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## Mechanical rejuvenation in polymer glasses: fact or fallacy?

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### Abstract

There has been considerable interest in the impact of mechanical stresses on the thermodynamic state of glassy materials over the past quarter century—beginning with Struik's hypothesized erasure of ageing by large stresses. In particular, there has been a recent application of the ideas of erasure or rejuvenation in the general literature on glasses and glass-like substances. For this reason we here examine the evidence for and against rejuvenation and show several sets of data that argue strongly against rejuvenation or erasure of ageing as viable explanations for the interactions between large mechanical stimuli and the structure of the glass. Two particular experimental conditions are of significance here. First, measurements that are made in the sub-yield region and close to the glass transition allow the direct measurement of the evolution of the glassy response both with and without applying any stress. For example, in torsional dilatometry experiments where the volume recovery is measured simultaneously and in the same apparatus as the mechanical response, it is found that the baseline volume recovery is unaffected by the applied stress. The second class of experiments has been post-yield experiments, where the rejuvenation hypothesis is more difficult to reject. However, observations that post-yield ageing leads to evolution into a different 'equilibrium' state as measured by the recovered yield stress suggest that yielding does not rejuvenate the glass, but it may lead to a sort of polyamorphism or new deformation induced phase. We also present results of mechanically induced 'implosion' in polymers far below the glass temperature that suggest that mechanical stimuli may actually accelerate ageing rather than rejuvenating the glass. Finally, the origins of the power-law dependence on ageing time (also termed elapsed or waiting time) of the mechanical relaxation time are discussed, and the use of the elapsed time as a natural variable to describe ageing is shown not to be appropriate for structural glasses.

## 1. Introduction

Glassy materials are out of equilibrium and, consequently, exhibit a continuous evolution of the thermodynamic state of the material towards equilibrium [1–6]. The evolution of the thermodynamic state is referred to as structural recovery and experimental measurements of these changes are generally made using volume dilatometry or calorimetric experiments. The general features of structural recovery have been well documented, and we do not deal with them here. A practical aspect of structural recovery is that, as it occurs, it is accompanied by changes in other properties such as mechanical or dielectric relaxation, yield stress, fracture resistance, etc, in a process referred to as physical ageing [6–10]. Physical ageing interests us in the present paper because the apparent reversal of ageing due to large mechanical or other stimulus has become a topic of significant import in recent years, not only in structural glasses but in colloidal systems, ferroelectric relaxors and spin glasses [11–21]. Therefore, it is important to understand this phenomenon in structural glasses to set the stage for an understanding of rejuvenation that may be important in other, related, systems.

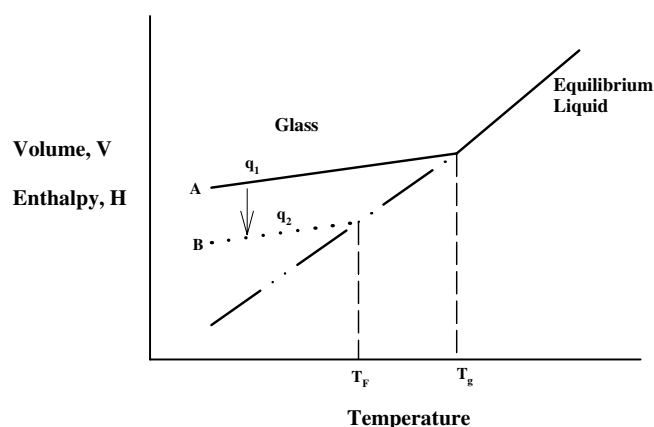
Historically, Struik [6] was the first to remark on what he referred to as erasure of ageing due to the application of large deformations to a sample. The simple ageing experiment is straightforward and the results for the erasure counterpart are not in question. The questions that have arisen are due to interpretation, and this will be one focus of the present work. First, we describe the simple ageing and erasure scenarios. Referring to figure 1, which depicts a schematic of a volume–temperature surface for a glass-forming system, such as an amorphous polymer where no crystallization occurs, we define a temperature-jump experiment which begins at equilibrium above the glass transition temperature. Upon cooling rapidly, the sample volume (and enthalpy) departs from equilibrium—hence the glassy state. Note here that extrapolation to the equilibrium line along a line parallel to the glassy line from any point in the glassy state leads to the definition of the fictive temperature  $T_F$  that will be discussed later. If we stop the cooling at a temperature  $T_a$  (ageing temperature) and sit isothermally and isobarically, the thermodynamic state variables (volume and temperature) evolve towards equilibrium, namely, they undergo structural recovery. Typical volume recovery curves are shown in figure 2 for polystyrene subjected to temperature jumps from above to below  $T_g$ . Associated with the changing structure are changes in mechanical properties. Figure 3 shows a mechanical loading sequence proposed by Struik to probe the viscoelastic response of the glass as structural recovery occurs [6, 24]. Note that the loading time  $t_i$  is always less than or equal to the elapsed ageing time  $t_e$  by a factor of ten. This ensures that the mechanical probe is not influenced significantly by the ongoing structural recovery and a true ‘snapshot’ of response is obtained. Figure 4 shows the response of the creep compliance of an epoxy glass as a function of ageing time and we see that it shifts to longer timescales as the time elapsed after the quench increases. This response is referred to as physical ageing. Struik [6] put physical ageing on a firm footing in his seminal work when he demonstrated that time–ageing time superposition can be applied to such curves and a ‘master’ curve could be obtained. In Struik’s work he used a stretched exponential to fit the creep data:

$$D(t) = D_0 e^{(t/\tau)^\beta} \quad (1)$$

where  $D_0$  is a zero time compliance,  $\tau$  is a characteristic retardation time and  $\beta$  is a stretching exponent that is related to the breadth of the retardation process. Then, the time–ageing time shift factor  $a_{te}$  is written:

$$a_{te} = \frac{\tau}{\tau_{ref}} \quad (2)$$

where the subscript *ref* refers to a reference ageing time (and, in the general case, temperature).



**Figure 1.** Schematic of the volume or enthalpy behaviour upon cooling of a glass-forming liquid. The  $q_i$  represent different cooling rates with  $q_1 > q_2$ . The arrow denotes structural recovery during isothermal ageing.  $T_g$  is the glass transition temperature on cooling at  $q_1$ .  $T_F$  denotes the fictive temperature for a material aged isothermally along the arrow to the glassy line B.

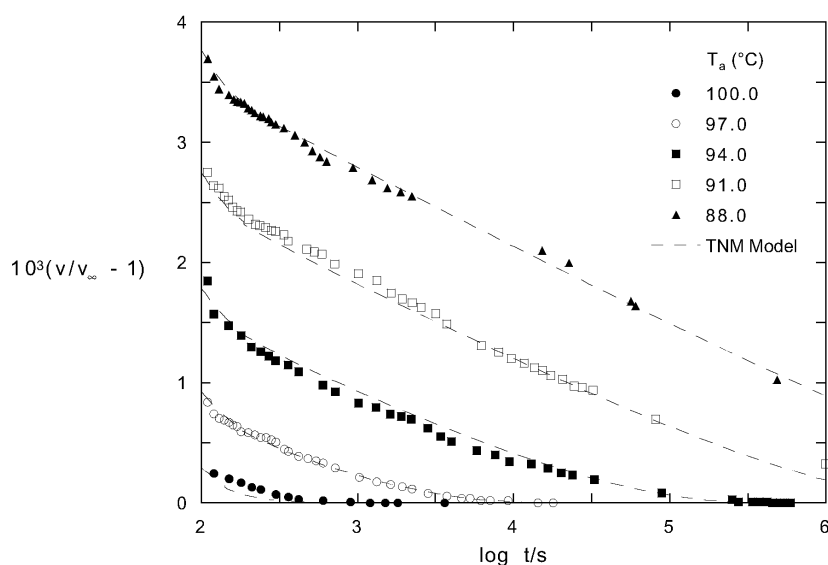
A double logarithmic plot of the shift factors versus ageing time is presented in figure 5 for a polycarbonate glass where we see that there is a general power-law behaviour for the material response [6, 24]:

$$a_{te} = At_e^\mu. \quad (3)$$

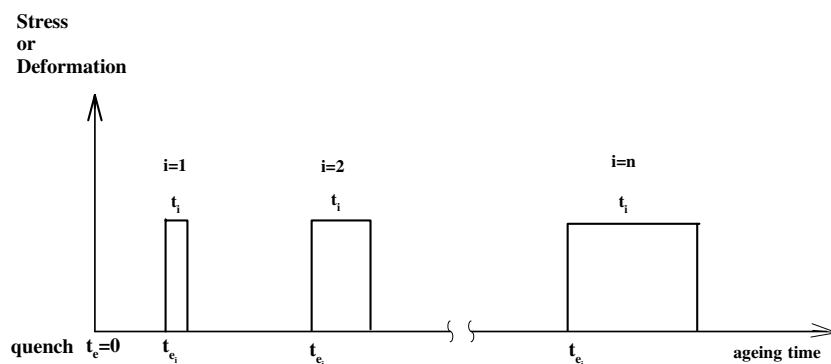
Struik found that the power law exponent  $\mu$  was in the neighbourhood of unity, though it varied considerably with temperature, as illustrated in figure 6. This power-law relationship has recently been used in the description of ageing in spin glasses, pastes and colloids and has been alluded to as the Struik elapsed time theory [18, 20, 22]. We discuss this subsequently. The ageing range where the exponent was nearly constant was generally found to be broader than in figure 6, but it is clear that at high temperatures and near to the glass temperature  $\mu$  tends towards zero. The lower temperature limits for ageing were originally related to the sub-glass relaxations [6], although this explanation is no longer widely accepted [26–28].

Struik then did a very interesting set of experiments in which the mechanical probes of figure 3 were increased in magnitude. The result is illustrated schematically in figure 7. In the illustration we show that at small stress levels the amount of time–ageing time shifting is significantly greater than it is at large stresses. The effect is to reduce the slope of the  $\log a_{te}$  versus  $\log t_e$  plot, as illustrated in figure 8 for an epoxy glass. Struik referred to this effect as erasure of prior ageing. McKenna and Kovacs [29] were the first to use the term ‘rejuvenation’ to refer to the effects of large stresses on physical ageing, and it has caught on, perhaps because Smith was captivated by the word<sup>1</sup>. Regardless, as we discuss subsequently, it is unclear whether or not glasses rejuvenate (or are erased) by mechanical deformations. Hence the question in the title of the present work: ‘fact or fallacy.’ In the rest of this work we discuss the interpretations of the simple erasure experiment described above and present

<sup>1</sup> It is of historical interest that T L Smith visited A J Kovacs in the summer of 1983, just after the present author had completed a 20 month stay as a visiting scientist at the CRM (now ICS) in Strasbourg. Smith found that Kovacs’ use of the word ‘rejuvenation’ resonated and took it back and used it frequently when referring to the potential impact of large mechanical stimuli on the structure of polymer glasses. When Kovacs and I used the word, however, it had been tongue in cheek as he was old and I was young (at the time). Note that, in fact, the first usage of the meaning was in French and Kovacs discussed *vieillessement* (ageing) and I discussed *rajeunissement* (rejuvenation) in internal meetings at the CRM.



**Figure 2.** Volume recovery in a polystyrene glass after temperature jumps from 104 °C to the temperatures indicated. The volume departure from equilibrium is depicted on the ordinate and the logarithm of the time after the beginning of the quench is depicted on the abscissa. (After [23] with permission.)

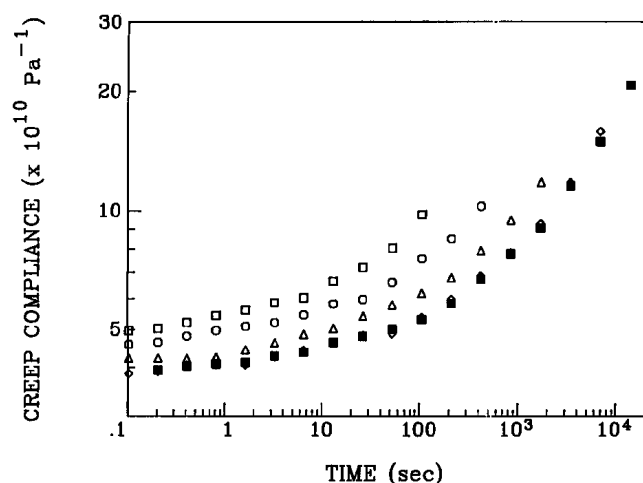


**Figure 3.** Schematic of sequential loading history applied to samples after a quench from above  $T_g$  to below it. Note that the  $t_{ei}$  represent increasing ageing times where  $t_{ei+1} \propto 2t_{ei}$ . The  $t_i$  are the loading times and  $t_i/t_{ei} \leq 0.10$ .

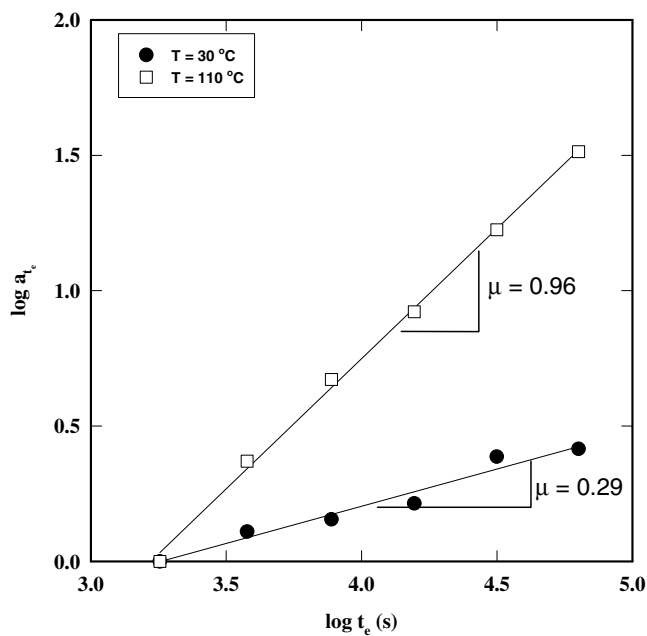
data that refute that interpretation. We also present other ‘evidences’ for rejuvenation from more complex mechanical histories and provide other experimental and analytical evidence that supports the view that rejuvenation is not the only interpretation of the results. In the last section of the paper we remark on the meaning of physical ageing and the apparent power-law dependence of the relaxation time on the elapsed time after a quench.

## 2. The simple erasure experiment—evidence against rejuvenation

The results of the simple erasure experiment have been interpreted in the rejuvenation framework to conclude that the application of large mechanical stresses to the polymer glass

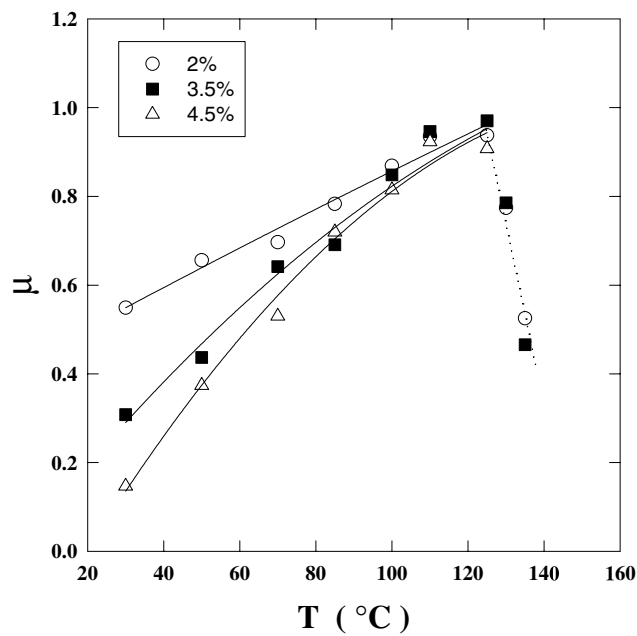


**Figure 4.** Creep compliance curves for an epoxy glass tested according to the protocol shown in figure 3 after a quench from above to approximately 9 K below the glass temperature. The ageing times in minutes are: (□) 28; (○) 126; (△) 503; (◇) 2013; (■) 4026. (After [11].)

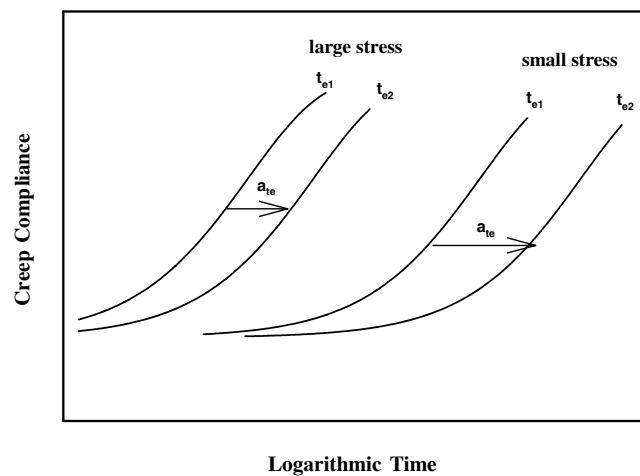


**Figure 5.** Typical behaviour for the ageing time shift factor as a function of ageing time in the ‘power-law regime’ for a polycarbonate tested at a torsional strain of 3.5% and at two test temperatures, as indicated. Shift rate  $\mu$  is indicated as the slope of the lines. (After [24].)

has the same effect as moving the thermodynamic state closer to the freshly quenched state. This is illustrated in figure 9, as adapted from the work of Ricco and Smith [14]. Another possible way of looking at the problem is that proposed by Struik and illustrated schematically in figure 10 [6]. Here we see that the application of a large mechanical perturbation is conceived to cause a deviation of the volume recovery path away from that which the structure would

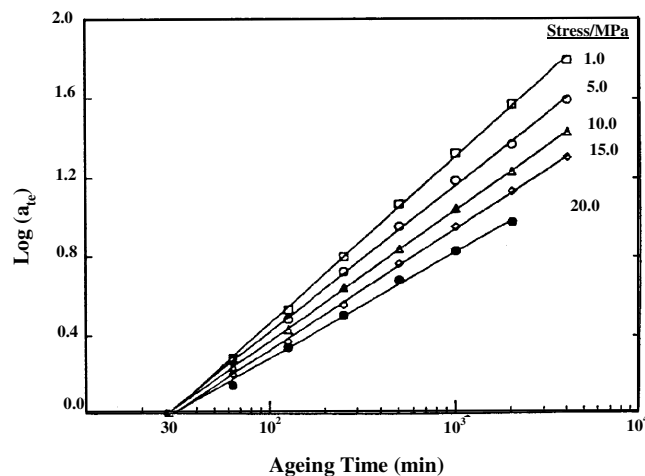


**Figure 6.** Shift rate in the power-law regime for a polycarbonate glass as a function of temperature and strain magnitude. The glass transition of the material is approximately 142  $^{\circ}\text{C}$ . (After [24].)



**Figure 7.** Schematic of the impact of large stresses on the ageing time shift factor in a creep experiment. See text for discussion. (After [10].)

follow without a mechanical perturbation. Since figures 9 and 10 present conceptions of how rejuvenation should look we use them to form the basis of the present discussion. It is important that, if erasure or rejuvenation takes place, the material should be ‘kicked’ back towards the freshly quenched state. Furthermore, because it is moved back towards the freshly quenched state, one would expect that the underlying structural recovery should change. This latter observation is important because it suggests that the mechanical stimulus to the material



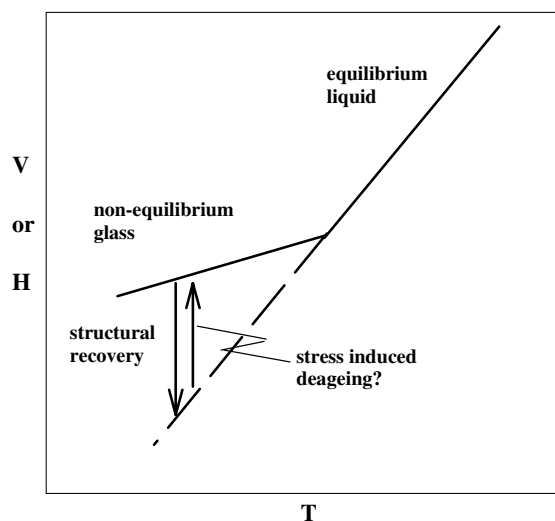
**Figure 8.** Plot of shift factor versus ageing time in the power-law ageing regime at different probe stresses, as indicated. The reduction in the slope of the lines, i.e. the shift rate, is illustrative of one ‘rejuvenation’ signature. (After [11].)

not only results in a departure from the local equilibrium, such as one would observe in a fluid at equilibrium, but that it also alters the underlying structure of the glass. Resolution of the problem is of great importance because it defines the level of complexity required to describe the mechanical response of glassy materials. If the mechanical perturbation alters the underlying structure of the glass, this must be accounted for explicitly in any constitutive law description of the behaviour. On the other hand, if the rejuvenation hypothesis is not correct, the mechanical response is a function only of the current state of the glass and one is not required to consider explicitly any alterations in the glassy structure due to the mechanical perturbations. In this section we consider two evidences for an independence of the glassy structure from mechanical perturbations—hence results that are contrary to the rejuvenation hypothesis.

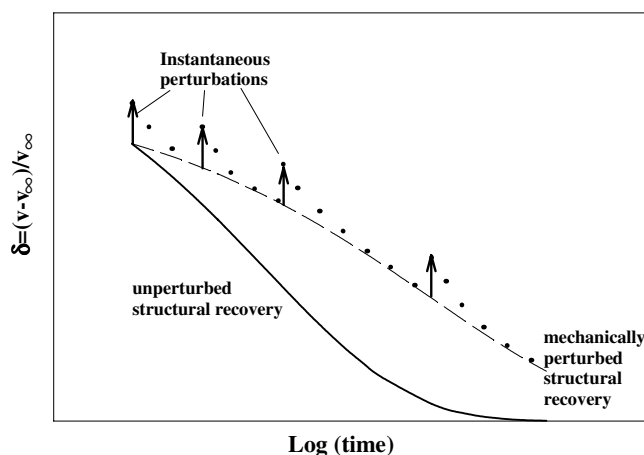
### 2.1. The $t^*$ experiment

Just as the volume or enthalpy of the glass recovers towards its equilibrium value during structural recovery, one expects that the mechanical response will also recover into an equilibrium behaviour. Figure 11 provides evidence that this is the case for a polycarbonate glass, where we see that the ageing time shift factor, normalized to zero at an ageing time of 1800 s for all temperatures, curves over at temperatures close to the glass transition, hence reaching equilibrium [24]. If the rejuvenation hypothesis were correct, one would expect that the time to attain equilibrium would become longer as the stress became higher because the applied stresses erase some of the prior ageing. Figure 12 illustrates several possible results based on the rejuvenation hypothesis, an acceleration hypothesis put forward by Sternstein [30] and discussed subsequently, and a decoupling hypothesis. By setting a parameter  $t^*$  as an estimate of the equilibration time, we can ask if  $t^*$  increases, decreases or remains the same in experiments in which the probe stress in the Struik protocol (figure 3) is varied systematically at temperatures close enough to the glass transition that equilibrium is attained. Figure 13 presents results from a study on an epoxy glass by Lee and McKenna in which the signature of rejuvenation is present, namely, the ageing rate  $\mu$  decreases as the applied (probe) stress





**Figure 9.** Schematic of the effects of large probe stresses on the thermodynamic state of the glass in the rejuvenation hypothesis. (Adapted from [14].)



**Figure 10.** Schematic of perturbed structural recovery expected to occur after large mechanical stimuli are applied to an ageing glass according to the rejuvenation concept. (Adapted from [6].)

increases. Yet the value of  $t^*$  remains unchanged within experimental uncertainty. This result is strongly suggestive that rejuvenation, in the sense of figures 9 and 10, does not occur. However, the mechanical measurement is, perhaps, not definitive because it has been variously shown that the timescales required to reach equilibrium may depend on what property is being measured [12, 23, 32–36]. For example, McKenna and co-workers [12, 32] report a shorter equilibration time for the mechanical response than for the volume, and Simon and co-workers [33, 34] have reported differences among mechanical, volume and enthalpy recovery times. The next section describes measurements of the volume response, one of the measures of glassy structure.

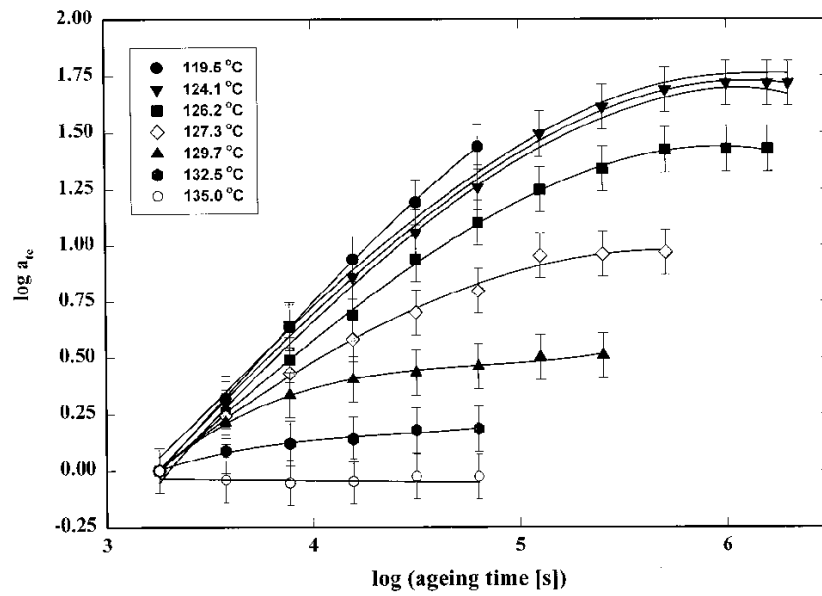


Figure 11. Double logarithmic representation of the ageing time shift factor versus the ageing time for a polycarbonate glass near to the glass transition temperature. (After O’Connell and McKenna [24].)

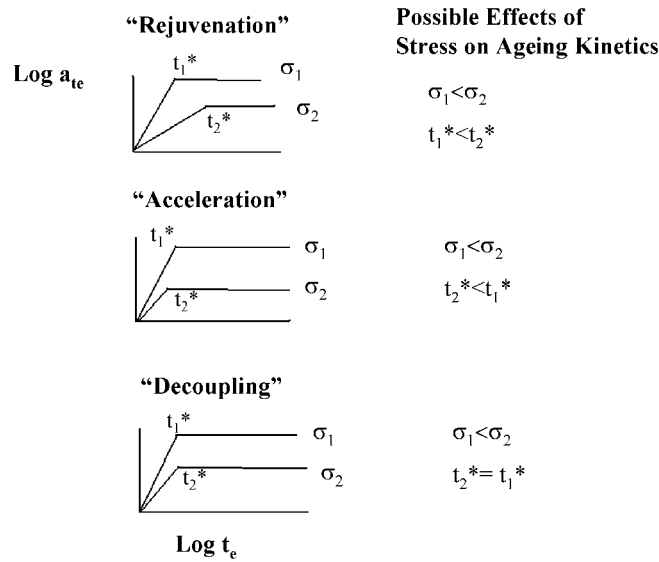
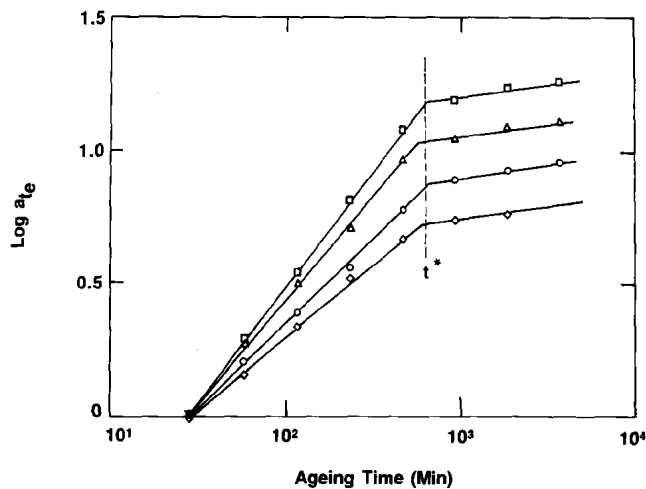


Figure 12. Schematic of the possible effects of mechanical probe on the equilibration time  $t^*$  as determined from the ageing time shift factor versus ageing time plot. Rejuvenation, acceleration and decoupling hypotheses are compared.

2.2. The torsional dilatometry experiment

The torsional dilatometry experiment addresses more directly the rejuvenation hypothesis that the volume recovery (that takes place after a quench and that is responsible for the time–



**Figure 13.** Effect of probe stress magnitude on nominal equilibration time  $t^*$  for an epoxy glass. The figure shows that there is no effect of stress on  $t^*$ . Stress magnitude: (squares) 1 MPa; (triangles) 5 MPa; (circles) 10 MPa; (diamonds) 15 MPa. (After [11].)

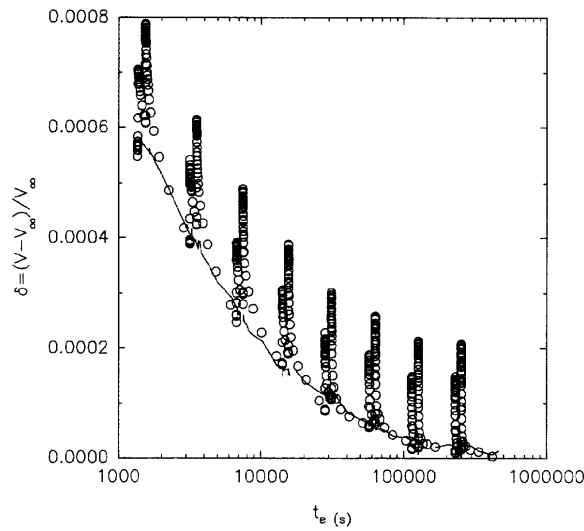
ageing time shifting of the mechanical response) is altered by large applied stresses or strains. In this experiment one simultaneously measures the mechanical and volumetric responses and directly tests the rejuvenation hypothesis. Using the torsional dilatometer built at NIST [37], McKenna and co-workers performed experiments in which both structural recovery (volume) and the mechanical relaxation response were measured after  $T$  jumps from above to below the  $T_g$ . Their results showed that, contrary to the rejuvenation suggestion illustrated in figure 10, large deformations do not affect the underlying volume recovery of the glassy material [12, 38]. Rather, for torsional experiments to strains well into the nonlinear viscoelastic regime, the underlying volume recovery response of the deformed material is identical to that of the undeformed material. This is illustrated in figure 14 where it is clear that, although the torsional deformation causes an instantaneous increase in the volume, it always relaxes back to the response of the undeformed specimen. This is direct evidence that, at least close to the glass transition temperature and at deformations below the yield point, the volume part of the glassy structure is not rejuvenated by the mechanical stimulus.

### 2.3. Rejuvenation in other mechanical histories

There are two other sub-yield mechanical histories that have been purported to support the concept of rejuvenation. These are experiments in which the material is subjected to a large deformation followed by a small probe deformation. One such experiment is illustrated in figure 15 where the large deformation remains on the sample while the probes are applied. The observation in such experiments is that the incremental response shifts to shorter times than the linear viscoelastic response and subsequently begins ageing again. Here, as in other experiments, there is no question of the results. The question is one of interpretation. The incremental modulus from experiments such as outlined in figure 15 is defined as

$$\Delta G(\gamma_1, t_e, t) = \frac{\Delta \sigma(t)}{\Delta \gamma} \quad (4)$$

where  $\Delta G$  is the incremental modulus,  $\gamma_1$  is the large deformation,  $t_e$  is the elapsed time after imposition of the large deformation,  $t$  is the time after imposition of the small probe strain  $\Delta \gamma$



**Figure 14.** Plot showing comparison of the structural recovery for the unperturbed glass (full curve) and for the sample loaded into the nonlinear regime using the Struik protocol. Results show the underlying structure is unchanged by the large deformations. (After [40].)

and  $\Delta\sigma$  is the incremental stress response (see figure). Figure 16 shows the response observed for a polymer glass [39] with the incremental modulus shifted to shorter times, implying that the material is softened relative to the linear viscoelastic response. The general features of the incremental modulus attributed to rejuvenation in this sort of experiment are [15, 39]:

- (1) Shift of response to shorter times (increased molecular mobility or softening).
- (2) Re-initiation of ageing. The incremental response shifts back towards the linear viscoelastic response.
- (3) The magnitude of the effect increases as the applied deformation increases.

McKenna and Zapas [39] used a nonlinear viscoelastic constitutive equation to address the interpretation of the above results. Without going into details of the analysis, we present the salient analytical expression for the incremental modulus based on the non-linear material model:

$$\Delta G(\gamma_1, t_e, t) = \phi(\gamma_1, t + t_e) + G(t) - G(t + t_e) \quad (5)$$

where  $\phi(\gamma, t)$  is the secant modulus at the nonlinear relaxation modulus at the relevant arguments and  $G(t)$  is the linear relaxation modulus. Equation (5) defines a very interesting set of results. First, at small deformations  $\phi(\gamma, t + t_e) = G(t + t_e)$  and equation (5) reduces to  $\Delta G(\gamma_1, t_e, t) = G(t)$ . That is, we recover the linear response. Second, at large elapsed times, i.e.  $t_e \rightarrow \infty$ ,  $\phi(\gamma, t + t_e) = G(t + t_e) = 0$  and therefore we again have  $\Delta G(\gamma_1, t_e, t) = G(t)$ . In addition, for most nonlinear materials strain softening occurs prior to yield and  $\phi(\gamma, t + t_e) \leq G(t + t_e)$ , which means that, for all deformations in the nonlinear range,  $\Delta G(\gamma_1, t_e, t) \leq G(t)$ . Therefore, we qualitatively reproduce items 1–3 above. Upon application of a large strain the incremental modulus is reduced (shifts to shorter times) and as elapsed time gets longer the values of  $\phi(\gamma, t + t_e)$  and  $G(t + t_e)$  become closer to zero and the incremental modulus response evolves towards the linear modulus. Hence it appears that one has softening followed by re-initiated ageing. Figure 17 shows the evolution of the response for the same PMMA glass as measured and as predicted by the nonlinear constitutive

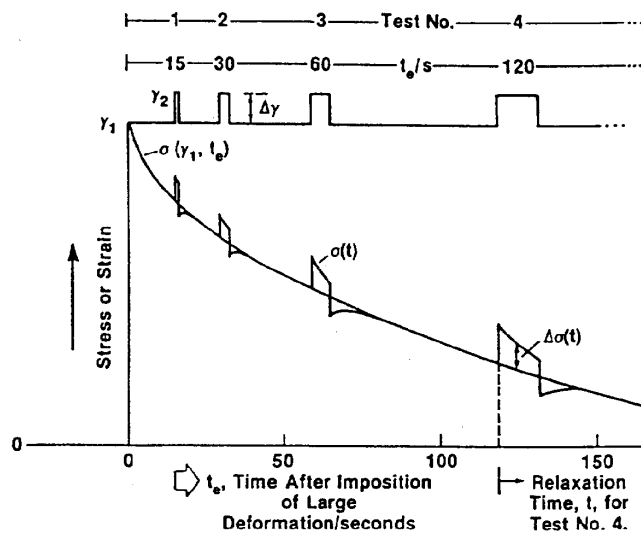


Figure 15. Schematic of strain history for superposition of small deformations on large, showing how the incremental modulus  $\Delta G(t)$  is determined from  $\Delta\sigma(t)/\Delta\gamma$ . (After [39].)

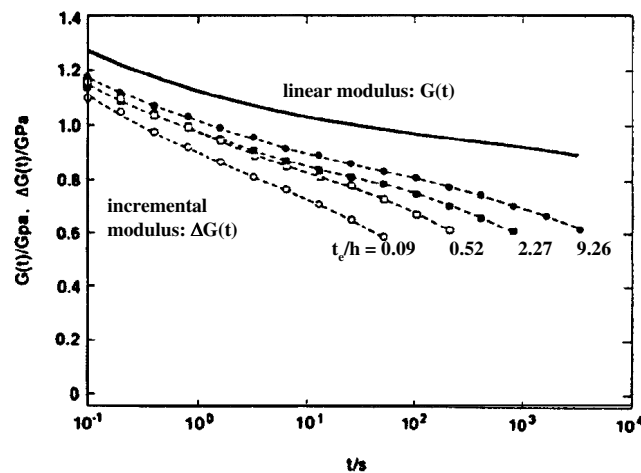
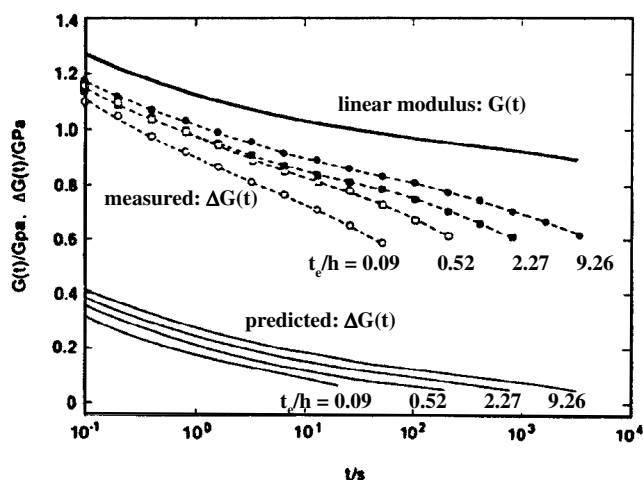


Figure 16. Comparison of incremental and linear viscoelastic response for a PMMA glass at room temperature. The magnitude of the large deformation was  $\gamma_1 = 0.05$  and the probe or incremental strain was  $\Delta\gamma = 0.005$ . (After [39].)

model. While the constitutive model does not capture the actual response quantitatively it does capture the qualitative features of the response, in particular the softening and re-initiation of ageing. It is interesting that the model over-predicts the degree of softening. This might be interpreted to imply that the large mechanical deformations harden the material rather than softening it. Regardless, it is clear that the material response contains at least a component of 'fading memory' that explains a portion of the results.

A similar experimental result is one in which the sample is partially aged, then a large stress or deformation is applied for a short time and this is followed by a series of probe experiments as shown in figure 18. Again, the results give an initial softening followed



**Figure 17.** As in figure 16 but with nonlinear viscoelastic model predictions for incremental response showing much greater softening than the actual measurement. (After [39].)

by a re-initiated ageing behaviour. Waldron *et al* [40] used a nonlinear constitutive law to quantitatively describe such behaviours in an epoxy glass. The analysis is beyond the scope of the present paper, but the conclusion is the same as that of McKenna and Zapas [39]. Much of the behaviour attributed to rejuvenation of polymeric materials subjected to sub-yield deformations or stresses is most likely due to memory effects in nonlinear viscoelastic materials rather than to a strong interaction between the large mechanical impulses and the underlying structure (thermodynamic state) of the glass. An interpretation of this behaviour is given in the 3D drawing of figure 19 where we illustrate a  $v$ - $T$ - $\sigma_{12}$  surface. In the  $v$ - $T$  plane, upon cooling, we go through a conventional glass transition and, upon sitting isothermally, find a structural recovery. If we allow the sample to age from A to B, and then apply a shear stress  $\sigma_{12}$  we move out the  $\sigma_{12}$  axis (B to B'). In the  $v$ - $T$  plane at this value of  $\sigma_{12}$  there is, of course, a corresponding thermodynamics. (For example the Gibbs-DiMarzio [41, 42] model would predict that a shear stress would increase the glass transition temperature.) Upon unloading, the diagram illustrates two possible paths. The first path from B' to B would be a 'decoupled' path in which the underlying thermodynamic state is unchanged. On the other hand, if rejuvenation occurs, the path B' to C would be followed. The sum of results presented to this point suggests strongly that the path followed is from B' to B and that rejuvenation does not occur.

### 3. Mechanical erasure above the yield point

In the deformation histories examined above, the material was always loaded in the regime below the yield regime. Yet there has been a significant amount of work in which the material response was measured above the yield point and rejuvenation was postulated [17, 43–47]. While it is possible that rejuvenation occurs here, the present author suggests that it is more likely that the material response is actually a form of phase transformation induced by yield [48–51]. Because the pre- and post-yield responses are between two glassy states, it is further speculated that the yield is accompanied by a polyamorphic transition similar to that seen in computer simulations of glassy H<sub>2</sub>O and other network glasses and which is induced by



experiment. The peak increases with increasing ageing time [2, 3, 5, 57–59]. The excess enthalpy peak is related to the loss of enthalpy during ageing due to structural recovery. Figure 20 illustrates the behaviour in enthalpy space and figure 21 illustrates the behaviour in heat capacity space. The latter is understood because it is a result of the fact that the apparent heat capacity is simply the slope of the enthalpy–temperature curve. Such behaviour is generally described fairly well using the so-called Tool [61]–Narayanaswamy [62]–Moynihan [63] model for structural recovery and can be expressed in integral form as follows:

$$\delta_H(z) = \Delta C_p \int_0^z R(z - z') \frac{dT}{dz'} dz' \quad (6)$$

where  $\Delta C_p$  is the heat capacity change at the glass transition,  $T$  is the temperature, the time variable is the reduced time  $z$ :

$$z = \int_0^t \frac{d\xi}{a_T a_{\delta_H}} \quad (7)$$

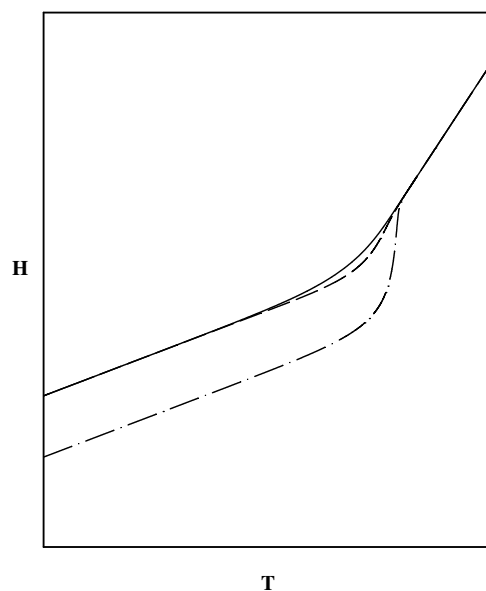
and  $a_T$  and  $a_{\delta_H}$  are the temperature shift factor and structure shift factor, respectively. Here we follow Kovacs' [1] approach and use the departure from equilibrium  $\delta_H(t)$  as the measure of structure where

$$\delta_H(t) = H(t) - H_\infty \quad (8)$$

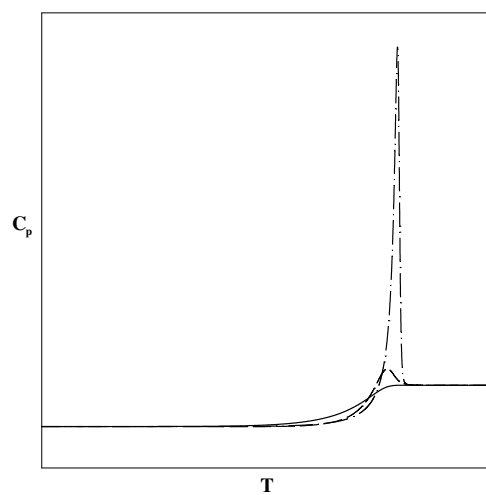
and  $H(t)$  is the present enthalpy and  $H_\infty$  is the equilibrium value of the enthalpy. The hereditary integral of equation (6) is nonlinear in the departure from equilibrium (enthalpy) because the equation is linear viscoelastic in reduced time. Equations of the form of equation (6) capture the major phenomena of structural recovery, namely intrinsic isotherms, asymmetry of approach and memory effect, and an extensive discussion of these phenomena is beyond the scope of the present work. It is important to remark, however, that the equations shown above illustrate that the structure of the glass (here the enthalpy) is path-dependent. Therefore, one might also expect that not accounting for the full viscoelasticity of the enthalpy of the system might lead to misinterpretation of the data. Unfortunately, a full incorporation of yielding phenomena into a formalism related to equation (6) has yet to be accomplished, although some progress has been made within the rational mechanics framework by Caruthers' group at Purdue University [64–67]. Therefore, we simply relate the observations that have been made in enthalpy measurements and ask if the rejuvenation interpretation is a unique interpretation. We present the data suggesting a polyamorphic transition in the subsequent section.

Figure 22 illustrates the effects of stressing a material on the apparent heat capacity of an aged polymer as measured by DSC [17]. As can be seen, as the magnitude of the stress increases, the magnitude of the excess enthalpy peak decreases [17, 68]. It is this specific feature that has been interpreted as rejuvenation of the glass due to the mechanical stimulus. However, we remark on two things. First, associated with the reduction of the excess enthalpy peak is the onset of a sub-glass transition minimum which has yet to be fully explained. In fact, were simple rejuvenation taking place, the DSC trace for the yielded material should look like the unaged or freshly quenched material. Since this is not the case, alternatives to rejuvenation need to be considered. In addition, we remark that similar effects are seen when glass-forming materials are subjected to hydrostatic compressions and ageing is performed [69]. This scenario is mechanically different from yielding, which is shear dominated. Such results need to be considered in building a picture of the calorimetric behaviour of mechanically stressed materials. One alternative view of yield and its effects on the glassy state is presented next.





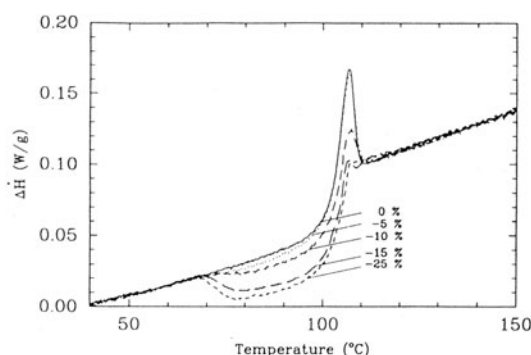
**Figure 20.** Schematic of the enthalpy versus temperature behaviour of a glass-forming substance in different thermal histories. The full curve is for a cooling history and the broken curve is for the immediate reheating scan at the same rate. The chain curve is for a heating scan after the material has been cooled, allowed to partially recover (age) and has then been reheated at the same rate. (After [60].)



**Figure 21.** Schematic representation of the heat capacity during DSC scans for different thermal histories: the full curve is for cooling at a rate  $q$ . The broken curve is for heating at a rate  $q$  immediately after cooling at the same rate. The chain curve is for heating at a rate  $q$  after ageing the sample. Note the large excess enthalpy for the peak and the shifting of the apparent position of the glass transition. (After [60].)

### 3.2. A mechanically induced polyamorphism

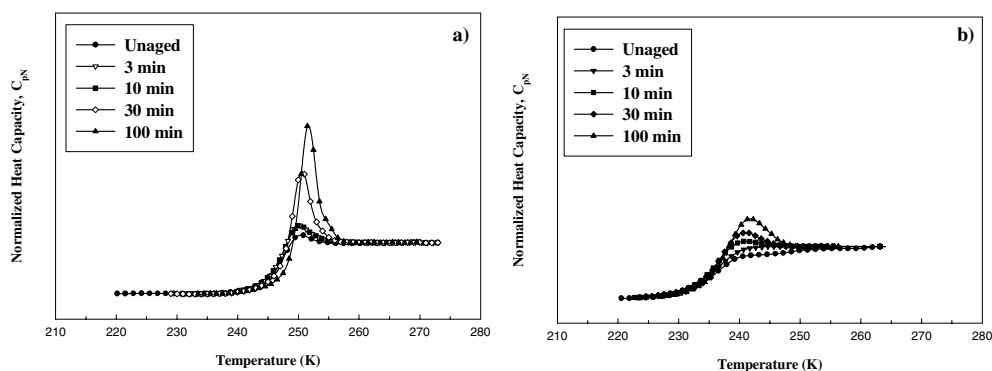
Before showing the results of ageing and yield of an epoxy glass that suggest polyamorphism, we present a brief result that shows a reduced excess enthalpy upon ageing but that is attributed



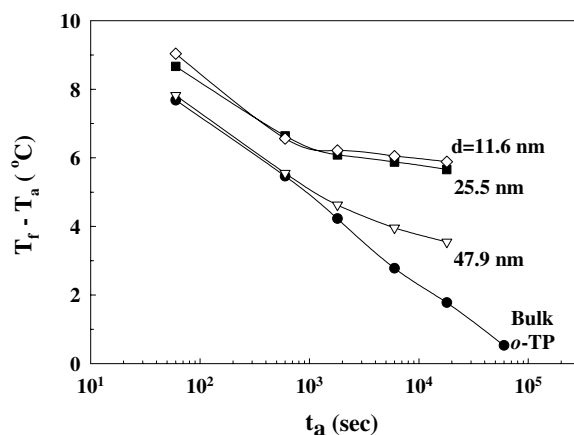
**Figure 22.** Heat flow versus temperature for a polystyrene subjected to strain levels from unstrained (0%) to strains above the yield (>10%) in compression, showing the influence of mechanical deformations on the excess enthalpy peak. Also note the large pre-transition minimum in the heat flow that also increases as the magnitude of the strain increases. (After [17], with permission.)

to the ageing taking place to a different thermodynamic state from that expected [70]. The experiment is as follows. Take a glass-forming liquid and confine it in a nano-porous matrix. Quench from above  $T_g$  to below and follow the structural recovery using the DSC approach described above. The evolution of the excess enthalpy peak in the pores is very different from that in the bulk glass as shown in figure 23. In fact, analysis of the data in terms of the fictive temperature (see the introduction) results in the surprising finding that the material confined in the pores ages to a different state than that in the bulk, as evidenced by the fact that  $T_a - T_F > 0$ . This is illustrated in figure 24. Simon *et al* [70] have analysed this problem in the context of the TNM model [61–63] and find that the new state is that formed by a hydrostatic tension induced isochoric (constant volume) [71] glass transition. This suggests that DSC measurements of glass-forming materials subjected to different thermo-mechanical (*PVT*) paths may not be easily analysed without a proper model of the interactions of the mechanical path and the enthalpy path (in the case of DSC). The signature of reduced excess enthalpy has nothing to do with rejuvenation and can be modelled in terms of normal enthalpy recovery in an isochoric state followed by a DSC scan in which the material goes from the isochoric state into the isobaric state. Might such behaviour apply to the yielded material with a difference in the equilibrium properties between the yielded state and the isobaric, non-yielded state? While further work is probably needed in experimentation (perhaps deformation calorimetry similar to the deformation dilatometry described previously) and modelling of the condition, we now provide one piece of evidence to suggest that yield is a polyamorphic transition.

Take a glassy epoxy and quench it to below the  $T_g$  and perform ageing experiments for long enough times that equilibrium can be reached, similar to figure 11. However, we now measure the evolution of the shear yield stress after the thermal quench. Aboulfaraj *et al* [72] have carried out such tests. In addition, they performed tests in which the sample was ‘mechanically quenched’ by shearing through the yield point and then reversing the shear to zero deformation. The rebuilding of the yield stress after the ‘mechanical quench’ was followed as a function of elapsed time. The build-up of the yield stress after a thermal quench and after the large shear is shown in figure 25. As seen, the material responses follow a similar rate  $d\sigma_y/d \log t_e$  and also have similar times to equilibration. The important point to take from figure 25 is that the ‘equilibrium’ values of the yield stress  $\sigma_y$  for the thermally quenched and for the ‘mechanically’ quenched material differ greatly. If the sample was truly rejuvenated then the equilibrium value of the yield stress should be identical for the two cases. Hence the suggestion that yield is a

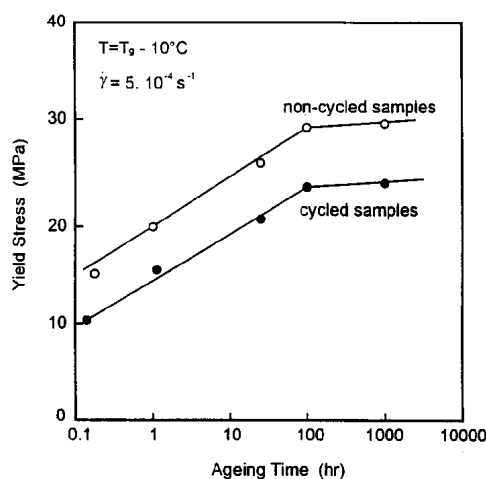


**Figure 23.** A comparison of the development of the enthalpy overshoot as a function of time for *o*-terphenyl (a) in bulk and (b) in 11.6 nm pores. The ageing temperature was  $T_g - 11$  °C. Ageing times are indicated in figures. (After [70].)



**Figure 24.** Structural recovery of *o*-TP in the bulk and in nanometre pores of the size indicated. The fact that  $T_f - T_a$  does not go to zero in the pores is taken as evidence for an isochoric glass transition. The test temperature is  $T_g - T_a = 8$  °C. (After [70].)

phase transition, proposed previously in the literature for crystalline solids [48–51], begins to make sense in the context of an amorphous–amorphous transition between the unyielded and yielded polymer. This would also provide, at least qualitatively, an explanation for the apparent ‘erasure’ or rejuvenation of the DSC signal after yielding in a well-aged glass, in analogy to the isochoric transition in the nano-pore confined glass former. The difference here is that the transition between the two amorphous states—yielded and unyielded—takes place in the glass rather than between the liquid and the glass. Furthermore, unlike the polyamorphous transition proposed for  $H_2O$ , the present transition appears irreversible except by heating above the glass transition and repeating the set of ageing and mechanical histories that are relevant. Clearly, further research needs to be performed to clarify these interesting speculations.

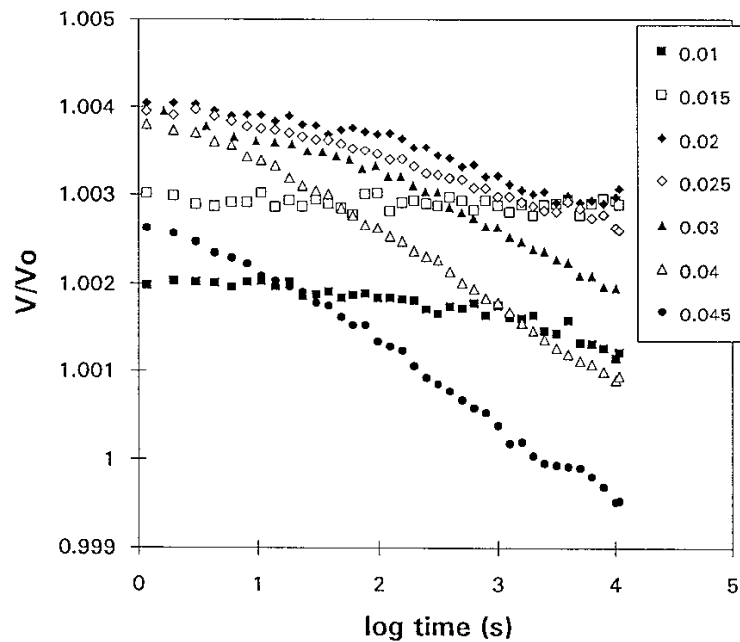


**Figure 25.** Comparison of build-up of yield stress after a thermal quench (non-cycled samples) and after a mechanical cycle through the yield point for an epoxy glass near to  $T_g$ . The fact that the yield stress does not equilibrate at the same value suggests that yield is a polyamorphic transition. (After [72].)

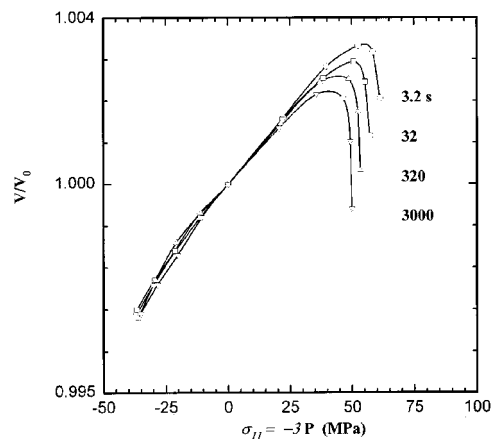
#### 4. Mechanically induced implosion

In section 3 we made a case that large mechanical stimuli do not cause ‘rejuvenation’ of aged glasses and showed evidence from experiments run near to the glass transition temperature. Here we present a set of results that indicate that the behaviour further below the glass transition may be more complicated than that shown in the previous sections. But rather than providing evidence for rejuvenation of the glassy structure, the present discourse revolves around results that suggest the possibility that large, but sub-yield, deformations may cause ‘accelerated’ ageing.

The experiment is the following. Take a polymeric glass, such as polycarbonate, and subject it to simple elongational experiments in stress relaxation conditions at a temperature that is well below the glass temperature. Measure both the stress relaxation and the lateral contraction (Poisson’s effect) at the constant elongation. Figure 26 shows the results for the change in volume calculated from the lateral contraction for a polycarbonate glass at room temperature as a function of time and for increasing applied strains [73]. The interesting result here is that, as the tensile strain increases, we see an increase in volume, as expected at short times due (primarily) to the hydrostatic component of the tensile stress. These relax with time also as expected for a viscoelastic material. However, at strains above about 0.03 the behaviour changes and the volume shows increasingly rapid relaxation. At the highest strains tested, the material actually densified after about 3000 s. Another way of looking at the phenomenon is to plot isochronal values of the volume versus the stress [74]. This is done in figure 27 and we see that the volume goes through a maximum whose position moves to lower stresses as the relaxation time (isochronal value) increases. We also see distinctly the long-time densification of the material. Importantly, stress–strain isochrones, while being nonlinear, do not go through a maximum in the regime presented here, i.e. yield has not occurred. Further studies are required to completely elucidate this phenomenon, but it shows a mechanically induced densification that cannot happen in simple extension in an isotropic viscoelastic material that is in equilibrium. Referring back to figures 9 and 10, this experiment



**Figure 26.** Volume change as a function of time in stress relaxation experiments in tension for a polycarbonate glass at room temperature ( $T_g = 115$  K) at different strain levels. Note that a sample at a strain of 0.045 densifies ( $V/V_0 < 1$ ) at times greater than approximately 3000 s. (After [73].)



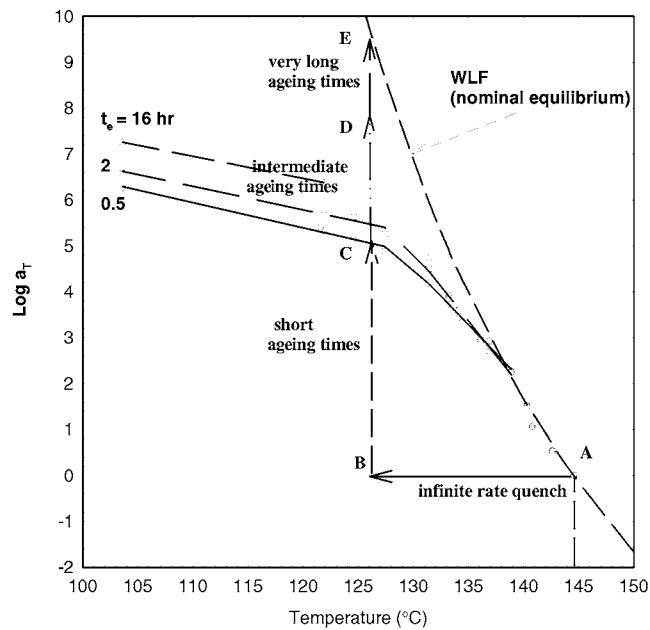
**Figure 27.** Plot of relative volume versus applied stress for a polycarbonate glass in single step stress relaxation conditions showing non-monotonic behaviour at stresses below the yield point. Times indicate the time after loading (isochronal values). Implosion ( $V/V_0 < 1$ ) occurs for the 3000 s isochrone. (After [75].)

differs from the rejuvenation concept in that it shows that the mechanical stimulus accelerates the ageing or densifies the material. This implosion, while not explained, is certainly contrary to the mechanical rejuvenation of glassy materials hypothesis described above.

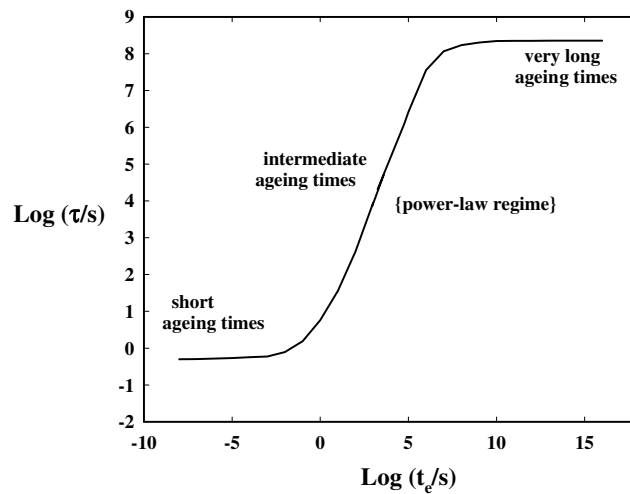
## 5. The power-law dependence of the relaxation time on elapsed time

We now turn to the observation of a power-law dependence of the relaxation time for the mechanical response on the ageing or elapsed time after a quench during ageing experiments. One reason that a full understanding of this observation is important arises from the continued use of similar power-law dependences to describe ageing phenomena in other systems such as spin glasses and ‘shear melted’ pastes or colloidal glasses and then making analogies to the structural glass system [18–21, 75–80]. The first comment to make about work in structural glasses is that it is clear that the ageing time dependence of the relaxation time is not truly a power law even in the simplest experiments described above. The real response should be sigmoidal in form for a perfect quench, with the power law dependence being what is observed in experiments carried out in a limited ageing time window. Figure 11 actually shows the long time end of the sigmoidal curve where the shift factors bend over towards a constant value as the equilibrium state is approached. Clearly, this must happen because the structure (e.g. volume) of the glass asymptotically approaches equilibrium, as shown in figures 2 and 14. However, it is also important to consider the physical limits possible at the short time end of the response that is not readily accessible by experiment. To help in this development we consider a combination of figure 28, where the total shift factor for different ageing times and at different temperatures is shown versus temperature, and figure 1 where we show the  $v$ - $T$  plot schematic for a glass-forming liquid. Imagine cooling along the glassy line in figure 1. The relaxation time for the perfect quench cannot be any shorter than the relaxation time relevant to the highest departure from equilibrium and the ageing temperature. For an extreme case, we could use the relaxation time relevant to that of the higher temperature, i.e.  $T_F$ . Hence, in figure 28, we could imagine a material whose smallest shift factor was  $\log a_T \approx 0$  if we performed the perfect quench along line A–B from  $\approx 145^\circ\text{C}$  to the ageing temperature ( $\approx 126^\circ\text{C}$ ). Then, as ageing takes place the shift factors would vary between  $\log a_T \approx 0$  and 10. The latter is the value of the shift factor in equilibrium at the ageing temperature of  $\approx 126^\circ\text{C}$ . Assuming a relaxation time of 1 s at  $145^\circ\text{C}$ , the curve should look like that depicted in figure 29. The power law cannot continue to zero time because this implies a zero relaxation time, which is not physically admissible. In fact, at zero ageing time the relaxation time cannot be less than 1 s, the value at  $145^\circ\text{C}$ . The physics of the structural recovery govern the relaxation time evolution curve depicted in figure 29. It is such that the mechanical relaxation time depends on the glassy structure and the glassy structure evolves in a way that results in an intermediate ageing time regime where there is a power-law dependence of the relaxation time or shift factor on the elapsed time, which is a laboratory variable.

Another interesting example that is difficult to mimic in the spin glass or the shear melted colloid is that of the glass undergoing a so-called memory or crossover event. In this case, the temperature history is a two-step history in which one partially ages the sample and then jumps up to a temperature where the glass is near to zero departure from equilibrium. The result is that the volume goes through a maximum and relaxes back to equilibrium [1, 2, 4, 8]. Measurements of the relaxation time shift factors show the same non-monotonic behaviour. In fact, for a range of complicated thermal histories, Struik showed a consistent one-to-one relationship of relaxation time to the volume of the sample independent (or nearly) of the history [82]. Hence, for structural glasses it is clear that the observation of a power law dependence of the relaxation time or shift factor on ageing time is purely an artefact of choosing a specific experiment (down-jump) and a limited time window for the experiments (missing short and long times). In fact, the parameter of importance is the structure of the glass and not the waiting time. Kovacs *et al* [83] recognized this earlier when they performed the first experiments focusing on the relationships between the evolution of the mechanical properties

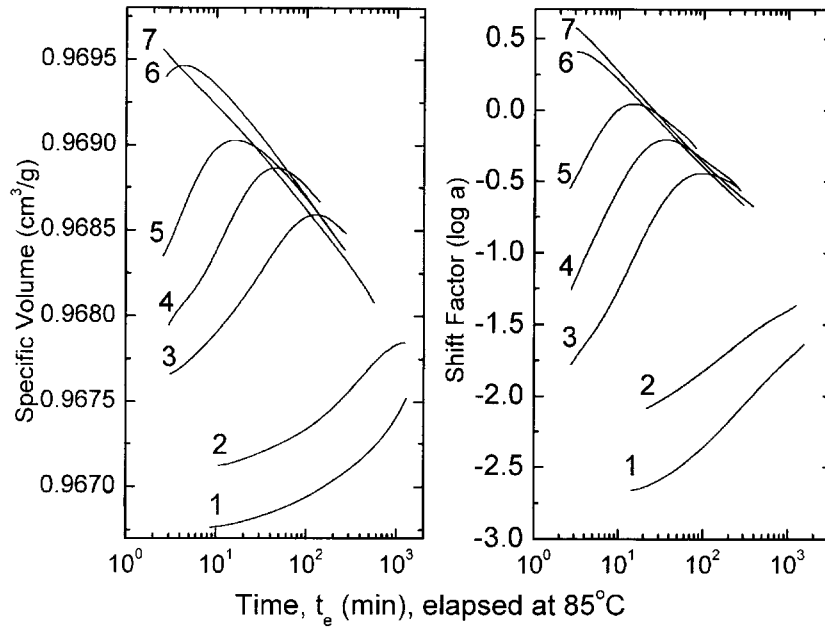


**Figure 28.** Total shift factor versus temperature for a polycarbonate glass former at different ageing times. Quench and ageing paths and their significance are discussed in the text. (Data reported in [26].)



**Figure 29.** Semi-quantitative schematic of the shift factor versus ageing or elapsed time for a material in a down-jump experiment showing the sigmoidal shape that the curve must have due to physical limitations at the short times and the fact that the material reaches equilibrium at long times. (See the text for a discussion.)

with changes in the volume of a poly(vinyl acetate) glass after both up- and down-temperature jumps (asymmetry of approach). Struik [6] also discusses this relationship extensively. A representation of their thoughts can be made beginning with an equation for the changing



**Figure 30.** Memory or crossover experiments in polystyrene showing that both the volume and the shift factor (retardation time) are non-monotonic because the viscoelastic response during ageing depends on the specific volume or other state variable and not on the elapsed time *per se*.

shear creep compliance:

$$J(t, t_e) = J(t, \delta(t_e)) = J(t/a_\delta) \quad (9)$$

where  $\delta(t_e)$  can be determined by equation (6) for any relevant thermal history. The structure shift factor is determined in these models through appeals to free volume or entropy-type theories of the glass transition. The characteristic mechanical (creep retardation) time of glassy materials is often presented through an equation of the form proposed by Struik [6]:

$$J(t) = J_0 e^{(t/\tau)^\beta} \quad (10)$$

where  $\tau$  is the relevant material time. The shift factors that are important to the current discussion are  $a_{t_e}$  and  $a_\delta$ . They are defined as follows:

$$a_{t_e} = \frac{\tau(t_e)}{\tau(t_{e,ref})} \quad (11)$$

$$a_\delta = \frac{\tau(\delta)}{\tau(\delta_{ref})}$$

These are not equivalent and only in special circumstances will we find that  $a_{t_e}$  follows a power law because the glassy structure happens to change in a certain way in down-jump histories. An excellent description of the differences between shift factors for different ageing-type histories is presented by Cerrada and McKenna [26] where both isochronal (physical ageing) and isostructural (intrinsic isotherm) types of information are used to consider material behaviour. Furthermore, in the so-called memory experiment, in which non-monotonic changes in structure can be induced [1, 84], the shift factors or retardation times for the mechanical tests are also non-monotonic as shown in figure 30. It seems to this author that the equivalent to structure in structural glasses has yet to be adequately included in models



of ageing in spin glasses and the shear-melted colloidal systems. Perhaps these systems are different but, if so, the analogy to the Struik [6] elapsed time model should not be made—in fact, the behaviours should be contrasted because they may be fundamentally different if a similar structural parameter (state-like variable, ordering parameter, etc) on which the relaxation response depends is not considered in the analysis.

### 5.1. Some other considerations

The above presented a survey of experimental results in structural glasses that bear on the issues of ageing and rejuvenation, with the emphasis being on interpretations that have to do with structural changes in the glass and why other systems that show similar phenomenology should consider similar aspects of the system because, otherwise, the attempted analogies to, e.g. elapsed time theories or rejuvenation models, may not be meaningful. To make an attempt at closure without going into detail, we mention that there is work in computer simulations that deals with mechanically induced changes in the energy landscape [19, 84] in glass-forming systems. Such efforts may benefit from a closer look at the empirical information presented, which forms a fairly complete set of the known phenomena independent of the interpretation placed on them.

## 6. Summary and conclusions

The behaviour of polymeric materials subjected to both thermal and mechanical histories has been briefly reviewed, with particular emphasis on the question of the effects of large mechanical stimuli on the structure of glassy materials in a process that has come to be called rejuvenation. Results are presented which counter the existence of rejuvenation in the sense that a large mechanical stimulus pushes the glass back towards the more freshly quenched state or erases the prior ageing. Two specific experimental results are presented that demonstrate a lack of rejuvenation in the sub-yield regime. The mechanical equilibration time is unchanged by the magnitude of probe stresses in ageing experiments and torsional dilatometric results show that the glassy structure, as measured by volume, attains equilibrium along the same underlying path as the unperturbed material. For experiments performed in the post-yield regime, the results are different, yet seem to not conform to the rejuvenation picture. After subjecting the glassy polymer to a large yield–unload cycle the yield stress builds up to a different equilibrium value than that obtained via a thermal quench path. The suggestion is made that yield in the polymer is the result of a polyamorphic phase transition. Behaviour of a glassy material subjected to large deformations, but sub-yield, at temperatures further below the glass transition on the other hand suggest that large stimuli can lead to accelerated ageing because the material densifies or implodes due to the large, but sub-yield, strains. Finally, a critique of the use of the Struik [6] elapsed time theory or power-law behaviour to describe spin glasses or shear-melted colloids is presented.

## Acknowledgments

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*Note added.* While the work described in the present paper does not include other structural glasses, there is no fundamental reason to believe that the results should not be generally applicable, i.e. to polymer glasses, inorganic glasses and small molecule glasses. There may be differences in detail and, for example, it may be difficult to cycle an inorganic glass to 50% deformation and back to zero because of the lack of chain connectivity that is present in

polymers. But, otherwise, the present author tends to think that the behaviours described above are general to all structural glasses.

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