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Plastic deformation and physical ageing in PMMA

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Abstract

Ageing and rejuvenation of PMMA are investigated just above T_β and just below T_g by means of tensile creep experiments, in the non-linear range, i.e. for high stress levels. The molecular mobility is probed using torsional microcreep. Rejuvenation is induced by tensile Struik's 'type II' experiments, i.e. long-term ones. It is shown that, at low temperature, creep induces rejuvenation due to anelastic (or reversible) deformation, and so does recovery after the load removal. When the creep (or recovery) rate becomes very low, ageing proceeds at the same rate as natural ageing does. At high temperature, plasticity occurs and represents the main cause for rejuvenation that is no more reversible. In this case, plasticity seems to have a very significant influence on the thermodynamic equilibrium state reached after full ageing. These observations are finally interpreted in terms of microstructural mechanisms of deformation.

Keywords: Physical ageing; Rejuvenation; Plastic deformation

1. Introduction

Glasses and, more specifically, amorphous polymers below their glass transition point, are, in most cases, out of thermodynamical equilibrium. As such, they evolve spontaneously towards their supercooled liquid equilibrium state. The only condition for this process, named structural relaxation or physical ageing, is the availability of minimum molecular mobility. This condition is fulfilled above secondary relaxation temperatures and, most often, above the beta-transition point.

During the course of ageing, several concomitant phenomena are observed: the shrinkage of specific volume, the decrease in specific enthalpy and entropy, and the decrease in molecular mobility. Probing molecular mobility by means of low amplitude creep tests, several authors (see in particular the textbook of Struik [1]) showed the applicability of the time-ageing time equivalence. Moreover, low amplitude creep tests on ageing materials can be adequately described by the theory of linear viscoelasticity incorporating the notion of reduced time (or internal clock) driven by the ageing duration [1,2], thus allowing creep master curves to be built. Therefore, such low stress creep experiments can be said to pertain to the linear regime, in the sense that the ageing rate does not depend on the level of the creep stress.

If, however, creep experiments are performed at medium or high stress, this picture no longer applies, and the above-mentioned internal clock is seen to depend upon the stress amplitude [1]. It is always observed that the molecular mobility increases, sometimes strongly, such that spontaneous ageing is slowed, stopped, or even counteracted. This latter phenomenon has been termed 'de-ageing' or 'rejuvenation' by Struik [1]. Notice that what precedes concerning creep processes also applies to relaxation ones; in this case, the above-mentioned internal clock will depend upon the level of strain.

The question has long been to understand whether rejuvenation is the consequence of microstructural changes [1,3], or rather the expression of a non-linear viscoelastic behavior involving no major molecular rearrangement [2,4]. Under a low stress level, the ageing process is not perturbed: this is even the basis for measuring the ageing rate via repeated mechanical testing. Increasing the stress level biases the process; Santore [5] showed, using volumetric measurements, that the specific volume increases at the time of application (and removal as well) of a shear strain, this having in turn the effect of rejuvenating the material, i.e.

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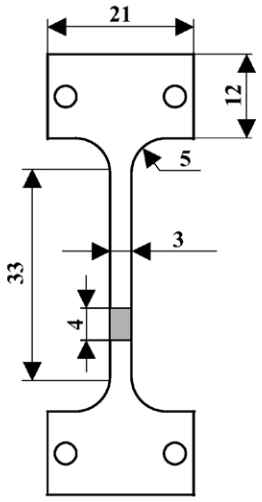

Fig. 1. Geometry of the test specimen.

increasing the molecular mobility. For short creep durations (and the range of temperatures considered), the effect seems reversible: the course of ageing is soon restored or, in other words, the memory of the effect of a (high) stress pulse fades away rapidly. This has led McKenna and co-workers (see in particular Ref. [4]) to claim that rejuvenation is nothing but a non-linear effect, without any major structural rearrangement involved.

Growing evidence seems to support the ideas of Struik [1,3], according to whom applying a large stress may deeply modify the microstructure of the polymer. These modifications are witnessed by calorimetric studies and energy balance analyses [6–9]. A large creep stress first produces an instantaneous (elastic) strain, rapidly followed by a delayed (also called viscoelastic or anelastic) strain. This latter part of the creep strain is recoverable below T_g; it is associated with enthalpy storage [6–8]. Kung and Li [10], studying recovery, showed that anelastic strain is associated with volume variations.

For sufficient temperature or duration, a new mechanism takes place, involving a part of the creep strain that is no more recoverable. Oleinik [7] and Quinson [11] showed it to be recoverable only by heating above T_g, and called it 'plastic strain'. Studying very low stress creep in PMMA not too far from T_g, Cherrière et al. [12] showed that this part of the strain can be attributed to the motion of entanglements. They called it 'rubbery creep strain', and showed it to follow a power law time dependence of the form:

$$\varepsilon^{R}(t) \propto t^{m}$$

with $m \approx 0.8$. This value of the exponent m is quite coherent with the results of Plazek [13], who found the same time dependence during creep above (and slightly below) T_g, i.e. in the rubbery domain. These experimental findings are in line with the views of Boyce [14] and Wu and Van der Giessen [15], for whom the plastic part of the strain is entropic by nature. Therefore, it generates entropic back-stresses that become significant only at high elongations. Otherwise, they are so low that they cannot induce any measurable recovery, except perhaps on geological time-scales, below T_g. This is further substantiated by Kung and Li [10] who showed that recovery above T_g involves a major part of the strain with but little volume variations; Hasan and Boyce [6] established that the enthalpy storage associated with plastic strain is quite negligible for small to moderate elongations, only becoming significant above, say 50%.

The present work aims at providing elements in understanding the interactions between physical ageing and plasticity, by probing the instantaneous molecular mobility during high stress creep and subsequent recovery.

Early low stress creep experiments intended to measure the molecular mobility during the course of ageing; they were thus conducted over short periods of time (generally less than 10% of the total ageing time) in order that ageing time be considered as constant over the measurement duration. This procedure, designed by Struik [1] and termed 'type I experiment', insures that creep results can be interpreted as a probe and reflect the instantaneous molecular mobility during ageing.

In order to study the effect of high stresses on ageing, different experiments were imagined [2]. The so-called 'type III experiments' consist in applying, at a given ageing time, a high stress short creep pulse, followed by regular subsequent low stress short creep pulses, in order to probe ageing eventually perturbed by the high stress pulse. 'Type II experiments', on the other hand, consist in applying, at a given ageing time, a high stress *over a long period of time*; low stress short creep pulses are then superimposed, in order to probe ageing under the continued action of a high creep stress. The investigations reported in the present paper involve type II experiments that appear to be the only ones capable of producing plastic straining. Moreover, the recovery process following the stress removal is also studied in order to discriminate the respective effects of reversible (i.e. anelastic or viscoelastic) and non-reversible (i.e. plastic) deformation on ageing.

2. Experimental procedure

The experimental investigations reported below used a specific apparatus described elsewhere [16], the main characteristics of which are simply outlined here. It allows simultaneous longitudinal tensile creep and torsional creep on dumbbed-shaped specimens (gauge length: 33 mm; gauge section: $3 \times 4\ \text{mm}^2$), as shown schematically in Fig. 1. The tensile loading may be applied in the non-linear range, and the longitudinal strain is recorded with an accuracy of 10^{-5}, either during creep or recovery. Torsional creep is specifically devoted to probing instantaneous molecular mobility, either during spontaneous ageing, longitudinal creep or recovery. As such, it involves very low levels of torsional stress (< 0.1 MPa) and strain

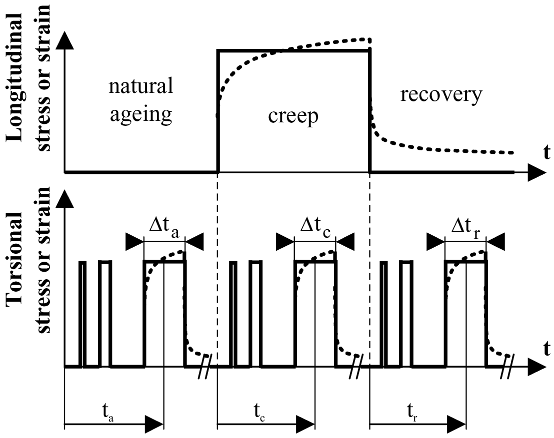

Fig. 2. Time sequence of the experimental procedure.

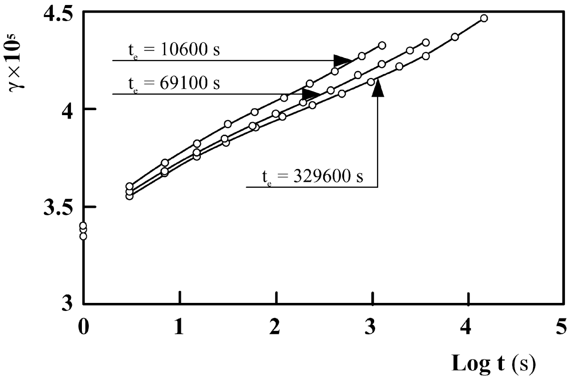

Fig. 3. Example of microcreep curves performed during natural ageing at 42 °C.

($<10^{-4}$), the latter being measured with an accuracy better than 5×10^{-8}. In order to avoid any confusion, the term 'creep' will designate longitudinal creep, whereas torsional creep will be termed 'microcreep' in the sequel.

The studied material is PMMA, on account of the great deal of experimental studies and results accumulated to date on this material. Specimens are machined out of 3 mm thick commercial Altuglass® sheets, and mounted on the testing apparatus. They are then heated to 140 °C (i.e. 25 °C above T_g) for half an hour, in order to erase any thermo-mechanical history, and to insure reproducible and isotropic initial state. They are then mildly cooled to the test temperature, by simply switching off the power supply of the furnace. The heat treatment is not a strong quench, and the material begins to age during cooling. However, ageing times will be counted from the time at which the test temperature is reached. It is then stabilized within 0.25 °C.

The experimental procedure is as follows:

(i) the first phase simply consists in letting the material age freely for a hundred hours or so;
(ii) in the second phase, a pre-selected value of the creep (tensile) stress, as defined by the applied force divided by the undeformed cross-section, is applied to the specimen for a pre-selected (long) duration;
(iii) the creep stress is then removed, and recovery is recorded until the recovery rate reaches very low values involving unreasonable experiment durations.

During each phase, microcreep tests are performed following the aforementioned Struik's procedure [1], i.e. for durations not exceeding 10% of the duration *of the considered phase*. The microcreep stress is then removed, until 95% of the microcreep strain is recovered at least, after what a new microcreep test is performed. Fig. 2 sketches out the total experimental procedure. As a verification, a sample was subjected to (longitudinal) creep without applying any microtorque. The creep curves obtained with and without microtorque could be strictly superimposed: microcreep has no detectable influence on creep.

It is well known that the crucial mechanism for the creep deformation of glassy polymers is the α-relaxation process. Therefore, experiments are done between T_β (~20 °C) and T_g (~115 °C), at temperatures of 42, 61, 68, 82, 90, and 100 °C, respectively. However, the main results having been obtained just above T_β and just below T_g, the test temperatures of 42 and 100 °C are selected here for report.

The stress level must be sufficient to allow significant rejuvenation (i.e. above 10 MPa for PMMA according to Read [17]), but not too high, in order to avoid failure during creep, especially at low temperature. The selected values of tensile stress are 26 MPa at 42 °C, and 4.0 and 8.2 MPa at 100 °C.

The molecular mobility is quantified as follows. It was systematically shown [18] that the microcreep results can be described within a very good accuracy by:

$$\gamma = \gamma_i \exp\left(-\frac{t}{t_0}\right)^m \qquad (1)$$

where γ is the microcreep torsional strain, t, the time elapsed from the application of the microstress, and γ_i, t_0, and m are obtained as best-fit constants (obviously differing from a microcreep test to another). An example corresponding to natural ageing at 100 °C is shown in Fig. 3.

It was shown [18] that t_0 is closely linked to the average relaxation time, thus reflecting the main aspects (but not all) of the molecular mobility. The exponent m ($0 \le m \le 1$) is related to the width of the relaxation spectrum; a low value of m indicates a broad distribution, whereas $m = 1$ represents a single relaxation mechanism, i.e. the limiting case of a narrow distribution. As a general rule, m always decreases during the course of ageing.

Though the three parameters γ_i, t_0, and m are worth a detailed analysis, attention will be mainly focused here on t_0, considered to reflect the instantaneous molecular mobility.

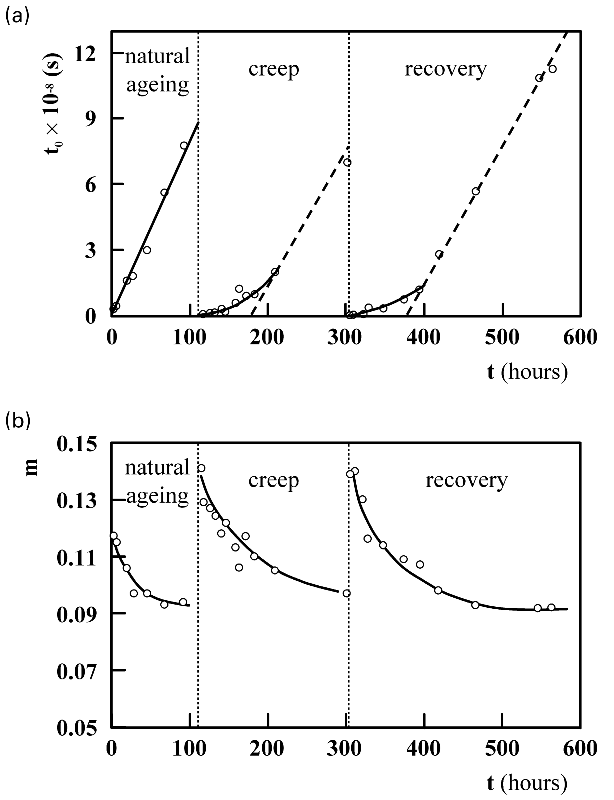

Fig. 4. (a) Evolution of t_0 at 42 °C and 26 MPa. (b) Evolution of m at 42 °C and 26 MPa.

3. Low temperature results

Fig. 4a and b shows the evolution of t_0 and m at 42 °C. After cooling from the rubbery state, the parameter t_0 is seen to increase linearly from 5×10^5 s just after cooling to 7.7×10^8 s after 100 h of ageing. The latter value is extremely high. At this quite low temperature, the exponent m is of the order 0.1. For such a value, the limits of an analysis via the stretched exponential function (1) are probably reached, and the value of t_0 should only be taken as indicative.

However, loading the sample with a stress of 26 MPa induces a creep elongation that also follows a stretched exponential form (Fig. 5):

$$\varepsilon = 86 \times 10^{-4} \exp\left(-\frac{t}{7.8 \times 10^5}\right)^{0.104} \tag{2}$$

where ε stands for the creep (longitudinal) strain, and time is given in seconds, as will be the case in the remainder of this paper also. The 'relaxation time' of 7.8×10^5 s and the exponent of 0.104 are surprisingly close to those indicated by the microcreep results at the very beginning of the ageing process ($t_0 = 7.7 \times 10^5$ s and $m = 0.1$). The application of the stress confers to the material a molecular mobility quite similar to the one of the unaged material. This is coherent with a phenomenon of rejuvenation, not surprising since the stress is about three times larger than the value of 10 MPa found by Read [17] for rejuvenation to occur in tension for PMMA.

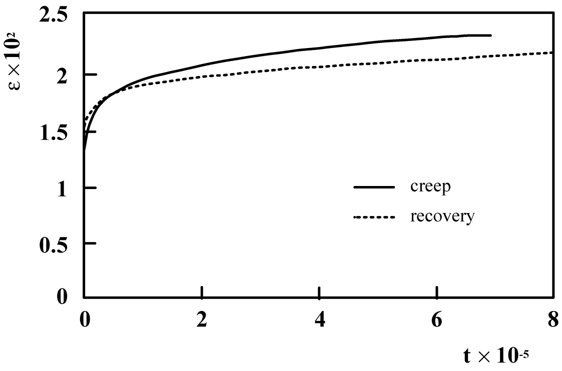

Fig. 5. Evolution of elongation during creep and recovery at 42 °C.

The proof is given by the microcreep results. The first microcreep test is performed 2 h after the application of the creep stress, and indicates a value of 1.8×10^6 s for t_0. This value is close to 7.7×10^5 s obtained after cooling from the rubbery state, and corresponds to a vigorous rejuvenation. The effect of preliminary ageing seems completely erased. The first five values of t_0 determined during creep increase slowly. Beyond 100 h of creep, t_0 increases linearly with creep time, as during stress-free ageing. At this time, the high tensile stress has no more influence on the ageing rate of PMMA.

After removing the creep stress, the specimen contracts. Just after unloading, the contraction rate is higher than just after loading, as shown in Fig. 5. Beyond 10 h, the contraction rate rapidly decreases and becomes negligible after 50 h. During the first 20 h, the sample recovers about 90% of the creep elongation (i.e. about 2% total strain). The parameter t_0 behaves exactly as after loading: the initial drop at unloading is followed by a slow increase for 100 h, and then by a linear increase with recovery time for the remainder of the experiment.

It must be noticed that in both cases, the drop in t_0 is accompanied by a jump of the exponent m from 0.1 to 0.15 roughly, showing a narrowing of the relaxation spectrum induced by loading and unloading as well (Fig. 4).

4. High temperature results

During stress-free ageing at 100 °C, t_0 increases no more linearly with ageing time (Fig. 6a), as indicated by the following:

$$t_0 = 3.4 \times t_e^{0.75} \tag{3}$$

where t_e is the ageing time. Struik [1], who defined the ageing rate μ as $\mu \equiv \partial \ln t_0 / \partial \ln t_e$, already noticed that μ is close to unity at low temperature, and progressively decreases to 0 near T_g. Since $\mu = 0$ means that ageing has no influence on the molecular mobility, this value is

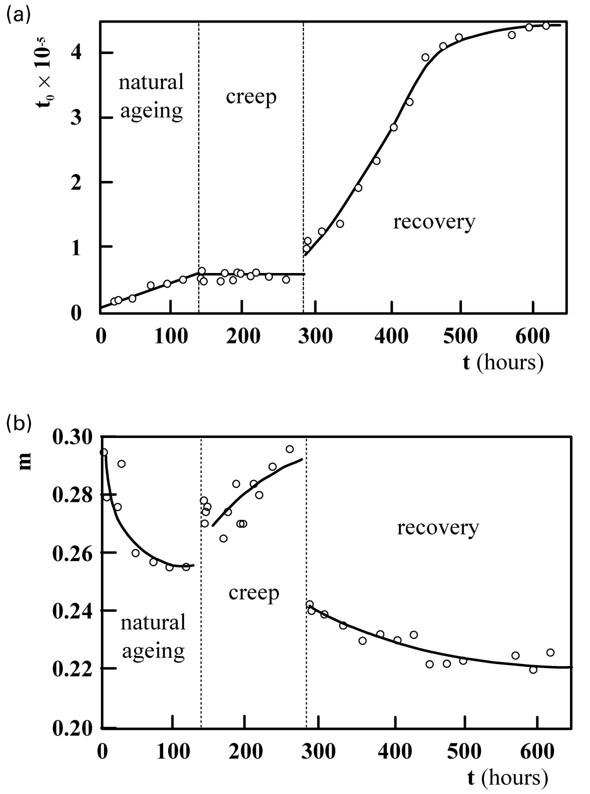

Fig. 6. (a) Evolution of t_0 at 100 °C and 4 MPa. (b) Evolution of m at 100 °C and 4 MPa.

characteristic of the supercooled equilibrium state, as noted by McKenna and co-workers [2,4].

This means that t_0 is not very far from its equilibrium value, that can be estimated to be about 10^5 s after some weeks of ageing. This is confirmed by the asymptotic decrease in the exponent m, which reaches a minimum value of 0.25 after 90 h of ageing (Fig. 6b).

When a stress of 4 MPa is applied after 140 h of ageing, the creep strain can be described by (Fig. 7):

$$\varepsilon = 2.25 \times 10^{-3} \exp\left(-\frac{t}{2.56 \times 10^3}\right)^{0.301} \quad (4)$$

where the initial elongation (2.2×10^{-3}) is four times lower than at 42 °C, the relaxation time t_0 (2.56×10^3 s) is about 30 times lower, and the exponent m, as expected, takes the value of 0.3 instead of 0.1 at low temperature.

This leads to a creep rate which decreases slowly down to $3 \times 10^{-8}\ \mathrm{s}^{-1}$ after 170 h of creep. Further creep occurs at a nearly constant rate, and a steady-state regime is seemingly established. All the torsional microcreep tests made during creep are identical, and there is no drop in t_0 at the time of stress application, as shown in Fig. 6a.

Although t_0 does not change during creep, the slight increase of the exponent m suggests that the structure of PMMA evolves somewhat. The steady-state regime may therefore be interpreted as the competition between two mechanisms, namely ageing and rejuvenation.

The contraction after the stress removal is quite small, about 1%. Nevertheless, the recovery rate during the first 2 h is higher than the creep rate at the same time (Fig. 7). Recovery stops quickly, and the major part of it is accomplished in 25 h. The final elongation is about 2%.

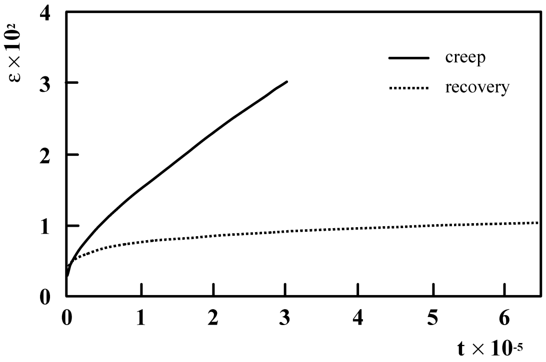

Fig. 7. Evolution of elongation during creep and recovery at 100 °C and 4 MPa.

The microcreep tests performed during recovery reveal the great influence of a quite small creep elongation (~3%). During the first 200 h of recovery, the relaxation time t_0 increases following:

$$t_0 = 8 \times 10^4 + 0.5 t_\mathrm{r} \quad (5)$$

where t_r is measured from the time of stress removal; meanwhile, the exponent m drops from 0.29 to 0.24, then slowly decreases to 0.22.

Ageing ceases suddenly after 200 h of recovery. For the last 100 h, t_0 and m remain constant at 4.5×10^5 s and 0.22, respectively: the specimen seems to have reached an equilibrium state. It is clear that though small, the irreversible strain (about 2%) has strongly enhanced ageing: the ageing rate during recovery is more than five times the rate of natural ageing.

The apparent equilibrium state is characterized by $t_0 = 4.5 \times 10^5$ s and $m = 0.22$, to be compared with $t_0 \approx 10^5$ s and $m \approx 0.25$ obtained after preliminary ageing. Though differences are not large, these respective values indicate that the 2% irreversible (i.e. plastic) strain has induced significant changes in the final equilibrium state.

The situation is quite different if the creep stress is 8.2 MPa instead of 4.0 MPa. In this case, creep occurs in two successive stages. The creep rate first decreases for 7 h, passes through a minimum, then continuously increases until the stress is removed after 33 h of creep (Fig. 8).

The first 7 h of creep can be described by:

$$\varepsilon = 4.4 \times 10^{-3} \exp\left(-\frac{t}{1.03 \times 10^3}\right)^{0.33} \quad (6)$$

The exponent 0.33 has about the same value as found at 4 MPa, but the relaxation time is shorter, 10^3 s instead of 2.5×10^3 s. It can be assumed that in this stage of creep, the mechanisms are similar to those acting under 4 MPa, except that due to the higher stress, the rejuvenation process is more efficient, leading to a lower value of t_0.

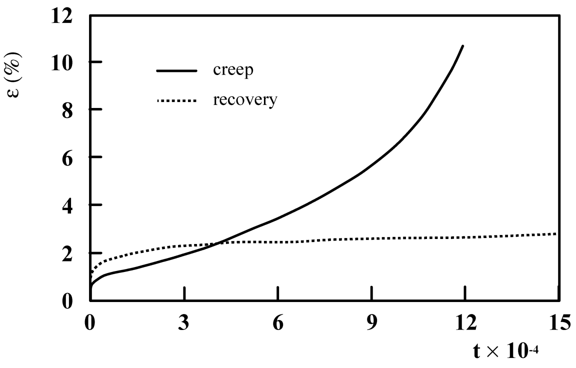

Fig. 8. Evolution of elongation during creep and recovery at 100 °C and 8.2 MPa.

After 7 h, the elongation is about 1.8%, and the creep rate has reached a minimum value of $3.16 \times 10^{-7}\ \mathrm{s}^{-1}$. It then increases to reach $2.5 \times 10^{-6}\ \mathrm{s}^{-1}$ at 33 h of creep, when the stress is removed. The final elongation is 10.5%; no striction is apparent, but many crazes of about 0.3 mm in length are observed at the sample surface. Beyond the minimum creep rate, the relaxation time t_0 decreases sharply from 5×10^4 to 1.4×10^3 s and surprisingly, the exponent m diminishes slightly too (Fig. 9a and b).

During the first hours following the stress removal, the specimen contracts very rapidly up to 1.5% of recovery. Then, the recovery rate decreases, and beyond 25 h the recovered strain remains at 2.2%. This value is about twice the recovery under 4 MPa.

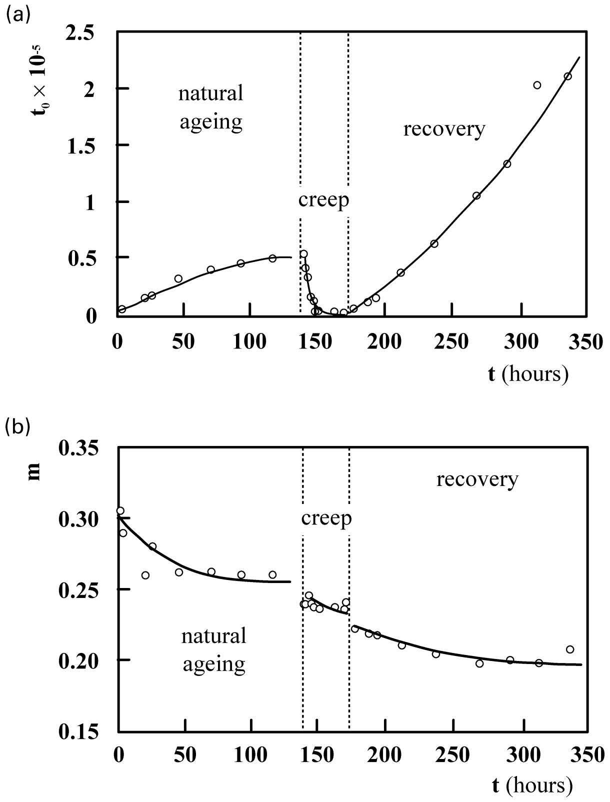

Fig. 9. (a) Evolution of t_0 at 100 °C and 8.2 MPa. (b) Evolution of m at 100 °C and 8.2 MPa.

As in the previous case, the microcreep tests reveal an important acceleration of ageing during recovery: after 100 h of recovery, t_0 increases linearly with the recovery time in nearly the same fashion as at 4 MPa, while m decreases to 0.19. This latter value is lower than for the case 4 MPa. Unfortunately, the experiment was interrupted before reaching an equilibrium state. However, such an equilibrium would be characterized by $t_0 > 2.5 \times 10^5$ s and $m \approx 0.19$, thus being clearly different from the supercooled liquid equilibrium state aforementioned.

5. Discussion and microstructural interpretation

Let us discuss the low temperature (42 °C) results first. At this temperature, just above T_β, the α-relaxation is hardly active. Natural ageing is quite slow, and the molecular mobility decreases almost linearly with ageing time. This is equivalent to Struik's finding [1] that, in the linear range, $\mu \equiv \partial \ln t_0 / \partial \ln t_e$ is close to unity at low temperature. Applying the creep stress has the following effects. In a first and quasi-immediate step, the molecular mobility increases abruptly, and comes close to its value prior to ageing: rejuvenation is rapid and strong. After this, a transient phase of slow decrease of the molecular mobility takes place, along with the essential part of the creep strain development. Once the creep rate has decreased to a very small value, ageing is seen to continue at the same linear rate as during spontaneous ageing. Removing the stress has the same effect as applying it: immediate rejuvenation, transient evolution of recovered strain, 'normal' ageing.

The evolution of the molecular mobility during creep is plotted in Fig. 10 versus creep rate. The solid line represents a linear approximation of available data, which shows that the molecular mobility and the creep rate are strongly

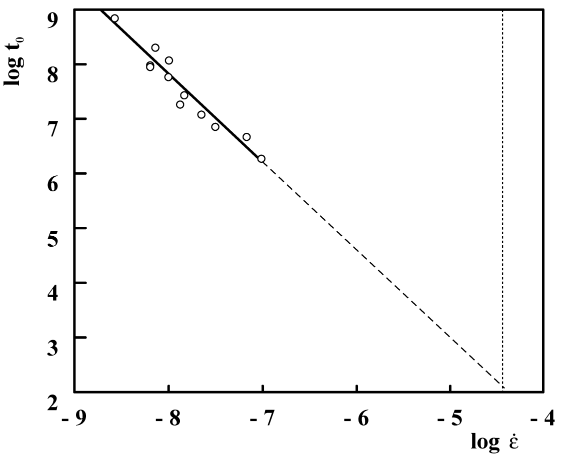

Fig. 10. Evolution of t_0 with the creep rate at 42 °C. Solid: linear regression of actual data; dashed: extrapolation towards low rates; dotted: strain rate at the time of stress application.

correlated, at least after two hours of creep (time at which the first microcreep measurement was made). This correlation applies through the entire range of the creep phase (corresponding to Fig. 4a), whether t_0 evolves linearly with creep duration or not, and even for strain rates as low as $3 \times 10^{-9}\ \mathrm{s}^{-1}$. This observation may be interpreted by assuming that rejuvenation is driven by the creep rate.

It is interesting to wonder about the early phase of creep. Unfortunately, no measurement is available at this time. Trying to extrapolate the linear plot of Fig. 10 (dashed line), one finds out that at this time, t_0 should be of the order 10^2 s. We remind that t_0 is 5×10^5 s at the beginning of the natural ageing phase. However, the cooling process is not a strong quench (the test temperature is reached after roughly 7 h of cooling). An infinitely rapid quench would provide the material with a molecular mobility characteristic to the glass transition temperature. This can be estimated to be $t_0 \approx 10^3$ s, i.e. the ratio of the viscosity at T_g ($\sim 10^{12}$ Poise) to the characteristic modulus (~ 1 GPa). One may also use the WLF equation and deduce t_0 at T_g from its *equilibrium* value at 100 °C ($\sim 10^5$ s) and conventional values of the WLF constants. Therefore, two tentative conclusions may be drawn: (i) the application of the creep stress is a very strong rejuvenation, equivalent to heating above T_g followed by a strong quench, and (ii) the rejuvenation process is rapid, and occurs probably during the application of the creep stress.

These features may be interpreted on structural grounds as follows. Since the creep strain is almost entirely recoverable, very little plastic deformation occurs, if any. Neglecting it, let us follow the ideas of Pérez [19], Escaig [20], or Hasan et al. [21,22]. According to these authors (and others), the anelastic strain is the result of the nucleation and growth of mutually non-interacting 'microsheared domains' [19], 'dislocation loops' [20,23,24], or 'transformed domains' [21,22]. These domains produce local back-stresses opposed to the direction of straining. This is coherent with the ability of the specimen to recover spontaneously almost the entire creep strain. Therefore, the material may be seen as an elastic, well-aged, matrix, containing isolated though numerous microsheared domains. These ones have experienced jumps over high-energy barriers. They are then presumably in a state of relatively high energy, and should possess a high molecular mobility. As such, they represent the rejuvenated (and thus able to age) part of the material. The microsheared domains are essentially formed at the beginning of creep, along with back-stress build-up. After what, they may start to age 'normally'. Removing the creep stress lets the material evolve under the sole action of back-stresses: microsheared domains experience backward jumps releasing back-stresses, but leaving again the material in a state of high molecular mobility, enabling it to age again towards the same supercooled liquid equilibrium as natural ageing.

Though this picture is no doubt simplistic, it raises no contradiction with experimental findings, and illustrates the material's behavior when (i) no plasticity takes place and (ii) the molecular mobility is too low to enable significant diffusion to occur, such that microsheared domains cannot interact. It also provides an explanation for the observed fact that initial recovery rate is higher than initial creep rate. During creep, microsheared domains are nucleated progressively; recovery only involves already present microsheared domains, all acting at the same time such that recovery is faster than creep is.

Low temperature results may be compared to those of Santore et al. [5], represented qualitatively in Fig. 11. Santore et al. [5] performed type III experiments and recorded volume evolutions during natural ageing, relaxation and recovery, for several creep amplitudes. They found (Fig. 11) that during natural ageing, the specific volume shrinks progressively towards a steady-state value, forming a baseline curve quite similar to Kovacs' findings [25]. The stress application immediately induces a volume increase, followed by an accelerated ageing phase witnessed by a rapid decrease of volume. The stress removal has a quite similar effect; note that the volume jump at stress removal and the initial recovery rate are higher than the initial creep ones are. Therefore, these results indicate a strikingly similar trend of the evolutions of the molecular mobility, as measured by our parameter t_0, and specific volume. It can be inferred that, at low temperature, the supercooled liquid equilibrium is biased by the applied stress, but is not fundamentally affected. In other words, inelastic—but recoverable—strain is the consequence of non-linear viscoelasticity, but the underlying structure of the material remains unchanged. Thus, the claim of McKenna and co-workers [2,4] appears as justified if restricted to low temperature, or more precisely, to loading paths that involve no plastic straining.

The high temperature situation is quite different, even under low creep stress. At 100 °C, i.e. 15 °C below T_g, the α-relaxation process is quite active. As discussed above, at the end of the natural ageing phase, the material is not so far

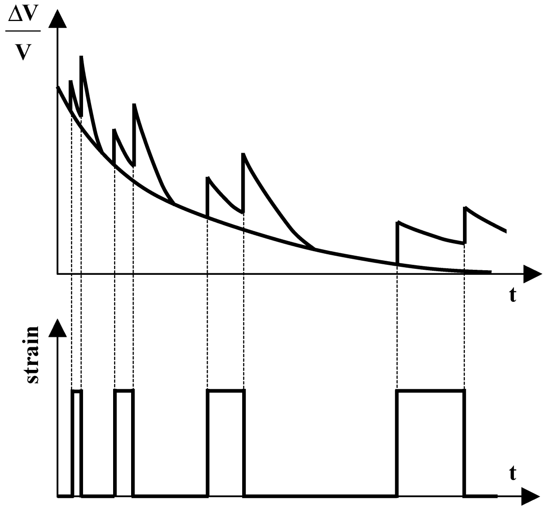

Fig. 11. Qualitative schematization of the results of Santore et al. [5].

from its supercooled liquid equilibrium state. Applying a creep stress of 4 MPa seems to stop ageing, since the molecular mobility, as measured by the parameter t_0, remains constant during the whole creep phase. This is only an apparent effect, since the parameter m evolves towards a relaxation spectrum narrowing. In fact, the material appears to reach a steady-state regime for which the strain rate keeps a constant value. This is once again coherent with the above interpretation of the creep rate as the 'driving force' for rejuvenation. This means that back-stresses do not equilibrate the external loading, as witnessed by the low level of final recovery. It is probable that back-stresses rapidly reach a steady-state value, which can be interpreted as a balance between microsheared domains nucleation and some mechanism of back-stress erasure. Therefore, rejuvenated material is continuously produced, each new site immediately beginning to age. The constancy of t_0 is then fortuitous, because the ageing rate is driven by the temperature, while the rejuvenation rate is fixed by the stress level primarily.

We saw above that back-stresses may be attributed to the nucleation and growth of microsheared domains, that distort the neighboring (well-aged) elastic matrix. However, this growth is not unlimited: it happens to move entanglements, then allowing molecular segments to adopt lower entropy and energy configurations. This picture is a plausible explanation for back-stress relaxation and its connection to plasticity.

When the creep stress is removed, recovery occurs rapidly and stops soon. The stress removal is accompanied by a strong enhancement of the ageing rate that keeps a *constant value during recovery*, regardless to the value of the recovery rate. It can be inferred that the recovery process has no strong influence on the molecular mobility. In other words, the strong observed ageing rate can be attributed to plasticity. This is coherent with the above-mentioned fact that after plastic straining, the material ages towards a specific equilibrium. If we assume that the ageing rate depends upon the distance to equilibrium, it can be inferred that the new equilibrium state is more stable than the former. If this is true, its characteristic molecular mobility should be lower, and this is precisely what is observed. However, this should not be taken as a definite proof, because the plastically strained equilibrium is an oriented one, and should exhibit an anisotropic molecular mobility deserving a more detailed experimental analysis.

Doubling the creep stress does not merely modify the beginning of the creep phase, since the creep strain (up to 2%) is well described by Eq. (6), in which the instantaneous strain has doubled, relative to the 4 MPa case, and the average relaxation time t_0 is reduced by a factor 2 approximately, indicating that the creep rate is two times faster. Microcreep results show that during this first creep phase, the parameter t_0 (about 5×10^4 s) has not changed much (Fig. 8), so that it is reasonable to consider that the same molecular mechanisms are at work. However, the rejuvenation process is necessarily faster, and happens to overcome ageing: an accelerated creep phase is observed. This feature is attributed to plasticity: the recovered strain at 8.2 MPa is twice the value recorded at 4 MPa, indicating that the back-stresses do not evolve much during this creep phase, since back-stresses are mainly generated during early phases of creep. Meanwhile, the molecular mobility is strongly enhanced, as it drops from 5×10^4 to 10^3 s approximately: rejuvenation is very effective. Once more, recovery does not change the molecular mobility; it only stops the rejuvenation process, such that accelerated ageing takes place towards a plastic strain dependent equilibrium state, as before.

6. Summary and final comments

Summarizing, the following picture is proposed. At low temperature, for the selected stress and time scale, no plasticity occurs (at least in a qualitative sense). Applying the creep stress induces anelastic strain. This one is seen as the macroscopic consequence of the nucleation (and growth) of microsheared domains, i.e. spots of deformed—and thus rejuvenated—material, surrounded by elastic—and aged—material. The anelastic or viscoelastic behavior is clearly non-linear, but is *reversible*. At this low temperature, the molecular mobility is low, and plasticity has hardly any time to occur, because it should then involve diffusion *in the aged part of the material* (remembering that microsheared domains may be viewed as non-mobile defects [19]). Hence, the intrinsic equilibrium state to which the material tends is not very much modified by the inelastic strain, though it should be modified somewhat. This explains why ageing proceeds at approximately the same rate during the three stages of the experiment.

The situation is different at high temperature, because diffusion can occur quite quickly. Microsheared domains are nucleated, can grow rather fast until entanglements become untrapped, thus generating plasticity while erasing back-stresses, at least partly. Plasticity is not reversible, and induces a very different supercooled liquid equilibrium state, i.e. a highly oriented one, as revealed, for example, by Haidar and Smith [26]. This explains why ageing proceeds so rapidly during recovery; it does not so during the creep phase, because rejuvenation happens continuously. This contrasts with the low-temperature situation for which rejuvenation only occurs during back-stress build-up.

This picture remains in line with the claim of McKenna and co-workers, because they used type III experiments, involving high stresses but only on short time scales, such that, even at high temperature, plasticity has but little time to occur. This point is even quoted by McKenna himself [27] in a recent paper. It is very likely that the results of McKenna and co-workers [2,4] would have been entirely different for type II experiments.

A puzzling point is represented by the ageing rate at high temperature during recovery. If we accept that this rate depends on the distance to equilibrium, then it should decrease as this distance is reduced. This is not what is observed, as this rate is rather constant until it stops abruptly, as also reported by McKenna and co-workers [4]. However, data are not sufficiently accurate to be fully conclusive, and additional work is clearly required.

One may also think that since molecular segments between entanglement points are elongated, the total number of permitted (iso-energy) configurations is reduced. As the frequency of attempts only depends on temperature, the probability of reaching lower energy states increases. This is a plausible explanation for the observed ageing rate enhancement after plastic straining.

Three spatial ranges are clearly involved in the process of straining, and have distinct consequences. The finest one is the beta;-process characterized by segments of a few atomic bonds along the molecular chain [28]. The concept of quasi-punctual defect put forward by Pérez [19] is clearly applicable to this process, and nothing happens when it is frozen (i.e. below T_β). The intermediate—and somewhat fuzzy—scale is the α-process, which involves longer-range interactions, and for which the notion of microsheared domains applies. Entanglement motions represent the broadest scale.

The scenario described above must of course be tested quantitatively. Such a work needs an appropriate model for describing anelasticity and plasticity as well, not available to date, to the authors' knowledge. The main obstacle seems to lie in the description of the glassy state, if possible in a non-equilibrium thermodynamic framework. This is clearly required, because our results show that the material behaves as if it 'knew' its internal equilibrium state.

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