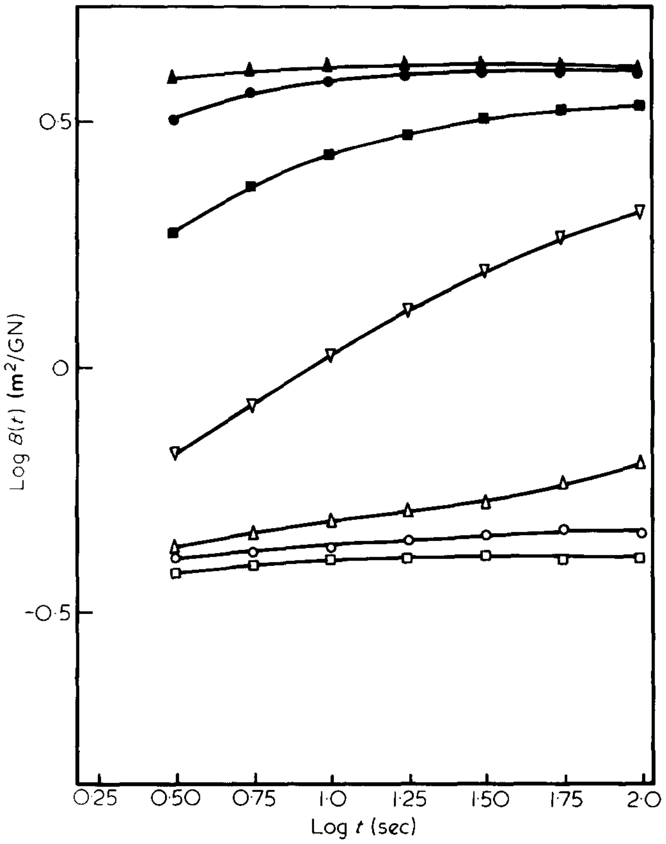

Figure 8 Log $B(t)$ versus log t in the transition region. Temperatures: □, 415.4 degK; ○, 420.6 degK; △, 426.0 degK; ▽, 430.8 degK; ■, 436.8 degK; ●, 442.6 degK; ▲, 446.6 degK

same specimen was used as for shear creep. As for shear creep the procedure was to raise the temperature to about 30°C above T_g and anneal for 10 min before allowing it to cool slowly to room temperature. This procedure served to standardize the physical state of the specimen prior to testing in both the bulk and shear modes. As a check on chemical degradation a separate specimen was heat treated at 180°C for 2 h. No significant differences were found between shear compliance values obtained before and after this treatment, and it was concluded that chemical degradation was negligible. Measurements were made at several different temperatures in the transition region (because of the difficulties outlined in the previous section it was not possible to obtain good creep curves in the glassy and rubbery regions) and the procedure adopted was to wait 30 min at each new temperature for the specimen to come to thermal equilibrium, to allow the specimen to creep for two minutes under load, and then to remove the load, and allow a further two minutes for creep recovery. Measurements were taken mainly for increasing temperature, since this allows strain which is unrecovered at the end of the four minute cycle to recover quickly when the specimen is heated to the next temperature. For this part of the work the temperature range covered was from 140° to 180°C.

At each temperature a curve for creep and creep recovery was obtained. By choosing suitable increments of time, chosen to be equally spaced when plotted on a logarithmic scale, values of the bulk compliance $B(t)$ were evaluated from the creep curve using the relation given in equation (5). The values of log $B(t)$ as a function of time for different temperatures are plotted in *Figure 8* versus log$t$. From these curves a superposition by horizontal shifts was attempted and the result is shown in *Figure 9*. Only values of log $B(t)$ at half integral values of log t are plotted for clarity. The experimental creep curves appear to superpose reasonably well without any form of correction, and values of log a_T are plotted against 1000/T(K) in *Figure 10*. From this graph it is evident that, over the temperature range for which data were obtained, the Arrhenius equation provides a good fit. For this reason an apparent activation energy was calculated from *Figure 10* from the relation

$$\log a_T = \frac{\Delta H}{2.303R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{1}$$

hence $\Delta H = 205$ Kcal/mole.

In bulk relaxation the normalization procedures described by McCrum and Morris[18], and McCrum and Pogany[19] are not generally valid because the temperature dependence of the relaxed and unrelaxed bulk compliances are different from those in shear. Perhaps the most usual bulk normalisation procedure is the one suggested by McKinney, Belcher and Marvin[23], and given in equation (4) and (5). For the case of bulk creep compliance the equation is

$$B^{T_0}(t/a_T) = \frac{B^T(t) - B_U T}{B_R^T - B_U^T} \tag{6}$$

The data should then superpose by horizontal shifts alone. Before this normalisation can be applied the temperature dependence of B_U and B_R must be known, and this is not possible for the data given here. However, McKinney and Belcher[24], and Morita, Kono and Yoshizaki[1] have approximated the temperature dependence of B_U and B_R by using their own data plotted against temperature at a certain arbitrary frequency. The data in the glassy and rubbery regions are extrapolated and $B_U(T)$ interpreted as the extrapolated line from the glassy data and B_R (T) from the

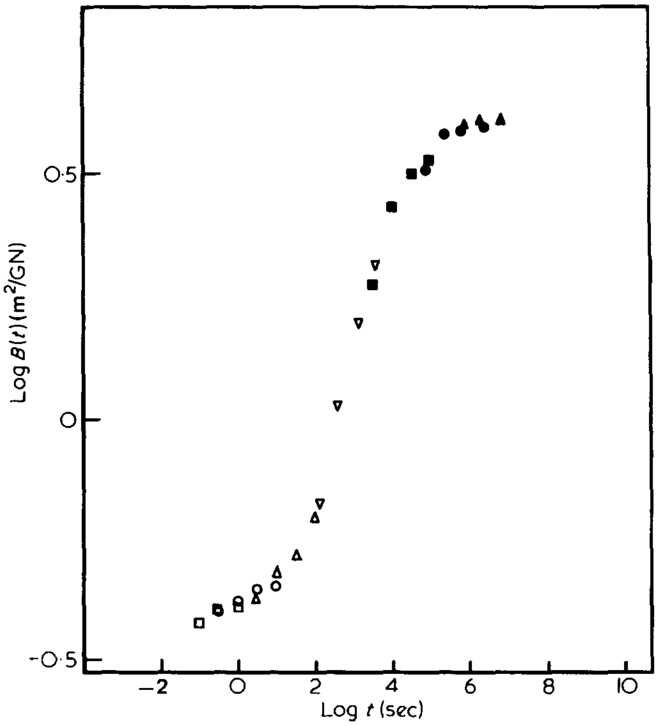

Figure 9 The composite curve reduced to T_g (= 426 K) for dilatational creep data. An explanation of the symbols is given in *Figure 8*

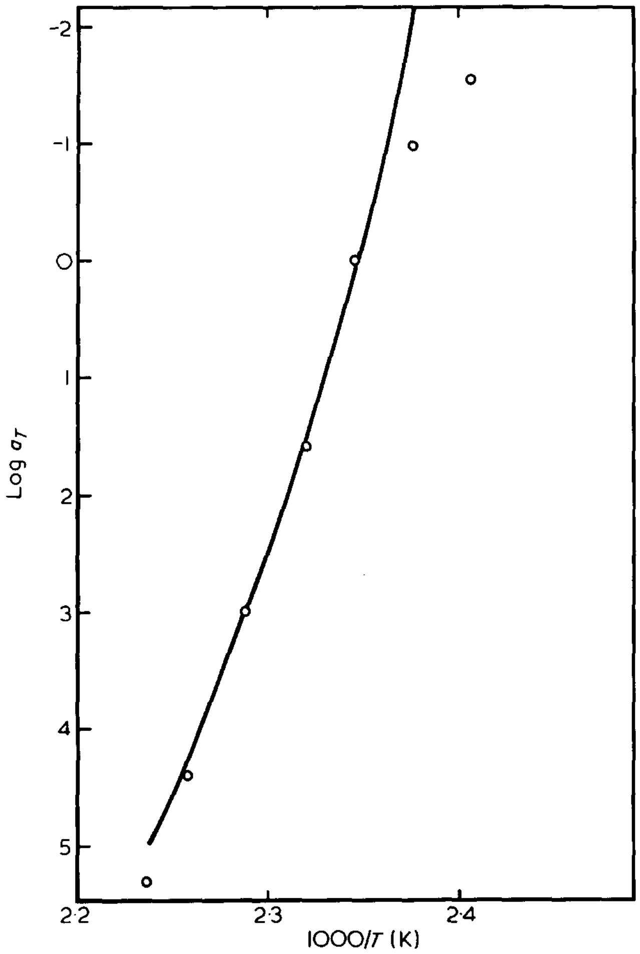

Figure 10 Log a_T versus 1000/T (K) for dilatational creep data. The solid line denotes the WLF equation

data in the rubbery region. From the data obtained in the present study the glassy region is very flat (see *Figure 11*). The data do not allow a conclusion to be drawn about the rubbery region, but the temperature dependence, if it exists, is very small. The above approximation procedure would then imply that B_U does not vary with temperature, and that B_R probably varies very little. Thus equation (6) would give

$$B^{T_0}(t/a_T) = \frac{B^T(t)}{B_R - B_U} - \frac{B_U}{B_R - B_U} \quad (7)$$

The effect of the second term is to shift all the log $B(t)$ versus log t curves vertically downwards by $B_U/(B_R - B_U)$ whilst the factor $1/(B_R - B_U)$ in the first term merely changes the vertical scale. Thus this normalisation procedure is unnecessary for our data, and will have no effect on the superposition, and for this reason it was not used here.

As with the shear creep data an alternative method, based on measurement of T_g shift with creep time, was used. The isochronous log $B(t)$ data are plotted against T in *Figure 11*, and the values of T_g found from these curves are shown in *Figure 12* as a plot of log t versus 1000/T_g(K). The procedure for finding T_g was the same as that used for the shear data. *Figure 12* is a straight line, from which the activation energy may be calculated by

$$\log t = \frac{\Delta H}{2.303R}\left(\frac{1}{T_g}\right) - \left(\frac{\Delta H}{2.303RT_{g0}} + \log t_0\right) \quad (3)$$

thus $\Delta H = 210$ Kcal/mole. (This value is obtained from a least squares fit of the data on *Figure 12*). The agreement between this figure and the value of 205 Kcal/mole obtained by temperature–time superposition is probably slightly fortuitous because the discrepancy between the two figures is only 2½%, which is rather less than the expected experimental error.

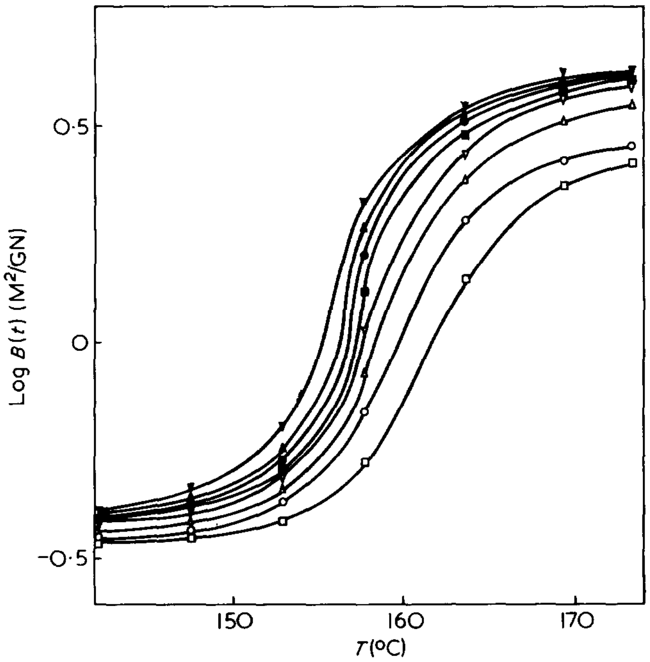

Figure 11 Isochronous plots of log $B(t)$ versus T. The values of log t are: □, 0.25; ○, 0.5; △, 0.75; ▽, 1.0; ■, 1.25; ●, 1.5; ▲, 1.75; ▼, 2.0

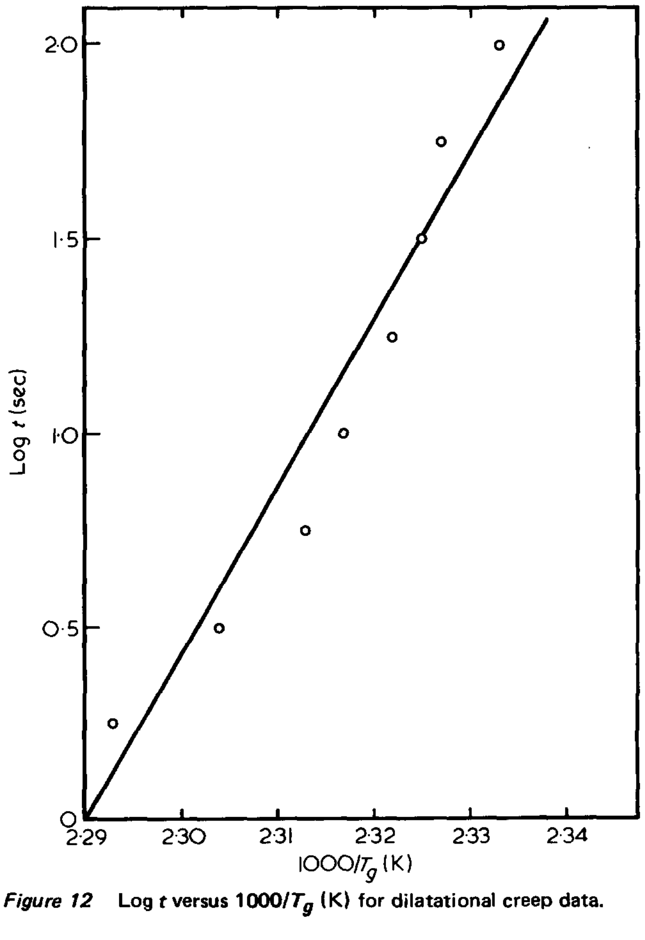

Figure 12 Log t versus 1000/T_g (K) for dilatational creep data.

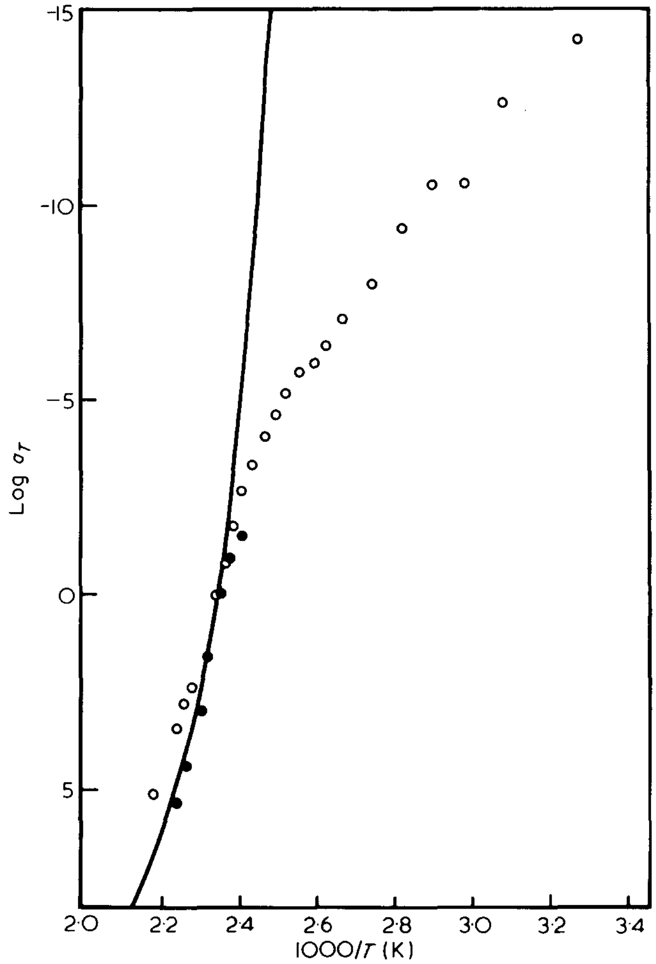

Figure 13 Log a_T versus 1000/T (K) for dilatational and shear creep data. Shear creep data are denoted by ○, dilatational creep data by ●. The solid line is the WLF equation

As in the case of shear measurements, the errors involved in calculation of activation energies for the bulk deformation may be appreciable. If the time–temperature superposition method is used the probable error in bulk activation energy is estimated to be about 13% compared with about 17% if ΔH is obtained from the T_g shift method.

Discussion of bulk and shear creep

Time–temperature superposition of the shear data by the Ferry normalisation method yields a smooth master curve. The McCrum and Morris method[18] is probably superior, but may be used only if $J_U(T)$ and $J_R(T)$ are known. The technique used by McCrum and Pogany to find $J_U(T)$ is rather unsatisfactory, and it would be preferable to use data obtained at ultrasonic frequencies to estimate this function. Since such data were not available here, and because there were insufficient data above T_g to extrapolate $J_R(T)$ by the McCrum–Pogany method[19] the McCrum–Morris normalisation[18] was not used in the present study. The Ferry normalisation[20], because it corrects only for the relaxed compliance, is expected to lead to worsening of the superposition below T_g, whilst giving improved superposition above T_g. At the moment it is not known to what extent the normalisation procedure affects the values of $\log a_T$, but the shape of the curve of $\log a_T$ versus $1/T$ is very similar to the curve obtained if no normalisation is used. The disadvantage of the Ferry method[20] is that although superposition below T_g is good, the $\log a_T$ values obtained may be incorrect. The $\log a_T$ values above T_g are more reliable, since it is in this region that the Ferry superposition procedure[20] has theoretical justification, and this is the temperature region of chief interest here, because it is only in this temperature region that we have obtained values of $\log a_T$ in bulk deformation

In bulk deformation the time–temperature superposition method used was the method of superposition by horizontal shifts alone. The McKinney, Belcher, and Marvin reduction equations[23] (equation (4) and (5)) may be an improvement, but cannot be used here because $B_U(T)$ and $B_R(T)$ are unknown. There is insufficient data here to estimate $B_R(T)$ by the method used in shear by McCrum and Pogany[19], but the indications are that $B_U(T)$ and $B_R(T)$ vary little with temperature, and thus the McKinney, Belcher, and Marvin technique[23] is not expected to differ significantly from the basic method of superposition by horizontal shifts for this material.

The value of $\log a_T$ obtained in bulk and shear have been plotted in *Figures 3* and *10* and are plotted on the same graph in *Figure 13*, together with the WLF equation[11]. In *Figure 13* the $\log a_T$ values in shear were obtained after multiplication by $T\rho/T_0\rho_0$. We are now in a position to consider whether the dependence of $\log a_T$ on T obeys the WLF equation[11], or whether a description by the Arrhenius equation is more appropriate. Below T_g the WLF equation[11] increases to infinity and clearly cannot be used in this region. The WLF equation[11] is intended for use in the temperature region $T_g < T < T_g +$ 100°C and from *Figure 13* the data fit the WLF equation[11] reasonably well between 150° and 180°C ($T_g \sim$ 155°C). No values of $\log a_T$ were obtained above this temperature, and so a comparison with the WLF equation[11] at its upper limit is not possible. Thus it seems that the WLF equation[11] is capable of giving reasonable estimates of the shifting factors, but better agreement may be possible if different values for the constants in the WLF equation are used. If a description of the shifting factors in shear is required across a wider temperature range, it is operationally convenient (although it may not be strictly correct theoretically) to use the Arrhenius equation with two different values of activation energy as described above. In bulk deformation the temperature range covered is smaller, and a single value of activation energy is sufficient for a description of the $\log a_T$ values. A description of the values of $\log a_T$ in shear by Arrhenius equations with two different values of ΔH would imply that the molecular mechanism responsible for the low temperature part of the glass transition is different from, and has a smaller value of ΔH than the mechanism responsible for the high temperature part of the transition.

The significance of this change in slope of the plot of $\log a_T$ against $1/T$ in shear is not known, but it is of interest that other authors have seen similar occurrences. McCrum and Pogany[19] obtained data for the glass transition in shear in an amine-cured epoxy resin, and their $\log a_T$ data show a similar dependence on T to that observed in the present study. Kono[5] presented a plot of the bulk and shear shifting factors against T for the glass transition region of polyvinylchloride, and the data show a similar behaviour to that seen here. Lipatov and Geller[30] studied the isothermal volume contraction of polymethylmethacrylate after being quenched from a constant temperature (above T_g) to various experimental temperatures spanning the glass transition region, and derived plots of $\log \tau$ against $1/T$ (where τ is the relaxation time at temperature T). They represented their data by two Arrhenius plots, the activation energy at high temperature being greater than that at low temperature. The $\log a_T$ data of Theocaris[31] were obtained for tensile creep and stress relaxation for amine-cured and anhydride-cured epoxy resin materials in their glass transition regions, and the creep and stress relaxation values of log a_T are in close agreement. The data are plotted as log a_T versus $1/T$. The behaviour at all but the lowest temperatures seems to be consistent with that observed in the present study, and it is at the lowest temperatures that the errors in log a_T are a maximum. Thus the decrease in slope of the curves from high to low temperature appears to be a general characteristic of the glass transition in amorphous polymers.

Although the WLF equation[11] may be preferable from a theoretical standpoint, and although it fits our experimental data adequately in the temperature region for which it is intended, the glass transition in amorphous polymers, is described equally well by the Arrhenius equation, given that ΔH has a higher value above T_g than below.

The difference in the apparent activation energies above and below T_g may perhaps be related to the state of equilibrium of the material. Above T_g volume equilibrium is achieved very rapidly (within a few seconds of the achievement of thermal equilibrium), but the time required to reach volume equilibrium increases drastically as the specimen is cooled below T_g, and may be of the order of years for polymers in their glassy state. The problem of the approach to volume equilibrium and the large effect this has on the mechanical properties has been studied by Struik[32,33]. In the experiments described in this paper the time taken for thermal equilibrium to be achieved is about ten minutes, and the time allowed between experiments at different temperatures is 30 min. Thus the time allowed for the establishment of volume equilibrium after the thermal equilibrium is achieved is about 20 min. For an experiment in the glassy region the volume will not reach equilibrium before the end of the experiment, whereas in the rubbery region the equilibrium volume will be reached before the experiment starts. At temperatures in the transition region the specimen may reach equilibrium during the experiment. It is tempting therefore to suggest that the low value of activation energy obtained below T_g is characteristic of the non-equilibrium material, and that the higher activation energy is typical of the equilibrium state above T_g.

The value of ΔH obtained here for bulk deformation (above T_g) is 210 kcal/mole, and for shear ΔH increases from 58 Kcal/mole below T_g to 165 Kcal/mole above T_g. In the WLF interpretation[11] ΔH would decrease with temperature, but over the temperature range used here the variation would be small. These values are comparable with values obtained for the glass transition in epoxy resin polymers by other workers. Kaelble[34] working on a DGEBA resin cured by various diamines obtained a value of $\Delta H = 167$ Kcal/mole from measurement of the dynamic Young's modulus. Theocaris's[31] curves of log a_T versus $1/T$ may be used to derive values of ΔH, for tensile creep and stress relaxation, of 160 Kcal/mole above T_g, and 55 Kcal/mole below T_g for a DGEBA resin cured with triethylene-tetramine.

Although the errors in the calculated activation energies are appreciable, because of the complicated method of processing the data, the difference between the apparent bulk and shear activation energies is considered to be significant for this material.

The only other comparison of bulk and shear activation energies known to the authors is that of Kono[3] who contends that the activation energy in shear is less than that in bulk for polystyrene. ΔH in shear was found to be 62 Kcal/mole, compared with 106 Kcal/mole for bulk deformation. If the bulk and shear activation energies are different, it would imply that the molecular mechanisms which cause the relaxation are not the same. This subject is one which requires further study before the origin of the differences in activation energy may be elucidated, and the methods described here are well suited to tackling this problem.

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