Craze-Initiation Kinetics in Polystyrene

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ABSTRACT: In this study it is shown, for a commercial polystyrene grade, that the strain-rate dependence of craze initiation is equivalent to that of yielding. This implies that the kinetics of craze initiation are determined by the nonlinear flow behavior, and that the actual cavitation process is governed by an additional, apparently rate-independent, criterion. © 2004 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 42: 2066–2073, 2004

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INTRODUCTION

Macroscopic brittle fracture of glassy polymers is normally preceded by the formation of crazes, small crack-like defects, bridged by fibrillar material. Unlike real cracks, crazes have load-bearing capacity, and when viewed on a microscopic level, they display large plastic deformations. Therefore, crazes are the most important source of fracture toughness in brittle glassy polymers, even though the volume fraction crazes during fracture is generally low. It is, therefore, not surprising that a vast amount of research has been done on all aspects of crazing: craze nucleation, growth and failure, the microstructure of crazes, the influence of molecular parameters, etc., and a number of excellent reviews are available.1–3

Craze initiation has received relatively little attention. It is generally accepted that craze initiation is enhanced by both the hydrostatic and the deviatoric stress state, and, consequently, craze-initiation criteria normally involve both the first and the second invariant of the stress tensor (Chapter 12 of ref.4). Unfortunately, two factors complicate the search for a macroscopic craze initiation criterion. First, it is well known that crazes always initiate on surface grooves or small imperfections in the bulk of the polymer, where the exact state of stress (or strain) is unknown. Second, especially at low stresses, there can be a considerable time lag between load application and the occurrence of the first visible craze, which indicates that craze initiation is a time-dependent phenomenon. Therefore, a meaningful craze initiation criterion can probably only be defined on a local scale, in a well-defined microstructure, where the state of stress is known.5 Such a local criterion would still be very useful in numerical aided design of morphologies where shear yielding prevails crazing.6

Figure 1 depicts some of the microscopic events that are likely to be involved in craze nucleation.1 First, plastic deformation starts at a local stress concentration. The nonlinear nature of the yield
process and the strain-softening character of polymer glasses will result in a localization of deformation as the plastic strain increases. Because the material at some distance of the local deformation zone is relatively undeformed, lateral stresses will develop. At this stage two possibilities exist. First, the strain-hardening response of the material can stabilize the strain-localization process, and the microshear band will spread out. Second, it has been shown that the hydrostatic stress required to plastically expand a microporous region is greatly reduced if the material is in a state of flow. Therefore, if the lateral stresses become sufficiently high, the material in the deformation zone will cavitate, and craze nucleation has been accomplished.

It is difficult to predict which of the events in Figure 1 will be the rate-determining step in craze nucleation. In one of the most detailed studies on craze initiation by Argon and Hannoosh, it was argued that nucleation of voids is a thermally activated process. The activation-free energy for pore formation consists out of two terms: the formation of a slip patch, which is started and arrested by molecular inhomogeneities, followed by the formation of a stable round cavity by plastic expansion of microporous regions inside the slip patch. This model was criticized by Kramer, because it ignores both surface-tension and chain-entanglement effects. Furthermore, in the study by Argon and Hannoosh, the true kinetics of craze initiation were obscured by the considerable time lag between the void formation and visible occurrence of the first craze. The void-initiation time could only be estimated indirectly by assuming a power-law relation between the equivalent stress and strain during the plastic expansion of the initial void until it becomes large enough to reflect light.

To avoid the difficulties associated with the unknown state of stress, Dekkers studied craze initiation around a well-adhering glass bead. Linear elastic finite-element calculations were used to determine the local state of stress and strain. Comparing these calculations with the spatial arrangement of crazes around the glass beads, it was concluded that the major principle stress and the dilatation were the most likely candidates for a craze-initiation criterion. In Dekkers' study, the kinetics of craze initiation were not considered. Moreover, the assumption of linear elastic behavior up to the point of craze initiation is questionable.

In a more recent study, van Melick et al. employed a hydrostatic time-independent craze criterion to describe craze initiation during microindentation in polystyrene. Nonlinear viscoelastic finite element calculations were used to estimate the local state of stress and strain as a function of indentation force. Using a critical hydrostatic stress of 40 MPa, a good agreement was found between the predicted and observed indentation force at which the first craze was formed. The critical hydrostatic stress was found to be independent of thermal history and loading rate, but strongly dependent on network density.

The study of van Melick et al. showed that the concept of a local, time-independent cavitation criterion is appealing and useful in finite element calculations on a microscopic level. Unfortunately, a direct experimental verification of the existence of such a criterion on a macroscopic level is not possible. However, the hypothesis of a local time-independent cavitation criterion implies that the rate-determining step in craze initiation is the onset of strain localization, followed by the evolution of the localized plastic zone up to the point of voiding. This would mean that the kinetics of craze initiation and the nonlinear yield behavior should be identical, the experimental verification of which is the objective of this article.

**THEORY**

Strain localization in polymer glasses is the result of the combined action of nonlinear material re-
response, comprising the nonlinear yield behavior, intrinsic strain softening and strain hardening, and the boundary conditions applied. The initiation of strain localization, however, is only determined by the yield process (and the boundary conditions applied). For polymer glasses, the rate dependence (the “kinetics”) of the yield behavior is fully described by the Eyring process, eq. 2b, and is not influenced by strain hardening or strain softening. The rigorous justification of this statement would require a full stability analysis. Here, however, a more qualitative argument will be used to illustrate the influence of the constitutive behavior on strain localization.  

To start, it will be assumed that, at the yield point, the material behavior can be approximated by a Kelvin-Voigt model, representing the nonlinear flow behavior and the strain-hardening response in shear (see Fig. 2), which results from a rubber–elastic response of the “entanglement” network.

At the yield point, to a good approximation, the total strain rate is equal to the plastic strain-rate. According to Figure 2, the relation between the shear-flow stress \( \tau \) and the plastic strain-rate \( \dot{\gamma}_p \) becomes:

\[
\dot{\gamma}_p = \frac{\tau - G_r \gamma_p}{\eta((\tau - G_r \gamma_p), \gamma_p)}
\]

where \( G_r \) is the “rubbery” strain-hardening modulus, and \( \gamma_p \) is the plastic strain.

All nonlinear flow characteristics (the “kinetics” of the yield process) are incorporated in the viscosity function \( \eta \) (Fig. 2):

\[
\eta = \eta_0 \alpha_\sigma \alpha_\gamma
\]

\[
\alpha_\sigma(\tau) = \frac{\tau}{\sinh(\tau/\tau_0)}
\]

\[
\alpha_\gamma = \exp(-D)
\]

\[
D = h \left(1 - \frac{D}{D_0}\right) \dot{\gamma}_p
\]

The function \( \alpha_\sigma(\tau) \) is the Eyring-shift factor, which describes stress activated flow. The last two relations, eqs. 2c and 2d, present a phenomenological description of intrinsic strain softening, using a scalar internal variable, \( D \) which is related to the number density of shear transformation sites (areas of increased mobility due to a high free volume). The constants \( D_0 \) and \( h \) are essentially fitting parameters. The shift factor \( \alpha_\gamma \) can be expressed as a function of the plastic strain \( \gamma_p \) by integration of eqs. 2c and 2d:

\[
\alpha_\gamma = \exp\left[-D_0 \left(1 - \exp\left[-\frac{h}{D_0} \gamma_p\right]\right)\right]
\]

At high stress levels, the hyperbolic sine function in eq. 2b can be approximated by an exponential. Using eqs. 1 and 2, the plastic strain rate can then be written as:

\[
\ln \dot{\gamma}_p = \ln \left(\frac{\tau_0}{2\eta_0 \alpha_\sigma}\right) + \frac{\tau - G_r \gamma_p}{\tau_0}
\]

The nonlinear character of the Eyring process is depicted in an Eyring plot of the yield stress versus the logarithm of the plastic strain rate (Fig. 3). From this plot, it is clear that the Eyring process can trigger inhomogeneous behavior. A small fluctuation of the stress field will result in a large deviation of the local plastic strain rate, depending on the value of the activation volume (which determines the slope \( \tau_0 \), see Fig. 3). Dependent on the specific boundary conditions, this can lead to strain localization.
Crazing, as an extreme form of strain localization, is not determined by the Eyring process alone. Figure 4 depicts a combined Eyring plot of several polymers. From this figure it can be seen that polymers sensitive to crazing, like polystyrene, can have a smaller activation volume (larger $\tau_0$) than polymers like polycarbonate, which are insensitive to crazing and generally fail through shearing.

Intrinsic strain softening and strain hardening amplify respectively stabilize small stress fluctuations. This is depicted in Figures 5 and 6, where some typical values of the material constants in eq. 4 for polycarbonate were used,\textsuperscript{17} to show the effect of strain softening- and hardening on the plastic strain as a function of time, at different stress levels.

As is clear from Figure 5, the plastic strain as a function of time increases dramatically if the material displays strain softening behavior. Dependent on the balance between strain hardening and strain softening, and the specific boundary conditions, this will promote strain localization. Particularly, elimination of strain softening by means of mechanical preconditioning will result in a more homogeneous deformation behavior,\textsuperscript{16} and can even induce macroscopic ductile behavior during uniaxial extension of polystyrene.\textsuperscript{19}

From eq 1 it can also be seen that the value of the strain-hardening modulus $G_r$ determines the level at which the plastic strain stabilizes. A high value of $G_r$ promotes homogeneous behavior.

It was shown that according to the Eyring process for plastic flow, the yield point can be envisaged as a stress-induced glass transition.\textsuperscript{10} Therefore, a plastically expanding zone is effectively a rubber. From rubber-cavitation theories, it is known that dense networks have a higher cavitation stress.\textsuperscript{20} As a consequence, a high

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**Figure 3.** A graphical representation of the nonlinear yield behavior as described by the Eyring process. A small fluctuation in the stress results in a large deviation of the plastic strain rate (logarithmic x-axis).

**Figure 4.** A combined Eyring plot for several well-known polymers. The polystyrene data are a prediction, using eq. 14.

**Figure 5.** Plastic strain as a function of time, according to eqs. 1 and 2, at a shear stress $\tau = 40$ MPa. Parameters used for polycarbonate: $D_e = 43$ [ ] and $h = 120$ [ ], $G_e = 26$ MPa, $\tau_0 = 0.888$ MPa and $\sigma_0 = 4.656 \cdot 10^{20}$ MPa $\cdot$ s.

**Figure 6.** Plastic strain as a function of time, according to eqs. 1 and 2, at different constant shear stress. Parameters as in Figure 5.
strain-hardening modulus will inhibit voiding of the slip patch. An alternative point of view is that the cavitation stress is higher, because the covalent-bond contribution to the surface energy of a glassy polymer increases with entanglement density.\textsuperscript{1} Therefore, due to its dense entanglement network, polycarbonate is not very sensitive to crazing, despite its rather strong strain-softening response and its small activation volume.

Using eq.4, the sensitivity of the local plastic strain rate to deviations in the stress field, can be expressed as:

\[
\frac{d}{d\tau} \left( \frac{\ln \dot{\gamma}_p}{\tau_0} \right) = \frac{1}{\tau_0} \tag{5}
\]

Thus, the kinetics of the yield process, responsible for the initiation of strain localization, are fully described by the Eyring process and, in particular, independent of strain hardening and softening. Consequently, if the initiation of strain localization is the rate-determining step in craze initiation, the kinetics of craze initiation should be described by the same Eyring parameters as the yield process.

**EXPERIMENTAL**

The polystyrene grade (Styron 638\textsuperscript{TM}), used in this study, was specially selected for its extreme brittle behavior, creating a situation where the craze-initiation stress is approximately equal to the macroscopic breaking stress. The strain rate dependence of the craze-initiation stress was studied using biaxial flexure (ball-ring) tests.\textsuperscript{21} In these tests, the maximum stress region is limited to a very small volume, thus minimizing the influence of surface flaws and other defects on the experimentally determined strength. The biaxial flexure tests were performed on 3 mm-thick polystyrene disks with a diameter of 45 mm. The support (ring) consisted of thrust bearing of 30 mm diameter with balls of 3 mm radius. The load was applied in the center of the disk with a 3-mm radius ball. As the loading path was linear the nominal fracture stress \(\sigma_f\), and the corresponding strain rate \(\dot{\varepsilon}\) were evaluated according to linear elastic theory:\textsuperscript{22}

\[
\sigma_f = \frac{3(1 + \nu)F}{4\pi d^2} \left[ 1 + 2 \ln \left( \frac{a}{b} \right) + \frac{(1 - \nu)}{1 + \nu} \right] \left( \frac{a^2}{R^2} \right) \left( 1 - \frac{b^2}{2a^2} \right) \tag{6a}
\]

\[
\dot{\varepsilon} = \frac{1}{t} \left[ \frac{1 - \nu}{E} \right] \sigma_f \tag{6b}
\]

where \(a\) is the support radius, \(b\) the effective contact radius, \(R\) the specimen radius, \(d\) the specimen thickness, \(E\) Young’s modulus, \(F\) the force at fracture, \(t\) the loading time and \(\nu\) Poisson’s ratio. The effective contact radius \(b\) can be calculated from the Hertzian contact radius \(c\): (page 163 of ref. 23):

\[
b = \sqrt{1.6c^2 + d^2 - 0.675t} \tag{7}
\]

To study the strain-rate dependence and pressure sensitivity of the yield behavior of polystyrene two other test methods were employed:

1. Tensile tests under a superimposed hydrostatic pressure (500 MPa), performed on polystyrene specimens with dimensions: 35 \(\times\) 10 \(\times\) 2 mm. The experiments were performed, with generous permission, at the IRC of Polymer Science & Technology (University of Leeds). The experimental setup at the IRC has been described extensively by Sweeney et al.\textsuperscript{24}

2. Planar compression tests, performed on polystyrene specimens with a gauge length of 40 \(\times\) 12 \(\times\) 3 mm. The specimens were supported by two steel plates to create a plane strain condition. To minimize friction, the steel plates were covered with a single layer of polytetrafluoroethylene (PTFE) tape (3M 5480, PTFE skived film tape). The contact area was additionally lubricated with a 1:1 solution of dish washing soap and water.

All specimen were produced by compression molding, and were carefully polished to minimize the effect of surface defects.

**RESULTS AND DISCUSSION**

Uniaxial tensile tests under superimposed hydrostatic pressure and planar compression tests were performed to suppress crazing.\textsuperscript{25} The yield stresses obtained from these tests and the results of the ball-ring tests are depicted in Figure 7.

A convenient way to verify whether the rate dependence of the yield and fracture process
(craze initiation) are identical, is to compare the results of Figure 7 in a single Eyring plot. Because different loading geometries are involved, the state of stress and the strain rate at the yield and fracture points must be expressed in terms of equivalent shear stress \( \tau_{eq} \) and equivalent shear strain rate \( \dot{\gamma}_{eq} \) respectively:

\[
\tau_{eq} = \frac{1}{\sqrt{2}} \text{tr}(T_d \cdot T_d) \quad (8a)
\]
\[
\dot{\gamma}_{eq} = \sqrt{2} \text{tr}(D_p \cdot D_p) \quad (8b)
\]

where \( T_d \) is the deviatoric Cauchy stress tensor, \( D_p \) the plastic strain rate tensor, and \( \text{tr} \) denotes the trace.

The pressure-modified Eyring relation (Chapter 11 of ref. 4) in terms of equivalent quantities, is given by:

\[
\dot{\gamma}_{eq} = \frac{1}{A} \sin \left( \frac{\tau_{eq}}{\tau_0} \right) \exp \left( -\frac{P}{\omega_0} \right) \quad (9)
\]

which at high stress leads to:

\[
\tau_{eq} = \tau_{eq}^0 + \tau_0 \ln \dot{\gamma}_{eq} + \mu P \quad (10)
\]

where \( \tau_{eq}^0 = \tau_0 \ln(2A) \) is a constant, \( P \) the hydrostatic pressure, and \( \mu = \tau_0 / \omega_0 \), with \( \omega_0 \) related to the pressure activation volume. In general loading situations, the hydrostatic pressure \( P \) and the equivalent (yield) stress \( \tau_{eq} \) are not independent. For example, in the case of uniaxial extension under a superimposed pressure \( P_0 \), \( \tau_{eq} \) and \( P \) are equal to:

\[
\tau_{eq} = \frac{1}{\sqrt{2}} \text{tr}(T_d \cdot T_d) = \frac{1}{3} \sqrt{3} \sigma \quad (11)
\]
\[
P = P_0 - \frac{1}{3} \sigma \quad (12)
\]

Therefore, \( P \) can be written as a function of \( \tau_{eq}^0 \):

\[
P = P_0 + \alpha \tau_{eq}^0 \quad (13)
\]

with \( \alpha = -\frac{1}{3} \sqrt{3} \). For other loading geometries, the coefficient \( \alpha \) can be calculated in a similar way (see Table 1).

Introduction of the coefficient \( \alpha \), eq. 13, into the Eyring flow equation, eq. 10, leads to:

![Figure 7. Combined plot of yield stress (closed symbols) and fracture stress (open symbols) as a function of deformation rate. Yield stress from planar compression tests (○) and uniaxial tensile tests under superimposed hydrostatic pressure (●). Fracture stress from ball-ring tests (□).](image7.png)

![Figure 8. Equivalent stress versus equivalent strain rate for polystyrene (Styron 638™) in various loading geometries. Open symbols: crazing; closed symbols: yielding (see Fig. 7). The solid lines are a best fit of all data according to eq. 14, using a single set of Eyring parameters.](image8.png)

**Table 1. Geometry Factor \( \alpha \) for the Different Loading Geometries in Figure 8**

<table>
<thead>
<tr>
<th>Loading Geometry</th>
<th>Geometry Factor ( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniaxial extension</td>
<td>-133</td>
</tr>
<tr>
<td>Biaxial extension</td>
<td>-233</td>
</tr>
<tr>
<td>Planar compression</td>
<td>122</td>
</tr>
</tbody>
</table>

![Figure 8](image8.png)
\[
\tau_{eq} = \frac{\tau_{eq}^0 + \tau_0 \ln \dot{\gamma}_{eq} + \mu P_0}{1 - \mu \alpha}
\]  

(14)

This equation facilitates a direct interpretation of the experimental data of Figure 7, the results of which are presented in Figure 8. The drawn lines in this figure, are a best fit of all data using a single set of Eyring parameters: \(\tau_{eq}^0 = 60.0\) MPa, \(\tau_0 = 2.2\) MPa and \(\mu = 0.09\) \([-\cdot]\). From Figure 8 it is clear that this single set of parameters accurately describes both yield and craze initiation. In our opinion, this is a strong indication that the rate-determining step in craze initiation is the formation of a localized plastic zone. The evolution and cavitation of these patches are either relatively fast or even time-independent processes.

CONCLUSIONS

It was illustrated how the combined action of nonlinear plastic flow behavior, strain hardening, and intrinsic strain softening can give rise to strain localization. It was argued that the initiation of strain localization is only determined by the yield process. The aim of this article was to investigate whether craze initiation can be envisaged as a plastic localization process, followed by (time-independent) cavitation of the deformed zones. An extremely brittle polystyrene grade was selected as a model material, to ensure that, during a fracture test, the time between craze initiation and macroscopic fracture is negligible small. A ball-ring test was used to minimize the effect of inhomogeneities on the fracture process. The strain rate dependence of the yield process was determined using plane-strain compression tests and uniaxial tensile tests under superimposed hydrostatic pressure. Expressing the results of these tests in equivalent quantities, it was shown that both fracture and yield have the same strain-rate dependence, which is described by one and the same Eyring process only. This is a strong indication that the occurrence of small deformation zones ("slip patches") is indeed the rate-determining step in craze initiation. The evolution of these microshear bands is determined by the combined action of constitutive behavior, and the local boundary conditions. Given a certain microstructure, the evolution of these slip patches can, in principle, be calculated using finite element methods, employing the detailed constitutive equation discussed in this article. This offers possibilities for defining a local craze-initiation criterion, by comparing these detailed finite element calculations with experimental craze studies. Such a local craze-initiation criterion is essential in computer-aided design of new heterogeneous polymer systems, where the morphology is optimized in such a way that shear yielding prevails crazing.

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