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Work-hardening rate of glassy polymers: evolution with curing of thermo-set resins

J. M. LEFEBVRE, C. BULTEL, B. ESCAIG
Laboratoire de Structures et Propriétés de l'Etat Solide, CNRS (LA 234), Université des Sciences et Techniques de Lille, 56955 Villeneuve d'Ascq Cedex, France

A new parameter, the work-hardening rate, *K*, is introduced to characterize the non-elastic deformation behaviour of glassy polymers. Related to the defects nucleation in the preyield stage, this parameter is shown to be a very sensitive probe of the structural evolution of materials. The variation of *K* with cross-linking in the curing of a polyimide resin is reported.

1. Introduction

In a previous paper [1] we introduced a new parameter to characterize the non-elastic behaviour of glassy polymers. This quantity, the work-hardening rate K, is measured in the pre-yield stage. It has been applied to the physical ageing of atactic PMMA, and shown to provide a sensitive probe to account for mechanical changes in the range 3% to 6% total strain. The application to another example, the progress of the cross-link reaction in a thermo-set resin during curing, is reported. Measuring the work-hardening rate allows one to investigate, in this case, variations of mechanical properties with cross-link density in the range 5% to 10% strain, i.e. in a stress/strain range much closer to practice than in standard viscoelastic dynamic tests. Moreover, K measurements give an insight into a basic quantity of the physics of deformation: the nucleation rate of defects in the chain arrangement.

The necessary existence of such defects for propagating non-elastic local strain through solid atactic polymers, and their importance in the understanding of yield processes has been elucidated in recent years [2]; These defects have been described both theoretically as kinks on molecular rods [3] or as Volterra or Somigliana dislocation loops [2, 4–7], and experimentally as emissary defects at the tip of elementary shear bands or diffuse shear zones [8–10]. As a result, an internal stress field, σ_i, grows up with increasing strains during the pre-yield stage, originating from these defects much as in crystalline materials when dislocation multiplication hardens the deforming solid. Parallelling this last situation, the non-elastic work-hardening rate, K, can be defined as [1, 9]:

$$K = \frac{d\sigma_i}{d\epsilon_p} = \left(\frac{\partial \sigma}{\partial \epsilon_p}\right)_{\dot{\epsilon},T}$$

where $\sigma = \sigma_i(\epsilon_p) + \sigma^*(T, \dot{\epsilon}_p)$ is the flow stress corresponding to a total strain: $\epsilon_t = \epsilon_H + \epsilon_p$ made of a Hookean elastic contribution, ϵ_H, and a non-elastic remaining part, ϵ_p (comprising both the irreversible plastic and the recoverable anelastic strain).

From the point of view of a defect based (or "metallurgical") analysis, K is related to the defect nucleation rate. If e is the total non-elastic strain, each molecular defect contributes once it has wholly developed, the nucleation of dN defects at some point in the pre-yield stage results in a non-elastic strain increment $d\epsilon_p = e\,dN$. These dN defects are nucleated from the stress increment, $d\sigma$, during a constant strain-rate test, so that:

$$K = \frac{1}{e}\left(\frac{\partial \sigma}{\partial N}\right)_{\dot{\epsilon},T} \sim \left(\frac{dN}{d\sigma}\right)^{-1}_{\dot{\epsilon},T}$$

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 controlling. Thus K is a measure of the material resistance to non-elastic strain: a purely elastic

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behaviour ($d\epsilon_p = dN = 0$) means K is infinite, whereas at yield ($\dot{\epsilon}_H \simeq 0$) $K \simeq 0$.

The ability of a polymer to deform non-elastically can be investigated as long as K is a readily measurable quantity. From what is known of the physical metallurgy of crystals, K is most sensitive to any slight change in microstructure such as local ordering, microprecipitation, etc. By analogy, it is tempting to investigate how polymers can keep close to this pattern. A previous study [1] has proved K is clearly sensitive to changes in the thermal jump frequency of monomer units due to standard differences in ageing treatment (physical ageing) of atactic PMMA much more than the yield stress or the creep rate at comparable stress levels, for example. As a second test, we would investigate here the influence of cross-link density on the mechanical properties of a polyimide resin at high stresses (about two thirds of the yield stress), or reversely, whether K measurements are a way of obtaining information on the degree of cross-linkage and on its increase during curing, since it is known that the usual methods (swelling, infrared spectroscopy, etc) are largely ineffective in this case except, perhaps, ^{13}C NMR in the solid state.

Owing to the relatively new character of the experimental technique used, i.e. the measurement of K by repeated stress relaxation tests, we feel it is necessary to give first, in the next section, the theoretical framework. Subsequently, we shall define the PABM polyimide resin and its curing conditions, describe the mechanical tests and finally discuss the results obtained.

2. Measurement of *K* by stress relaxation

The stress relaxation test can be viewed as an experimental method of uncoupling elastic and non-elastic strains [11, 12], which are mixed together in the pre-yield stage with a ratio varying from pure elastic to largely dominant non-elastic strain. During this test, in which the total strain rate $\dot{\epsilon}_t = 0$, any non-elastic component, $\Delta\epsilon_p$, produced in a time Δt (such as at point A$'$ in Fig. 1) is easy to measure from the simultaneous stress drop, $\Delta\sigma < 0$, provided that the effective modulus, M, of the machine–sample association is known, since $\Delta\epsilon_p + \Delta\epsilon_H = \epsilon_t \Delta t = 0$, or $\Delta\epsilon_p = -(\Delta\sigma/M)$; or else:

$$\dot{\epsilon}_p = -\dot{\sigma}/M \qquad (1)$$

What are the underlying physical ingredients in the kinetics of the stress drop $\Delta\sigma(t)$? Equation 1 shows that the kinetics are primarily controlled by the non-elastic strain rate, $\dot{\epsilon}_p$, and their stress derivative is the apparent activation volume, V_0 (see below). In fact, Equation 1 also contains information about the slight variation in microstructure entailed by the extra strain, $\Delta\epsilon_p$, produced by a slight nucleation of defects during the relaxation itself, which introduces the non-elastic work-hardening rate, K. Therefore, the stress drop at any point A$'$ depends on three deformation parameters: $\dot{\epsilon}_p(\mathrm{A}')$, $V_0(\mathrm{A}')$ and $K(\mathrm{A}')$, which can, in turn, be extracted from experimental curves.

Early in the stress relaxation, and usually in the first 4 or 5 min, the time variation $\Delta\sigma(t)$ can be analysed in terms of the only deformation parameters at the starting state A in Fig. 1, from a first order expansion of the strain rate at state A$'$, $\dot{\epsilon}_p(\mathrm{A}')$. Accordingly we can probe any state A of the stress–strain curve for $\dot{\epsilon}_p$, V_0 and K with this test. This point of view is, of course, quite different from standard rheological analysis of the same test, which is aimed at obtaining from it a whole spectrum of relaxation times. We think that in solid polymers, the short time span of this spectrum should be identified with our stress-decreasing activation energy of deformation process, $\Delta G_a(\sigma - \sigma_i, T)$, which means under test conditions, time-increasing, hence merely with V_0. On the other hand, the long time span should be interpreted as activation energies of recovery processes [13–15].

For the purpose of our analysis, one only needs to consider the non-elastic strain rate, $\dot{\epsilon}_p$, as a function of stress, temperature and microstructure. Then $\dot{\epsilon}_p(\mathrm{A}')$ at some point A$'$ of the relaxation curve (at time Δt and strain increment $\Delta\epsilon_p$) can be expanded and related to $\dot{\epsilon}_p(\mathrm{A})$ at the start A ($\Delta t = 0$, $\Delta\epsilon_p = 0$, see Fig. 1). Let us first neglect, for the sake of simplicity, the slight change in microstructure from A to A$'$, i.e., the defect number: $N(\mathrm{A}) = N(\mathrm{A}')$. Then the $\dot{\epsilon}_p$ expansion occurs at constant structure and temperature and reads:

$$\ln \dot{\epsilon}_p(\mathrm{A}') = \ln \dot{\epsilon}_p(\mathrm{A}) + [V_0(\mathrm{A})/kT] \\ [\sigma(\mathrm{A}') - \sigma(\mathrm{A})]$$

or

$$\dot{\epsilon}_p(\mathrm{A}') = \dot{\epsilon}_p(\mathrm{A}) \exp(V_0(\mathrm{A})\Delta\sigma/kT) \qquad (2)$$

with $V_0(\mathrm{A}) = kT(\partial \ln \dot{\epsilon}_p/\partial\sigma)_{T,\mathrm{str}}$ V_0 is termed

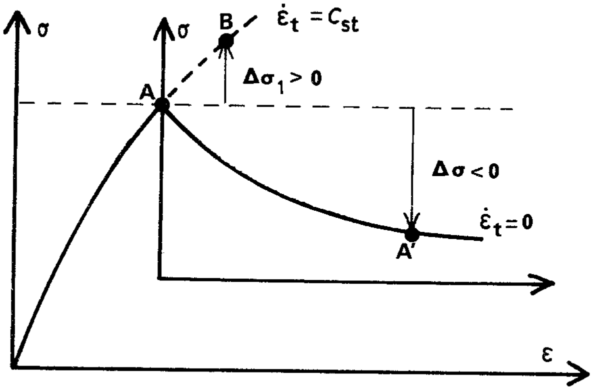


Figure 1 The stress relaxation test.

the "apparent" activation volume. Substituting for $\dot{\epsilon}_p(A')$ in Equation 1 leads to a straightforward differential equation in $\sigma(A')$, the resolution of which gives the well-known law:

$$\Delta\sigma = -\frac{kT}{V_0(A)} \ln\left(1 + \frac{t}{c}\right) \qquad (3)$$

where $c = [kT/MV_0\dot{\epsilon}_p(A)]$ from which the recorded chart $\Delta\sigma(t)$ yields a measurement of $V_0(A)$ [12, 14, 15].

In order to appreciate the validity of this expansion, it is worth noting typical figures for solid polymers: $\Delta\sigma$ is smaller than a few per cents of the applied stress σ, and with M of the order 3 to 4 GPa, the strain $\Delta\epsilon_p$ experienced by the sample during relaxation is, from Equation 1, smaller than 10^{-3} for a test duration of 5 min (about four times the time constant c).

Now, the change in microstructure, $N(A') \neq N(A)$ has to be introduced. Let us define B in Fig. 1 as a point a little beyond A on the same constant strain rate curve, which represents the isostructural state to A′, i.e. the point at which the polymer contains as many defects, $N(A') = N(B)$ and has been given an equal strain amount, $\Delta\epsilon_p$, from A. So, we can compute the stress increment, $\Delta\epsilon_1$, from A to B, simply as:

$$\Delta\sigma_1 = \int_A^B \left(\frac{\partial\sigma}{\partial\epsilon_p}\right)_{\dot{\epsilon}_p} d\epsilon_p = K\Delta\epsilon_p \qquad (4)$$

where K is taken at A on the stress–strain curve and is assumed to be constant between A and B since these states are presumably very close to each other. Note also that $K(A) = K(B)$ entails $\dot{\epsilon}_p(A) = \dot{\epsilon}_p(B)$, since, from $\epsilon_t = \epsilon_H + \epsilon_p$, it is straightforward to show that $\dot{\epsilon}_p = M\dot{\epsilon}_t/(M + K)$ with the same total strain rate $\dot{\epsilon}_t$ at A and B.

The derivation of $\dot{\epsilon}_p(A')$ then follows along the same lines as above, but starts now from B instead of A, so that:

$$\dot{\epsilon}_p(A') = \dot{\epsilon}_p(B) \exp\,[V_0(B)/kT]\,(\Delta\sigma - \Delta\sigma_1)$$

or

$$\dot{\epsilon}_p(A') = \dot{\epsilon}_p(A) \exp\,[V_0(A)/kT]\,(\Delta\sigma - \Delta\sigma_1)$$
$$= \dot{\epsilon}_p(A) \exp\,(V_{\text{exp}}\Delta\sigma/kT) \qquad (5)$$

since $\sigma(A') - \sigma(B) = \Delta\sigma - \Delta\sigma_1 = \Delta\sigma(1 + K/M)$ from Equation 1 and 4 and $V_0(B) = V_0(A) = V_0$ within the same approximation as that used in expanding $\dot{\epsilon}_p$ between states separated by a strain increment, $\Delta\epsilon_p$. Equation 5 has the same form as Equation 2, where V_0 is replaced by V_{exp}:

$$V_{\text{exp}} = V_0\left(1 + \frac{K}{M}\right) \qquad (6)$$

V_{exp} is termed the "experimental" activation volume, which has to be substituted for V_0 in the relaxation kinetics given in Equation 3. The corrective term V_0K/M stems from work-hardening by the defects nucleated during the relaxation test itself, and is usually larger than V_0 in the pre-yield stage.

Since K slows down the relaxation kinetics by increasing V_{exp}, it is clear that K can be obtained from the gradual increase in duration of repeated relaxation tests by a given stress amount, $\Delta\sigma_0$ (Fig. 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, $V_0\Delta\sigma_0 < kT$, it is easy to show [11], following Kubin [16], that the duration of the nth relaxation ($n = 1, 2, \ldots$) increases exponentially with n:

$$\Delta t_n = \Delta t_1 \exp\,[(n-1)KV_0\Delta\sigma_0/MkT], \qquad (7)$$

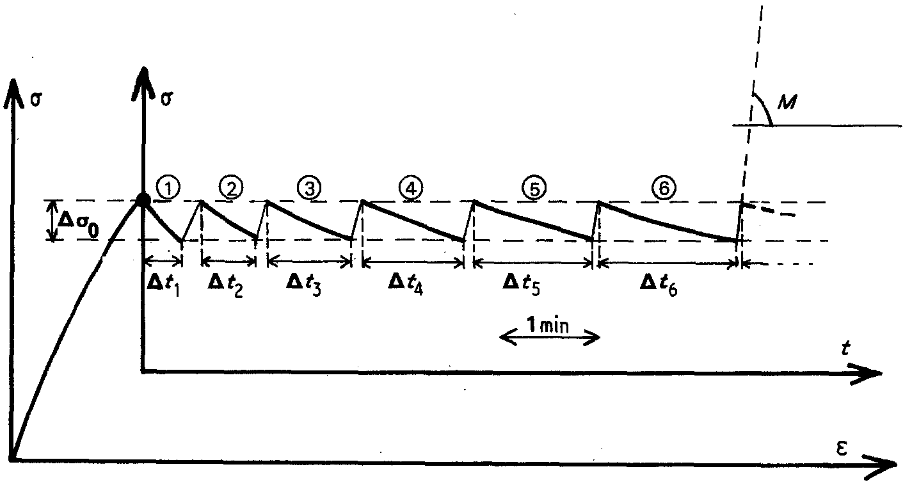


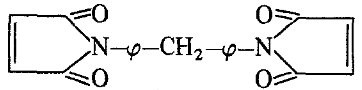
Figure 2 The repeated relaxations test, Δt_i refers to $t_c = 3$ h.

as soon as n is larger than a few units, $n > 4$ to 6, in practice. Therefore a plot of ln $(\Delta t_n/\Delta t_1)$ against n yields the value of V_0K/M; since the first run gives the experimental volume $V_{\text{exp}} = V_0 + (V_0K/M)$, then both V_0 and K/M can be measured. Finally, M can be deduced from the last loading slope, $p_n = \mathrm{d}\sigma/\mathrm{d}\epsilon_t$, since it is shown that the ratio $(M - p_n)/M$ also decreases exponentially with n and, practically speaking, $M \simeq p_n$ from $n \simeq 4$ or 5 and beyond.

This method is applied later to the determination of K at a given non-elastic strain in the pre-yield stage, on samples of a polyimide resin of different curing times and conditions in order to investigate the advancement of cross-linkage and its influence on mechanical behaviour.

3. Preparation and curing conditions of PABM polyimide samples

Polyamino-bismaleimide (PABM) samples were obtained from Rhone Poulenc Industries. These were prepared by reaction at 180° C of 2.5 mol 44′ diphenylmethane bismalemide:



with 1 mol diamino 44′ diphenylmethane:

$$H_2O{-}\varphi{-}CH_2{-}\varphi{-}NH_2$$

Both homopolymerization and polyaddition with diamine occur during reaction and curing, and result in a strongly cross-linked thermoset resin, the glass transition temperature of which is over 300° C.

Parallelepipedic PABM resin plates, 120 mm × 70 mm × 12 mm, are then cured following different treatments:

1. 1 h at 200° C;
2. 2 h at 200° C;
3. 8 h at 200° C;
4. 24 h at 200° C;
5. 24 h at 200° C plus 24 h at 250° C.

All these treatments were performed in air. Finally a sixth treatment was carried out under primary vacuum, i.e. 24 h at 200° C plus 24 h at 250° C. After treatment, the resin plates were just left free to return to room temperature. Compression samples were then cut from the sheets and machine turned into small cylindrical specimens (6 mm diameter and 11 mm long); they were mechanically polished carefully to ensure that end sections were parallel to better than 0.01 mm.

4. Mechanical tests

Compression tests at constant strain rate, $\dot{\epsilon}_t = 3 \times 10^{-5}\ \text{sec}^{-1}$, and constant temperature, $T = 17^\circ$ C, have been performed using an Instron machine, and the work-hardening rates, K, measured by stress relaxation from some stress value σ_0.

In these experiments, K is taken as a function of non-elastic strain, ϵ_p, and curing time, t_c, $K(\epsilon_p; t_c)$, t_c standing for the sample microstructure prior to deformation. Therefore, in order to determine the sole influence of t_c, different samples have to be tested for K at the same non-elastic strain ϵ_p, which in turn has to be

TABLE I Summary of experimental results

Curing time, t_c	σ_y (MPa)	σ_0 (MPa)	M (MPa)	V_{exp} (nm^3)	V_0 (K/M) (nm^3)	V_0 (nm^3)	ϵ_p ($\times 10^{-3}$)	K (MPa)
1 h at 200° C	195	125	3950	2.870	1.990	0.880	4.3	9 100
3 h at 200° C	180	123	3830	2.610	1.310	1.300	4.2	3 830
8 h at 200° C	192	123	3700	2.910	1.770	1.140	4.1	5 735
24 h at 200° C	194	125	3650	3.210	2.050	1.160	4.1	6 570
24 h at 200° C + 24 h at 250° C in air	185	108	3500	3.160	2.390	0.770	4.4	10 850
24 h at 200° C + 24 h at 250° C under vacuum		131	3480	3.900	2.735	1.165	1.2	8 060

known from the equation:

$$\epsilon_p = \epsilon_t - (\sigma/M)$$

where ϵ_t and M are measured.

The total strain, ϵ_t, of the sole sample is measured by an LVDT transducer rigidly attached to the mobile compression plate with its tip at the fixed plate [17]. The effective modulus, M, has to be read from the very beginning of the load–extension chart (typically between 10 and 30 MPa), once the setting of the device is fixed under the load. This allowed the computation of ϵ_p from the reading of ϵ_t and σ during the test, and the measurement of K in each investigated sample at a given non-elastic strain, which scatters experimentally from one sample to another between 4.1 and 4.4×10^{-3}.

The corresponding stresses, σ_0, are close to $2\sigma_y/3$, with σ_y the yield stress (slightly increasing with t_c). This is an optimized value for the method, since at too low a stress, and here in practice below 0.5 σ_y, behaviour is almost purely elastic and the magnitude of any stress relaxation would be much too small to be properly measured, while at too high a stress, and currently when approaching yield, K decreases to very small values, and the duration of successive relaxations, Δt_n in Equation 7, do not vary enough to permit an accurate determination of K.

Each measurement of K requires that two specimens with the same curing time undergo stress relaxation from the same compressive stress, σ_0. One relaxation test is designed to yield a reliable value for the experimental activation volume, V_{exp} in Equation 6. This is done by standard analysis of the stress drop $\Delta\sigma(t)$, following Equation 3 with V_{exp} instead of V_0 [12, 14, 15]. Typical conditions are a duration of 5 min, a corresponding stress drop $\Delta\sigma = 2$ MPa, and a time constant $c = 70$ sec. The experimental scatter of V_{exp} is smaller than 0.05.

The other relaxation test is designed to provide us with a reasonably precise value for (V_0K/M) in Equation 7. This implies that we are able to repeat eight to ten successive relaxations, with a reasonable duration of the last run, Δt_n; typical values are $\Delta t_n \simeq 9\Delta t_1 \simeq 4$ min, with a constant stress drop $\Delta\sigma_0 \simeq 0.35$ MPa.

The illustration given in Fig. 2 relates to $t_c = 3$ h. Each test thus generates one straight line in Fig. 3, as Equation 7 predicts.

The determination of K requires some experimental care since V_0 must be known; this is obtained by the difference of two experimental quantities of ratio 1.5, V_{exp} and the slope (V_0K/M) in Fig. 3. Therefore, it is important to obtain experimental points in this plot which clearly define a unique slope. We chose here as a criterion to have the only points for $n > 3$ to 5 aligned, since Equation 7 is only valid for a sufficiently large value of n. In this way, the experimental scatter of (V_0K/M) is reduced to only 0.06, which leads to a scatter of less than 0.2 for (K/M).

Table I gives as a function of curing conditions, the deformation parameters V_0 and K measured at states such as A in Figs. 1 or 2, together with the corresponding stress, σ_0 (applied force divided by initial section) and non-elastic strain, ϵ_p, the effective Young's modulus, M, and the intermediate quantities V_{exp} and (V_0K/M). For information, the yield stress obtained for each type of curing treatment is also given.

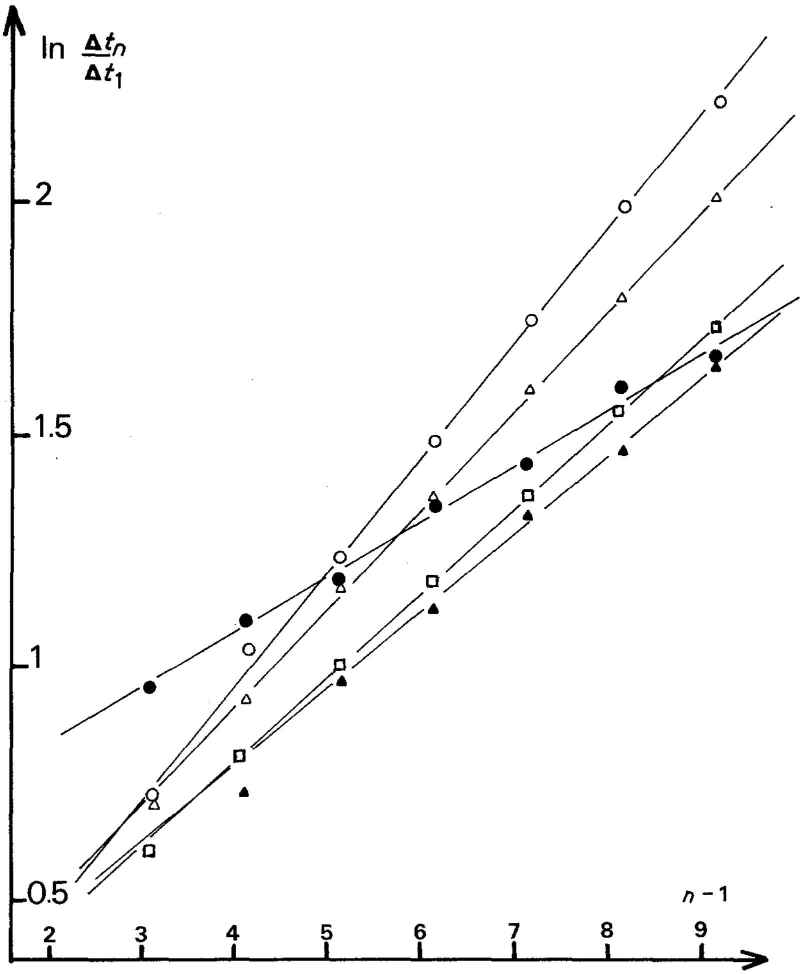


Figure 3 Duration of the *n*th repeated stress relaxation with relaxation number. Key to curing times t_c: □ 1 h at 200° C; ● 3 h at 200° C; ▲ 8 h at 200° C; □ 24 h at 200° C; △ 24 h at 200° C + 24 h at 250° C; ○ 24 h at 200° C + 24 h at 250° C under vacuum.

5. Discussion

It has been possible to perform up to ten repeated relaxation tests on differently cured samples. Fig. 3 shows how the experimental duration of the *n*th test varies with test number *n*; it can be seen how good is the fit to Equation 7 once *n* is sufficiently large (from 3 to 5 and beyond). This gives a clear indication of the feasibility of the method, as it has been proved elsewhere for atactic PMMA [1] as well as on metals [18]. Moreover, it can be seen that *K* is a quite sensitive probe for microstructural evolutions. The values of *K* in Table I exhibit variations due to the sole effect of curing time, since they are all taken at the same non-elastic strain. Thus *K* increases by almost a factor three between a minimum treatment (3 h at 200° C) and the most complete curing (24 h at 200° C plus 24 h at 250° C in air), with a uniform evolution for intermediate conditions (except for the 1 h treatment, see below).

This is to be contrasted with the behaviour of other usual mechanical parameters. On the one hand, the yield stress is almost unaffected; this might come from a cross-link spacing smaller than the persistence length which is expected to be rather large in such rigid chains: further cross-linkage should not result in a higher yield stress [2]. On the other hand, the effective Young's modulus decreases slightly by about 10%, an observation similar to that found in other resins [19–21].

Clearly, inspection of stress–strain curves only cannot show the progress of cross-linkage. Note, for example, that at a stress of 125 MPa, the elastic strain, ϵ_H, contributes ~90% to the total strain; if, due to the elastic modulus, ϵ_H increases then by 10% while ϵ_p, due to K, decreases at the same time by 30%, the net increase in total strain should be reduced to only 2%. Therefore, even at yield, the total strain would not be sensibly changed, for longer curing times, as is observed.

Furthermore, small strain, viscoelastic properties such as elastic moduli, do not reflect properly the change in mechanical properties of interest in practical use, i.e. at higher (total) strains ranging from 5% to 6%. It is noteworthy, in this aspect, that values of M show a slight softening, or the compliance increases, with longer curings while K shows the opposite, i.e. a much greater resistance to non-elastic strains. Along the same lines, values of M are insensitive to changes in curing environment (air or vacuum) in contrast to K. The origin of this last effect is not clear. However, study of weight loss during the curing treatment shows a slightly larger loss under vacuum than in air during the first 24h at 200° C (3% compared to 2.5%), while at 250° C the curves cross over each other, presumably due to surface reaction at contact with air (which does not affect the bulk). This might be in favour of a greater loss of the diamine (which is more volatile) while curing under vacuum, which would result in a less complete cross-linkage, hence a smaller value of K.

From the point of view of deformation physics, K varies as the inverse of the defect nucleation rate (see Section 1); accordingly, the above results indicate that in polyimide resins, cross-linkage should affect only the thermally activated nucleation of "plasticity" defects. Since yield stresses are not sensibly changed, this should concern only the pre-exponential factors rather than activation energies. Thus, comparing the 3h resin to the most completely cured one, it might be tentatively proposed that plasticity defects either extend, or nucleate, at sites three times less than when the curing treatment is more complete and the cross-linkage tighter, as can be reasonably expected.

It has not been possible to correlate the above K variation with the decrease in remaining double bonds during curing treatments, which can be directly followed in the solid by FTIR spectroscopy. Experiments done in the laboratory of Professor Monnerie at ESPCI Paris show this method is not sensitive enough in the present case. The remaining double bonds decrease from 50% to 30% in the first 2h curing; beyond, further modification of absorption spectrum cannot be resolved. ^{13}C NMR has also been used in the solid state; at 100MHz, resolution is not high enough, but at 300MHz there might be some hope of obtaining better results [22]. Therefore, for the time being, measurements of K, although being less directly related to cross-linkage than spectroscopic methods, appear to be the only way to characterize it; moreover, this test is relatively simple to apply, and gives mechanical information over a strain range of interest.

Finally, the 1-h resin appears in Table I as a singular case. At first sight, it behaves as a crumbly material and is hardly machinable as opposed to the other samples. The curing time is presumably not long enough to build up a reasonably homogeneous network of cross-link nodes and/or a well polymerized solid, which is visible in FTIR spectroscopy. Accordingly, we do not take it to be a significant state of cross-linking.

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