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Craze growth mechanics

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Abstract

Crazing is an important fracture mechanism in polymers. In this paper, crazes are treated as cracks bridged by fibrils. Fibril stresses are treated as external loads on the crack flanks. This perception of a craze allows an analysis in terms of linear elastic fracture mechanics. A "Paris law" type of crack growth behaviour is adopted and the two constants for the Paris equation are estimated. The results of the approach explain experimental results from the literature, including the well-known empirical logarithmic craze growth equation. The model prediction compares favourably with craze growth data, obtained by Wales on PVC. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Stress intensity factor; Paris low; Craze growth rate

1. Introduction

Crazes often represent the first stage of the fracture process in polymers. Crazes may initiate, grow into a real crack and eventually cause catastrophic fracture of the polymer, or they may, after their initiation and growth, slow down and finally arrest. An arrested craze may quite well be acceptable from a structural point of view. However, it still remains necessary to consider craze growth dynamics since it allows a prediction to be made, as to whether a craze will grow into a dangerous condition, or whether it will arrest under a given loading situation.

Craze growth studies have been published by many authors [1–25]. In these studies, many relevant observations have been reported and described mathematically. An example of such a mathematical description is the so-called logarithmic craze growth law for crazes, growing under long time constant stress conditions, as e.g. presented by Wales [1] and by Verheulpen and Bauwens [2]:

$$a = \beta \ln(t/t_i) \qquad \text{for } t > t_i. \tag{1}$$

In this equation, a is the craze length at time t, t is the loading time, t_i is the initiation time and β is the constant logarithmic growth rate (using a logarithmic time scale). Eq. (1) is valuable because it fits the craze growth behaviour of many glassy polymers under various loading conditions. However, a mechanistic explanation for Eq. (1) is lacking.

A craze is a rather complex feature. Fig. 1 shows a schematic representation of a craze, which has developed from a defect. The defect is assumed to be present in the polymer as produced, and may be associated with impurities. The exact nature of the defect is of no importance in the context of the present study. The craze is presented as a crack, partly bridged by fibrils, which extend between the crack flanks. The assumed initial defect is obviously not bridged. Rupture of the fibrils may also be a cause for the absence of bridging. Four individual and distinct damage processes at different locations along the craze can be identified:

1. The pure craze tip. This is the location where longitudinal craze growth takes place.
2. The fibrils, highly oriented polymer, experiencing a large true stress. This stress may promote fibril elongation due to creep.
3. The drawing zone, where fibrils are drawn from the bulk polymer.
4. The tip of the true crack, i.e. the site where the fibrils most remote from the tip may break. In this study, the true crack size corresponds to the size of the initial defect only, since fibril fracture is assumed to be absent. Nevertheless, the model is valid irrespective of the cause for non-bridging.

The area where fibril rupture occurs, has been studied by Brown [3]. He derived a mathematical description of the local fibril peak stress near the true crack tip, and subsequently draws conclusions on fibril breakage and the polymer fracture energy. He demonstrates the importance of the cross-tie fibrils. However, his elaborations do not take into account the other three damage processes. Consequently, the description is not complete and is not a suitable example

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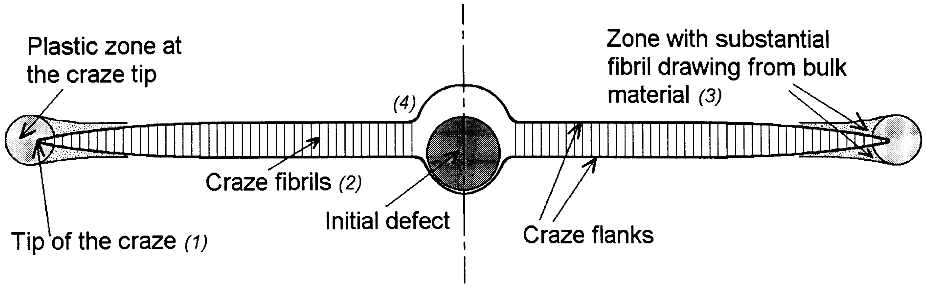

Fig. 1. Schematic representation of a craze, developed from a defect. The craze is envisaged as a crack, bridged by fibrils, except at the location of the initial defect.

for the prediction of craze growth rates. In more recent papers by Hui et al. [4], and Sha et al. [5,6], more detailed and accurate solutions are derived. However, the focus is still on fibril rupture only. Kramer and others devoted many studies to the drawing zone, [7,8]. Creep elongation of the fibrils has also been studied. Ward studied the creep behaviour of stretched polymers. This behaviour has been related to craze fibril creep. Some of such related publications are [9,10]. The pure craze tip has hardly been studied in detail in an isolated way, as far as known to the present author. A mechanistic study has been presented by Donald et al. [11]. However, practical tools for the prediction of craze growth rates were again not given. In the present study, and in contrast (and addition) to the previous work summarised above, the craze tip is considered to be the dominating location. The other damage areas and processes are incorporated in the present model, but only to the extent that they influence the local loading state at the craze tip. The results of the present model will be compared to experimental craze growth studies performed on PVC by Wales [1].

2. Fracture mechanics modelling

A craze may be considered as a crack, loaded by a remote, externally applied stress and by a stress acting on the crack flanks due to the presence of stretched craze fibrils. This perception of a craze allows an analysis of craze dynamics in terms of conventional fracture mechanics, where the crack flank stresses may be treated as external loads. A simple two-dimensional (2-D) analogue of this perception of a craze is outlined in Fig. 2. This approach allows to describe the highly complex loading state at the crack tip with one parameter only: the stress intensity factor K! K is, in general, a unique crack tip loading parameter. In the present context, it is a unique craze tip loading parameter. Moreover, the model does not need an assumption with respect to the mechanical properties of the crazed material, such as the assumed ideal elastic–plastic craze behaviour in the Dugdale model [9]. The solution for K, including the effect of the average crack flank stress (total fibril force divided by crack flank area) caused by the fibrils, for this 2-D case can be found in standard text books, in Ref. [26]. It is given by the following equation:

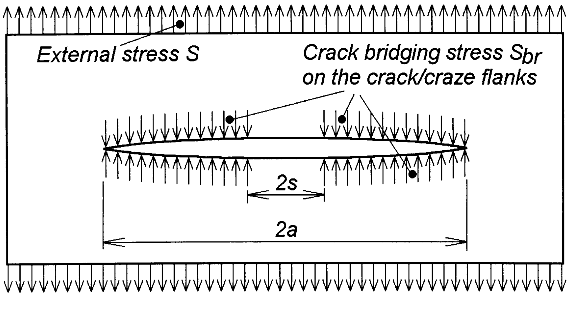

Fig. 2. Loading system for a craze, modelled as a partly bridged crack.

$$K = S\sqrt{(\pi a)} - 2S_{\mathrm{br}}\sqrt{(a/\pi)}\,\arccos(s/a). \qquad (2)$$

In this equation, K is the stress intensity factor, including the effect of the craze fibrils, a is half the craze length, s is half the length of the non-bridged area, S is the applied external stress, and S_{br} is the average (smeared out) fibril stress on the crack flanks. The non-bridged area s may be due to the fibril breakage during growth of the "true crack". However, in the following it will be considered to be half the extension of the initial defect from which the craze initiated. Fibrils are not present within the initial defect, due to the very nature of a defect.

Eq. (2) has been applied successfully by the present author [27–29] in predicting crack growth of ARALL® laminates, with cracks in aluminium sheet material, bridged by non-broken aramid fibres. These laminates also comprised a non-bridged area, e.g. a bore hole or a saw cut was present as an initial defect.

The stress intensity factor K is a unique loading parameter for a crack tip and, provided that the fibril stresses are accounted for, also for a craze tip, if the conditions for applicability of linear elastic fracture mechanics are fulfilled. Fibril stresses are accounted for in the stress intensity factor K by the presence of the arccos-term in Eq. (2). The applicability condition of linear elastic fracture mechanics requires small scale yielding at the crack tip, e.g. the dimensions of the yielding zone must be much smaller than the crack length and the length of the remaining ligament. For a pure and uniformly applied tensile stress,

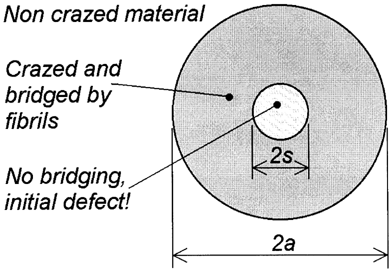

Fig. 3. Schematic illustration of a circular craze, starting from a circular defect, modelled as a partly bridged crack.

small scale yielding may be checked with a crude rule of thumb: small scale yielding is present, if the applied stress is smaller than 0.6 times the polymer yield stress, and K may be applied without any modification. If the stress is larger, but does not exceed 0.8 times the yield stress, the use of K becomes inaccurate, but may remain applicable qualitatively. Eventually a plastic zone size correction like Irwins correction [30] may be applied for better accuracy. Crazes in polymers may occur within the region requiring a plastic zone correction for accurate results, but in practice conditions the applied stress will usually be below 0.6 times the yield stress. However, even if such a correction is not applied at higher stress levels, the results remain valid in a qualitative way. A plastic zone correction will not be applied in this paper, for reasons of mathematical simplicity, though there is no fundamental difficulty to include it in the model. Moreover, the following sections show that the absence of such a correction does not obstruct an illustrative description of craze growth behaviour. It should be noted in the present context, that plasticity means “irreversible” non-linear deformation. The crazing process itself is often considered as a plasticity mechanism. Here, all relevant effects of the craze (fibril stresses) are explicitly considered, e.g. by the arccos term in Eq. (2), so non-linear material behaviour due to crazing is excluded from small scale yielding and stress intensity validity considerations.

The stress intensity factor K is a linear elastic concept. Polymers are generally considered to exhibit visco-elastic behaviour. Nevertheless, as long as the polymer shows linear visco-elastic behaviour, the stress intensity factor K can still be applied in a rigorous way. This can be understood from the fact that Young’s modulus does not even appear in the crack tip stress field equations related to the stress intensity factor K. Hence time dependency of Young’s modulus does not occur either and linearity is important only. A good introduction to the basics of fracture mechanics is presented by Tada et al. [26], or by Broek [31].

Eq. (2) describes a 2-D craze situation. However actual crazes occur in a three dimensional (3-D) environment. A model situation much closer to the reality of a craze, is a circular craze, initiated from a circular (spherical) defect in a large solid under tensile stress. This situation is outlined in Fig. 3.

The stress intensity factor K for Fig. 3 can also be found in standard text books, e.g. Tada’s book [26], and is given by Eq. (3):

$$K = 2S\sqrt{\frac{a}{\pi}} - 2S_{\mathrm{br}}\sqrt{\left(\frac{a}{\pi}\right)\left\{1-\left(\frac{s}{a}\right)^2\right\}}. \tag{3}$$

In the remainder of this paper, the 3-D situation, described by Eq. (3) will be considered. The stress intensity factor K quantifies the loading state at the craze tip. Consequently, the craze growth rate can be described as a function of K only. The relation must be of a type as observed for true cracks, because the effect of the craze fibrils is already accounted for by the right-hand side of Eq. (3). Publications describing the creep (true) crack growth rate in polymers as a function of K are rather rare. Only some publications are found in Refs. [32–39]. These investigations are almost completely devoted to PE and PMMA. They indicate that the material behaviour can be fitted with a Paris [40] type equation, over a large range of K and $\mathrm{d}a/\mathrm{d}t$ values:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = CK^n. \tag{4}$$

Here $\mathrm{d}a/\mathrm{d}t$ is the (true) crack growth rate on a linear scale, unlike β in Eq. (1), which is defined on a logarithmic time scale, which makes craze growth according to Eq. (1) actually time dependent. C and n are material properties, which depend on temperature, but not on stress. A Paris type equation for the sub-critical crack growth rate, as a function of a fracture mechanics loading parameter has been found for many materials, metals [40], polymers [32–39], and ceramics [41] under various types of loads. Of course, C and n are dependent on the type of load (static or fatigue), the temperature, environment and material. Fett [41] related Eq. (4) for creep rupture of ceramics to the Lennard–Jones potential of the covalent bonds in ceramics. For polymers, the potential of weak inter-chain bonds would be the relevant potential. The small value of the inter-chain potential would explain the observed strong dependency of, especially, C on the temperature [37], and on the eventual presence of solvents, like benzene vapour in a number of experiments described by Wales [1]. The choice for the weak interaction inter-chain potential would also be consistent with the meniscus like micro-morphology at the craze tip, as proposed by Donald et al. [11]. Further elaborations on the physical background of Eq. (4) are interesting, but beyond the scope of this paper.

Substitution of Eq. (4) in Eq. (3) gives:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = C\left[2S\sqrt{\frac{a}{\pi}} - 2S_{\mathrm{br}}\sqrt{\left(\frac{a}{\pi}\right)\left\{1-\left(\frac{s}{a}\right)^2\right\}}\right]^n. \tag{5}$$

Integration of Eq. (5) with appropriate boundary conditions

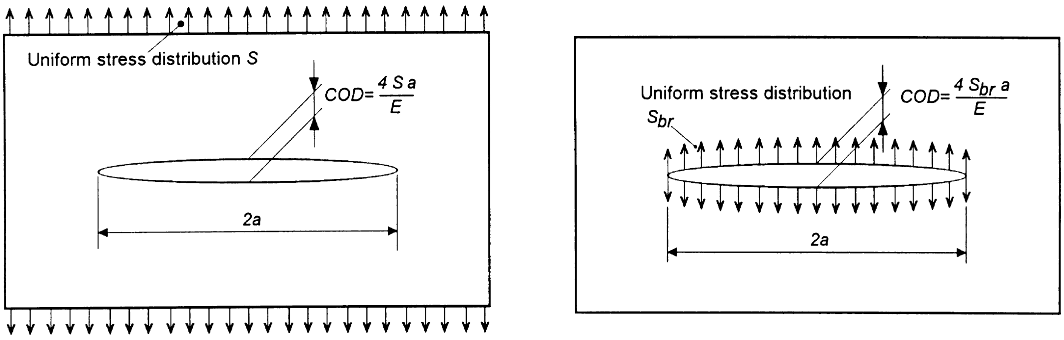

Fig. 4. COD equivalence for external and crack flank stresses.

directly after the onset of craze growth yields:

$$a = s + C \int_{t_i}^{t} \left[2S\sqrt{\frac{a}{\pi}} - 2S_{\mathrm{br}}\sqrt{\left(\frac{a}{\pi}\right)\left\{1 - \left(\frac{s}{a}\right)^2\right\}} \right]^n \mathrm{d}t, \quad (6)$$

where t_i is the time for craze initiation ($t > t_i$).

3. Determination of model parameters

The model given above contains four parameters, which have not unambiguously been determined as yet:

1. the size of the initial defect s;
2. the fibril bridging stress S_{br};
3. the material constants C and n;
4. the initiation time.

The size of the initial defect s can in principle be measured, using a microscope. Several published fracture surfaces [12,15,16,19], and numerous personal unpublished observations suggest that initial defects with a size of around 50 μm are common in polymers. However, not all authors mention the defects explicitly. An average order of magnitude of about 50 μm will be adopted here. Further, the defect size s will be treated as a variable in the following considerations. It will also be assumed that this is the only area without fibril bridging. The situation after first fibril fracture (increase of s) will consequently not be addressed in this study.

Measuring the fibril bridging stress S_{br} is difficult. Nevertheless, substantial experimental information is available. Several publications [4–6,18] refer it to a fibril drawing stress. Consequently, the smeared out average bridging stress in a craze is assumed to be about equal to the drawing stress during necking in a tensile specimen. Indeed, "fibrils necking from the bulk" is a plausible scenario and might therefore be adopted. Riemslag [17] attempted to measure the fibril stresses at a tip craze more or less directly. His results confirm the drawing stress scenario for relatively short tip crazes. However, for crazes substantially longer than the size of the initial defect, and bridging stresses larger than the applied stress, the physically impossible situation arises that the force transfer along the craze flanks becomes larger than the remote force transfer. This of course violates force equilibrium. Consequently, the smeared out bridging stress for long crazes must be lower than the drawing stress. The only solution is to conclude that the drawing stress occurs only at a small region behind the craze tip, where active fibril drawing occurs. The bridging stress at a larger distance will be slightly lower than the tensile stress S. This is consistent with the results obtained on ARALL® laminates [27–29], mentioned before, in the case that the bridging fibres (here fibrils) have a rather high stiffness. A further argument to motivate that S_{br} is about equal to S, is presented below.

For an unbridged crack, the crack opening displacement at the crack centre COD is known from continuum mechanics:

$$\mathrm{COD} = \frac{4Sa}{E}, \quad (7)$$

where E is Young's modulus and S and a are defined as above. The same equation is valid for a crack opening stress on the crack flanks (see Fig. 4). Superposition and sign reversal yields the COD for a bridged crack (denoted as $\mathrm{COD}_{\mathrm{br}}$) and a crack closing stress on the crack flanks (and $s \ll a$):

$$\mathrm{COD}_{\mathrm{br}} = \frac{4a(S - S_{\mathrm{br}})}{E}. \quad (8)$$

Combination of Eqs. (7) and (8) yields:

$$\frac{S_{\mathrm{br}}}{S} = \left(- \frac{\mathrm{COD}_{\mathrm{br}}}{\mathrm{COD}} \right). \quad (9)$$

A rough estimation, based on typical values for a polymer such as PVC, as applied by Wales [1], namely a craze length of 0.3 mm, a Young's modulus of 1.5 GPa (short term measurement, long term value may be even lower), and a tensile strength of 30 MPa, yields a COD of 0.025 mm. The thickness $\mathrm{COD}_{\mathrm{br}}$ of crazes observed in reality is much smaller. A fracture mechanics estimation by Breen [21] yields a critical opening between 0.003 and 0.0125 mm. Actual crazes in the long term are non-critical and, consequently, are even thinner. A micrograph of a long term craze, presented by Breen et al. (Fig. 2 of Ref. [22]) allows a rough estimation by measurement. A craze thickness of about 0.003 mm, or even smaller is observed. Other published micrographs [23] on long crazes also indicate an extremely small thickness. Consequently, it must be concluded that in accordance with Eq. (9), $S_{\mathrm{br}} \approx S$ with a quite reasonable accuracy! Actually, equating $S_{\mathrm{br}} \approx S$ over the entire craze length except for the distance crossed by the initial defect is a schematic stress distribution which is quite similar to distributions presented elsewhere [7,13–15]. Obviously, fibril drawing and the associated relatively high drawing stress in these fibrils, remains limited to the region closely behind the craze tip. Consequently, long crazes show a large area of more or less “inactive” static fibrils, bridging the craze flanks.

Adopting $S_{\mathrm{br}} = S$ simplifies the previous Eqs. (3), (5) and (6) to:

$$K = 2S\sqrt{\frac{a}{\pi}}\left\{1 - \left(\frac{s}{a}\right)^2\right\} \qquad (\text{with } a \geq s), \tag{10}$$

$$\frac{\mathrm{d}a}{\mathrm{d}t} = C\left[2S\sqrt{\frac{a}{\pi}}\left\{1 - \sqrt{1 - \left(\frac{s}{a}\right)^2}\right\}\right]^n, \tag{11}$$

$$a = s + C\int_{t_i}^{t}\left[2S\sqrt{\frac{a}{\pi}}\left\{1 - \sqrt{\left(\frac{s}{a}\right)^2}\right\}\right]^n \mathrm{d}t. \tag{12}$$

The material constants C and n can be obtained by fitting to true crack growth experiments in, ideally, uncrazed polymers. Unfortunately, the experiments reported in the literature were obtained on cracks which probably contained a tip craze, thereby including some bridging already. Nevertheless, if the tip craze is small compared to the total crack length, C and n can be estimated with reasonable accuracy. This also means that the so-called threshold region at low stress intensity factors (and therefore long tip crazes) should not be considered for determining C and n.

Only a limited amount of publications exist, which explicitly deal with true crack growth experiments, suitable for obtaining C and n for creep crack growth in polymers [32–39]. Moreover, almost all reported experiments were performed on PE or PMMA. Stern and Stern et al. [32–34] present rather detailed data for these polymers. Those results indicate values of $n \approx 2.2$ for PE and $n \approx 2.5$ for PMMA. These values were obtained by fitting the data with Eq. (4), but excluding all data being within the threshold range as indicated above, as well as the range of large stress intensities where the critical value for the unstable growth is approached.

The model results will later be compared with craze growth results obtained by Wales on PVC [1]. Since PVC and PMMA are both amorphous polymers and therefore more similar than PVC and PE, the n-value, $n \approx 2.5$, obtained for PMMA will be adopted as a model constant. The difference between $n \approx 2.2$ and $n \approx 2.5$ is small anyhow.

The constant C for PMMA can also be obtained from the data of Stern [32–34]. A value of $C = 2 \times 10^{-4}$ is obtained. Again the difference with PE is not large. (Note dimensions taken for K and $\mathrm{d}a/\mathrm{d}t$ are MPa $\mathrm{m}^{1/2}$ and in mm/s, respectively). The dimension of C is dependent on the value of n. A physical discussion of this peculiarity of Eq. (4) is beyond the scope of this paper. The Paris equation is treated here as a fit. Depending on the testing conditions, the constants C and n can vary with polymer type, temperature and environmental conditions. In later model predictions therefore, the constants C and n will be varied, to study their effect on craze growth predictions.

The initiation time does not directly result from a particular growth law. From the experiments by Wales [1], it can be inferred that the initiation time is often quite small compared to the time elapsing during craze growth. Many material failure initiation times can be fitted with a Manson–Coffin type equation [42,43]. A modified Manson–Coffin type equation will be postulated here as a fit, and has the form:

$$t_i = DS^{-m}, \tag{13}$$

where t_i is the craze initiation time and D and m are material properties >0. Eq. (13) with a positive value for the parameter m, reflects the fact that the initiation time will be shorter for higher applied stress levels S. It shows some similarity to an equation presented by Lang et al. [33]. It might be that the physical processes of growth and initiation are related. A pure relation (identical physical processes, only different in length-scale) would imply that $m = n$. An estimation from Fig. 2 in the publication by Breen and van Dijk, for craze initiation in PVC loaded in air [24], yields a value of $m = 11$. This value is quite different from the value for n ($n = 2.5$) adopted before. This suggests that the physical processes of initiation and growth of crazes are probably rather different. However, explanations for a possible difference are beyond the scope of this paper. From the data by Breen and van Dijk [24], the empirical fitting parameter D is found to be about $D = 8 \times 10^{20}$ (dimensions for stress and time are MegaPascal and second, respectively. The dimension of D shows a similar peculiarity as mentioned before for C. This will not be discussed here). This value provides a quite good fit to the average data for initiation in air. The figure in Ref. [24] showing the initiation data contains a considerable scatter. The size of the initial defect may be expected to influence the initiation time, scatter in size of the defects could explain the data scatter. However, a defect size effect on the craze initiation is not incorporated in Eq. (13), because no indications could be found regarding the magnitude of the effect. Anyhow, since the initiation time is typically much shorter than the craze growth period (note the logarithmic time axes in Ref. [1]), a high accuracy is actually not required for Eq. (13). Moreover, initiation is not the main subject of the present study. Its influence becomes manifest only by the usual choice of a logarithmic time scale in the available experimental data. Some consequences of

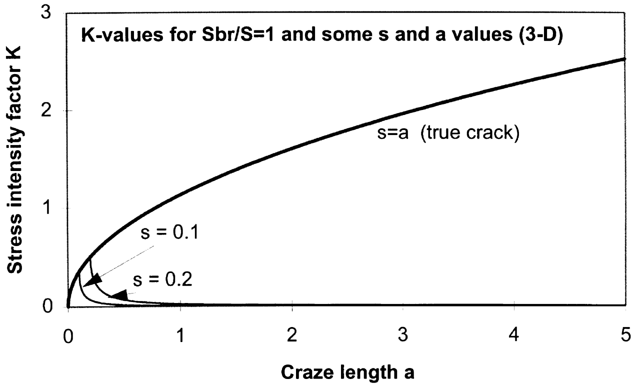

Fig. 5. Illustration of the effect of fibril bridging on the stress intensity factor K, Normalised to $S = 1$, for $S_{br} = S$, and for two values of the initial defect s. (Note that the curves for $s = 0.1$ and $s = 0.2$ do not start at $a = 0$, but at $a = 0.1$ and $a = 0.2$, respectively.)

the logarithmic time scale will be discussed later in more detail.

4. Some calculations

The behaviour of the model for K, as given by Eq. (3), has been studied systematically, by varying the ratio of S_{br}/S and by varying the size s of the initial defect and the craze length a. The results are presented in Figs. 5–8. The figures have been normalised by setting the applied stress level $S = 1$. The dimensions in Figs. 5–8 are arbitrary.

The most realistic scenario $S_{br} \approx S$ is presented in Fig. 5. The figure also shows the stress intensity factor for an unbridged craze (true crack), for which of course $s = a$. From the curves it is apparent that:

- Crack bridging is highly effective in reducing the stress intensity factor at the craze tip.
- The stress intensity factor decreases with increasing craze length. Consequently the craze growth rate is expected to decrease (on a linear scale)!
- The size of the initial defect remains important for the stress intensity factor (and thus craze growth rate) during the entire craze growth life (Figs. 5 and 7), except when $S_{br} < S$ (Fig. 6).

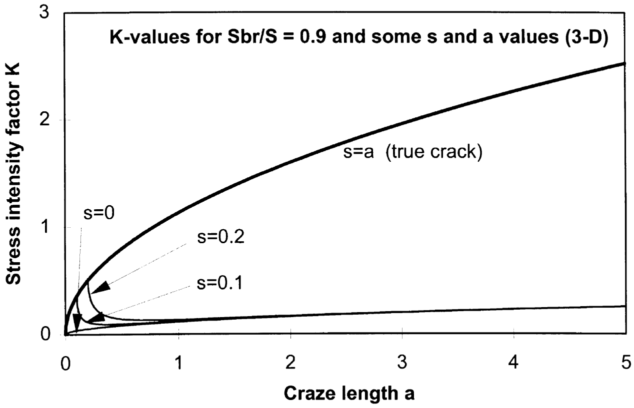

Fig. 6. Illustration of the effect of fibril bridging on the stress intensity factor K, Normalised to $S = 1$, for $S_{br} = 0.9S$, and for two values of the initial defect s. (Note that the curves for $s = 0.1$ and $s = 0.2$ do not start at $a = 0$, but at $a = 0.1$ and $a = 0.2$, respectively.)

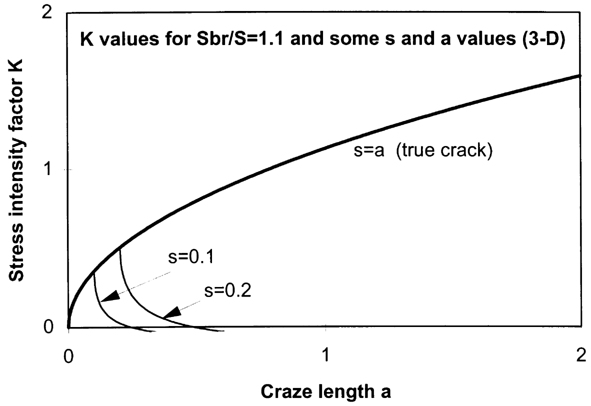

Fig. 7. Illustration of the effect of fibril bridging on the stress intensity factor K, Normalised to $S = 1$, for $S_{br} = 1.1S$, and for two values of the initial defect s. (Note that a crack (craze) is closed for a calculated value $K < 0$. The physical result should than be interpreted as $K = 0$.)

Fig. 6 shows the situation for an average bridging stress being slightly lower than the external stress. Bridging is still extremely effective. However, it can be seen that after an initial decrease, the stress intensity factor increases again at large craze lengths. The effect of the size of the initial defect disappears now, if the craze is several times larger than the defect.

Fig. 7 shows a situation for an average bridging stress being slightly larger than the external stress. Now the stress intensity will become zero after some craze growth, and the craze is expected to stop growing.

The stress intensity factors as displayed in Fig. 5, can be used to predict craze growth rates according to Eq. (4). Fig. 5 displays what is also evident from Eq. (10), The stress intensity factor decreases continuously during further craze

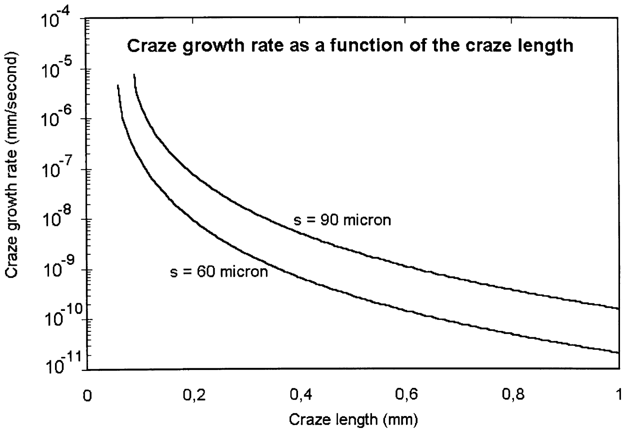

Fig. 8. Predicted craze growth rate as a function of craze length for two values of the initial defect.

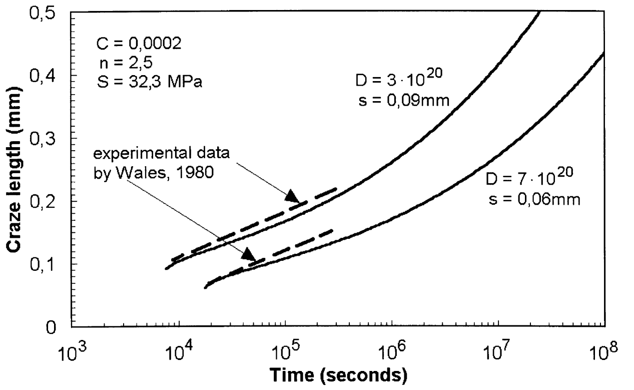

Fig. 9. Predicted craze growth as a function of time, together with the experimental results of Wales (1980, broken lines), for $S = 32.3$ MPa.

growth, but it never does reach zero. Its value remains positive, and the size of the initial defect remains important during the entire craze growth life (the last statement is not visible anymore in Fig. 5, but is clear from Eq. (10)).

Fig. 8 displays the craze growth rate (note, logarithmic scale) as a function of the craze length, calculated according to Eq. (4) and the constants C and n found for PMMA, for the case where $S_{\mathrm{br}} = S$. Two values of the initial defect size s are assumed: 60 μm (0.06 mm) and 90 μm.

It is easily observed from Fig. 8 that the size of the initial defect remains important, also for craze lengths much larger than the initial defect length. This is typical for a bridged crack situation; i.e. for a craze. Pure cracks "forget" the effect of the initial defect rapidly. It can also be seen in Fig. 8 that the craze growth rate decreases continuously with increasing craze length. This seems to be in contrast with the constant logarithmic craze growth rate law as presented in Eq. (1). This apparent contrast is discussed below.

A numerical integration of Eq. (12), with the constants derived before, yields the craze length as a function of time. In the Figs. 9 and 10, the model prediction is compared to experimental data from Wales [1], taken from Fig. 4 in Ref. [1]. A logarithmic time scale has been used as in Ref. [1]. The procedure was as follows: Wales presents two data series, for craze growth at stress levels of 32.3 and 42 MPa. For both stress levels, the model value for the initial defect is chosen equal to the craze length of the first data point of the respective data series. This presupposes that Wales observed the crazes shortly after their initiation, when craze growth was still small. The result is that two values for the initial defect size s are presented in Fig. 9: 0.06 and 0.09 mm. The initiation parameter D was fitted in such a way that the craze initiation time in the model coincides with first experimental data point (similar choice as for the defect size). This variation of the initiation parameter D from the earlier obtained value $D = 8 \times 10^{20}$ was well within the range of experimental scatter observed in Ref. [24]. After equalising the initiation conditions to those of the experiments, the craze growth was modelled entirely with the craze growth equations discussed above and the growth characteristics obtained for PMMA as discussed before. The same procedure was followed for Fig. 10.

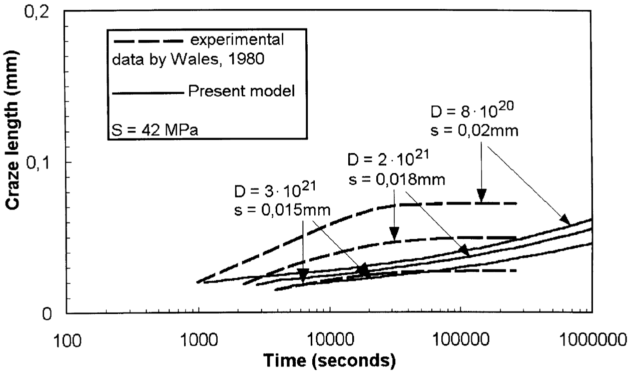

Fig. 10. Predicted craze growth as a function of time, together with the experimental results of Wales (1980), for $S = 42$ MPa.

The model data in Fig. 9 agree quite well with the experimental results of Wales, indicating the validity of the present model. The agreement in Fig. 10 is only moderate. However, the stress of 42 MPa is close to the polymer yield stress. Wales even reported necking at 3×10^5 s. The validity limits of fracture mechanics is discussed at the beginning of this paper. Necking means that the yield stress is surpassed, so the rough validity criteria, a stress smaller than 0.6 times the yield stress, or 0.8 times if a correction for plasticity is applied, are both violated. Considering this violation, the moderate and only qualitative agreement to the experimental date should instead be considered as surprisingly good.

It is further observed from Fig. 9, that after a craze has been initiated, an almost linear behaviour is predicted over a long time range (more than two decades)! This corresponds exactly with the experimentally observed behaviour from which the logarithmic growth rate law of Eq. (1) was concluded. It should be noted that the almost linear behaviour is obviously a consequence of opposing trends of decreasing craze growth (as demonstrated in Fig. 8) and a "compression" of the right part of the curve due to the choice of a logarithmic time axis, rather than the result of a logarithmic physical time dependent damage process in the material. The predicted curves in Fig. 9 are extended to a much longer time than available for the experimental data. The predictions indicate that the experimental trends may be expected to remain similar during much longer times than investigated. Only a slight increase in the logarithmic craze growth rate β with time is predicted beyond the experimental range. The crazes remain stable as long as the relevant conditions remain similar, in other words, as long as the fibrils remain intact.

The difference in the experimental results obtained for two growing crazes in the same material and loaded at the same stress, can obviously be explained by a difference in

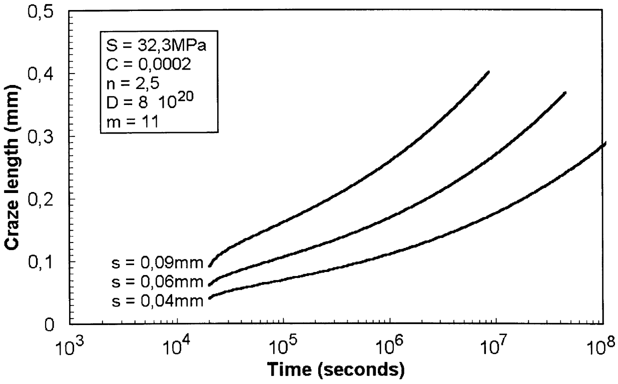

Fig. 11. Predicted effect of the size of the initial defect.

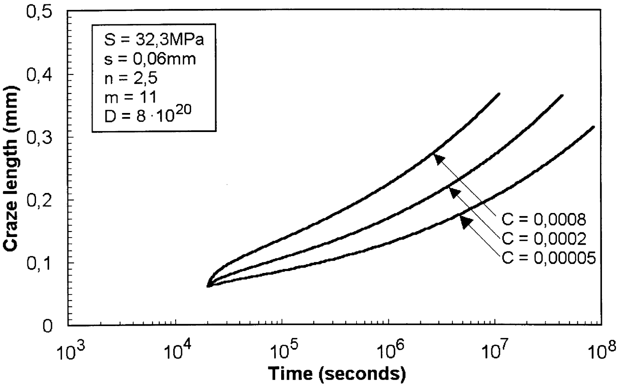

Fig. 13. The theoretical effect of the craze growth material constant *C*.

the initial defect size for the two crazes. This is shown in Fig. 11, for both crazes of Fig. 9, and for a smaller one, but now, all three with the same initiation time. Obviously, the size of the initial defect remains important during the entire craze growth life. Moreover, the "predicted" logarithmic growth rate law results in a β being about proportional to the size of the defect for the three crazes. In Fig. 9, β was about the same for the different defect sizes, similar to the experimental observation. The explanation is that on a logarithmic scale, β is influenced by the initiation time, which on its turn will be influenced by the defect size. Consequently, the experimentally observed trend of a constant β for different crazes loaded under the same stress should be considered as more or less coincidental, in view of the different consequences of initial defect size on craze initiation and growth on the one hand, and the pure presentation effect of the choice of a logarithmic time scale on the other hand. Moreover, a physical process referring to a constant β was not at all adopted in the equations. Consequently, the logarithmic growth rate law must be considered to be a kind of mathematical coincidence. Considering the fact that the "linearity" of the growth behaviour is a mathematical coincidence, it is interesting to vary some other model parameters and observe the ensuing differences in behaviour.

Fig. 12 shows the predicted effect of a change in craze initiation sensitivity, modelled by varying the parameter *D* in a systematic way. The effect is only visible at the beginning of the curves. The curves coincide at large time values. This is again an effect of the logarithmic horizontal axis, and of the fact that the craze growth life is much longer than the initiation life. Apparently, β (as it would be approximated from an experimental programme, covering only the first time decades of craze growth) is larger for long initiation lives. However, as discussed before, the craze growth rate is not really affected. Consequently, the larger β is a misleading result of later initiation and larger "compression" at the right-hand part of the logarithmic time axis.

The effects of a variation of the model parameters *C* and *n* and of the applied external stress *S* are shown in Figs. 13–15, respectively.

Fig. 13 demonstrates the effect of a variation of *C*. A 16-fold increase of *C*, causes a factor two larger predicted craze length in the beginning of the curve, and about 50% increase of the craze length at the right part of the curve at long times. Obviously, the predicted craze length is hardly influenced by *C*. However, a factor of about 16 is found again if the time difference is observed at the same craze length.

Fig. 14 shows the effect of the exponent *n*, again the effect is limited, especially in the first (left-hand) part of the curves. The moderate effect of *C* and *n*, observed, gives (at last) an additional indication as to why the crude way of estimating them (adopting PMMA data) still allows for

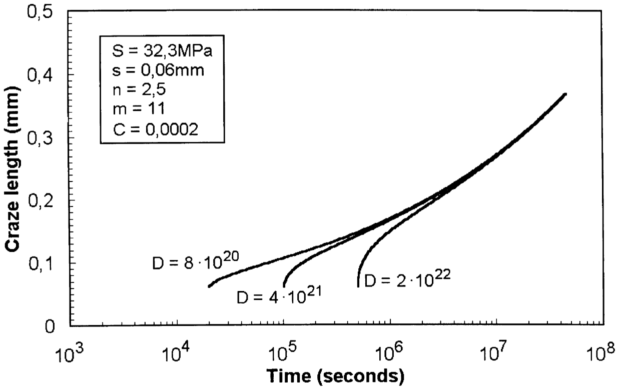

Fig. 12. The theoretical effect of sensitivity to craze initiation.

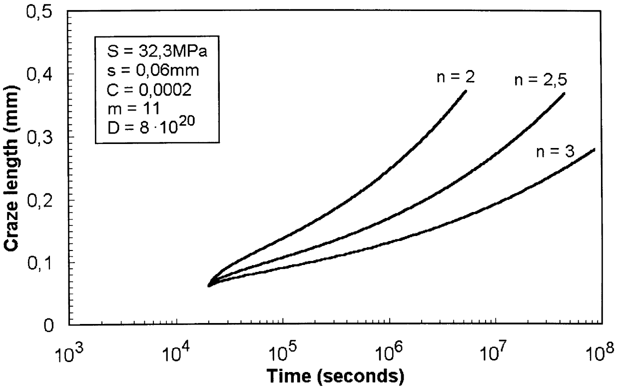

Fig. 14. The theoretical effect of the craze growth material constant *n*.

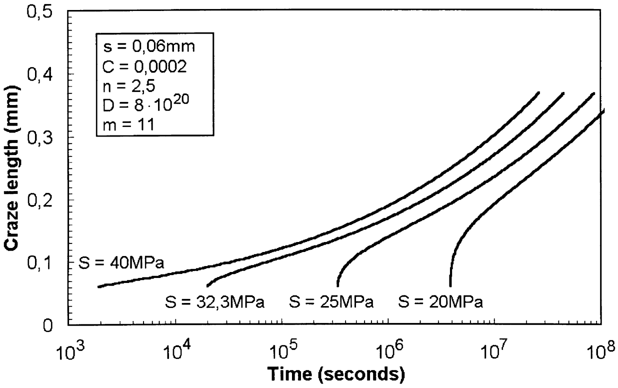

Fig. 15. The theoretical effect of a variation of the external stress *S*.

the acceptable prediction result as demonstrated in Fig. 9. Obviously, the character of the equations, together with the traditional choice of a logarithmic time axis, makes the result rather insensitive to variations of material constants.

Fig. 15 shows seemingly strange behaviour. The slope of the curves increases with a decreasing stress. In other words, a decreasing stress is related to an increasing logarithmic craze growth rate β! Consequently, a first impression may be that crazes grow faster for lower stresses. However, this is not the case. It is again the consequence of the distortion by the logarithmic time axis and the fact that craze initiation is more sensitive to the stress level than craze growth, because $m > n$, ($m = 11$, and $n = 2.5$). The shift to the right-hand side on the logarithmic axis is larger for the lower part of the curves than for the upper part. Discussions with Struik [44] revealed that unpublished experimental data, obtained by TNO in The Netherlands, indeed show an increasing β with a decreasing stress. The present results show that it is useless to try to explain the apparent faster craze growth rate (larger β) at lower stresses. It is simply just not faster, but only looks faster due to the chosen logarithmic time axis.

5. Discussion and conclusions

It was demonstrated in the previous chapters that a craze may be considered as a crack, loaded by an external stress and by fibril stresses applied on the crack flanks. This allows the use of fracture mechanics. Both stress systems together result in a stress intensity factor which can be used to obtain the craze growth rate. Constitutive equations translating a stress intensity factor to a crack growth rate were not found for PVC (for which experimental craze growth data are available). Therefore PMMA data were used, arguing that PVC and PMMA are similar enough to make PMMA data acceptable. A plausible value for the size of the initial defect was adopted. Fracture mechanics on crazes has been used earlier [9]. Although, always in a Dugdale type of approach. This means that it has been argued that the stress intensity factor at a craze tip, including (all) non-linearities, is always zero, because nature does not show singularities. Then all non-linearity is attributed to the fibril bridging mechanism and the stress intensity factor has been taken to be zero, allowing the calculation of the fibril stresses or bridging distance. Usually the 2-D Eq. (2) or a simplification of it has been used with $K = 0$ for this type of approach. The difference with the present approach is clear: the bridging distance and the average bridging stress are determined at the beginning and the stress intensity factor is subsequently calculated. The stress intensity factor determines the plastic zone size at the crack tip. In a more general analysis, the stress intensity factor determines the size of the zone in which with various types of non-linear physical processes occur. However, for the present model, crazing is not included in these processes, because it is explicitly taken into account. That leaves true plasticity and viscous processes as processes occurring in the "plastic zone" related to the stress intensity factor resulting from the present model. For small scale yielding conditions, where the use of a stress intensity factor is valid, the processes will be directly related to that plastic zone size, and consequently to the stress intensity factor. Such processes will be related to the growth behaviour of the craze, which is consequently related to the stress intensity factor. Moreover, a 3-D Eq. (3) is applied in the present model. This equation is more accurate for the real craze geometry, although the small effect of the free edge on the stress intensity factor of surface crazes is still neglected. Summarising, it can be stated that the "switch" from the often applied Dugdale approach to the present explicit calculation of the stress intensity factor is useful indeed. This is also confirmed by the observation that the craze growth model results agree reasonably well with the experimental results described by Wales.

Wales performed most of his experiments in the presence of benzene vapour. Benzene influences the material behaviour significantly. The present model could be adapted to the modified material by finding the appropriate values (especially *C* and *n*) for the altered material constants, and including the effects of a gradient of the benzene content (decreasing away from the surface). This will not be pursued here. The presently available information is unfortunately insufficient for PVC containing benzene. Consequently, a confrontation of the present model with experimental results could only be performed for the few data for crazes growing in air. Nevertheless, a good agreement with those data is observed.

The present model allows to indicate possible ways for improving the crazing resistance of polymers. An obvious way would be to improve the crack growth resistance of the polymer, e.g. by developing materials with small values of the constant *C*. Large improvements will be necessary to obtain a significant shift to the right on the logarithmic time axis. An improvement of the craze initiation behaviour (e.g. an increase in *D*) is almost useless. The initiation time is too short as compared with the time spent during the growth of the craze. A very effective way to improve the material is to reduce the size of the initial defect, by the production of clean polymers. Figs. 9 and 11 show a significant reduction of the craze length, during the entire loading time, obtained with only a moderate reduction of the size of the initial defect.

Of course the most important condition is the situation adopted here from experience. It is the fact that for natural craze growth in PVC, all fibrils stay intact during craze growth. Fibril fracture will instantaneously cause a significantly increased stress intensity factor (as if the initial defect size were larger) and consequently the craze growth rate will also increase considerably. Polymers for which the craze fibrils are strong and durable are highly preferred, because while fibrils remain intact, a continuing deceleration of the craze growth rate (on a linear scale) will occur.

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