

Ageing in glassy polymers under various thermal histories

H Montes, V Viasnoff¹, S Jurine and F Lequeux²

UMR 7615, CNRS, PPMD, ESPCI, 10 Rue Vauquelin, 75005 Paris, France
E-mail: helene.montes@espci.fr, virgile.viasnoff@espci.fr and
francois.lequeux@espci.fr

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Abstract. Glasses are known to age continuously, thus exhibiting self-similar temporal evolution of their relaxation spectrum. We investigated the effect of a temperature step on physical ageing at a given temperature, on an amorphous polymer—polybutylacrylate. Measuring the dynamics of the system through creep measurements, it appeared that a negative temperature step induces both a slowing down of the physical ageing and a thinning of the relaxation spectrum. The situation was more complex for a positive temperature jump. Shortly after its completion, the system appeared younger—there was an apparent speeding up of the relaxation dynamics, in other words, a rejuvenation. Later, the system appeared older—it behaved as if an apparent acceleration of the physical ageing occurred through ‘overageing’. In addition there was in each case a widening of the relaxation spectrum. In conclusion, the effect of a temperature jump could not be described by a simple shift of the time-relaxation distribution of the system. An evolution of the relaxation spectra following thermally activated processes is at first sight compatible with the observed phenomena, even if some results—the effective time as a function of the total time—are not compatible with this latest approach. This suggests a complex spatial arrangement of the dynamics.

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¹ Present address: ESPCI Nanobiophysique UMR 7083, CNRS, France.

² Author to whom any correspondence should be addressed.

Contents

1. Introduction	2
2. Experimental details	3
2.1. Samples	3
2.2. Protocol	4
2.3. Measurement procedure	4
2.4. Thermal history parameters	6
2.5. Simple physical ageing results	6
2.6. Influence of a temperature step on the physical ageing behaviour	6
2.7. Effective time	7
2.8. Effective time dependence with ΔT	9
2.9. Effective time dependence with probe time	10
2.10. Discussion	11
3. Conclusion	13
Acknowledgment	14
Appendix A: Creep	14
Appendix B: Trap model	14
References	16

1. Introduction

Glassy systems, such as molecular glasses, polymers glasses, or spin glasses, exhibit very slow dynamics [1]. In general their dynamics is so slow that they can only be studied in an out-of-equilibrium regime. Consequently, their dynamical properties evolve continuously with time. The usual way to measure these time-dependent dynamics is by quenching a system. The sample is then kept at rest at constant temperature for a given waiting time t_w . Then its dynamical properties—for instance its mechanical linear response—are measured.

The evolution of the dynamical properties of a glass with the waiting time, known as ageing, exhibits a very remarkable behaviour. The spectrum of relaxation times evolves nearly self-similarly with t_w . In the literature, various scaling laws for the time-dependent response are proposed—the most popular being t/t_w^μ —where t is the time elapsed after the solicitation and μ an exponent generally close to unity. This scaling law was popularized by Struik on polymer glasses in the 1970s [2], but more recent experiments and models on various systems led to similar scaling laws. However, the profound meaning of this scaling is still unclear. It is likely that—in a classical ageing experiment—the system evolves towards configurations of increasing stability and thus that its dynamics slow down. Thus, in a coarse-grained approach, the evolution rate of the average relaxation time is proportional to the average relaxation time itself and thus tends to infinity. This simple scaling argument leads to a t/t_w scaling for the response function, and thus an

exponent μ of 1 for the ageing. In practice the time spectrum is extremely wide—leading to the well-known stretched KWW exponential relaxation. It follows that ageing can be described as a self-similar shift of the whole relaxation time spectrum with an evolution rate that depends on the spectrum itself. Such a time spectrum self-arrangement is well pictured by the Monthus and Bouchaud traps model [3]. In this model, a wide spectrum of energy wells is available for fictive particles hopping from well to well under simple thermal activation. The solution of this model—in the case of an exponential distribution of the well depth, below a critical temperature and for classical ageing conditions—is a time-dependent self-similar distribution law of population in the energy wells, leading to a t/t_w rescaling. Otherwise, very different models—spin glasses, mode coupling—also lead to similar scaling laws [4].

Beyond this ageing scaling law, the role of thermal or mechanical history on ageing has been also widely investigated in order to get insight into the ageing phenomena. Struik has performed some ‘annealing’ experiments on polymer glasses [5]. He annealed a glassy polymer sample at a temperature T_1 and measured its ageing behaviour at a temperature T_2 . He concluded that a system ages faster as T_2 is larger than T_1 with the existence of an optimal temperature for which ageing is the fastest. Kovacs [6] also annealed a polymer glass at some temperature, and demonstrated that the subsequent time evolution of glass density at constant temperature is not only determined by its average density, but by its whole thermal history. More recently, Bellon *et al* [7], following spin glass experiments [8], annealed a polymer glass at some temperature T_a , before cooling it at a lower temperature. Consequently, they observed—while heating the sample up to the glass transition temperature—a specific response around T_a known in spin glasses as a memory effect. They argued that a temperature-dependent spatial arrangement of the glassy dynamics is revealed by this memory effect. Otherwise temperature square-steps during ageing of spin glasses have been reported to modify their relaxation-time spectrum [9]. In addition, we have recently shown that a mechanical perturbation applied during the ageing of a colloidal glass deeply modifies its relaxation-time spectrum and eventually speeds up the ageing process. We have called this speeding up of ageing under stress overageing [10].

In this paper, we demonstrate that the phenomenology observed on a polymer glass submitted to temperature jumps is similar to the one of a colloidal glass under shear. More precisely, we will show that a transient temperature rise (respectively fall) cannot be merely described as a ‘speeding up’ (respectively ‘slowing down’) of the ageing dynamics. More precisely, the whole spectrum evolves from its self-similar shapes, not only by a shift in time but also by a widening—or sharpening. We discuss this effect and suggest that thermally activated processes are able to explain the observed phenomena.

2. Experimental details

2.1. Samples

Measurements were performed on a statistic copolymer composed of two isomers: n-butylmethacrylate and tert-butylmethacrylate in equal proportion. The copolymer chains were polymerized and cross-linked simultaneously as described in [11]. Its glass transition temperature $T_g = 328$ K is defined here by the temperature at which the loss modulus at

0.1 Hz is maximum. Physical ageing was observed through creep experiments performed on an MTS 831 instrument.

2.2. Protocol

In order to maximize the reproducibility and precision of the effects of thermal annealing, we compared experiments performed on the same sample in the exact same geometry. This implied that a given sample had to experience successive thermal sequences with full rejuvenation in between, all this within the experimental set-up. Thus the sample had to remain solid-like above its T_g . This is why we chose to work with cross-linked polymer chains. Moreover, as the elastic modulus of the sample varies across more than three decades with temperature, it was necessary to switch the instrument between strain and stress control modes during the experiment. In fact, since in the rubber state displacement is very sensitive to weak force variation, we operated with a strain control at a temperature above the glass transition temperature. In the glassy state a stress control mode was chosen.

Ageing measurements were made on dog-bone shape samples (the sample dimensions were $15 \times 3 \times 30 \text{ mm}^3$ in its middle part). In order to avoid slip, the sample was embedded in a hollow dog-bone shaped grip. It was fixed into the grips in the temperature chamber in its rubbery state, and under a elongation of about 3%. Under this elongation, the force is equal to zero within the precision of the apparatus. Then successive measurements were performed using cycles of thermal and mechanical histories. An example is shown in figures 1(a) and (b).

2.3. Measurement procedure

Each cycle was composed of seven steps during which the control mode of the apparatus was adapted to the sample state. During each step, the variations with time of temperature T , force F and displacement δ were measured. (1) First we chose the sample annealed at a temperature of 25 K above its T_g for 1 h, in a strain-imposed mode ($\delta = 0$). We checked that all the history effects were erased during this thermal treatment. (2) The temperature was then decreased to T_g (328 K) in 10 min in a strain-imposed mode $\delta = 0$. After this, the instrument mode was switched from strain control mode to stress control mode at force $F = 0$ (3), and the temperature set point fixed at $T_g - 25$ K. In practice the temperature decreased for 15 min and levelled off after 30 min. (4) The temperature was increased to $T + \Delta T$ for a duration $t_{\Delta T}$ equal to 3.75 h, while the instrument remained in force-controlled mode at force $F = 0$. (5) The temperature was then regulated back to $T_g - 25$ K at time t_{eop} —marking the end of the thermal perturbation, (6) and the force was set to 50 N for 5 h (stress = 1 MPa). We carefully checked that this force remains in the linear response regime. (7) The sample was thus brought back to the initial conditions (5% stretching in the rubbery state at $T = T_g + 25$ K). In practice, the sample did not slip, nor was it damaged during at least 20 cycles. No noticeable force drift was observed. Figures 1(a) and (b) show the raw data measured during an experiment made of two successive cycles. Figure 1(a) presents the temperature and force variations during the two cycles while figure 1(b) shows the corresponding displacement variations. From each cycle, we extracted the time dependence of the compliance $J(t, t_w, \Delta T)$ from the time evolution of the sample length during step (6) ($\delta_F = \delta(t, t_w, \Delta T, F = 50)$).

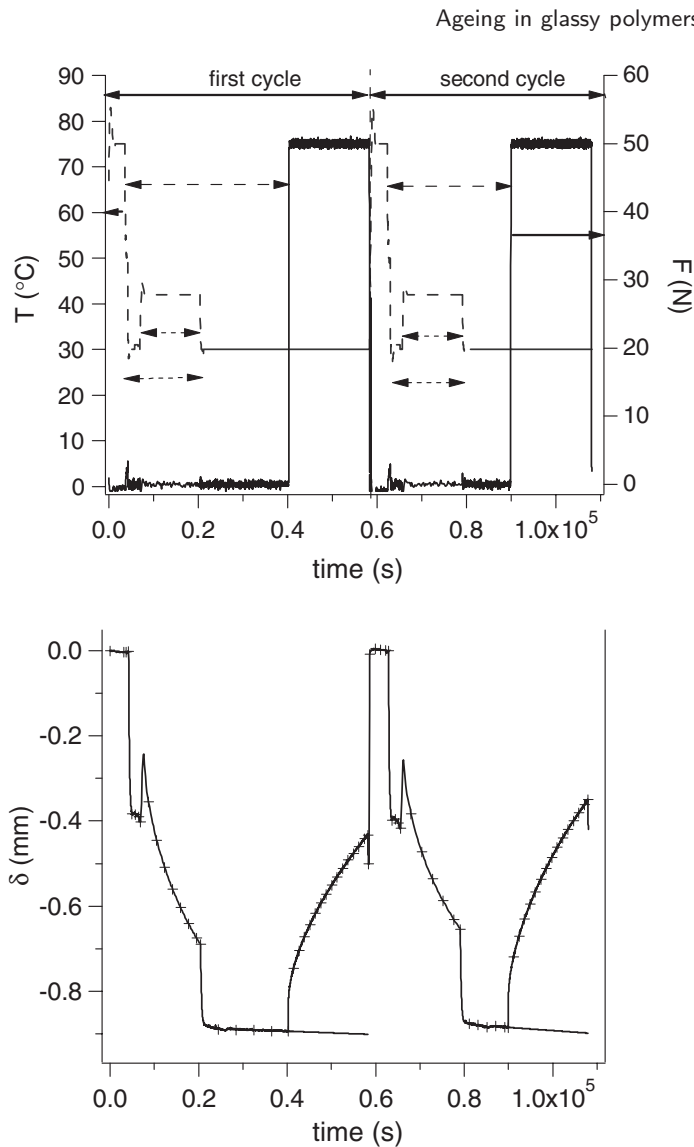


Figure 1. Example of experiment composed of two cycles allowing us to measure the physical ageing after an ageing time of $t_{w1} = 10$ h and an ageing time of $t_{w2} = 7.5$ h. $t_{eop} = 4.5$ h and $t_{\Delta T} = 3.75$ h. In the upper part, the dashed line is a plot of the temperature of the sample as a function of time. The full line is the force applied to the sample. Below is plotted the displacement measured respectively in the presence and in the absence of applied force for the creep test.

Even in the absence of stress, the sample undergoes an isotropic compression due to the spontaneous decrease of its volume as is shown in figure 1(b). This volume decrease, due to ageing, is small but not completely negligible. Thus the compliance was deduced from the difference between the displacement under stress $\delta_F = \delta(t, t_w, \Delta T, F = 50)$, and that in the absence of stress $\delta_0 = \delta(t, t_w, \Delta T, F = 0)$. Finally, the compliance $J(t, t_w, \Delta T)$ was measured successively two or three times in similar conditions, and the largest error bars were about 2%. In this work, we compared only data measured on successive cycles performed on a same sample. More precisely, in the figures presented here, experiments on

two different samples have been performed. One corresponds to data in figures 3, 4, and 7. The second sample gives the results shown in figures 5 and 6. Some small discrepancies between these two sets of data may have arisen from a slightly different value of T_g .

2.4. Thermal history parameters

We defined t_w as the macroscopic ageing time since the polymer quench. In all the following experiments, t_{eop} was fixed to 4.5 h. Thus, the macroscopic ageing time was only varied by changing the delay between the end of the thermal step and the beginning of the creep measurement. The compliance $J(t, t_w, \Delta T)$ was measured as a function of three parameters: the time t elapsed since the beginning of the step force, the macroscopic ageing time t_w and the amplitude of the temperature step ΔT .

2.5. Simple physical ageing results

In order to establish a reference history for the evolution of $J_{\text{sa}}(t, t_w)$, we first performed a simple ageing experiment. We thus reproduced Struik's results. Successive cycles with different t_w were performed for $\Delta T = 0$, and figure 2 shows $J_{\text{sa}}(t, t_w)$ versus t , for different t_w . The self-similar shape of these curves on a log scale can be accounted for by using a time shift factor [2]. We define α so that

$$J_{\text{sa}}(t, t'_w) = J_{\text{sa}}(t \cdot e^\alpha, t_w). \quad (1)$$

Thus defined, α corresponds to the Struik shift factor a through the relation $\alpha = \ln(a)$.

In addition, and as observed by Struik, α is found to have a logarithmic dependence with t'_w/t_w but does not vary with t . Indeed, we found

$$\alpha = \mu \ln(t'_w/t_w) \quad (2)$$

with $\mu = 0.64$ independent of t .

Hence all the creep compliances rescaled on one single master curve, $J_{\text{sa}}(t/t_w^\mu)$, as demonstrated by the inset of figure 2. This well-known scaling law is the signature of simple physical ageing as abundantly described in the literature. As creep compliances are closely related to the relaxation-time distribution of the system, such a scaling law indicates that the time spectrum evolves self-similarly with the time t_w . In the following section the creep compliances following temperature shifts will be compared to the reference ones using the shift factor α .

2.6. Influence of a temperature step on the physical ageing behaviour

In this part, we focus on data measured for different values of t_w after a temperature step of amplitude ΔT was applied during the sample ageing. Let us recall here that the duration of the thermal square-step is 3 h 45 min and that the delay between the initial quench and second one— t_{eop} —is 4 h 30 min. These values were kept constant for all the experimental data presented in the paper. We varied only the delay of the beginning of the creep test. Let us also recall that the delay of the creep test with respect to the initial quench is t_w . Table 1 presents the values of ΔT and t_w for which measurements were made.

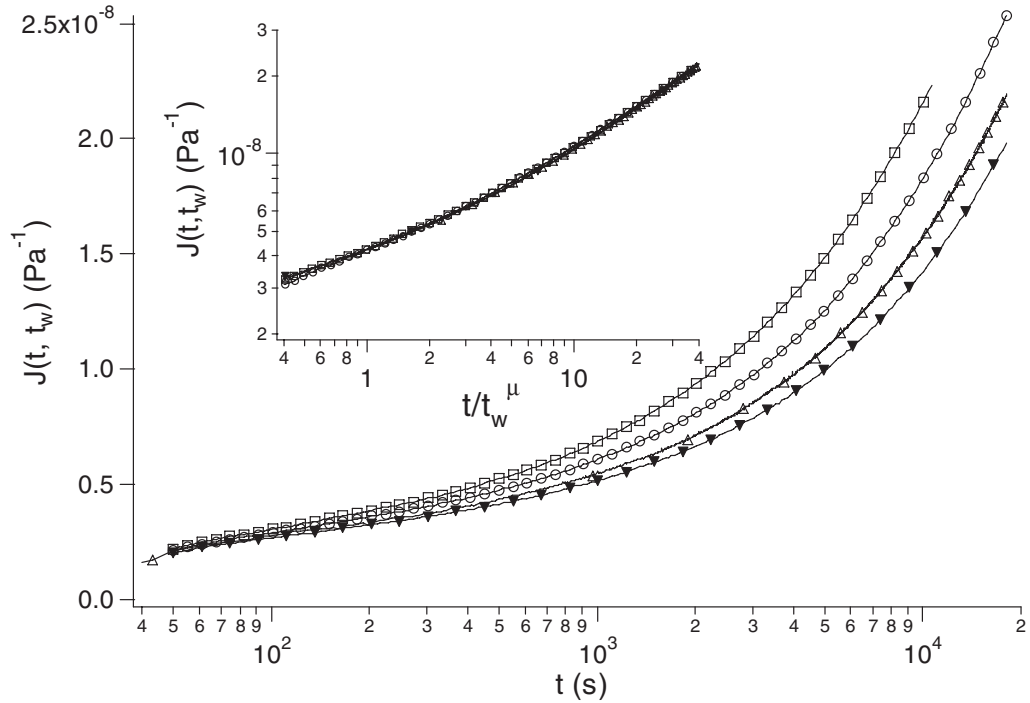


Figure 2. $J_{sa}(t, t_w)$ versus t during a force step of 50 N (step 6 of figure 1) for different ageing times t_w . The inset presents the master curves obtained using the reduced variable $t/(t_w)^\mu$ where $\mu = 0.64$. For $t_w = 3$ h (square); $t_w = 5$ h (circle); $t_w = 7.5$ h (triangle); $t_w = 10$ h (filled inverse triangle).

Table 1. List of the ΔT and t_w values for which physical ageing was studied.

ΔT	-15	-5	-2	+2	+5	+7	+10	+12
t_w	5 h	5 h	5 h	5 h	5 h	5 h	5 h	5 h
				7.5 h	7.5 h	7.5 h	7.5 h	7.5 h
		10 h		10 h	10 h	10 h	10 h	10 h

In figures 3(a) and (b), we compare the compliance $J(t, t_w, \Delta T)$ measured after the temperature step to that observed in a simple ageing experiment for the same waiting time t_w . Measurements performed for two t_w values are presented in figures 3(a) and (b): $t_w = 10$ h (figure 3(a)) and $t_w = 5$ h (figure 3(b)). In these figures it is apparent that the physical ageing behaviour was significantly modified by a temperature step.

2.7. Effective time

From the experimental results, the creep functions in the case of a complex ageing and in the case of a simple ageing were significantly different.

As for the classical physical ageing experiments reported above, within the context of glass polymer studies, the definition of the shift parameter—introduced first by Struik can be extended to complex thermal history:

$$J(t, t_w, \Delta T) = J_{sa}(t.e^\alpha, t_w). \quad (3)$$

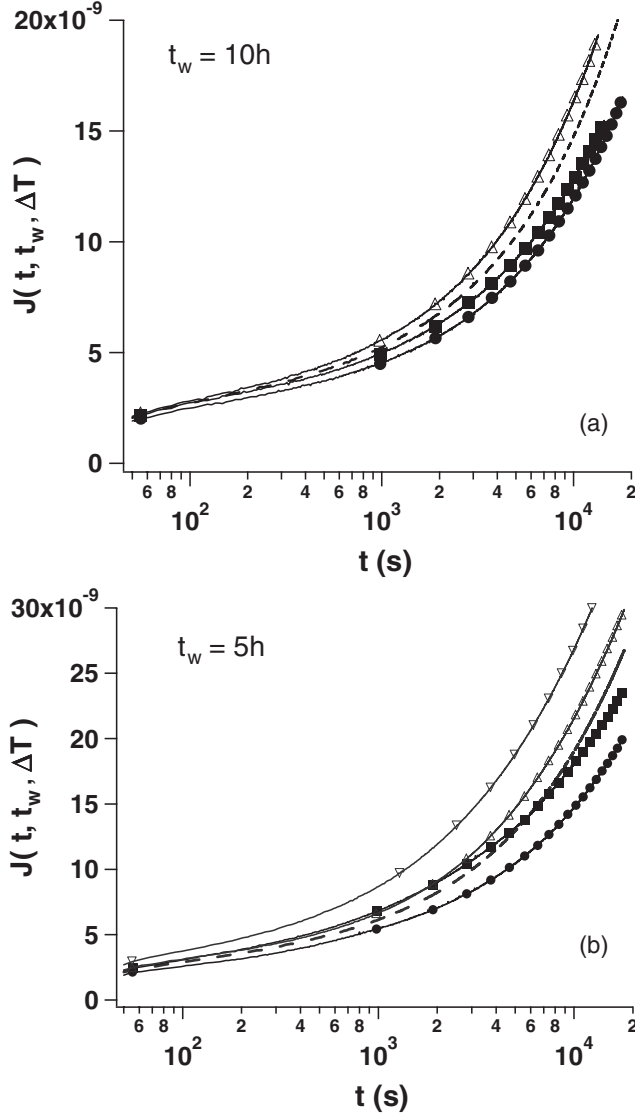


Figure 3. $J(t, t_w, \Delta T)$ with time t after application of a temperature step for two ageing times. Respectively for (a) $t_w = 10$ h and for (b) $t_w = 5$ h, and for the following temperature amplitudes. For $\Delta T = 0$ K (- - -); $\Delta T = 2$ (filled circle); $\Delta T = 10$ (filled square); $\Delta T = -5$ (triangle); $\Delta T = -15$ (inverse triangle).

When dealing with spin glasses, an effective time is usually introduced. The state of the system is sometimes approximated to the one it would have been if it had been ageing for $t_w + t_{\text{eff}}$. In that case, the following relation is used:

$$J(t, t_w, \Delta T) = J_{\text{sa}}(t, t_w + t_{\text{eff}}). \quad (4)$$

Actually, the two approaches are equivalent, as t_{eff} and α are related through

$$t_{\text{eff}} = t_w \cdot (e^{\alpha/\mu} - 1). \quad (5)$$

In figure 4, we have plotted t_{eff}/t_w for $t_w = 5$ h and different values of ΔT . One can see that the situation is somewhat confusing since the effective time varies with the probe

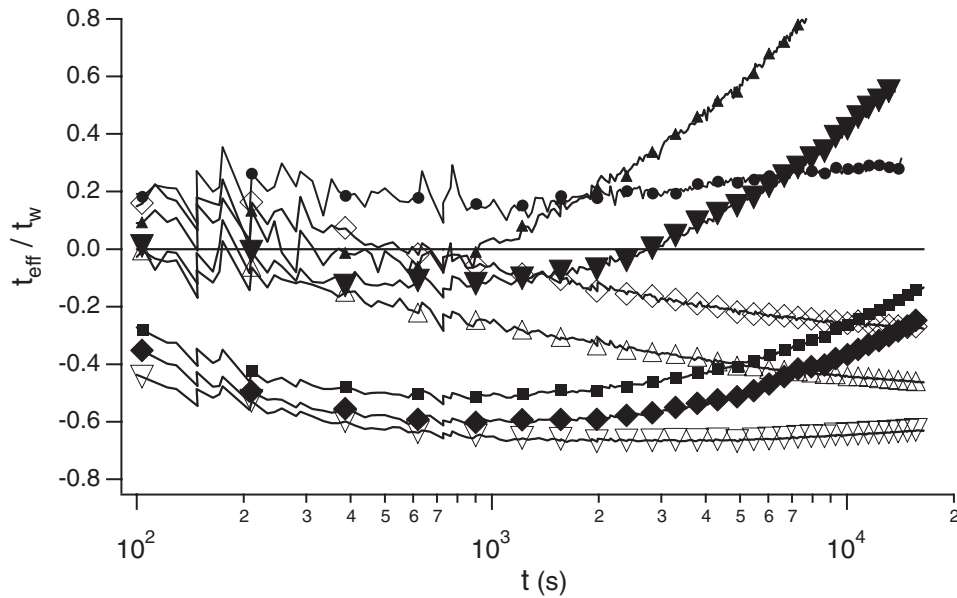


Figure 4. t_{eff}/t_w versus t for $t_w = 5$ h and different ΔT . The solid line ($t_{\text{eff}} = 0$) corresponds by definition to $\Delta T = 0$. For $\Delta T = 12$ K (filled diamond); $\Delta T = 10$ (filled square); $\Delta T = 7$ (filled inverse triangle); $\Delta T = 5$ (filled triangle); $\Delta T = 2$ (filled circle); $\Delta T = -3$ (diamond); $\Delta T = -5$ (triangle); $\Delta T = -15$ (inverse triangle).

time for nearly all the values of ΔT . Indeed, some effective times change their sign during the measurement!

2.8. Effective time dependence with ΔT

While figure 4 is confusing, it is much clearer to plot the variation of t_{eff}/t_w for given values of J as a function of ΔT , as done in figure 5 for a waiting time of $t_w = 5$ h. By construction, all the curves cross at $t_{\text{eff}} = 0$ for $\Delta T = 0$. It is interesting to remark also that t_{eff}/t_w is expected to tend asymptotically towards two values. First $\Delta T = -T$ corresponds to a cooling to 0 K, hence to a complete arrest of the ageing process. In that case, the ageing process occurs only at T and for a time equal to $t_w - t_{\Delta T}$. Thus, according to (2) and (3), t_{eff}/t_w has then to converge towards $(t_w - t_{\Delta T})/t_w$, whatever the value of J , for ΔT going towards $-T$.

Second, if now ΔT exceeds $T_g - T$, the temperature shift amounts to another quench from the molten phase and an ageing time of $t_w - t_{\text{eop}}$. Consequently t_{eff}/t_w converges towards $(t_w - t_{\text{eop}})/t_w$ independently of J . These two asymptotic values are indicated in figure 5.

The plot revealed the following behaviour. t_{eff} increased with J for positive values of ΔT : the compliance curve was stretched for positive values of ΔT . In contrast, it was compressed for negative values of ΔT .

Moreover, the average shift was always negative for negative values of ΔT . But for positive values of ΔT , the average time shift was first positive and then negative. The increase of the width of the creep function coupled with its average time delay

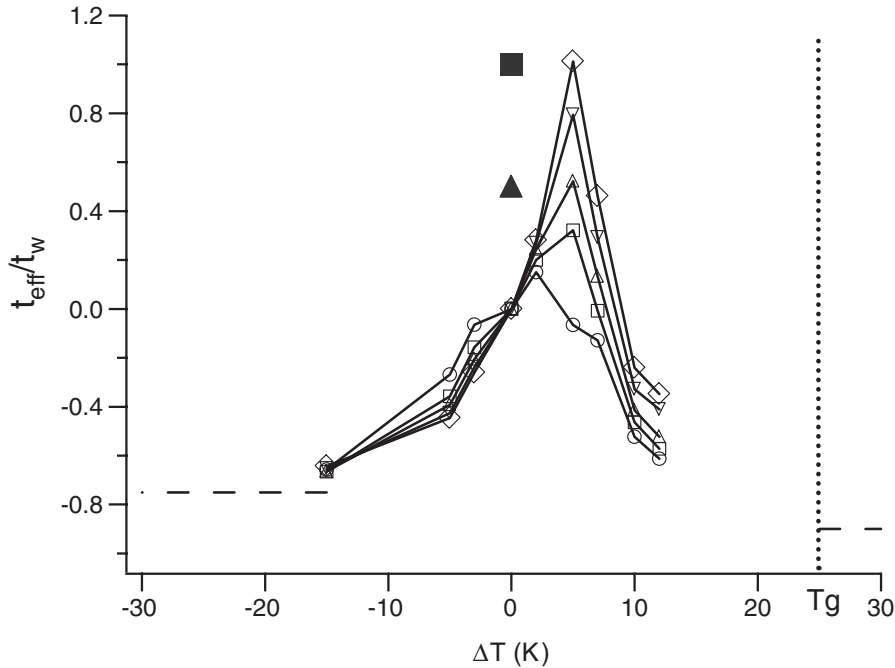


Figure 5. t_{eff}/t_w versus ΔT , at constant J and for $t_w = 5$ h. For respectively the following values of J in Pa^{-1} : 5×10^{-9} (circle); 8×10^{-9} (square); 10×10^{-9} (triangle); 13×10^{-9} (inverse triangle); 16×10^{-9} (diamond). The dashed lines correspond to the asymptotic values of α . Whatever the value of J , α must tends towards $0.64 * \ln[(t_w - t_{\Delta T})/t_w]$ while $T + \Delta T$ tends towards zero, and towards $0.64 * \ln[(t_w - t_{\text{eop}})/t_w]$ while T tends towards T_g . The same values but for $\Delta T = 0$ and $t_w = 7.5$ h and 10 h are represented by the symbols (filled triangle) and (filled square). Because of the simple ageing superposition, they can be superimposed.

was responsible for complex effects. Depending on the time window of the experiment, one could observe either an apparently older or younger system after a positive step of temperature. This behaviour is very similar to the one observed in colloidal glasses after a mechanical perturbation. As t_{eff} could be positive, we have called this effect ‘overageing’ in a previous publication [10].

In figure 6, similar data to those in figure 5 have been plotted but with waiting times of $t_w = 7.5$ and 10 h. One can see that the stretching of the creep function decreased with t_w . As expected, the relaxation functions tend toward their asymptotic scaling.

2.9. Effective time dependence with probe time

As shown above, a constant effective time does not allow a description of ageing after complex thermal history. One thus could ask whether a time-dependent effective time should describe the above phenomena.

In order to check if a time-dependent effective time could describe ageing after a temperature square-step, we plotted the effective time t_{eff} as a function of the total time $t + t_w$ for the same thermal history— $\Delta T = 10$ K in the present case—but for various

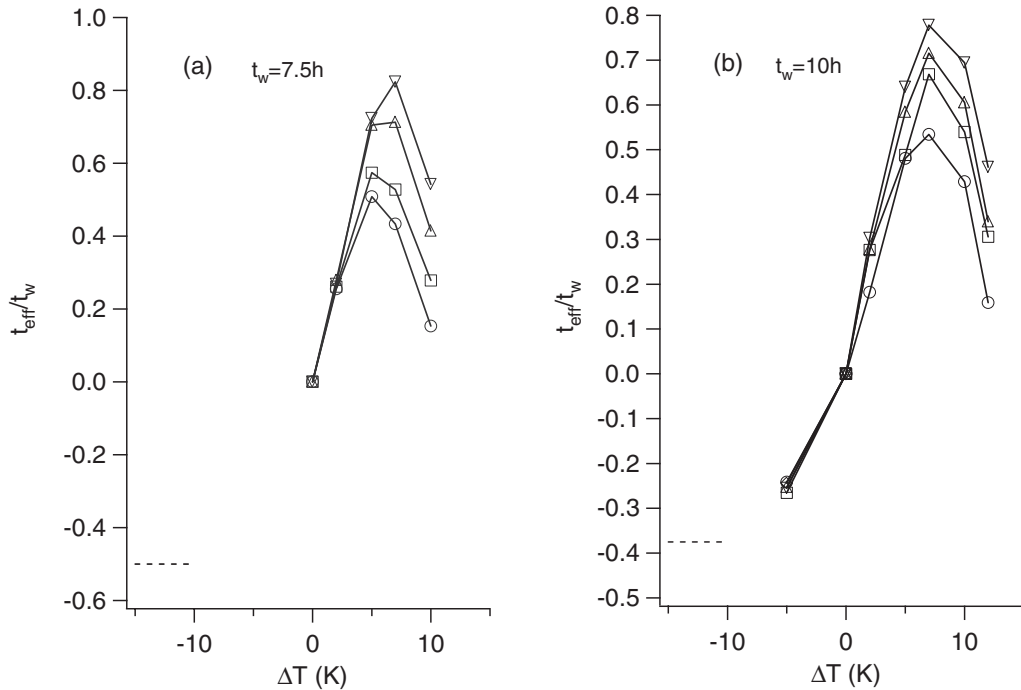


Figure 6. t_{eff}/t_w versus ΔT at constant J and for respectively $t_w = 7.5$ h (a) and $t_w = 10$ h (b). For the following values of J in Pa^{-1} : 5×10^{-9} (circle); 8×10^{-9} (square); 10×10^{-9} (triangle); 13×10^{-9} (inverse triangle); 16×10^{-9} (diamond). The dashed lines correspond to the asymptotic values of α for negative temperature amplitudes $\alpha = 0.64 * \ln[(t_w - t_{\Delta T})/t_w]$.

value of the time of the stress loading t_w . The data are presented in figure 7. If a single effective time could describe the complex ageing, all the curves would superimpose. This was clearly not the case. Thus, neither a constant effective time nor a time-dependent effective time was able to describe ageing after complex thermal history.

2.10. Discussion

The creep measurement is actually a probe for the spontaneous rearrangement dynamics at rest under thermal motion, as explained in appendix A. Thus the creep measurement gives access to the time-relaxation spectrum of the system. Roughly speaking, a small time measurement probes the relaxation of the fast domain, while a long time measurement probes the slow domain relaxation. Here we show that the time-relaxation spectrum evolves in a complex manner after a temperature step. It stretches for a positive temperature step and shrinks for a negative temperature step. On the other hand, the average relaxation time is smaller than the one associated with simple ageing after a negative temperature square-step. But after a positive temperature step, it can be larger for a small step, but it becomes smaller when the temperature during the step approaches the glass transition. All these results are rather intuitive. Starting from a classical ageing situation, a negative step will modify the time evolution of the system. A lower temperature appears to be more selective in dynamics, like for activated processes:

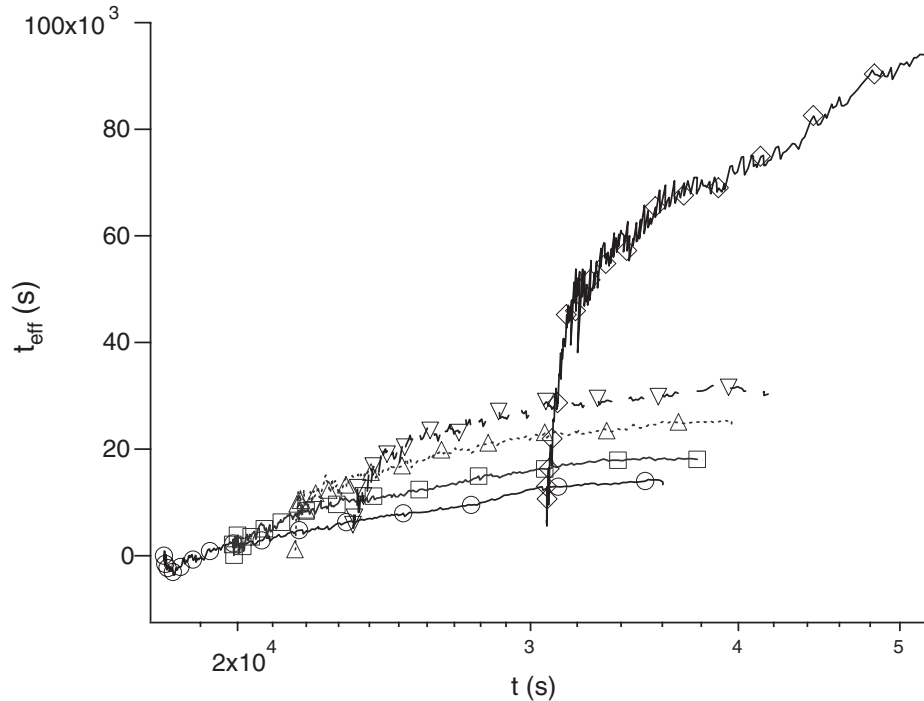


Figure 7. t_{eff} versus $t_w + t$, for the same value $\Delta T = 10$ K but for various values of t_w . Respectively $t_w = 5$ h (circle), $t_w = 5.5$ h (square), $t_w = 6$ h (triangle), $t_w = 8.5$ h (inverse triangle).

the faster domains—with a small activation energy—relax comparatively more quickly than the slow ones, when compared to those in the reference situation. This leads to a shrinking of the time-relaxation spectrum in addition to an average decrease of the dynamics.

Hence the observed shrinking of the time-relaxation spectrum under negative ΔT can be described as the consequence of an evolution of an energy wells distribution under the action of activated process. This is indeed the ansatz of the trap mode—see in appendix B.

In contrast, for a small positive temperature square-step, the average relaxation increases, leading to overageing of the system. At the same time, the domains with the larger energy activation relax more quickly than in the reference situation. This leads to a stretching of the time-relaxation spectrum.

Finally, if temperature during the square-step approaches the glass transition, the system tends to equilibrate, pulling back the time-relaxation spectrum to an after-quench situation.

These results are also in agreement with the Struik optimization of the annealing temperature. In figure 5, the maximum of t_{eff} corresponds to the ideal annealing temperature. But as remarked also by Struik, this temperature depends on the timescale considered. These results are finally quite straightforward as they could also been qualitatively accounted for by the trap model—see appendix B.

It is interesting to remark that the effective time depends not only on time during a single experiment, but also on the typical timescale considered for the relaxation, as shown

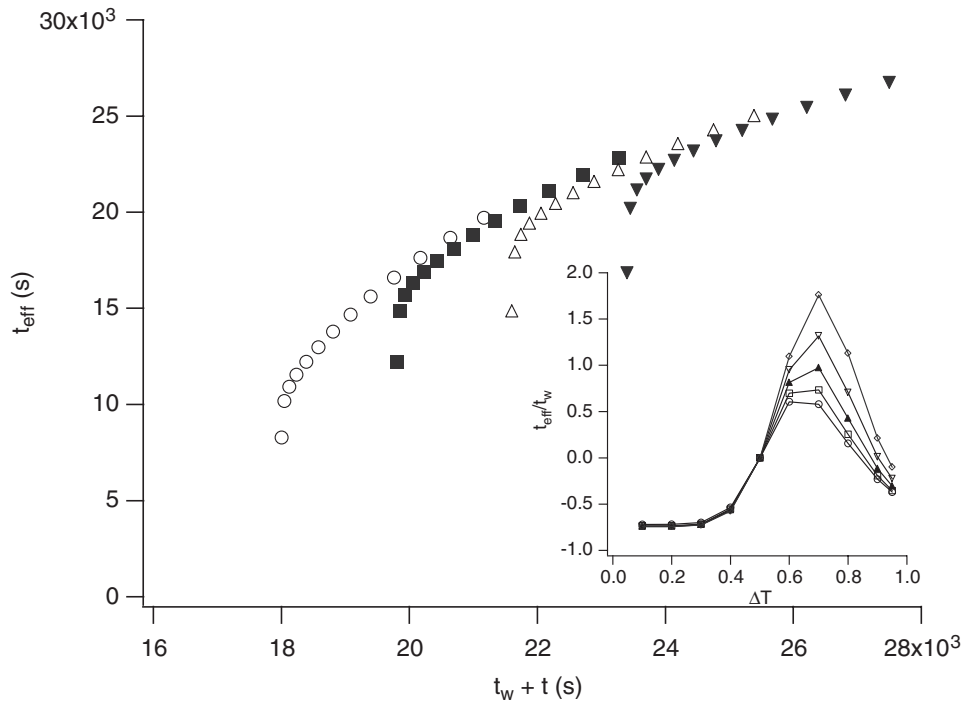


Figure 8. t_{eff} versus $t_w + t$ for $T = 0.5$ and $\Delta T = 0.1$ deduced from the trap model, with the following parameters: $t_{\Delta T} = 13\,500$, $t_{\text{eop}} = 16\,200$, for $t_w = 18\,000$, $19\,800$, $21\,600$, $23\,400$. Inset: t_{eff}/t_w versus ΔT , for $T = 0.5$, and $t_w = 18\,000$. For respectively the following values of C : 0.05 to 0.25 in steps of 0.05 .

figure 7. More precisely, we observe that the effective time experimentally increases with t_w , while the trap model—see figure 8—gives the opposite result. This definitively proves that the effective time is not an intrinsic quantity, suggesting as many other experiments a complex—probably spatial—organization of the dynamics. This time dependence of the effective time, for a given age of the system, cannot be qualitatively described by the trap model (it gives an opposite variation of the effective time). Hence the t_w -dependence of the effective time is likely to be a good candidate to test theoretical models for the ageing of glassy systems. More precisely, the trap model could be seen as a mean field approach of the structural evolution of a glass. However, it is clear that the spatial arrangement of the relaxation is a key point in the understanding of glass dynamics [13, 14]. Annealing at a given temperature modifies the spatial arrangement of the dynamics in a specific way. This is probably the reason why the t_w -dependence of the effective time cannot be described by a trap model. We are however aware that the experiments described in this paper are not good candidates for looking specifically at this effect of spatial arrangement of the relaxation.

3. Conclusion

Experimental results on polymer glass ageing shows that the relaxation spectrum—which evolves self-similarly at constant temperature—evolves in a complex manner under thermal perturbation. A negative thermal step both slows down and narrows the

relaxation spectrum. A positive thermal step widens the spectrum but the average relaxation time is advanced or delayed depending on the temperature step amplitude. In any case these effects can be described by an effective time or an effective delay. The apparent effective time is found to depend on the timescale, but also on the waiting time. If the thermal history dependence of the time-relaxation spectrum is easy to understand in terms of activated process and can be described by the trap model, this is not the case for the waiting time dependence of the effective time.

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Appendix A: Creep

Creep is not very straightforward to understand. But it appears that for small strain values, it can be understood in a rather intuitive way. The system initially at rest is submitted to a small stress at time zero. The stress is kept constant afterwards. Just after the stress loading, the system behaves like an elastic matrix submitted to a stress. Let $G(0)$ be the (instantaneous) elastic modulus of the system. After some time, thermal fluctuations lead to rearrangements of some domains of the system. In the Eyring approach [12], they are usually called cage rearrangements. Let $\Phi(t, t_w)$ be the volume fraction of domains that have experienced a rearrangement during t_w and $t + t_w$. One can assume reasonably that each rearrangement cancels the stress locally. If the total strain variation during the experiment is not excessive, one can assume that the rearranged domains do not contribute any more to the elastic modulus of the system. Thus the apparent elastic modulus of the system can be written as

$$G(t) = G(0) \cdot (1 - \frac{5}{3}\Phi(t, t_w) + O(\Phi_2)). \quad (\text{A.1})$$

And the compliance immediately follows:

$$J(t, t_w) = G(0)^{-1} \cdot (1 + \frac{5}{3}\Phi(t, t_w) + O(\Phi_2)). \quad (\text{A.2})$$

Hence, for small deformation, the compliance is related to the number of domains that have relaxed since the application of the stress.

Appendix B: Trap model

We can discuss the relaxation spectrum in the framework of a very naïve model: the trap model. In general, the remarkable self-similarity of the glass relaxation functions can be pictured as follows. The system in its asymptotic state would have a nearly infinite relaxation time. However, it evolves following its own dynamics. The evolution rate of its dynamical time distribution towards an infinitely slow situation is governed by its time distribution itself. This self-arrangement of the time spectrum appears to be self-similar. This is well pictured qualitatively by the traps model. This model enables us to describe the domain rearrangement dynamics in a qualitative mean field approach.

In this model, the system is described by fictive particles that hop randomly from well to well under the action of thermal activation. Each hop of a fictive particle

corresponds in fact to some domain rearrangement. A wide spectrum of energy wells is available for these fictive particles. The lifetime of a particle in a well is simply given by thermally activated dynamics allowing escape from the well. The density of wells is given by $n(E) = \exp(-E/kT_c)$ and the hopping rate from a well of depth E is given by $\tau^{-1}(E) = \exp(-E/kT)$. After a particle escapes from its well, it chooses randomly a new well among the distribution $n(E)$. Thus the probability density $P(E)$ evolves following the equation

$$\frac{dP(E)}{dt} = -\frac{P(E)}{\tau(E)} + n(E) \cdot \int \frac{P(E')}{\tau(E')} dE'. \quad (\text{B.1})$$

The first term of the right-hand side counts the number of particles that escape from the well of depth E , and the second term counts the particles that hop from a well of depth E' to a well of depth E .

A stationary solution exists only for $T > T_c$. If $T < T_c$ a self-similar asymptotic solution appears and evolves following a $\exp(-E/kT)/t_w$ rescaling [3]. The system tendency is to fill infinitely deep wells. But it would take an infinite time to do that. Thus, after a transient regime, depending on the initial solution, the population tends towards a bell-shape distribution that evolves with time, $P(E, t_w)$. This distribution exhibits the following ageing scaling:

$$P(E, t_w) \approx f(e^{-E/kT}/t_w) \quad (\text{B.2})$$

which corresponds also to a scaling in t/t_w for any response function as the relaxation time τ scales in $\exp(-E/kT)$. The self-similarity of the ageing solution is robust in a trap model since qualitatively similar results are obtained if a non-exponential distribution of well density is used instead of an exponential.

Going back to the creep, in the trap model we can thus estimate the volume fraction of rearranged domain—which corresponds to the hop of fictive particles. It is written as

$$\Phi(t, t_w) = \int_0^t P(E, t_w) \exp(-t/e^{(\beta E)}) dE. \quad (\text{B.3})$$

Thus using relation (A.2), one gets immediately the relation between the time spectrum of the relaxation, and the creep—in the limit of small strain variations:

$$J(t, t_w) \approx G(0)^{-1} \left(1 + \frac{5}{3} \cdot \int_0^t P(E, t_w) \exp(-t/e^{(\beta E)}) dE \right). \quad (\text{B.4})$$

In figure 8 we have plotted the results of this model with reasonable values for the parameters. We have plotted t_{eff} versus $t + t_w$ for different value of t_w , and in the inset t_{eff}/t_w as a function of the step temperature T . It appears that the trap model can mimic the variations of t_{eff} at constant J as a function of the step temperature. Indeed figure 5 is similar to the inset of figure 8. But the trap model gives the wrong sign for the dependence of t_{eff} on t_w , thus figure 8 is not able to mimic the figure 7. More precisely, it results in an opposite dependence on t_{eff} versus t_w .

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