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New method for measuring the non-elastic work-hardening rate of solid polymers

Ph. FRANÇOIS, D. MELOT, J. M. LEFEBVRE, B. ESCAIG
Université de Lille Flandres Artois, Laboratoire de Structure et Propriétés de l'Etat Solide, URA CNRS 234 59655 Villeneuve d'Ascq, France

Probing the non-elastic deformation of solid polymers in the pre-yield range has proved to be a very sensitive test of the structural response to plasticity nucleation. A work-hardening rate parameter, *K*, deduced from repeated stress relaxations was thus introduced to quantify this behaviour. It is shown that considerable improvement and more extensive information may be gained by measuring the work-hardening rate by the so-called direct method from a simple stress–non-elastic strain plot. A comparison is given of the two methods in the case of unsaturated polyester resins, together with a careful evaluation of potential sources of discrepancy.

1. Introduction

It is now generally well agreed that the non-elastic behaviour of solid polymers can be usefully described, in the absence of crazing, in terms of the nucleation and growth of local defects in the chain arrangement of the deforming polymer [1, 2]. These defects should be nucleated merely below the yield stress, during the pre-yield stage, as small (Somigliana) dislocation loops, or micro-shear zones probably not larger than 10–100 nm, throughout the polymeric glassy phase; yielding would then occur, once stress and temperature conditions allow for their catastrophic growth and coalescence.

The defect nucleation rate in the pre-yield stage can be measured by the non-elastic work-hardening rate, *K*, under the mere assumption that the sole defect nucleation is responsible for the increasing non-elastic strain, ε_p, in the material. It has been shown in previous papers [3, 4] that this nucleation rate, and thus the parameter, *K*, was a reliable probe to the polymer mesostructure (10 nm) and its time or temperature evolution, i.e. ageing, curing degree, or nature and state of a dispersed second phase. It is also a way to characterize and classify materials depending on their ability to exhibit local non-elastic, or plastic deformation so that, recently, correlations have been found between *K* and the toughness of polymer blends [5].

The method for measuring *K* has been given previously [3, 4, 6]; it is based on the gradual increase in duration of repeated stress relaxation runs from the same stress value, due to the accumulating work hardening. This method might be found difficult to apply in some cases for several reasons.

(i) Two samples deformed exactly at the same strain, ε_p, are needed for each value of the strain: one is for measuring the apparent activation volume, $V(\varepsilon_p)$, from a single stress relaxation test, and the other for measuring the quantity VK/M, where M is the elastic modulus, by the repeated relaxations test.

(ii) The measurement gives only the value of *K* at a given ε_p. Because *K* depends on ε_p as ε_p^{-1} [4], comparing two different materials, for example, should necessitate comparing both the whole curves $K(\varepsilon_p)$ all over the pre-yield stage, which is rather time consuming to obtain, even if measurements can now be computer aided.

(iii) In the case of brittle materials, like organic composites for example, deformation damage (microcracks) may occur from the slight strains experienced during the repeated relaxations, which hinders the method from being applied correctly. Therefore, a new method for measuring $K(\varepsilon_p)$ has been developed which is merely another way to plot the load–elongation chart obtained from the standard constant (total) strain rate test, correcting only for the non-constant plastic strain rate. That is, from the data of the stress–strain curve, $\sigma_a(\varepsilon)$, plus that of the apparent activation volume, $V(\varepsilon)$, which a few samples are enough to establish, the whole curve $K(\varepsilon_p)$ can be determined. Thus, this new method of measurement brings about a clear improvement which allows us to obtain both faster and better results; for a rapid probing of materials, the correction terms (hence the need for $V(\varepsilon)$) can even be skipped, so that results are still faster.

It is the purpose of this paper to establish the method, which we will call the direct method, and to check it against the more conventional repeated stress relaxation (RSR) method. The theoretical aspects are first discussed, then the experimental procedure is developed, and the two materials tested for comparison (two unsaturated polyester resins) are described. In order to have a valid comparison, the RSR method has, itself, to be reviewed for possible physical ageing and strain effects on *K* during repeated relaxations. These corrections are introduced in Section 4, and the measurements of *K* by the two methods are then compared.

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2. Theory

The basic idea of this approach is to model the stress needed to deform non-elastically the material as [6]

$$\sigma_a = \sigma_i(\varepsilon_p) + \sigma^*(T, \dot{\varepsilon}_p) \quad (1)$$

where σ_a is the applied stress corresponding to the total strain $\varepsilon_t = \varepsilon_H + \varepsilon_p$, with ε_H the Hookean elastic part and ε_p the defect part of the strain, σ_i is the internal stress built up as ε_p increases, and σ^* is the so-called thermal component of stress.

The internal stress field, σ_i, grows up from ε_p, i.e. from the defect development. Either, as in crystalline materials, it stems from the elastic interaction of growing dislocation loops, or, as is more likely in amorphous materials, it originates from the back stress which the molecular misfits trailing behind, on the wake of the nucleated loop, apply on its contour [1, 2]. Accordingly, $\sigma_i = \gamma/b$ with b the mean shear vector of the micro-shear zone, and γ the energy per unit area of the faulted interface corresponding to the inferred bad molecular stackings. As the non-elastic strain, ε_p, increases in the pre-yield stage, shear zones should be nucleated into more and more compact regions of the polymeric glass, so that the interface energy should be an increasing function of $\varepsilon_p, \gamma(\varepsilon_p)$ and so should $\sigma_i(\varepsilon_p)$. Thus the σ_i variation should be merely controlled by the structure of the glassy phase, while the σ^* variation should come from the activated growth of the nucleated defects, i.e. it should depend primarily on temperature and non-elastic strain rate, $\dot{\varepsilon}_p$. During the pre-yield stage, this term is at first quite small, as is ε_p, then it increases as does ε_p up to yielding, at which $\dot{\varepsilon}_p$ is equal to the total strain rate $\dot{\varepsilon}_t$.

The non-elastic work-hardening rate, K, is the structure dependent parameter defined by

$$K = \frac{d\sigma_i}{d\varepsilon_p} = \left(\frac{\partial\sigma_a}{\partial\varepsilon_p}\right)_{\dot{\varepsilon}_p, T} \quad (2)$$

while in a standard, constant total strain rate test, only the parameter K' can be easily obtained as the load–elongation slope

$$K' = \left(\frac{\partial\sigma_a}{\partial\varepsilon_p}\right)_{\dot{\varepsilon}_t} = \frac{d\sigma_i}{d\varepsilon_p} + \left(\frac{\partial\sigma^*}{\partial\dot{\varepsilon}_p}\right)_T \left(\frac{\partial\dot{\varepsilon}_p}{\partial\varepsilon_p}\right)_{\dot{\varepsilon}_t} \quad (3)$$

following Equation 1. The strain rate derivative of σ^* can be deduced from the knowledge of the apparent activation volume, V, defined [6] by

$$V = kT\left(\frac{\partial \ln \dot{\varepsilon}_p}{\partial\sigma_a}\right)_{T, \sigma_i} = kT\left(\frac{\partial \ln \dot{\varepsilon}_p}{\partial\sigma^*}\right)_T \quad (4)$$

again from Equation 1. It follows from Equations 3 and 4 that

$$K' = K + \frac{kT}{V}A \quad (5a)$$

$$A = \left(\frac{\partial \ln \dot{\varepsilon}_p}{\partial\varepsilon_p}\right)_{\dot{\varepsilon}_t} \quad (5b)$$

Now, V is measured from the relaxation of the applied stress which follows the modified Guiu and Pratt relationship [6]

$$-\Delta\sigma = \frac{kT}{V_{exp}}\ln\left(1 + \frac{t}{C}\right) \quad (6a)$$

$$V_{exp} = V\left(1 + \frac{K}{M}\right) \quad (6b)$$

with t, the time, C a time constant, and M the elastic modulus.

Finally we obtain K from Equations 5 and 6

$$K = \left[K' - \left(\frac{AkT}{V_{exp}}\right)\right] \Big/ \left[1 + \left(\frac{AkT}{MV_{exp}}\right)\right] \quad (7)$$

which shows that K can be known at any strain ε_p from experimental determination of M, $K'(\varepsilon_p)$, $A(\varepsilon_p)$ and $V_{exp}(\varepsilon_p)$. All these quantities can be computed using experimental data stored on floppy disks in a standard constant total strain rate compression test.

The materials investigated, the experimental procedure and the results of measurements of K by the direct method are described below [7].

3. Experimental determination of $K(\varepsilon_p)$ by the direct method for two unsaturated polyester resins

The polyester prepolymers consist of alternating sequences of maleic anhydride associated with a diol; the latter is either diethylene glycol (DEG) or propylene glycol (PG). This prepolymer is diluted in styrene (31% wt/wt) and network formation occurs by radical copolymerization of styrene with the maleic anhydride double bonds.

Curing has been achieved at room temperature with cobalt octoate as an accelerator and MEK peroxide as a catalyst.

There are, on average, two to three styrene unit per cross-link. A post-curing treatment has been applied to all networks. Based on previous work in our laboratory, post-curing optimization is achieved by controlling network evolution from a mechanical point of view [3, 7]. The theory outlined above can be used for this control: network structure is thus probed by work-hardening rate, K, measurements and it is postulated that curing efficiency is reached when K levels off to an upper plateau value. According to these results, a curing time of 1 h at 130 °C was retained.

Compression tests have been performed at room temperature ($T = 20$ °C) and constant total strain rate $\dot{\varepsilon}_t = 3 \times 10^{-5}$ s^{-1} using an Instron machine driven by a microcomputer. Compression samples were machine turned into small cylindrical specimens (6 mm diameter and 11 mm long); they were mechanically polished to ensure parallel end sections to better than 0.01 mm. The total strain is measured by an LVDT transducer rigidly attached to the fixed compression plate with its tip at the mobile plate.

Three types of experimental data are stored by the computer: the elapsed time, t, since the start of the test, the force and the total strain, ε_t, of the sample. From these data one computes:

(a) the time derivative, $\dot{\sigma}_a(t)$, using a least square routine between the applied stress and the elapsed time;

(b) the elastic modulus, which is taken as the maximum slope of the curve $\sigma_a(\varepsilon_t)$ and is computed from $M = \dot{\sigma}_a(t)/\dot{\varepsilon}_t$, where $\dot{\varepsilon}_t$ is the imposed constant strain rate;

(c) the non-elastic strain, $\varepsilon_p(t)$, is obtained at any time from the data $\varepsilon_t(t)$ and $\sigma_a(t)$ using $\varepsilon_p = \varepsilon_t - (\sigma_a - \sigma_0)/M$, where σ_0 is a stress constant due to mechanical looseness which tightens early during the test; σ_0 is taken at the intersection of the ε_t-axis and the preceding M-tangent to the $\sigma_a(\varepsilon_t)$ curve;

(d) the plastic strain rate, $\dot{\varepsilon}_p(t)$, is computed from $\dot{\sigma}_a(t)$, using $\dot{\varepsilon}_p = \dot{\varepsilon}_t - (\dot{\sigma}_a/M)$;

(e) $K'(\varepsilon_p)$ is computed from $K' = \dot{\sigma}_a/\dot{\varepsilon}_p$;

(f) the curve $\dot{\varepsilon}_p(\varepsilon_p)$ is approximated by a polynomial which allows us to compute its strain derivative, i.e. $A(\varepsilon_p) = (1/\dot{\varepsilon}_p)(d\dot{\varepsilon}_p/d\varepsilon_p)$;

(g) finally the curve $V_{exp}(\varepsilon_p)$ is obtained with five samples tested for stress relaxation, each at a given point $(\sigma_a, \varepsilon_p)$ of the curve $\sigma_a(\varepsilon_p)$ with ε_p in the range 5×10^{-4}–25×10^{-4}: $\varepsilon_p = 5 \times 10^{-4}, 10^{-3}, 1.5 \times 10^{-3}, 2 \times 10^{-3}$, and 2.5×10^{-3}.

Fig. 1 shows the K' and K values obtained by this procedure for resins PG and DEG, respectively, as functions of ε_p; Table I gives intermediate parameters which have been used and the values of K obtained for these plastic strains.

4. Measurement of *K* by the RSR method

4.1. RSR method reviewed

Let us consider a repeated stress relaxation run performed from a point $(\sigma_a^{(1)}, \varepsilon_p^{(1)})$ of the $\sigma_a(\varepsilon_p)$ curve, in a constant total strain rate test. The duration, Δt_n, of the nth run needed to relax a given stress amount $\Delta\sigma_0$ is given by an equation like Equation 6a

$$-\Delta\sigma_0 = \frac{kT}{V_{exp}} \ln\left(1 + \frac{\Delta t_n}{C_n}\right) \qquad (8)$$

with the time constant C_n, proportional to $1/\dot{\varepsilon}_{pn,i}$, the plastic strain rate at the start of the run [6]. The experimental activation volume V_{exp} relates to the

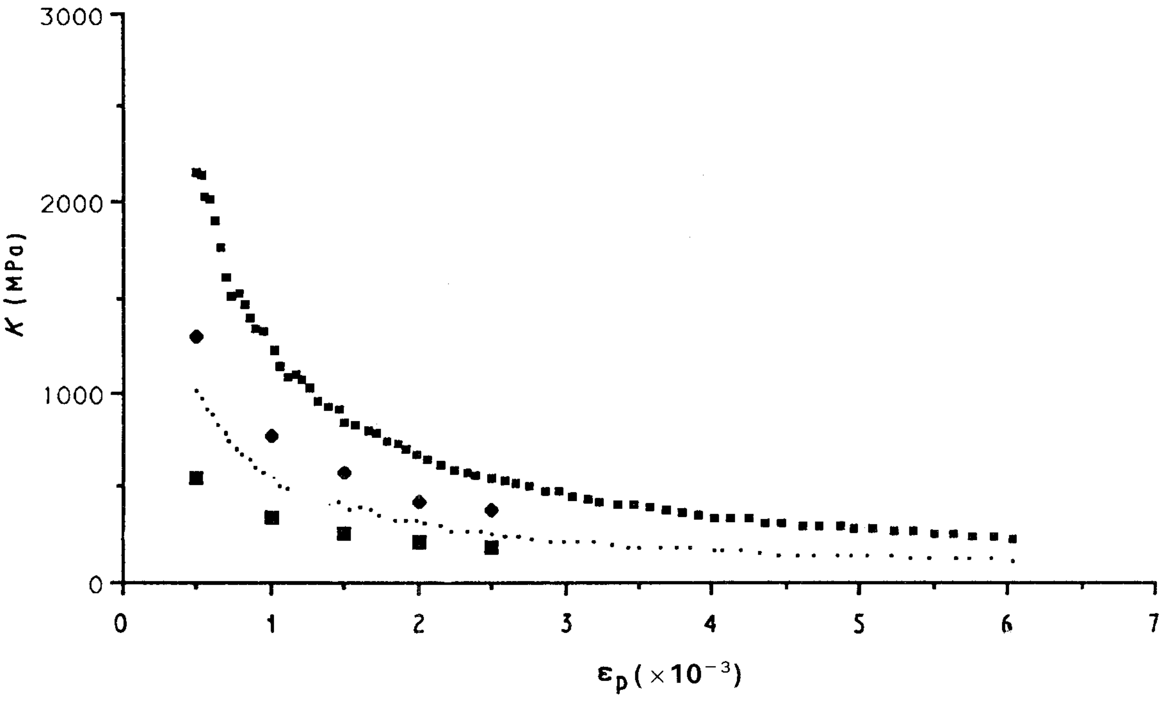

Figure 1 $K'(\varepsilon_p)$ values for the two unsaturated polyester resins, PG and DEG. Work-hardening rate, K, values as obtained from K' by the direct method are also shown (▪) K'(PG), (◆) K(PG), (•) K'(DEG), (■) K(DEG).

TABLE I K' and K values for the PG and DEG resins and intermediate mechanical parameters: M (elastic compressive modulus). V_{exp} (activation volume)

	0.5×10^{-3}		1.0×10^{-3}		1.5×10^{-3}		2.0×10^{-3}		2.5×10^{-3}	
	PG	DEG	PG	DEG	PG	DEG	PG	DEG	PG	DEG
M(MPa)	3100	2500	3100	2500	3100	2500	3100	2500	3100	2500
V_{exp}(nm^3)		3.900		3.050		2.590		2.030		1.900
K'(MPa)	21600	10000	12200	5450	8510	3860	6410	3140	5430	2580
K(MPa) direct meth.	13000	5550	7750	3375	5730	2530	4230	2045	3830	1770
K(MPa) RSR		5100		3025		2500		2250		1975

stress derivative $(\partial \ln \dot{\varepsilon}_p/\partial \sigma_a)_R$ in relaxation conditions, taken at its starting time when $\sigma_a = \sigma_a^{(1)}$; for the sake of simplicity, its value is assumed to be the same whatever the number, n, of the run, and is measured on a distinct sample by a single stress relaxation test from the same point $(\sigma_a^{(1)}, \varepsilon_p^{(1)})$, as in Section 3(g). Because $\Delta\sigma_0$ and V_{exp} are independent of n, Equation 8 shows that $\Delta t_n/C_n$, i.e. $\dot{\varepsilon}_{pn,i}\Delta t_n$ is independent of n as well, which means that Δt_{n+1} is related to Δt_n by

$$\Delta t_{n+1} = \Delta t_n \cdot (\dot{\varepsilon}_{pn,i}/\dot{\varepsilon}_{pn+1,i}) \qquad (9)$$

From Equation 1, $\dot{\varepsilon}_p$ is a function of $\sigma^* = \sigma_a - \sigma_i$, and T. Therefore, the strain rate ratio can be evaluated from a limited expansion of $\ln \dot{\varepsilon}_p$ in terms of σ^*, for a thermal component increment $\Delta\sigma^* = -\Delta\sigma_i$ between the two successive initial strain rates, and corresponding to the plastic strain increment gained during one run

$$\Delta\varepsilon_p = \Delta\sigma_0/M \qquad (10a)$$

$$\Delta\sigma^* = -\Delta\sigma_i = -K_n \cdot \Delta\sigma_0/M \qquad (10b)$$

So that, using Equations 4 and 6 finally [6]

$$\frac{\Delta t_{n+1}}{\Delta t_n} = \exp\left(\frac{V_{exp}\Delta\sigma_0}{kT}\,\frac{K_n}{M + K_n}\right) \qquad (11)$$

where K_n is the work-hardening rate during the nth run.

Let us first neglect any physical ageing during relaxation runs. Then K_n decreases from run to run because of the increasing plastic strain and because it has been shown elsewhere that K varies as $1/\varepsilon_p$ [4, 7]. Therefore, while assuming, for the sake of simplicity, that K remains constant during one run, we change its value at each new run. For the value of K_n, we take the value of K at the terminal strain, at the end of the nth run (i.e. at time t_n), i.e. at $\varepsilon_p = \varepsilon_p^{(1)} + n\Delta\sigma_0/M$. Hence denoting the K values without physical ageing, $K(0)$, the recurring relationship between $K_n(0)$ and $K_{n-1}(0)$ is

$$K_n(0) = K_{n-1}(0)\left[\varepsilon_p^{(1)} + (n-1)\frac{\Delta\sigma_0}{M}\right] \Big/ \left[\varepsilon_p^{(1)} + n\frac{\Delta\sigma_0}{M}\right] \qquad (12a)$$

from which $K_n(0)$ can be evaluated as soon as $K_1(0)$ is known. $K_1(0)$ is known in turn from Δt_1 and Δt_2, following Equation 11

$$\frac{K_1(0)}{M} = \frac{kT\ln(\Delta t_2/\Delta t_1)}{V_{exp}\Delta\sigma_0 - kT\ln(\Delta t_2/\Delta t_1)} \qquad (12b)$$

Thus from the two input data $(\Delta t_1, \Delta t_2)$ or $(\Delta t_1, K_1(0))$ all the other Δt_ns can be computed together with the $K_n(0)$s using Equations 11 and 12. The fit with experimental values $\Delta t_1, \Delta t_2, \ldots, \Delta t_n, \ldots$ for each given starting strain $\varepsilon_p^{(1)}$ can be optimised (see Section 4.2) so that the best curve of $K_n(0)$ versus n is obtained. It can be approximated by polynomial and extrapolated to $n = 0$, so that finally the work-hardening rate at zero relaxation strain, $K = K_0(0)$ can be obtained and compared to the K value measured by the direct method at the same strain $\varepsilon_p^{(1)}$ (see Section 5).

Now the recovery of σ_i by physical ageing during the repeated runs, an additional cause of a decrease in K along the test, can be introduced. Let us choose a stress recovery function $f(\tau)$, $\tau = t/t_0$ with t the elapsed time, so that the internal stress is written as

$$\sigma_i(\varepsilon_p, t) = \sigma_i^0(\varepsilon_p)f(\tau) \qquad \tau = \frac{t}{t_0} \qquad (13)$$

with $f(0) = 1$, σ_i^0 is the internal stress at the origin time. An usual ageing function is, for example

$$f(\tau) = \exp(-\tau^\beta) \qquad (14)$$

where β is a constant ranging typically between one-third (Andrade law) and two-thirds, depending on the recovery phenomena. With this time dependence, K may be written

$$K(\varepsilon_p, t) = \left(\frac{\partial\sigma_i}{\partial\varepsilon_p}\right)_t = K(0)f(\tau),\ K(0) = \frac{d\sigma_i^0}{d\varepsilon_p} \qquad (15)$$

while during a stress relaxation run, the total strain derivative of σ_i may be written as

$$K''(\varepsilon_p, t) = \frac{d\sigma_i}{d\varepsilon_p} = \left(\frac{\partial\sigma_i}{\partial\varepsilon_p}\right)_t + \frac{1}{\dot{\varepsilon}_p}\left(\frac{\partial\sigma_i}{\partial t}\right)_{\varepsilon_p} \qquad (16)$$

so that for the nth run of average strain rate $\dot{\varepsilon}_p = \Delta\sigma_0/M\Delta t_n$,

$$\frac{K_n''(\varepsilon_p, t)}{M} = \frac{K_n(0)}{M}f(\tau) + \frac{\sigma_{i,n}^0}{\Delta\sigma_0}\,\frac{\Delta t_n}{t_0}f'(\tau) \qquad (17)$$

where $f'(\tau)$ is the τ-derivative of $f(\tau)$, and $K_n(0)$ is strain dependent as given still by Equation 12, as is $\varepsilon_{pi}^0(\varepsilon_p)$ (see below).

In Equation 17, time is flowing during the nth relaxation run. As in Equation 12, for the sake of simplicity, we take $K_n(0)$ as a constant over the run and equal to its value at the run end, i.e. at time t_n and strain $\varepsilon_p^{(1)} + n\Delta\sigma_0/M$. The new recurring relationship between Δt_{n+1} and Δt_n is obtained by substituting Equations 16 and 17 into Equation 11, with K'' instead of K, hence

$$\frac{kT}{V_{exp}\Delta\sigma_0}\ln\left(\frac{\Delta t_{n+1}}{\Delta t_n}\right) = \left[\frac{K_n(0)}{M} - \beta\frac{\sigma_i^0\,\Delta t_m}{\Delta\sigma_0 t_m}\tau^\beta\right](\exp - \tau^\beta) \Big/ \left[1 + \left(\frac{K_n(0)}{M}\right)\right] \qquad (18)$$

$$\tau = t_n/t_0; \qquad t_n \approx \sum_{i=1}^{n} \Delta t_i$$

where we have neglected in t_n the quite short reloading times before each new run, and where we have made the simplifying assumption $\tau = 0$ (i.e. no ageing) in the denominator in which K_n comes as a corrective term between $V_{\exp}$ and V. By doing this, we slightly force the ageing decrease of K as expressed in the numerator, only through a corrective term; because the ageing function is itself only a crude approximation, this assumption is acceptable.

In Equation 18 σ_i^0 is strain dependent. Recalling that its strain derivative, $K(0)$, varies as $1/\varepsilon_p$ [4, 7], σ_i^0 varies like $\ln \varepsilon_p$. Taking again $\sigma_{i,n}^0$ equal to its terminal value at the nth run end, a recurring relationship similar to Equation 12 is obtained

$$\sigma_{i,n}^0 = \sigma_{i,n-1}^0 + K_{n-1}(0)\left[\varepsilon_p^{(1)} + (n-1)\frac{\Delta\sigma_0}{M}\right]\ln\left[\left(\varepsilon_p^{(1)} + n\frac{\Delta\sigma_0}{M}\right)\Big/\left(\varepsilon_p^{(1)} + (n-1)\frac{\Delta\sigma_0}{M}\right)\right] \quad (19)$$

from which $\sigma_{i,n}^0$ can be evaluated as soon as $\sigma_{i,1}^0$ is known. Now $\sigma_{i,1}^0$ can be approximated as the applied stress from the stress, σ_E, at which the curve $\sigma_a(\varepsilon)$ deviates from linearity (where the above M straight line is tangent to this curve)

$$\sigma_{i,1}^0 = \sigma_a(\varepsilon_p^{(1)}) - \sigma_E \quad (20)$$

By the same procedure as above, using Equations 18 and 12a, b, 19 and 20, the run durations $\Delta t_1, \Delta t_2, \ldots, \Delta t_n, \ldots$ can be computed from the two input data ($\Delta t_1, \Delta t_2$), and after fitting with the experimental durations, the zero relaxation strain K value, $K_0(0) = K$, can be deduced, provided that the two ageing parameters which have been introduced, β and t_0, be determined. The derivation of these parameters, and the K values obtained at five strains $\varepsilon_p^{(1)}$ are given below.

4.2. Ageing parameter determination and *K* values by the RSR method

The fitting exercise has been performed for one of the two preceding unsaturated polyester resins (the DEG resin), which was tested in RSR from five strain values $\varepsilon_{pi}^{(1)} = 5\times10^{-4}$, 10^{-3}, 1.5×10^{-3}, 2×10^{-3}, and 2.5×10^{-3}. Here the relaxed amount of stress is $\Delta\sigma_0 = 0.71$ MPa and the elastic modulus is $M = 2500$ MPa, so that the plastic strain gained in each relaxation run, $\Delta\sigma_0/M = 2.84\times10^{-4}$ is by no way negligible as compared to $\varepsilon_p^{(1)}$ values. The five values $V_{\exp}(\varepsilon_p^{(1)})$ are the ones already measured in Section 3(g) and given in Table I.

The fit is done on the five experimental Δt_n versus n curves, using the following procedure implemented in a PC computer.

(a) The process starts from a given value of β (between 0.25 and 1) and of t_0 (between 2000 and 82 000 s). For the plastic strain $\varepsilon_{p1}^{(1)}$, we take a given value Δt_1 (near the experimental one); we then determine a Δt_2 value, or equivalently a ratio $\Delta t_2/\Delta t_1$, i.e. a $K_1(0)$ value, which gives the best fit with experiment. That is, starting from some Δt_2 value, the others durations $\Delta t_3, \Delta t_4, \ldots \Delta t_n, \ldots$ are computed so that the quantity I,

$$I(\beta, t_0, \varepsilon_{p1}^{(1)}, \Delta t_2, \Delta t_1) = \sum_n (\Delta t_n^{\text{comp}} - \Delta t_n^{\exp})^2 \quad (21)$$

can be calculated. Another value Δt_2 is then tried, which gives another value for I, and the process is repeated until I reaches some minimum value I_0.

(b) Another Δt_1 value is taken, and the same process leads to another minimum I_0, and so on until the minimum minimorum for I is reached, $I_m(\beta, t_0, \varepsilon_{p1}^{(1)}, \Delta t_2, \Delta t_1)$, which determines the best predicted values $\Delta t_1, \Delta t_2, \ldots \Delta t_n, \ldots$ either by choice for $\Delta t_2, \Delta t_1$, or by computation for $\Delta t_3, \Delta t_4, \ldots \Delta t_n, \ldots$ (we make no claim for uniqueness).

(c) Another strain value, $\varepsilon_{p2}^{(1)}$ is chosen and we compute the quantity S, such that

$$S(\beta, t_0) = \sum_{i=1}^{5} I_m(\beta, t_0, \varepsilon_{p,i}^{(1)})$$

(d) The surface $S(\beta, t_0)$ is investigated in varying t_0 with fixed β, and vice versa. Fig. 2 shows how this surface looks. The minimum of S is found for the (β, t_0) values given by $\beta = 0.65$; $t_0 = 50000$ s. Fig. 3 shows the fit of the Δt_ns calculated from these parameters, for each strain value $\varepsilon_{pi}^{(1)}$, with the corresponding experimental values, and Fig. 4 shows the five corresponding $K_i(n)$ versus n curves, from which the K values for each strain value $\varepsilon_{pi}^{(1)}$ are extrapolated; these values are reported in Table I.

It is worthy of note that the value found for t_0, about 14 h, means any σ_i recovery by physical ageing during the relaxation runs is quite negligible, because durations are always much shorter than t_0($\Delta t_n < 300$ s so that $t_n = \Sigma\Delta t_n < 2000$ s, i.e. $t_n < t_0/25$). Therefore, the main cause of decrease of K

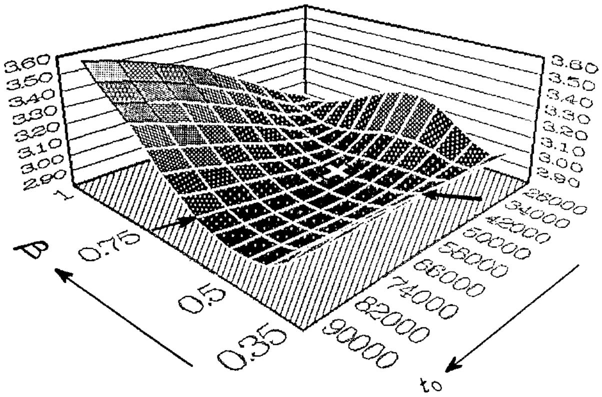

Figure 2 Surface $S(\beta, t_0)$ as a function of b and t_0; the part of the surface corresponding to $t_0 \in [2000\text{ s}, 26000\text{ s}]$ and $\beta \in [0.25, 0.35]$ is beyond the minimum and is not shown here for the sake of clarity. Arrows show the isoparameter lines $\beta = 0.65$ and $t_0 = 50000$ s which define the minimum locus (white cross).

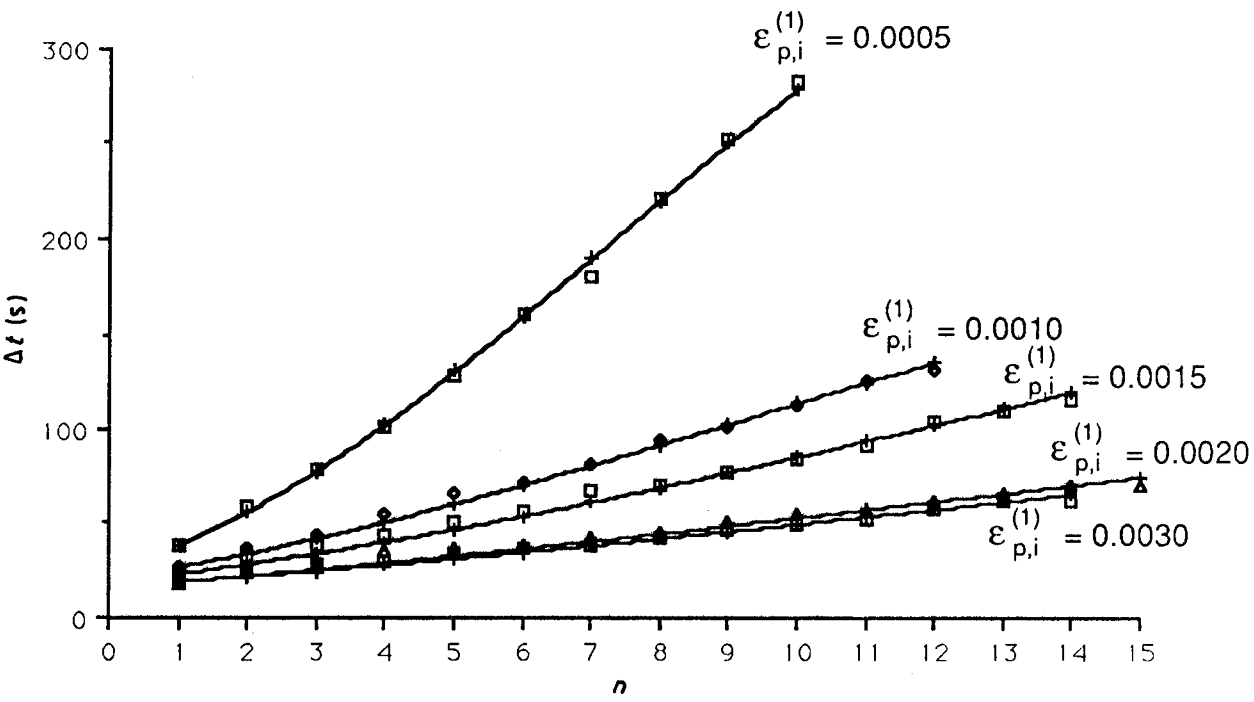

Figure 3 Measured values of $\Delta t_n^{\mathrm{comp}}$ versus n (number of the relaxation). The line shows the calculated $\Delta t_n^{\mathrm{mes}}$ versus n.

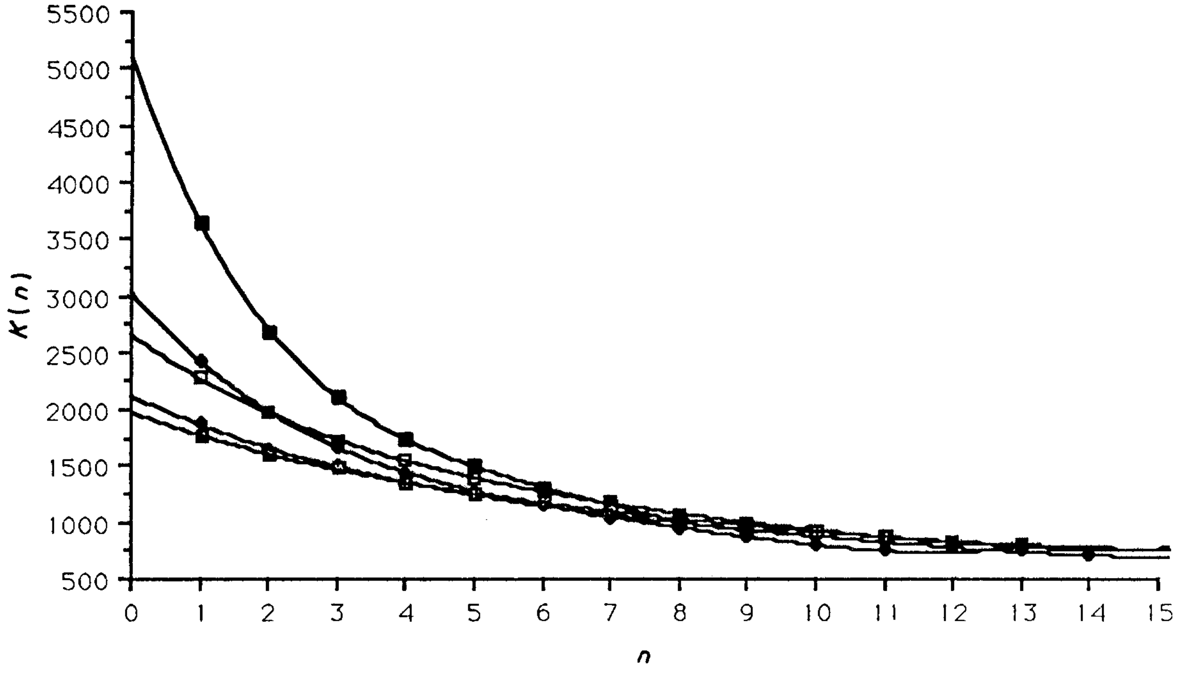

Figure 4 $K(n)$ values versus n (number of the relaxation) (■) $\varepsilon^{(1)}_{p,i} = 0.0005$, (◇) $\varepsilon^{(1)}_{p,i} = 0.0010$, (□) $\varepsilon^{(1)}_{p,i} = 0.0015$, (◆) $\varepsilon^{(1)}_{p,i} = 0.0020$, (⊞) $\varepsilon^{(1)}_{p,i} = 0.0030$.

during stress relaxation runs, and of $(\Delta t_{n+1}/\Delta t_n)$ as well, is the plastic strain increment gained at each run.

5. Comparison between the two methods

The agreement between the work-hardening rate, K, values measured either by the direct method, or by RSR is very good: Table I shows an agreement within 10% only.

This agreement has to be appreciated in comparison with two causes of uncertainties. The first is the experimental scatter of the activation volume values, V_{exp}, which is certainly of order of 5%–10%. Numerical simulation shows that a 10% decrease in V_{exp} in K from the direct method, and a 12%–16% increase in K from the RSR depending on the strain $\varepsilon^{(1)}_{p,i}$. These changes lead to largely overlapping K values, the direct method spread being narrower and enclosed in the RSR spread.

The second cause of error is the crude approximation used in accounting for physical ageing recovery of internal stresses, σ_i. The parameters β and t_0 of the chosen ageing function should depend on the level of applied stress, i.e. on the strain $\varepsilon_{p,i}^{(1)}$ at the start of the ith RSR run [8]; accordingly, the coordinates $[\beta, t_0]$ of the minimum locus of the function $I_m(\beta, t_0, \varepsilon_{p,i}^{(1)})$ should be found for each given $\varepsilon_{p,i}^{(1)}$ value instead of the one of the $S(\beta, t_0)$ function in Section 4(c) above. Although this procedure would be unavoidable when investigating ageing processes for themselves, it is less necessary here because of the range of small investigated strains (smaller than 25×10^{-4}) and because we merely want to check the validation of the direct method against the RSR one; therefore, in order to save computer time, we choose to perform only the 4(c) procedure. The computed minimum coordinates $[\beta, t_0]$ as given above are thus only some averaged ageing parameters in the investigated strain range; the good experimental fits obtained on Δt_n versus n curves in Fig. 3 show that they are nevertheless acceptable values.

Despite of the approximation used for physical ageing, our analysis shows that physical ageing accounts about as much as strain effects upon K, for the correction to be brought in the K measurement by RSR. This is shown in Table II in which for each strain value $\varepsilon_{p,i}^{(1)}$ are displayed for the DEG resin:

(i) the K value obtained from RSR without any correction, following the standard method given in previous papers [3, 4, 6];

(ii) the K value after correcting only for the strain dependence of K during an RSR run;

(iii) the K value after correcting for both the ageing and the strain effects.

Consistent with the above discussion, this table cannot give indications of the varying amounts the ageing contributes to the correction term depending on the level of applied stress.

6. Conclusions

This study establishes the validity of the new method of measurement of the non-elastic work-hardening rate, K, the so-called direct method. While being consistent with the RSR method, this new method has several advantages over the latter:

(i) it is much less time-consuming to set out;

(ii) it gives the whole curve $K(\varepsilon_p)$ in one experiment, thus allowing an easier comparison between various temperature behaviours of the same material, or various materials at the same temperature;

(iii) it is much less strain-damaging, allowing thus brittle materials like organic composites to be investigated;

(iv) it gives more precise measurements of K, because it is less sensitive to scatter in V_{exp} values as shown in the above section.

TABLE II Different K values obtained for the DEG resin at different plastic strains $\varepsilon_{pi}^{(1)}$: K_1, standard procedure without any correction; K_2, after correcting only for the $K(\varepsilon_p)$ dependence during an RSR run; K_3, after correcting both the ageing and strain effect

ε_p	K_1(MPa)	K_2(MPa)	K_3(MPa)
0.5×10^{-3}	1560	3500	5100
1.0×10^{-3}	1280	2275	3025
1.5×10^{-3}	1390	2025	2500
2.0×10^{-3}	1220	1700	2250
2.5×10^{-3}	1110	1550	1975

The measurements can be made even faster when only K' values are needed, avoiding the need of correction from K' to K (Equation 7), i.e; the experimental determination of $V_{exp}(\varepsilon_p)$ and $A(\varepsilon_p)$. This is the case either with some materials like epoxy resins or epoxy composites in which it happens that the correction is quite small [9], or when there is only the need of classifying materials depending on their ability to deform plastically: most of the time, $K'(\varepsilon_p)$ gives the same classification as does $K(\varepsilon_p)$. As an example, Fig. 1 shows that PG resin is harder to deform non-elastically than DEG resin (as is expected from their molecular structure [7]) because K is always higher in that case; but this conclusion is already seen from K' data which fall in the same order. The same behaviour has been observed with a number of other polymers in our laboratory.

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