Temperature dependence of the steady state recoverable compliance of amorphous polymers

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The steady state recoverable compliance, J_e (cm^2/dyne), of a poly(dimethyl siloxane) with an estimated weight-average molecular weight of 4.1×10^5 was determined over the temperature range −45° to 152°C. It was found that J_e was inversely proportional to the absolute temperature in the range of reduced temperatures, $T_r = T/T_g$ from about 2 to 3. However, at temperatures where $T_r < 2$ the steady state recoverable compliance appeared to become independent of temperature. A reduced plot of the normalized reciprocal J_e utilizing additional data obtained on a polyisobutylene and a low molecular weight polystyrene confirm the temperature insensitivity of J_e in the temperature range $1.2 < T_r < 2.0$. At $T_r < 1.2$ the normalized reciprocal J_e increases rapidly reflecting a sharp decrease of J_e with decreasing temperature.

INTRODUCTION

Viscoelastic liquids, such as linear amorphous polymers, are characterized, in part, by the recoverable component of deformation which increases under constant stress with time to a limiting value. This long time limit of the recoverable strain, divided by the constant applied stress, is the steady state compliance, J_e (cm^2/dyne). In the usual representation of the shear creep compliance[1] as a function of time, t:

$$J(t) = J_g + J_d\psi(t) + t/\eta \qquad (1)$$

$J_e = J_g + J_d$, where J_g is the time independent glassy compliance, $\psi(t)$ is the normalized retardation function and J_d is the normalizing constant. At time, $t = 0$, $\psi(t) = 0$ and at $t = \infty$, $\psi(t) = 1$. η is the shear viscosity.

Up to now, when measurements of the recoverable compliance of undiluted high polymers have been possible, values have been obtained only over a narrow temperature range; certainly less than 50°C. One of the principal reasons for this lack of temperature dependence data of a steady state parameter is the strong temperature dependence of rate processes found in most polymeric systems; that is to say that the time period, within which measurements of J_e are possible, is limited. It is bracketed at short times by instrumental limitations (recording speed coupled by instrumental drift or phase angle error) and at long times by one's patience or ability to wait. In the temperature range from T_g to T_g + 100°C the viscosity of most linear amorphous polymers will decrease in value over a dozen orders of magnitude. The time to reach steady state deformation decreases by a similar amount. Consideration of this fact alone leads to the conclusion that the measurements of J_e over the indicated temperature range on a single polymer can be considered impossible; at least for the present.

One of the principal reasons for our attempts to measure the temperature dependence of the steady state compliance was the fact that the viscosity dependence of poly(dimethyl siloxane), PDMS, fails to conform to a free volume analysis that appears to be highly successful for most linear amorphous polymers[2]. Measurements on low molecular weight polystyrene samples have provided evidence that the temperature dependence of the viscosity is a composite as expressed by $\eta(T) = \tau(T)/J_e(T)$ where $\tau(T)$ (sec) is a characteristic time that is a true rate process characterizing parameter[3]. The rate behaviour of PDMS would not therefore be anomalous if its J_e were strongly dependent on temperature and $\tau(T)$ behaved as expected. It must be noted that the expected temperature dependence for J_e (inverse proportionality to the absolute temperature)[4] is slight and would not obviate the anomaly. The weak temperature dependence of the viscosity of PDMS allows for the determination of J_e over an exceptionally large temperature range.

EXPERIMENTAL

The poly(dimethyl siloxane) studied was generously given to us by Mr Kenneth Rumon of the Mellon Institute, who anionically polymerized it using hexamethyltrisiloxane dissolved in pyridine *in vacuo*. The initiator was 2-ethyl-1-lithio-1,2-dihydropyridinium. The reaction was terminated by methyl iodide. The sample had a weight-average molecular weight, of 4.1×10^5 as indicated by its shear viscosity[5,6]. At 25°C the viscosity was found to be $9.2_7 \times 10^4$ Poise. Using this value and a density, ρ, at 25°C of 0.973[7] a kinematic viscosity, η/ρ, of $9.5_2 \times 10^4$ Stoke is obtained. This value substituted into Merker's equation (17) of ref 5 yields a molecular weight of 3.9×10^5. Interpolation between viscosity results reported by Plazek *et al.*[6] gave a weight-average molecular weight $\bar{M}_w$, of 4.2×10^5. Creep recovery measurements were made with a frictionless magnetic bearing torsional creep apparatus[8]. At the highest temperatures of measurement where the angular velocity of the rotor was too great for our recording system to follow a photorelay was used to automatically turn off the torque producing drag cup motor at a predetermined angular position. The light spot tracking recorder was then

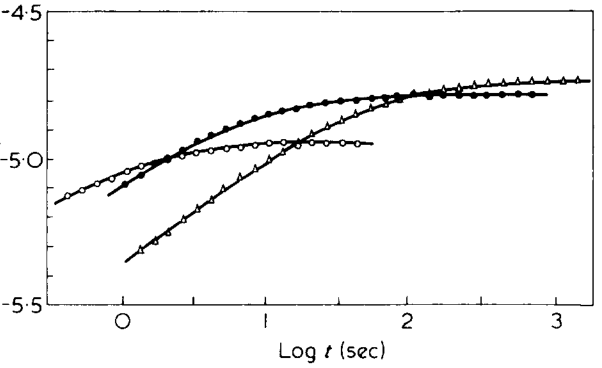

Figure 1 Logarithmic plot of the recoverable shear creep compliance, $J_r(t)$ (cm^2/dyne) as a function of time (sec), for poly(dimethyl siloxane) at three temperatures as indicated: △, −45.2°C; ●, 34.4°C; ○, 152.3°C

manually locked on to the light lever beam to follow the recoverable deformation.

Torsional creep and recovery measurements [from which the limiting low rate of shear viscosity, η, and the recoverable shear compliance, $J_r(t) = J(t) - t/\eta$, were calculated] were carried out at eleven temperatures from −45° to 152°C.

Falling ball viscosities were measured at six temperatures between 25° and 120°C. The Faxén wall correction as described by Bacon[9] was applied to the data. A simple Arrhenius plot yielded an apparent heat of activation of 3.5 kcal, which is in reasonable agreement with the value of 3.6_5 kcal given in ref 6 for a sample of similar molecular weight. Log η (Poise) values of 4.967, 4.857, 4.641, 4.462, and 4.356 were obtained at 25.0°, 40.0°, 70.0°, 100.0° and 120.0°C respectively.

RESULTS AND DISCUSSION

Illustrative curves of the recoverable shear compliance, $J_r(t)$, are presented in *Figure 1*; where $J_r(t) = J_g + J_d\psi(t)$. The $J_r(t)$ curves were obtained from measurements of deformation recovered upon removable of the applied creep torque. The time of creep preceding the recovery was always chosen to be several times greater than the time for complete recovery. The required condition of steady state deformation for producing a unique characteristic recoverable compliance curve was thereby ensured. Note that an experimentally constant creep velocity is insufficient evidence that the steady state condition is achieved. Only measurements of recovery can indicate if $\psi(t)$ has reached unity. The curves presented are corrected for an instrumental drift which is linear in time. At each temperature usually three determinations were carried out and the J_e values reported here are the averages obtained. The didactic procedure for obtaining the recoverable compliance from the creep compliance by subtracting the viscous contribution (the t/η term in equation 1) does not work dependably because of rapidly accumulating difference errors. The practical limit of this subtraction procedure is reached when $t/\eta \geqslant J_r(t)$. Data reflecting differences taken when the viscous deformation is more than one half of the total creep deformation generally prove to be unreliable and misleading.

At most of the temperatures of measurement the determinations were made using a range of applied torques to ascertain that the results were in the linear viscoelastic range. At 34.4° and 152.3°C the maximum stress in the sample, σ_m, was varied from 1800 to 4600 dyne/cm^2 (180 to 460 N/m^2) which constitutes a 2.6 fold change. At −21.8°C, σ_m was changed over a factor of 6.5 from 1100 to 7200 dyne/cm^2. No systematic variation of the results was observed to indicate the presence of a non-linear response.

In spite of the nearly 200°C temperature range the time to achieve complete recovery varied only by a factor of 50, as will be seen below. The amount of information reflecting the viscoelastic response of PDMS in the recovery curves shown in *Figure 1* is minimal since only the approach to steady state is seen. The form of the approach is a sensitive function of the molecular weight distribution of the material[4]. Without detailed knowledge of the molecular weight distribution we can only concern ourselves with the determined time independent parameters J_e and η as functions of temperature.

The $J_r(t)$ curves are reduced with empirical vertical (magnitude) and horizontal (time scale) shifts to the response at the chosen reference temperature of 34.4°C. The limited but successfully reduced recovery curve is shown in *Figure 2*, where the data points are represented by the same distinguishing features as in *Figure 1*. The time scale shift factors obtained from the reduction are log a_T (−45.2°C) = 0.91 and log a_T(152.3°C) = -0.77_5.

The reciprocal average J_e values obtained at the eleven temperatures of measurement are plotted in *Figure 3*. Their scatter and uncertainty is largely attributed to the determination of the geometrical shape factor which is routinely calculated from a sample height measurement[8]. To reduce this principal source of error we have taken advantage of the greater precision afforded by the falling ball viscosity determinations. Using the combined falling ball data from above and from ref 6, with the latter suitably shifted by a single factor to take into account the modest molecular weight differences between the samples, precise viscosities could be determined for each of our temperatures of measurement. With the creep terminal velocities which immediately preceded the determination of the recoverable response and the known viscosities sample geometrical factors were calculated. With the more precise and hopefully more accurate geometrical factors J_e values were recalculated and are presented in *Figure 3*. The reciprocal compliances have been plotted as a function of the absolute temperature, T(K) to ascertain whether or not these steady state recoverable compli-

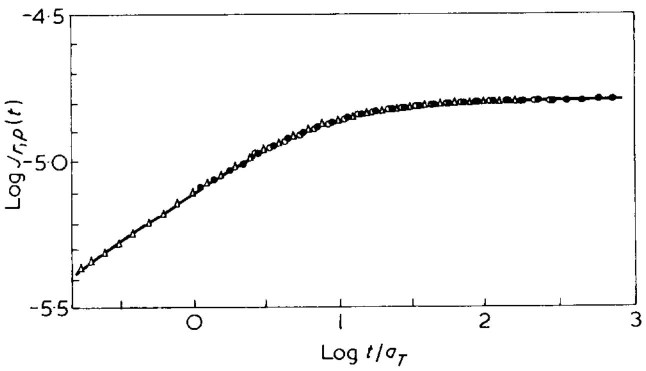

Figure 2 Logarithmic plot of the reduced recoverable shear creep compliance, $J_{r,p}(t)$, as a function of reduced time, t/a_T. Empirically determined values used for both magnitude and time scale shifts to accomplish superposition. The temperature of reduction, T_0 = 34.4°C

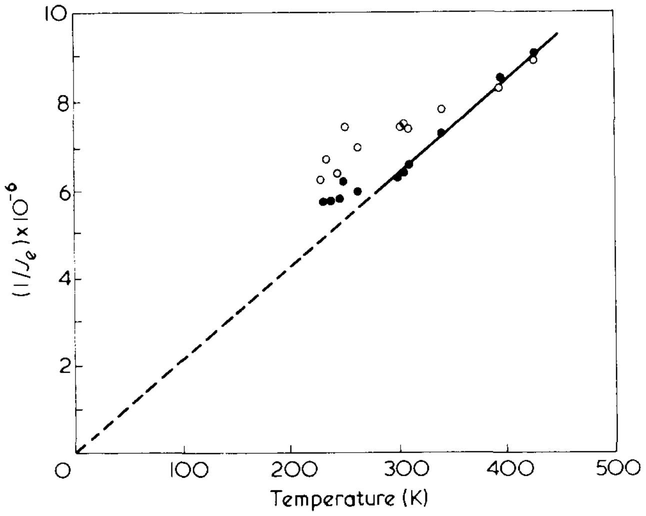

Figure 3 The reciprocal steady state recoverable compliance, J_e^{-1}, shown as a function of the absolute temperature T(K). ○, Sample coefficients calculated with measured sample height; ●, sample coefficients calculated from terminal creep velocities and known viscosity values

ances were completely entropic in origin. The expected direct proportionality[4] is represented by the straight line in *Figure 3* and above 300K the recalculated values do seem to fall along the line. Below 300K, as far as they go, the determinations appear to be high, but the discrepancy involving these data points alone is not convincing.

Effectively lower temperature response can be obtained from the response of polystyrene, PS[3], and polyisobutylene, PIB[10]. The steady state recoverable compliances for polyisobutylene were determined on a sample with a molecular weight of 78 500 and a very narrow distribution which had been obtained from Johnson and Porter[11]. The values of J_e are 1.86×10^{-6} (62.9°C), 1.95×10^{-6} (27.7°C), 1.91×10^{-6} (10.5°C), 1.84×10^{-6} (−0.8°C), and 1.84×10^{-6} cm^2/dyne (−11.7°C). All of the J_e values for the three polymeric systems PDMS, PS and PIB are presented in a composite plot of a normalized reciprocal recoverable compliance, $J_{e,\max}/J_e$ as a function of a reduced temperature, T/T_g (see *Figure 4*). J_e appears to go through a maximum value at a reduced temperature of about 1.5. It is this value, $J_{e,\max}$ that is used to normalize the three sets of data points.

T_g values used were: 343K for the 3.4×10^3 molecular weight polystyrene[3]; 203K for the PIB sample; and 150K for PDMS. The deviation noted at lower temperatures in *Figure 3* appears to be substantiated. The composite plot suggests a general pattern of response for linear amorphous polymers. At reduced temperatures greater than 2.0 direct proportionality with absolute temperature is observed. At lower reduced temperatures, between 1.2 to 2.0 a broad minimum is apparent. Finally at the lowest temperatures, below $T/T_g = 1.2$, a sharp increase is observed. Beyond the range of the graph a value of $J_{e,\max}/J_e = 51$ has been measured at $T/T_g = 1.00$.

Although the curve in *Figure 4* gives the impression that it is a unique representation of the temperature dependence of J_e for the three polymers involved and suggests that data for all linear amorphous polymers should fall onto it, this is certainly not the case. Some deviation from this curve can be expected for several reasons. The most convincing reason is that data for other low molecular weight polystyrenes do not quantitatively follow the rapid rise at reduced temperatures near $T/T_g = 1.00$[3]. In addition near the glass temperature, because of the success of the Williams, Landel and Ferry free volume analysis of rate processes in amorphous polymers, one expects a corresponding state reduced temperature to be an additive increment above T_g; $T_r = T - T_g$ and not a ratio as is used in *Figure 4*. However, the more recent Magill–Li equation[12] uses the same temperature ratio as a corresponding state variable and this equation has been rationalized in the light of free volume concepts[13].

It is unlikely that measurements of J_e can ever be made on a single polymer over the range of reduced temperatures from 1 to 3. For the 3400 molecular weight polystyrene a reduced temperature of 3 is above an actual temperature of 1000K, which is in the red heat range. For poly(dimethyl siloxane) measurements near the glass temperature are precluded because of the intervention of crystallization at temperatures below 220K. Most studies of the viscoelastic response of polymers are made in the reduced temperature range $T/T_g = 1.2$ to 2.0. Since this is where J_e is virtually independent of temperature it appears the amplitude reduction factor T/T_0 (where T_0 is the reduction temperature) is not needed for temperature reduction procedure. However, there is some evidence[15] that polymer solutions do not behave as bulk polymers do in this regard and the T/T_0 factor appears to be necessary. Unfortunately, at the present time one cannot always be sure when vertical shifting is necessary. The vertical shift in any case is usually small and for most problems is not significant. For others it may be and, therefore, this ambiguity should be kept in mind.

If, the temperature dependence of the rubber-like plateau parallels that of the steady state compliance it should be noted that the procedure for calculating the molecular weight per entanglement, M_e, must be changed from the present practice. This significant characterizing parameter is determined from the rubber-like plateau modulus, G_{eN}, (or compliance, J_{eN}) with the simple kinetic theory expression:

$$M_e = \frac{\rho RT}{G_{eN}} \equiv \rho RTJ_{eN}$$

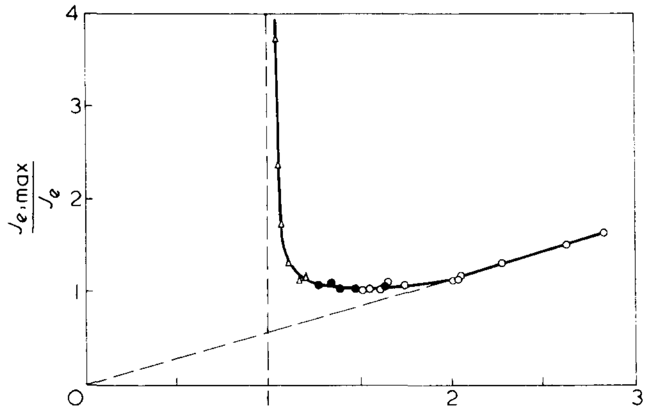

Figure 4 Normalized reciprocal steady state recoverable compliance, $J_{e,\max}/J_e$, for three polymers, poly(dimethyl siloxane), polyisobutylene, and polystyrene *versus* the reduced temperature, T/T_g; T_g is the glass temperature and the normalizing compliance, $J_{e,\max}$, is the largest experimentally indicated value which appears to occur at $T/T_g \simeq 1.5$. The broken line through the origin indicates the expected kinetic theory result for a rubber-like modulus. ○, Poly(dimethyl siloxane); ●, poly(isobutylene); △, polystyrene

where ρ is the polymer density in g/cm^3 and R is the universal gas constant, 8.314 x 10^7 erg/°C mol. This, of course, is the equation for the straight line in *Figure 4*. Therefore if a rubber-like modulus is determined that falls off the rubber-like theory line it should be corrected to a corresponding point on the line before M_e is calculated. Such a correction indicates that the values reported in the literature[14] are probably about 25% too low.

Evidence does exist that the rubbery plateau level of compliance is essentially independent of temperature in the usual range of measurement of high molecular weight poly(methyl methacrylate)[16] and polystyrene.

The temperature dependence of the recoverable compliance rate is greater than that of the viscosity at temperatures just above T_g[3]. Therefore, as T_g is approached from above the rate of recovery slows down more rapidly than the viscosity increases; in other words although the absolute value of the viscosity increases with decreasing temperature relative to the rate of recovery the material appears more fluid. This relative increase in the rate of viscous flow apparently aids the rate of diffusion to a greater degree than it does the orientation effect of the transmitted stress, thus shifting the dynamic balance and yielding a smaller amount of recoverable strain per unit stress.

In conclusion we can say that the temperature dependence of the steady state recoverable compliance of PDMS is slight in the accessible temperature range and its behaviour cannot be invoked to explain the lack of adherence of the viscosity to free volume theory expectations. Most likely then, the unusually large thermal expansion coefficient (1.2 x 10^{-3} °C) and the distance above T_g yield such a large free volume (as evidenced by a high compressibility) that additional increments with increasing temperature do not have as great an effect as they do under more crowded conditions near T_g. Such a diminishing effect of the free volume on the viscosity has been proposed to explain a similar deviation from the Doolittle[17] form by a non-polymeric organic glass-former, 1,3,5-trinaphthylbenzene[18].

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