Dynamic recovery and embrittlement in poly(aminobismaleimide) [PABM] resin

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Dynamic recovery and embrittlement have been demonstrated in PABM resin by means of mixed deformation tests: fatigue/creep tests and creep/fatigue tests. By fatigue test, we mean an oscillating stress test of low amplitude, the maximum stress always being below the yield stress; the mean stress value corresponds to the creep stress. Creep time and fatigue time were 12 h. The measurement of the work-hardening rate K in the pre-yield stage and optical microscopy observations seem to show that fatigue induces dynamic recovery while creep would be responsible for the embrittlement observed in the case of fatigue/creep tests.

(Keywords: work hardening; polyimide resin; plastic deformation; creep; fatigue; glassy polymers)

INTRODUCTION

In a previous paper[1] we showed the influence of creep or oscillating stress tests on the 'plasticity' defect nucleation rate in the case of PABM thermoset resin by measuring the work-hardening rate K in the pre-yield stage, defined as:

$$K=\left(\frac{\partial\sigma}{\partial\varepsilon_p}\right)_{\dot{\varepsilon},T}\sim\left(\frac{\partial N}{\partial\sigma}\right)^{-1}_{\dot{\varepsilon},T} \quad (1)$$

where σ is the flow stress corresponding to the total strain $\varepsilon_t=\varepsilon_H+\varepsilon_p$ (ε_H is the Hookean elastic part of the strain and ε_p is the non-elastic part) and N is the number of 'plasticity' defects nucleated at a given stress value σ.

Deformation processes in the solid glassy phase are quite localized events[2]: distortions in bonding have to be strictly confined within cores of defects in the molecular arrangement (much like dislocation lines of the Somigliana type[3]), the propagation of which produces a local shear strain. These shear nuclei (or 'plasticity' defects) nucleate and expand in the pre-yield stage and are the precursors of the non-elastic macroscopic strain.

In both cases, after 12 h tests, we found that K was increased by a factor of 6 and that the activation volume V_0 decreased by a factor of 5. Such a behaviour allowed us to conclude that both fatigue and creep tests involved a decrease of the ratio of mobile 'plasticity' defects because of the internal stress field σ_i built up in the sample during these tests.

For both cases, the time dependence of the variation of the non-elastic strain $\Delta\varepsilon_p$ induced by fatigue or creep followed a logarithmic law, but the final magnitude of $\Delta\varepsilon_p$ induced by a 12 h fatigue test was twice as large as that induced by a 12 h creep test. This logarithmic behaviour of $\Delta\varepsilon_p(t)$, similar to the α-creep of metals occurring at low temperature, led us to assert that defect nucleation was not a thermally activated process. The twice as great increment in $\Delta\varepsilon_p$ after a fatigue test was interpreted as 'dynamic' recovery due to the intermittent applied stress.

However, it remained to be seen whether the oscillating stress tests do or do not induce embrittlements inside the material. In order to answer this question successive tests of creep followed by fatigue and of fatigue followed by creep have been performed. In parallel with this, optical microscope observations have been made on the corresponding tested samples.

The experimental procedures are reported next, while the last section is devoted to the discussion of results.

EXPERIMENTAL

The preparation of PABM polyimide samples has been described in a previous paper[1]. Compression samples are of cylindrical shape (6 mm diameter and 11 mm long).

Deformation procedures

All the deformation tests were performed at room temperature with an Instron machine. Typical deformation procedures *versus* time t are shown in *Figure 1*.

- $0<t<t_1$: constant-strain-rate compression test with $\dot{\varepsilon}=3\times10^{-5}\,s^{-1}$
- $t_1<t<t_2$: K measurement at $\sigma=\sigma_1$ such as $\varepsilon_p=4.5\times10^{-3}$
- $t_2<t<t_3$: constant-strain-rate compression test up to $\sigma=\sigma_0=158$ MPa
- $t_3<t<t_4$: fatigue test for 12 h; period of intermittent stress $T=96$ s, amplitude $\Delta\sigma=39$ MPa
- $t_4<t<t_5$: fast unloading with $\dot{\varepsilon}=7.5\times10^{-4}\,s^{-1}$
- $t_5<t<t_6$: same procedure as for $0<t<t_3$
- $t_6<t<t_7$: creep test for 12 h at $\sigma=\sigma_0=158$ MPa
- $t_7<t<t_8$: fast unloading with $\dot{\varepsilon}=7.5\times10^{-4}\,s^{-1}$
- $t>t_8$: same procedure as for $0<t<t_2$

K measurements

The method has already been described in a previous paper[1], so we just want to recall briefly how it is used to determine the values of the work-hardening rate K and of the activation volume V_0 (ref. 4).

Two different tests are needed: a single relaxation test which leads to the value of the experimental activation volume V_{exp} and successive relaxation tests which yield the

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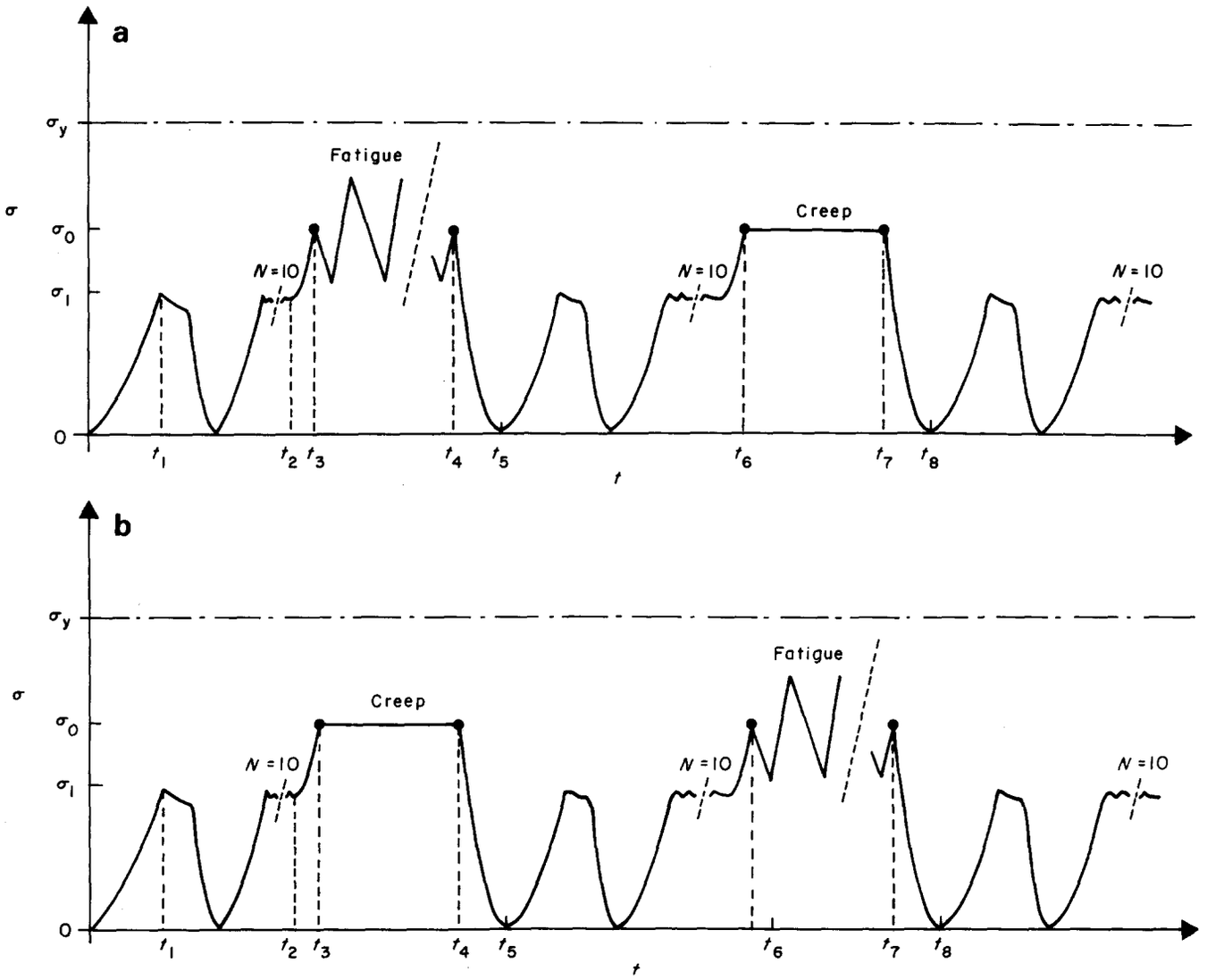

Figure 1 The two typical deformation procedures *versus* time: (a) the fatigue/creep test; (b) the creep/fatigue test

Table 1 Activation volumes and work-hardening rates before, in between and after mixed tests

	Blank sample	12 h creep test +	12 h fatigue test	12 h fatigue test +	12 h creep test
V_0 (Å^3)	1200±20	280±20	185±20	260±30	620±100
K/M	1.45±0.10	8.20±1.00	14.0±1.5	8.90±1.00	2±1
K (MPa)	4495±450	25 420±2540	43 400±4650	27 590±2760	6200±3100

quantity V_0K/M where M is the Young modulus. By measuring M at the beginning of the stress–strain curve and by using the relation

$$V_{exp} = V_0(1 + K/M)$$

the values of K and V_0 can be obtained:

$$\frac{K}{M} = \frac{V_0K/M}{V_{exp} - (V_0K/M} \qquad (2)$$

$$V_0 = V_{exp} - (V_0K/M)$$

RESULTS AND DISCUSSION

Table 1 provides the true activation volume V_0 and the work-hardening rate K, measured at a non-elastic deformation $\varepsilon_p = 4.5 \times 10^{-3}$ before, in between and after the mixed tests. The Young modulus is equal to $M = 3100 \pm 50$ MPa.

The main features are as follows: (a) In the creep/fatigue test, the increase of K after 12 h creep is greater when followed by a 12 h fatigue, so that the work-hardening rate is finally increased by a factor of up to 10 in comparison with its blank value. (b) In the fatigue/creep test, the behaviour is quite different. KM increases up to 8.9 after the 12 h fatigue test, but decreases to 2 (close to the blank value) after successive 12 h creep tests. This might be taken as meaning that the PABM resin would be made younger by the fatigue/creep test; this apparent softening is in fact due to induced embrittlement in the sample.

Optical microscopy observations were performed systematically on all the tested samples in order to detect any visible existing cracks. As shown in *Figure 2*, the cylindrical-shaped samples have been carefully polished

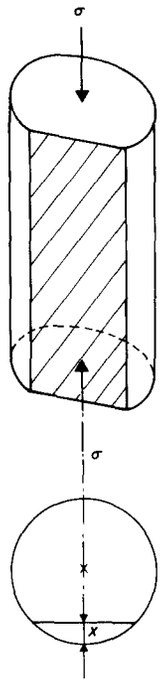

Figure 2 Geometry of the surfaces observed by optical microscopy

with alumina paste along planes parallel to the compression axis at different depths x beneath the external surface. Optical observations were made at four different depths: $x=0.01$, 0.07, 0.3 and 0.6 mm.

In the case of samples tested for 12 h by fatigue only, as well as in the case of samples subject to a 12 h creep/12 h fatigue test, there were no perceptible cracks inside the material nor on its external surface.

On the contrary, in the case of the 12 h fatigue/12 h creep test, many cracks were visible on the external surfaces. As shown in *Figure 3*, the main crack axis is tilted about 10° relative to the compression axis. At a 0.01 mm depth, their averaged longitudinal extent is about 260 μm and the number of cracks per square millimetre is about 4. Their density is uniform on the whole observed surface. *Figure 4* represents optical micrographs performed at a depth equal to 0.07 mm: the observed cracks can be divided into two kinds, their averaged longitudinal extent is only 200 μm and their number per square millimetre is smaller, proving that cracks observed at $x=0.07$ mm are nothing other than persistent traces of the ones observed at $x=0.01$ mm. At depth $x=0.3$ mm and beyond, only scarce cracks, located at random, are visible; at 0.6 mm depth there are no more cracks.

So, it is clear that embrittlement occurs only within a superficial shell, of about 0.3 mm width. It has often been observed, especially in metals, that fatigue cracks nucleate preferentially at free surfaces rather than within the bulk[5,6]. This embrittlement is responsible for the decreasing of the work-hardening rate K at the end of the fatigue/creep test.

If we look back to *Table 1*, the high value of the true activation volume V_0 ($=620$ Å^3) is to be noted and may appear quite suprising. Indeed, it is well known that stress relaxation due to cracks is greater than that due to 'plasticity' defects and thus one could expect to measure at the end of the fatigue/creep test a much smaller activation volume V_0. In fact, this behaviour can be easily explained. The K and V_0 measurements have been made, as for the other tests, at a non-elastic strain $\varepsilon_p = 4.5 \times 10^{-3}$. But, in the present case, the measured ε_p results from both the nucleation of 'plasticity' defects plus the added compliance of cracks, so that the part of the non-elastic strain ε_p due to the 'plasticity' defects is in fact smaller than 4.5×10^{-3}. As the activation volume V_0 is expected to increase with decreasing ε_p[4,7], it is right to find a higher value of V_0.

It is worthy of note that, in contrast to the fatigue/creep test, there is no discernible embrittlement after the creep/fatigue test. This confirms the fact that an intermittent applied stress induces a 'dynamic recovery', as was suggested in a previous paper[1].

Contrary to what we thought, low-amplitude fatigue does not produce embrittlement. Moreover, it is well known that, in metals, fatigue is the only way to obtain greater densities of dislocations, i.e. to induce a large plastic deformation. In the case of PABM resin, we have actually noticed[1] that the non-elastic deformation increment, induced during fatigue, was twice as great as that induced by a creep test of the same duration.

Therefore, as is the case in the creep/fatigue test, fatigue when it is performed at the end of a mixed test (i.e. even after a plastic deformation of the sample of about 0.7%[1]) does not lead to embrittlement. Because of its oscillating character and consequently because of the backward and forward motion of the 'plasticity' defects, fatigue induces recovery in the material. But, in the reverse order, when fatigue is performed at the beginning of the mixed test, there is no possibility of recovery at the end of the mixed

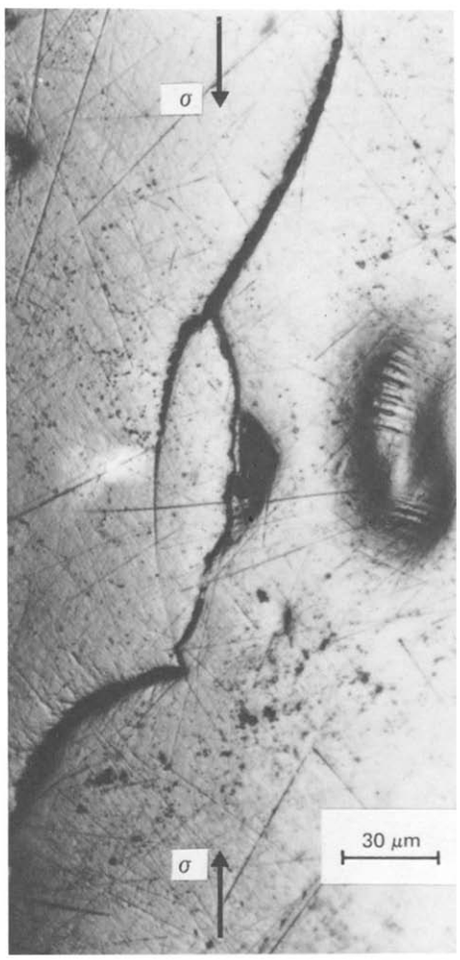

Figure 3 Optical micrograph at 0.01 mm depth: cracks induced by a fatigue/creep test. (The arrows show the compression axis)

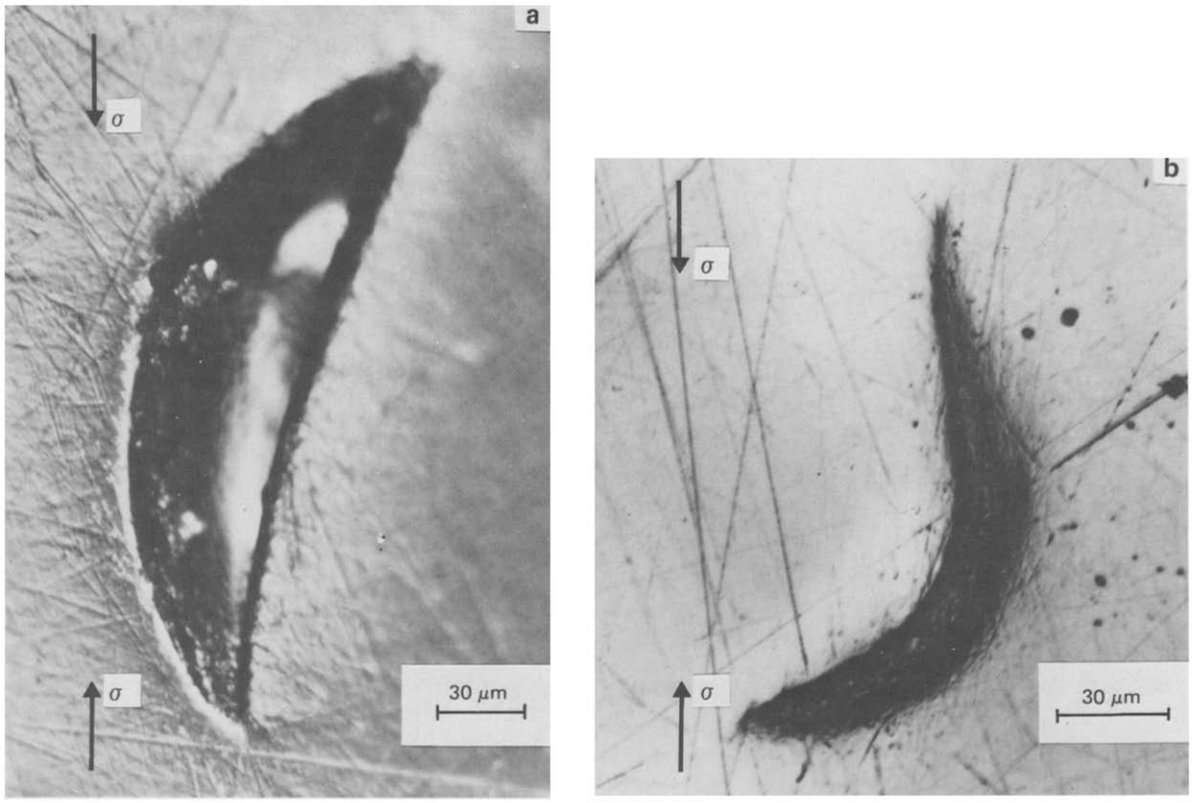

Figure 4 Optical micrograph at 0.07 mm depth: (a) crescent-shaped crack; (b) comma-shaped crack. (The arrows show the compression axis)

test because creep, due to its monotonic character, cannot induce recovery, but, on the contrary, embrittles the sample (K decreases). Indeed, in the fatigue/creep test, creep is performed on a sample which has been already deformed plastically by about 1.4% so that the ratio of mobile defects is quite low and the only way for the sample to sustain the constant applied stress is to deform by cracking.

In the case of the creep/fatigue test, there is no visible embrittlement just after the creep test (K increases); this results simply from the fact that creep is performed in this case on a sample which has been deformed plastically by about 0.7% only. We think that if creep had been performed for three months[1], i.e. in order to obtain a plastic deformation of 1.4%, embrittlements could be detected in the sample.

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