Influence of monotonic or oscillating stress tests on the work-hardening rate in PABM resin

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The influence of creep and oscillating stress tests on the nucleation rate of 'plasticity' defects is investigated in the case of poly(aminobismaleimide) (PABM) thermoset resin by measuring the work-hardening rate K in the pre-yield stage. In both cases, after 12 h tests, K is multiplied by a factor 6, V_0 is divided by a factor 5, and $\Delta\varepsilon_p$, the variation of the non-elastic strain, follows a logarithmic law with time. Thus, the creep is similar to the α-creep observed in metals at low temperatures, where the defect nucleation is not thermally activated. The 'fatigue' test differs from the creep test in having a $\Delta\varepsilon_p$ value twice as large, because of dynamical recovery.

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

INTRODUCTION

It is well known that a material subjected to an intermittent stress will ultimately fail at a stress level that is small in comparison to that required for failure due to a monotonic stress. Up to now, most fatigue tests in polymers have been performed in order to understand and to prevent ultimate fracture[1]. Typically 'S–N' curves depicting stress *versus* the number of cycles to failure are used to select materials, but they tell us nothing about phenomena such as the initiation and propagation of crazes, yielding or the storage or dissipation of energy. But careful examination of fine-scale fracture surface details can provide significant information about polymeric fatigue crack propagation processes[2,3].

We are not interested here in the ultimate stage of deformation (fracture) but in the deformation behaviour of polymers under normal service conditions, that is, in the so-called pre-yield stage, which corresponds to the 5–10% total deformation range.

In a monotonic test, it is well known that deformation zones appear clearly below the conventional yield stress, so that from a 'metallurgical' point of view critical shear nuclei (or defects) should nucleate and expand in the pre-yield range. The closer the applied stress σ approaches the yield stress, the more profuse is the shearing, leading to flow of the solid at yield.

In previous studies[4–6] it has been pointed out how the property of nucleating defects is related to polymer microstructure. In the specific case of thermoset resin[5] it has been found that the nucleation of 'plasticity' defects becomes harder and harder when the degree of crosslinking increases. Indeed, it has been shown[7] that the nucleation rate is related to the work-hardening rate K measured in the pre-yield stage and defined as:

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

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 one, and N is the number of defects nucleated at a given stress value σ.

Whereas the usual macroscopic mechanical quantities such as the Young modulus M or the yield stress σ_y did not vary noticeably with curing time, in contrast the parameter K, measured at a constant non-elastic strain $\varepsilon_p=4\times10^{-3}$, increased uniformly by a factor almost 3 between the minimum curing (3 h at 200°C) and the most complete one (24 h at 200°C plus 24 h at 250°C). Indeed, K measurements proved to be very efficient in following the evolution of crosslinking with curing time.

The purpose of this paper is to report the influence of 'fatigue' and creep, occurring in the pre-yield stage, on the defect nucleation process. We first produce a stock of mobile defects by compressing the polymer at constant strain rate up to a stress $\sigma_0<\sigma_y$; then, the material is submitted either to a creep test or to a 'fatigue' test. In the case of the 'fatigue' test, the stress oscillates around the $\bar{\sigma}$ value with an amplitude such that the maximum stress does not reach the yield stress σ_y; thus the defect propagation process does not interfere with the nucleation process. On the other hand, the period of the alternative stress is chosen in order to prevent any temperature rise in the material, that is any alteration of the initial defect microstructure. Finally, the effect of creep and 'fatigue' on defect nucleation is tested by measuring the work-hardening rate K and comparing it with its value for a blank sample. The time evolutions of the non-elastic deformation induced during fatigue and creep tests are analysed similarly and allow us to go further in the understanding of the process.

We have chosen to investigate the influence of fatigue and creep on a PABM resin cured for 24 h at 200°C in air. From recent thermodynamical analysis[8], the mechanical behaviour of this highly crosslinked resin over the whole temperature range exhibits only one deformation mode: a

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low-temperature, high-strain-rate mode called the 'glide mode'. Experimental procedures are reported in the next section, while the last section is devoted to a discussion of the results.

EXPERIMENTAL

Preparation of PABM polyimide samples

Details of the polymerization and of the curing treatment are given in Appendix 1. Compression samples were cut from cured resin sheets and machined into small cylindrical specimens (6 mm diameter and 11 mm long); they were carefully mechanically polished to ensure that end sections were parallel to better than 0.01 mm.

Deformation procedure

All the deformation tests have been performed at room temperature with an Instron machine. A typical deformation procedure *versus* time t is shown in *Figure 1*. The regions can be split up as follows:

$0<t<t_1$	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 $\sigma=\sigma_0$,
$t_3<t<t_4$	fatigue or creep test during various times t,
$t_4<t<t_5$	fast unloading with $\dot{\varepsilon}=7.5\times10^{-4}\ s^{-1}$,
$t>t_5$	procedure identical to those in the time range $0<t<t_2$.

K measurements

General points. The method has already been explained in detail in previous papers[5,7,9], so we will mention here only the main features. During compression tests at constant strain rate $\dot{\varepsilon}_t$ and constant temperature, K is measured by repeated stress relaxations from some stress value σ_1. In the experiments, K is a function of both the non-elastic strain ε_p and the defect microstructure. So, if we want to investigate only the influence of any microstructure variation, all K measurements have to be performed at the same value of ε_p in the pre-yield stage.

The evaluation of K needs two different types of test: a single relaxation test, which leads to the value of the experimental activation volume V_{exp}, and successive relaxation tests, which yield the quantity V_0K/M, where M is the Young modulus and V_0 the apparent activation volume[5,7]. By measuring M at the beginning of a stress–strain curve and by using the relation[5,7]

$$V_{exp}=V_0\left(1+\frac{K}{M}\right)$$

the values of K and V_0 can be determined:

$$\frac{K}{M}=\frac{V_0K/M}{V_{exp}-(V_0K/M)}$$
$$V_0=V_{exp}-(V_0K/M) \qquad (2)$$

M is measured in the linear part of the $\sigma(\varepsilon)$ curve; it lies typically between 18 and 36 MPa.

The total strain ε_t is measured with an LVDT transducer, rigidly attached to the mobile compression plate with its tip at the fixed plate. The non-elastic strain ε_p is thus continually known from the following relation:

$$\varepsilon_p=\varepsilon_t-(\sigma/M) \qquad (3)$$

Comments on the measurements. In previous studies[4–6] the parameter K was measured by performing the two types of relaxation test on two different samples. Here these two tests have been performed on the same sample (*Figure 1*) in order to avoid the experimental uncertainty in the Young modulus M and to ensure a more precise evaluation of ε_p given by (3).

For K measurements, the simple stress relaxation test has always been performed before the repeated relaxation test. Indeed, it has been observed that this procedure yields K values that do not differ from those obtained with measurements on two samples. That is not the case for the reverse procedure.

Fatigue test/creep test

The fatigue test is performed at time t_3 (*Figure 1*), when the applied stress σ reaches the mean stress value σ_0, which has been chosen so that $\frac{1}{2}\sigma_y<\sigma_0<\sigma_y$, where σ_y is the flow stress.

The experimental value of the flow stress is $\sigma_y=237$ MPa. The mean stress level has been taken to be $\sigma_0=158$ MPa and the period of the intermittent stress to be $T=96$ s in order to avoid any temperature variation in the sample. The amplitude of the intermittent stress $\Delta\sigma=39$ MPa has been chosen to keep $\sigma_{max}=\sigma_0+\Delta\sigma$ smaller than σ_y.

The creep test is performed alternatively on the same Instron machine at time t_3, under the constant stress $\bar{\sigma}=\sigma_0=158$ MPa.

At time t_4, the test is interrupted and the sample is quickly unloaded down to zero stress in order to freeze the microstructure built up during testing. This microstructure is then probed at time t_5 in measuring K during a final test at constant strain rate.

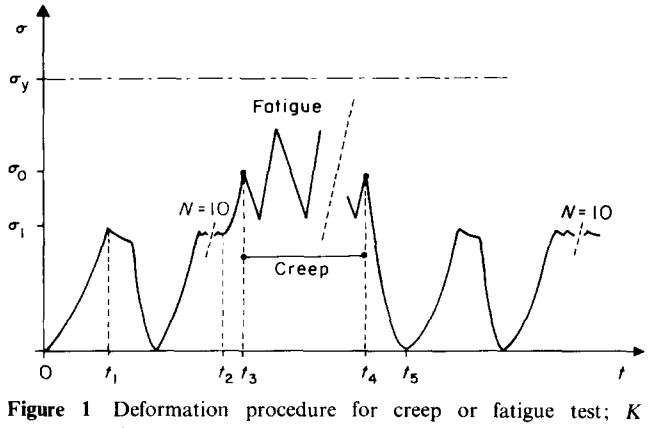

Figure 1 Deformation procedure for creep or fatigue test; K measurements

RESULTS AND DISCUSSION

Table 1 gives the true activation volume V_0 and the work-hardening rate K *versus* fatigue (or creep) time, measured at a non-elastic deformation $\varepsilon_p=4.5\times10^{-3}$. The Young modulus is not affected by the fatigue or creep test, and is

Table 1

	Original sample	After fatigue			After creep
		1500 s	10000 s	12 h	12 h
V_0 (Å^3)	1200±20	800±20	500±20	260±30	280±20
K/M	1.45±0.10	2.20±0.15	3.70±0.20	8.90±1.00	8.20±1.00
K (MPa)	4495±450	6820±1000	11470±2300	27590±2760	25420±2540

equal to $M = 3100 \pm 50$ MPa. The main features are as follows.

(i) *Fatigue.* The V_0 value decreases with time. Its value goes from $V_0 = 1200$ Å^3 for a blank sample, down to 260 Å^3 for a sample tested for 12 h, i.e. is divided by a factor 5.

The work-hardening rate K increases with time. The value of K varies from 4495 MPa (blank sample) up to 27 590 MPa after 12 h, i.e. is multiplied by a factor 6.

(ii) *Creep.* The V_0 value after a 12 h creep test ($V_0 = 280$ Å^3) is close to that measured after a 12 h fatigue test (260 Å^3). This volume (260–280 Å^3) is similar to the activation volume obtained beyond the flow stress[8]. It is the lowest possible volume, within which correlated motions of segments occur.

The K value after 12 h creep is also nearly equal to the K value after 12 h fatigue: $K \sim 27\,000$ MPa. It has been observed that, for intermediate times, the K and V_0 values measured after creep tests are close to those obtained after fatigue tests.

The non-elastic behaviour of PABM resin during fatigue or creep is shown in *Figure 2*, where the increment $\Delta\varepsilon_p$ of the plastic deformation induced by fatigue or creep is plotted *versus* time. It must be noted that, for both cases, the time dependence of $\Delta\varepsilon_p$ follows a logarithmic law, although the final magnitude of $\Delta\varepsilon_p$ induced by a 12 h fatigue test is twice as great as that induced by a creep test. This behaviour is similar to the low-temperature creep observed in metals[10].

What is the influence of fatigue or creep on the pre-yield behaviour of PABM resin? From a metallurgical point of view, as mentioned above, the non-elastic mechanical behaviour of PABM resin exhibits only a low-temperature deformation mode[8]: the so-called activated glide mode, characterized by stress-dependent energy of activation.

If we assume that recovery processes are not active, as can be expected, internal stresses σ_i increase with strain at the work-hardening rate $K = d\sigma_i/d\varepsilon_p$. The corresponding energy of activation, which is required for nucleating a 'plasticity' defect, is then given by[7]:

$$\Delta G_a = KV_0\Delta\varepsilon_p \tag{4}$$

so that the creep law can be written as:

$$\begin{aligned}\dot{\varepsilon}_p &= \dot{\varepsilon}_p(0)\exp\{-[\Delta G_a(\sigma-\sigma_i,T)/kT]\} \\ &= \dot{\varepsilon}_p(0)\exp\{-[KV_0\Delta\varepsilon_p/kT]\}\end{aligned} \tag{5}$$

The integration of equation (5) leads to

$$\Delta\varepsilon_p = \varepsilon_p - \varepsilon_p(0) = \frac{kT}{KV_0}\ln\left(1+\frac{t}{c}\right) \qquad c = \frac{kT}{KV_0\dot{\varepsilon}_p(0)} \tag{6}$$

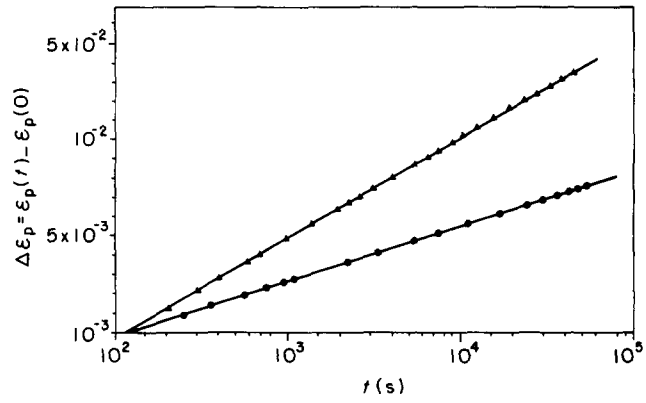

Figure 2 Variation of the non-elastic strain with time: (▲) fatigue, $c \sim 100$ s; (●) creep, $c \sim 140$ s

This logarithmic law describes the progressive slowing down of strain due to strain-induced hardening. As has been shown in metals[12], such behaviour means that the nucleation of defects, which already occurs below the yield stress, it not thermally activated.

In the case of PABM resin, the experimental logarithmic creep (*Figure 2*) can thus be explained as follows. A stock of 'mobile' plasticity defects resulting from the preceding constant-strain-rate compression test is available. These 'mobile' defects are allowed to develop following their own kinetics. As the test time increases, the ratio of 'mobile' defects decreases, while the number of obstacles rises, so that the internal stress field σ_i (and consequently the energy of activation) due to these obstacles becomes more and more important and little by little prevents the strain from continuing. Then when the sample is subjected, after rapid unloading, to a constant-strain-rate compression test, the internal field σ_i acts against the nucleation of new defects. The longer the creep time, the higher is σ_i and consequently the work-hardening rate K is expected to increase, as is experimentally observed. So the logarithmic behaviour of $\Delta\varepsilon_p(t)$ is to be compared to the α-creep of metals occurring at low temperatures and proves that defect nucleation is not a thermally activated process.

Although the fatigue and creep tests lead to close values of K and V_0, and to logarithmic $\Delta\varepsilon_p(t)$ laws, it can be noticed as mentioned above that the final non-elastic increment $\Delta\varepsilon_p$ after a fatigue test is twice as great as that after a creep test. This behaviour can be interpreted as a 'dynamical recovery' due to the intermittent applied stress; it has already been observed in metals[11].

Although, in our tests, the amplitude of the alternative stress is quite a bit lower than the amplitude of 'classical' fatigue tests, it may be asked whether the oscillating stress tests induce embrittlement. To this end, experimental procedures are presently in progress in our laboratory.

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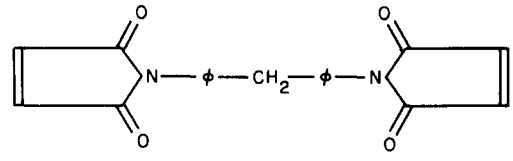
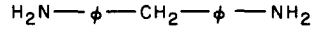
APPENDIX 1

Poly(aminobismaleimide) (PABM) samples were obtained from Rhône Poulenc Industries. These were prepared by reaction at 180°C of 2.5 mol 4,4'-diphenylmethane bismaleide



with 1 mol diamino-4,4'-diphenylméthane



Both homopolymerization and polyaddition with diamine occur during reaction and curing. The glass transition temperature is over 300°C. Parallelepipedic resin plates were cured in the laboratory for 24 h at 200°C in air. The cooling rate was 2.5°C min^{-1}.