The constant stress behaviour of polystyrene–low density polyethylene blends

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The constant-stress behaviour of low-density polyethylene toughened polystyrene has been analysed. It was found that the initial strain–time behaviour during constant-stress tensile tests is well described by a simple model that predicts a proportionality between strain and the square of time, provided a correction for craze formation during the application of stress is made. By analysing strain–time curves at different stresses it has been determined that the product of the rates of craze initiation and of craze growth is exponentially dependent on stress. The attainment of a constant strain rate during constant-stress experiments and the attainment of a constant-stress level during constant strain–rate experiments result from a strong decrease in the rate of craze initiation. This effect allowed the determination of the stress and temperature dependences of the rate of craze growth. This rate was found to be well described by the Eyring equation, which is in agreement with earlier results obtained from constant stress- and strain-rate experiments.

1. Introduction

In a previous paper [1] a model has been presented to describe the stress–strain behaviour of toughened polymers such as low-density polyethylene toughened polystyrene (TPS). It was found that the volume-fraction, v, of polystyrene (PS) that has been converted into craze material can be expressed in terms of stress, σ, and strain, ϵ, of a homogeneously deforming tensile specimen such that

$$v = \frac{\epsilon - \sigma/E_{TPS}}{f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})}, \qquad (1)$$

where f^{-1} is the volume-fraction PS within a craze and E_{cr} and E_{TPS} are the tensile moduli of crazes and TPS, respectively. Furthermore, v, can be expressed in terms of rates of craze initiation (k_i, the rate of craze area formation normal to the stress direction per unit volume TPS) and craze growth (k_g, the rate of craze thickening, which corresponds to craze growth in the stress direction):

$$v = \frac{1}{f} \int_0^t k_i(\tau) \int_\tau^t k_g(\zeta)\, d\zeta\, d\tau, \qquad (2)$$

where τ is a time in the interval between times 0 and t at which a craze is initiated, and ζ a time in the interval between times τ and t in which such a craze is growing.

Experimental results indicate [2] that the stress and temperature dependences of k_i and k_g are well described by the Eyring activated flow equation:

$$k_{i,g} = A_{i,g} \exp\left(\frac{-\Delta H^*_{i,g}}{kT}\right) \exp\left(\frac{\gamma_{i,g}\sigma V^*_{i,g}}{4kT}\right), \qquad (3)$$

where k is the Boltzmann constant, T is the absolute temperature and $\Delta H^*_{i,g}$, $\gamma_{i,g}$ and $V^*_{i,g}$ are the activation energy, stress concentration factor and activation volume of the transition states i or g, and σ is the applied stress.

In a simplified form,

$$k_i = a \exp(b\sigma) \qquad (4)$$

and

$$k_g = c \exp(d\sigma), \qquad (5)$$

where $a = A_i \exp[-\Delta H^*_i/RT]$, $c = A_g \exp[-\Delta H^*_g/RT]$, and $b = \gamma_i V^*_i$ and $d = \gamma_g V^*_g$.

The combination of Equations 1, 2 and 4 results in a general stress–strain equation that has been experimentally verified for constant strain-rate and constant stress-rate tensile tests [2].

It can be shown that for constant-stress experiments, the model predicts the following relation between strain, ϵ, and time, t:

$$\epsilon = \frac{f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})}{2f}$$

$$\times ac\{\exp(b + d)\sigma\}t^2 + \frac{\sigma}{E_{TPS}}. \quad (6)$$

As the constants, f, E_{cr} and E_{TPS} are known [1], stress–strain curves obtained from constant-stress experiments can be analysed to verify Equation 6 and to determine values for the craze parameters ac and $b + d$.

2. Experimental procedure

The tensile tests were performed on blends of polystyrene (PS, Styron 634, from Dow Chemical Co., USA) and low-density polyethylene (ldPE, Stamylan 1500 from DSM, The Netherlands). Blending was carried out on a Schwabenthan laboratory mill. Tensile specimens (ASTM D 638 III) were machined from compression-moulded sheets. The blend composition was 85 wt %/15 wt % PS/ldPE. Blends of this composition deform only by crazing [3, 4]. Constant-stress experiments were performed on an Instron machine using dead loads. The stress range was 13 to 23 MPa and the test temperature was 22° C. The cross-head of the Instron machine served as a plateau for the dead load attached to the tensile specimen. The creep experiments were started by lowering this cross-head at a speed corresponding to an elongation rate of 100% min^{-1}, thus assuring identical load application for all experiments. Strain was monitored using a linear voltage displacement transducer (LVDT). Constant strain-rate experiments were performed on a thermostatically temperature controlled Instron tensile tester equipped with a LVDT to monitor strain.

3. Constant stress behaviour
3.1. General features of the creep curves

A typical strain–time curve obtained from a constant-stress experiment is shown schematically in Fig. 1. In Fig. 1 the fluctuations indicated at B, which are sometimes observed immediately after
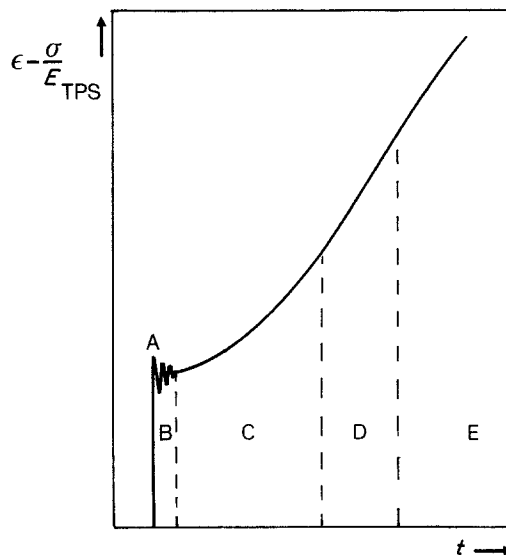

Figure 1 Schematic strain–time curve from a constant stress tensile test.

the application of stress indicated at A, are due to a swinging movement of the dead load and have no significant effect on the further course of the curve. It was found in all cases that the beginning of the strain–time curve had a positive slope. The first part of the strain–time curve (C in Fig. 1) is concave and is followed by the second, linear, part of the curve (D in Fig. 1). The curve eventually becomes convex (E in Fig. 1) until failure of the tensile sample takes place. This behaviour can be interpreted as follows.

The positive initial slope of the strain–time curve of the constant-stress experiment indicates that, during the application of the stress, crazes have been initiated causing a positive strain rate due to craze growth immediately after the stress has reached its ultimate value. The concave shape of the curve (at C) is due to the combination of craze initiation and craze growth. This can be compared with yielding in a constant strain-rate experiment. The linear and the convex part of the curve (in D and E) indicate that at higher elongation craze termination mechanisms have become more predominant [5]. The process in the linear part (in D) of the strain–time curve may correspond with the attainment of a constant stress level after yielding during a constant strain-rate experiment. Likewise, the convex part (in E), strain hardening, may correspond with the increase of stress that is sometimes observed at high strains during constant strain-rate experiments.

3.2. The concave part of the creep curves

As only the concave parts (in C) of the strain—time curves fulfill all the conditions of the model, the analysis of the curves to determine the craze parameters ac and $b + d$ is limited to these parts. However, Equation 6 must be corrected for two effects, being

(a) the occurrence of craze initiation during the application of stress; and

(b) the possible occurrence of craze growth during stress application and errors in absolute strain due to inaccuracies that arise immediately after stress application.

With regard to Correction a, if the craze area normal to the stress-direction per unit volume TPS formed during the application of stress is taken to be A_0, then the contribution of these crazes to the strain equals

$$\frac{f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})}{f} A_0 c \exp\left[(d\sigma)\right] t. \tag{7}$$

With regard to Correction b, an error in strain due to craze growth during stress application or due to inaccuracies can be corrected by allowing a constant ϵ_e in Equation 6 where ϵ_e is the sum of the elastic strain belonging to a stress σ plus a possible error in the measured strain.

Thus, Equation 6 is transformed into

$$\epsilon = Pt^2 + Qt + R, \tag{8}$$

where

$$P = \frac{f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})}{2f}$$

$$\times ac \exp\left[(b + d)\sigma\right], \tag{9}$$

$$Q = \frac{f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})}{f}$$

$$\times A_0 c \exp(d\sigma) \tag{10}$$

and

$$R = \sigma/E_{TPS} + \epsilon_e. \tag{11}$$

By applying Equation 8 it is possible to determine $ac \exp\left[(b + d)\sigma\right]$ from a least-squares curve fitting procedure on the points of the concave part of the strain—time curve. The stress dependence of the values for $ac \exp\{(b + d)\sigma\}$ thus obtained can be used to calculate ac and $(b + d)$.

3.3. The linear part of the strain—time curves, craze termination

The attainment of a constant strain-rate during constant-stress tensile tests indicates some craze termination mechanism. This mechanism causes a stop in the rate of craze initiation, which would imply the existence of a maximum craze area, A_{max}, normal to the stress direction (per unit volume TPS), or it causes a decrease in the rate of craze growth in the stress direction or it causes a combination of these two possibilities.

If the stress is increased in steps while the strain—time curve during a constant-stress test is linear, then the slope of the strain—time curve will increase (see Fig. 2). As the slope is given by

$$\dot{\epsilon}_t = \frac{f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})}{f}$$

$$\times \left(\int_0^t k_i(\tau)\, d\tau + A_0\right) k_g, \tag{12}$$

this can be interpreted as a consequence of an increase of the (stress-dependent) rate of craze growth, k_g, or as a consequence of an increase of the craze area normal to the stress-direction, $\int_0^t k_i(\tau)\, d\tau$, or as a consequence of a combination of both effects. However, upon the reduction of the stress to its original level the slope regains its original value, indicating that the value of $\int_0^t k_i(\tau)\, d\tau$ has not changed. Apparently $\int_0^t k_i(\tau)\, d\tau$ has practically reached a maximum value A_{max}, while the stress dependence of A_{max} must be small. This can be explained by mutual interference of the crazes. Craze growth normal to the stress direction is strongly suppressed by the presence of another craze nearby in the stress direction [6], or, more generally, craze growth normal to the stress direction is a decreasing function of the total craze-area normal to the stress direction [7]. However, another explanation will be offered in a subsequent paper [8].

If the rate of craze initiation is zero then the slope, $\dot{\epsilon}$, of the strain—time curve is constant, and equals

$$\dot{\epsilon} = \frac{f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})}{f}$$

$$\times A_{max} c \exp(d\sigma). \tag{13}$$

As A_{max} is not stress dependent, Equation 13 predicts a linear relationship between $\ln\{\dot{\epsilon}/[(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})]\}$ and σ, and thus allows the determination of the craze parameter, d. The transition from linearity to a convex curvature of a strain—time curve can now be ascribed to a decrease in the rate of craze growth.
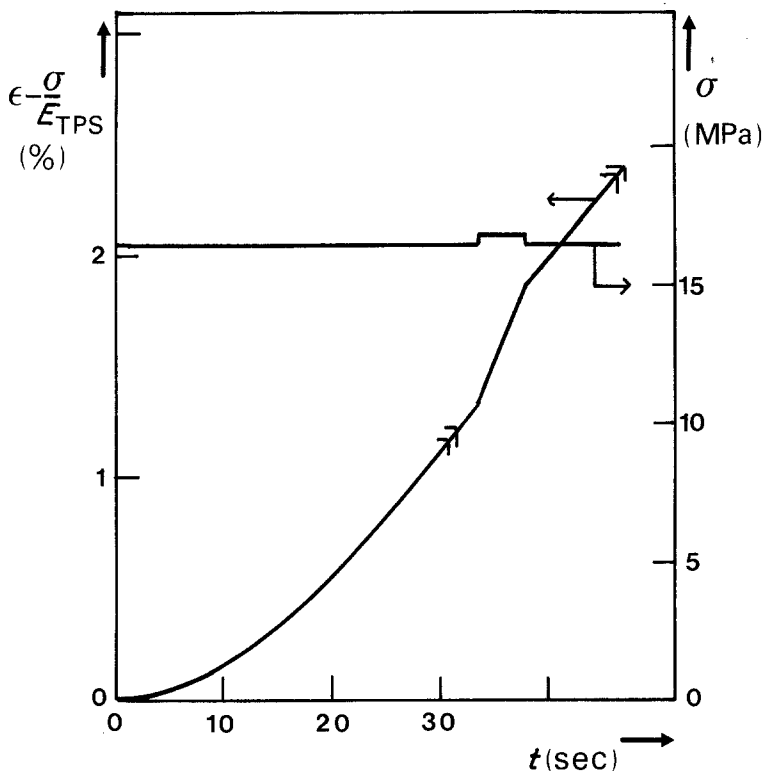
Figure 2 Response of the strain to a stepped increase and decrease of the stress at a time when the strain rate has reached a constant value (constant-stress experiment).

4. Results from constant-stress experiments
4.1. Results from the analysis of the concave part of the strain—time curves

The quadratic curve-fitting procedure through the points on the concave part of the strain—time curve gave, in all cases, a good fit. Some examples are shown in Fig. 3. The coefficients P from Equation 8 were multiplied by a factor $2f/[f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})]$ in order to obtain the product $k_i k_g$. A plot of $\ln k_i k_g$ against stress
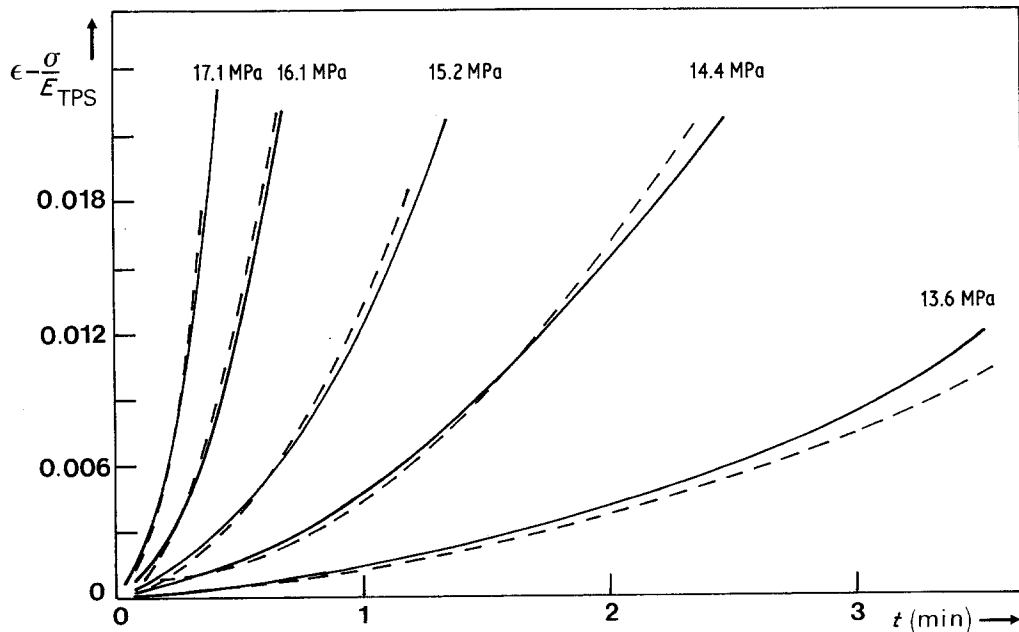

Figure 3 Experimental strain—time curves (full curves) and theoretical strain—time curves (broken curves) of five constant-stress experiments. The constant stress for each curve is indicated.
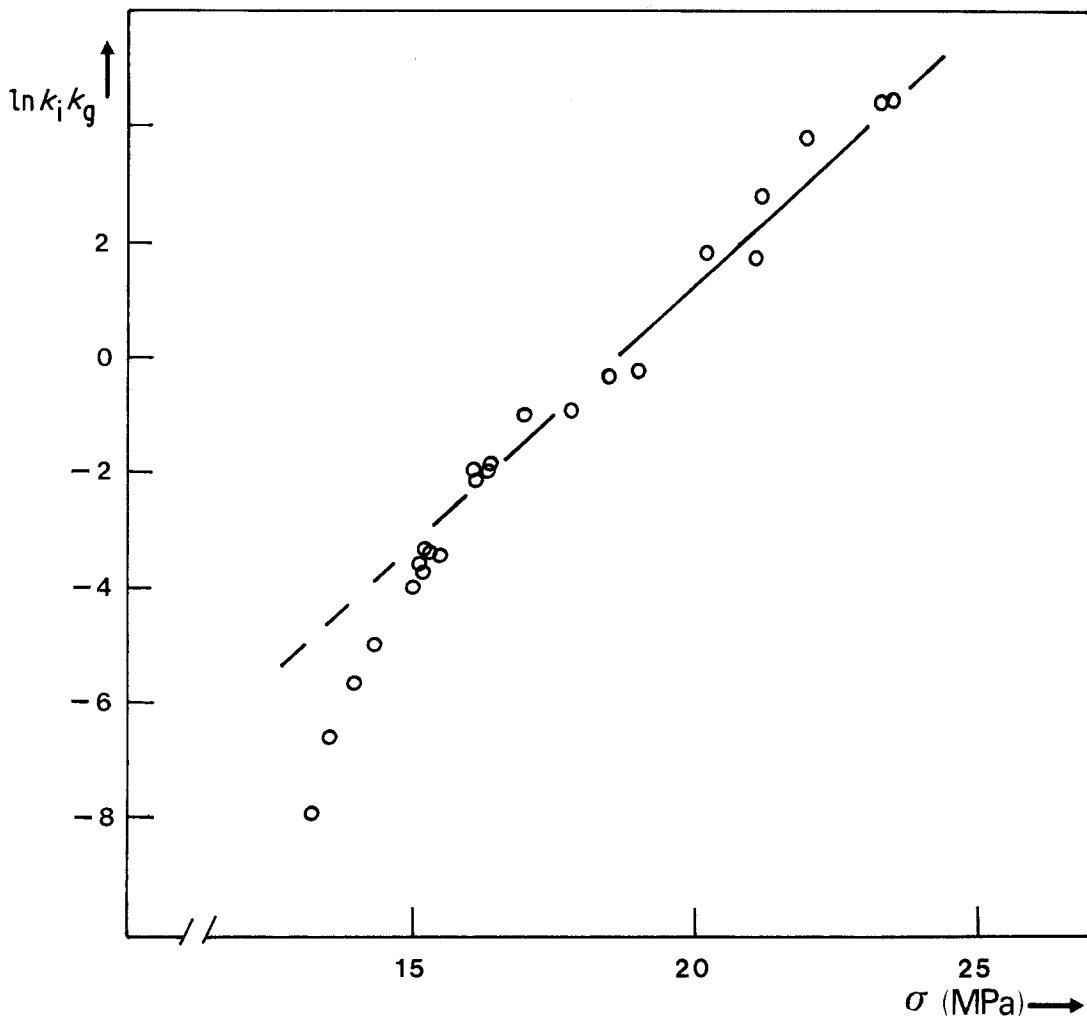
Figure 4 Dependence of ln $k_i k_g$ on stress, as determined from constant-stress experiments.

(given in Fig. 4) is linear at stresses higher than 15 MPa. Below 15 MPa a drop in the ln $k_i k_g$ values takes place. This drop was also found from constant strain-rate experiments [2] and was ascribed to the existence of a critical stress, below which either no crazes or few crazes are initiated.

From the slope of the linear part of the plot of ln $k_i k_g$ against stress the sum $(b + d)$ can be calculated while extrapolation to zero stress gives ln ac. For $b + d$ and ln ac values of respectively $0.85 \pm 0.04 \, \text{MPa}^{-1}$ and -16.0 ± 0.8 (ac in min^{-2}) were obtained. These values are to be compared with values for $b + d$ and ln ac obtained from constant strain-rate experiments [2]: $b + d = 0.70 \pm 0.02 \, \text{MPa}^{-1}$, ln $ac = -14.3 \pm 0.4$.

4.2. Results from the analysis of the linear part of the strain–time curves

A plot of ln $\{\dot{\varepsilon}/[f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})]\}$

against σ is given in Fig. 5. Indeed, a linear relationship is found, in agreement with Equation 13. This allows the determination of the craze parameter, d. From the slope a value of $d = 0.74 \, \text{MPa}^{-1}$ is obtained. In earlier research [2] a value of the craze parameter of $d = 0.55$, was determined from constant strain-rate and constant stress-rate experiments.

4.3. Results from the analysis of the constant stress part of constant strain-rate curves

Equation 13 may also be valid for constant strain-rate experiments as, during these experiments, a constant stress level is attained after yielding. A stepped increase of the strain-rate followed by a stepped decrease to the original strain-rate, which causes a temporary increase of stress, does not affect the original (constant) stress level (Fig. 6).
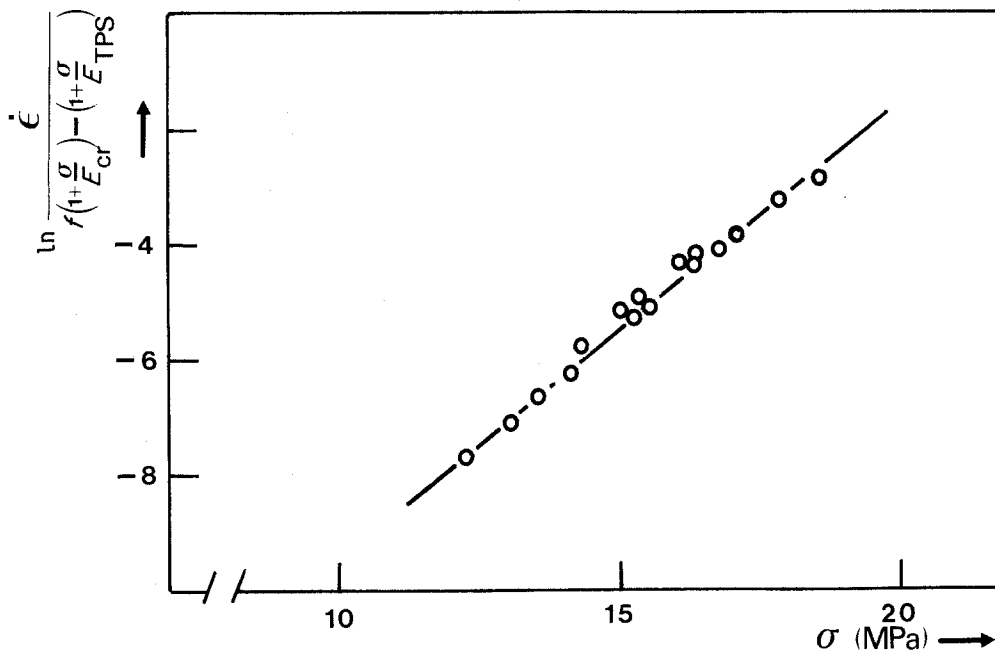
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Figure 5 Dependence of $\ln\{\dot{\epsilon}/[f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})]\}$ on stress if $\dot{\epsilon}$ is constant, as determined from constant-stress experiments.

This again indicates a stop in craze initiation. Plots of $\ln\{\dot{\epsilon}/[f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})]\}$ against stress at several temperatures are given in Fig. 7. At lower temperatures these plots are linear and have equal slopes. From these slopes the craze parameter, d, was calculated to be $d = 0.52\,\text{MPa}^{-1}$. This value compares well with the value $d = 0.55\,\text{MPa}^{-1}$ as obtained from constant stress-rate experiments [2]. At higher temperatures a pronounced downward curvature as the stress decreases is again observed. Due to the existence of a lower critical craze initiation stress, the maximum value of craze area, A_{max}, is not reached under these conditions, which prohibits the separate determination of the rate of craze growth.
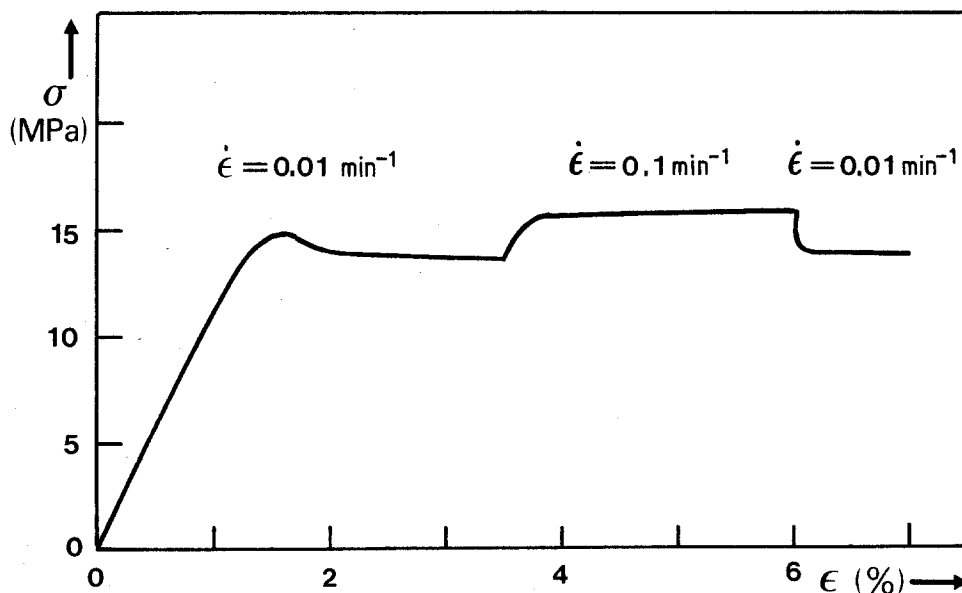

Figure 6 Stress response to a stepped increase and decrease in the strain-rate at an elongation where the stress has become constant (constant strain-rate experiment).
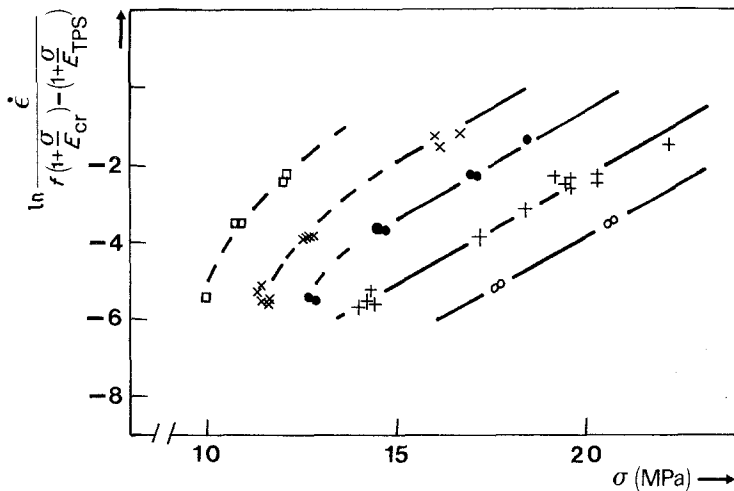
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Figure 7 The stress and temperature dependence of $\ln \{\dot{\epsilon}/[f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})]\}$ if the stress is constant, as determined from constant strain-rate experiments. Temperatures: $\circ$, $10°$ C; $+$, $18°$ C; $\bullet$, $30°$ C; x, $40°$ C; $\square$, $50°$ C.

4.4. Applications of the Eyring activated flow equation

By applying the Eyring activated flow equation, Equation 3, which was found to describe the stress and temperature dependence of the product $k_i k_g$ [2], the terms b and d can be regarded as a measure of the apparent activation volume of, respectively, craze initiation and craze growth. The sum of the apparent activation volumes of craze initiation and craze growth, $\gamma_i V_i^* + \gamma_g V_g^*$, was calculated to be $14 \, nm^3$ from constant-stress experiments, while the apparent activation volume $\gamma_g V_g^*$ at $22°$ C for craze growth was $12 \, nm^3$. From the constant-stress part of constant-strain rate curves, $\gamma_g V_g^*$ was calculated to be $8.5 \, nm^3$. The combined results from constant strain-rate and constant stress-rate experiments indicated $\gamma_g V_g^* = 9 \, nm^3$ [2]. The apparent activation volume of craze initiation then is calculated to be variously $2 \, nm^3$ (from the linear part of strain–time curves obtained during a constant stress experiment), $3.5 \, nm^3$ (from the linear part of stress–strain curves from constant strain-rate experiments) and $2.5 \, nm^3$ (from the combined results of constant strain-rate and constant stress-

rate experiments [2]). These results are summarized in Table I.

The term $\ln (A_{max} c/f)$ can be determined by extrapolation to zero stress of the linear plots of $\ln \{\dot{\epsilon}/[f(1 + \sigma/E_{cr}) - (1 + \sigma/E_{TPS})]\}$ against the stress. As c equals $A_g \exp (- \Delta H^*/kT)$ (from Equation 3) a linear relationship between $\ln (A_{max} c/f)$ and the reciprocal temperature is predicted. This linear relationship indeed exists (see Fig. 8) allowing the determination of the activation enthalpy of the rate of craze growth,

TABLE I Summary of the data obtained from the apparent activation volumes of craze initiation and craze growth

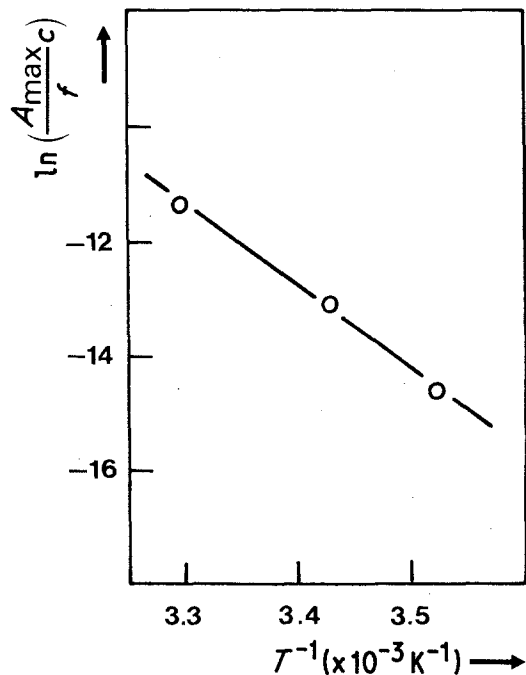| Experiment	$\gamma_i V_i^*$ (nm^3)	$\gamma_g V_g^*$ (nm^3)	$\gamma_i V_i + \gamma_g V_g^*$ (nm^3)
From constant-stress curves	2	12	14
From constant strain-rate curves	3.5	8.5	11 [2]
From constant strain-rate and constant stress-rate curves [2]	2.5	9	11

Figure 8 Dependence of $\ln (A_{max} c/f)$ on the reciprocal temperature.

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ΔH_g^*. This activation enthalpy was calculated to be $\Delta H_g^* = 110\,\text{kJ}\,\text{mol}^{-1}$. As the sum $\Delta H_i^* + \Delta H_g^*$ equals $150\,\text{kJ}\,\text{mol}^{-1}$ [2] the activation enthalpy of craze initiation is $\Delta H_i^* = 40\,\text{kJ}\,\text{mol}^{-1}$.

5. Conclusions

The initial quadratic time dependence of strain during constant stress tensile tests shows that the model for stress–strain behaviour [1] is applicable for constant-stress tensile tests as long as no significant craze termination takes place. The linear dependence of $\ln k_i k_g$ on stresses higher than $15\,\text{MPa}$ confirm an earlier conclusion from constant strain-rate tests that the product of the rates of craze initiation and craze growth is exponentially dependent on stress [2].

The strain–time response to a stepped increase of stress shows that at 22°C the attainment of a constant strain rate during constant-stress tensile tests, and the attainment of a constant stress level during constant strain-rate tensile tests are a consequence of a strong decrease in the rate of craze initiation at higher elongations. It thus appears that under these circumstances craze termination results from the attainment of a maximum craze area (per unit volume TPS) normal to the stress direction, while at higher strains craze termination due to a decrease in the rate of craze growth becomes important as well.

Applying this result it was found that the rate of craze growth is exponentially dependent on the stress and the reciprocal temperature, in accordance with the Eyring equation.

Taking into account the simplicity of the model the agreement between the values for the craze parameters obtained from constant stress tensile tests and those obtained from constant strain-rate and constant stress-rate tensile tests can be considered to be good.

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