Influence of physical ageing on the impact embrittlement of uPVC pipes

H.A. Visser[*], T.C. Bor, M. Wolters, L.L. Warnet, L.E. Govaert

dr. Hendrikus A. Visser[*], dr. Ton C. Bor, prof. Mannes Wolters, dr. Laurent L. Warnet
Faculty of Engineering Technology, University of Twente, P.O.Box 217, NL-7500 AE Enschede, the Netherlands
e-mail: h.a.visser@ctw.utwente.nl

dr. Leon E. Govaert
Materials Technology (MaTe), Eindhoven University of Technology, P.O.Box 513, NL-5600 MB Eindhoven, the Netherlands

Abstract

Most failures of the unplasticised poly(vinyl chloride) (uPVC) pipes used in the Dutch gas distribution network originate from third-party damage. Brittle pipes should therefore be replaced to ensure safe operation of the network. In this study, the relation between physical ageing and embrittlement of uPVC is investigated using instrumented falling weight impact tests. The ductile-to-brittle transition temperature was first measured for a water pipe grade uPVC at different stages of ageing. As a hypothesis a critical stress criterion is proposed above which failure is brittle. The evolution of the ductile-to-brittle transition temperature, that followed from the use of this hypothesis and a model for the polymers yield stress, agrees qualitatively with the experimental data. A minor increase of the transition temperature was observed for the water pipe grade with ageing. Applying the same hypothesis to a uPVC gas pipe grade shows a more pronounced influence of physical ageing.

1 Introduction

One of the largest industrial applications for unplasticised poly(vinyl chloride) (uPVC) is its use in pipe systems. In the Netherlands uPVC is extensively used for water and sewer distribution systems. Moreover, uPVC pipes were installed in the low pressure gas distribution network between the mid-fifties up to 1974. Currently, about 22,500 km of these uPVC pipes is still in service and reaches its initially specified 50 years of service life in the near future. Replacing these pipes exactly after 50 years of service would result in an extremely labour intensive, and thus costly, project in the next decade. Postponement should, however, never compromise the safety of the distribution network, which emphasises the need for knowledge on the current status of the network and its subsequent development in time.

The operating pressure of uPVC gas distribution pipes generally does not exceed 100 mbar, resulting in only low wall stresses in service conditions, when assuming a negligible influence of the surrounding soil on the embedded gas pipes. Consequently, failure data on the existing gas distribution network show that spontaneous failure of uPVC gas pipes hardly occurs and most failures originate from third-party damage (impact loads).[1] Therefore, it is important in which way the uPVC behaves upon an impact load; more specifically, whether it fails in a ductile or a brittle way. A uPVC pipe that behaves in a ductile way upon impact can absorb significantly more energy before it fails. These pipes can therefore survive heavier impact events than brittle pipes. Furthermore, it is easier to stop the gas flowing from a pipe that failed in a ductile way, since it allows the instalment of a temporary stopper without a risk of further damage. If a pipe fails in a brittle manner a relatively large part of a pipe is usually destroyed instantly. The sharp, irregular fracture surfaces makes it more difficult to stop the gas flow. For these reasons, the probability of (fatal) incidents is higher for brittle pipes, making embrittlement a limiting factor for the service life of the pipe in a gas distribution network. It is evident that the uPVC pipes should have a good impact performance during their entire service life and not just during installation, since third-party damage can occur at any moment in service. Glassy polymers, such as PVC, are known to become more brittle in course of time due to physical aging. Therefore, the influence of physical ageing on the impact behaviour of uPVC is studied in this paper.

Since the studies of Peilstöcker[2,3] and LeGrand[4] it is known that physical ageing can have a significant influence on the impact behaviour of polycarbonate (PC, a glassy polymer like uPVC). Physical ageing is caused by the fact that glassy polymers are not in thermodynamic equilibrium, but continuously strive towards it. Although the mobility in the glassy state (below approximately 80 °C for uPVC) is low, the polymer chains are still capable of small conformational changes,[5] which results in a change of the thermodynamic state of the polymer towards its equilibrium. The mobility of the polymer chains increases at higher temperatures, shortening the timescales at which conformational changes occur. As a result of the conformational changes, the polymer density increases, the molecular mobility decreases and the resistance against plastic deformation increases. The latter is proven by a significant increase in the yield stress of glassy polymers during physical ageing,[6] which was also demonstrated for uPVC in a previous publication.[7]

The influence of physical ageing on the intrinsic deformation behaviour of glassy polymers is schematically shown in Fig. 1. Annealing[a] accelerated the physical aging process . The stress response on the applied strain shows an increase in yield stress with an unaffected strain hardening. This results in an increase of the yield drop, known as strain softening. The interplay between the amount of softening and the strain hardening modulus determines the degree of localisation of the plastic deformation when subjected to a tensile load.[8-11] The degree of localisation has a strong influence on the failure behaviour of glassy polymers. An increase in strain softening results in e.g. a decrease in elongation at break on a macroscopic scale[12-14] and can eventually lead to crazing and even brittle fracture. The latter failure behaviour might seem counter intuitive to originate from plastic deformation, but can be understood in the following way.[15] On a microscopic scale the formation of crazes is preceded by local plastic deformation (e.g. near an imperfection) in a plastic zone. Depending on the mechanical properties of the polymer the formation of the plastic zone is succeeded by global plastic deformation, or the plastic zone grows further on a local scale. In the latter case the hydrostatic stress within the plastic zone builds up because its deformation is constrained by the surrounding material.

---

[a] Annealing is defined here as a heat treatment at elevated temperatures, but below the glass transition temperature of the polymer.

Voiding occurs when the strain is localised to such an extent that the local hydrostatic tensile stress (near the edge of the yield zone) surpasses a critical value.[16] These voids grow and interconnect with the remaining highly oriented polymer ligaments between the voids: the craze fibrils. At this stage a craze is nucleated. The value of the critical hydrostatic stress at which crazing occurs is hardly influenced by physical ageing as was shown for PC,[17,18] poly(methyl methacrylate) (PMMA)[17] and polystyrene (PS).[19] The change in failure behaviour can be related to the process of physical ageing by calculating the thermodynamic state at which the deformation of the polymer localises to such an extent that the hydrostatic stress in the material surpasses the critical value.

The ageing induced changes in intrinsic behaviour can thus lead to a transition from ductile towards (macroscopically) brittle behaviour, which is indeed observed in studies on the influence of physical ageing on the Izod[13,20,21] and Charpy[22] impact performance of uPVC. It is known that the decrease in impact performance leads to a shift of the ductile-to-brittle transition temperature towards higher temperatures. Both Adam et al.[9] and Ryan[23] reported a marked increase of the ductile-to-brittle transition temperature of polycarbonate (PC) after an annealing treatment. The goal of this paper is to investigate whether the ageing induced embrittlement can be related to physical ageing via the evolution of the yield stress resulting from an annealing treatment. In the next section the annealing embrittlement data of LeGrand[4] on PC are analysed to find that the ductile-to-brittle transition indeed occurs at a constant thermodynamic state and thus a constant yield stress. This observation is then used to pose a hypothesis which enables the prediction of the ductile-to-brittle transition temperature ($T_{d \to b}$) based on the influence of temperature and physical ageing on the yield stress. The experiments which are required to characterise the influence of physical ageing on the deformation and impact behaviour of uPVC are described first, followed by a comparison between the experimental data and predictions based on the posed hypothesis. The comparison is followed by a discussion where the results for the water pipe grade uPVC used in this paper are translated to the behaviour which can be expected for the gas pipe grade uPVC of the pipes which have been in service for almost 50 years now.

5

2 Annealing embrittlement of polycarbonate

Following the path outlined in the introduction, one can expect the ductile-to-brittle transition to be related to the thermodynamic state and thus the yield behaviour of the polymer. As already stated, the value of the critical hydrostatic stress at which crazes initiate in PC remains constant after annealing.[17,18] The ductile-to-brittle transition upon annealing can therefore be directly related to a critical amount of strain localisation, thus a critical thermodynamic state, with a corresponding yield stress (for a given strain rate and temperature).[18] Consequently, the ductile-to-brittle data of PC as presented by LeGrand[4] can be coupled to the evolution of the yield stress upon an annealing treatment. Klompen et al.[24] proposed to describe the evolution of the yield stress (σ_y) of PC after annealing time t at annealing temperature T_a using the following relation:

$$\sigma_y = \sigma_{y,0}(\dot{\varepsilon}, T) + c \cdot \log\left(\frac{t_{eff}(t, T_a) + t_{ini}}{t_0}\right),$$ (1)

with c a constant equal to the slope of the yield stress versus the logarithm of the annealing time (t), t_{ini} the initial age, $t_0 = 1$ s and $\sigma_{y,0}$ the yield stress at the hypothetical case of $t_{eff} + t_{ini} = 1$ s, which depends on the strain rate ($\dot{\varepsilon}$) and absolute temperature (T). Klompen et al. used $\sigma_{y,0} = 26.1$ MPa, $c = 3.82$ MPa per decade and $t_{ini} = 7.3 \cdot 10^{10}$ s to describe the true tensile yield stress evolution of injection moulded PC tensile bars measured at a strain rate of 10^{-2} s^{-1} and a temperature of 23 °C. The effective time (t_{eff}) is a measure for the annealing time at the reference condition and is defined using an Arrhenius type time-temperature superposition:

$$t_{eff}(t, T_a) = t \cdot \exp\left[\frac{\Delta U_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T_a}\right)\right],$$ (2)

where ΔU_a is the activation energy that quantifies the difference in timescale of the influence of ageing at absolute annealing temperature T_a compared to the timescale at which ageing becomes apparent at the absolute reference temperature (here, $T_{ref} = 23$ °C). Klompen et al. found a value of 205 kJ·mol^{-1} for the activation energy of PC. With these values the evolution of the true tensile yield stress as a function of the annealing time can be described for different

annealing temperatures as shown in Fig. 2 (bottom).

As mentioned before, not only yield, but also impact properties are influenced by physical ageing. The Izod impact data for notched PC specimens of LeGrand[4] are reproduced in Fig. 2 (top). The data measured after annealing at 100 °C to 125 °C are used for further analysis. The data measured at 130 °C are disregarded since the annealing times at this temperature are shorter than the time required to obtain thermal equilibrium within the specimens. The solid lines in Fig. 2 (top) represent the best fit of the Izod impact data to the inverse tangent fit function employed and can be used to determine the time frame in which the ductile-to-brittle transition occurs for each annealing temperature. The ductile-to-brittle time frames are marked with the vertical grey areas. The same time frames are also marked in the evolution of the yield stress shown in Fig. 2 (bottom). Remarkably, the yield stresses corresponding to the ductile-to-brittle transitions at the four annealing temperatures all fall within a range of only 2.5 MPa. This observation supports the existence of a critical thermodynamic state (and thus critical yield stress) at which the ductile-to-brittle transition occurs. This is in line with the results of Engels,[18] who proposed the use of a critical yield stress to calculate the lifetime at a certain service temperature. It should be noted, however, that the value found for the critical yield stress cannot be applied to predict the transition towards brittle failure in other loading geometries. The critical yield stress value depends, for example, on the deformation field imposed by the impactor. It can merely be used as a tool to predict the ductile-to-brittle transition for these specific testing conditions.

3 Predicting $T_{d \to b}$ for uPVC

In the previous section a critical yield stress was found at which the ductile-to-brittle transition occurred for Izod tests performed on PC at a constant testing temperature. In the present study impact tests are performed on uPVC at a range of temperatures and for various annealing treatments to find the influence of physical ageing on the ductile-to-brittle transition temperature $T_{d \to b}$. The evolution of $T_{d \to b}$ with physical ageing (a change in thermodynamic state) is related to the evolution of the yield stress by posing the following hypothesis: *brittle*

fracture occurs when the yield stress (σ_y) of the uPVC specimens surpasses a critical (tensile)

stress (σ_{cr}). This critical tensile stress is independent of the annealing treatment (defined by the

annealing temperature T_a and annealing time t) and testing temperature (T) as long as both

temperatures are below the glass transition temperature of the polymer. In mathematical terms

this means that the pipe behaves brittle if:

$$\sigma_y(T,t,T_a) \geq \sigma_{cr}. \tag{3}$$

This hypothesis is used to relate the impact behaviour of uPVC with its yield behaviour.

The proposed hypothesis can only be employed when the influences of strain rate, temperature

and physical ageing on the yield behaviour of uPVC are characterised, such as done in previous

work.[7,25] In these papers the yield behaviour of uPVC was assumed to be thermorheologically

simple: only one relaxation mechanism, the α-process related to the glass transition

temperature, was considered to contribute to the yield behaviour. This assumption holds for

low strain rates and/or moderate temperatures. At high strain rates and/or low temperatures,

such as encountered during the instrumented falling weight impact tests, the secondary, or β-

transition, also contributes to the yield behaviour. Roetling[26-28] showed that the strain rate ($\dot{\varepsilon}$)

and temperature (T) dependence of thermorheologically complex yield behaviour of polymers

can be described with a Ree-Eyring relation.[29] This is a modification of the Eyring reaction rate

relation,[30] in which the contribution of two (or more) relaxation mechanisms to the tensile yield

stress (σ_y) are decomposed into two parallel contributions:

$$\sigma_y(T,\dot{\varepsilon}) = \sum_{x=\alpha,\beta} \frac{RT}{v_x^*} \cdot \sinh^{-1}\left[\frac{\dot{\varepsilon}}{\dot{\varepsilon}_{0,x}} \cdot \exp\left(\frac{\Delta U_x}{RT} \right) \right], \tag{4}$$

with R the universal gas constant, v_x^* the activation volume, ΔU_x the activation energy and

$\dot{\varepsilon}_{0,x}$ the pre-exponential factor that is related to the entropy of the system. The subscript x in

the parameters is substituted by α or β to refer to the parameter for the corresponding

relaxation mechanism. The influence of physical ageing on the yield stress of uPVC can be

described by making the pre-exponential factor a function of time.[7] In the characterisation

procedure it was found that, in agreement with the behaviour of PC,[31,32] the pre-exponential

factor for the β-process ($\dot{\varepsilon}_{0,\beta}$) in uPVC does not change for the range of annealing temperatures investigated in the present study (from 45 °C to 60 °C). The local twisting mode around the main chain, to which the β-process is presumed to be related in PVC,[33,34] is in thermodynamic equilibrium in this temperature range, and therefore does not change upon annealing. As a result, the ageing kinetics can be incorporated in equation (4) by making only $\dot{\varepsilon}_{0,\alpha}$ a function of time (similar to the procedure described in a previous publication[7]):

$$\dot{\varepsilon}_{0,\alpha} = b_0 \cdot \left(\frac{t_{eff}(t,T_a) + t_{ini}}{t_0} \right)^{b_1}, \tag{5}$$

with b_0 and b_1 constants, $t_0 = 1$ s and t_{ini} the initial age of the material. The effective time (t_{eff}) accounts for the influence of temperature on the ageing rate and was already defined in equation (2). Combining equations (2), (4) and (5) gives the following expression that relates the yield stress with the strain rate and temperature and includes the influence of physical ageing:

$$\sigma_y(T,\dot{\varepsilon},t,T_a) = \frac{RT}{v_\alpha^*} \cdot \sinh^{-1} \left[\frac{\dot{\varepsilon} \cdot \exp\left(\dfrac{\Delta U_\alpha}{RT} \right)}{b_0 \cdot \left(\left\langle t \cdot \exp\left[\dfrac{\Delta U_{a,\alpha}}{R} \left(\dfrac{1}{T_{ref}} - \dfrac{1}{T_a} \right) \right] + t_{ini} \right\rangle \cdot t_0^{-1} \right)^{b_1}} \right] \cdots$$
$$+ \frac{RT}{v_\beta^*} \cdot \sinh^{-1} \left[\frac{\dot{\varepsilon}}{\dot{\varepsilon}_{0,\beta}} \cdot \exp\left(\frac{\Delta U_\beta}{RT} \right) \right]. \tag{6}$$

4 Experimental

4.1 Material and specimen preparation
A large amount of material is required for the type of instrumented falling weight tests used in this study. It is impossible to obtain this amount of material from uPVC gas pipes taken out of service, as multiple pipes are required and it is unknown whether these are all processed under the same conditions and have the same thermo-mechanical history. Therefore, all specimens were made from new, unused uPVC pipes all taken from a single processing batch. The pipes have a diameter of 110 mm, a wall thickness of 2.7 mm and are produced for water distribution

9

purposes. Unfortunately, the uPVC used for these pipes has a different grade/formulation than the gas pipes produced between 1960 and the mid-seventies. Therefore, the characterisation described elsewhere[7,25] cannot be used directly; the yield behaviour of the water grade pipes should be characterised for this type of uPVC as well.

The specimens for the instrumented falling weight tests were produced by cutting pipe segments with a length of 55 mm from the pipe with a lathe. These pipe segments were sawed in half (in the axial direction) to obtain two identical semi-cylindrical specimens. Five different sets of specimens were prepared that consisted of at least 180 specimens per set. Each set was given a different heat treatment (as summarised in Table 1) resulting in different thermodynamic states.

The characterisation of the yield stress behaviour was carried out with the use of tensile tests. The tensile specimens were produced by cutting a section of 70 mm from the pipe with a bandsaw. Subsequently, such a section was sawed in half in axial direction and then pressed into flat plates in a press at 100 °C , thus approximately 15 °C–20 °C above the glass transition temperature of uPVC, in 25 minutes at a compressive stress of around 1 MPa. Tensile bars with a gauge section of approximately $30 \times 5 \times 2.7$ mm^3 were milled from the plate material (parallel to the axial direction of the pipe). The pressing procedure erased all prior effects of physical ageing. In some cases a heat treatment above the glass transition temperature can change the crystallinity of the uPVC, which in turn influences the β-relaxation as shown by Harrell and Chartoff.[35] They varied the crystallinity levels between 0% and 34% by selecting specimens with different amounts of stereoregularity and/or chain branching. Here, only one uPVC formulation was used. Consequently, the increase in crystallinity during the 25 minutes at 100 °C is expected to be only minor. The influence of the processing treatment on the β-relaxation and the associated physical ageing kinetics (as studied by Tsitsilianis et al.[36]) was therefore neglected.

4.2 Test method
The experimental setup for the impact tests is similar to the one described by Meijering[37] and is (partly) schematically shown in Fig. 3. All impact tests were carried out on a Dynatup 8250

impact machine. The specimens were placed on a temperature controlled anvil and impacted with a semi-spherical tup with a top radius of 7.5 mm. The tup was mounted on a falling weight of 23 kg at a height of 460 mm above the specimen prior to testing. The velocity at impact was around 3 m·s^{-1}, resulting in a kinetic impact energy of 100 J. The force during impact was measured with a 15 kN Kistler force cell (9011A) and recorded with a Yokogawa DL 1540 digital oscilloscope. The displacement of the weight was measured using a Meter Drive ZAM 301 AAS linear encoder with a resolution of 0.1 mm.

The impact tests were carried out at various temperatures. Prior to testing the temperature of the specimens was controlled in a Sanyo MIR 583 Incubator. The temperature of the anvil was controlled by an ethylene glycol flow through a cooling circuit inside the anvil. The temperature of the ethylene glycol was controlled in a Haake F3 thermal bath. A thin layer of vaseline was applied on the anvil to ensure that any ice formed at the surface of the anvil could be easily removed prior to testing. In most cases 30 specimens were tested per temperature.

The uniaxial tensile tests were carried out on an MTS Elastomer Testing System 810 equipped with a 25 kN force cell and a thermostatically controlled chamber. These experiments were carried out at a constant crosshead speed, resulting in constant *engineering* strain rates. The tensile tests were carried out at strain rates ranging from 10^{-4} s^{-1} to 1 s^{-1} and temperatures ranging from -20 °C up to 40 °C . The value of the yield stress was calculated using the average of the cross-sectional surface areas as measured at three locations in the gauge section. All stresses and strains reported in this paper are *engineering* values.

5 Characterisation

The uPVC pipe material used for the experiments presented in this paper, differs from the grade used in previous publications.[7,25] Moreover, the β-contribution to the yield behaviour has not been characterised in these publications. The characterisation of the temperature and strain rate dependence of the yield stress and the influence of physical ageing is presented in the following two sections.

5.1 Characterising the deformation kinetics

The results of the tensile yield stress measurements plotted in Fig. 4 clearly show a transition from α dominated yield towards $\alpha+\beta$ dominated yield; at room temperature the influence of the β-relaxation becomes apparent at strain rates higher than 0.03 s^{-1}. The solid lines represent the result of equation (4) using the parameters summarised in Table 2 . The parameters related to the α-relaxation were calculated from the parameters as determined earlier[25] for the different uPVC grade. The parameters that account for the contribution of the β-relaxation were adopted from a study of Bauwens-Crowet et al.[38]. The pre-exponential factors $\dot{\varepsilon}_{0,\alpha}$ and $\dot{\varepsilon}_{0,\beta}$ were obtained using a reference point in the α-regime and one in the $\alpha+\beta$-regime, respectively. The excellent agreement of the solid lines compared to the experimental data allows two conclusions to be made. Firstly, for the α-regime the deformation kinetics of the gas pipe grade uPVC characterised in[25] is equal to the deformation kinetics of the uPVC grade used here. Secondly, for the the $\alpha+\beta$-regime, the combination of the above mentioned data from the α-regime and the parameters adopted from Bauwens-Crowet et al. also proves to give an excellent desciption of the experimental data presented here.

5.2 Characterising the ageing kinetics

The physical ageing kinetics of the α-contribution to the tensile yield stress of (a different grade of) uPVC was characterised in a previous publication.[7] Both Bauwens-Crowet et al.[31] and Ho-Huu[32] showed that the β-contribution to the yield stress of PC is not influenced by its thermal history. The same behaviour can be expected for uPVC; its β-transition temperature is about $-40\,°C$ and, therefore, the mobility that is related to the β-relaxation, is in thermodynamical equilibrium at the annealing temperature of 60 °C. To verify whether the β-contribution to the yield stress indeed remains constant during annealing treatments, the experimental data are compared with the predictions of the model taking only the ageing kinetics of the α-contribution to the yield stress into account neglecting the β-contribution.

The yield stress data at a strain rate of 10^{-4} s^{-1} and at 25 °C after different annealing treatments, are shown as unfilled markers in Fig. 5 (left). From the shift between the data at the annealing

temperature of 45 °C and 65 °C, the activation energy in equation (2), $\Delta U_{a,\alpha}$, can be calculated and was found to be 238 kJ·mol^{-1}. With this activation energy the location of the filled markers in Fig. 5 (left) can be calculated using equation (2) to calculate the effective ageing time at a certain reference temperature. The filled markers represent the yield evolution of the uPVC aged at a reference temperature (chosen to be 25 °C, here). The values of the constants b_0 and b_1 in equation (6) were determined using a non-linear least square fitting routine on the shifted yield stress data, resulting in values of $b_0 = 7.34 \cdot 10^{41}$ s^{-1} and $b_1 = -0.45$, respectively.

As shown above, the strain rate and temperature dependence of the yield stress in at least the α-region of the water pipe grade used here is identical to that of the gas pipe grade used in earlier publications.[7,25] Remarkably, the ageing kinetics are significantly different. The activation energy for the gas pipe grade is about half the value found for the material used in this paper. Moreover, the constant b_1 is about half the value found for the gas pipe grade, resulting in a twice as steep slope of the mastercurve for the gas pipe grade. Apparently, the cooperative motions of the polymer chain segments which are related to yielding is identical for the two grades, whereas the mechanism which enables small conformational changes of the polymer chains, which are related to the ageing behaviour, differs significantly. The physical background behind this difference is unknown at this stage, but a few possible explanations can be given. (i) First of all, the difference might be related to the different content and type of additives and fillers in the PVC grades used for the two pipes. A small amount of plasticiser in the water pipe grade, could cause an "anti-plasticisation" effect.[39,40] The small amount of plasticiser can (partly) supress the secondary transition and therewith increase the modulus and yield stress, and can also affect the ageing kinetics.[41] If the "anti-plasticisation" effect is present one would also expect a change in the contribution of the secondary transition to the yield stress: the $\alpha+\beta$-regime should shift towards higher temperatures and lower strainrates. Future yield stress measurements in the $\alpha+\beta$-regime of the gas pipe grade are required to confirm this explanation. (ii) The difference in ageing kinetics can also originate form a difference in polymerisation process for the PVC powders used for the production of the pipes. The tacticity of PVC chains polymerised from a suspension is different to that of PVC polymerised from an emulsion.

Assuming that the PVC used for the two pipes where indeed polymerised via the two different routes, a difference in tacticity can be expected, leading to a difference in the molecular arrangement of the amorphous phases and therefore the ageing kinetics. (iii) Although unlikely, differences in the crystalline structures could also explain the observed difference in ageing kinetics. Despite the low crystallinity of PVC, its crystalline structure can influence the ageing kinetics.[36] Differences in the crystalline structure can originate from differences in tacticity, leading to a different primary crystalline structure.[42] Furthermore, the processing conditions during pipe extrusion determine the level of destruction of the primary crystaline structure and the level of recrystalisation[43] and will thus also affect the crystalline structure and consequently might influence the ageing kinetics. (iv) A last explaination could be a difference in the level of gelation of the water and gas pipe investigated. This level of gelation (the level of primary particle structure breakdown) of the PVC is also closely related to the processing conditions.[43,44] Currently, a research program is carried out at laboraties involved in the present study that addresses the influence of gelation on the ageing kinetics of PVC pipes.

The influence of the strain rate on the yield stress at 0 °C was measured for specimens that were annealed for $2.7 \cdot 10^6$ s at 60 °C and specimens that did not receive a heat treatment. The results are shown in Fig. 5 (right). The solid line for the annealed specimens is predicted using equation (6) and the parameters listed in Table 2 . Note that the β-contribution to the yield stress was considered to be independent of the thermodynamic state of the material. The quantitative agreement between the prediction and the experimental data supports the assumption that the β-contribution to the yield stress is not influenced by physical ageing. Hence, only the physical ageing kinetics of the α-contribution is taken into account.

6 Impact results

6.1 Types of failure
The conditions during the instrumented falling weight tests were such that an excess kinetic impact energy was exerted to ensure all specimens failed. The behaviour of the specimens during impact can be divided into three categories: ductile, semi-ductile and brittle behaviour. A

typical force-displacement diagram for each of these three types of failure is shown in Fig. 6. At critical points in the force-displacement curves the corresponding image, obtained using a high speed camera, is shown.

The force-displacement diagram of a ductile failure, Fig. 6 (top left), shows a continuous increase of the force up to a value between 5 and 6 kN. A "shoulder" can be distinguished during the start of deformation, between the first two image stills (a and b). The deformation occurring before this shoulder can be ascribed mainly to elastic deformation, whereas the deformation occurring after the shoulder is mainly plastic. A considerable amount of stress whitening takes places in the material underneath the tup. At the moment the force reaches its maximum value the sides of the specimen have deflected upwards and lose contact with the anvil. Furthermore, the material underneath the tup is drawn into the anvil in a similar way as the ductile failures described by Chivers and Moore.[45] In the highly drawn regions the material starts to rupture locally. These ruptures grow and coalesce, followed by the formation of a crack that is large enough for the tup to penetrate the specimen. The material folds around the tup, between the tup and the hole in the anvil. The force does not decrease directly to zero after the puncture of the tup, as a result of friction between the moving tup and the stationary specimen.

The semi-ductile specimens follow the same path as the ductile specimens up to the point where the force reaches its maximum. After this point, at still c, the tup punches out a piece of material that has roughly the size of the hole of the anvil. This part of the fracture is still ductile, but the remaining part of the specimen fractures in a brittle way. As a result of the build-up of elastic energy, the fractured pieces scatter around at high velocity.

Brittle fracture occurs somewhere on the (left side of the) curve of the ductile specimens, far before the maximum force is reached. Most of the brittle fractures occur before the shoulder can be distinguished, thus before a significant amount of plastic deformation has been built up. After fracture, dynamic effects cause some oscillations in the force signal although no forces are exerted on the (fractured) specimen anymore (see the bottom left graph of Fig. 6).

6.2 Impact energy analysis

During impact testing the kinetic energy of the impactor is partly stored as elastic energy and partly dissipated in the specimen as a result of plastic deformation, friction and fracture. The amount of energy absorbed by the specimen (E) is a measure for the ductility of the specimen upon impact. When all frictional losses are neglected, the absorbed energy can be calculated with:

$$E = \int_{s(t_{contact})}^{s(t_f)} F(s)\,\mathrm{d}s, \qquad\qquad (7)$$

where F is the force exterted on the specimen, s the displacement of the tup head, $t_{contact}$ the time at which the tup makes contact with the specimen and t_f the time when failure occurs.

The latter time depends on the definition for failure that is employed. Here, failure is defined as the moment at which the exerted force reaches its maximum value. The amount of energy that follows from this criterion is referred to as the energy up to the maximum force (E_{max}) throughout this paper and its definition is graphically shown in Fig. 7. Other definitions of failure can be employed, but will eventually lead to similar results and conclusions. The force displacement signals of ductile failures are identical to those of semi-ductile failures up to the maximum force. The E_{max} of these two types of failure are therefore identical making it easy to distinguish brittle fracture on the one side from (semi-) ductile failures on the other side. This is illustrated in Fig. 8 (left) which shows a histogram of E_{max} as calculated for all experiments carried out during this study. The figure clearly shows the existence of two distinct populations. The population of brittle fractures have a mean energy up to the maximum force of about 3 J. As the force-displacement behaviour during a semi-ductile failure is equal to that of a ductile failure up to the maximum force, these populations coincide and are brought together under the ductile population. The mean energy up to the maximum force of this population of failures is about 34 J.

The energy up to the maximum force (E_{max}) was determined for a range of test temperatures for each set of specimens listed in Table 1. All determined values are plotted versus the test

16

temperature in Fig. 9 for the as-received specimens (left) and the specimens that were annealed for $3 \cdot 10^6$ s at 60 °C (right). As already stated, the difference between ductile and brittle failure is very distinct, as can be seen in Fig. 9 as well. The transition from ductile failures at higher temperatures towards brittle fractures at lower temperatures is, however, not very distinct. In the transition range both brittle and ductile failures occur, causing large standard deviations around the average of E_{max} at temperatures in this transition region (also for the temperatures at which a large number of experiments was carried out). Nonetheless, it is clear from the experimental data that the as-received specimens do show a transition towards brittle fracture at a lower temperature than the annealed specimens. An attempt to quantify this shift of the ductile-to-brittle transition temperature as a result of physical ageing is presented in the following section.

7 Ductile-to-brittle transition analysis

A failure is categorised here as "brittle" when E_{max} is lower than 25 J. The choice for this value is rather arbitrary as the analysis that follows is not sensitive for values between 10 J and 30 J. The percentage of ductile failures at each test temperature is shown in Fig. 10 for the as-received specimens (left) and the specimens that were annealed for $3 \cdot 10^6$ s at 60 °C (right). The transition temperature is obtained by fitting an error-function (erf) to the percentage of ductile failure at each temperature:

$$Percentage\ of\ ductile\ failures = 50 + 50 \cdot \mathrm{erf}(d_0 + d_1 \cdot T), \tag{8}$$

using d_0 and d_1 as fit parameters that determine the temperature at which the transition occurs and the width of the transition range, respectively. The number of experiments differs per testing temperature, as can be seen in Fig. 9. The non-linear fitting routine was carried out on all individual experimental data points to account for this difference in number of data points per temperature. The resulting best fits are shown as a solid line for the as-received (left) and the annealed specimens (right) in Fig. 10.

The ductile-to-brittle transition is defined here as the temperature region in which the percentage of ductile failure is between 30% and 70%. This transition temperature region can

17

be calculated with the fitted function and is shown as the darker grey area in Fig. 10. The transition temperature is found to be between $-3.5\ °C$ and $-1\ °C$ for the as-received specimens and between $0.4\ °C$ and $2.8\ °C$ for the annealed specimens, thus showing an increase of approximately $4\ °C$ of the average $T_{d \to b}$ as a result of physical ageing . The transition regions for the specimens that received intermediate annealing treatments (set 2, 3 and 4 in Table 1) were calculated using the same procedure and shown as grey areas in Fig. 11. On the abscissa of the figure the ageing time at $10\ °C$ (the average service temperature of uPVC gas pipes) is given. This ageing time at $10\ °C$ was calculated from the annealing treatment of each set, equation (2) and the activation energy $\Delta U_{a,\alpha}$ as found during the characterisation of the ageing kinetics (see above). The transition temperature region for the as-received specimens is shown as a light grey area as its ageing time at $10\ °C$ is 0 seconds which cannot be shown on a logarithmic scale. The experimental data do not show a significant, increasing trend of the transition temperature with an increase in ageing time.

The evolution of $T_{d \to b}$ resulting from an annealing treatment can be predicted assuming that the ductile-to-brittle transition occurs when a critical, temperature independent, tensile stress is reached (equation (3)). As a first step, the value for this critical stress (σ_{cr}), pertaining to the conditions of the current impact experiments, was determined. From equation (6) and the parameters listed in Table 2 the tensile yield stress at any given strain rate and temperature can be calculated as a function of the thermal treatment. The yield stress for the specimens of set 3 at its $T_{d \to b}$ was calculated to be 113 MPa for a strain rate of $10^2\ s^{-1}$, which is a rough estimate of the overall strain rate of the material during impact (neglecting local differences).[b] This yield stress value is assigned as the critical stress σ_{cr} . Once again, it should be emphasised that σ_{cr} is not a material parameter, but is merely a tool to calculate the evolution of $T_{d \to b}$ for these specific experimental conditions.

---

[b] The value of the strain rate has an influence (albeit small) on the resulting evolution of $T_{d \to b}$, as the lines in Fig. 4 are not exactly parallel in both the α and the $\alpha+\beta$-region.

The procedure to obtain the evolution of $T_{d \to b}$ with the age of the material is outlined in Fig. 11 (right). The $T_{d \to b}$ for specimens with a different annealing treatment was determined by calculating at which temperature the yield stress of these specimens is equal to the critical stress. For this calculation it is necessary to know the thermal history of the material, expressed as t_{ini} (initial age) in equation (6). The initial age was estimated from the age of the pipe material; at the time of testing the pipe material was 3 years old. Assuming a storage temperature of 23 °C the initial age was estimated to be equivalent to about 225 years at the service temperature of 10 °C using equation (2) . The solid line shown in Fig. 11 (left) is the result of employing the hypothesis on the yield evolution and qualitatively agrees with the experimentally obtained $T_{d \to b}$ in the sense that the increase with age is marginal. The predicted gradient of $T_{d \to b}$ versus the logarithm of age is somewhat higher than the gradient found experimentally, but is still a good estimate. Furthermore, the predicted transition temperature of the as-received specimens (the level of the initial plateau of the solid line) is lower than the measured value. A possible explanation for this difference is that the initial age of the pipe material was actually higher than expected because of a higher storage temperature or a slow cooling rate after processing. Another explanation is that the posed hypothesis is not valid. Ishikawa et al.[46] showed that the critical hydrostatic stress at which crazes nucleate decreases with temperature, which contradicts the hypothesis posed in this paper. Employing a decreasing critical stress with temperature would, however, result in an even more pronounced increase of $T_{d \to b}$ with (effective) annealing time as it would mean that the horizontal line in Fig. 11 (right) would have a negative slope. This would result in a wider range of $T_{d \to b}$ for the four thermodynamic states shown. The posed hypothesis thus results in a better description of the evolution of $T_{d \to b}$ and is used to describe the evolution throughout the rest of the paper.

The practical implication of these results is that physical ageing does not lead to embrittlement during 50 years of service life for *this water pipe grade* of uPVC for unloaded pipe conditions. The 50 years of service at 10 °C only adds about 0.2 °C to $T_{d \to b}$ for the prediction based on the estimated initial age of 225 years (see above). As already stated, the yield behaviour of the uPVC

grade that was used for gas distribution pipes is much more influenced by physical ageing. In the next section the consequences of this difference are discussed. It should, however, be emphasized that the observed difference in ageing kinetics relates only to the specific PVC grade of the pipes used in this study. A more extensive study on a wide range of PVC pipes grades used for water and gas distribution pipes is required, before fundamental differences between water and gas pipes can be confirmed.

8 Discussion

Both the experimental and the modeling results show that the influence of physical ageing has but a small effect on the $T_{d \to b}$ of the uPVC water pipe grade: 50 years of ageing at 10 °C hardly changes the $T_{d \to b}$, independent from the initial age of the material (see also Fig. 11). The ageing kinetics of this water pipe grade were found to differ significantly from a pipe grade used for gas distribution pipes, which was characterised elsewhere.[7] For the operators of the gas distribution network the influence of this difference on the prediction of the ductile-to-brittle transition is of interest. As a first approximation the same critical yield stress was used to calculate the evolution of the transition temperature. This choice for the critical yield stress determines the temperature at which the transition occurs at a given state of ageing, but not the rate at which $T_{d \to b}$ changes with the age of the pipe. The initial age of the uPVC gas pipe material was chosen to correspond to a yield stress of 50 MPa (at a strain rate of 10^{-3} s^{-1} and at an ambient temperature of 23 °C) and a moderate cooling rate after processing. The resulting relation between the age and $T_{d \to b}$ for the gas pipe grade is shown in Fig. 12. Note that both the time and the temperature range along the axes in Fig. 12 are different from those in Fig. 11 (left).

The model predicts that the transition temperature for the gas pipe grade is clearly more sensitive to physical ageing than the water pipe grade; the $T_{d \to b}$ increases 5.7 °C per decade for the gas pipe grade and 2.5 °C per decade for the water pipe grade. Within a service life of 50 years at 10 °C the ductile-to-brittle transition temperature can be expected to increase about

7 °C;[c] depending on the initial age of the pipe at the moment it is installed. In this case the initial age was chosen such that it complies with cooling rates encountered during the extrusion process of PVC pipes. Storing the pipe for 3 years at 23 °C (as assumed for the water pipe grade) results in an increase of 5 °C of the $T_{d \to b}$. Subsequent ageing in the ground (at 10 °C), only results in minor changes as the changes in $T_{d \to b}$ occur on a logarithmic timescale. The storage time *and* temperature prior to installation of the pipes therefore have an important influence on the quality of the pipe at the moment it is installed.

For the operators of the gas distribution network it is important to determine a criterion for the uPVC pipes at which the pipes become too brittle. In this study it is shown that this criterion can be related to the age, and thus to the thermodynamic state, of the material. The network operators are advised to create a procedure comparable to the one used by LeGrand[4] to determine such a criterion. First, a temperature should be chosen at which the uPVC pipe should still be ductile. An impact load comparable to that encountered by digging activities should be applied on specimens of uPVC pipe material at this temperature. Subsequently, the age of the specimens is increased until a brittle failure is encountered. The thermodynamic state of this brittle specimen corresponds to the critical age. The experimental data presented in the present paper can be used to estimate at which age this transition occurs.

9 Conclusions

Instrumented falling weight tests have been used to measure the influence of physical ageing on the ductile-to-brittle transition temperature of uPVC pipes. Experiments that were carried out on a water pipe grade of uPVC show that this transition temperature is hardly influenced for the range of ageing times tested: an increase of only 4 °C was observed after prolonged annealing the specimens for $3 \cdot 10^6$ s at 60 °C, equivalent to almost half a million year at the service temperature of uPVC gas pipes. This marginal increase was found to comply at least qualitatively with the description of the evolution of $T_{d \to b}$ with physical ageing using the

---

[c]Nonetheless, the effect of ageing on the embrittlement of this grade of uPVC is still much less pronounced than the annealing induced embrittlement reported for PC.[9,23]

hypothesis that the transition from ductile-to-brittle behaviour occurs when the tensile yield stress surpasses a critical, temperature independent stress value. The calculated increase in $T_{d \to b}$ is 0.2 °C for a water pipe grade after 50 years of service at 10 °C. It can thus be concluded that the physical ageing during the service life of the pipe will not affect the fracture behaviour of the pipe, but the thermal history of the pipe prior to installation will determine the fracture behaviour of the pipe during its service life. Applying the same hypothesis on the evolution of the yield stress of the uPVC gas pipe grade upon ageing, suggests that the $T_{d \to b}$ for these pipes is much more influenced during service life; an increase of about 7 °C is predicted. Additional impact tests on this pipe grade are required to determine wheter the yield stress is indeed a key parameter in determining the residual lifetime of the uPVC gas pipes that are currently in service.

Aknowledgements

References

[1] Hendriks, A. Storingsrapportage gasdistributienetten 2008. Technical report, Netbeheer Nederland, Arnhem, the Netherlands, 2009.
[2] Peilstöcker, G.: *Kunststoffe*, 1961, 51(9), 509-512.
[3] Peilstöcker, G.: *Brit. Plast.*, 1962, 35(7), 365-369.
[4] Legrand, D.G.: *J. Appl. Polym. Sci.*, 1969, 13(10), 2129-2147.
[5] Hutchinson, J.M.: *Prog. Polym. Sci.*, 1995, 20(4), 703-760.
[6] Golden, J.H. and Hammant, B.L. and Hazell, E.A.: *Journal J. Appl. Polym. Sci.*, 1967, 11(8), 1571-1579.
[7] Visser, H.A. and Bor, T.C. and Wolters, M. and Wismans, J.G.F. and Govaert, L.E. Lifetime assessment of load-bearing polymer glasses; The influence of physical ageing, *Macromol. Mater. Eng.*, accepted, 2010.
[8] Brady, T.E. and Yeh, G.S.Y.: *J. Appl. Phys.*, 1971, 42(12), 4622-4630.
[9] Adam, G.A. and Cross, A. and Haward, R.N.: *J. Mater. Sci.*, 1975, 10(9), 1582-1590.
[10] Cross, A. and Haward, R.N. and Mills, N.J.: *Polymer*, 1979, 20(3), 288-294.
[11] van Melick, H.G.H. and Govaert, L.E. and Meijer, H.E.H.: *Polymer*, 2003, 44, 3579-3591.
[12] Illers, K.-H.: *J. Macromol. Sci. -Phys.*, 1977, B14(4), 471-482.
[13] Rabinovitch, E.B. and Summers, J.W.: *J. Vinyl Techn.*, 1992, 14(3), 126-130.
[14] Yarahmadi, N. and Jakubowicz, I. and Hjertberg, T.: *Polymer Degrad. Stabil.*, 2003, 82, 59-72.

[15] Kramer, E.J.: *Adv. Pol. Sci.*, 1983, 52/53, 1-56.

[16] Ishikawa, M. and Narisawa, I. and Ogawa, H.: *J. Polym. Sci. Pol. Phys.*, 1977, 15(10), 1791-1804.

[17] Ishikawa, M. and Narisawa, I.: *J. Mater. Sci.*, 1983, 18(9), 2826-2834.

[18] Engels, T.A.P. *Predicting performance of glassy polymers; Evolution of the thermodynamic state during processing and service life*. PhD thesis, Eindhoven University of Technology, the Netherlands, 2008.

[19] van Melick, H.G.H. and Bressers, O.F.J.T. and den Toonder, J.M.J. and Govaert, L.E. and Meijer, H.E.H: *Polymer*, 2003, 44, 2481-2491.

[20] Lacatus, E.E. and Rogers, C.E.: *J. Vinyl Techn.*, 1986, 8(4), 183-188.

[21] Zerafati, S. and Black, J.: *J. Vinyl Addit. Techn.*, 1998, 4(4), 240-245.

[22] Fillot, L.-A. and Hajji, P. and Gauthier, C. and Masenelli-Varlot, K.: *J. Appl. Polym. Sci.*, 2007, 104, 2009-2017.

[23] Ryan, J.T.: *Polym. Eng. Sci.*, 1978, 18(4), 264-267.

[24] Klompen, E.T.J. and Engels, T.A.P. and Govaert, L.E. and Meijer, H.E.H.: *Macromolecules*, 2005, 38, 6997-7008.

[25] Visser, H.A. and Bor, T.C. and Wolters, M. and Engels, T.A.P. and Govaert, L.E.: *Macromol. Mater. Eng.*, 2010, 295(7), 637-651.

[26] Roetling, J.A.: *Polymer*, 1965, 6(6), 311-317.

[27] Roetling, J.A.: *Polymer*, 1965, 6(11), 615-619.

[28] Roetling, J.A.: *Polymer*, 1966, 7(7), 303-306.

[29] Ree, T. and Eyring, H.: *J. Appl. Phys.*, 1955, 26(7), 794-800.

[30] Eyring, H.: *J. Chem. Phys.*, 1936, 4, 283-291.

[31] Bauwens-Crowet, C. and Bauwens, J.C.: *Polymer*, 1983, 24, 921-924.

[32] Ho Huu, C. and Vu-Khanh, T.: *Theor. Appl. Fract. Mec.*, 2003, 40(1), 75-83.

[33] Ishida, Y.: *J. Polym. Sci. Pol. Phys.*, 1969, 8(11), 1835-1861.

[34] Utracki, L.A. and Jukes, J.A.: *J. Vinyl. Techn.*, 1984, 6(2), 85-94.

[35] Harrell, Jr. , E.R. and Chartoff, R.P.: *Polym. Eng. Sci.*, 1974, 14(5), 362-365.

[36] Tsitsilianis, C. and Tsapatsis, M. and Economou, Ch.: *Polymer*, 1989, 60, 1861-1866.

[37] Meijering, T.G.: *Plast. Rub. Compos. Pro., 1985,* 5, 165-171.

[38] Bauwens-Crowet, C. and Bauwens, J.C. and Homès, G.: *J. Polym. Sci. Pol. Phys.*, 1969, 7(4), 735-742.

[39] Vincent, P.I.: *Polymer*, 1960, 1(1), 425-444.

[40] Skibo, M. and Manson, J.A. and Hertzberg, R.W. and Collins, E.A.: *J. Macromol. Sci. -Phys.*, 1977, B14(4), 525-543.

[41] Kierkels, J.T.A. and Dona, C.L. and Tervoort, T.A. and Govaert, L.E.: *J. Polym. Sci., Part B: Polym. Phys.*, 2008(46) 134-147.

[42] Juijn, J.A. and Gisolf, J.H. and de Jong, W.A.: *Kolloid Z. Z. Polym.*, 1973, 251(7), 456-473.

[43] Covas, J.A. and Gilbert, M. And Marshall, D.E.: *Plast. Rub. Proc. Appl.*, 1988(9), 107-116.

[44] Benjamin, P.: *J. Vinyl. Techn.*, 1980(4) 254-258.

[45] Chivers, R.A. and Moore, D.R.: *Meas. Sci. Technol.*, 1990, 1(4), 313-321.

[46] Ishikawa, M. and Ogawa, H. and Narisawa, I. , *J. Macromol. Sci. -Phys.*, 1981, B19(3):421-443.

Figure captions

Figure 1: Schematic representation of the intrinsic behaviour of a glassy polymer, such as uPVC, as measured in compression before (solid line) and after (dashed line) an annealing treatment below the glass transition temperature.

Figure 2: The influence of annealing treatments at four different temperatures on the notched Izod impact strength and yield stress. **Top:** Izod impact data of notched PC specimens tested at room temperature after an annealing treatment at 100 °C, 115 °C, 125 °C or 130 °C for different annealing times (reproduced from LeGrand[4]). The data at 130 °C are not taken into account in the analysis and are shown in grey. **Bottom:** the evolution of the yield stress at 23 °C and at an applied strain rate of 10^{-2} s^{-1} according to equation (1) as proposed by Klompen et al.[24] The vertical grey hatches correspond to the annealing time at which the transition from ductile-to-brittle behaviour is observed in the data of LeGrand[4] shown in the top figure. The horizontal grey hatches indicate the corresponding yield stresses.

Figure 3: Cross-sectional view of the setup (schematically) for the instrumented falling weight test.

Figure 4: The markers show the yield stress as measured in uniaxial tension at a range of strain rates and temperatures. Two regimes are indicated: the α-regime and the $\alpha + \beta$-regime. The solid lines represent the description of equation (4) using the material parameters given in Table 2.

Figure 5: Influence of physical ageing on the deformation kinetics of uPVC. **Left:** yield stress at 10^{-4} s^{-1} and 25 °C versus the annealing time. The unfilled markers represent the yield stress versus the ageing time at the specific annealing temperature (T_a). The filled markers represent the same measurements where the annealing time is calculated for the reference temperature of 25 °C (the effective time in equation (2)). The master curve that follows from equation (6) is shown as solid black line. **Right:** the tensile yield stress versus strain rate at 0 °C for two sets of uPVC specimens. One set did not receive a heat treatment after production ("as-manufactured") and one set was annealed for $2.7 \cdot 10^6$ s at 60 °C ("annealed"). The solid lines represent predictions using equation (6).

Figure 6: Typical force versus displacement signals including video stills from a high speed camera for three failure types encountered during falling weight tests. The letters indicated on top of the figures on the left correspond to the video stills displayed on the right. **Top:** ductile failure. **Middle:** semi-ductile fracture. **Bottom:** brittle fracture.

Figure 7: Typical force versus displacement signal for a ductile failure. The energy up to the maximum force (E_{max}) is defined as the surface area of the filled, grey areas.

Figure 8: Histogram of the energy taken up by the specimens up to the maximum force in the force-displacement plot, E_{max}, of all tested specimens.

Figure 9: Energy taken up by the specimens up to the maximum force in the force-displacement plot (E_{max}) during a falling weight versus the test temperature. **Left:** for the as-received specimens. **Right:** for specimens annealed for $3 \cdot 10^6$ s at 60 °C.

Figure 10: Percentage of (semi-)ductile failures versus the test temperature. At the even temperature values, five measurements were conducted. At the uneven temperature values 30 measurements were carried out. The solid lines are the best fit to equation (8) . **Left:** for the as-received specimens. **Right:** for specimens that were annealed for $3 \cdot 10^6$ s at 60 °C.

Figure 11: **Left:** the ductile-to-brittle transition temperature range (grey patches) versus the calculated age at 10 °C in years (using equation (2)). The solid line represents a prediction using equation (6) and the hypothesis given by equation (3). **Right:** the tensile yield stresses of uPVC specimens at four ages (1, 100, 10,000 and 1,000,000 years at 10 °C, shown in grey towards black lines respectively) and a strain rate of 10^2 s^{-1} versus the test temperature are shown in solid black lines. The critical stress, σ_{cr}, is shown as a horizontal, dashed black line and the resulting $T_{d \to b}$ for each age is shown as vertical dashed grey lines.

Figure 12: Prediction of the ductile-to-brittle transition temperature of uPVC gas pipes using the ageing parameters as determined elsewhere,[7] assuming an initial age that corresponds to a tensile yield stress of 50 MPa (at a strain rate of 10^{-3} s^{-1} and an ambient temperature of 23 °C) and the same critical yield stress as used for the water grade uPVC from Fig. 11.

Tables

Table 1: Heat treatments of the five sets of specimens.

#	Annealing time	Annealing temperature
1	as-received	
2	$2 \cdot 10^6$ s	45 °C
3	$1 \cdot 10^5$ s	60 °C
4	$1 \cdot 10^6$ s	60 °C
5	$3 \cdot 10^6$ s	60 °C

Table 2: The values for the parameters in equation (6) for the α and β relaxation mechanisms in uPVC.

	α	β	
$\dot{\varepsilon}_{0,x}$	$1.88 \cdot 10^{38}$	$2.21 \cdot 10^{0}$	[s^{-1}]
v_x^*	$1.29 \cdot 10^{-3}$ [†]	$8.39 \cdot 10^{-4}$ [‡]	[m$^3 \cdot$mol^{-1}]
ΔU_x	$2.97 \cdot 10^{5}$ [†]	$5.86 \cdot 10^{4}$ [‡]	[J·mol^{-1}]
$\Delta U_{a,x}$	$2.38 \cdot 10^{5}$		[J·mol^{-1}]
b_0	$7.39 \cdot 10^{41}$		[s^{-1}]
b_1	-0.45		[-]

[†] value adopted from Visser[25] (includes pressure dependence)

[‡] value adopted from Bauwens-Crowet et al.[38]