Crazing limit of polymers in creep and stress relaxation

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The appearance of the first visible damage in polymers in the form of crazes or microcracks may be assumed to be a sign of failure. Experimental investigations have shown that in uniaxial creep and stress relaxation experiments, under isothermal conditions, a certain time between the quasi-spontaneous loading and visible crazing is needed. This 'incubation time' is very strongly dependent on the magnitude of the quasi-spontaneously applied stress or induced strain. Based on the Reiner–Weissenberg theory of strength, simple relations allowing the prediction of crazing are developed. The agreement between theoretical computation and experiment is very good.

INTRODUCTION

Strength theories developed over the past few years define some particular function of stress and/or strain, the limiting value of which is determined empirically. When this limiting value is exceeded the associated failure takes place. All these theories are time independent and therefore not applicable to viscoelastic materials, where the stress–strain relation is highly time dependent.

A theory of strength in which time is also considered was developed by Reiner and Weissenberg[1]. During loading the work done by external forces on a viscoelastic material is converted into a stored part (potential energy) and a dissipated part, each of which may be divided into two other parts: the isotropic one, connected with volume changes and the deviatoric one, associated with shape changes. According to the Reiner–Weissenberg theory of strength, failure occurs when the stored deviatoric strain energy reaches a certain value, defined by Reiner as 'resilience' and assumed to be a material constant.

The existence of such a value is demonstrated in constant strain rate experiments[2] over four decades of strain rate for two different materials, poly(methyl methacrylate) (PMMA) and epoxy resin. As with failure, the transition limit from linear to non-linear viscoelasticity is considered. The computed value of the specific stored deviatoric energy at transition from linear to non-linear viscoelasticity is:

$$W_{sd,lim} = 0.084 \text{ Nmm/mm}^3 \qquad (1)$$

Different experimental results collected in ref 3 as well as experiments carried out by the author allow us to state that below the limit of the appearance of the first visible crazes, Poisson's ratio is practically a constant.

As a result, the ratio of deviatoric energy/total energy becomes constant and, consequently, the value of the total stored energy can be considered as a limiting value for the linear range. For PMMA it is[4]:

$$W_{st,lim} = 0.090 \text{ N mm/mm}^3 \qquad (2)$$

Based on the limiting value given in equation (2), the limit of linear viscoelasticity of PMMA has been presented for different simple loading histories[5]. The available experimental points are in good agreement with the theoretical values.

Successful attempts to apply the Reiner–Weissenberg theory of strength to crazing in creep have already been carried out[4,6,7]; these are discussed in the next section.

CREEP CRAZING

Crazing of transparent and translucent polymers under creep-loading conditions has been investigated in a large number of publications, for example refs 6–8. One can state that crazes always appear perpendicularly to the maximal normal stress. They are not hollow spaces but stretched material and therefore they still carry load. The number and magnitude of crazes as well as the time at which they become visible is strongly dependent on the magnitude of the working stress. At high stresses a large number of small crazes become visible after a relatively short time, while small stresses lead to a small number of larger crazes which become visible after a very long loading time. In other words, the 'incubation time' of the crazes decreases rapidly with increasing stresses. This is shown in *Figure 1* for PMMA, where uniaxial isothermal creep curves at room temperature

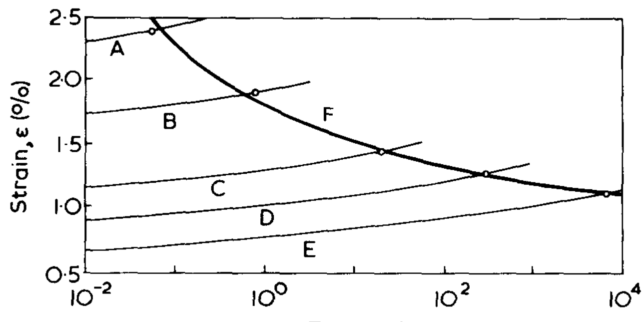

Figure 1 Creep curves of PMMA at 23°C (ref 7). σ_0 values: A, 50 N/mm^2; B, 40 N/mm^2; C, 30 N/mm^2; D, 25 N/mm^2; E, 20 N/mm^2; F, ϵ_c

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are presented as well as the ϵ_c curve connecting the points where first crazes become visible. Further experimental results have been presented in refs 6, 7 and 9, dealing with other polymers at different temperatures below the glass transition temperature.

Computations of the creep energy and its components, based on experimental data for PMMA at room temperature[4], have demonstrated the existence of a strong interconnection between the appearance of first visible crazes and the time-dependent part of the stored energy. (The time-dependent part of the stored energy is equal to the difference between the total stored energy and the quasi-spontaneously stored energy during the loading phase.) Under different stress levels, first crazes always become visible when this time-dependent part of the stored energy reaches a certain value. This happens mostly in the so-called non-linear viscoelastic range of the materials, but the possibility of the appearance of crazes directly in the linear viscoelastic range is not excluded[8]. In this case the stresses acting are relatively small and the incubation time required will be very large. Similar results have been obtained for polycarbonate (PC) at room temperature[4].

It should be pointed out that computations of the creep energy and its components are laborious and require computer time. They are based on the approximation of the creep compliance by a Prony–Dirichlet series, the material parameters of which are determined by numerical methods[4].

A very significant simplification to the computations is permitted by the important observation that when the first crazes become visible, not only the time-dependent part of the stored energy, but also the dissipated energy are practically constant. This can be explained mathematically as well as by using the well-known spring–dashpot mechanical model[8]. The dissipated energy starts growing after the quasi-spontaneous loading phase is accomplished. Its growth is comparable with that of the time-dependent part of the stored energy. The simplification of the procedure occurs since, if at the appearance of first visible crazes, both the time-dependent part of the stored energy and the dissipated energy are constants, then their sum is also constant. The determination of this sum is very simple. The sum represents the difference between the creep energy when crazes become visible and the creep energy stored in the material during the loading phase. If this energy difference, which can be called 'crazing incubation energy' is denoted by W_c, then the following mathematical relation is valid:

$$W_c = \sigma_0(\epsilon_c - \epsilon_{\mathrm{sp}}) \tag{3}$$

where σ_0 is the acting creep stress; ϵ_c is the strain when crazes become visible; and ϵ_{sp} is the quasi-spontaneous strain.

The experimental determination of the limit where crazes become visible is quite simple. Photoelectrical methods[9], for example, are applicable especially with semicrystalline polymers which are usually translucent, while in amorphous polymers they can be detected with sufficient accuracy by simple observation.

The major experimental difficulty is the determination of the strain reaction of the polymer to a quasi-spontaneously applied stress. The prefix 'quasi' is used since the procedure does not allow any phenomena which take place instantaneously. With creep experiments the load increases from zero to its final value in a finite time (1–2 sec are generally needed in order to avoid strong vibrations). During this relatively short loading period, the material responds 'viscoelastically' to the applied load, and besides, the pure elastic stored energy, a supplementary amount of energy is in part stored, in part dissipated. (The abovementioned mechanical model helps to explain this phenomenon.) Taking into account the infinity of possible loading histories, it can be seen that the uncertainty about what happens during the loading phase of creep experiments produces some uncertainty in the following creep phase.

Nevertheless, good results have been obtained using experimentally possible approximations for the spontaneous response of the material ϵ_{sp}. Two methods were used:

(a) ϵ_{sp} was approximated by the value of the creep strain obtained as soon as possible after the loading phase (extrapolated);

(b) ϵ_{sp} was approximated from high speed experiments with constant rate of strain or stress (extrapolated).

The first method was applied to experimental data obtained on PMMA and PC, the second one to polyoxymethylene (POM), both leading to accurate results[8].

For PMMA and PC the crazing incubation energy was found to be[8]:

$$W_c \simeq 0.1 \text{ Nmm/mm}^3 \tag{4}$$

For POM its value is larger:

$$W_c \simeq 0.3 \text{ Nmm/mm}^3 \tag{5}$$

Starting from the known value of the crazing incubation energy W_c, a prediction of the strain at which the first crazes become visible can be made by rewriting equation (3) in the form:

$$\epsilon_c = \epsilon_{sp} + \frac{W_c}{\sigma_0} \tag{6}$$

In *Figure 2* the theoretically deduced curve described by equation (6) is shown for PMMA at room temperature together with some experimental points[7]. A very good agreement is observed.

INFLUENCE OF TEMPERATURE

The association between time and temperature is well known for plastics. For the so-called thermorheologically simple materials (the group in which most polymers are included) the usual form of this association is due to Williams, Landel and Ferry. For such materials an increase of temperature causes an acceleration of viscoelastic phenomena and *vice versa,* at lower temperature, viscoelastic phenomena develop over a longer period of time.

On the other hand, regarding equation (6), shown for PMMA in *Figure 2,* we conclude that the crazing strain limit is a direct function of stress only. In other words, under a given working stress, crazes appear when a certain value of the strain is reached. How this value is reached is not the crucial point (of course it is clear that at higher temperatures the value is reached sooner than at lower temperatures). In any case we repeat that only the actual value of the creep strain is conclusive for the prediction of eventual crazing. This is confirmed by creep experiments with observations of the crazing carried out on PMMA at 40° and 60°C[7]. The results, presented in *Figure 3,* are in relatively good agree-

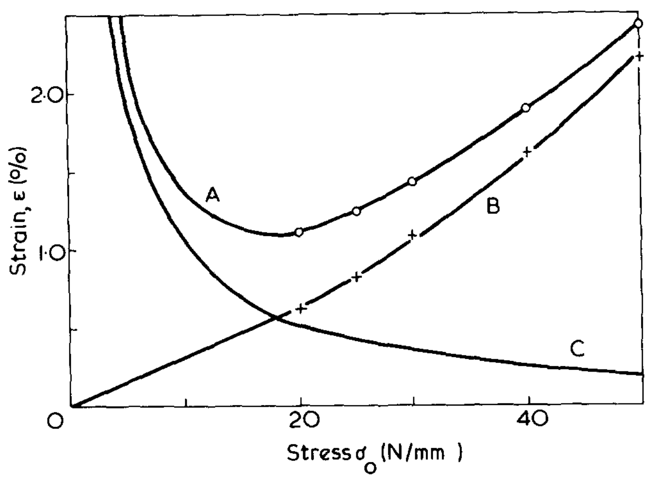

Figure 2 Visible crazing limit of PMMA in creep *versus* stress. $T = 23°C$. A, $\epsilon_c = \epsilon_{sp} + W_c/\sigma_0$; B, ϵ_{sp}; C, W_c/σ_0. +, ○ Experimental points from ref 7

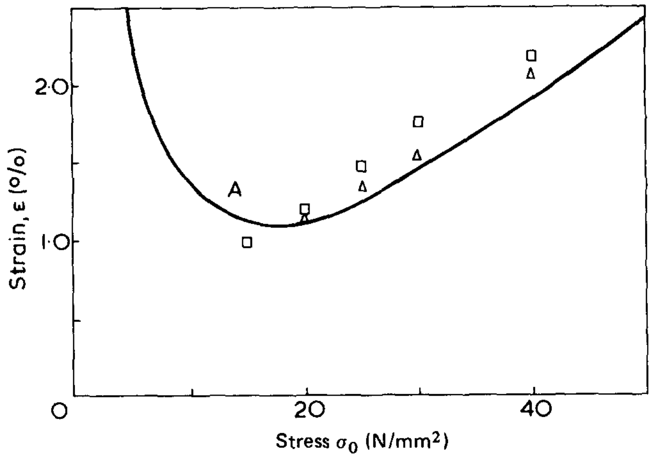

Figure 3 Visible crazing limit of PMMA in creep at different temperatures. A, $\epsilon_c = \epsilon_{sp} + W_c/\sigma_0$; △, Experimental points at 40°C; □, 60°C. Experimental points from ref 7

ment with the theoretical suppositions. The slightly higher values of the crazing strain at elevated temperatures are due, we believe, to observation difficulties caused by the temperature chambers.

For PC, experimental values collected from ref 10 at 23°, 40° and 60°C are close together. These are shown in *Figure 4*.

Turning back to equation (6), using these experimental confirmations, we can state that the crazing incubation energy is a material constant, independent of time and temperature.

STRESS RELAXATION CRAZING

In stress relaxation the situation is quite different. After the quasi-spontaneous loading phase, no more external energy is supplied to the material. Internal time-dependent redistribution of energies takes place and a part of the stored energy is dissipated. The amount of specific energy in the material decreases as well as the stress level (*Figure 5b*). In creep, additional energy is supplied to the material (in part stored, in part dissipated) and the amount of specific energy increases, as well as the strain (*Figure 5a*).

A simple but efficient explanation of the phenomena can be given by using a generalized Kelvin–Voigt mechanical model of springs and dashpots as shown for example in ref 8.

In spite of the apparent differences between creep and stress-relaxation, the laws governing the behaviour of the

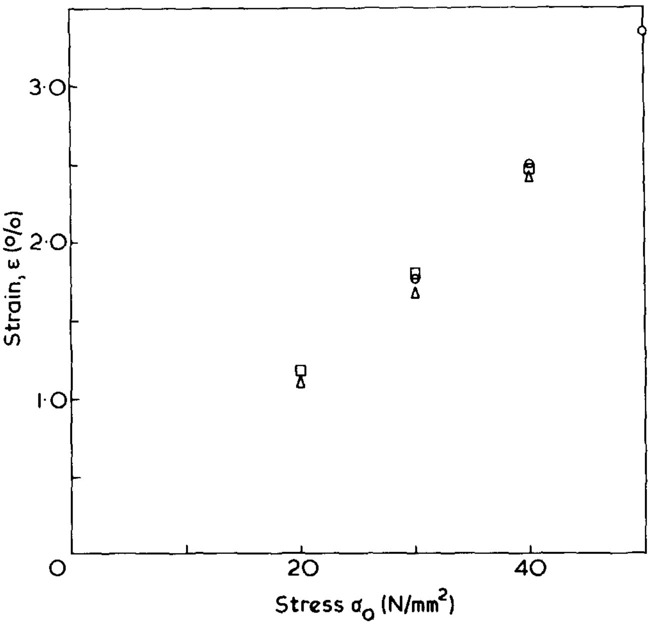

Figure 4 Visible crazing limit of PC at different temperatures. ○, Experimental points at 23°C; △, 40°C; □, 60°C. Experimental points from ref 10

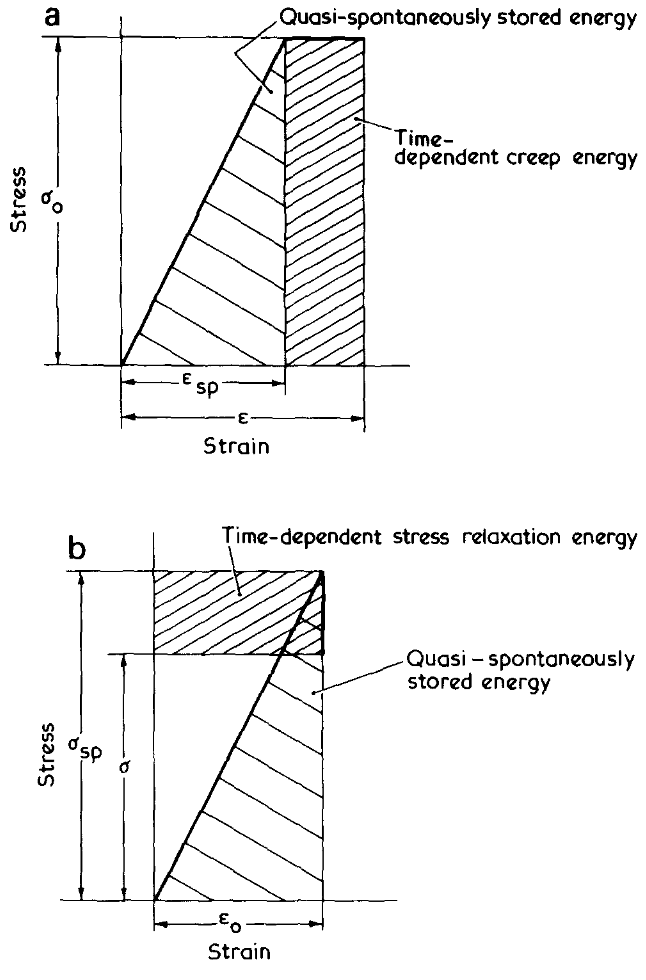

Figure 5 (a) Stress–strain representation of (a) creep; (b) stress relaxation

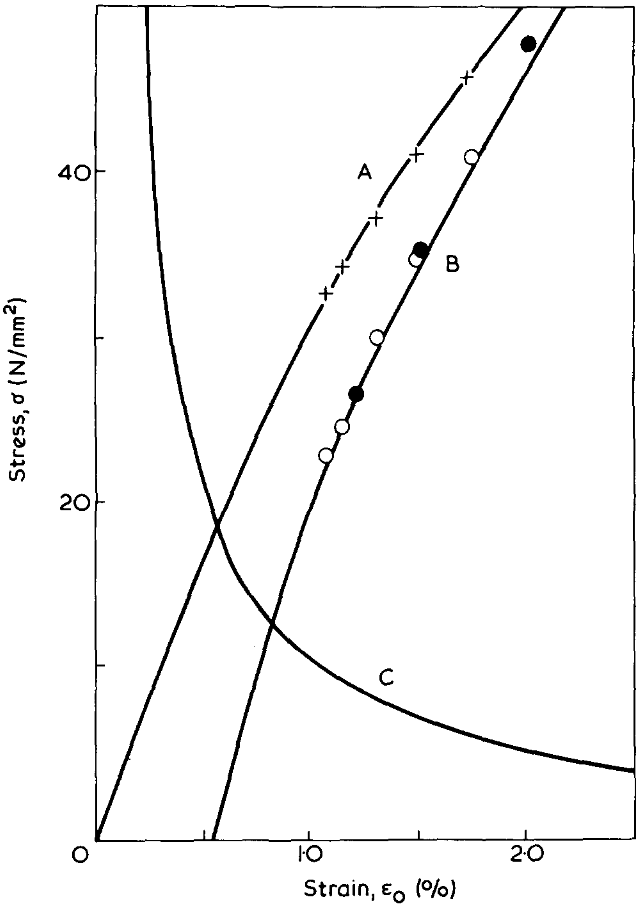

Figure 6 Visible crazing limit of PMMA in stress relaxation *versus* strain. $T = 23°C$. A, σ_{sp}; B, $\sigma_c = \sigma_{sp} - W_c/\epsilon_0$; C, W_c/ϵ_0. ●, Experimental points from ref 7; +, O, from ref 11

material have to be the same. In the present case we can postulate that the crazing incubation energy, W_c, has the samevalue for both creep and stress relaxation.

Considering the case of stress relaxation crazing, based on the observations which have led to equation (6), the following relation can be deduced (see also *Figure 5b*):

$$W_c = (\sigma_{sp} - \sigma_c)\epsilon_0 \qquad (7)$$

where W_c is the crazing incubation energy; σ_{sp} is the quasi-spontaneously obtained stress; σ_c is the stress when first crazes become visible; and ϵ_0 is the induced strain.

As for creep, equation (7) can be rewritten in the form:

$$\sigma_c = \sigma_{sp} - \frac{W_c}{\epsilon_0} \qquad (8)$$

from which the stress limit of appearance of visible crazes in stress relaxation can easily be computed.

Only a few experimental results are available[7,11]. For PMMA at 23° they are plotted together with the theoretical curve described by equation (8), with the value for W_c as determined from creep crazing ($W_c \cong 0.1$ Nmm/mm^3). Only small discrepancies are observed.

CONCLUSIONS

In spite of the fact that creep and stress relaxation are quite different loading cases, as shown in the example of PMMA, the incubation energy needed for the appearance of first visible crazes is the same for both cases.

The interpretation of the results of creep experiments conducted on PMMA and PC allow the additional statement that this energy is a material constant and does not depend on time or temperature.

Using very simple relations, developed on the basis of the Reiner–Weissenberg theory of strength, very accurate predictions of crazing in creep or stress relaxation can be made.

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