The physical ageing response of an epoxy glass subjected to large stresses

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Physical ageing studies were made using model epoxy network glasses. Non-linear viscoelastic responses were measured after quenching the glasses from above T_g to the temperature of interest. The physical ageing responses at different magnitudes of applied load, for different duration times of the load application and at different temperatures were studied. The creep compliance curves at different ageing times were able to be superimposed to form a single master curve, demonstrating the validity of a time–ageing time superposition principle for this epoxy network. Similar to many other physical ageing studies, we observed that the double-logarithmic shift rate μ decreases as the stress amplitude increases. However, this study differs from others in that the glasses were aged close to T_g and it was possible to age them into structural equilibrium, i.e. the glasses cease to age. Thus, t^*, the time required to reach structural equilibrium, was obtained. Results showed that t^* did not change with the magnitude of applied stress; therefore, it will be argued that ageing is not 'erased' by large mechanical stimuli. Furthermore, the creep response after reaching equilibrium for the glass that had been subjected to the repeated stresses as it aged into equilibrium was compared with that of the same glass that was aged thermally into equilibrium without any stress application. There was no significant difference between the responses in these two conditions. This demonstrates that, in spite of the mechanical stimulus, the response of the glass in the equilibrium state has not changed. All these results support the argument that the volume recovery that occurs during ageing impacts the small-deformation response differently than it does the large-deformation response.

(Keywords: physical ageing; glass; stress; epoxy network)

INTRODUCTION

Upon cooling from above the glass transition to below it, glass-forming systems, such as polymers, exhibit non-equilibrium behaviour[1–3]. In the glass, and under isothermal conditions, the volume of the polymer evolves continuously towards its equilibrium value[2,3]. During this volume evolution the mechanical properties of the material also change[3–5]. It is the change in mechanical properties during the volume recovery that has come to be known as physical ageing.

During physical ageing it has been found that the changes in the viscoelastic properties of the glass can be represented by a time–ageing time correspondence[5]†, i.e. the spectrum of relaxation or retardation times obtained at a given ageing time t_e can be shifted to superimpose onto the spectrum obtained at a reference ageing time t_{er}. This superposition results in a single master curve for a given viscoelastic property, which can be described in terms of a reduced time $t_R = t/a_{te}$, where a_{te} is the shift factor required to do the superposition and is defined as $a_{te} = \tau_i/\tau_r$, where τ_i and τ_r are the characteristic times in an arbitrary state of ageing and the reference state respectively. In addition, Struik[5] defined a shift rate:

$$\mu = \mathrm{d}\log(a_{te})/\mathrm{d}\log(t_e)$$

which he found to be of order unity in the small-deformation or stress range (i.e. linear viscoelastic).

The above definition of physical ageing as the change in the viscoelastic behaviour (or molecular mobility) of the glass as the thermodynamic state or structure (as measured by volume or enthalpy) of the glass evolves is widely accepted when discussing the behaviour in the linear viscoelastic range. On the other hand, the ageing response of the glass when subjected to large deformation or stresses, i.e. in the non-linear viscoelastic range, has been the subject of a certain amount of controversy, which we outline briefly in the following paragraphs.

There are several types of experiments in the non-linear viscoelastic range that have been carried out in order to attempt to define the impact of volume changes (or changes in thermodynamic state) in the glass during physical ageing on the glass's non-linear viscoelastic response. These experiments have been interpreted so as to imply that the application of large stresses or deformations has a major impact on the thermodynamic state of the glass. (Here we need to emphasize that by thermodynamic state we mean the state defined by the *PVT* (pressure–volume–temperature) surface or the *SPT* (entropy–pressure–temperature) surface, recognizing that the application of a stress or deformation has thermodynamics involved with it as well. For simplicity we will keep the mechanical response part of the thermodynamics separate from the *PVT* or *SPT* response.) The experiments can generally be categorized as one of two types.

First, a classical ageing experiment is performed in which the polymer is quenched from above the glass transition to some temperature below it and then is aged isothermally. The shift rate μ of the glass during ageing is

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† Kovacs *et al.*[4] found that time–ageing time correspondence was only approximately valid

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measured as a function of the magnitude of the applied stress or deformation. It is found that μ decreases as the applied stress or deformation increases[5,6]. *Figures 1a* and *1b* show these effects schematically. *Figure 1c* shows an interpretation of the result as erasure[5], rejuvenation[6,7] or deageing of the glass. It is significant that this interpretation implies that the thermodynamic state of the glass is changed by the application of the large mechanical stimulus. In this paper we will present results that challenge this interpretation.

The second type of experiment that has been used to examine the rejuvenation of ageing or aged glasses is one in which a large deformation or stress is applied to the sample. In one experiment of this type a small deformation is subsequently superimposed upon a large one in the same sequence as after a thermal quench, i.e. at increasing 'ageing times' t_e. As shown in *Figure 1d*, the result is that the incremental or superposed modulus is smaller than the linear modulus and increases with increasing time after imposition of the large deformation. This set of results has been observed in both glasses[5,7–11] and in polymer solutions[11,12] and has been interpreted either as rejuvenation (of the glass) followed by renewed ageing or as a simple memory effect[11,12], which one would expect simply due to the non-linear viscoelastic behaviour of the material. Another experiment that falls into this category is one in which a glass is aged normally and then a single large stress or deformation is applied followed by small 'probe' deformations[5]. Again, we would expect there to be a memory effect due to the non-linear viscoelastic response of the material and a simple interpretation of the behaviour in such an experiment is extremely difficult. Because the interpretation of the experiments described here is complicated by any non-linear effects that occur, the reader is referred to the original references for further information concerning their interpretation[5,7–12]. It should be noted, however, that the present authors feel that rejuvenation is not an appropriate explanation for these types of experiment. We will not deal with this second type of experiment further.

The concept of rejuvenation in polymer glasses has received considerable attention lately as several groups[5,7–10,13,14] have used the concept to explain various types of non-linear behaviour that have been observed in polymer glasses. Importantly, we do not dispute any of the experimental results, rather we dispute their interpretation in terms of rejuvenation, deageing or erasure of ageing. In this paper, we present new results relevant to the first type of experiment, which show that applying large stresses to an epoxy network glass does not change the length of time required for that glass to attain equilibrium. Furthermore, the non-linear response of the glass aged into equilibrium is the same whether or not the large (intermittent) stresses are applied. These results argue strongly that the thermodynamic state of the glass (in the *PVT* sense described above) is unaffected by application of large mechanical stimuli. Rather, we will

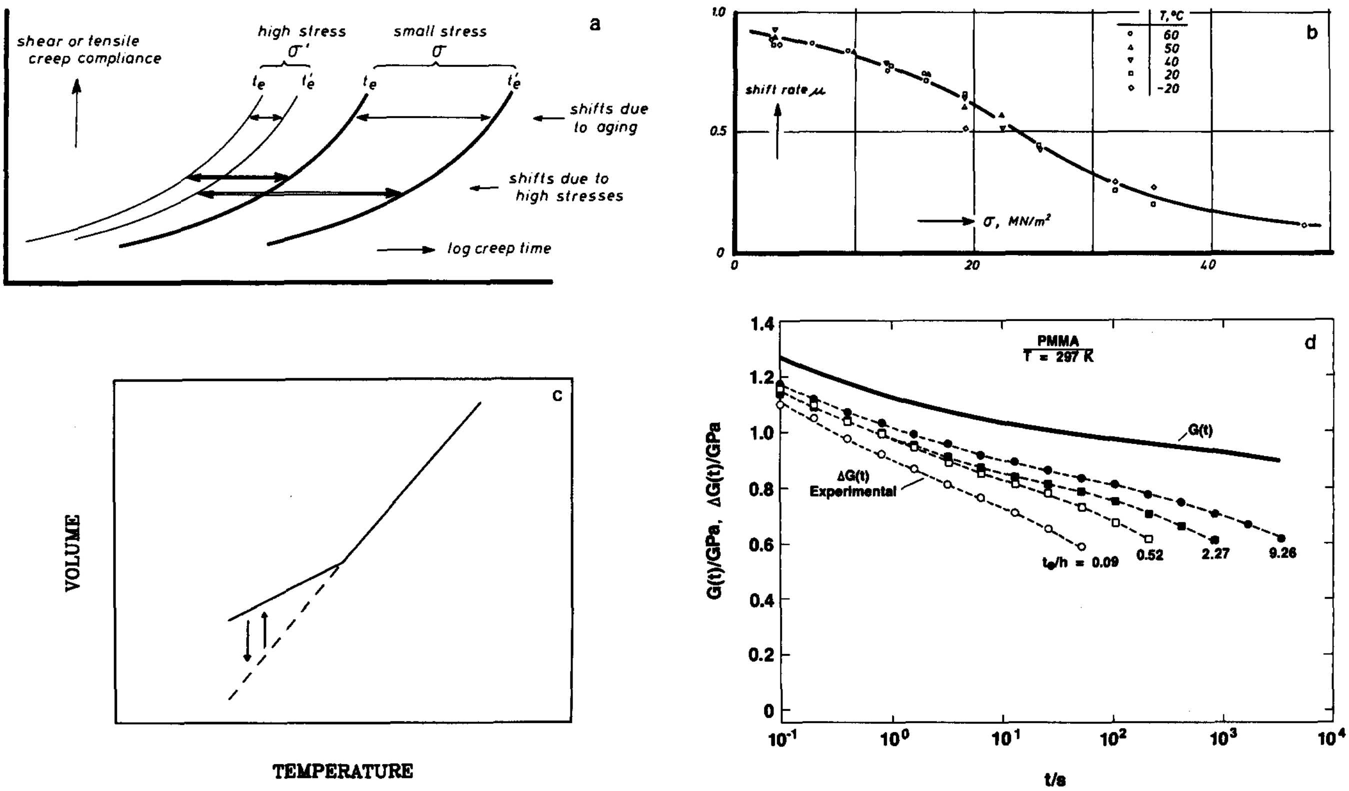

Figure 1 (a) Schematic of the relative effects of ageing on the small-stress and large-stress creep compliances of a glass; t_e and t'_e are two different ageing times ($t'_e > t_e$). (From Struik[5].) (b) Double-logarithmic ageing time shift rate μ *versus* applied stress for a poly(vinyl chloride) quenched from 90°C to various temperatures. (From Struik[5].) (c) Schematic of volume–temperature plot showing ageing and rejuvenation hypothesis. Arrow showing volume decrease represents normal isothermal response of a glass after rapid cooling to a non-equilibrium state. Physical ageing is change in viscoelastic properties accompanying the volume decrease. Arrow showing volume increase depicts expected rejuvenation response of a glass due to application of a large stress or strain after ageing has occurred. (After Ricco and Smith[7].) (d) Comparison of the incremental modulus $\Delta G(t)$ and linear modulus $G(t)$ for a poly(methyl methacrylate) glass subjected to torsional deformations; $\gamma = 0.05$, $\Delta\gamma = 0.005$; t_e is the 'ageing' time after application of the large deformation at which time the incremental deformation was applied. We remark that at shorter t_e, $\Delta G(t)$ is shifted to shorter times. As t_e increases, $\Delta G(t)$ appears to 'age' and shifts to large times. (After McKenna and Zapas[11])

argue that the results support the contention that the volume recovery (change in thermodynamic state) that occurs during ageing impacts the small-deformation behaviour differently than it does the large-deformation response.

EXPERIMENTAL PROCEDURES

Materials

Pure diglycidyl ether of bisphenol A (DGEBA, DER 332, Dow Chemical, USA)* epoxide monomer was used in this study and cured with amine-terminated poly(propylene oxide) (Jeffamine, designation of Texaco Chemical Co.)* of molecular weight 400 g mol^{-1} to form a network.

The DGEBA epoxide monomer was preheated at 55°C for 2 h to melt any crystals present. The amine was then added and the mixture was stirred by hand until clear. The mole ratio of the epoxide to amine was that of the stoichiometric ratio. The mixture was degassed for 10 min at room temperature (23°C), then cast into a mould with dimensions of $11 \times 9 \times 1/8$ inch ($28 \times 23 \times 0.32$ cm) and cured at 100°C for 24 h. The sample was then allowed to cool slowly in the oven to 23°C overnight. Strips of $3/4 \times 9 \times 1/8$ inch ($1.9 \times 23 \times 0.32$ cm) were cut from the cast sheets, milled into dumbbell-shaped samples and kept in a sealed desiccator prior to performing the physical ageing experiments.

The glass transition temperature for this network polymer was determined to be 42.4°C by heating in a differential scanning calorimeter (Perkin–Elmer DSC-2)* at 20°C min^{-1}. The heating scan was performed immediately after cooling (at 20°C min^{-1}) samples that had been held in the DSC at 160°C for 30 min.

Physical ageing experiments

The mechanical tests were performed using a computer-controlled servo-hydraulic testing machine (Instron model 132.25)* equipped with an oven for temperature control. Measurements of the temperature between the top and bottom of the sample showed that the gradient was less than 0.5°C. Oven stability was better than ±0.2°C during each experiment. The dumbbell-shaped specimens were first annealed for 30 min at 64.4±2°C (T_g+22°C) and then placed in the testing machine at the testing temperature where the glass began to age.

The mechanical tests were carried out in uniaxial extension under creep conditions. Loads were applied periodically at ageing times t_e that approximately doubled with each test, i.e. $t_e = 30$ min, 60 min, 120 min, etc. The duration t_1 of the load application was varied so that the ratio t_1/t_e was constant throughout the ageing experiment. The values of t_1/t_e used in this study were 0.028, 0.056 and 0.112. The (engineering) stresses applied to the samples were 1, 5, 10, 15 and 20 MPa. The strain was measured with an extensometer attached to the specimen. Because the specimens did not return to zero deformation at the larger stresses and/or high values of t_1/t_e the residual strain was subtracted from the total strain and the specimen gauge length was corrected for each loading interval of the ageing test. When yielding occurred the tests were stopped. The creep compliance was then calculated at $\varepsilon(t)/\sigma$, where $\varepsilon(t)$ is the corrected strain and σ is the engineering stress, determined from the original cross-sectional area of the specimen.

METHOD OF ANALYSIS

Each creep compliance curve was analysed by using a Kohlrausch–Williams–Watts (KWW)[15,16] type creep function:

$$D(t) = D_0\{1 + \exp[(t/\tau)^{\beta}]\} \tag{1}$$

where $2D_0$ is the zero-time compliance, τ is a characteristic retardation time and β is a shape parameter for the creep curve. The numerical analysis for the curve fits at each experimental condition was performed using the DATAPLOT[17] non-linear least-squares data analysis package available on the NIST Cyber 205 computer.

When the values of D_0 and β are independent of ageing time, one can perform a time–ageing time superposition of the creep data by reducing them to a reference ageing time via a shift along the time axis. Then the ageing time shift factor a_{te} is defined in terms of the KWW function as:

$$a_{te} = \tau(t_e)/\tau(t_{er}) \tag{2}$$

where $\tau(t_e)$ is the value of τ in equation (1) at the ageing time t_e and $\tau(t_{er})$ is its value at the reference ageing time.

Having obtained the values of a_{te}, we use the conventional method of analysing the effect of ageing time on a_{te} of making double-logarithmic plots of a_{te} *versus* t_e. Struik has defined the double-logarithmic shift rate μ as:

$$\mu = \mathrm{d}\log(a_{te})/\mathrm{d}\log(t_e) \tag{3}$$

In the results described in the next section we will present creep curves for various ageing times. Double-logarithmic plots of a_{te} *versus* t_e for different temperatures, stresses and values of the ratio of t_1/t_e will be compared.

RESULTS

Ageing in the linear viscoelastic range: definition of t^*

We have previously published results from a study of the effects of isothermal volume recovery on the linear viscoelastic response of epoxy network glasses[18]. This physical ageing study led to the definition from mechanical measurements of the time t^* for the glass to reach its equilibrium state. In *Figures 2a* and *2b* we can see the effects of ageing a glass near to its glass transition. In *Figure 2a*, the creep curves are plotted at increasing ageing times for the D400 epoxy/diamine network at 9°C below the d.s.c.-measured T_g. It is readily apparent from this curve that after approximately 400 min of ageing the creep curves no longer shift to longer times, i.e. ageing has ceased and equilibrium has been reached. This result is shown in another perspective in *Figure 2b* where we show a double-logarithmic representation of a_{te} *versus* t_e. As can be seen in *Figure 2b*, there is a rather abrupt transition where the shift rate μ (the slope of the plot) changes from a value near unity to virtually zero. Again this corresponds to the point where ageing has arrested and equilibrium has been attained. We have chosen to define t^* as the point of intersection of the lines in the ageing and equilibrium region.

The importance of this definition of t^* stems from the

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* Certain commercial materials and equipment are identified in this paper in order adequately to specify the experimental procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily the best available for the purpose

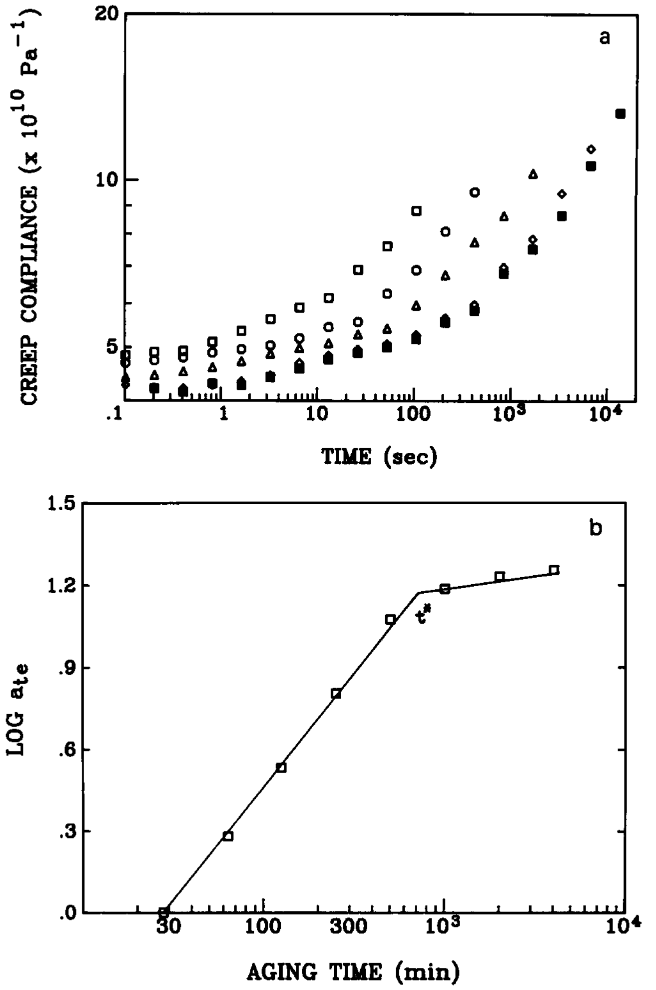

Figure 2 (a) Creep compliance curves for DGEBA/D400 diamine glass quenched from 64°C to 33.2°C and kept at 33.2±0.2°C for a period of 3 days. The T_g of this glass was determined with d.s.c. and is 42.4°C. The applied stress is 1 MPa. The different curves were measured for various values of ageing time, time elapsed after quenching: (□) 28 min; (○) 126 min; (△) 503 min; (◇) 2013 min; (■) 4026 min. (b) Log a_{t_e} *versus* ageing time for DGEBA/D400 glass aged at 33.2°C with applied stress equal to 1 MPa. The transition from ageing to non-ageing behaviour is quite abrupt. Here, we define the intersection of the lines in the ageing and non-ageing regimes at t^*, which is the time required to attain equilibrium

ability to use now a mechanical technique to determine when the glass has been aged into the equilibrium state. Following Struik[5] and others[7–10], their argument being that large mechanical stimuli affect the ageing of the glass (i.e. rejuvenate it) as evidenced by a reduction of μ when the stress magnitude increases, one would expect that the value of t^* should correspondingly increase. In the next section we present results on the effect of stress magnitude and the ratio of step duration to ageing time on t^*.

Ageing in the non-linear viscoelastic range

Effect of stress magnitude on t^* and μ. We have already shown in *Figures 2a* and *2b* the effects of ageing on the creep response of the D400 epoxy/diamine glass at 1 MPa. In *Figures 3–5* we show double-logarithmic plots of the creep compliance at the indicated ageing times *versus* time for stress levels of 5, 10 and 15 MPa. The value of t_1/t_e in these experiments was 0.056. The KWW parameters for these data are tabulated in *Table 1*. Importantly, the values of D_0 and β do not vary with

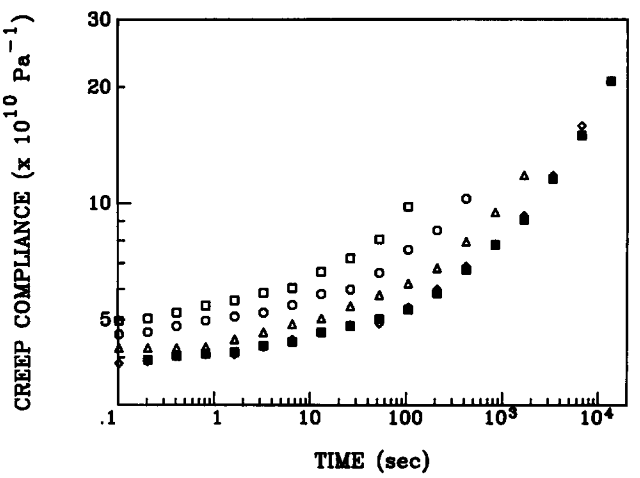

Figure 3 Creep compliance curves for DGEBA/D400 glass quenched from 64°C to 33.2°C and kept at 33.2±0.2°C for a period of 3 days. The applied stress is 5 MPa. The different curves were measured for various values of ageing time: (□) 28 min; (○) 126 min; (△) 503 min; (◇) 2013 min; (■) 4026 min

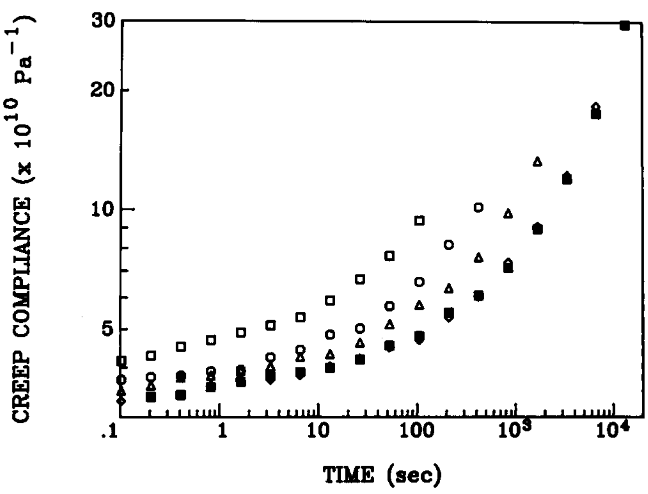

Figure 4 Creep compliance curves for DGEBA/D400 glass quenched from 64°C to 33.2°C and kept at 33.2±0.2°C for a period of 3 days. The applied stress is 10 MPa. The different curves were measured for various values of ageing time: (□) 28 min; (○) 126 min; (△) 503 min; (◇) 2013 min; (■) 4026 min

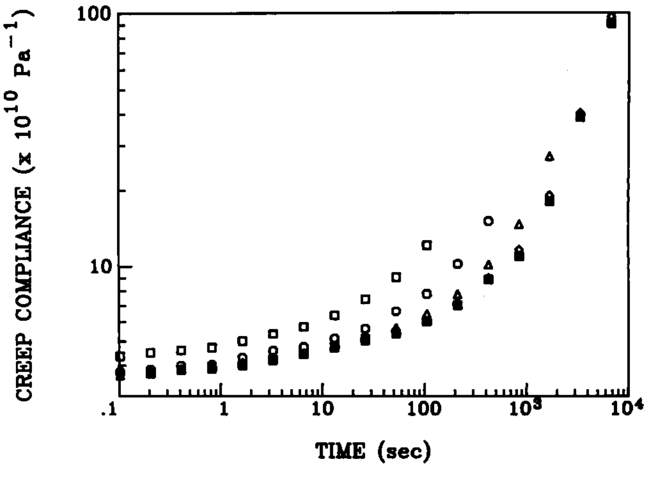

Figure 5 Creep compliance curves for DGEBA/D400 glass quenched from 64°C to 33.2°C and kept at 33.2±0.2°C for a period of 3 days. The applied stress is 15 MPa. The different curves were measured for various values of ageing time: (□) 28 min; (○) 126 min; (△) 503 min; (◇) 2013 min; (■) 4026 min

Table 1 Kohlrausch–Williams–Watts curve-fitting parameters[a] ($T=33.2°C$, $t_1/t_e=0.056$)

σ (MPa)	t_e (min)	D_0 ($\times 10^{10}$ Pa^{-1})	τ (s)	β
1	28	2.01	62.5	0.276
	63	2.00	119.4	0.270
	126	1.97	212.5	0.273
	252	1.99	398.7	0.272
	503	1.93	741.2	0.275
	1006	2.01	975.5	0.272
	2013	1.94	1063.1	0.277
	4026	1.95	1121.8	0.271
5	28	1.92	45.8	0.280
	63	1.96	83.8	0.275
	126	1.92	141.9	0.281
	252	1.86	229.5	0.282
	503	1.85	413.6	0.278
	1006	1.89	502.9	0.275
	2013	1.87	555.6	0.281
	4026	1.89	576.2	0.277
10	28	2.01	38.3	0.302
	63	2.01	60.5	0.297
	126	2.02	93.1	0.299
	252	1.97	136.3	0.296
	503	1.93	224.4	0.296
	1006	1.96	291.5	0.303
	2013	1.96	318.6	0.294
	4026	1.98	338.2	0.303
15	28	2.01	32.0	0.338
	63	1.95	45.4	0.333
	126	1.95	68.8	0.340
	252	1.94	104.3	0.341
	503	1.93	147.5	0.337
	1006	1.93	173.4	0.345
	2013	2.00	180.3	0.338
	4026	2.13	186.5	0.339

[a] Fit to equation (1) using a non-linear least-squares regression analysis[17]

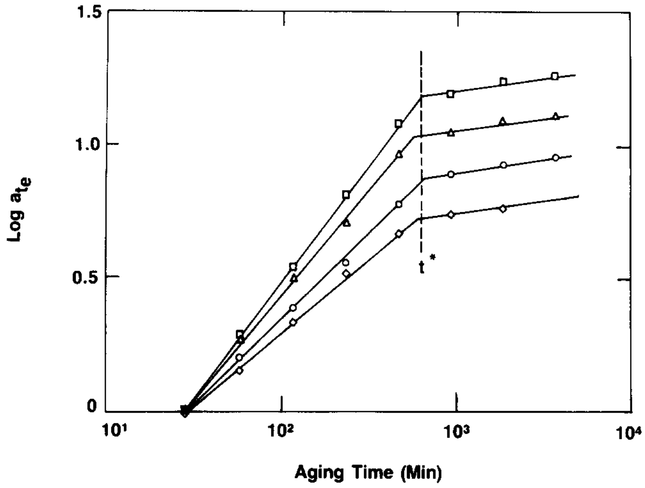

Figure 6 Log a_{te} *versus* ageing time for DGEBA/D400 glass aged at different values of applied stress: (□) 1 MPa; (△) 5 MPa; (○) 10 MPa; (◇) 15 MPa. Test temperature $=33.2\pm0.2°C$

ageing time for any given stress magnitude. However, β does vary with the stress magnitude and, although time–ageing time superposition appears to be valid for this system, time–stress superposition is not.

In *Figure 6* we show a double-logarithmic plot of a_{te} *versus* t_e for each stress magnitude. There are two features of interest in this figure. First, the signature of rejuvenation is apparent in that the value of the shift rate μ decreases as the stress amplitude increases. These values are tabulated in *Table 2*. Secondly, for each stress level there is a change in slope on the plot for an ageing behaviour to a non-ageing behaviour, which allows definition of t^* for each stress. A vertical line has been drawn at the value of t^* for the 1 MPa stress level. As can be seen, this line passes, within experimental uncertainty, through the points that define t^* for all of the stress magnitudes depicted. This is contrary to the rejuvenation hypothesis and will be discussed in detail in a subsequent section.

In *Figure 7* we compare the creep response after reaching equilibrium for the D400 glass that was subjected to the repeated stresses as it aged into equilibrium with that of the same glass that was aged isothermally into equilibrium without any stress application. As can be seen, there is no significant difference between the responses in these two conditions. This demonstrates that, in spite of the mechanical stimulus, the response of the glass in the equilibrium state has not changed.

Effects of t_1/t_e on t^* and μ. We have also studied the influence of the stress history applied at early ageing times on the response at later ageing times by changing the relative values of the step duration t_1 and the ageing time t_e. This explores the so-called 'stress memory' effect on apparent ageing behaviour.

In *Figures 8* and *9* we show the creep compliance response at $T_g-T=9°C$ and at different ageing times for the D400 glass at 10 MPa and at values of t_1/t_e of 0.028 and 0.112, respectively. These figures should be compared with *Figure 5* where the value of $t_1/t_e=0.056$. All creep

Table 2 Double-logarithmic ageing time shift rate μ for $t_e<t^*$ ($T=33.2°C$, $t_1/t_e=0.056$)

σ (MPa)	μ
1	0.858
5	0.733
10	0.622
15	0.542

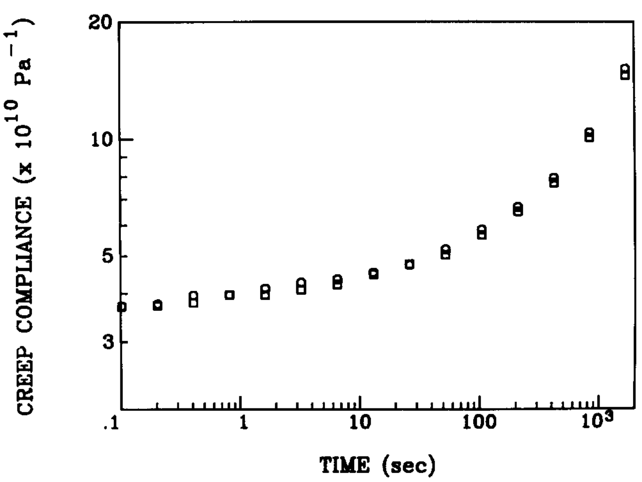

Figure 7 Double-logarithmic representation of the large-stress creep compliance at $\sigma=15$ MPa *versus* time for samples aged into equilibrium at 33.2°C. (○) Sample aged while intermittent large stress (15 MPa) was applied. (□) Sample aged into equilibrium without stress. The fact that the responses are the same shows that the process of attaining equilibrium is not changed whether or not a stress has been applied during ageing

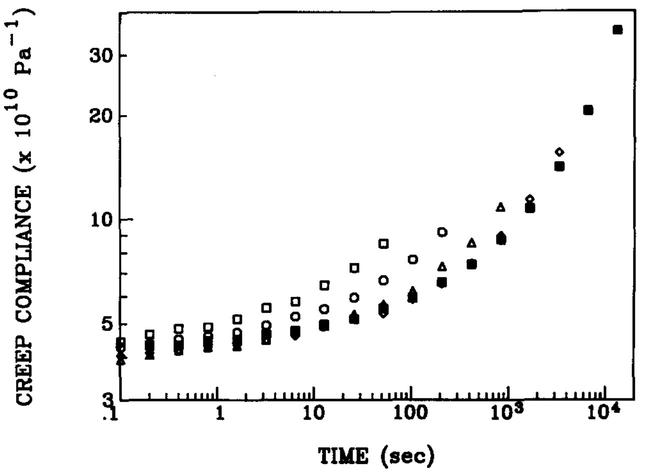

Figure 8 Double-logarithmic representation of the creep compliance *versus* time for different ageing times at $T=33.2°C$. The applied stress is 10 MPa and $t_1/t_e=0.028$. Ageing times: (□) 28 min; (○) 126 min; (△) 503 min; (◇) 2013 min; (■) 8052 min

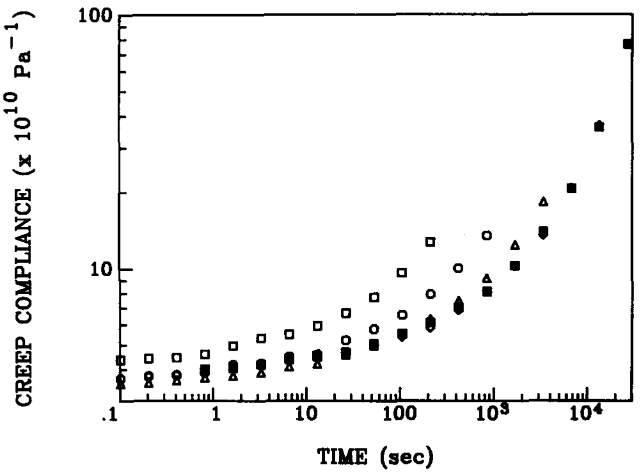

Figure 9 Double-logarithmic representation of the creep compliance *versus* time for different ageing times at $T=33.2°C$. The applied stress is 10 MPa and $t_1/t_e=0.112$. Ageing times: (□) 28 min; (○) 126 min; (△) 503 min; (◇) 2013 min; (■) 4026 min

compliance data were analysed using the KWW function and we found that time–ageing time superposition was valid. The values of τ and β are tabulated in *Table 3*. We note that while time–ageing time superposition is valid, time–stress superposition is not. In *Figure 10* we show a double-logarithmic representation of a_{te} *versus* t_e for the data obtained at 10 MPa. Interestingly, while there is a decrease in the value of μ with increasing t_1/t_e, the value of t^* appears to remain constant.

We also carried out experiments at $T_g-T=13°C$ and at stress magnitudes of 5, 10, 15 and 20 MPa. The results of the KWW analysis are tabulated in *Table 4*. Again, time–ageing time superposition was found to be valid but time–stress superposition was not, and the values of D_0 were nearly independent of stress while β varied with stress amplitude much as it did at $T_g-T=9°C$ (*Table 1*). In *Figure 11* we show a double-logarithmic representation of a_{te} *versus* t_e for each value of t_1/t_e and a stress level of 20 MPa. Again μ decreases with increasing t_1/t_e. The values of μ for the different stress levels are tabulated in *Table 5*. Note that, at this temperature, t^* was not reached in the time elapsed during these ageing experiments, i.e. $\simeq$64 h.

DISCUSSION AND CONCLUSIONS

As stated in the 'Introduction', the results of this study will be used to argue that large mechanical stimuli (deformations or stresses) do not act to rejuvenate polymer glasses. We have found that we can age glasses

Table 3 Kohlrausch–Williams–Watts curve-fitting parameters[a] ($T=33.2°C$)

σ (MPa)	t_1/t_e	t_e (min)	τ (s)	β
1	0.028	63	120.3	0.275
	0.028	252	401.4	0.277
	0.028	1006	985.6	0.272
	0.028	4026	1168.9	0.271
1	0.112	63	115.9	0.274
	0.112	252	378.5	0.273
	0.112	1006	966.7	0.270
	0.112	4026	1097.8	0.274
5	0.028	63	92.4	0.274
	0.028	252	252.3	0.276
	0.028	1006	601.9	0.276
	0.028	4026	687.6	0.272
5	0.112	63	75.9	0.289
	0.112	252	207.3	0.285
	0.112	1006	421.0	0.293
	0.112	4026	496.4	0.286
10	0.028	63	67.3	0.293
	0.028	252	162.0	0.299
	0.028	1006	339.5	0.296
	0.028	4026	406.9	0.293
10	0.112	63	56.1	0.312
	0.112	252	132.9	0.313
	0.112	1006	255.8	0.309
	0.112	4026	293.1	0.313
15	0.028	63	50.9	0.324
	0.028	252	112.9	0.321
	0.028	1006	195.2	0.318
	0.028	4026	206.3	0.322
15	0.112	63	42.1	0.353
	0.112	252	99.2	0.348
	0.112	1006	160.0	0.351

[a] Fit to equation (1) using a non-linear least-squares regression analysis[17]

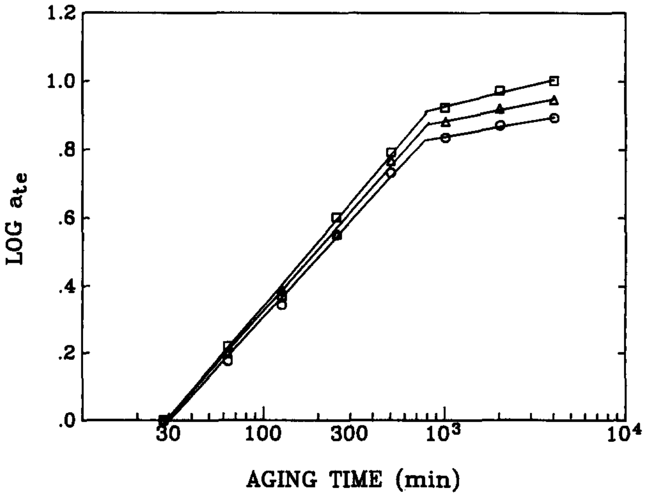

Figure 10 Log a_{te} *versus* ageing time for various values of t_1/t_e. The applied stress is 10 MPa. Results show the near-constancy of t^*, the time required to attain equilibrium. Values of t_1/t_e: (□) 0.028; (△) 0.056; (○) 0.112

Table 4 Kohlrausch–Williams–Watts curve-fitting parameters[a] (T=29.2°C, t_1/t_e=0.056)

σ (MPa)	t_e (min)	D_0 (×10^{10} Pa^{-1})	τ (s)	β
1	28	1.80	162.7	0.271
	63	1.79	313.6	0.275
	126	1.79	556.4	0.270
	252	1.80	1024.2	0.272
	503	1.80	1898.8	0.273
	1006	1.79	3417.3	0.271
	2013	1.80	6019.9	0.272
	4026	1.80	10087.5	0.270
5	28	1.74	128.2	0.281
	63	1.74	238.4	0.279
	126	1.75	391.0	0.276
	252	1.71	679.5	0.282
	503	1.70	1148.1	0.279
	1006	1.70	1961.5	0.282
	2013	1.69	2985.3	0.278
	4026	1.71	5011.7	0.276
10	28	1.85	98.5	0.304
	63	1.85	171.4	0.298
	126	1.82	266.4	0.296
	252	1.82	433.0	0.303
	503	1.84	678.5	0.300
	1006	1.84	1084.8	0.299
	2013	1.85	1678.5	0.303
	4026	1.85	2659.7	0.298
15	28	1.74	62.8	0.340
	63	1.73	99.8	0.334
	126	1.72	148.2	0.336
	252	1.72	227.0	0.341
	503	1.69	364.2	0.345
	1006	1.72	558.9	0.338
	2013	1.69	847.7	0.341
	4026	1.73	1261.7	0.337
20	28	1.87	42.2	0.389
	63	1.86	59.1	0.401
	126	1.86	92.8	0.402
	252	1.86	135.0	0.396
	503	1.91	202.6	0.404
	1006	1.86	282.7	0.400
	2013	1.97	396.6	0.402

[a] Fit to equation (1) using a non-linear least-squares regression analysis[17].

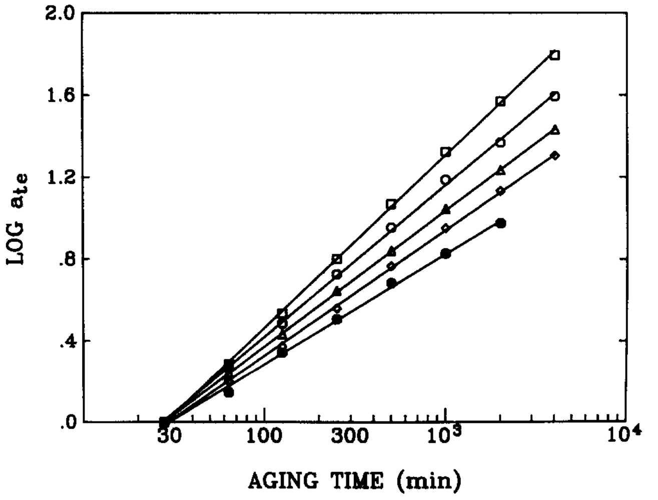

Figure 11 Log a_{te} *versus* ageing time for DGEBA/D400 glass aged at different applied stresses: (□) 1 MPa; (○) 5 MPa; (△) 10 MPa; (◇) 15 MPa; (●) 20 MPa. Test temperature = 29.2 ± 0.2°C

into an equilibrium state and that the time t^* required to reach equilibrium does not change when the amplitude of the intermittent stress applied to probe the ageing is increased. This is in spite of the fact that the 'signature' of rejuvenation is observed, i.e. the shift rate μ decreases as the stress magnitude increases. In addition, we have shown mechanical data that indicate that the state of equilibrium that is attained is the same whether or not large stresses are applied to the sample during the isothermal ageing into the equilibrium state.

Our interpretation of this result is that after a quench from above the glass transition temperature to below it, the volume recovery that occurs as the glass's structure (thermodynamic state) evolves towards equilibrium affects the viscoelastic response of the glass. At small deformations this can be decribed to a reasonable approximation by a time–ageing time superposition principle as first explored by Kovacs *et al.*[4] and subsequently developed extensively by Struik[5]. An increase in the amplitude of the stress applied in the physical ageing experiment results in a decrease in the shift rate μ simply because the changes in structure accompanying volume recovery affect the non-linear response differently at large stresses than at small ones. We emphasize that it does not mean that the structure of the glass is changed by the large mechanical stimuli.

An interesting way in which to envision this phenomenon is to imagine a three-dimensional volume–temperature–stress plot. We depict such a diagram in *Figure 12*. Note that we have chosen to label the stress axis

Table 5 Double-logarithmic ageing time shift rate μ (T=29.2°C, t_1/t_e=0.056)

σ (MPa)	μ
1	0.843
5	0.740
10	0.664
15	0.613
20	0.538

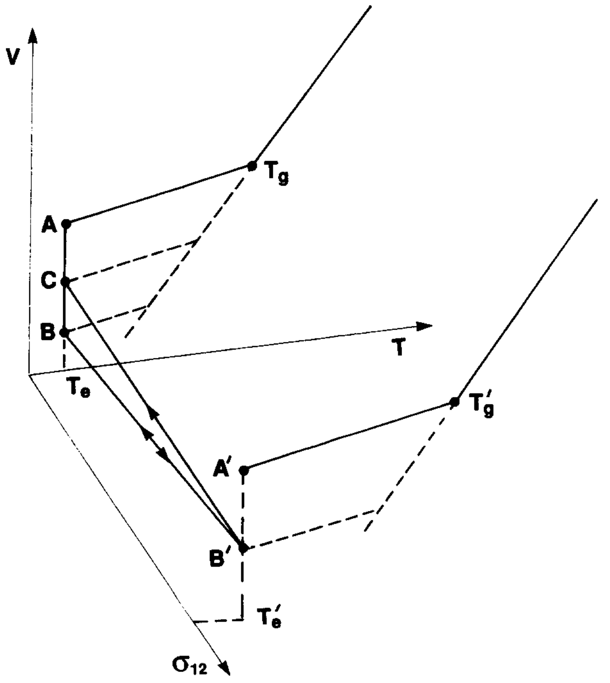

Figure 12 Schematic of the V–T–σ_{12} diagram showing comparison of stress-induced rejuvenation and no-rejuvenation hypotheses. We have depicted $T_e = T'_e$ as the temperature where the glass is aged. (See text for detailed discussion)

as σ_{12}, which is the deviatoric stress. We refer to this as a V–T–σ_{12} diagram[†]. Further imagine that, after the glass ages isothermally for a time t_e (line AB), we apply a large stress (line BB′). If the stress does not change the structure of the glass (i.e. no rejuvenation), then upon release of the stress the glass would return to the same point (B) on the V–T plane as prior to the application of the stress[†]. In the case of rejuvenation, the application of stress would effect a change in the glassy structure. In this case, upon release of the stress, the glass would return to a point (C) on the V–T plane that has a greater volume than that which the glass had prior to the stress application. Struik[5] argues that such a change may not be necessary and a change in the distribution of free volume could result in rejuvenation. We do not agree with this hypothesis. Furthermore since the observed kinetics of volume recovery do not appear to change (i.e. t^* does not change), we argue that the glass follows the path B′B upon unloading.

Examination of the V–T–σ_{12} diagram leads us to believe that, at any given state of volume and temperature, the stress response to a given deformation or the deformation response to a given stress would be influenced by the current values of volume and temperature. However, the large-deformation response would be less changed than the small-deformation response for a given volume change. The result is that the apparent stress–strain behaviour changes as the ageing (volume recovery) proceeds. This is depicted in *Figure 13* where we plot 105 s isochrones of the creep compliance *versus* the stress for different ageing times at $T_g - T = 13$°C. As can be seen, the small-stress response changes more upon ageing than does the large-stress response and the curves for the different ageing times begin to converge as the stress increases. This explains why there is a decrease in the shift rate μ while t^* does not change when the stress applied to probe the ageing increases.

Importantly, this interpretation implies that the mechanical response is coupled to the structure of the glass. However, the structure of the glass is not coupled to the mechanical stimulus. Thus, the V–T plane is independent of the σ_{12} axis in *Figure 12*. Obviously the details of the thermodynamics of systems subjected to mechanical stimuli is more complicated than outlined here. However, this picture suggests that it is simpler than previously thought.

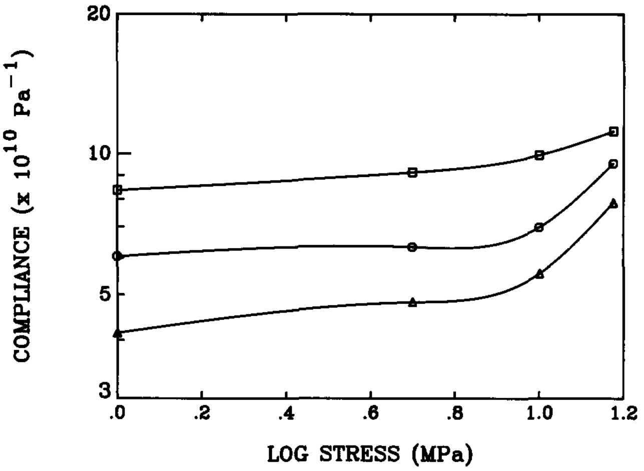

Figure 13 Double-logarithmic plot of compliance *versus* stress for 105 s isochrones at different ageing times: (□) 28 min; (○) 252 min; (△) 2013 min. Test temperature = 33.2 ± 0.2°C

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[†] This discussion of the V–T–σ_{12} diagram is simplified by assuming that the stress–strain response is elastic. The basic premise is not changed by viscoelasticity. However, the return to point B upon unloading might require a certain recovery time for the viscoelastic material. Presumably, the 'mechanical' recovery time would be related to the time for which the sample was subjected to the load. In typical ageing experiments this time would be shorter than the total ageing time. In fact, when t_1/t_e becomes very large it is conceivable that apparent rejuvenation could be observed because of the long 'mechanical' volume recovery time