On the workhardening rate of glassy polymers:
1. Application to the physical ageing of atactic PMMA

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The aim of this paper is to introduce a new parameter to characterize the non-elastic behaviour of glassy polymers, namely the workhardening rate. The change in molecular microstructure induced by non elastic deformation during the pre-yield stage is treated as a defect nucleation rate. Such defect nucleation is very sensitive to the past thermomechanical history of the material and therefore the parameter K, which characterizes the ability of the polymer to deform non-elastically, will be influenced by any structural variation. Application to physical ageing of atactic poly(methylmethacrylate) PMMA is presented.

Keywords Workhardening; physical ageing, poly(methylmethacrylate); plastic deformation; glassy polymers

INTRODUCTION

Non-elastic straining of solid polymers in the glassy state causes changes in their molecular microstructure. Basically, these changes occur locally in the polymer sample, and are heterogeneously distributed either within more or less diffuse shear bands[1,2], or within localized crazes[3]. At the tip of such deformed regions the chain arrangement might be described as some number of molecular defects[4,5] propagating the 'plastic' strain forward (the partially recoverable character of which is not essential in this description). It is well known that these deformation zones nucleate clearly below the conventional yield stress, so that the above molecular defects, which can be looked upon as their precursors, should also nucleate and multiply during the pre-yield stage. These defects have been described either as kinks along molecular rods[6,7] or as Volterra or Somigliana dislocations[5,8]; their probable limited motion through the bulk results in a more and more profuse shearing leading to a flow of the solid at yield, of more or less irreversible character. Therefore it is of prime importance to observe and understand the special defect nucleation rate a given polymer exhibits during the pre-yield stage, in order to characterize its ability to deform non-elastically.

Let us assume each molecular defect contributes a given total plastic strain e once it is nucleated, so that if dN defects are nucleated at some point in the pre-yield stage, a plastic strain increment $d\varepsilon_p = edN$ is obtained. It can clearly be seen that the plastic work-hardening rate,

$$K = \left(\frac{d\sigma}{d\varepsilon_p}\right)_{\dot{\varepsilon}}$$

as observed during a constant (total) strain rate test, is determined by the net number of defects produced per unit stress, $dN/d\sigma$; for the stress increment $d\sigma$ produces the strain $d\varepsilon_p = edN$, from the nucleation of dN defects, hence $K = (dN/d\sigma)_{\dot{\varepsilon}}^{-1}$ assuming the defect strain e is not stress dependent, which should be the case in the pre-yield stage where defect nucleation may be thought to be dominant. Thus K is a measure of the resistance of the material to plastic strain: a purely elastic behaviour $(d\varepsilon_p = dN = 0)$ means K is infinite, while during yielding $(\dot{\varepsilon}_{e1} \simeq 0)K \simeq 0$. We will show below how K can be readily measured in the pre-yield stage; thereby showing the ability of a given polymer to deform non-elastically can be experimentally investigated.

A number of physical properties can be thought to have some influence on this ability and hence also on K. Examples are the crosslink density of a resin, the thermal jump frequency of monomer units, or the local density of monomer units available for local cohesion in thermoplastics, etc. ... In such cases, the measurement of K can be used as a sensitive tool to follow and characterize processes like the curing of resins, their irradiation, the crack healing kinetics, or the physical ageing of thermoplastics and its influence on non-elastic properties. This paper is devoted to an investigation of the latter through K measurements, choosing as an example atactic PMMA. Applications to the curing evolution in resins are currently in progress and will be published in a subsequent paper.

Physical ageing is a process which results from the influence of thermal history on molecular mobilities, i.e basically on the jump frequency of monomer units[9] depending on various free volume (or point defects) contents and distributions. The temperature of those secondary mechanical relaxations (measured at frequencies ca. 1 Hz) which entail the smallest local distorsion of the chain backbone, i.e., usually the β-relaxation (but which might be called γ in
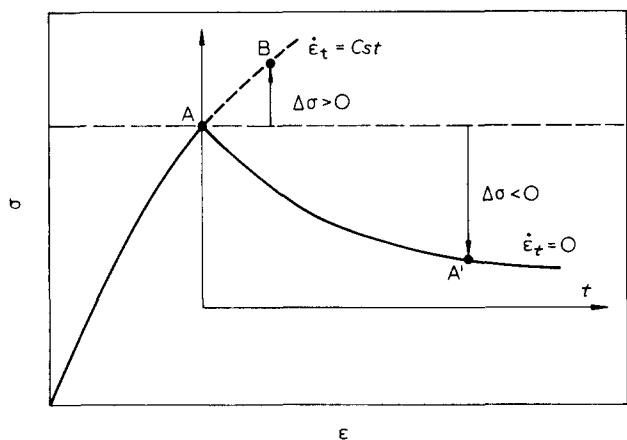
Figure 1 Definition of a state B at $\dot{\varepsilon}_t$ = Cst, isostructural to the state A' of the stress relaxation test

polycarbonate[10]) is frequently taken as being the temperature threshold above which mass transport over a limited range can occur within a reasonable length of time. This is similar to short range diffusion of monomer units, a process depending on their jump frequency. Accordingly, physical ageing seems to have only negligible effects on the physical properties of polymers below these temperatures[9,10].

We have recently proposed, on the basis of a careful experimental investigation of the plastic deformation in glassy PMMA[11], that the rising of such diffusional movements above some critical temperature T_c, akin to T_β (or, more exactly, to the low temperature foot of the 1 Hz β peak in PMMA, $T_c \simeq 220$ K), changes the deformation mode from a defect-glide, chain-orientational mode below T_c, to a diffusional mode, in which orientation relaxation occurs locally in rather diffuse shear bands above T_c.

In order to check the assumed differences in the deformation mechanisms, it has been possible to study the effect of molecular mobility on the pre-yield work-hardening rate K, i.e. on the defect nucleation mechanism By giving different free volume contents and distributions to PMMA samples, i.e., different ageing histories, the K dependence *versus* ageing time has been observed Preliminary experiments have been done at a constant total strain (at a given deformation time), and at two temperatures chosen in each of the deformation modes, 195 K and 290 K. At the lower temperature, K is quite insensitive to marked ageing differences, hence to free volume content and distribution; in contrast, K is found to increase strongly with ageing time (or a decrease in jump frequency) at the higher temperature. These results thus support our previous conclusions[11] and show defects nucleate by a fundamentally different mechanism in the two modes.

In the next section we will discuss the method used for measuring K, by repeated successive stress relaxations, and in subsequent sections we will define the thermal treatment and ageing conditions given to the different samples, describe the mechanical tests used and finally discuss the results we achieved.

MEASUREMENT OF THE WORK-HARDENING RATE, K

In the pre-yield stage, both elastic and non-elastic strains

are mixed, with a ratio varying from pure elastic to largely dominant non-elastic strain. In order to investigate non-elastic or plastic properties in this stage, it is essential to have an experimental method of uncoupling them. This is readily done by stress relaxation. During this test, in which the total strain rate $\dot{\varepsilon}_t = 0$, any non-elastic strain component $\Delta\varepsilon_p$ produced in a time Δt, such as at point A' in *Figure 1*, is easy to measure from the simultaneous stress drop $\Delta\sigma < 0$[12] provided that the effective elastic modulus M of the machine-sample association be known:

$$\Delta\varepsilon_p + \Delta\varepsilon_{e1} = \dot{\varepsilon}_t\Delta t = 0, \text{ or } \Delta\varepsilon_p = -(\Delta\sigma/M) \qquad (1)$$

In fact the observed time variation $\Delta\sigma(t)$, or $\Delta\varepsilon_p(t)$, also contains some information about the slight variation in microstructure brought about by the extra strain $\Delta\varepsilon_p$, i.e. information about the corresponding slight nucleation of defects in the polymer sample during the relaxation test. We show below how to evaluate this effect, which introduces K into the relaxation equation, a method that parallels that followed by Kubin in the case of crystals[13].

Let us assume the non-elastic strain follows the Eyring equation:

$$\dot{\varepsilon}_p = \dot{\varepsilon}_0 \exp - (\Delta G/kT) = f(\sigma, T, \text{Structure}) \qquad (2)$$

This relation can be expanded in terms of stress during relaxation so that, substituting ε_p into equation (1), the time evolution $\Delta\sigma(t)$ can be predicted and confirmed by experiment. This expansion relates the rate $\dot{\varepsilon}_p(A')$ at some point A' during relaxation, for a time Δt and strain increment $\Delta\varepsilon_p$ (see *Figure 1*), to $\dot{\varepsilon}_p(A)$ at the start at point A ($\Delta t = 0$, $\Delta\varepsilon_p = 0$). Let us first neglect, for the sake of simplicity, the slight change in microstructure from A to A', i.e. in the defect number: $N(A) \simeq N(A')$. Then $\dot{\varepsilon}_p(\sigma, T, \text{Structure})$ can be expanded in terms of stress at constant structure and temperature and reads:

$$\dot{\varepsilon}_p(A') = \dot{\varepsilon}_p(A) \exp(V_0\Delta\sigma/kT)$$

with V_0, the apparent activation volume:

$$V_0 = kT\left(\frac{\partial \ln \dot{\varepsilon}_p}{\partial \sigma}\right)_{T, \text{Structure}} \qquad (3)$$

which is the same as the true activation volume: $-(\partial\Delta G/\partial\sigma)_{T, \text{Structure}}$ when $\dot{\varepsilon}_0$ is not stress dependent. Substituting this value of $\dot{\varepsilon}_p(A')$ into equation (1) leads to the usual time evolution:

$$\Delta\sigma = -\frac{kT}{V_0}\ln\left(1 + \frac{t}{c}\right)$$

from which the recorded chart $\Delta\sigma(t)$ yields a measurement of V_0.[12]

Now the change in microstructure, $N(A') \neq N(A)$, has to be introduced. Let us define B as this point a little beyond A on the same constant strain rate curve in *Figure 1*, which represents the isostructural state to A', that is to say the point at which the polymer contains as many defects, $N(A') = N(B)$, and has been given an equal strain amount from A, $\Delta\varepsilon_p$. So, we can compute the stress increment $\Delta\sigma_1$ of B relative to A, simply as:
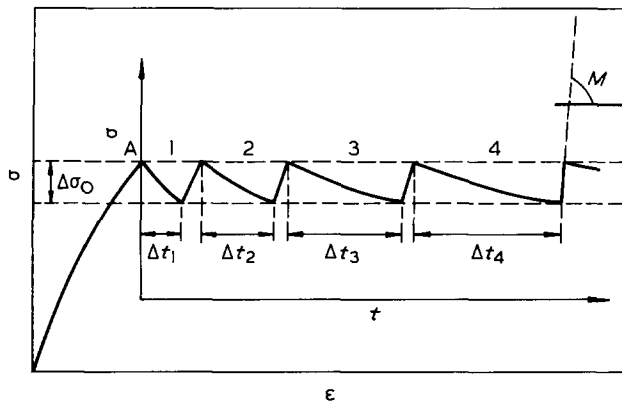
Figure 2 Repeated stress relaxation tests (schematic)

$$\Delta\sigma_1 = \int_A^B \left(\frac{d\sigma}{d\varepsilon_p}\right)_{\dot{\varepsilon}} d\varepsilon_p = K\Delta\varepsilon_p \qquad (4)$$

where K is taken at A on the stress–strain curve, and is assumed to be constant between A and B since A and B are presumably very near to each other. The derivation of $\dot{\varepsilon}_p(A')$ then follows along the same lines as above, but now starts from B instead of A, so that: $\dot{\varepsilon}_p(A') = \dot{\varepsilon}_p(B)$ $\exp(V_0/kT)(\Delta\sigma - \Delta\sigma_1)$. Since $\dot{\varepsilon}_p(B) \simeq \dot{\varepsilon}_p(A)$, for as much as K is the same at A and B, and $\Delta\sigma - \Delta\sigma_1 = \Delta\sigma(1 + K/M)$ from equations (1) and (4), the plastic strain rate at A' is now given by an equation quite similar to the above simple equation, $\dot{\varepsilon}_p(A') = \dot{\varepsilon}_p(A)\exp(V^*\Delta\sigma/kT)$, with V^*, the experimental activation volume as:

$$V^* = V_0\left(1 + \frac{K}{M}\right) \qquad (5)$$

Here the corrective term, $V_0 K/M$, is due to work-hardening by the defects nucleated during the relaxation test itself; it is usually *larger* in the pre-yield stage than V_0.

Since K slows down the stress relaxation kinetics, it is clear that K can be obtained from the gradual increase in duration of repeated relaxation tests by a given stress amount $\Delta\sigma_0$ (*Figure 2*). The idea is to accumulate enough work-hardening by repeating successively from A a number of such relaxations, to increase steadily the duration of each run. Provided that $\Delta\sigma_0$ be chosen small enough, $V_0\Delta\sigma_0 < kT$, Kubin has shown the duration of the nth relaxation ($n = 1,2,...$) increases exponentially with n[13]:

$$\Delta t_n = \Delta t_1 \exp[(n-1)K V_0 \Delta\sigma_0/MkT] \qquad (6)$$

as soon as n is larger than a few units, $n > 6$ in practice. Therefore a plot of $(\Delta t_n/\Delta t_1)$ versus n yields the value of $V_0 K/M$; since the first relaxation run gives the quantity $V^* = V_0 + (V_0 K/M)$, then both V_0 and K/M values can be found experimentally. Finally M can be deduced from the last loading slope, $p_n = d\sigma/d\varepsilon_t$, since it is shown the ratio $(M - p_n)/M$ also decreases exponentially with n, and practically speaking $M \simeq p_n$, from $n \simeq 4$ or 5.

Below we apply this method to the determination of K at a given total strain (chosen in the pre-yield stage) on samples prepared with different ageing treatments.

THERMAL TREATMENT AND AGEING CONDITIONS OF PMMA SAMPLES

Atactic PMMA was obtained as in ref 11, from the Ecole d'Application des Hauts Polymères (Strasbourg, France) by anionic polymerization ($M_w = 2.2$ 10^5 and polydispersity $p = 2.29$). This PMMA powder is compression moulded as follows. The powder is first compressed at room temperature, then vacuum heated under compression at 197°C for 4 h. After this, mould and sample are left free to return to room temperature. As moulded cyclindrical samples (7 mm diameter and 30 mm long) are then annealed for 90 min at 140°C ($\simeq T_g + 30°C$) to relieve the internal stresses at the origin of the strong initial birefringence. Finally they are machine turned into smaller cylindrical specimens (5 mm diameter, and 8.6 mm long) and mechanically polished carefully to ensure that the end sections were parallel to better than 0.01 mm.

Our specimens were aged in pairs. They are first put into fitted brass jackets preheated at 130°C, and kept in an oven at this temperature for 30 min to reach thermal equilibrium. Then the whole set, jackets and specimens, is water-quenched down to 15°C for *ca.* 2 min, and finally the pair of specimens is kept in a regulated oven at a fixed temperature of 62°C for the ageing time t_a until deformation testing starts.

Some specimens have simply been slowly cooled from equilibrium ($T = 130°C$) down to room temperature, at a cooling rate 3°C/h. With so slow a rate, it can be considered that an equilibrium free volume is retained in the sample down to a temperature only slightly higher than the conventional T_g, and is therefore reduced to a value about as small as the value which would have been retained after quenching, followed by an extended ageing time of a year or longer, as Struick has verified experimentally[9]. Such samples will be therefore labelled as samples having been aged for 'infinite' time.

MECHANICAL TESTS

Compression tests at a constant strain rate, $\dot{\varepsilon}_t = 2.10^{-4} s^{-1}$, have been performed with an INSTRON machine at two temperatures, $T = 290$ K and $T = 195$ K.

For each measurement of the work-hardening rate K, two specimens with the same ageing time have to be tested under stress relaxation with the same compressive stress. One relaxation test is designed to yield a reasonably precise value for the experimental activation volume, V^* in equation (5); typical conditions are a duration of 10 min, and a corresponding stress drop $\Delta\sigma = 6$–10 MPa. The other relaxation test is designed to provide us with a reasonably precise value for $(V_0 K/M)$, (see equation (5)) which implies that we are able to repeat 8 to 10 successive relaxations with a reasonable duration, of the last one Δt_n; typical values are $\Delta t_n \simeq 12\Delta t_1$, $\simeq 6$ min, with a constant stress drop $\Delta\sigma_0 \simeq 0.5$–1.5 MPa.

To be able to investigate the ageing effect on mechanical properties by the stress relaxation technique, the stress range to be chosen in the pre-yield stage has to be optimized since at too high a stress, strain induced, structural changes would rub out any previous ageing structure (in other words, the solid is made younger by straining[9]), while at too small a stress, behaviour is almost purely elastic and the stress relaxation strength would be much too small to be properly measured. The optimum

Table 1 Mechanical parameters at 290 K of samples with different ageing times t_a. The elastic modulus of the machine-sample association is M = 2845 MPa

t_a	σ (MPa)	ϵ_t (×10²)	$\epsilon_{el} = \dfrac{\sigma}{M}$ (×10²)	V^* (Å³)	V_0 (Å³)	$\dfrac{K}{M}$	K (MPa)
30 min	49.1	2.9	1.7	1525	880	0.73	2077
90 min	53.0	3.1	1.9	1625	880	0.85	2418
7 hours	53.8	3.0	1.9	1840	930	0.98	2788
5 days	55.7	3.0	2.0	1960	970	1.02	2902
15 days	56.2	3.0	2.0	2130	1040	1.05	2987
∞	57.7	3.0	2.0	1905	905	1.10	3130

Table 2 Mechanical parameters at 195 K of samples with different ageing times t_a. The elastic modulus of the machine-sample association is M = 3924 MPa

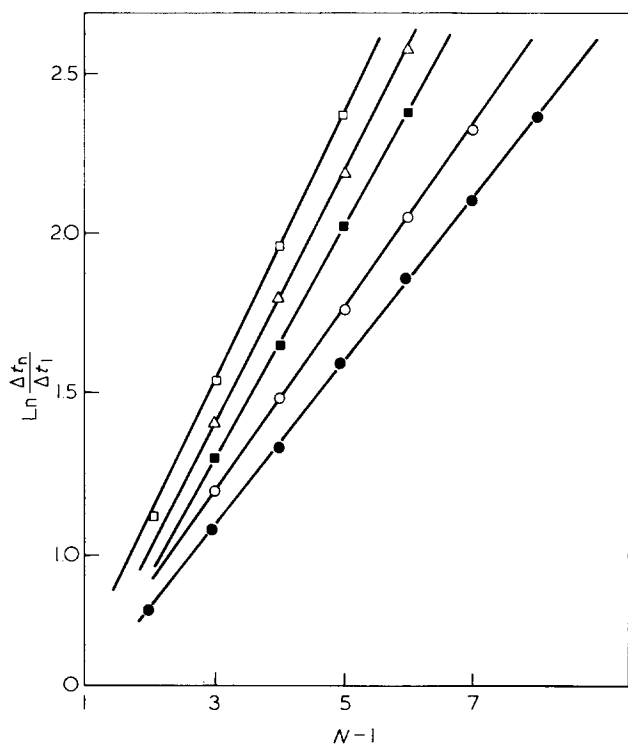| t_a	σ (MPa)	ϵ_t (×10²)	$\epsilon_{el} = \dfrac{\sigma}{M}$ (×10²)	V^* (Å³)	V_0 (Å³)	$\dfrac{K}{M}$	K (MPa)
1 hour	176.1	5.8	4.5	1210	240	4.04	15 853
5 days	175.8	5.8	4.5	1180	230	4.13	16 206
15 days	169.0	5.7	4.3	1090	205	4.32	16 952

Figure 3 Duration of the nth stress relaxation test, Δt_n versus test number n for differently aged samples (●, t_a = 30 min; ○, t_a = = 90 min.; ■, t_a = 7 h; △, t_a = 5 days; □, t_a = 15 days)

range depends on the nature of the polymer. In PMMA, a range near to 0.5 σ_y, with σ_y being the yield stress, has been found convenient. In this respect the present method is complementary to viscoelastic studies of ageing using time temperature shifts of creep curves under very small stresses, in the range 0.1 σ_y^9, beyond which shifts are much reduced.

In fact experiments at a given temperature have been done for a fixed deformation time, i.e. for a constant total strain in all compared specimens. From *Tables 1* and *2*, ε_t

lies from 5.7 to 5.8 10^{-2} at 195 K, and from 2.9 to 3.1 10^{-2} at 290 K. These figures are very approximate as they are simply read from load-extension charts and they are clearly overestimations because of the setting of some loose-fitting screws and bolts in the INSTRON machine at very early strains. However, the corresponding true total strains not withstanding should be constant. Besides, at stress level 0.5 σ_y, any looseness should be tied up and M measurements read from loading slopes of the last relaxation should then yield reasonably good values for the machine-sample association. These values are also given in *Tables 1* and *2*. Moreover they represent only a slight underestimation of the sample elastic modulus itself (of order 5%) as direct further extensometry using an LVDT transducer has shown. It is therefore possible to compute a reliable corresponding elastic strain σ/M.

It has been possible to perform up to ten repeated relaxation tests on differently aged samples. *Figure 3* is an example of the experimental duration of the nth test *versus* test number n; it shows how good the fit with equation (6) is. As explained above, such fits allow us to obtain, together with the V^* value measured on an identical sample in a separate relaxation test, both V_0 and (K/M) values. These are gathered in *Tables 1* and *2* with corresponding stresses (applied force divided by initial section), and axial strains taken at state A in *Figures 1* or *2*.

DISCUSSION

The above results are only preliminary measurements aimed at the feasability of the experimental method and at the role of temperature on the mechanical effect of ageing processes.

Table 1 shows that ageing has a sensible effect on K at 290 K. Recalling that $K = (d\sigma/dN)_\varepsilon$, it means that in a short-aged sample (t_a = 30 min) about half as many more defects are nucleated per unit stress than in a long-aged sample ($t_a \rightarrow \infty$), for a given deformation time, or total strain, or also, at about the same ratio of stress to yield stress (0.46). Therefore K is proved to be a quantity that is very sensitive to ageing. For comparison, this behaviour is

consistent with the evolution of plastic strain $\varepsilon_p = \varepsilon_t - (\sigma/M)$, which is seen here to be decreasing with t_a (since σ increases) but in a much smaller ratio $(\Delta\varepsilon_p/\varepsilon_p = -\Delta\sigma/\sigma \simeq 0.16)$.

In contrast, *Table 2* shows that K at 195 K and presumably, the whole stress–strain curve, is practically unaffected by ageing. This is of course expected if we recall that below temperatures in the range of β peak, no short range diffusion of monomer units is believed to occur, and secondly, if it is accepted as in ref 11 that below $T_c = 220$ K, the deformation mode should not entail any mass diffusion process contrary to that at higher temperatures.

K is known to decrease steadily all along the pre-yield stage. Then the question of how corresponding stress ranges at 195 K and 290 K, i.e. corresponding states in the pre-yield stage, have to be chosen in order to give a meaningful comparison, has of course to be raised. The value of the total strain in *Table 2* has been chosen so that the ratio of stress to yield stress (0.48) be about the same as in *Table 1* (0.46). This seems reasonable in view of the very similar plastic strains which are reached, as judged from the remark that almost all the difference in total strain with *Table 1*, is accounted for by elastic contributions. It therefore can be considered that *Tables 1* and *2* effectively compare two relatively similar states in the pre-yield stage.

However, the large variation in K values shown in *Table 1* is not presumably due only to variations in t_a since K is likely to be a function of both ε_p and t_a, $K(\varepsilon_p, t_a)$, and ε_p

varies in *Table 1* from a line to another one. Therefore, while this study is clear evidence for the strong influence the temperature has on the effect of ageing on non-elastic properties, it is not conveniently designed to investigate separately the ε_p and t_a dependence of K, and for checking them against theoretical predictions. A more complete study of K dependences is thus underway and will be published in a following paper.

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