Influence of the degree of crosslinking on the plastic deformation behaviour of epoxy resins

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(Received 24 June 1987; revised 3 August 1987; accepted 25 September 1987)

The yielding behaviour of solid epoxy resins has been studied in the temperature range 77 K < T < 350 K as a function of the degree of crosslinking. From a metallurgical point of view, we show that, below the secondary transition temperature T_β, the deformation mechanism that governs the yielding does not depend on the degree of crosslinking. This mechanism, which mainly affects the hexamethylene groups (curing agent), can be pictured as a dislocation glide mode. Above T_β, the degree of crosslinking comes into play for yielding through its T_g effect; the flexibilities of the hexamethylene and DGEBA (diglycidyl ether of bisphenol A) groups become equivalent and the whole molecular network is involved in the plastic shear deformation.

(Keywords: yielding; epoxy resin; plastic deformation; glassy polymers)

INTRODUCTION

In previous papers[1,2], it has been shown that the non-elastic deformation of glassy polymers can be successfully described as the nucleation and propagation of mobile plasticity defects similar to dislocations in crystalline materials. This assessment relies merely on the way in which thermomechanical parameters influence the mechanical behaviour relationship. Furthermore, previous neutron experiments[3] on deformed glassy polymers have emphasized that deformation processes in the solid glassy phase are quite localized events: distortions in bonding have to be confined within cores of defects in the molecular arrangement (much like dislocation lines of the Somigliana type), the propagation of which produces a local shear strain. As shown in the following, the free activation energy of the yield mechanism is quite low (about 0.1 eV). As a consequence, the plastic deformation of materials such as solid epoxy resins occurs by uncoiling covalent links rather than breaking them, and only van der Waals interactions are involved in the propagation of dislocations. Their probably limited motion through the polymer bulk, owing to its random nature, results in more and more repeated nucleation processes leading to a more and more profuse shearing, i.e. to a flow of the solid at yield. It is noteworthy that an elementary slip step has a value close to a molecular spacing and thus results in a shear strain of 100% in the shear band[1], so that only some chain slippages are needed to reach the rather low plastic strain (5%) of the sample measured at yield.

The nucleation process should occur mainly in the early pre-yield stage of a constant-strain-rate deformation test. It has already been pointed out that the degree of crosslinking modifies the ability of glassy polymers to nucleate plasticity defects. Indeed, the plastic work-hardening rate K, which varies as the inverse of the nucleation rate[2], increases with the degree of crosslinking for both polystyrylpyridine (PSP) and polyamino-bismaleimide (PABM) thermoset resin[4,5].

In contrast, the propagation of defects, which prevails beyond the flow stress σ_y, should be insensitive to the degree of crosslinking, as far as each crosslink point can be expected to act independently from its neighbours. The yield behaviour, which depends mainly on obstacles to the propagation of defects, is thus thought to be influenced mainly by the polymer microstructure at a finer scale, i.e. by chain flexibility[1,2]. Indeed, in the particular case of PABM resin[5], it has been found that the yield stress σ_y does not vary noticeably with the degree of crosslinking (or with curing time): only about 6% from the minimum curing time (3 h at 200°C) up to the most complete one (24 h at 200°C and 24 h at 250°C). However, the yield stress σ_y of the PSP resin does depend on the degree of crosslinking[4]: at 20°C, in the most highly crosslinked state σ_y is about 33% greater than in the less-crosslinked one. This inverse trend may only be reconciled with the above one if crosslink points in this resin no longer act as independent obstacles, owing to either a smaller chain flexibility or a higher degree of crosslinking (or both) than in the PABM case. It is therefore of basic importance to have a systematic study of the influence of these two microstructural factors on the flow stress.

To this end, we have chosen to investigate model thermoset resins in which the degree of crosslinking and the chain flexibility can be modified independently at will. The present paper is the first part of a more general study devoted to determining by experiment the separate influences of these two structure parameters. It reports on a thermodynamic analysis of the yielding behaviour of two model resins, which are characterized by the same chain flexibility but differ in the degree of crosslinking*.

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* In solid epoxy resins, the microstructure on a submicrometre level has been discussed by several authors; some of them have suggested that the resin has well defined areas of different crosslink density while others are convinced that the crosslinking is homogeneous. At the present time, this point is still a subject of controversy[6,7]. In the present study, the crosslinked polymer is assumed to be homogeneous. However, we have recently performed small-angle neutron scattering experiments on solid epoxy resins; the analysis of this investigation is in progress and will be reported in a forthcoming paper.

0032-3861/88/050808-06$03.00

Our measurements describe the stress-aided thermally activated growth of plasticity defects and the overcoming of energy barriers responsible for yielding. The thermodynamic and kinetic analysis is aimed at establishing the characteristic features of the elementary mechanism, namely its energy and spatial extent. This method has already been described in detail in previous papers[8,9], so here we will mention only the main features. The aim is to obtain the plastic strain rate law:

$$\dot{\varepsilon}_p = \dot{\varepsilon}_0 \exp[-\Delta G_a(\sigma_a - \sigma_i, T)/kT] \qquad (1)$$

and more especially the Gibbs free energy of activation $\Delta G_a(\sigma_a - \sigma_i, T)$, where σ_a is the applied stress and σ_i the internal stress due to long-range elastic interactions between plasticity defects. Knowing $\Delta G_a(\sigma_a - \sigma_i, T)$, it is thus possible to identify the deformation mechanism involved at yield depending on the temperature range.

The T dependence of $\Delta G_a(\sigma_a - \sigma_i, T)$ can be determined in two different ways: First,

$$\Delta G_a = \frac{\Delta H_0(T) + (T/\mu)(\mathrm{d}\mu/\mathrm{d}T)V_0\sigma_y}{1-(T/\mu)(\mathrm{d}\mu/\mathrm{d}T)} \qquad (2)$$

where the operational apparent enthalpy $\Delta H_0(T)$ is given by:

$$\Delta H_0(T) = -V_0 T\left(\frac{\mathrm{d}\sigma_y}{\mathrm{d}T}\right)_{\dot{\varepsilon}_p,\sigma_i} \qquad (3)$$

V_0 is the operational apparent volume measured by stress relaxation at yield defined by:

$$V_0 = kT\left(\frac{\mathrm{d}\log\dot{\varepsilon}_p}{\mathrm{d}\sigma_a}\right)_{T,\sigma_i} \qquad (4)$$

The T dependence of the shear modulus μ to be entered in equation (2) has to be taken at a relevant frequency for the molecular mechanism responsible for the non-elastic behaviour[10]; this frequency is the inverse of the waiting time of the activation process. Secondly,

$$\Delta G_a(T) = \frac{\mu(T)}{\mu_0(T)}\int_{\tau(T)}^{\tau(0)} V_0(\tau)\,\mathrm{d}\tau \qquad (5)$$

$$\tau = \frac{\mu(0)}{\mu(T)}\sigma_y \qquad (6)$$

As long as the experimental quantity V_0 has the physical meaning of an activation volume V_a (defined as the stress derivative of the Gibbs free energy ΔG_a), i.e. $V_0 = V_a$, the determination of ΔG_a from (5) has to agree with the one from (2). The disagreement between the two routes indicates that the stress dependence in the pre-exponential term in (1) is not negligible[8,10].

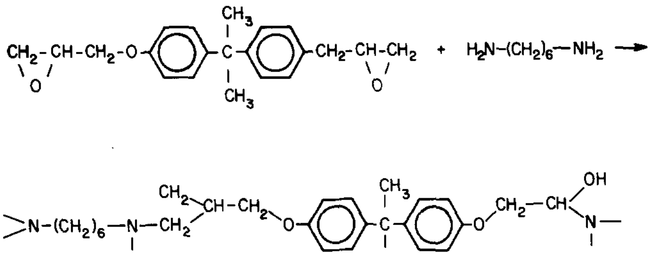
In the following section, experimental procedures and results are given. The last section is devoted to the discussion.

EXPERIMENTAL PROCEDURES AND RESULTS

Experimental details

Compression-moulded epoxy samples (diameter = 8 mm, length $L = 80$ mm) have been supplied by the Office National d'Etudes et de Recherches Aérospatiales (ONERA), France. Two kinds of solid epoxy resins have been studied:

(i) The EPO 100/0 is obtained by mixing the prepolymer diglycidyl ether of bisphenol A (DGEBA) with pure hexamethylenediamine (HMDA) as a curing agent in stoichiometric proportions. The reaction mechanism is as follows:



(ii) The EPO 40/60 is based on the same DGEBA prepolymer; the curing agent is now a mixture of 60% hexamethyleneamine (HA) with 40% HMDA (the amounts of HA and HMDA are given relative to the total number of amine functional groups). The stoichiometry of the system DGEBA/curing agent is equal to 1.

For both EPO 100/0 and EPO 40/60 resins the curing treatment is as follows: 20 h at 293 K plus 2 h at 393 K ($T = 393$ K is quite a bit higher than the T_g values of both systems). No evidence of incomplete cure has been observed by differential scanning calorimetry.

The schematic networks of both systems are shown in *Figure 1*. Both these networks are characterized by the same chain flexibility, but differ in the number of crosslink points. The EPO 100/0 is a very highly crosslinked system; in the case of the EPO 40/60 the number of crosslink points is decreased by about 60%. As a consequence, the characteristic relaxation temperatures are as shown in *Table 1*. Temperatures T_g have been obtained by a d.s.c. technique at ONERA[11] and T_β have been measured using a Metravib viscoelastometer in our laboratory.

Solid epoxy resins have been machine turned into cylindrical specimens (diameter = 4 mm, length

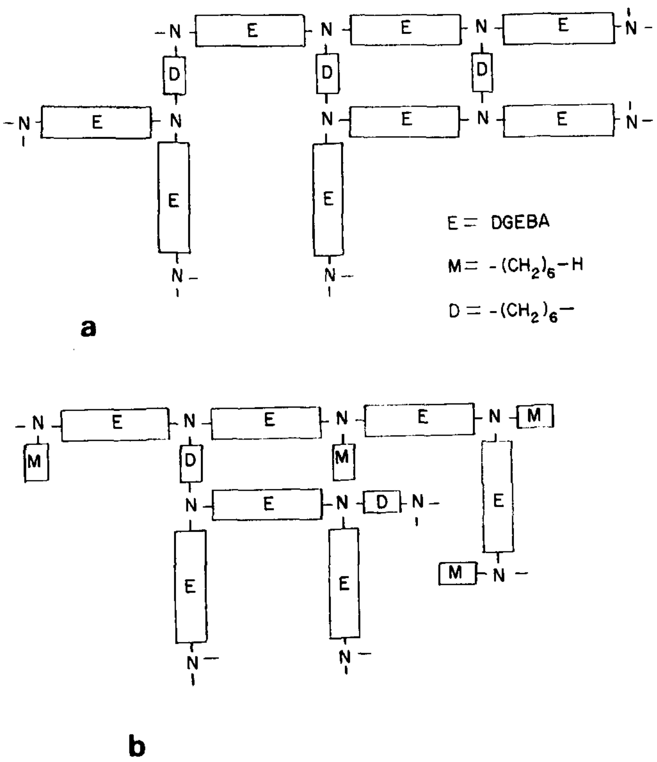


Figure 1 Schematic diagrams of (a) EPO 100/0 network and (b) EPO 40/60 network

Table 1 Characteristic relaxation temperatures of the two solid epoxy resins

	EPO 100/0	EPO 40/60
T_g (K)	380	335
T_β (K) at 1 kHz	245	220

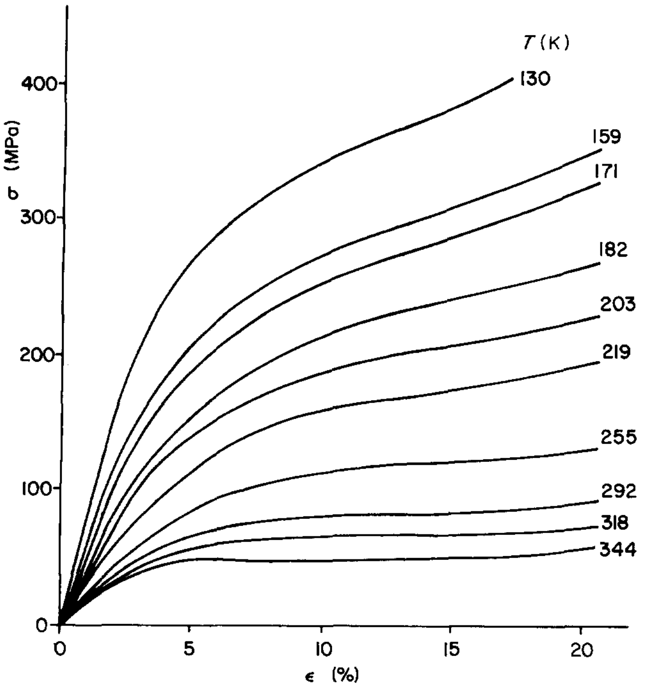


Figure 2 Stress–strain curves for EPO 100/0

$L = 7.3$ mm). Compression tests have been performed on an Instron machine at a constant applied strain rate $\dot{\varepsilon}_T = 4.5 \times 10^{-5}\,\mathrm{s}^{-1}$. In the low-temperature range (77–293 K), a sufficiently compact deformation system (rigidity $M = 3700$ MPa) has been used so that it can be immersed in a liquid-nitrogen cryostat; the temperature of the sample was measured with an accuracy of ± 0.5 K. In the 293–473 K temperature range, another deformation system ($M = 8300$ MPa), well suited to high temperatures, has been used; it was inserted in an oven with PID regulation so as to yield a thermal stability of ± 0.1 K. Both these deformation apparatuses have been designed in order to ensure a perfectly guided compressive load.

Results

The experimental stress–strain curves $\sigma(\varepsilon)$ are shown in *Figures 2* and *3*. In the case of EPO 100/0, the $\sigma(\varepsilon)$ curves exhibit a stress plateau for temperatures higher than 230 K; below 230 K, a bending point appears on the $\sigma(\varepsilon)$ in place of the stress plateau. For EPO 40/60, the stress–strain curves show a plateau whatever the temperature. It is apparent that all the isothermal $\sigma(\varepsilon)$ curves do not exhibit an identical elastic–plastic transition. It was thus necessary to find an acceptable definition of the compressive yield stress σ_y, valid for each particular behaviour. As a consequence, the σ_y value has been derived as follows. When the experimental apparent volume V_0 is followed vs. ε all along the $\sigma(\varepsilon)$ curve by successive standard stress relaxations, it is observed that it falls rather sharply to a weakly sloping straight line (*Figure 4*) characteristic of the pseudo-plastic flow regime[8,12]. This sharp-cup behaviour is conveniently used as an experimental definition of the yielding state, thus locating 'corresponding' microstructural states at any temperature[13]. In summary, depending on the $\sigma(\varepsilon)$ curve shape, the yield stress σ_y coincides either with the stress plateau or with the stress value corresponding to the bending point. The experimental determination of the bending point is performed directly from the $F(t)$ load chart because the bending of the $F(t)$ curve is much more pronounced than that of the stress–strain curve; so, σ_y is defined in a unique way.

Figures 5 and *6* show the experimental variation of the yield stress σ_y and the apparent volume V_0 with temperature. It is of interest to note that the apparent volume V_0 measured at low temperatures is identical for both epoxy resins and stays rather constant at a low value (120–160 Å^3). In the particular case of EPO 100/0, a cusp is observed at 220 K.

For the sake of simplicity, only Gibbs free energy values ΔG_a as deduced from equation (2) are reported here. It has been checked that the ΔG_a values obtained from equations (2) and (5) are in agreement, proving that the pre-exponential term in the strain-rate law (equation (1)) is stress-independent. Hence, the measured apparent volume V_0 is actually a true activation volume (i.e. a stress derivative of the free energy of activation) and represents the volume in which correlated motions of monomers occur[8].

The T dependence of the apparent enthalpy ΔH_0, given by equation (3), is shown in *Figure 7*. The difference observed between the behaviours of the EPO 100/0 and EPO 40/60 resins, i.e. the enthalpy plateau at 0.75 eV from 220 to 270 K for EPO 40/60 resin, is consistent with

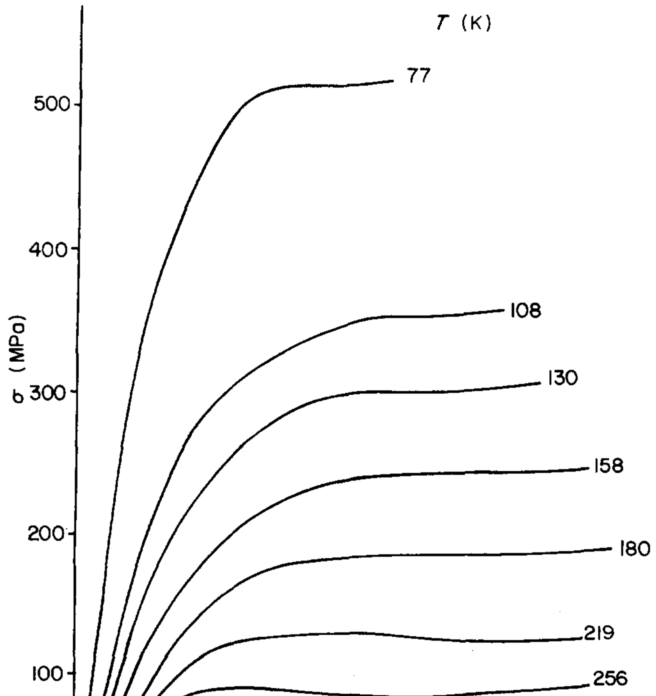


Figure 3 Stress–strain curves for EPO 40/60

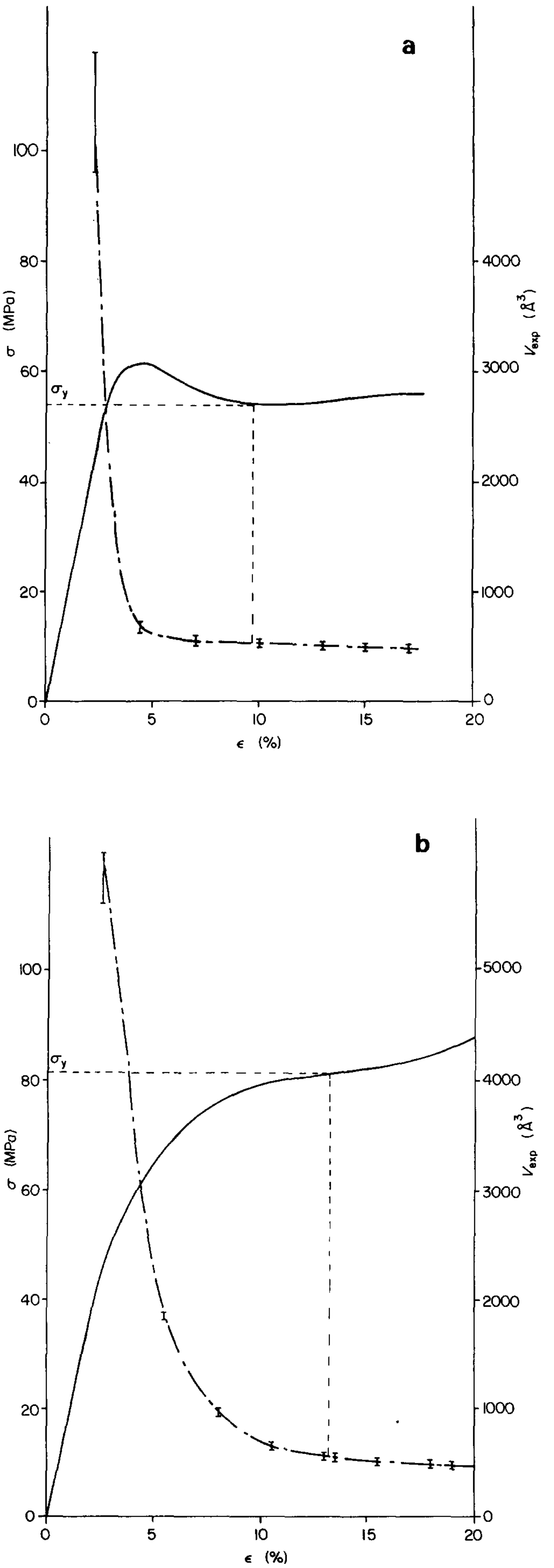


Figure 4 Definition of the yield stress σ_y: (a) EPO 100/0 network; (b) EPO 40/60 network ($T = 20°C$ for both)

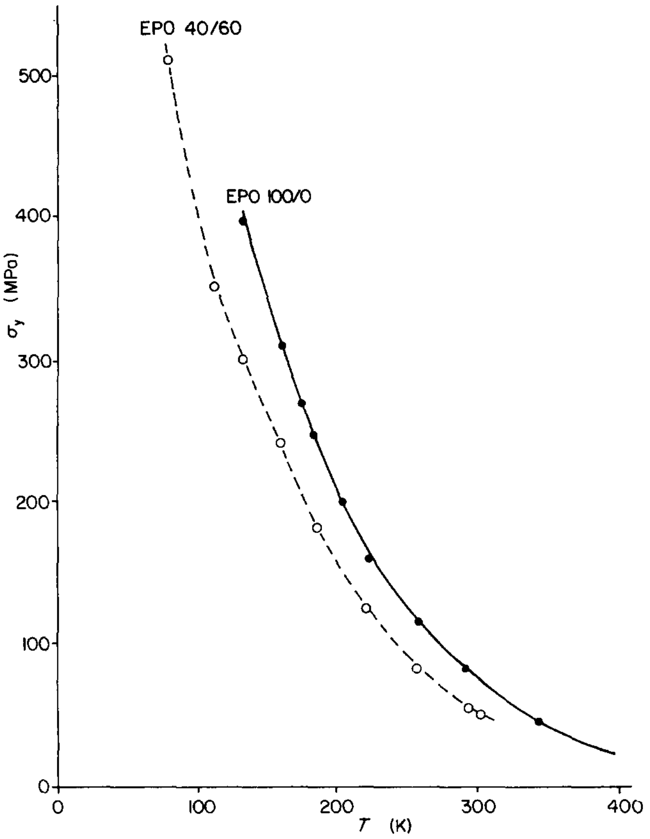


Figure 5 The temperature dependence of the yield stress σ_y

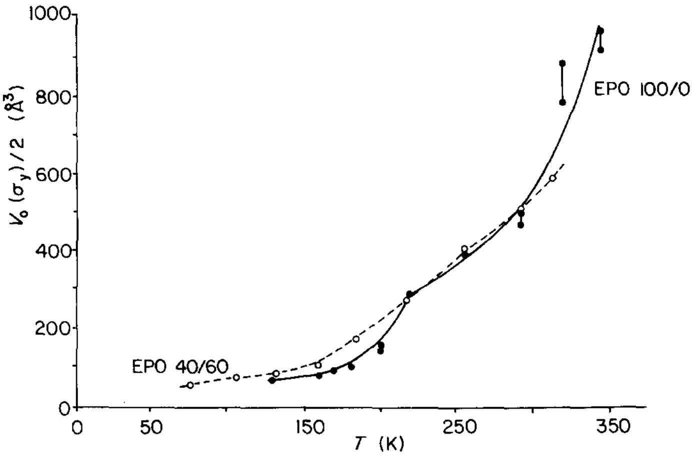


Figure 6 The temperature dependence of the apparent volume $V_0/2$ measured at yield

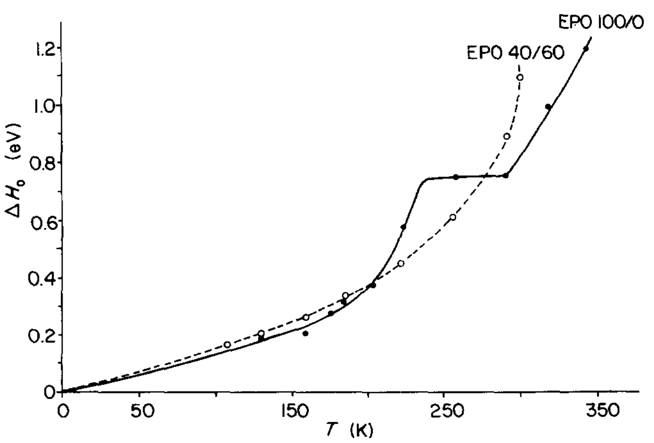


Figure 7 The experimental apparent enthalpy ΔH_0 *versus* temperature

the cusp noted above in the $V_0(T)$ values, as has been previously shown in metal plasticity[14].

The Gibbs free energy ΔG_a *versus* temperature is represented in *Figure 8*, from values of the shear modulus $\mu(T)$ measured at 1 kHz on a Metravib viscoelastometer. Up to 220 K, the ΔG_a values of both epoxy resins coincide: experimental points of ΔG_a *versus* T can be lined up with the origin, as they should. Above 220 K, the behaviour of both epoxides differs: in the case of EPO 100/0 a plateau ($\Delta G_a = 0.08$ eV) is observed from 220 to 270 K, which corresponds to the enthalpy plateau (*Figure 7*). Above 270 K, ΔG_a is again linear with temperature. For EPO 40/60, there is no plateau; ΔG_a still varies linearly with temperature above 220 K but the slope of the straight line is rather steeper than below 220 K.

DISCUSSION

It is clear that up to 220 K, i.e. below activation of β molecular motions, the deformation mechanism that governs the yielding of epoxy resins does not depend on the degree of crosslinking. The linear dependence of ΔG_a *versus* T suggests that this mechanism is analogous to the low-temperature dislocation glide in crystals[8]. It is characterized by two main features:

(a) low Gibbs free energy of activation ΔG_a (<0.08 eV), and

(b) low apparent volume V_0 (120–160 Å^3) at lower temperatures.

In terms of plasticity defects (dislocations) the low-temperature volume V_0 is equal to the volume V_c of the critical shear nuclei. As a consequence, it can be deduced that plastic events are strongly localized. Moreover, the value obtained for V_c suggests that they affect mainly the hexamethylene groups, which are more flexible than the stiff DGEBA groups in the low-temperature range. The higher flexibility of these groups has already been pointed out in several studies[15,16]. Knowing that the volume occupied by one hexamethylene group is about 150 Å^3, the volume V_c represents 5–6 carbon bonds, so it suggests that the shearing of hexamethylene groups is made by *cis–trans* movements in the carbon chains[17].

Indeed, it is quite paradoxical that crosslinked amorphous polymers can undergo a 'low-temperature dislocation glide' mechanism, i.e. undergo a plastic shear strain without breaking covalent links. However, as has been pointed out in the 'Introduction', the low value of the apparent volume V_0 and the low value of the free energy of activation prove that plastic shearing is quite localized and that dislocation glide does not involve the rupture of molecular chains. Moreover, the stress–strain curves shown in *Figures 2* and *3* confirm this behaviour; it is noteworthy, beyond yielding, that the more crosslinked is the epoxy network, the stronger is the plastic work-hardening rate.

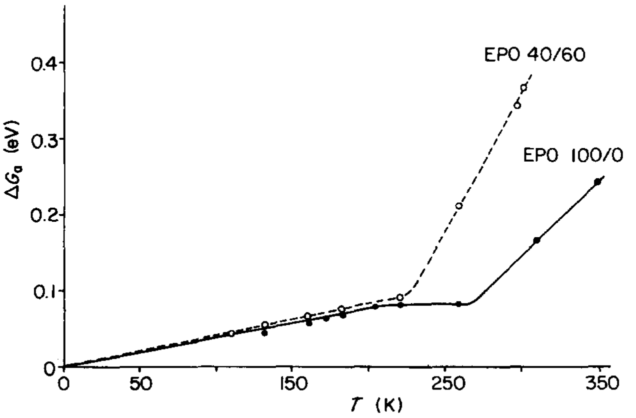


Figure 8 The Gibbs free energy of activation ΔG_a *versus* temperature

The relevant frequency ν_{def} for the molecular mechanism responsible for the non-elastic behaviour can be deduced from the T slope of the curve $\Delta G_a = \alpha kT$. Indeed, it has been shown[8] that the frequency ν_{def} is given by:

$$\nu_{def} = \nu_N \exp(-\alpha) \qquad (7)$$

where $\nu_N = \nu_D/10$ (ν_D is the Debye frequency). With the present data, $\alpha \simeq 5$, so that equation (7) yields $\nu_{def} = 10^{10}$ Hz (with $\nu_N = 10^{12}$ Hz). It should be noted that the Gibbs free energy ΔG_a has been determined here using elastic shear modulus measurements at only 1 kHz. A consistent analysis would have involved measuring $\mu(T)$ in the 10^{10} Hz range[10]. The lack of experimental methods available in our laboratory in the range 10^3 to 10^{10} Hz has made it impossible to measure $\mu(T)$ at the right activation frequency ν_{def}. However, it has been shown that the choice of frequency does not noticeably influence the qualitative shape of the $\Delta G_a(T)$ curve[10], except for α, which would probably be higher, thus inducing a lower characteristic frequency ν_{def} and a slightly higher plateau value of ΔG_a.

Above 220 K, the degree of crosslinking comes into play for yielding. In the case of EPO 40/60, the lack of a plateau might be related just to the difference in the T_g values ($\simeq 50$ K). For, while a second deformation mechanism starts to operate in this epoxy as soon as T reaches 220 K (the T_β value at 1 kHz), it is worth noting that for EPO 100/0 the temperature has to be as high as 270 K for this new mechanism to start, a value that can be deduced from 220 K by a shift just equal to that in the T_g values (and which does not follow from T_β, here 245 K). Therefore, it is apparent that the degree of crosslinking intervenes here through its T_g effect. Previous studies[18–20] have shown that, above the secondary transition β, the flexibilities of the hydroxy ether and diphenylpropane groups become equivalent to the flexibility of the hexamethylene group, so that the whole molecular network is now involved in the plastic deformation.

A similar variation of the Gibbs free energy of activation ΔG_a *versus* temperature has already been observed in the case of pure aluminium by Dorn *et al.*[21]. They showed that the $\Delta G_a(T)$ curves can be related to the resolved yield stress $\sigma_y/\mu(T)$ curves. In this particular case, they concluded the existence of two deformation mechanisms acting in parallel according to the temperature. The intermediate plateau of the $\sigma_y/\mu(T)$ curves, which corresponds to the energy plateau $\Delta G_a(T)$, yields the value of the internal stress σ_i built up in the material by the first (i.e. lower-temperature) deformation process[21,22].

Following the same lines for the case of EPO 100/0, it can be seen in *Figure 9* that the $\sigma_y/\mu(T)$ curve also exhibits a plateau from 220 to 270 K, which corresponds to the activation energy plateau at $\Delta G_a \simeq 0.1$ eV. This means that no extra thermal activation is then required for the low-temperature deformation mode. Here, *Figure 9* yields the internal stress value $\sigma_i \simeq \mu/100 = 100$ MPa, and the corresponding athermal temperature $T_a(\sigma_i) = 270$ K.

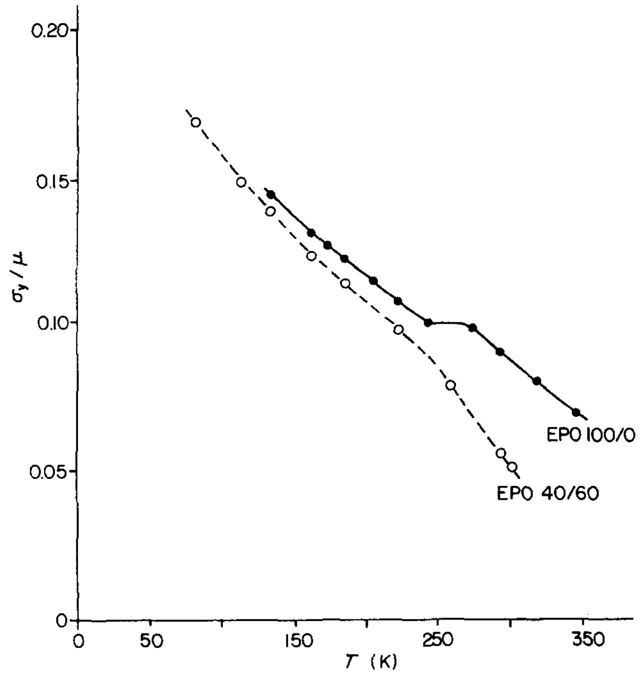


Figure 9 The resolved yield stress σ_y/μ *versus* temperature

This high value of σ_i suggests the existence of severe mismatch sticking of the DGEBA groups, resulting from the shearing through hexamethylene groups[1]. Above T_β, the second deformation mode might reflect merely the relaxation of these mismatch stickings made possible because of the higher mobilities gained by the DGEBA groups.

The existence of two distinct mechanisms responsible for yielding of the epoxy resins EPO 100/0 and EPO 40/60 depending on the temperature range is in agreement with previous data published in the literature[15–20]. However, there are some apparent discrepancies concerning the transition temperatures and the corresponding values of the energy of activation. Torsion pendulum measurements performed at frequencies of 0.1 and 1 Hz reveal the existence of three transition temperatures: $T_\gamma = 150$ K[15,16], due to the local mobilities of the carbon atoms, with an energy of activation of about 0.5 eV; $T_\beta = 215$ K, assigned to the movements of the hydroxy ether and diphenylpropane groups[18,20], with an energy of activation of about 1 eV; and $T_g = 375$ K.

For plastic deformation, the local molecular mobilities to be considered are the β movements[10]. Our measurements on EPO 100/0 at 1 kHz ($T_\beta = 245$ K) compare well with the value $T_\beta = 215$ K, which was taken at 1 Hz. As in polystyrene (PS) or poly(methyl methacrylate) (PMMA), these β movements seem to characterize the plateau in activation energy $\Delta G_a(T)$ ascribed to shearing through the hexamethylene groups (T (plateau) between 220 and 270 K).

On the other hand, the energy of activation reported for the β transition (1 eV) is clearly higher than the value of the Gibbs free energy given by the plateau of $\Delta G_a(T) \simeq 0.1$ eV. This discrepancy can be accounted for by noting two points. First, dynamic measurements provide only an enthalpy of activation ΔH, while thermodynamic analysis of plastic behaviour yields a Gibbs free energy, which as we have seen is much smaller. Secondly, as noticed by Read[23], β relaxation is generally complex and results from the convolution of several elementary peaks, which have their own enthalpy of activation. It has been shown, in the case of PS and PMMA[10], that the enthalpy of activation ΔH_0 measured from compression tests compares well with the lower-temperature component only of the secondary relaxation peak. Unfortunately, at the present time, there are no data available in the literature concerning the detailed convolution of secondary relaxation peaks in solid epoxy resins. Though it is not possible to make quantitative conclusions on our activation energy, we can state however that the value obtained from compression tests is not inconsistent with the value given by dynamic measurements.

Further experiments are in progress in order to study the influence of other parameters, such as chain flexibility, on plastic flow. To this end, we mean to investigate other model epoxy resins with different flexibilities: either, for a given epoxy prepolymer, by using aliphatic/aromatic curing agents, or for a given curing agent, by using DGEBA or DGEBU (diglycidylether butane diol) epoxy prepolymers.

ACKNOWLEDGEMENTS

The authors wish to thank ONERA for providing the epoxy resin and acknowledge financial support from the DRET under Contract No. 84/168.

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