An Interpretation of the Critical Strain Measure for Polymers

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Synopsis

During creep deformation many polymeric materials exhibit small cracklike zones, crazes. In the literature it is reported that crazing will not occur if the strain is kept under a critical value, specific for each material. This fact has importance in avoiding rupture. In this work a uniaxial theory is put forward that is based on a creep law describing the buildup of internal stress and on the Kachanov damage law. Crazing is here regarded to be a stage in the damage accumulation process, the final stage of which is rupture. Relations among the critical strain, the corresponding critical stress, and the minimum stress leading to creep rupture are derived. Some conditions that are necessary for the critical strain concept to work are formulated.

INTRODUCTION

During recent years there have been numerous works published on the crazing phenomenon in glassy polymers. Crazing is a part of a time- and stress-dependent deterioration process where the final state can be rupture. As design against fracture has become more important, increasing efforts have also been directed towards the problem of crazing.

Today craze formation is considered to be a mode of plastic deformation. Crazes are not believed to be true cracks, although they reflect light in a similar way. They contain polymer material that interconnects the normal polymer material on both sides of the craze. The material in the craze is plastically oriented with the molecules approximately normal to the plane of the craze, i.e., in the direction of the tensile stress which produced the craze.[1]

Experimentally, it has been found, e.g., by Menges et al.,[2,3] that there exists a critical value of strain ϵ_{cr} below which crazing is never observed. This value is specific for each material within a large group of polymers. In fast creep tests, i.e., at high load levels, this critical strain value can be exceeded significantly without any observable crazing. Furthermore, they claim that the critical strain is about 0.8%–1% for most glassy polymers. Other values can be found in literature. However, there are also materials where no critical strain value can be found.[1,4]

For semicrystalline polymers like polyethylene, polyoxymethylene, etc., crazing can hardly occur in the amorphous regions. For such materials, special methods have been employed (dilatation, optical methods, etc.) by Menges et al.[2,5] to determine the strain level at which irreversible changes occur. A corresponding critical strain can be defined, being on the order of 2%–3%.

From an engineering point of view, it would be more important to determine the critical stress value than the critical strain. Menges et al.[2,3] have determined

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ϵ_{cr} for numerous polymeric materials, including reinforced plastics, but no value of a corresponding critical stress has been given. This problem has been recognized by Gotham,[4] who consequently has given values of the critical stress σ_{cr} for craze initiation.

In the following, a continuum theory is presented, which gives a relation between σ_{cr} and ϵ_{cr}. The theory is based on the internal stress concept. By internal stress is here meant a quantity entering the constitutive relation in such a way that the deformation rate is changed with deformation. Alternative terms would be back-stress or deformation resistance.

The theory is an attempt to clarify the relations between critical strain and other material parameters such as the critical stress for crazing or for rupture and the constants in the creep law and in the Kachanov damage law, as well as to clarify the dependence of the critical strain value on the sensitivity of the experimental method for indicating crazes.

THEORETICAL MODEL

The first assumption is that the deformation of the material can be described by the uniaxial constitutive equation

$$\dot{\epsilon}_c = B(\sigma - K\epsilon_c)^n \qquad \sigma > K\epsilon_c \tag{1}$$

where the quantity $K\epsilon_c$ can be interpreted as the internal stress. As was shown in an earlier paper by Bråthe and Rigdahl,[6] this is roughly the case for many polymeric materials, although it is arguable whether the power function rather than some other function of the effective stress $\sigma - K\epsilon_c$ fits the experimental data best.

For a constant-load creep test with the initial stress σ_0, using the condition of constant volume and the linear strain concept, i.e., for small strains, we will get the creep strain as a function of time for an initially virgin material[6]:

$$\epsilon_c = \frac{1 - (1 + \lambda t)^{1/(n-1)}}{K/\sigma_0 - 1} \tag{2}$$

where $n > 1$ and

$$\lambda = B\sigma_0^n(n-1)(K/\sigma_0 - 1) \tag{3}$$

The effective stress, defined as applied stress minus internal stress, can now be expressed as

$$\sigma_{eff} = \sigma_0(1 + \lambda t)^{-1/(n-1)} \tag{4}$$

The next assumption is that the rate of material deterioration is a function of the effective stress, viz.,

$$\dot{\omega} = C[\sigma_{eff}/(1 - \omega)]^\nu \tag{5}$$

where ω is the damage parameter, $0 \leq \omega \leq 1$. This equation was introduced by Kachanov[7] for metals.

It is now possible to use some of the results for creep relaxation from Bråthe[8] for the combination of eqs. (4) and (5),

$$\frac{d\omega}{dt} = C\frac{\sigma_0^\nu(1 + \lambda t)^{-\nu/(n-1)}}{(1 - \omega)^\nu} \tag{6}$$

which was integrated with the initial value $\omega = 0$ at $t = 0$ to give

$$\omega = 1 - \left(1 - \frac{\beta}{\lambda}\left[(1 + \lambda t)^{(n-\nu-1)/(n-1)} - 1\right]\right)^{1/(\nu+1)} \tag{7}$$

if $n - \nu \neq 1$ and where

$$\beta = C\sigma_0^\nu \frac{(\nu + 1)(n - 1)}{n - \nu - 1} \tag{8}$$

Let us now assume that when the damage has increased to a fixed value, say ω_*, then the crazes will become visible.

This value ω_* is reached after the time $t_*(\sigma_0)$ and at the strain $\epsilon_*(\sigma_0)$. The time t_* can be found immediately by inserting ω_* in eq. (7),

$$t_* = \frac{1}{\lambda}\left[\left(1 + \frac{\lambda}{\beta}\left[1 - (1 - \omega_*)^{\nu+1}\right]\right)^{(n-1)/(n-\nu-1)} - 1\right] \tag{9}$$

and the strain is given for the time t_* by eq. (2),

$$\epsilon_* = \frac{1 - (1 + \lambda t_*)^{-1/(n-1)}}{K/\sigma_0 - 1} \tag{10}$$

Equation (7) in (10) yields

$$\epsilon_* = 1 - \left(\frac{\lambda}{\beta}\left[1 - (1 - \omega_*)^{\nu+1}\right] + 1\right)^{-1/(n-\nu-1)} \times \left(\frac{K}{\sigma_0} - 1\right)^{-1} \tag{11}$$

In Figure 1 creep curves according to eq. (2) are shown together with the time dependence of the critical strain from eq. (10) corresponding to various levels of damage. They have roughly the same shape as the experimental curves in Refs. 2 and 3.
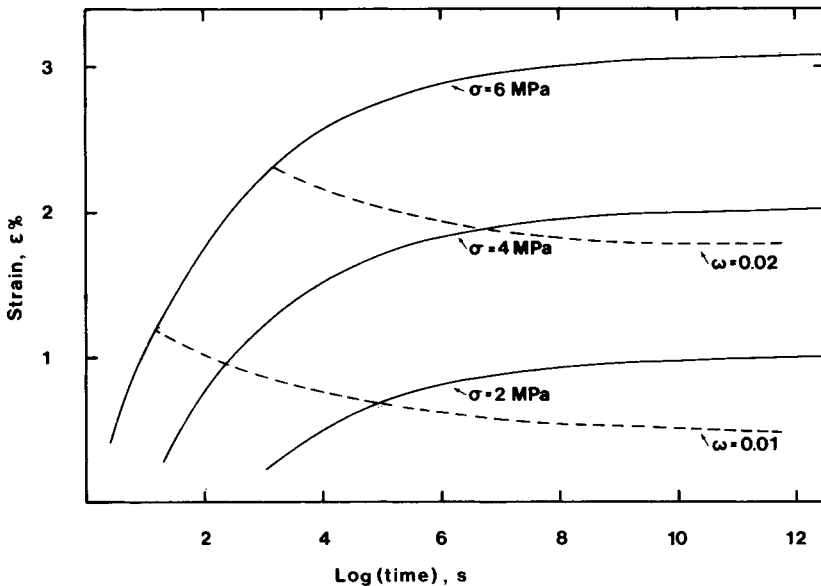

Fig. 1. Creep curves (solid lines) for various constant stresses according to eq. (2), with $E = 1$ GPa, $B = 10^{-7}$ (MPa)$^{-n}$s^{-1}, $K = 200$ MPa, and $n = 6$, with critical strain as a function of time (dashed lines) for two damage levels and the values of E, B, K, and n as above and $C = 10^{-5}$ (MPa)$^{-\nu}$s^{-1} and $\nu = 5.5$.

We will now consider the consequences of a long time under load.

(i) If $n > \nu + 1$, we will, according to Bråthe,[8] exceed ω_* after a finite time no matter how small the initial stress is. This means that for such material there exists no critical strain.

(ii) If $\nu < n < \nu + 1$, we have to distinguish between three cases depending on the initial stress σ_0: (a) if $\sigma_0 > \sigma_r$, we will have rupture in a finite time; (b) if $\sigma_r > \sigma_0 > \sigma_{cr}$, we will pass the damage level ω_* but will not have rupture in a finite time; (c) if $\sigma_{cr} > \sigma_0$, we will have neither visible crazes nor rupture for finite times.

The minimum stress to cause crazes σ_{cr} can be determined from eq. (7), since

$$(1 + \lambda t_*)^{-(\nu+1-n)/(n-1)} \rightarrow 0 \text{ as } t_* \rightarrow \infty$$

This gives

$$1 - (1 - \omega_*)^{\nu+1} = \frac{C\sigma_{cr}^{\nu-n}(\nu+1)}{B(K/\sigma_{cr} - 1)(\nu + 1 - n)} \tag{12}$$

where σ_{cr} can be solved for, at least numerically.

The corresponding strain is given by eq. (2):

$$\epsilon_{cr} = \left(\frac{K}{\sigma_{cr}} - 1\right)^{-1} \tag{13}$$

These expressions can be simplified, if $\sigma_{cr} \ll K$ and if $\omega_* \ll 1$, by use of the binominal series expansion of the power expression, which yields

$$\sigma_{cr} \approx \left(\frac{BK(\nu + 1 - n)\omega_*}{C}\right)^{1/(\nu+1-n)} \tag{14}$$

and

$$\epsilon_{cr} \approx \sigma_{cr}/K \tag{15}$$

The minimum stress causing rupture, σ_r, is solved from eq. (7) with the condition $\omega = 1$ (see Ref. 8), which gives

$$1 = \frac{C\sigma_r^{\nu-n}(\nu + 1)}{B(K/\sigma_r - 1)(\nu + 1 - n)} \tag{16}$$

If $\sigma_r \ll K$, then

$$\sigma_r \approx \left(\frac{BK(\nu + 1 - n)}{C(\nu + 1)}\right)^{1/(\nu+1-n)} \tag{17}$$

and the corresponding strain is σ_r divided by K.

Finally, the approximate relation between the minimum stress required to cause crazes and the minimum stress to cause creep rupture can be found by combining eqs. (12) and (16) for $\sigma \ll K$:

$$\sigma_{cr}/\sigma_r \approx [1 - (1 - \omega_*)^{\nu+1}]^{1/(\nu+1-n)} \tag{18}$$

If also ω_* is small, then

$$\frac{\sigma_{cr}}{\sigma_r} \approx \frac{\epsilon_{cr}}{\epsilon_r} \approx [(\nu + 1)\omega_*]^{1/(\nu+1-n)} \tag{19}$$

DETERMINATION OF MATERIAL CONSTANTS

Determination of K, B and n

Apart from the well-known parameters B and n, the constitutive equation (1) contains an "elastic modulus" K relating the value of the internal stress to the creep strain, $\sigma_i = K\epsilon_c$. The specific value of K for a given material can be obtained either by stress relaxation tests or by estimating the final strain of the ceasing creep process by an extrapolation method. Both techniques are analyzed in detail in Ref. 6. For a relaxation experiment it consists of plotting the derivative $-\partial\sigma/\partial\ln t$ versus σ and extrapolating the resulting curve to $-\partial\sigma/\partial\ln t = 0$. The value of the stress at the intercept with the σ-axis is equal to the stress level of the relaxation test reached after infinite time and given by $\sigma_\infty = KE\epsilon_0/(K + E)$, where $E\epsilon_0$ is the initial stress of the relaxation experiment. From this relation the parameter K can be evaluated knowing the value of the tensile modulus E. For constant-load creep, a corresponding procedure could be applied with σ replaced by ϵ.

Returning to relaxation, the slope of the $-\partial\sigma/\partial\ln t$ (σ) curve at $-\partial\sigma/\partial\ln t = 0$ is easily shown[9] to be $1/(n - 1)$, and from this relation a value of the exponent n is obtained. Several techniques can now be employed for the determination of B. For example, if the decaying stress in a relaxation experiment is plotted versus $\ln(\text{time})$, a sigmoid curve is normally obtained. The inflexion point of this curve along the time axis t_1 is given by

$$t_i = \left[\left(\sigma_0 - \frac{K\sigma_0}{K + E}\right)^{n-1} BE\right]^{-1} \tag{20}$$

Provided the parameters K, E, and n are known, a value of B is found from eq. (20).

Determination of C and ν

Information regarding the magnitudes of C and ν in the damage law, eq. (5), can be obtained from constant strain rate experiments. For reasons of simplicity we assume that the elastic term $\dot{\sigma}/E$ in eq. (1) can be neglected. Then we have the creep strain equation

$$\dot{\epsilon} = B(\sigma - K\epsilon)^n \tag{21}$$

and

$$\epsilon = v_0 t \tag{22}$$

where v_0 is the constant strain rate.

Combining eqs. (21) and (22) results in

$$\sigma = (v_0^{1/n} + B^{1/n} K v_0 t)/B^{1/n} \tag{23}$$

The effective stress is

$$\sigma_{\text{eff}} = \sigma - K v_0 t = v_0^{1/n} B^{-1/n} \tag{24}$$

where eq. (23) has also been used.

The effective stress being constant, eq. (5) can be integrated with the initial condition $\omega = 0$, which will give an expression of damage as a function of time.

Following Kachanov,[7] we insert the rupture condition $\omega = 1$ and get the rupture time

$$t_R = 1/C(\nu + 1)\sigma_{\text{eff}}^\nu \qquad (25)$$

Performing tests at different strain rates, i.e., different effective stresses, will lead to different rupture times. Using eq. (25) to make a $\log t_R$ versus $\log \sigma_{\text{eff}}$ plot of the experimental data will give the constants C and ν.

Using eqs. (5) and (24), assuming that the damage ω is small and that $\omega(t = 0) = 0$, gives the time dependence of ω:

$$\omega = C(v_0^{\nu/n}/B^{\nu/n})t \qquad (26)$$

As before, we now assume that the crazes are observed when the damage has reached the value $\omega = \omega_*$, and this happens when $t = t_*$ and $\epsilon = \epsilon_*$:

$$\omega_* = C(v_0^{\nu/n}/B^{\nu/n})t_* \qquad (27)$$

or using eq. (22),

$$\omega_* = C(v_0^{\nu/n-1}/B^{\nu/n})\epsilon_* \qquad (28)$$

From eq. (28) it can be seen that if $\nu < n$, the strain ϵ_* will decrease with decreasing applied strain rate v_0, and in the limit $v_0 \to 0$, ϵ_* is zero. Hence our theory predicts that the critical strain concept is not applicable for small constant strain rate situations.

For $n = \nu$, eq. (28) reduces to

$$\omega_* = (C/B)\epsilon_* \qquad (29)$$

which is independent of the applied strain rate.

A more accurate analysis would also include the elastic strain, which is not considered here.

DISCUSSION

Review of the Assumptions

The first assumption in the preceding analysis relates to the constitutive equation, eq. (1), which fairly well describes the creep behavior of a number of polymers as was shown by Bråthe and Rigdahl.[6] However, under certain circumstances a variation in the constant B with the applied stress is noticed, indicating that another function of the effective stress $(\sigma - K\epsilon_c)$ would be more appropriate, e.g., of the $\sinh$ type. Still the constitutive relation used leads to the concept of a decaying effective stress, which is important here when describing the creep deformation and crazing behavior of polymeric materials subjected to constant loading. The damage is not assumed to influence the strain rate.

The second assumption is that the rate of damage is assumed to be a power function of the stress, eq. (5). This is in analogy with current theories for metallic materials. In contrast to the common damage theory, as described by Kachanov,[7] $\dot\omega$ is here assumed to be related not to the applied, but to the effective stress. The effective stress is taken as the difference between the applied stress and the internal stress.

The third assumption deals with the observation of crazes at a specific damage level ω_*. Although we describe both the craze size and craze distribution with only one parameter, this assumption does not seem to be controversial. By changing the value of ω_*, the sensitivity of the craze observation method can be taken into account by the theory.

The last assumption is that rupture occurs at $\omega = 1$. Other rupture conditions could possibly be applied.

Consequences of the Theory

The damage theory and the concept of internal stress used in a constitutive equation of the power law type thus provide a correlation between the minimum stress leading to rupture σ_r, the critical strain ϵ_{cr} for the onset of crazing, and the corresponding stress σ_{cr}. A correlation of this kind has implicitly been assumed in experimental analysis but has never been shown to exist.

It follows from the approach adopted in this paper that only those materials exhibiting a diminishing creep rate, i.e., ceasing creep, prior to the eventual tertiary creep stage due to instability, will have a critical strain limit ϵ_{cr}. Another formulation of this condition is that a stress relaxation test can be extrapolated to end at a nonzero level. Evidently this implies that there may exist materials that do not have a critical strain value ϵ_{cr}.

Menges et al. have on a number of occasions presented results showing that ϵ_{cr}, within a certain temperature interval, is roughly independent of the temperature. In the theory outlined here this is easily interpreted as arising from the constants B and C having the same temperature dependence, since only the ratio between those parameters enters the equation for ϵ_{cr}, eq. (11). This means that the activation energies for the creep deformation process and for the deterioration process are of the same magnitude.

The design of components subjected to a multiaxial state of stress is more complicated. Menges et al.[2,3] have proposed two different methods. One method is to perform creep tests on the construction under study and to evaluate the isochronous stress–strain curves. This is costly and time-consuming. Another method is to use an extension of the elastic theory. However, it appears to be difficult[3] to establish the value of Poisson's ratio for polymers, since it obviously varies with time and state of stress.

In our interpretation these difficulties stem from the fact that one can not assume *a priori* that the value of $K\epsilon_c$ in one direction is independent of the creep deformation in perpendicular directions. However, some results from the well-established frozen-in stress technique in photoelasticity seem to indicate that in the limit state where all creep has ceased, Poisson's ratio is very near 0.5.[10] Thus for the limiting deformation state, which is associated with K, the theory of elasticity with Poisson's ratio equal to 0.5 can probably be used. For the instantaneous part, however, which is associated with E, a quite different Poisson's ratio must be employed. In which way the development of crazes in the material depends on the different components of a multiaxial state of stress does not seem to be clear. Our suggestion for future work is that the multiaxial case be evaluated both theoretically and experimentally.

We believe that the present theory can also be applied to composite materials, and especially to the process of delamination between the different components of such a material.

CONCLUSIONS

The theory presented in this work, although based on a number of assumptions, establishes the conditions for the existence of a critical strain concept as introduced by Menges.

To each value of the critical strain there corresponds a critical stress value, which is also connected to the minimum stress causing creep rupture.

Different sensibilities when observing craze initiation can, in principle, be accounted for by varying the associated characteristic damage value.

The theory indicates that the critical strain as determined by creep experiments can adopt lower values at low constant strain rate experiments.

The theory could be of value when developing new polymeric materials with high resistance to creep rupture.

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