Lifetime Assessment of Load-Bearing Polymer Glasses: The Influence of Physical Ageing

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The timescale at which ductile failure occurs in loaded glassy polymers can be successfully predicted using the engineering approach presented in a previous publication. In this paper the influence of progressive physical ageing on the plastic deformation behaviour of unplasticised poly(vinyl chloride) (uPVC) is characterised and incorporated in the existing approach. With the modification it is possible to quantitatively predict long-term failures which show a so-called endurance limit. The predictions are compared with failure data of uPVC specimens which were subjected to constant or dynamic loads. In dynamic loading conditions a second type of failure mode was observed: fatigue crack growth. A brief study on the influence of the frequency and stress ratio of the applied stress signal shows that crack growth failure is not expected to occur within experimentally reasonable timescales for constant loading conditions.

Introduction

Since the 1950s polymer pipes have been installed in water and gas distribution systems throughout the world. The same holds for the Dutch gas distribution network, in which a significant number of polymer pipes has been installed in the first decade after the discovery of the Slochteren gas field in 1959. The service life of these pipes was initially specified to be 50 years. This means that replacement based on the time a pipe has been in service will lead to the renewal of thousands of kilometres of pipelines in the near future. Since replacement of these distribution systems is labour intensive, its postponement will result in huge economic savings for society. On the other hand, the integrity of the network should not be compromised, especially in the case of gas distribution networks where failure can lead to life threatening situations.[1,2] Consequently, the prediction of the residual lifetime of polymer pipes has received considerable attention (see, e.g. [3–6]). As the lifetimes of the pipes can exceed 50 years, accelerated tests have been developed to determine the lifetime based on short-term tests. The most well known tests used for this purpose are experiments where the failure time of a pipe segment that is subjected to a constant internal pressure is measured. The lifetime is estimated by extrapolating the time-to-failure measured at testing conditions (mostly at elevated temperatures) towards a reference condition according to a method described in ISO 9080. A typical result is shown schematically in Figure 1 (left). In general three regions can be observed with each having different failure mechanisms.[7,8] In the high stress region (region I) the pipe segment shows a considerable amount of plastic deformation before failure. The pipe bulges until the tensile...
The stabilisation of uPVC and the influence of distribution networks in the Netherlands. Increased knowledge of unplasticised poly(vinyl chloride) (uPVC) pipes, which have been used extensively in the gas, water and sewer networks, has led to prolonged region III and region II failure times. As a result, the long-term behaviour of the pipes is improved significantly and region I failure has become the limiting region for a wider range of failure times. The predictive approach for region I failure as presented in a previous paper has led to prolonged region III and region II failure times. As a result, the long-term behaviour of the pipes is improved considerably and region I failure has become the limiting region for a wider range of failure times. The predictive approach for region I failure as presented in a previous paper is based on the hypothesis that the polymer fails when the accumulated plastic strain reaches a critical value and the polymer enters its softening regime. This approach proved successful in quantitatively predict long-term failure of pipes subjected to a constant internal pressure as shown in Figure 2 (left). Remarkably, the predictions not only hold for the ductile failures, but also for pipes which failed as a result of hairline cracks. This is in line with the statement of Niklas and Kausch von Schmeling that slow crack growth did not significantly contribute to the failure time of the PVC pipes they subjected to an internal pressure. Based upon the experimental observation that all failure modes showed similar circumferential strain behaviour up to failure, they stated that all failure modes followed a common path up to failure. Where Niklas and Kausch von Schmeling modelled the complete viscoelastic creep behaviour to predict failure for pressurised pipes, it was demonstrated that capturing the secondary creep alone is sufficient for quantitative failure predictions.

Here, the hypothesis is posed that the transition from ductile failure towards hairline cracking is caused by time-dependent changes in the mechanical properties of uPVC as a result of physical ageing. This phenomenon finds its origin in the fact that glassy polymers like uPVC are not in a state of thermodynamic equilibrium, but display a continuous strive towards it. As a consequence, the volume decreases, whereas the yield stress increases gradually over time. The increase of the yield stress leads to increased strain softening, which has a strong influence on the failure mode of this type of materials. In general, increased strain softening leads to a stronger strain localisation. Eventually, the plastic zone localises to such an extent that cavitation takes place and a craze is initiated. When the craze breaks down, a crack is formed which acts as an extremely sharp notch. The subsequent crack growth occurs at such a high rate that the time it takes for the crack to grow to a critical level does not significantly contribute to the overall failure time. This explains why a different failure mode is observed macroscopically, whereas the path up to failure (accumulation of plastic strain up to a critical value) is, in essence, the same.

Klompen et al. observed a similar transition from ductile to a brittle failure mode for polycarbonate tensile bars subjected to a static load. They showed that the transition can indeed be attributed to an increase in yield stress resulting from progressive physical ageing, i.e. ageing occurring during the experiment itself, confirming the posed hypothesis. They also showed that the increase in yield stress not only influences the failure mode, but the progressive increase in resistance against plastic deformation also leads to the occurrence of a so-called endurance limit. Such a limit under which no failure is observed within experimentally acceptable timescales has been observed for several glassy polymers under deadweight load. Despite the change in failure mode, such a change in kinetics is not apparent in the experimental data of Niklas and Kausch von Schmeling. Comparable measurements by Benjamin, as reproduced in Figure 2 (right), do show that slow crack growth did not significantly contribute to the failure time of the PVC pipes they subjected to an internal pressure. Based upon the experimental observation that all failure modes showed similar circumferential strain behaviour up to failure, they stated that all failure modes followed a common path up to failure. Where Niklas and Kausch von Schmeling modelled the complete viscoelastic creep behaviour to predict failure for pressurised pipes, it was demonstrated that capturing the secondary creep alone is sufficient for quantitative failure predictions.
an endurance limit. The solid lines represent predictions of the current approach that do not take physical ageing into account. The predictions clearly underestimate the failure time observed experimentally, especially at 60 °C.

In the present study the physical ageing kinetics is incorporated in the existing engineering approach as presented in a previous paper. The procedure employed in this work is similar to the procedure of Klompen et al. used to incorporate the kinetics of physical ageing into their constitutive model. In the resulting engineering approach the time-to-failure follows from a closed form expression. Moreover, it is shown that the more laborious characterisation and numerical calculations of the constitutive approach of Klompen et al. can be circumvented for simple structures subjected to 3D loads. In the next section this procedure for implementing the ageing kinetics is described and the relevant expressions are elucidated. Subsequently, the physical ageing kinetics including its dependence on temperature and stress, is characterised using short-term tensile experiments. To conclude, the approach is validated on experimentally obtained failure data for tensile specimens subjected to either constant or dynamic loads.

**Theoretical Background**

The existing approach was employed to calculate the equivalent plastic strain rate \( \dot{\gamma} \) for a given temperature \( T \), pressure \( p \) and equivalent stress \( \sigma \):

\[
\dot{\gamma}(T, p, \sigma) = \gamma_0 \exp\left(\frac{-\Delta U}{RT}\right) \sinh\left(\frac{\tau}{RT}\right) \exp\left(-\frac{\mu \nu}{RT}\right) \tag{1}
\]

with \( R \) to denote the universal gas constant. The pre-exponential factor \( \gamma_0 \) in Equation (1) is related to the entropy of the system and thus the thermodynamic state of the polymer. The more the polymer has aged, the lower the value of \( \gamma_0 \) will be, reflecting the increased resistance against plastic deformation of the aged glassy polymer. The first exponential term includes the influence of temperature on the plastic strain rate using activation energy \( \Delta U \). In the second term the activation volume \( \nu \) determines the sensitivity of the plastic strain rate to the stress. The third term is included to take the influence of the hydrostatic pressure \( p \) into account via the pressure dependence parameter \( \mu \), making Equation (1) valid for any 3D loading geometry. Each of the parameters was determined using short-term tensile tests on the uPVC pipe material. The definitions of the equivalent plastic strain rate \( \dot{\gamma} \), the equivalent stress \( \sigma \) and the hydrostatic pressure \( p \) are given in Table 1.

Brady and Yeh showed that the stress and temperature dependence (and hence the activation volume and energy) of polycarbonate are influenced by an annealing treatment. In other studies was shown, however, that the deformation kinetics can still be described accurately using constant values for the activation volume and energy. Klompen et al. proposed

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**Table 1.** Definition of the equivalent plastic strain rate \( \dot{\gamma} \), the equivalent stress \( \sigma \) and the hydrostatic pressure \( p \) as used in Equation (1) as a function of the strain tensor and stress tensor.

**Definitions**

\[
\dot{\gamma} = \sqrt{2(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2 + 2\varepsilon_{12}^2 + 2\varepsilon_{23}^2 + 2\varepsilon_{13}^2)}
\]

\[
\sigma = \frac{1}{6}[(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2 + \sigma_{11}^2 + \sigma_{22}^2 + \sigma_{33}^2]
\]

\[
p = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})
\]
to make only $\dot{\gamma}_0$ in Equation (1) a function of time ($t$) to incorporate the influence of physical ageing. Here, a similar function is used to describe the behaviour of uPVC:

$$\dot{\gamma}_0(T, \tau, t) = b_0 \left( \frac{t_{\text{eff}}(T, \tau, t) + t_0}{t_0} \right)^{b_1}$$

(2)

where $b_0$ and $b_1$ are constants\(^b\) and $t_0 = 1$ s. The initial age of the specimen is denoted as $t_0$, which is related to the thermo-mechanical history of the material. As it is well known that the process of physical ageing is accelerated by temperature\(^{19}\) and stress and strain,\(^{31,36-40}\) the effective time ($t_{\text{eff}}$) is introduced. The effective time is a measure for the ageing time $t$ at reference conditions (zero stress and $T = T_{\text{ref}}$) and is related to the ageing time at temperature $T$ and stress $\tau$ via the acceleration factors $a_\tau$ and $a_\sigma$, respectively. The effective time is defined as:

$$t_{\text{eff}} = \int_0^t \frac{dt'}{a_\tau(T) a_\sigma(T, \tau)}$$

(3)

where $a_\tau$ is the temperature-induced acceleration factor and $a_\sigma$ the stress-induced acceleration factor. These acceleration factors are equal to unity for the reference condition. The relation for the plastic deformation rate including the influence of physical ageing can now be obtained by combining Equation (1), (2) and (3):

$$\dot{\gamma}(T, p, \tau, t) = b_0 \left( \frac{t_{\text{eff}}(T, \tau, t) + t_0}{t_0} \right)^{b_1} \times \exp\left(\frac{-\Delta U - \mu p\nu^+}{RT}\right) \sinh\left(\frac{\rho \nu^+}{RT}\right)$$

(4)

As failure occurs when the accumulated plastic strain reaches a critical level, the time-to-failure can be found by integrating the rate of plastic deformation (Equation 4) up to the critical equivalent strain

$$\int_0^t \dot{\gamma}(T, p, \tau, t) dt, \quad \text{failure occurs if:}$$

$$\int_0^t \dot{\gamma}(T, p, \tau, t) dt = \gamma_{\text{cr}}$$

(5)

This relation can be used to deduct analytical expressions for the time-to-failure for different load cases. In the validation procedure, which follows after the characterisation of the physical ageing kinetics of uPVC, the expressions for a constant and a dynamic (triangular) tensile load are given.

**Experimental Part**

**Material and Specimen Preparation**

The uPVC specimens were taken out of an excavated uPVC gas distribution pipe that was in service for several decades. The pipe has a diameter of 160 mm and a wall thickness of about 4.1 mm. A section of 70 mm was cut from the pipe with a bandsaw and subsequently sawed in half in axial direction. These parts were then pressed into flat plates in a press at 100 °C,\(^c\) thus approximately 20 °C above the glass transition temperature of uPVC, in 25 min at a pressure of approximately 1 MPa. This procedure erased all prior effects of physical ageing, thus $\dot{\gamma}_0$ of the specimens that are manufactured in this way is only dependent on the cooling rate in the cold press and subsequent heat treatments. Tensile bars with a gauge section of approximately $30 \times 5 \times 4.1$ mm$^3$ were milled from the plate material with the length direction of the tensile bars parallel to the axial direction of the pipe. The specimens which were used to characterise the ageing kinetics were given an annealing treatment in a convection oven (at a temperature of 45, 55 or 65 °C) or by storing them at ambient conditions (25 °C).

The compact tension specimens were milled from plates that were produced in the same way as the ones used for producing the tensile specimens. The geometry of the compact tension specimens is in accordance with the ASTM E-647 standard, and have a characteristic width of 32 mm (from backside to centre of holes). The notch was machined in the axial direction of the original pipe.

**Experimental Setup**

All uniaxial tensile, creep and fatigue crack growth measurements were carried out on an MTS Elastomer Testing System S810 equipped with a 25 kN force cell or a Zwick 2010 equipped with a 2.5 kN force cell. Engineering stresses were calculated using the average of the cross-sectional surface areas as measured at three locations in the gauge section of the specimen. The tensile experiments were carried out at a constant load, thus at a constant engineering strain rate. The creep tests were conducted at a constant load, thus at constant engineering stress. For all fatigue experiments a triangular signal was used. Two sets of fatigue tests were conducted. For the first set of experiments the minimum stress was kept at a constant level of 2.5 MPa while varying the maximum stress level and frequency of the stress signal. The second set of fatigue experiments was conducted at three different levels of the stress ratio (minimum stress/maximum stress level) for a range of maximum stresses and a frequency of 1 Hz.

\(^c\) It is known that a heat treatment at 100 °C can influence the crystallinity of the uPVC.\(^{40}\) A change in crystallinity can have a marked effect on the physical ageing behaviour of uPVC.\(^{40}\) As all specimens used throughout this study received the same preparation procedure, differences in ageing behaviour are not to be expected.
The fatigue crack growth measurements were carried out with a sinusoidal stress signal with a frequency of 1 Hz and at four different stress ratios. The crack growth was monitored with the use of a video camera.

**Ageing Kinetics of uPVC**

At room temperature uPVC is about 60°C below its glass transition temperature, \( T_g \), and about 60°C above its \( \beta \)-transition. Although the main chain segmental mobility is low at room temperature, it is sufficient to allow for small conformational changes towards their thermodynamically favoured positions.\(^{[18]}\) With annealing, defined here as a heat treatment at a temperature below \( T_g \), this process can be accelerated, which makes the ageing effect more apparent at shorter timescales.

The influence of annealing at four different temperatures on the yield stress of uPVC tensile specimens as measured at 25°C and a strain rate of \( 10^{-3} \text{s}^{-1} \) is shown in Figure 3. The yield stress increases about 20% after an annealing treatment of \( 2.3 \times 10^5 \text{s} \) (corresponding to almost a month) at 65°C. The data for the different annealing temperatures can be shifted towards one single curve, using only horizontal shift factors. The natural logarithm of the horizontal shift factors are plotted versus the inverse of the annealing temperatures in Figure 4. The data can be accurately described with a linear relation. This suggests that an Arrhenius type of time-temperature superposition can be employed to calculate the shift factor \( a_T \):

\[
 a_T(T_a) = \exp \left( \frac{\Delta U_a}{RT_a} \left( \frac{1}{T_a} - \frac{1}{T_{ref}} \right) \right) \quad (6)
\]

where the activation energy (\( \Delta U_a \)) can be calculated from the slope of the best fit in Figure 4, resulting in a value of 115 kJ·mol\(^{-1}\). The temperature during annealing is denoted as \( T_a \) and \( T_{ref} \) is the reference temperature. A clear distinction should be made between \( T_a \) and \( T_{ref} \) in Equation (6) and the temperature \( T \) in Equation (1) at which the tensile test is carried out. \( T_a \) influences the ageing kinetics, \( T_{ref} \) the timescale of the mastercurve and \( T \) the plastic deformation rate. The mastercurve resulting from shifting the yield data in Figure 3 to a reference temperature of 25°C with Equation (6) is shown in Figure 5. This mastercurve can be described with Equation (4), for which the initial age of the specimens \( t_0 \) and the constants \( b_0 \) and \( b_1 \) were obtained using a nonlinear least squares fitting routine. The value for the initial age determines the length of the time-independent initial plateau and depends on the thermo-mechanical history of the material. The values of \( b_0 \) and \( b_1 \) determine the position and slope of the time-dependent yield behaviour. The value for \( b_0 \) depends on the choice of the reference temperature and \( b_1 \) is only material dependent.

With the nonlinear least squares fitting routine a best fit was found with \( b_0 = 1.13 \times 10^{14} \text{s}^{-1} \) (at \( T_{ref} = 25°C \)), \( b_1 = 0.95 \) and \( t_a = 4.9 \times 10^5 \text{s} \). The latter value implies that ageing will occur already after 1 week at \( T_a = T_{ref} \) and \( t_a = 0 \text{MPa} \). The fit is shown as a solid line in Figure 5 and accurately follows the experimental results.

As already stated, the segmental mobility of polymer chains in a glassy polymer is also known to increase by applying a mechanical load, resulting in mechanically enhanced ageing.\(^{[31,36–40]}\) (also...
referred to as stress/strain induced ageing). The kinetics of stress-induced ageing are characterised by first subjecting specimens to a constant tensile stress of 25 or 32.5 MPa for a range of ageing times. Subsequently, the cross-sectional area of the specimens is measured again and a tensile test is performed at a strain rate of 10\(^{-3}\) s\(^{-1}\) and a temperature of 25°C. The solid line represents the mastercurve for uPVC at 25°C. The dashed lines show the shifted mastercurve to the ageing condition of the respective specimens. For the shift as given by Equation (7) an activation volume \((\nu_3)\) of 9.65 \(\times\) 10\(^{-4}\) m\(^3\) mol\(^{-1}\) has been used.

\[ a_s(T_a, t_a) = \frac{T_a \nu_3}{RT_a} \sinh \left( \frac{T_a \nu_3}{RT_a} \right) \]  

(7)

Constructing a mastercurve of the experimental data with the use of Equation (7) with \(\nu_3\) as a fit parameter, resulted in a value of 9.65 \(\times\) 10\(^{-4}\) m\(^3\) mol\(^{-1}\). With this value of \(\nu_3\) a good fit of the dashed lines is obtained (see Figure 6).

The parameters that followed from the characterisation of the temperature and stress-induced ageing kinetics of uPVC are summarised in Table 2. The next step is to verify whether the approach can successfully predict the influence of progressive physical ageing during creep and fatigue experiments.

Table 2. The values for the parameters for uPVC used in this work.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu)</td>
<td>0.14</td>
</tr>
<tr>
<td>(\nu^*)</td>
<td>2.06 (\times) 10(^{-3}) (m(^3) mol(^{-1}))(^a)</td>
</tr>
<tr>
<td>(\Delta U)</td>
<td>2.97 (\times) 10(^5) (J mol(^{-1}))(^a)</td>
</tr>
<tr>
<td>(\bar{\gamma}_{ca})</td>
<td>0.015</td>
</tr>
<tr>
<td>(v_s)</td>
<td>9.65 (\times) 10(^{-4}) (m(^3) mol(^{-1}))</td>
</tr>
</tbody>
</table>

\(^a\)Value determined in Visser et al.\[9\]

Validation Using Uniaxial Tensile Creep Failure Data

The method is validated first with the use of creep failure data. In a previous paper,\[9\] it has been shown that the time-to-failure could be predicted employing Equation (1) to calculate the accumulation of the plastic strain up to a critical equivalent plastic strain \((\varepsilon_{pl})\) for uPVC subjected to a constant tensile load. The predictions proved to agree quantitatively with experimental measurements as long as physical ageing did not have a significant influence. Beyond this point the influence of physical ageing emerges as the resistance against plastic deformation increases, leading to progressively longer failure times. With the use of Equation (4) and (5), this influence of physical ageing is taken into account for failure time predictions.

The deduction of the closed form solution of Equation (5) for isothermal, constant stress conditions (creep tests) can be found in Appendix A. The equivalent stress and the hydrostatic pressure for specimens subjected to uniaxial tension can be calculated using the definitions given in Table 1 and are given in Table 3. During a creep test the ageing temperature is equal to the testing temperature and the ageing stress equal to the applied stress \((\sigma)\), thus \(T_a = T\) and \(t_a = \sigma / \sqrt{3}\). For the time-to-failure this results in:

\[ t_f(T, \sigma) = \frac{T(\sigma / \sqrt{3})}{\bar{\gamma}_{ca} a_s} \left[ \frac{\varepsilon_{pl}}{t_f} \right] + b_0 - b_1 \left[ \sinh \left( \frac{\sigma}{\sqrt{3}RT} \right) \right]^{1/b_2} \]  

(8)

Table 3. Relations for the equivalent stress and hydrostatic pressure as defined in Table 1 for uniaxial tension and a pipe with outer diameter \(D\) and wall thickness \(t\) subjected to an internal pressure \((p)\).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniaxial tension</td>
<td>(\frac{(D - 2t)p}{4t})</td>
</tr>
<tr>
<td>Internal pressure</td>
<td>(-\frac{\sigma}{3})</td>
</tr>
</tbody>
</table>
The only unknown parameter in this relation is the initial thermodynamic state represented by the initial age \( t_0 \). This parameter can be calculated from the yield stress of a specimen which has the same thermo-mechanical history as the specimens used in the creep tests. The relation between initial age and the yield stress as measured at a certain strain rate \( \dot{\varepsilon} \) and temperature is obtained by rewriting Equation (4):

\[
t_0 = \left( \frac{V_0^{3/2}}{b_0 \sinh \left( \frac{\alpha \gamma_i}{\sqrt{3} T} \right)} \right)^{1/b_1} \exp \left( \frac{3U_0 - \mu_0 \sigma_0^{1/3}}{3RT} \right)
\]

The experimentally obtained time-to-failure data are shown for two different sets of specimens in Figure 7. The first set is referred to as ‘annealed’ and was annealed for \( 5 \times 10^3 \) s at \( 20^\circ C \). The other set is referred to as ‘as manufactured’ and did not receive a heat treatment after the production procedure as described in the experimental section. The annealed specimens were tested at a temperature of \( 20^\circ C \), whereas the as-manufactured specimens were tested at \( 24^\circ C \). Therefore, the difference between the failure times of the two sets of specimens cannot be attributed solely to the difference in thermal history, but is partly a testing temperature effect (for about \( 3 \) MPa).

The initial age as determined using the tensile yield stress of each set of specimens is found to be \( 9.1 \times 10^7 \) and \( 1.4 \times 10^6 \) s for the annealed and as-manufactured specimens respectively (\( T_{ref} = 25^\circ C \)). The time-to-failure predictions which follow from Equation (8) are shown as solid lines in Figure 7. The dashed lines in this figure represent failure predictions of the approach excluding the influence of physical ageing. Ageing does not influence the failure kinetics for short failure times. In this regime both predictions are in agreement with the experimental data. At longer failure times the influence of ageing becomes apparent. For the as-manufactured specimens this occurs at failure times longer than about \( 10^3 \) s. At these timescales the resistance against plastic deformation of the specimen changes during the creep test, mainly owing to stress-induced ageing. The predicted endurance limit is in quantitative agreement with the one observed experimentally. For the annealed specimens no endurance limit was observed experimentally, which is in agreement with the theoretical prediction that ageing effects appear for failure times longer than about \( 10^3 \). This marked difference with the as-manufactured specimens is a direct result of the difference in the initial age of the two sets of specimens caused by the ageing procedure of the annealed specimens.

Employing Equation (8) to predict the long-term failure data of PC as presented by Klompen et al.[26] results in a prediction that is comparable to their prediction. It is noteworthy that whereas Klompen et al. used a model incorporating the full constitutive behaviour of PC to calculate the failure times, here the predictions follow from a closed-form analytical relation (Equation 8).

**Validation Using Failure Data for Internally Pressurised Pipes**

In a previous publication[9] it was shown that the engineering approach is able to predict the time-to-(ductile)failure of glassy polymers subjected to different loading geometries, such as that found in a pipe subjected to an internal pressure. The extended version of the engineering approach as presented in the present paper is validated by predicting the time-to-failure for two sets of failure data for pressurised pipes from different sources. The first set comprises failure data of pipes under an internal pressure as measured at three temperatures (reproduced from Niklas and Kausch von Schmeling[17]). The white, grey and black filled markers represent the failure modes ductile rupture, hairline cracking and brittle fracture, respectively. Predictions with the approach including the influence of physical ageing on the deformation kinetics are shown in solid lines and predictions excluding ageing effects in dashed lines.

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\( e \) Although no mathematical lower stress limit exists in Equation (8) where \( t_0 \) becomes infinite, such a limit is experienced within experimentally realistic timescales. As mentioned earlier, this ‘limit’ is referred to as the endurance limit.
The dashed lines represent the prediction for the approach in which physical ageing effects were not taken into account. The predictions represented as solid lines do include these effects. The initial age is calculated using one reference point and Equation (9), resulting in a value of $2.3 \times 10^8$ s which is relatively high when compared to the initial age values found for the tensile specimens used in this study. This explains why the prediction that neglects the influence of physical ageing, holds so well up to very long failure times. Furthermore, it is noteworthy that the transition from ductile failure to hairline cracking indeed occurs in the region where the solid lines start to deviate from the dashed lines; thus, where the approach predicts a change in yield behaviour as a result of physical ageing. This supports the hypothesis that the transition to hairline cracking is governed by physical ageing, leading to a more localised deformation behaviour. The transition sets in when a certain thermodynamic state is reached, which, in this case, occurs directly when ageing becomes apparent. These two transitions do not necessarily have to be connected as can be seen in the other set of experimental pipe failure data that is predicted next.

The second set of failure data of pipes was presented by Benjamin[44] who studied the influence of the level of gelation on the time-to-failure of pipes. As already stated in the introduction, the increased knowledge on stabilisation and processing has led to improved service lifetimes of uPVC pipes. Especially the processing conditions have a significant influence on the mechanical properties of the uPVC product. The degradation temperature of PVC is lower than the melting temperature at which the primary particle structure of the PVC grains is destroyed, thus uPVC, unlike most other polymers, cannot be processed from the melt. Destroying the primary particle structure is therefore difficult, and poor processing can result in a PVC product in which the primary particle structure is still partly intact. This primary particle grains can act as stress concentrators in the final product, influencing its mechanical properties. The level of gelation is related to the degree in which the primary PVC particle structure is destroyed during processing and thus a measure for the homogeneity of the molecular structure (e.g.[45,46]). A significant part of the Dutch gas distribution network was installed in the period from the 1960s up to the mid-1970s using uPVC pipes, when the primary particle structure is still partly intact. This primary particle structure of PVC is given by Portingell.[45]

The initial age is calculated using one reference point and Equation (9), resulting in a value of $2.3 \times 10^8$ s which is relatively high when compared to the initial age values found for the tensile specimens used in this study. This explains why the prediction that neglects the influence of physical ageing, holds so well up to very long failure times. Furthermore, it is noteworthy that the transition from ductile failure to hairline cracking indeed occurs in the region where the solid lines start to deviate from the dashed lines; thus, where the approach predicts a change in yield behaviour as a result of physical ageing. This supports the hypothesis that the transition to hairline cracking is governed by physical ageing, leading to a more localised deformation behaviour. The transition sets in when a certain thermodynamic state is reached, which, in this case, occurs directly when ageing becomes apparent. These two transitions do not necessarily have to be connected as can be seen in the other set of experimental pipe failure data that is predicted next.

The predictions for the evolution of yield stress are shown to hold equal for all four levels of gelation. The initial age is calculated using one reference point and is only $1.2 \times 10^8$ s. This supports the strong influence of physical ageing at relatively short failure times in the experimental data. The predicted influence of the ageing kinetics agrees reasonably well with the measurements at 20 °C, but is somewhat conservative for the measurements at 60 °C. Nonetheless, the approach gives quite an accurate prediction for the level of stress that can be sustained for a certain amount of time.

Like the data of Nikias and Kausch von Schmeling, the data of Benjamin show a transition towards a brittle failure mode. In the data of Benjamin, however, this transition in failure mode is accompanied by a transition in failure kinetics and a knee is observed. Only for the lowest level of gelation region II failure is observed. For low levels of gelation the primary particle structure is still partly present, which can act as a stress concentrator, leading to slow crack growth failure. For increased levels of gelation, the size of the initial flaws caused by the primary particle structure are expected to decrease, shifting region II failure towards longer failure times. Some remarks on region II (crack growth) failure are given at the end of this paper.

Validation Using Dynamic Fatigue Data

The predictions for the evolution of yield stress are shown to hold for constant loads. In water distribution networks oscillations in the applied stress are known to accelerate the stress-induced ageing process, when compared to a constant mean stress.[53] Oscillations in the applied stress are known to accelerate the stress-induced ageing process, when compared to a constant mean stress.[53] Predictions of the proposed engineering approach are compared with data for uPVC tensile bars under a cyclic load in this section, to verify whether the proposed approach can adequately take dynamic stress effects into account.

Modelling Dynamic Fatigue Failure

The triangular stress signal as applied on the tensile bars is shown schematically in Figure 10. By calculating the equivalent plastic...
strain rate for small timesteps with Equation (1), the accumulation of the plastic strain can be determined. The accumulated plastic strain (excluding the influence of physical ageing) is plotted as a function of time in Figure 11. The figure clearly shows that the plastic strain accumulates differently for a triangular stress signal than during a creep test at the mean stress level ($\sigma_m$) of the triangular signal. Therefore, the solution for the time-to-failure as found for constant loads (Equation 8) cannot be employed directly for a dynamic load. An acceleration factor for the deformation kinetics ($a_{d,\tau}$) similar to the one proposed by Janssen et al.\textsuperscript{[55]} is applied to circumvent a numerical procedure to find the failure time for dynamic stress signals. The acceleration factor is defined as the accumulated plastic strain after one triangular stress cycle (excluding physical ageing effects), divided by accumulated plastic strain for a constant stress with a value equal to $\sigma_m$ during the time of one cycle ($= 1/f$):

$$a_{d,\tau}[T, \sigma(t')] = \frac{\int_0^{1/f} \left( \frac{\exp(\frac{\alpha \sigma(t') \nu}{3RT}) \sinh(\frac{\alpha \sigma(t') \nu}{\sqrt{3RT}})}{\frac{1}{2} \exp(\frac{\mu \sigma_m \nu}{3RT}) \sinh(\frac{\sigma_m \nu}{\sqrt{3RT}})} \right) dt'}{\frac{1}{2} \exp(\frac{\mu \sigma_m \nu}{3RT}) \sinh(\frac{\sigma_m \nu}{\sqrt{3RT}})}$$

(10)

The solution for a triangular and a square wave of this acceleration factor is deducted in the appendix of Janssen et al.\textsuperscript{[55]} For a triangular waveform the solution is given by:

$$a_{d,\tau} = \frac{\sinh\left(\frac{\sigma_{amp}}{\sigma_0}\right)}{\sinh\left(\frac{\sigma_{amp}}{\sigma_0}\right)}$$

with: $$\sigma_0 = \frac{3RT}{(\mu + \sqrt{3})\nu}$$

(11)

According to this result the acceleration factor for the triangular signal is independent of the frequency of the stress signal, which is consistent with the experimental data of Janssen et al.\textsuperscript{[55]} The equivalent plastic strain rate for a dynamic stress signal can be calculated by multiplying Equation (10) with Equation (1), resulting in the dashed line in Figure 11. The dashed line deviates from the solid line during each cycle, but the accumulated plastic strains are equal after each whole cycle. The error in the predicted failure time is smaller than $(t_f)^{-1}$ when using the acceleration factor. The accuracy of the predictions thus increases when the cycle time of the stress signal becomes much shorter than the time-to-failure.

Not only the plastic deformation kinetics, but also the ageing kinetics are influenced by a dynamic stress signal. The evolution of the effective time as defined in Equation (3) for a dynamic stress signal can also be calculated using an acceleration factor ($a_{d,age}$), which is defined in a similar way as $a_{d,\tau}$:

$$a_{d,age}[T, \sigma(t')] = f_a \left( \frac{T}{T^*_s} \frac{\sigma_m}{\sqrt{3}} \right) \int_0^{1/f} \frac{dt'}{a_c \left( \frac{T}{T^*_s} \frac{\sigma(T') \nu}{\sqrt{3}} \right)}$$

(12)

The deduction of the analytical solution for a triangular wave form is given in Appendix B. This acceleration factor is also found to be independent of the frequency. The effective time for a dynamic stress signal can be calculated by multiplying Equation (3) with Equation (12).

The closed form solution of the time-to-failure for a creep test can be rewritten to give the time-to-failure for a specimen under isothermal, uniaxial, dynamic tensile stress conditions using the two acceleration factors $a_{d,\tau}$ and $a_{d,age}$:

$$t_f(T, \sigma_m, \sigma_{amp}) = \frac{a_1(T) a_c(T, \sigma_m)}{a_{d,age}(T, \sigma_m, \sigma_{amp})} \times \left( \frac{a_{d,age}[T, \sigma_m, \sigma_{amp}] \sigma_m^{\nu_8} (b_1 + 1)}{a_1(T) a_c(T, \sigma_m)} a_{d,\tau}(T, \sigma_m, \sigma_{amp}) \sigma_m^{\nu_8} \sinh\left(\frac{\sigma_m \nu}{\sqrt{3RT}}\right) \right) \times \exp\left( \frac{\Delta U (\mu \sigma_m \nu)}{3RT} + \frac{\mu \sigma_m \nu}{3RT} \right) = t_a.$$  

(13)

Both $a_{d,\tau}$ and $a_{d,age}$ are frequency independent, which makes the time-to-failure also frequency independent.
Frequency Dependence

In this section the frequency independent failure behaviour as predicted by the relations presented in the previous sections is verified. Two different sets of uPVC tensile specimens were subjected to a triangular cyclic load at a range of maximum stresses and a constant minimum stress of 2.5 MPa, for various frequencies. One set was annealed for $2.2 \times 10^6$ s at a temperature of 60 °C (‘annealed’), the other set of specimens did not receive any additional heat treatment (‘as manufactured’). The experimental results for the time-to-failure are shown in Figure 12. The most striking result is that two types of failure kinetics are observed. The failure kinetics in the high stress region (region I, referred to as ‘yield line’ in fatigue studies) is dominated by plastic deformation and has been the failure mode of interest in the present research so far. The region II failure mode observed at lower stresses (grey markers) is presumably related to fatigue crack growth failure, as visual inspection of these specimens points out the existence of crack sites at which the failures initiated.

As anticipated, the yield line is frequency independent, whereas the fatigue crack growth failures shift towards longer failure times with a decrease in frequency. Furthermore, the yield line is clearly influenced by the annealing treatment; the line is shifted almost two decades towards longer failure times. On the other hand, crack growth appears to be uninfluenced by the annealing treatment. More data for multiple sets of specimens at different thermodynamic states are required to confirm this observation. Only the yield line is of interest for validating the presented approach for plastic deformation and ageing kinetics. The region II failures will be discussed in more detail at the end of this paper.

The predictions are again shown as solid and dashed lines for the approach including and excluding ageing kinetics. The initial age of each set of specimens is calculated from one reference point. The short failure times are predicted accurately, but the experimental data for the as-manufactured specimens level off at somewhat shorter failure times than the theoretical predictions. The ageing trend is captured reasonably well by the engineering approach, but is somewhat conservative. A similar but much more pronounced deviation was reported by Janssen et al.\cite{54} for polycarbonate. This seems to suggest that the material ages somewhat faster for dynamic loading conditions than predicted. The subtle difference between the influence of a constant and dynamic stress signals on the ageing rate is not yet fully understood.

Stress Ratio Dependence

The experimental failure data presented in the previous section was measured for signals with a changing $\sigma_{\text{max}}$, but a constant $\sigma_{\text{min}}$ ($= 2.5 \text{ MPa}$). In this section the influence of a change in stress ratio ($R = \sigma_{\text{min}}/\sigma_{\text{max}}$) is studied. The difference in stress signal for three levels of $R$ and for a creep test ($R = 1$) is shown in Figure 13. The resulting (predicted) failure times are shown in Figure 14 for these four stress signals. The failure times are shorter for ductile (yield) failures when the stress ratio increases towards unity; the time at high stress levels increases, increasing the rate at which the plastic deformation accumulates. Consequently, the critical level of plastic strain is reached in a shorter timeframe, and the failure time decreases. The failure time for creep tests shifts about 1.4 decade...
Some Preliminary Remarks on Crack Growth

A knee was observed in the failure data of the fatigue measurements. The specimens that failed in the region after the knee are filled with surface cracks, which suggests the specimens have failed because of a fatigue crack growth mechanism. This mechanism is comparable to slow crack growth failure of a specimen subjected to a constant load in the sense that in both cases an inherent flaw grows as a result of a load and eventually causes the specimen to fail. Remarkably, the creep failure data of the tensile bars (Figure 7) and the data of Niklas and Kausch von Schmeling (Figure 8) did not show any transition towards slow crack growth failure. The question arises as to why this failure mechanism was not (yet) observed and at which timescale this second type of failure kinetics may become apparent. Therefore, a procedure to predict region II failure (slow crack growth) in creep tests, using region II failure data of fatigue tests (fatigue crack growth), is discussed in this section. Such a procedure implicitly assumes that the underlying mechanism for slow crack growth failure and fatigue crack growth failure is similar and can be described with the similar relations. In the next sections it is shown that it is important to take the influence of both the frequency ($f$) and the stress ratio ($R$) of the dynamic stress signal into account. The influence of frequency is studied using a relation proposed by Kim and Wang$^{[56]}$ to describe the dynamic fatigue failure data in the next section. Subsequently, the influence of an increase of the stress ratio of the dynamic stress signal towards unity ($f$ = creep) on the fatigue crack growth is discussed.

Influence of Frequency on Fatigue Crack Growth

Region II failure for tensile bars under dynamic loads is generally attributed to fatigue crack growth. Most fatigue crack growth models are based upon the Paris law$^{[57]}$ which relates the range of the stress intensity factor ($\Delta K$) to the rate of crack propagation per cycle ($da/dN$):

$$\frac{da}{dN} = A\Delta K^m$$  \hspace{1cm} (14)

with $A$ and $m$ constants. Although these constants are sometimes assumed to be only material dependent, they are known to depend on the frequency$^{[56,58-60]}$ ($f$), stress ratio$^{[61-63]}$ ($R$), temperature$^{[56,63,64]}$ and molecular weight distribution.$^{[65-67]}$ The dynamic fatigue experiments presented in Figure 12 are conducted at a wide range of frequencies, which rules out the use of Equation (14) to completely describe the measured data set with the use of only one parameter set.$^6$ Therefore, a modification to Equation (14) as proposed by Kim and Wang$^{[56]}$ is employed here. Their empirical relation takes the influence of frequency and temperature into account and is shortly summarised in Appendix C. The initial flaw size was used as a fit parameter, resulting in a value of 50 $\mu$m. This value is in agreement with the range of inherent defect sizes in uPVC pipes reported in other studies.$^{[68,69]}$

The resulting calculated time-to-failure at different frequencies are shown in Figure 15 as solid lines. The good agreement between the experimental data (markers) and the model description supports the statement that the failure mechanism for failures after the knee is fatigue crack growth. The relation and parameters of Kim and Wang accurately describe both the slope and the frequency dependence of the maximum stress versus time-to-failure. It is important to note that where failure in region I is insensitive for the frequency of the stress signal (as shown in

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$^6$ The stress ratio $R$ for the data in Figure 12 varies between 0.05 and o.1. The experimental data of Kim et al.$^{[56]}$ suggests that the fatigue crack growth is only marginally influenced by the variation of $R$ within this range. Therefore, this effect is neglected here.
Equation 13), fatigue crack growth failures are influenced significantly by the frequency. A decrease in frequency results in an increase in the time-to-failure. The same data, plotted in Figure 15 (right) as a function of cycles-to-failure, shows a frequency dependent response for the failures in both region I and region II. The latter does not comply with the Paris law (Equation 14), but is in agreement with the relation proposed by Kim and Wang: the number of cycles-to-failure increases with an increase in frequency of the applied stress. These observations should be taken into account when estimating the slow crack growth rate from fatigue crack growth measurements, as discussed in the next section.

**Influence of the Stress Ratio on Fatigue Crack Growth**

The stress ratio, $R$, of the dynamic signal influences the kinetics of Region II failures in uPVC.$^{[60,70]}$ At the University of Leoben an approach has been developed that correlates the fatigue crack growth rate to the slow crack growth rate.$^{[6,63]}$ They extrapolate fatigue crack growth kinetics for a range of stress ratios towards $R = 1$ (creep). Here, a similar strategy is followed. Preliminary fatigue crack growth rate measurements were carried out on uPVC compact tension specimens. The crack growth rate was determined at four different stress ratios (from 0.1 up to 0.7). The results of the measurements are shown as markers in Figure 16, where the fatigue crack growth rate $\frac{da}{dt}$ is plotted versus the maximum stress intensity factor $K_{\text{max}}$. A clear decrease in the crack growth rate is observed for an increase in $R$. The slope of the crack growth rate versus maximum stress intensity factor in a double logarithmic plot remains more or less constant for the range of stress ratios investigated. The solid lines represent the fatigue crack growth rates as predicted using Equation (C.1). The dashed lines represent the extrapolation of these results out of the range of $K_{\text{max}}$ values in which Kim and Wang$^{[56]}$ characterised their material. These extrapolated lines are in reasonable agreement with the experimental data for the range of maximum stress intensity factors lower than 5 MPa $\cdot$ m$^{0.5}$. The slope of the crack growth rate is similar and the lines coincide with the markers at $K_{\text{max}} = 30$ MPa $\cdot$ m$^{0.5}$. Apparently, the molar mass of the material used by Kim and Wang is comparable to that of the material used here.

The predictions of the time-to-failure at different (constant) values of $R$ (again using an initial flaw size of 50 $\mu$m) are shown as solid lines in Figure 17. The predictions are in good agreement with the experimental data (shown as markers). As previously discussed, both the predictions of the yield lines and the measured ductile failure times decrease with an increase in $R$. The failure time for crack growth failure (region II) is more sensitive to an increase in $R$ and increases. For an increase in $R$ from 0.1 to 0.5 the failure times increase about 1.2 decades (compared to a decrease of only about 0.3 decades for the yield failures).

The fatigue crack growth rate at a particular $K_{\text{max}} (\approx 3$ MPa $\cdot$ m$^{0.5})$ is plotted against the stress ratio in Figure 18. The experimental data (shown as markers) and the model predictions using Equation (C.1) are in close agreement.$^h$ As Brown et al.$^{[71]}$ already noted, two regimes can be distinguished. At low stress ratios the crack growth rate is hardly influenced by a change in stress ratio, whereas at high stress ratio this influence on the crack growth ratio

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$h$ In this case the frequency is kept constant and the use of Equation (14) with corresponding values for $A$ and $m$ would therefore result in identical results.
becomes much more pronounced. With the use of SAXS measurements they showed that at low $R$ values the craze fibrils in polystyrene buckle during fatigue loading, due to compressive forces imposed by the material surrounding the crack tip on the fibrils. For ratios higher than about 0.6 the craze fibrils remain straight and the fibrils only contract in length and increase in diameter as the minimum stress level is approached. This difference in deformation behaviour of the fibrils can be the cause of a different failure mechanism, explaining the sharp decrease in crack growth rate as the stress ratio approaches unity.

The relation between $R$ and $\frac{d\Delta a}{dt}$ is used to calculate the time-to-failure for uPVC subjected to a dynamic load with a stress ratio ranging from 0.1 up to 0.9. The resulting failure times are shown as solid lines in Figure 19. These lines lead to the important observation that with an increase in $R$ the time-to-failure decreases slightly for region I failures, whereas, in region II, failure times dramatically increase. In region I, failure is dependent of the level of the applied stress. Failure thus occurs on shorter timescales for high $R$ values as the polymer is subject to a high stress for a longer part of the cycle. In region II, failure mainly depends on the amplitude of the stress. Specimens can sustain a cyclic load with a high $R$-value for longer periods of time as the amplitude of the stress signal decreases with an increase in $R$.

The predicted fatigue crack growth failure at $R = 0.9$ becomes apparent after $5 \times 10^6$ s; significantly longer than the longest fatigue time measured by Niklas and Kausch von Schmelting at 20 °C for pipes subjected to a constant load (see Figure 8). This explains why the second region of failure kinetics was not observed in their experimental data. This observation complies with predictions of Trus$^{(72)}$ who estimated that region II failure occurs after at least $3 \times 10^9$ s for a well-processed uPVC pipe at 20 °C.

The model cannot be used to obtain a realistic value for the slow crack growth rate as extrapolation towards $R = 1$ leads to a crack growth rate of 0 m/s. The uPVC pipes used in the gas network are operated at a pressure of only 100 mbar resulting in a very low wall stress during their service life. The prediction at $R = 0.9$ rules out slow crack growth failure for these pipes within their service life. The water and sewer networks are, however, operated at higher and sometimes oscillating pressures. As a consequence, it is of interest for the water and sewer network operators to characterise and model region II failure kinetics.

More research is required to obtain a more reliable estimate of the slow crack growth kinetics of uPVC. The research should focus on characterising the influence of the stress ratio up to $R$ values close to unity. In a previous section it was shown that the frequency also influences the fatigue crack growth rate. As the frequency is undefined for a static signal, one should be careful in extrapolating fatigue crack growth rates measured at one frequency only. It is therefore imperative that the influence of frequency is taken into account when extrapolating towards $R = 1$. Furthermore, it should be verified whether compressive forces at the crack tip for fatigue loads with a low stress ratio indeed results in a different failure mechanism than that occurring for fatigue failure at higher stress ratios. More knowledge on the failure mechanisms is required to improve the extrapolation procedure. Other approaches such as the one proposed by Hu et al.$^{(60)}$ may also be viable. They proposed a model where the (fatigue) crack growth rate is the product of a creep contribution, that depends only on the maximum stress intensity factor, and a fatigue contribution, that depends on the local strain rate. The slow crack growth rate follows from the creep contribution. Another issue that should be addressed is the temperature dependence of the crack growth failure mechanism. This temperature dependent response should be characterised, as the service temperature of uPVC pipes is generally lower than room temperature at which most laboratory experiments are conducted.

**Conclusion**

The influence of physical ageing on the resistance against plastic deformation is successfully implemented in a pressure-modified Eyring relation by introducing a time dependent pre-exponential factor. The influence of temperature and stress on the physical ageing kinetics was characterised using tensile yield stress measurements on specimens that were aged under different conditions. With the resulting parameters it is possible to predict long-term ductile failure for not only tensile bars, but also pipe segments subjected to a constant load. The endurance limit, observed for specimens that age significantly during the measurement, is also predicted accurately. The predictions for specimens subjected to a dynamic load are in reasonable agreement. Both the predictions and the measurements of the time to ductile failure are shown to be frequency independent. The engineering approach presented in this paper has the advantage that a less laborious characterisation procedure is required compared to the ones required for existing constitutive models that are also capable of producing long-term failure predictions.

During the dynamic fatigue tests fatigue crack growth failure was observed as a second type of failure kinetics in the maximum stress versus time-to-failure plots. This fatigue crack growth failure appeared to be highly dependent on both the frequency and the stress ratio of the applied stress signal. Preliminary fatigue crack growth experiments suggest that slow crack growth failure does not occur within the service life of uPVC gas pipes.
Additional research to the fatigue and slow crack growth behaviour of uPVC is required to confirm this preliminary estimate.

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Appendix A: Deduction of the Time-to-Failure Under Constant Loads

The time-to-failure for a glassy polymer that is subjected to a constant load is calculated using the hypothesis that failure occurs after reaching a critical value of the equivalent plastic strain (\(\gamma_e\)), resulting in Equation (5). The rate of plastic strain accumulation including ageing kinetics is a function of time as given in Equation (4). Combining Equation (4) and (5) results in the following relation for the critical plastic strain, from which the time-to-failure for isothermal creep tests can be calculated:

\[
\gamma_e = \frac{b_0}{t_0} \exp \left( \frac{-\Delta U - \mu p v^s}{RT} \right) \times \sinh \left( \frac{\gamma_v^s}{RT} \right) \int_0^t \frac{t'}{\alpha(T) a_s(T, \tau)} + t_a \, dt'
\]  

(A.1)

An analytical solution can be found by substituting \(x = \{t'/[\alpha(T)a_s(T, \tau)]\} + t_a\) and \(dx/dt' = 1/\alpha(T) a_s(T, \tau)\):

\[
\gamma_e \exp \left( \frac{\Delta U + \mu p v^s}{RT} \right) = \alpha(T) a_s(T, \tau) \int_0^t x^b \, dx
\]

\[
= \frac{\alpha(T) a_s(T, \tau)}{b_1 + 1} \left[ \left( \frac{t_1}{\alpha(T) a_s(T, \tau)} + t_a \right)^{b_1+1} - t_a^{b_1+1} \right]
\]

Rewriting this equation gives the analytical solution for the time-to-failure:

\[
t_f(T, \tau) = \alpha(T) a_s(T, \tau)
\]

\[
\times \left( \frac{\gamma_e^{b_1} (b_1 + 1) \exp \left( \frac{\Delta U + \mu p v^s}{RT} \right)}{\alpha(T) a_s(T, \tau) b_0 \sinh \left( \frac{\gamma_v^s}{RT} \right) + t_a^{b_1+1}} + t_a^{b_1+1} - t_a \right)
\]

(A.2)

Appendix B: Analytical Solution for a Triangular Waveform

A stress signal with a triangular waveform (see Figure 10), \(\sigma_{\text{tria}}\), can be described with the continuous function:

\[
\sigma_{\text{tria}}(t) = \sigma_m + \frac{2\sigma_{\text{amp}}}{\pi} \arcsin \left[ \sin(2\pi ft) \right]
\]  

(B.1)

where \(\sigma_m\) is the mean stress, \(\sigma_{\text{amp}}\) the stress amplitude and \(f\) is the frequency. To find an analytical solution for the deformation and ageing kinetics for this wave form, a more appropriate, discontinuous function for the triangular waveform was used:

\[
\sigma_{\text{tria}}(t) = A + Bt
\]  

(B.2)

with

- \(A = \sigma_m\) \quad \text{for} \quad 0 \leq t < \frac{1}{2f}
- \(A = \sigma_m + 2\sigma_{\text{amp}}\) \quad \text{for} \quad \frac{1}{2f} \leq t < \frac{3}{2f}
- \(A = \sigma_m - 4\sigma_{\text{amp}}\) \quad \text{for} \quad \frac{3}{2f} \leq t < \frac{5}{2f}

Janssen et al.\(^{55}\) already provided a solution for the acceleration factor of the deformation kinetics for a triangular wave (in tension) and with the approximation that \(\sinh(x) \approx 0.5 \exp(x)\) for \(x \gg 1\):

\[
a_{\sigma, \text{age}} = \frac{3RT}{(\sqrt{3} + 1)\nu^s\sigma_{\text{amp}}} \sinh \left( \frac{\sqrt{3} + 1}{3RT} \sigma_{\text{tria}} \right)
\]  

(B.3)

The acceleration factor for the ageing kinetics can be calculated using Equation (12). Assuming isothermal conditions and combining the result with Equation (B.2) and (12) the relation is as follows:

\[
a_{\sigma, \text{age}} = a_o \left( T, \sigma_{\text{amp}} \sqrt{3} \right) f \int_0^1 \frac{\sqrt{3RT}}{(A + B) \nu_a} \sinh \left( \frac{(A + B) \nu_a}{\sqrt{3RT}} \right) \, dt
\]  

(B.4)

Using the substitutions \(\sigma_{\text{tria}} = A + Bt\), \(dt = (d\sigma_{\text{tria}}/B)\) and \(\tau_a = (RT/\nu_a)\), in Equation (B.4) results in:

\[
a_{\sigma, \text{age}} = \frac{\sqrt{3} f \tau_a a_o \left(T, \frac{\sigma_{\text{amp}}}{\sqrt{3}} \right) A^{\frac{2\nu_a}{\nu_a}} \sinh \left( \frac{\sigma_{\text{tria}}}{\sqrt{3RT} \nu_a} \right)}{B} \, d\sigma_{\text{tria}}
\]  

(B.5)

For the analytical solution the following standard integral will be used:

\[
\int \frac{\sinh(ax)}{x} \, dx = \sum_{n=0}^{\infty} \frac{(ax)^{2n+1}}{(2n+1)(2n+1)!} = F(x)
\]  

(B.6)
Applying this relation and solving it for each of the three sections of the wave results in:

\[
a_{\text{age}} = \frac{\sqrt{3}f_{\text{sa}}a_r(T, \sigma_m)}{4f\sigma_{\text{amp}}} \begin{cases} 
F(\sigma_m + \sigma_{\text{amp}}) - F(\sigma_m) \\
0 \leq t < \frac{1}{4f} \\
F(\sigma_m - \sigma_{\text{amp}}) - F(\sigma_m + \sigma_{\text{amp}}) \\
\frac{1}{4f} \leq t < \frac{3}{4f} \\
F(\sigma_m) - F(\sigma_m - \sigma_{\text{amp}}) \\
\frac{3}{4f} \leq t < 1/f
\end{cases}
\]

This can be reduced to the final solution:

\[
a_{\text{age}} = \frac{\sqrt{3}RTa_r(T, \sigma_m)}{2\nu a_{\text{amp}}}
\]

\[
\times \left( \sum_{n=0}^{\infty} \frac{(2n+1)/(2n+1)!}{(2n+1)/(2n+1)!} \right)^{2n+1} \left( \sum_{n=0}^{\infty} \frac{(2n+1)/(2n+1)!}{(2n+1)/(2n+1)!} \right)^{2n+1}
\]

where \( Y \) is a geometrical factor. The geometrical factor for the tensile bars as used in the current study can be calculated with the empirical solution for a Single End Notched Beam (SENB) specimen subjected to tensile loads:

\[
Y = \frac{\sqrt{2w}\tan\left(\frac{\pi d}{2w}\right)}{\sqrt{a}\cos\left(\frac{\pi d}{2w}\right)} \left(0.752 + 2.02\frac{a}{w} + 0.37[1 - \sin\left(\frac{\pi d}{2w}\right)]^3\right)
\]

This can be reduced to the final solution:

\[
Y = \frac{1}{n}\tan\left(\frac{\pi d}{2w}\right)
\]

(C.3)

where \( w \) is the width of the specimen, which is chosen to be equal to the wall thickness of the original pipe (\( \approx 4.1 \) mm) as most cracks in the tensile bars grow in the radial direction of the original pipe geometry. The cycles to failure follow from solving differential Equation (C.1) for the initial crack size up to the critical crack size. This critical crack size taken as the crack size at which \( K_{\text{max}} \) is equal to the critical stress intensity factor \( (K_{\text{ic}} \approx 4 \text{ MPa}\cdot\sqrt{\text{m}} \text{ for PVC}^{[73]}) \). The initial crack size \( (a_{\text{ini}}) \) was used as a fit parameter. The experimental data are accurately described with a value of \( a_{\text{ini}} = 50 \mu \text{m} \).

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Appendix C: Summary of Fatigue Crack Growth Model

Kim and Wang\(^{[56]} \) proposed a modified version of the Paris law to take the influence of frequency and temperature on the fatigue crack growth kinetics of uPVC into account:

\[
\frac{da}{dN} = \left( \frac{f}{f_{\text{ref}}} \right)^{-n} \left[ B \exp\left( -\frac{\Delta H_{\text{th}} - \gamma \log(\Delta K)}{RT} \right) \right]_{\text{ref}}
\]

(C.1)

where \( \gamma \) is a geometrical factor. The geometrical factor for the tensile bars as used in the current study can be calculated with the empirical solution for a Single End Notched Beam (SENB) specimen subjected to tensile loads:

\[
Y = \frac{\sqrt{2w}\tan\left(\frac{\pi d}{2w}\right)}{\sqrt{a}\cos\left(\frac{\pi d}{2w}\right)} \left(0.752 + 2.02\frac{a}{w} + 0.37[1 - \sin\left(\frac{\pi d}{2w}\right)]^3\right)
\]

(C.3)

where \( w \) is the width of the specimen, which is chosen to be equal to the wall thickness of the original pipe (\( \approx 4.1 \) mm) as most cracks in the tensile bars grow in the radial direction of the original pipe geometry. The cycles to failure follow from solving differential Equation (C.1) for the initial crack size up to the critical crack size. This critical crack size taken as the crack size at which \( K_{\text{max}} \) is equal to the critical stress intensity factor \( (K_{\text{ic}} \approx 4 \text{ MPa}\cdot\sqrt{\text{m}} \text{ for PVC}^{[73]}) \). The initial crack size \( (a_{\text{ini}}) \) was used as a fit parameter. The experimental data are accurately described with a value of \( a_{\text{ini}} = 50 \mu \text{m} \).

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