Towards condition based asset management of uPVC pipes

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TOWARDS CONDITION BASED ASSET MANAGEMENT OF uPVC PIPES

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Summary

The Dutch gas and water distribution networks consist of considerable amounts of unplasticised poly(vinyl chloride) (uPVC) pipes: about 21,000 km (20%) in the gas distribution network and about 60,000 km (48%) in the water distribution network. Most of these uPVC pipes were installed between the mid-fifties and mid-seventies of the last century and have been in service ever since. The oldest uPVC pipes have surpassed their already extended specified service lifetime of 50 years. Replacing uPVC pipes which have exactly passed their specified lifetime would lead to an extremely labour intensive and costly project. Postponing replacements is therefore favourable, but only without compromising the safety and the integrity of the networks. The main goal of this thesis is to answer the question: how can we determine when a uPVC pipe should be replaced?

The development of a framework for determining the current condition and the residual lifetime of uPVC pipes started in 2005 in collaboration with the Dutch network companies. It was soon realized that most of the failures in uPVC gas pipes are caused by impact loading events from (third party) digging activities. The risk of (fatal) incidents after impact damage is higher for brittle pipes than for ductile pipes. The occurrence of brittle failure was considered the main limit for the service life of uPVC gas pipes. Hence, brittle pipes should be located and replaced. The first PhD project within the framework indicated that the extent of physical ageing and the level of gelation are the two important factors which can cause brittle failure of uPVC pipes. Methods were developed to determine the kinetics of the physical aging process and to estimate the parameters that could be used as a criterion for replacement of uPVC tubes.

In this second PhD project within the framework the emphasis is on improving the existing residual lifetime assessment method towards a level that in-situ application in uPVC pipes becomes realistic (Chapter 2). A new method to determine the critical condition has been developed (Chapter 3) and a systematic investigation to the variation in physical aging kinetics, as observed in the previous PhD project, has been carried out (Chapter 4). Finally, the in-situ determination of the level of gelation of uPVC pipes has been investigated (Chapter 5). The research on each of these subjects is described in four consecutive chapters followed by a proposal for practical implementation, conclusions and recommendations.

After the extrusion of a uPVC pipe the material is in a non-equilibrium thermodynamic state and undergoes physical ageing leading to changes in its yield

stress. In Chapter 2 of this thesis a new measurement approach is presented to non-destructively assess changes in the thermodynamic state of uPVC pipes. The measurement system employed is selected such that miniaturisation to a size compatible with the typical inner dimensions of uPVC pipe networks is realistic. The measurement approach consists of indentation of a uPVC pipe surface with a micro-Vickers indenter employing relatively low loads to minimally affect the uPVC pipes and confocal microscopy to determine the topography of the indents. The hardness was determined from the indent depth. The development of the yield stress and the hardness with the ageing time follow the same behaviour, which enables changes in the thermodynamic state to be determined from corresponding changes in the hardness measured. The residual lifetime of uPVC pipes can be non-destructively assessed using the ageing kinetics of the uPVC pipe investigated and assuming a critical limit to the yield stress and/or hardness. The measurement approach suffers from scatter in the hardness values determined. The scatter originated from surface roughness of the uPVC pipe as no pre-treatment to the pipe surfaces was carried out to keep the measurement approach simple with a view to future in-situ application in pipes. Statistical analysis has shown that the number of hardness measurements required can be estimated from a desired degree of precision in the residual lifetime. The approach presented has a similar sensitivity to physical ageing as the one used in the previous PhD project, but it is more robust and hence one step closer to practical implementation.

The residual lifetime of a uPVC pipe can only be determined when the critical thermodynamic state at which the failure behaviour of a pipe turns from ductile into brittle is known and quantified. A yield stress criterion was proposed in Chapter 3, which implies that a ductile-to-brittle transition occurs when the tensile yield stress of uPVC surpasses a critical, temperature and time independent value. Tensile impact tests were performed to determine the ductile-to-brittle transition temperature upon isothermal annealing. The yield stress criterion was applied and enabled a good prediction of the ductile-to-brittle transition temperature with annealing time, which shows that the proposed criterion holds for uPVC. Subsequently, saw tests performed on a single excavated uPVC gas pipe showed that physical ageing can induce brittle failure of a uPVC pipe. This result enables a quantitative assessment of a limiting tensile yield stress for loading conditions encountered in practice, which can then be used in lifetime assessment calculations.

In Chapter 4 the origin of the variation in the ageing kinetics of uPVC pipes has been studied. The ageing kinetics of a pipe has to be known to determine the residual lifetime of a pipe from the current yield stress, as measured with the micro-Vickers approach, and a limiting (maximum) value of the yield stress, where the material's failure behaviour turns brittle. The ageing rates of a broad range of uPVC pipes have been determined using uniaxial tensile experiments. Significant differences in the ageing rate up to a factor of four have been observed. These

differences are believed to be caused by differences in the material's physical and/or chemical structure and composition and might originate from one or more stages in the lifetime of uPVC pipes (polymerisation, processing, service life). The relation between a number of selected uPVC (material) properties and the ageing rates has been studied. It is shown that the properties related to the polymerisation stage (i.e. the PVC polymer chain structure, the average chain length and the crystallinity) cannot explain the variation in the ageing rates of the pipes investigated. The characterisation of the processing stage concentrated on a number of additives (stabilisers, lubricants, fillers, etc.), typically expected in the uPVC pipes in the Dutch gas and water distribution networks. Their relative or absolute concentrations were determined employing a large number of analyses. No conclusive relation between the presence/concentration of a single additive or combination of additives could be established that explains the variation in the ageing rates. However, to a certain degree correlations with the lead content and the presence of polyethylene wax have been observed. The year of production of the uPVC pipe could be a worthwhile piece of information as well, as there seems to be a considerable difference between the ageing behaviour of pipes produced before 1980 mainly for gas distribution purposes and those produced after this year for water distribution purposes. An elaborate study considering an even broader range of additives should be carried out to elucidate the origin of the variations in ageing rates observed. In addition, a relation between the ageing rate and the temperature at the maximum loss angle of the β -relaxation has been found. The latter enables a quicker way to determine the ageing kinetics and may be a possible route to determine the residual lifetime quantitatively in the future by also assessing the ageing rate in addition to the yield stress.

The level of gelation is the second important property that affects the failure behaviour of uPVC pipes. The level is controlled by the production process of the uPVC pipe and remains constant during the lifetime of the pipe. The gelation level is mostly lowest in the interior of the pipe wall. First, a systematic literature search was carried out to identify possible methods that allow in-situ, non-destructive and through thickness determination of the gelation level. Possible methods were studied in detail and evaluated, but currently no method is available that meets all requirements. A possible method developed in this thesis that is destructive to a small extent only is the micro-Methylene Chloride (MC) test. It is the small scale, more local version of the commonly applied MC test. The microMC experiments carried out on unused uPVC gas pipes have shown that it is indeed possible to determine the level of gelation of these pipes by milling a small hole to a depth of about 30% of the wall thickness of the (gas) pipe. The newly developed microMC method may be particularly suitable for thick-walled pipes as used in water distribution networks. Here, more problems with the level of gelation are observed and the required milling depth vs wall thickness ratio decreases drastically (to below 5%). Further study, especially to the temperature dependence of the method, can minimise the degree

of material removal. The almost non-destructive method would be useful to locate suspected uPVC pipes having low levels of gelation, if the major drawback of getting permission to perform in-situ measurements with MC in water pipes is overcome.

The research conducted in this PhD thesis forms an important step towards answering the main question posed: How can we determine when a uPVC pipe should be replaced? The research provides clear suggestions to the practical implementation of an in-situ residual lifetime assessment method based on the effects of physical ageing and the level of gelation on the failure behaviour of uPVC pipes used for gas and water distribution networks.

Samenvatting

Het Nederlandse gas- en waterdistributienetwerk bestaat voor een significant deel uit ongeplastificeerd polyvinylchloride (uPVC) buizen: ongeveer 21.000 km (20 %) in het gasdistributienetwerk en 60.100 km (48 %) in het waterdistributienetwerk. Het overgrote deel van deze leidingen is geïnstalleerd van halverwege de vijftiger jaren tot halverwege de zeventiger jaren van de vorige eeuw en transporteren sindsdien gas of water. Oorspronkelijk is de levensduurverwachting van de uPVC leidingen op 50 jaar geschat. Gezien de periode van installatie heeft een deel van de leidingen deze leeftijd inmiddels overschreden. De vervanging van de leidingen op basis van de initieel verwachte levensduur zou leiden tot een enorm werkintensief en kostbaar project. Het uitstellen van vervanging heeft de voorkeur, maar is echter alleen mogelijk wanneer de veiligheid en de integriteit van het netwerk niet in gevaar komt. Het voornaamste doel van dit proefschrift is om antwoord te geven op de vraag: hoe kunnen we bepalen wanneer een uPVC buis vervangen moet worden?

In 2005 startte in samenwerking met de Nederlandse netwerkbeheerders de ontwikkeling van een methodiek om de huidige conditie en de restlevensduur van uPVC buizen te bepalen. Al in een vroeg stadium werd duidelijk dat de meeste storingen aan uPVC gasleidingen veroorzaakt worden door slagbelasting van graafwerkzaamheden (van derden). Bij brosse breuk is het risico op (fatale) incidenten groter dan bij taaie breuk. Het optreden van brosse breuk wordt beschouwd als de belangrijkste limiet voor de restlevensduur van uPVC gasbuizen. Brosse buizen zouden daarom gelokaliseerd en vervangen moeten worden. In het eerste promotietraject binnen dit restlevensduurproject is naar voren gekomen dat de mate van fysische veroudering en de geleringsgraad twee belangrijke factoren zijn die zorgen voor brosse breuk. Methoden zijn ontwikkeld om de kinetiek van het verouderingsproces te bepalen en om de parameters te bepalen welke gebruikt zouden kunnen worden voor een vervangingscriterium voor uPVC buizen.

In dit tweede promotietraject ligt de nadruk op het doorontwikkelen van de bestaande restlevensduurmethode tot op het niveau waarbij in-situ toepassing in uPVC buizen realistisch wordt (hoofdstuk 2). Een nieuwe methode is ontwikkeld om de kritische conditie te bepalen (hoofdstuk 3). Een systematisch onderzoek naar de variatie in de verouderingskinetiek is uitgevoerd (hoofdstuk 4). Als laatste is onderzoek uitgevoerd naar de in-situ bepaling van de geleringsgraad. Het onderzoek naar elk van deze onderwerpen is beschreven in opeenvolgende hoofdstukken, gevolgd door een voorstel voor praktische implementatie van de

restlevensduurmethode en de belangrijkste conclusies en aanbevelingen.

Na de extrusie van een buis is het PVC materiaal niet in een thermodynamisch evenwicht en ondergaat het fysische veroudering. Tijdens dit proces vinden veranderingen in de thermodynamische toestand plaats en stijgt de vloeispanning van het materiaal. In hoofdstuk 2 is een nieuwe methode ontwikkeld om veranderingen in de thermodynamische toestand op niet-destructieve wijze te kunnen kwantificeren. De ontwikkelde methode is erop geselecteerd dat miniaturisatie tot de typische binnenafmetingen van uPVC buisnetwerken realistisch is. De meetmethode bestaat uit een indentatie met een micro-Vickers indenter met een lage toegepaste belasting om de buis zo minimaal mogelijk te beïnvloeden en uit een bepaling van de topografie van de indrukkingen met confocaal microscopie. De hardheid wordt bepaald uit de diepte van de indrukking. De vloeispanning en de hardheid vertonen hetzelfde gedrag bij fysische veroudering, wat het mogelijk maakt om veranderingen in de thermodynamische toestand te bepalen aan de hand van de corresponderende veranderingen in de gemeten hardheid. Vervolgens kan de restlevensduur op niet-destructieve wijze bepaald worden met de verouderingskinetiek en door het aannemen van een kritische limiet van de vloeispanning en/of hardheid. De meetmethode is onderhevig aan variatie in de gemeten hardheid. De variatie in hardheidswaardes komt voort uit de aanwezige oppervlakteruwheid. Vanwege de aanwezigheid van oppervlakteruwheid is bewust niet gekozen voor een voorbehandeling van het oppervlak om de meetmethode simpel te houden met het oog op praktische implementatie in buizen. Een statistische analyse laat zien dat het aantal benodigde metingen bepaald kan worden uit de gewenste precisie van de restlevensduur. De gepresenteerde methode heeft een vergelijkbare gevoeligheid voor fysische veroudering als de methode gebruikt in het vorige promotietraject, maar de gepresenteerde methode is meer robuust en daarom een stap dichterbij praktische implementatie.

De restlevensduur van een uPVC buis kan alleen bepaald worden indien de kritische thermodynamische toestand, waarbij het faalgedrag van de buis overgaat van taai naar bros, bekend en gekwantificeerd is. In hoofdstuk 3 is een vloeispanningscriterium geformuleerd. Dit criterium impliceert dat een taai-bros overgang plaatsvindt wanneer de vloeispanning van PVC een kritische temperatuurs- en tijdsafhankelijke waarde bereikt. Trekslagproeven zijn uitgevoerd om de verandering van de taai-bros overgangstemperatuur door isotherme verwarming beneden T_g te bepalen. Het vloeispanningscriterium is toegepast en geeft een goede voorspelling van de toename in de taai-bros overgangstemperatuur met de verwarmingstijd hetgeen laat zien dat het criterium geldig is voor PVC. Met de uitgevoerde zaagtesten is verbrossing door fysische veroudering aangetoond. Dit resultaat maakt het mogelijk om een limiterende waarde van de vloeispanning voor praktijkcondities te bepalen welke vervolgens gebruikt kan worden voor restlevensduurbepalingen.

In hoofdstuk 4 is de oorsprong van de variatie in de verouderingskinetiek van uPVC buizen onderzocht. De verouderingskinetiek moet bekend zijn om de restlevensduur van een buis te kunnen bepalen met de huidige vloeispanning (bepaald met een hardheidsmeting) en een limiterende waarde van de vloeispanning (waarbij het faalgedrag bros wordt). De verouderingssnelheid is voor verschillende uPVC buizen bepaald met trekproeven. Significante verschillen tot een maximum van een factor vier in de verouderingssnelheid zijn waargenomen. Deze variatie komt mogelijk voort uit verschillen in de fysische en/of chemische structuur en de samenstelling van de PVC buismaterialen en is mogelijk te herleiden tot de drie fases in de levensduur van PVC buizen: polymerisatie, verwerking en/of service. De relatie tussen een aantal geselecteerde (materiaal) eigenschappen van PVC en de verouderingssnelheid is onderzocht. Er is naar voren gekomen dat de eigenschappen die gerelateerd zijn aan de polymerisatiefase (dat wil zeggen de ketenstructuur, de ketenlengte en de kristalliniteit) niet de variatie in de verouderingssnelheid van de onderzochte uPVC buizen kunnen verklaren. De karakterisatie van de verwerkingsfase concentreerde zich op een aantal toevoegstoffen (stabilisatoren, glijmiddelen, vulmiddelen etc.) welke normaal gesproken verwacht worden in uPVC buizen in het Nederlandse gas- en waterdistributienetwerk. De relatieve en absolute concentraties zijn bepaald met een groot aantal analyses. Er is geen overtuigend verband gevonden tussen de aanwezigheid of concentratie van een enkel additief of een combinatie van additieven en de verouderingssnelheid. Echter, tot op zekere hoogte zijn er correlaties met het gehalte aan lood en de aanwezigheid van polyetheenwas. Daarnaast lijkt er een aanzienlijk verschil te zijn tussen het verouderingsgedrag van gasbuizen van voor 1980 en waterleidingen na dit jaartal. Een studie aan buizen met een zelfs groter bereik aan verschillende toevoegstoffen zou uitgevoerd moeten worden om de oorzaak van de verschillen in de verouderingssnelheid te kunnen achterhalen. Daarnaast is een verband gevonden tussen de verouderingssnelheid en de temperatuur op het maximum van de verlieshoek van de β -relaxatie. Deze laatste eigenschap maakt het mogelijk om de verouderingssnelheid op een snellere manier te bepalen dan voorheen en zou een mogelijke route kunnen zijn om in de toekomst naast de vloeispanning ook de verouderingssnelheid te kunnen bepalen.

De geleringsgraad is de tweede belangrijke eigenschap die het faalgedrag van uPVC buizen beïnvloedt. De graad wordt bepaald door het productieproces en is constant nadat de buis geproduceerd is. De geleringsgraad is voornamelijk het laagste in het midden van de buiswand. Als eerste is een systematische literatuurstudie uitgevoerd om mogelijke methoden te identificeren om de geleringsgraad op niet-destructieve en in-situ wijze tot in het midden van de buiswand te bepalen. De mogelijkheden met potentiële methoden zijn in detail onderzocht en geëvalueerd. Echter, er is geen methode gevonden die aan alle gestelde eisen voldoet. Een mogelijke methode, ontwikkeld in dit proefschrift, is de microMethyleenChloride (microMC) test welke alleen op een lokale schaal destructief is. Het is de op lokale schaal toegepaste versie van de veel gebruikte MC methode. De microMC-experimenten uitgevoerd op niet-

gebruikte uPVC gasbuizen laten zien dat het mogelijk is om de geleringsgraad van deze buizen te bepalen door het frezen van een kleine holte aan de binnenwand van de buizen met een diepte van ongeveer 30 % van de wanddikte van de buizen. Deze nieuw ontwikkelde methode is voornamelijk geschikt voor dikwandige buizen zoals gebruikt in het waterdistributienetwerk. Met deze buizen zijn meer problemen met de geleringsgraad waargenomen en de verhouding tussen de vereiste diepte van de holte en de wanddikte neemt drastisch af (tot beneden 5 %). Verder onderzoek naar vooral de invloed van temperatuur kan leiden tot reductie van het benodigde materiaal wat verwijderd moet worden. Deze bijna niet-destructieve methode zou bruikbaar kunnen zijn voor het lokaliseren van uPVC buizen met een te lage (of te hoge) geleringsgraad mits het grote nadeel van het toestemming krijgen voor metingen met MC in waterleidingen, verleend is.

Het uitgevoerde onderzoek in dit promotietraject is een belangrijke stap in het beantwoorden van de vraag: hoe kunnen we bepalen wanneer een uPVC buis vervangen moet worden? Het onderzoek levert duidelijke suggesties op voor de praktische implementatie van een in-situ restlevensduurmethode welke gebaseerd is op de invloed van fysische veroudering en de geleringsgraad op het breukgedrag van uPVC buizen gebruikt in gas- en waterdistributienetwerken.

Nomenclature

Roman symbols:

A_ω	absorbance at wavenumber ω	[-]
a_T	temperature induced acceleration factor	[-]
b_0	pre-exponential factor in ageing kinetics	[s ⁻¹]
b_1	exponent in ageing kinetics	[-]
CV	coefficient of variation	[%]
E	margin of error in Equation 2.8	[%]
$E_{t_{Fmax} \leq t \leq t_f}$	absorbed energy from the point of maximum force to fracture	[kJ/m ²]
F	force	[N]
F_{max}	maximum force	[N]
H	activation energy	[J/mol]
H	enthalpy	[J/g]
H_δ	hardness in Equation 2.5	[kgf/mm ²]
NA	numerical aperture	[-]
n	sample size in Equation 2.8	[-]
R	universal gas constant	[J/(mol · K)]
R_a	arithmetic average roughness	[μm]
R^2	coefficient of determination	[-]
R^2_{adj}	adjusted coefficient of determination	[-]
S	standard deviation in Equation 2.8	[kgf/mm ²]
s	displacement	[mm]
$s_{t_{Fmax} \leq t \leq t_f}$	extension at break from the point of maximum force to fracture	[mm]
T	temperature	[K]
T_a	annealing temperature	[K]
T_g	glass transition temperature	[K]
T_{ref}	reference temperature	[K]
$T_{d \rightarrow b}$	ductile-to-brittle transition temperature	[K]
t	time	[s]
t_a	annealing time	[s]
t_{eff}	effective time	[s]
t_{ini}	initial age	[s]
t_f	failure time	[s]
t_{Fmax}	time at maximum force	[s]

t_0	constant with the value 1 s	[s]
z	critical value in Equation 2.8	[-]

Greek symbols:

ΔU	activation energy	[J/mol]
ΔU_a	ageing activation energy	[J/mol]
δ	indent depth	[μm]
$\dot{\epsilon}$	strain rate	[s^{-1}]
$\dot{\epsilon}_0$	pre-exponential factor	[s^{-1}]
ν^*	activation volume	[m^3/mol]
σ	(tensile) stress	[Pa]
σ_{cr}	critical tensile yield stress	[Pa]
σ_{lim}	limiting tensile yield stress	[Pa]
σ_y	yield stress	[Pa]
$\sigma_{y,\text{mh}}$	yield stress determined from micro-hardness measurements	[Pa]
$\dot{\sigma}_y$	ageing rate	[MPa/decade]

Subscripts:

α	refers to α -relaxation
β	refers to β -relaxation

Abbreviations:

AFM	atomic force microscopy
DMA	dynamic mechanical analysis
DOP	dioctyl phthalate
DSC	differential scanning calorimetry
ESC	environmental stress cracking
IR	infrared
MCT	methylene chloride temperature
MC	methylene chloride
NMR	nuclear magnetic resonance
PC	polycarbonate
PE	polyethylene
PET	polyethylene terephthalate
PVC	poly(vinyl chloride)
uPVC	unplasticised poly(vinyl chloride)
THF	tetrahydrofuran

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Chapter 1

Introduction

1.1 Background and motivation

Recent pipe failures, such as the large water leakage in the south of Amsterdam due to a transportation pipe failure (September 2015) and the four gas pipe failures in Apeldoorn in the last two years, which were partly caused by water pipe failures, have increased the public awareness of the existence of the underground water and gas transportation and distribution networks. The implications of such failure events can be severe: a hospital had to be partially evacuated in the case of the failure incident in Amsterdam. Therefore, the network service providers are continuously trying to increase their knowledge of the condition of their network to maintain the current very low downtime and the high level of safety of the Dutch water and gas distribution networks. Only asset managers equipped with sufficient information on the current state of network assets can achieve this goal at acceptable cost, as replacement based on age would require huge investments both in labour and money in the upcoming years.

In the mid-1950s, PVC was the first polymer chosen for pipes as an attractive alternative to cast iron, steel and asbestos cement, because of its relatively high resistance to chemical components in the soil and its low cost [1, 2]. A drawback of unplasticised poly(vinyl chloride) (uPVC) pipes is that they are sensitive to impact loading events; it is known that some uPVC pipes can be very brittle. In the mid-sixties, the first generation of polyethylene (PE) gas pipes was introduced in the gas distribution network. These pipes are more resistant to impact loads than uPVC gas pipes. As a reaction to this development, impact-modified PVC gas pipes were developed and introduced in the mid-1970s [3], but no uPVC gas pipes have been installed since. The impact-modified PVC contains modifiers such as chlorinated polyethylene or an acrylate modifier, which make the impact resistance greater than that of uPVC pipes. For water distribution purposes uPVC is still the preferred material given the service conditions in the water distribution network [4]. More

recently biaxially-oriented PVC pipes have been introduced which have a higher impact resistance [3, 5] and resistance against internal pressure [3] than uPVC pipes. The material composition of gas and water distribution networks is shown in Figure 1.1. About 76% (78,000 km) of the gas distribution network consists of PVC pipes [6], of which 21,000 km are uPVC pipes and 57,000 km are impact-modified PVC pipes. For the water distribution network, about half (60,200 km) of the total length consists of PVC pipes. The majority of these pipes are unplasticised and only a few percent are biaxially-oriented.

Figure 1.1 Material composition of the gas distribution network (*left*) [6] and the water distribution network (*right*) [7, 8] (data from 2014 and 2012 respectively).

The oldest uPVC pipes were installed in the mid-1950s. These pipes have certainly passed their (already extended) service lifetime of 50 years. Replacing uPVC pipes as soon as they have passed their specified lifetime would lead to an extremely labour intensive and costly project. Most pipes were installed in densely populated areas and the qualified personnel involved in the installation of the network have retired. Hence, postponing the replacements over a larger time period is favourable, but only without if safety is not compromised.

Up to now, uPVC pipes in gas and water distribution networks have performed rather well. The number of failures of uPVC gas pipes is about 8% of the total number of failures occurring in the gas distribution network [9]. The failure rate of uPVC water pipes is about half of the failure rates of steel, cast iron and asbestos cement pipes, but about a factor two higher than for PE [4].

The gas and water network companies do not have a method available for determining the current condition of their uPVC distribution networks, which is not in keeping with their ambition to reduce future downtime. Replacement policies are currently based on parameters which are readily available within the distribution companies, such as installation data and post-mortem data. The latter information

comprises leakage data [9], failure data [4, 9] and laboratory test data on fractured uPVC pipes [10]. It would be very beneficial to network companies to have a method with which the current condition of the network components while in service can be determined. In fact, it would be even more beneficial if possible changes taking place over time could be monitored as well and an estimate of the residual lifetime could be made. Then, more data will become available to locate and preventively replace critical network components, reducing both unexpected high costs (repair costs and compensation costs of affected customers) and distrust of customers and supervising authorities. Hence, a method for monitoring and predicting the condition of pipes would be very valuable to support the development of more effective replacement policies.

The development of a framework for a residual lifetime assessment method for uPVC pipes started in 2005 in collaboration with a number of Dutch network companies. This is the second research project on this topic and is supported by eight industrial partners from the Dutch gas and water distribution sectors. For the development of the framework, the key aspects that influence the service lifetime of uPVC networks have to be described first.

1.2 Service lifetime of uPVC networks

The uPVC distribution networks consist of many components such as pipes, joints and saddles. Failure data shows that 75% of all failures in the uPVC gas network originate from pipes rather than from other components [9]. Moreover, pipe failure generally has greater implications than failures of joints or saddles. Therefore, the current research project focuses only on pipes; other network components will not be considered.

During the service life of a pipe, several factors may induce failure. Firstly, external factors like poor installation and soil subsidence may cause premature failure of uPVC pipes [11, 12]. Secondly, the internal pressure in the network may cause micro-cracks to develop prior to failure. However, the stresses in the pipe walls are low enough to prevent this kind of failure as the pressure in uPVC gas pipes does not surpass 100 mbar. In fact, only a small amount of occurrences of failures caused by internal or external loading are reported for the gas network [9].

For uPVC water distribution mains the wall stresses induced by the internal pressure are significantly higher and crack growth failure does occur and accounts for about 37% of all failure incidents [4]. Although relevant, the crack growth behaviour of uPVC water mains is outside the scope of this thesis.

In general, failures of uPVC gas pipes can be attributed to (third party) excavation activities [6] as they constitute about 50% of the total number of failures. For water mains third party damage is also an important cause of failures [4]. For this type

of failure it is of particular importance whether a uPVC pipe fails in a brittle or ductile way when hit during groundwork. Although a ductile pipe can absorb more energy before failing, it will not prevent failure, as in most cases there is an excess of impact energy due to the machinery used. Nonetheless, ductile failure is preferred for three reasons. Firstly, a relatively larger part of the pipe is damaged after a brittle failure event. Secondly, the sharp, irregular fracture surface makes it more difficult to stop the outflow of gas or water using a temporary stopper. In addition, there is an increased risk of crack propagation at the moment the pipe is plugged. Thirdly, the replacement of the temporary plugged pipe section usually involves sawing. For a brittle pipe, new cracks can readily form during sawing, which can result in additional brittle failure. For these three reasons, the probability of (fatal) incidents is higher for brittle pipes than for ductile pipes. Consequently, the quality and safety of the network is enhanced if pipes that behave in a brittle manner can be identified and replaced. In the next section it will be shown that uPVC pipes become more brittle in the course of time and, in some cases, are already brittle directly after production.

1.3 Factors causing brittle behaviour of uPVC pipes

There are various reasons why a uPVC pipe can display brittle behaviour. The reasons can be linked to the various stages during the lifetime of uPVC pipes: processing, installation and service. In this section, causes for brittle behaviour of uPVC are discussed in the order of the stages.

1.3.1 Processing

The raw material used for the extrusion of uPVC pipes is a powder. The PVC powder is mostly produced using suspension polymerisation, but emulsion or mass polymerisation have been applied too. For most other polymers, extrusion is possible using thermal energy only. However, PVC will degrade (at ~ 200 °C) before the crystallites in the material are fully molten (265 °C); hence PVC cannot be extruded from a melt. Different measures are taken to reduce the thermal degradation during processing. Firstly, PVC is processed below the crystalline melting temperature (180 - 200 °C) using high shear rates in addition to heat. Secondly, lubricants and thermal stabilisers are added to reduce the degradation during processing. Finally, PVC pipes are commonly produced using counter-rotating twin-screw extruders to ensure a low distribution of residence time of PVC material inside the extruder, further preventing thermal degradation.

A problem arising from this processing method is that it is difficult to completely destroy the particulate structure of the uPVC powder and get a homogeneous

material. The degree to which this homogenisation process is accomplished is referred to as the level of gelation. The level of gelation is an important parameter for the impact properties of a uPVC pipe. For example, when the particulate structure is still partly intact, it can act as a craze initiation site [13–15], leading to poor impact resistance [16–18] and brittle failure [19, 20]. In the early years of the production of uPVC pipes, the extrusion process was not always fully under control. As a result, uPVC pipes with a wide variation in the level of gelation were installed [10, 20]. The level of gelation is therefore considered an important factor which influences the impact resistance of buried uPVC pipes. The level of gelation is fixed after processing and does not change with time [10]. It is thus a measure for the initial (impact) quality of the pipe.

Other processing-related factors that can influence the impact resistance of uPVC pipes are molecular orientation [21, 22], residual stress [23] and molecular weight [24]. The studies cited show that effects of molecular orientation and residual stress on the impact properties are marginal. These factors are therefore not taken into account in the present research project. The molecular weight only has an influence on the impact resistance of uPVC pipes at relatively low molecular weights. As most of the pipes produced after the mid-1960s have a significantly higher molecular weight, variation in impact resistance as caused by molecular weight is not expected as long as chemical degradation does not take place.

1.3.2 Installation

Before installation, uPVC pipes can degrade during storage as a result of weathering, i.e. the exposure to outdoor conditions. The ultraviolet rays in the sunlight contribute most to the embrittlement. The rays cause a decrease in the molecular weight and subsequently in the impact resistance [25–28]. After installation the ultraviolet rays cannot reach the surface of buried pipes and do not contribute to embrittlement during service. Hence, weathering is not taken into account in this study.

1.3.3 Service

Four processes are known to degrade uPVC pipes during service life: (i) chemical degradation, (ii) slow crack growth, (iii) environmental stress cracking (ESC) and (iv) physical ageing. Each of the four processes is discussed below.

The presence of oxygen can cause chemical degradation, leading to a decrease in the molecular weight and, subsequently, to a decrease in impact resistance, similar to the influence of ultraviolet rays. Deterioration by oxygen was already known at the time of production of uPVC pipes, and measures have been taken to improve the resistance to degradation [29]. Furthermore, the concentration of oxygen and the temperature

during service are relatively low. It can therefore be expected that degradation of buried uPVC pipes by oxygen is very low.

When a uPVC pipe is subjected to a tensile stress, the existing imperfections in the pipe can evolve into cracks that slowly grow. This process is called slow crack growth. The presence of cracks decreases the impact resistance, making a pipe more prone to brittle failure. Cracks can grow from imperfections such as surface scratches [12] and/or internal flaws such as inhomogeneously dispersed additives, having a typical size of about 50-250 μm [20, 30]. However, the stresses exerted on buried uPVC gas pipes are relatively low, as gas pipes operate at a maximum pressure of 100 mbar above atmospheric pressure. A decrease in the impact resistance as a result of slow crack growth is therefore not expected, provided that the pipes are installed correctly. The uPVC water pipes operate at higher internal pressures and these pipes may suffer from slow crack growth. The influence of slow crack growth on the service lifetime and impact resistance of uPVC water pipes is beyond the scope of the present study, as already mentioned.

The ESC process is similar to slow crack growth except that the crack growth is now stimulated by the presence of a chemical agent. The formation of cracks was observed in some uPVC pipes, but exclusively on their pipe inner surfaces, showing that buried uPVC pipes do not suffer from ESC caused by chemical components in the surrounding soil [31]. The origin of the problem was that the distributed gas contained aromatic compounds that may cause ESC and a concomitant reduction of the impact resistance of the uPVC gas pipes [31–35]. However, these studies showed that ESC is unlikely to occur when uPVC gas pipes are subjected to the concentration of aromatic components conventionally present in Dutch natural gas. Even the presence of gas condensate, which can stimulate the formation of ESC related cracks, is hardly ever encountered in the Dutch gas network, so there are very few potential risk locations. Hence, the ESC process is not regarded as a critical factor to cause embrittlement during the service life of uPVC gas pipes and will not be considered further in this thesis.

The mechanical properties of uPVC pipes can also change without any influence from their surroundings as a result of physical ageing. The cause of this phenomenon is that glassy polymers like uPVC* are not in a state of thermodynamic equilibrium, but continuously strive towards it [37, 38]. As a result, the polymer molecules rearrange over time, resulting not only in a marginal change of the polymer density, but also in modified mechanical properties due to the increased intermolecular interaction. For example, the yield stress increases over time [39, 40]. The influence of physical ageing on the intrinsic deformation behaviour of a glassy polymer is shown schematically

*A glassy polymer is incapable of crystallising and the solid state is characterised by an amorphous arrangement of molecules. The crystallinity of uPVC is generally up to about 8-10% [36] and the mechanical properties of the uPVC match those of amorphous polymers, rather than semi-crystalline polymers. Therefore, uPVC is referred to as an amorphous or glassy polymer throughout this thesis.

Figure 1.2 *A schematic illustration of the influence of physical ageing on the intrinsic deformation behaviour of a glassy polymer like uPVC in compression. The solid and dashed lines represent, respectively, the true stress-strain response before and after annealing below T_g .*

in Figure 1.2. Clearly, the yield stress increases due to physical ageing and, since the hardening behaviour remains unchanged, also the softening part of the intrinsic deformation behaviour is increased. The latter effect promotes strain localisation leading to a decrease in impact resistance [41–44] and can eventually lead to brittle failure [45]. It is important to note that physical ageing always occurs in uPVC pipes if kept at a temperature between its glass transition temperature ($T_g \approx 85^\circ\text{C}$ for uPVC) and its secondary glass transition temperature [46] ($T_\beta \approx -50^\circ\text{C}$ for uPVC). Therefore, physical ageing occurs during the service life of water and gas pipes. It is considered an important contributor to the embrittlement of uPVC pipes. Significant differences in the ageing rates amongst uPVC pipes were observed [45], where a higher ageing rate leads to embrittlement occurring earlier.

To summarise this section, physical ageing and the level of gelation are considered the two most important factors that limit the lifetime of uPVC gas and water pipes. Hence, a residual lifetime assessment method for uPVC gas pipes should take these factors into account.

1.4 Objective

The objective of this second research project is to improve and extend the currently available non-destructive residual lifetime assessment method for uPVC gas pipes as developed in [47]. More specifically, the present study aims to improve the robustness and precision of the available assessment procedure, as well as to provide a way of measuring the level of gelation of uPVC pipes in a minimally invasive way. Moreover, the range of uPVC pipes studied is extended to give insight into the variation in ageing kinetics and the root cause of this variation. In other words: the project tries

to answer the underlying question: how can we determine when a uPVC pipe should be replaced? The outline of the thesis is described below.

1.5 Outline

A visual representation of the outline of this thesis is shown in Figure 1.3. The core of the thesis comprises five chapters (Chapters 2 to 6), which can be read independently.

Figure 1.3 Outline of the thesis.

In Chapter 2, a robust micro-hardness method is developed which can be used to determine non-destructively the yield stress of a uPVC pipe. Physical ageing causes the yield stress to slowly increase in the course of time. The condition of a uPVC pipe, also called the thermodynamic state, is related to the yield stress as was shown schematically in Figure 1.2. The variation in measured hardness values is an important factor limiting the resolution of the residual lifetime assessment method [47]. The origin of the variation in hardness values will be investigated as well.

The increase in the yield stress due to physical ageing ultimately leads to a brittle failure behaviour of the uPVC pipes. Network companies need a certain criterion to decide whether or not a uPVC pipe needs to be replaced. In Chapter 3 the effects of physical ageing on the failure behaviour are investigated. A stress criterion is described that allows the determination of the ductile-to-brittle transition temperature as a function of the extent of physical ageing. The residual lifetime of the pipe follows from the limiting yield stress and the kinetics of the ageing process.

The development of the yield stress as a function of time due to physical ageing, i.e. the ageing rate, is an important factor determining the residual lifetime of a uPVC pipe. If the ageing rate is high, a pipe quickly reaches a limiting yield stress value

and needs replacement. Prior work [47] has shown a range of ageing rates among the various uPVC pipes investigated. In Chapter 4 an in-depth study is performed on a large group of excavated and unused gas and water distribution uPVC pipes to elucidate the possible causes, grouped according to the different lifetime stages of a uPVC pipe (processing, installation and service). If the origin of the ageing rate differences becomes clear, an appropriate measurement technique may be developed in the future to determine in situ the ageing rate of a uPVC pipe.

The residual lifetime of a uPVC pipe depends not only on changes over time caused by physical ageing, but also by the initial product quality as characterised by the level of gelation. In Chapter 5 a systemic study is performed to identify possible methods that allow in-situ, non-destructive determination of the level of gelation over various thicknesses. Possible alternative measurement methods are considered as well.

In Chapter 6 the practical implementation of the residual lifetime assessment method is discussed based on the findings presented in Chapters 2 to 5. The conclusions and recommendations for future research are presented in Chapter 7.

Chapter 2

Quantitative assessment of the residual lifetime of uPVC pipes employing a robust non-destructive micro-hardness approach

2.1 Introduction

Unplasticised poly(vinyl chloride) (uPVC) pipe materials have been used for a long time in the Dutch gas and water distribution networks. In the course of time the mechanical properties of the materials change due to physical ageing, as explained in the introduction of the thesis. The physical ageing process is associated with small changes in conformation of the molecular chains of the polymer. After manufacturing of the uPVC pipe relatively rapid cooling has caused the material to be in a non-equilibrium thermodynamic state, which serves as the driving force for the physical ageing process. The conformational changes lead to an increase of the resistance against plastic deformation; the yield stress of the uPVC pipe increases, making the uPVC pipe stronger, but yet more prone to unwanted brittle failure if impacted. All pipes being too brittle should be located in good time and replaced for safe exploitation of the uPVC distribution network.

Non-destructive, in situ and autonomous monitoring of changes in the thermodynamic state of uPVC pipes would be a helpful approach for the development of cost-effective replacement strategies. Autonomous robots for inspection of low-pressure gas distribution networks are currently in development [48–50]. Such robots can carry out inspection and measurements from inside the pipe, making expensive excavation to expose the uPVC pipe network unnecessary.

Micro-indentation [47] and ultrasonic non-collinear wave mixing [51] are pos-

sible non-destructive measurement techniques for determining changes in the thermodynamic state of uPVC materials. The micro-indentation systems and ultrasonic transducers/receivers can be made quite compact to fit within uPVC pipes, increasing the potential to use these techniques for practical pipe inspection methods. However, a measurement procedure for determining changes in the thermodynamic state automatically employing the non-collinear wave mixing technique is less well developed than in the case of the micro-indentation technique. This chapter therefore continues with using the micro-indentation technique and the ultrasonic non-collinear wave mixing will not be elaborated on.

This research project focuses on (i) monitoring changes in the thermodynamic state of uPVC pipes using a micro-hardness approach and (ii) predicting the residual lifetime of uPVC pipes. The development of the monitoring system should lead to a simple and robust system that is easy to operate, performs in a reliable way and requires only small amounts of energy and maintenance. It was therefore decided to refrain from pre-treatment of the specimen surfaces. No grinding and/or polishing of the inner wall of the uPVC pipes has to be carried out. In this way additional pre-treatment functionality does not need to be integrated within future autonomous robot systems.

Recently, Visser et al. have shown that changes in the thermodynamic state of uPVC pipe specimens can be monitored non-destructively employing instrumented micro-indentation measurements [47]. A linear relation between the yield stress and the hardness, as deduced from the micro-indentation measurements, was found. This result shows that the hardness can be related to the ageing kinetics of the yield stress and allows the age of an uPVC pipe to be determined non-destructively using micro-indentation measurements. The residual lifetime of the uPVC pipe material could be predicted if a critical limit to the yield stress (at which the failure behaviour of the pipe become unacceptable) was assumed [45, 47].

However, the methodology faced two practical problems: (i) a rather complicated and sensitive instrument was required to assess the material's hardness and (ii) the precision of the residual lifetime assessment method was fairly low.

In this study a new and more robust measurement set-up is presented that is less sensitive to changes in environmental conditions and could form the basis for future in-situ pipe inspection systems. The set-up is based on micro-Vickers hardness measurements; it is presented in the first part of the chapter. The influence of surface roughness and (visco) elastic recovery on the precision of the micro-Vickers hardness measurements is studied in the next part of the chapter. Finally, hardness measurements have been performed employing the new set-up to assess the influence of physical ageing on the mechanical properties of a series of uPVC specimens taken from the gas and water distribution networks. A statistical approach is included to estimate the residual lifetime of aged uPVC pipes.

2.2 Micro-hardness approach

2.2.1 Selection of hardness measurement method

Various hardness measurement methods, such as Shore, Vickers, Brinell and Rockwell B & C [52–55], could be applied to determine the hardness of polymers. The hardness, as a measure of the resistance against plastic deformation, is determined from the depth or width of the resulting indent. The determination of the hardness in a relatively small uPVC pipe requires a measurement set-up that is correspondingly small or that has the potential to be manufactured to such dimensions. The thickness of a uPVC pipe wall is typically of the order of a few millimetres putting, constraints on the hardness measurement method. The depth of the indent should remain small to avoid interference of the hardness measurement by the material supporting and surrounding the buried uPVC pipe in the soil. The use of a micro-hardness approach is proposed for this reason and the micro-Vickers hardness measurement has been selected. This approach uses a small pyramidal diamond indenter, which is pressed into the specimen employing a constant mass. The hardness is usually determined from the average length of the indent diagonals. These lengths are commonly determined using a dedicated light microscope that goes with the micro-Vickers set-up. Older systems require manual determination of the diagonal lengths, but modern systems use automated image recognition techniques. The value of the mass can be selected on the basis of the anticipated indent dimensions. For measurement of the micro-Vickers hardness of uPVC pipes the indent widths are of the order of 100-200 μm , employing a mass of 200 g. In this case the indent depths are of the order of only 10-20 μm , which is sufficient to prevent any influence of the material supporting the uPVC specimen on the hardness determination. In this way, the micro-Vickers hardness measurement approach is virtually non-destructive for the uPVC pipe material.

2.2.2 Automated hardness determination

The in-situ inspection of many kilometres of gas and water pipes requires a fast, robust and reliable hardness measurement system. Automated hardness determination is essential to map the hardness distribution in the pipe network effectively. Indents are placed at numerous positions within the pipes and should be analysed quickly and reliably. The image recognition system works best if the images show sufficient contrast, i.e. the indents are clearly discernible from the adjacent unindented pipe material. This puts demands on the contrast and resolution of the indent images obtained and, related to this, on the quality of the material surface under study. In this thesis the pipe material on the inside of the uPVC pipes is not polished, for reasons explained in the introduction. As a consequence the

automatic determination of the hardness becomes challenging. This will be explained with the help of Figure 2.1. A schematic representation of a Vickers indent for a fully plastic material is shown in Figure 2.1 left by the grey lines. The indenter is still present although not drawn here. After removal of the indenter, the black lines show the typical outline of an indent in uPVC, indicating that the material shows considerable visco-elastic behaviour. As such, this does not pose a problem, however; the corresponding optical image of such an indent for a representative uPVC specimen is shown in Figure 2.1 right. The poor reflective properties of uPVC causes reduced image contrast. The outline of the indent is not visible in this image, making the determination of the diagonal lengths impossible. Hence, conventional image recognition techniques applied to optical images of indented uPVC pipes fail to accurately determine the diagonal lengths.

Figure 2.1 *Left: a schematic representation of a Vickers indent for a fully plastic material (grey lines) and for a uPVC pipe material (black lines). The arrow in the centre of the indent indicates the indent depth δ after (elastic and) visco-elastic recovery of a PVC material. The four dashed arrows indicate the edges of the indent. Right: an optical image (enhanced for clarity) of an indent in a PVC material taken using the optics on Vickers indentation system. The white arrow indicates the location of the indent tip.*

A different approach is followed here. The indents and an area in the vicinity of the indents are scanned by a confocal microscope after indentation. This microscope provides surface topology data that allows in principle the determination of the shape of the indent on a uPVC specimen surface. An example of the laser intensity picture obtained from an indented uPVC pipe specimen is shown in Figure 2.2 left. The outline of the indent is more clearly visible than in Figure 2.1 right, despite the presence of surface roughness. Unfortunately, the indentation procedure does not eliminate the surface roughness at the location of the indent. Small-scale asperities remain after indentation, possibly as a result of (visco) elastic recovery. This surface roughness hampers the straightforward determination of the diagonal lengths as it is difficult to locate the diagonal ends precisely. A control specimen with a polished surface has been indented as well under comparable conditions, see Figure 2.2 right. In that case determination of the diagonal lengths of the indent is very possible. It shows that the confocal microscope in principle allows for an accurate determination of the indent dimensions, but that the surface roughness reduces the accuracy.

Figure 2.2 *Laser intensity picture of an indent on an untreated specimen (left) and on a polished specimen (right), both taken from pipe 11.*

However, the numerical data of the confocal microscope can be analysed to determine the depth of the indents. Determination of indent depths is done routinely, for example, as part of the Rockwell hardness measurement, albeit a different indent body is used. In this work the indent depth is used as a way of characterising the micro-Vickers hardness of uPVC pipes. The definition of the hardness based on indent depth is provided in the next section. The influence of visco-elastic recovery on the indent shape and depth is relatively large as was also shown schematically in Figure 2.1 left. The indent depth will not only depend on the thermodynamic state of the material, i.e. the actual strength/hardness, but also on the time elapsed between the hardness indentation and the confocal microscope measurement. The influence of these effects will be dealt with in Section 2.4.

2.2.3 Measure for the thermodynamic state

The Vickers hardness is defined as the ratio between the load F given in kilograms-force and the area A of the resulting indentation in millimetres squared [56]. The area is related to the shape of the indenter according to:

$$A = \frac{d^2}{2 \sin\left(\frac{\theta}{2}\right)}, \quad (2.1)$$

with d the length of the indent diagonal and θ the apex angle of the indenter's square-based pyramid ($\theta = 136^\circ$). Hence, the Vickers hardness is defined as:

$$HV = \frac{F}{A} = \frac{2F \sin\left(\frac{\theta}{2}\right)}{d^2}. \quad (2.2)$$

The relation between the length of the diagonal d and the indent depth, δ , is given by:

$$\delta = \frac{d}{2\sqrt{2} \tan\left(\frac{\theta}{2}\right)}. \quad (2.3)$$

Combining Equations 2.2 and 2.3, the following relation can be derived:

$$HV = \frac{F \cos\left(\frac{\theta}{2}\right)}{4\delta^2 \tan\left(\frac{\theta}{2}\right)} = C \frac{F}{\delta^2}, \quad (2.4)$$

with $C \approx 0.0378$ if no (visco)-elastic recovery occurs. In general, recovery effects are expected after indentation of a thermoplastic material, such as uPVC. Hence, an alternative hardness scale is defined on the basis of the measured indent depths δ as:

$$H_\delta = \frac{F}{\delta^2}, \quad (2.5)$$

neglecting the term C . The last step is only allowed if the influence of the (visco)-elastic recovery is independent of the thermodynamic state and level of gelation of the uPVC pipe materials considered. It will be shown in Section 2.4 that this assumption is indeed valid for the materials studied in this thesis.

2.3 Experimental

2.3.1 Materials

All specimens were taken from unused uPVC gas pipes (pipes 10-13) and an unused uPVC water pipe (pipe 8). Pipes 10-13 have the same composition, but differ only in level of gelation. The diameter and wall thickness of the pipes are given in Table A.1 in Appendix A.

2.3.2 Specimens

Specimens of approximately $70 \times 70 \text{ mm}^2$ were taken from the unused uPVC pipes. A part of the specimens was pressed at 100°C (about 20°C above the glass transition temperature T_g) for 25 minutes between metal plates at a compressive stress of 2 MPa. This operation erased the thermodynamic history of the material (rejuvenation). The pressed specimens were subsequently cooled under pressure to room temperature within 5 minutes. The thickness of the flattened specimens was approximately equal

to the original wall thickness of the pipe, which shows that no large-scale plastic deformation occurred during the rejuvenation process. Tensile bars were milled from a number of flattened specimens. A gauge section was milled, having a width of 5 mm and a length of 35 mm. The length direction of the specimens was oriented along the extrusion direction of the pipe. A part of the prepared specimens was physically aged after rejuvenation by annealing at 40 °C, 50 °C and 60 °C for various times in climate chambers. The remaining rejuvenated specimens were stored at -40 °C to prevent (significant) ageing during storage. Micro-hardness experiments were carried out on (i) untreated and flattened specimens to investigate the influence of surface roughness, (ii) on flattened specimens to investigate the influence of recovery and (iii) on the end sections of the tensile bars. After determination of the hardness H_δ at the ends, the tensile bars were subjected to a tensile test enabling a direct comparison between micro-hardness and tensile test results.

2.3.3 Equipment

Micro-hardness experiments were carried out using an automated Leco AMH43 indenter. The indenter is equipped with a Vickers indenter diamond having an apex angle of 136 °. For all micro-hardness experiments, a load of 200 g was applied for 15 seconds. These values were selected to prevent influence of the material supporting the PVC specimen on the hardness measurement and to obtain indent dimensions that do not exceed the field of view of the microscope objective. The indents were made with 1 mm inter-distance. For this inter-distance, the influence of neighbouring indents was negligible as the typical diagonal length of an indent does not exceed 200 µm. The specimen was left on the indenter system for at least ten minutes to permit the temperature inside the specimen to equilibrate prior to each micro-hardness experiment. All micro-hardness experiments were performed at room temperature.

The indented surfaces were scanned by an automated Keyence VK-9700 laser scanning confocal microscope equipped with a 408 nm laser source. An objective lens having a magnification of 50 X and a numerical aperture of 0.95 was used. The vertical and lateral resolutions of the set-up are 1 nm and 276 nm respectively. Unless specified otherwise, all specimens were allowed to recover at least one day after indentation to minimise the influence of recovery effects on the experimental results. All indented specimens were kept at room temperature during this recovery period.

The tensile experiments were performed using a Zwick Z5.0 universal tensile testing machine equipped with a 2.5 kN force cell. All tensile experiments were carried out at a constant strain rate of 10^{-3} s^{-1} and at room temperature. The temperature of the specimens was equilibrated for at least ten minutes before each tensile test. The surface temperature of each specimen was kept within $22.1 \pm 0.5 \text{ °C}$. The engineering yield stress was determined using the average of the initial cross-sectional surface

areas measured at three locations along the gauge section and the maximum force in the force-displacement graph. Triplicate tensile measurements were performed after each annealing treatment.

2.3.4 Indent analysis

The hardness H_δ was determined from the confocal microscope topology data according to the following procedure: (i) a 5×5 median filter was applied to remove noise in the confocal microscope data (ii) a tilt correction was applied to correct for minor misalignment (iii) the reference plane was determined from the average surface position in the vicinity of the indent (iv) the depth at the indent tip was determined by locating the point having the maximal value in depth (v) the indent depth, defined as the distance between the reference plane and the indent tip, was determined and (vii) the hardness H_δ was determined from the indent depth using Equation 2.5.

In general, the measured H_δ values of a single specimen fall within a narrow range. The typical value of the coefficient of variation of the H_δ values measured is about 8%. Relatively large deviations of the H_δ values that could be attributed to indentations carried out on relatively large surface defects such as scratches were neglected for the determination of the thermodynamic state.

2.4 Precision of the Vickers indenter and the confocal microscope

The micro-hardness approach consists of using two experimental set-ups: the Vickers indenter and the confocal microscope as described in the previous section. The precision of each set-up was investigated using three measurement series:

1. Ten confocal microscope measurements of a single indent on a flattened specimen taken from pipe 11. This series captures the variation in H_δ values caused only by the confocal microscope.
2. Ten indents on several locations on a calibration specimen specified in JIS B 7730 [57]. This series captures the variation in H_δ values caused by both the confocal microscope and the Vickers indenter for a calibration specimen. It is assumed that the variation in the H_δ values over the calibration specimen is negligible.
3. Ten indents on several locations on the inner wall surface for a uPVC specimen taken from pipe 11. This series captures the variation caused by the confocal microscope, the Vickers indenter and the variation within the material itself.

The indents of the uPVC specimens were measured with the confocal microscope after an extensive recovery period of thirteen days. Preliminary experimental results show that the hardness value of a single indent decreases by about 3% between one day and eleven days of recovery time. This decrease is a factor four less than the typical variation of the H_δ values of several indents measured (about 8%). As the recovery progresses on a logarithmic timescale the recovery after eleven days will progress at an even lower rate. The influence of the recovery effects on the experimental results for a recovery period of thirteen days can therefore be neglected.

The coefficients of variation (CV) of the H_δ values for each measurement series are shown in Figure 2.3. The variation in the H_δ values caused by the confocal microscope (CV of series 1) is about eleven times smaller than the variation in the H_δ values over the surface of the uPVC specimen (CV of series 3). Furthermore, the CV for the calibration specimen (CV of series 2) is about five times lower than the value for a uPVC specimen (CV of series 3). This strong difference shows that the precision of the Vickers indenter and the confocal microscope are sufficient for this study. The relatively large variation in the H_δ values observed over the surface of the uPVC specimen is further studied in Section 2.6. First, the results of the study on the influence of visco-elastic recovery on the hardness H_δ are shown and discussed in the next section.

Figure 2.3 The coefficient of variation (CV) (= standard deviation/mean) of the H_δ values for three measurement series.
 (1) ten microscope measurements of a single indent on a flattened specimen taken from pipe 11.
 (2) ten indents on several locations on a calibration specimen specified in JIS B 7730 [57].
 (3) ten indents on several locations on the inner wall surface for a specimen taken from pipe 11.

2.5 Influence of visco-elastic recovery and physical ageing

The hardness H_δ of uPVC pipes is based on the indent depth, as explained in Section 2.2. After the indenter has been removed from the specimen surface, (visco) elastic recovery of the deformed volume takes place, effectively reducing the indent depth. A typical topography of an indent resulting from a micro-hardness test on uPVC is illustrated in Figure 2.4. It shows the topography data as measured by the confocal microscope along a diagonal of the indent of the uPVC specimen from measurement series 1 (see previous section). The location of the tip of the indent is clearly visible, along with small variations in height associated with surface roughness. A straight line is visible that represents the reference plane at this location. The indent depth is estimated as the distance from the indent tip to this (reference) line. It is approximately equal to 10 μm in this case. The diagonal length could also be estimated by measuring the distance between both intersection points of the line with the height / topography data. The distance is about 103 μm . If it is assumed that the diagonal lengths are not affected by the (visco) elastic recovery process, the location of the indent tip just before removal of the indenter at the end of the waiting time of the hardness measurement can be determined from the shape of the indenter using Equation 2.3. The location of the indenter is indicated in the figure by the dashed lines. Apparently, strong (visco) elastic recovery effect occurred after removal of the indenter.

The basis of the approach is the assumption that recovery effects work out in a similar fashion for all uPVC specimens. It means that if specimen A has a higher H_δ than specimen B at recovery time t , it should also have a higher H_δ value than specimen B at time $t + \Delta t$, irrespective of the value of Δt . If this is true, the H_δ values of uPVC specimens are uniquely determined at any recovery time, as long as all specimens are measured at the same recovery time.

The kinetics of the recovery process has been studied for uPVC pipes, that vary in the degree of physical ageing and/or the level of gelation. An indent was made on each specimen. The recovery behaviour of the indents was determined by performing confocal microscope measurements at various times after indentation. The recovery behaviour of the indents is shown in Figure 2.5. In all cases the indent depths reduce with the recovery time. The behaviour can be described reasonably well by a linear dependence on the logarithm of the recovery time [52] in the studied range for each uPVC pipe.

The recovery behaviours of pipes of the same uPVC grades are comparable. The slopes of the fitted lines of the “rejuvenated” and the “severely aged” uPVC specimens are very similar, see Figure 2.5 left. The same holds for all uPVC specimens with a different level of gelation in Figure 2.5 right. However, the slopes of the fitted

Figure 2.4 Topography data along a diagonal of an indent of a uPVC specimen of pipe 11 (measurement series 1). The estimated original position of the indenter before removal is shown by the dashed lines. Further explanation can be found in the text.

Figure 2.5 The indent depth versus the recovery time for indents made on a rejuvenated or severely aged specimen of pipe 8 (*left*) and specimens of pipes 10-13 differing in the level of gelation (*right*). The straight solid lines in the graphs are linear functions which were fitted on a logarithmic time scale using the least squares method.

lines of both uPVC grades differ to some extent, which suggests that for a precise determination of H_δ , the recovery behaviour should be included in the analysis. The differences in recovery behaviour between the uPVC grades are rather small: it is estimated that the error made in the indent depth is of the order of 0.5-1.0 μm , which corresponds approximately to a relative error of 5-10%. These values are still acceptable for application in practice and allow the use of Equation 2.5 as a means of defining the specimen hardness at a constant recovery time.

For practical applications, relatively short recovery times are preferred when determining the thermodynamic state of a uPVC pipe within an acceptable time frame. The results in Figure 2.5 show that differences in the thermodynamic state of uPVC specimens were observed for recovery times in the same order of magnitude as will be used in practical applications. The micro-hardness approach may therefore be

suited for use in practice.

2.6 Origin of the variation in H_δ values

The precision of the measurement approach was studied by measuring H_δ of a specimen from pipe 11 multiple times, as set out in Section 2.4. The coefficient of variation (CV) of the H_δ values reached almost 8%, which was much higher than could be accounted for by the variation inherent to the measurement system employed. The observed variation in H_δ values may be related to the presence of inhomogeneities in the bulk of the uPVC materials and/or surface roughness. The inhomogeneities include primary ($\sim 1 \mu\text{m}$) particles and filler particles (about 0.7-20 μm for CaCO_3) [58] in the bulk, which are typically smaller than the lateral dimensions of an indent (approximately 120 μm). The roughness on the inner surface of the wall of uPVC pipes varies and may originate from variations in processing temperature [59, 60], inner surface roughness of the extruder die [60], molecular weight [60] and/or additives [61].

The influence of surface roughness on the variation in the measured H_δ values was studied by comparing the CV of H_δ for uPVC specimens having different levels of surface roughness. Three uPVC specimens were taken from pipe 11. One specimen was pressed according to the procedure described in Section 2.3, one specimen was polished and one specimen was left untreated. Micro-hardness measurements were carried out at various positions on each specimen and H_δ was determined in the manner described in Section 2.3.4. The surface roughness was characterised by the parameter R_a which is based on local variations in surface height. The parameter R_a is defined as the arithmetic average of the absolute height values and is given by [62]

$$R_a = \frac{1}{n} \sum_{i=1}^n |y_i|, \quad (2.6)$$

where n is the number of equally spaced points over the surface and y_i is the height of the mean height for the i^{th} data point. For each micro-hardness experiment, the value of R_a was determined from the surface in the vicinity of the indent.

The variations in the H_δ values for the specimens from pipe 11 with different surface treatments are shown as a function of R_a in Figure 2.6 left. The variation in H_δ clearly reduces with decreasing R_a . The CV of the polished uPVC specimens is not much larger than the CV of series 1 (see Figure 2.3) that represents the CV of the measurement system. The results indicate that the large variation in H_δ values observed for the untreated uPVC specimens can be ascribed to the presence of surface roughness. If inhomogeneities were the main cause of the variation in H_δ , no decrease in the H_δ variation would be expected for specimens with a smoother surface as the

distribution of subsurface particles with different H_δ values does not depend on the surface conditions.

Figure 2.6 *Left:* the CV of the H_δ values versus the average surface roughness for an untreated specimen, a pressed specimen and a polished specimen (all taken from pipe 11). The values of R_a were determined using Equation 2.6. The horizontal line represents the value of CV caused by the confocal microscope taken from Figure 2.3. The horizontal error bars represent one standard deviation out of at least nine measurements. *Right:* the standard deviation in the depth versus R_a for the same specimens. The solid line represents the case where the standard deviation in the depth is equal to R_a .

The relationship between surface roughness and uncertainties in the hardness determination is shown in Figure 2.6 right. Here, the standard deviation of the indent depths of the specimens is plotted as a function of R_a . Micro-hardness experiments carried out on untreated specimens taken from other uPVC pipes and plates show the same linear relation. Thus, for practical purposes, the relation observed here may be used to estimate the expected variation in the H_δ values from surface roughness measurements.

The indent depth is determined from the difference in the position of the indent tip and the reference plane. Uncertainties in both positions affect the uncertainty in the indent depth. The indent tip position is found by means of the procedure described in Section 2.3.4. The indent tip position was determined from a single data point having the highest depth value (method 1). A certain level of surface roughness may be identified at the indent tip from the topology data of the confocal microscopy, see for example Figure 2.2 left. The surface roughness is still present even though the load near the indent tip location during the hardness testing was relatively high. A second method (method 2) was developed that determines the position of the indent tip with a dedicated software tool. The second method does not use a single data point to determine the position of the indent tip, but uses several data points by fitting the geometry of the indenter to the topology data available (method 2).

The performance of the second method was determined by comparing the corresponding CV values with those of method 1 for the specimens of measurement series 1 to 3, as used previously in Section 2.4. All results are collected in Figure 2.7.

Figure 2.7 The CV of the H_δ values for analysis methods 1 and 2 for the three measurement series which were described previously in Section 2.4.

At first sight, method 2 seems to be more robust than method 1 as the CV for series 1 decreased from 0.7% to 0.2%. Method 2 uses more data points to determine the exact location of the indent tip. The determined H_δ values are therefore less sensitive to variations in depth values of individual data points. However, for series 2 and 3 the CV employing method 2 is comparable to the values obtained from method 1. From these results it may be concluded that the determination of the depth location of the indent tip from the confocal microscope topology data is not the main source of variation of H_δ . Instead, the determination of the height of the reference plane from the data is the main source. Apparently, the presence of surface roughness leads to uncertainties in the exact location of the reference plane if the topology data in the neighbourhood of the indent is used to reconstruct the location of the indented surfaces before indentation.

A possible way to decrease the variation in measured depth values is to increase the mass used during the hardness measurements. In that way the indent depth would increase without any change in the surface roughness, i.e. R_a remains constant.

A series of micro-hardness measurements was performed employing a mass of 1 kg on the inner surface of an untreated specimen taken from pipe 11. No reduction in the variation of H_δ could be observed. This somewhat surprising outcome may be related to the fact that two out of nine measurements showed indentation depth values that were considerably different from the other seven. Without these two measurements, the standard deviation was less than the value obtained with the mass of 200 g. This suggests that using a higher load can be beneficial to the precision, but the number of measurements should be appropriate.

Further analysis of the specimen surfaces indicated that the surfaces can be characterised by a certain waviness along with the presence of grooves and spider lines. These features are inherent to the manufacturing process of the uPVC pipes as mentioned earlier.

The results indicate that the determined values of the indent depths contain a certain stochastic nature that should be incorporated accordingly. The results are also in line with common practice in measurement of hardness values where specimen surfaces are usually prepared in accordance with the requirements of the hardness measurement method employed [56]. Nevertheless, the accuracy and precision of the presented approach employing a Vickers indenter in conjunction with a confocal microscope is sufficient to study the development of the hardness of uPVC specimens over time, as a way to estimate the residual lifetime of uPVC pipe materials in practice.

2.7 Quantitative assessment of the residual lifetime of uPVC pipes

2.7.1 Influence of physical ageing

The yield stress of uPVC pipes increases over time due to physical ageing, as explained in the introduction to this chapter. Changes in the yield stress may be reflected in the material's hardness, as was observed by Visser et al. [47] (employing a different approach). In this section the relationship between the yield stress and the hardness H_δ of uPVC pipe materials with different thermodynamic states is studied employing the approach based on micro-Vickers hardness indentation and confocal microscopy as presented in the previous sections.

The study consists of a series of hardness and tensile test experiments. The tensile bars were annealed at several temperatures below T_g and for different annealing times. On the ends of each tensile bar, nine micro-hardness experiments were carried out prior to tensile testing. The average H_δ values obtained from these experiments are plotted against the annealing time for each annealing temperature in Figure 2.8. It can be seen that H_δ increases with the annealing time and the annealing temperature.

2.7.2 Relating the hardness H_δ to the yield stress

The yield stress values of the tensile bars were determined after the micro-hardness experiments were performed. These values are shown in Figure 2.9 left. The yield stress increases with annealing time and temperature showing that physical ageing occurred during the annealing treatments. The behaviour of the yield stress upon annealing is similar to the behaviour of H_δ , as can be concluded by comparing Figures 2.8 and 2.9; the yield stress and H_δ both increase with annealing time and temperature. The ageing activation volume, ΔU_a , can be determined from the yield stress data measured at different annealing times and annealing temperatures. A

Figure 2.8 The hardness H_δ versus the annealing time for different annealing temperatures T_a . The error bars represent one standard deviation determined from 27 micro-hardness experiments on three tensile bars. The tensile bars were taken from pipe 11. The recovery of the indents took place at 22–24 °C, and the indentation depths were measured approximately one day after indentation.

master curve of all yield stress data as a function of the ageing time at a certain reference temperature can then be composed.

Figure 2.9 **Left:** the engineering yield stress determined for tensile bars taken from pipe 11 which were annealed for various times at different temperatures. **Right:** the shifted yield stress versus the effective time. The effective time was determined using Equation 2.7 and an ageing activation energy of 185 kJ/mol. The dashed line is a guide to the eye. The error bars represent the maximum deviation from the average value for three measurements.

The yield stress can be shifted horizontally to a master curve by applying a time-temperature superposition [40, 63]. The horizontal shift factors a_T can be described with an Arrhenius equation [63]

$$a_T(T_a) = \exp \left[\frac{\Delta U_a}{R} \left(\frac{1}{T_a} - \frac{1}{T_{\text{ref}}} \right) \right], \quad (2.7)$$

where R is the universal gas constant, T_{ref} the reference temperature and T_a the annealing temperature. The logarithm of the shift factors for shifting each curve to the 60 °C annealing curve is plotted against the reciprocal annealing temperature in Figure 2.10. The ageing activation energy ΔU_a was calculated from the slope, resulting in a value of 185 kJ/mol for this uPVC pipe. The value is of the same order of magnitude as the values of the ageing activation energy found for other uPVC pipes (115 kJ/mol [40] and 238 kJ/mol [45] respectively). The origin of differences in the ageing activation energy of uPVC pipes is discussed in detail in Chapter 4. Using Equation 2.7 and the ageing activation energy of 185 kJ/mol, the yield stress values in Figure 2.9 left are shifted to a reference temperature $T_{\text{ref}} = 10$ °C, which is the average temperature of uPVC pipes in the ground, and shown in Figure 2.9 right. The figure clearly shows the increase of the yield stress over time due to physical ageing, where all data points obtained from different annealing treatments build up a common master curve.

Figure 2.10 The shift factor a_T plotted against the reciprocal annealing temperature as measured on pipe 11.

Applying the same ageing activation energy to the hardness data shown in Figure 2.8, results in a similar master curve, as shown in Figure 2.11. The resulting curve of H_δ is comparable to the curve of the yield stress visible in Figure 2.9 right, showing that the H_δ values can be shifted using the same Arrhenius relation as was used to shift the yield stress values. This observation confirms that H_δ determined from micro-hardness experiments can directly be related to the yield stress, similar to the procedure described by Visser [47].

The yield stress values are plotted against the corresponding H_δ values in Figure 2.12. A linear relationship is found, similar to the one observed by Visser et al. for another uPVC pipe employing a different indentation set-up and data reduction method [47]. The variation in the hardness values compared to the maximum increase in the hardness in the study of Visser is 7.5%. In this study, a value of 8.5% is found. Hence, the sensitivity of both hardness methods of monitoring the effects of physical

Figure 2.11 The hardness H_δ versus the effective ageing time. The dashed line is a guide to the eye.

ageing is similar. The advantage of the method applied in the current study is that it is more robust and thus more suitable for practical applications. The variation in the H_δ values is related mainly to surface roughness of the studied specimens, as discussed in the previous section. The variation in the measured yield stress is relatively small. The variation in H_δ values is therefore considered the main factor determining the precision of the residual lifetime assessment method presented in the next section.

Figure 2.12 The yield stress versus the hardness H_δ as determined for pipe 11.

2.7.3 From hardness H_δ to residual lifetime

The residual lifetime of a uPVC pipe is defined in this thesis as the time remaining for the pipe to reach a pre-defined yield stress, or equivalently, a pre-defined H_δ value, at the reference temperature. As mentioned in the previous section, the reference temperature used here is 10 °C. The pre-defined yield stress and/or H_δ

values provide upper limits that should not be exceeded, so as to prevent unwanted failure behaviour, such as brittle fracture, upon impact during excavation activities.

The procedure to determine the residual lifetime is as follows. First, the H_δ of a selected uPVC pipe is assessed with the newly developed micro-Vickers approach. The corresponding yield stress value is obtained using the relationship between H_δ and yield stress as displayed in Figure 2.12. The time to reach the limiting (predefined) value of the yield stress can then be determined from the known development of the yield stress over time, i.e. the kinetics of the physical ageing process. This time constitutes the residual lifetime of the (u)PVC pipe investigated. If the value of the yield stress obtained is above the limiting one, the particular PVC pipe is considered unsafe for application in service conditions and should be replaced.

The study of the micro-Vickers approach in the previous sections has shown that some degree of variation around an average H_δ value can occur. The H_δ distribution was studied in more detail by performing 50 hardness measurements on the inner surface of an untreated specimen taken from pipe 11. The hardness indents were allowed to recover for one month at room temperature.

The resulting H_δ distribution is shown in Figure 2.13 by the histogram. A normal (Gaussian) distribution function fits the data rather well ($R^2 = 0.93^*$) and the distribution can be characterised by a standard deviation S of 244 kgf/mm². In practice the number of indentations should be kept as low as possible. The required sample size n for approximating the true H_δ is given by [64]:

$$n = \left(\frac{Sz}{E} \right)^2, \quad (2.8)$$

where S is the standard deviation of the distribution of H_δ values, E is the desired margin of error in the approximated true H_δ and z is the critical value determined from the desired confidence level C of the confidence interval. The confidence interval has a total width of $2E$ centred around the average hardness $\bar{H}_\delta$ which is determined from n measurements. The formula can be used here since the distribution of H_δ values complies with the normal distribution, as exhibited in Figure 2.13.

The required sample size versus the confidence level was calculated for two confidence intervals: (i) 2% variation on the average hardness, $0.98\bar{H}_\delta < \bar{H}_\delta < 1.02\bar{H}_\delta$ and (ii) 5% variation on the average hardness, $0.95\bar{H}_\delta < \bar{H}_\delta < 1.05\bar{H}_\delta$. The number of micro-Vickers hardness measurements necessary to assure a certain level of confidence is given in Figure 2.14, utilising the standard deviation of the H_δ distribution shown in Figure 2.13. The sample sizes required for 95% confidence ($z = 1.96$ [64]) and 98% confidence are about 20 and 110 hardness measurements respectively. The required numbers of measurements are large, but still acceptable.

*Similar values of R^2 were found for measurement series on other uPVC pipes.

Figure 2.13 Histogram for fifty measurements of H_δ performed on the inner surface of an untreated specimen taken from pipe 11. The indents recovered for one month at room temperature. The solid line represents the best fit of a Gaussian function. The standard deviation S of the H_δ values of this measurement series is 244 kgf/mm^2 .

Figure 2.14 The sample size versus the confidence level for 5% (113 kgf/mm^2) and 2% (45 kgf/mm^2) margins of error using Equation 2.8 and the standard deviation $S = 244 \text{ kgf/mm}^2$.

The relation between the micro-Vickers hardness and the prediction of the residual lifetime of a uPVC pipe is shown schematically in Figure 2.15. The confidence intervals are given by the dark grey and light grey areas. The range of H_δ values within the confidence interval corresponds to a range of yield stress values employing the relationship between the yield stress and the hardness H_δ established previously. This corresponds to the horizontal light grey and dark grey bars in Figure 2.15 (left and right). Subsequently, the ranges of yield stress values correspond to ranges of effective times, utilising the known relationship between the yield stress and the effective time (i.e. the ageing kinetics). In this way the variation in H_δ values leads to certain variations in effective time as shown by the vertical light and dark grey bars in Figure 2.15 right.

The lower and upper limits in the ranges of residual lifetimes are determined

Figure 2.15 The procedure used to determine the residual lifetime from hardness measurements. The dark and light grey areas represent the confidence intervals with 5% (113 kgf/mm²) and 2% (45 kgf/mm²) margins of error in the average hardness $\bar{H}_\delta$ respectively, where n is the sample size for a confidence level C of 95% and a standard deviation S of 244 kgf/mm². The dashed lines indicate a fictive value of the limiting yield stress σ_{lim} and the corresponding time for pipe replacement.

assuming a hypothetical limiting yield stress, σ_{lim} , that corresponds to a certain maximum age of the PVC pipe. In this case, for 20 hardness measurements (5% confidence interval), the lower and upper limits of the residual lifetime will be 29 years and 51 years (22 year range) respectively. For 110 hardness measurements (2% confidence interval), the lower and upper limits will be 41 years and 49 years (8 year range) respectively. In conclusion: the approximation of the true H_δ improves and the precision of the residual lifetime assessment method increases if the number of hardness measurements is enlarged.

The required sample size can also be determined from a desired degree of precision in the residual lifetime instead of determining the degree of precision in the residual lifetime from the sample size. The required sample size depends not only on the standard deviation S and the confidence level C , but also on the functional behaviour of the yield stress versus H_δ and the yield stress versus the effective time. For example, the spread in the yield stress values in Figure 2.15 left is strongly dependent on the tangent of the yield stress versus H_δ line. The steeper the line, the greater the spread of the yield stress for a given confidence interval of H_δ values. A similar case holds for the yield stress versus the effective time in Figure 2.15 right. The less steep the yield stress versus the effective time line, the greater the spread of the effective time for a given spread in the yield stress.

The effective time axis of Figure 2.15 right is on a logarithmic basis. This has consequences for the precision of the residual lifetime prediction. If the widths of the dark grey and light grey areas on the effective time axis remain the same, but these areas are shifted to the right on the time axis, the corresponding range of years on a linear scale is strongly increased. Hence, the precision of the prediction of the

residual lifetime in number of years on a linear scale strongly reduces.

The prediction of the residual lifetime is also influenced by the standard deviation of the H_δ distribution, S , as the roughness amongst uPVC pipes will vary depending on the process conditions during manufacturing. A value of S may be estimated from roughness measurements and the relationship between the standard deviation of the indent depth and R_a shown in Figure 2.6 right.

2.8 Discussion

In the previous sections, it was shown that a number of micro-hardness measurements are required for determining the residual lifetime of a uPVC pipe with sufficient precision. A relatively fast measurement procedure is therefore required to determine the yield stress of a pipe within an acceptable time frame. Five possible ways to reduce the required time for the measurement procedure are discussed in the rest of this section.

The first option to speed up the measurement procedure is to reduce the recovery time. A recovery time of 1-2 days as applied in the current experiments is unacceptable for practical applications. A reduction of the waiting time requires the time between hardness indentation and confocal microscope measurement to vary less, because of stronger recovery at shorter recovery times (recovery follows a logarithmic time-path). Automated systems are very capable of following strict indentation and measurements schemes, allowing a substantial reduction of the overall time required to analyse pipe sections.

A further reduction in measurement time can be achieved when the time to scan an indented surface is decreased. In this study, it takes roughly two minutes to determine the position of the indent tip and the reference plane using a high resolution confocal microscope. A faster, less precise measurement technique will suffice in practice as the contribution to the variation in H_δ values caused by the confocal microscope is not significant, see Section 2.6.

Thirdly, the influence of the applied load during the micro-Vickers measurements needs to be further investigated. The number of measurements performed with a load of 1 kg instead of 200 g was relatively small. This may have led to indecisive results. Given the number of hardness measurements required to fully characterise the H_δ distribution in Figure 2.13, a more elaborate study might be able to disclose the relationship between the applied load and the measurement precision. The feasibility of a high load to measure the micro-Vickers hardness H_δ on thin-walled PVC pipes should be included as well.

A fourth option to speed up the measurement procedure is to reduce the number of micro-Vickers measurements. The number is related to the variation in H_δ values.

The H_δ values showed a considerable spread due to surface roughness on the inner wall of the PVC pipes. The surface roughness particularly affected the determination of the reference level around the indent. In the current procedure the reference level is determined from topology data of the surface region close to the indent. However, a more elegant approach would be to scan the uPVC surface region with the confocal microscope twice: prior to and after the hardness measurement. Then the indent depth could simply be determined from the difference between both confocal measurements without anything ado. It is expected that this new procedure strongly reduces the variation in H_δ values and improves the applicability and usefulness of the micro-Vickers approach as a way to estimate the residual lifetime of uPVC pipes.

As a final option, careful preparation of the inner wall of the uPVC pipe could also reduce the surface roughness and improve the precision and accuracy of the determination of H_δ . Such an approach strongly increases the complexity of the device required for in-situ hardness measurement in gas and water distribution networks and was therefore not part of this study.

Future research could focus on how to polish/prepare the inner surface of uPVC pipes without changing locally the thermodynamic state of the uPVC pipe under investigation. Whether polishing can reduce the overall time required to analyse pipe sections depends on the trade-off between the possible reduction of the number of micro-Vickers measurements required and the increase in the time used for surface preparation.

2.9 Conclusions

In this chapter, a new micro-Vickers hardness based approach was presented to determine changes in the thermodynamic states of uPVC pipes employed in gas and water distribution networks. Physical ageing of uPVC pipes causes an increase of the yield stress and the hardness H_δ in course of time that can be monitored with the developed methods.

The measurement approach consists of micro-Vickers hardness measurements with relatively low loads that affect the uPVC pipes minimally and confocal microscopy to determine the topography of the indents. All hardness measurements were performed on non-polished specimen surfaces to replicate the future use of in-situ pipe inspection systems. The hardness H_δ was determined from the indent depth; the diagonal length could not be determined accurately because of the presence of surface roughness. It was shown that the effects of (visco) elastic recovery hardly affected the results of the hardness measurements if the time between the indentation and the subsequent determination of the indent depth was kept constant among the specimens studied or was large enough on a logarithmic time scale. The scatter of the H_δ values determined originated from the surface roughness present and was

caused primarily by variations in the reference level that was used to determine the indent depths. To improve the hardness measurement method it was suggested that the exact topology of the indent region prior to indentation should be determined, instead of estimating its level from the topology data in the vicinity of the indent after indentation.

A linear relationship between the yield stress and the hardness H_δ has been established. The yield stress and H_δ follow the same behaviour over time. The residual lifetime of uPVC pipes can be determined assuming a critical limit to the yield stress and/or H_δ . Statistical analysis has shown that the required number of measurements can be estimated from a desired degree of precision in the residual lifetime.

In practice, a robust and relatively fast measurement procedure is required. From the fact that the sensitivity to physical ageing of the approach presented in this study is similar to the one used by Visser et al. [47] and that a more simple (constant load rather than force controlled) and less precise device is used, it can be concluded that the presented approach is more robust and one step closer to practical implementation.

Chapter 3

Predicting embrittlement of uPVC pipes

3.1 Introduction

The occurrence of brittle failure is the main limitation for the service life of unplasticised poly(vinyl chloride) (uPVC) pipes in the Dutch gas and water distribution networks, as already elucidated in Chapter 1. When brittle failure occurs, a relatively large part of the pipe is destroyed resulting in a large gas or water outflow. Moreover, the sharp, irregular fracture surface makes it difficult to stop the outflow of gas using a temporary stopper. In addition, there is an increased risk of crack propagation at the moment the pipe is plugged.

The subsequent repair procedure of an impact-damaged uPVC pipe usually involves sawing. For ductile pipe material it is relatively easy to obtain a clean saw cut. In contrast, new cracks can form when sawing a brittle pipe. These newly formed cracks can result in a sharp irregular cutting surface, which complicates further repair works. This distinct difference in the behaviour of uPVC pipes during sawing can be demonstrated by a so-called 'saw test' [65]. A photograph and a schematic cross-sectional view of the set-up of the saw test are shown in Figure 3.1 left and right respectively. The loading conditions encountered by sawing a uPVC pipe in practice (like the soil support) are mimicked in the test. A worst-case scenario is simulated by applying a bending moment to the pipe which constraints the pipe. This constraint makes the pipe more prone to brittle fracture when the pipe is sawed.

Figure 3.1 Photograph (*left*) and cross-sectional sketch (*right*) of the saw test set up. One end of the PVC pipe is clamped to simulate the force exerted by the surrounding solid soil. The protruding part is subjected to a bending moment by suspending a weight on the pipe at a fixed distance. A cross-cut saw was used to cut the pipe. Sawing can be done at different saw speeds and temperatures.

The saw test was performed by Weller et al. on two excavated uPVC pipes behaving differently during failure (the failure behaviour was verified using tensile impact tests) [65]. Photographs of saw cuts of the uPVC pipes are shown in Figure 3.2. Significant differences between the saw cuts of pipe A and pipe B were observed for each saw speed and temperature investigated, except for sawing fast at 5 °C. A straight saw cut shows that the pipe exhibited ductile behaviour. An irregular saw cut shows that the pipe failed in a brittle way during sawing. A comparison of the photographs shows that Pipe A fails in a brittle manner at temperatures of 5 °C or lower only if the sawing is done fast. In contrast to pipe A, pipe B performs much worse; only slow sawing at temperatures of 20 °C or higher prevents it from brittle failure. Therefore, sawing a brittle impact-damaged pipe (with similar material properties as pipe B) leads to a higher probability of incidents than sawing a pipe with similar material properties as pipe A. To conclude, brittle failure behaviour does not only cause larger gas outflow which is more difficult to stop, but also increases the chance of incidents during repair.

The facts given above support the statement that time dependent embrittlement is an important factor limiting the service life of uPVC pipes used in distribution networks. Replacement before the pipes become too brittle is necessary to guarantee safe operation of uPVC (gas) distribution networks in the future. Non-destructive methods for assessing the condition of uPVC pipes and for predicting the time scale in which a pipe becomes too brittle would be valuable tools for the development of a cost-effective replacement policy. A potential non-destructive method for assessing the condition (yield stress) of uPVC pipes was presented in Chapter 2. The present chapter focuses on linking the yield stress (evolution) to the impact failure behaviour and the behaviour during sawing.

Several factors can influence the failure behaviour of buried uPVC pipes. As elucidated in Chapter 1, physical ageing and the level of gelation are the two

Figure 3.2 Photographs of saw cuts made by sawing of two excavated uPVC pipes. Each uPVC pipe was sawed at test temperatures of 5 °C and 20 °C, and was sawed at two different speeds - slow and fast. These results were made available by Kiwa Technology [65].

most important factors that influence the impact behaviour of buried uPVC pipes, thus limiting the service life of uPVC gas pipes. Physical ageing is related to the densification of the polymer chains as a result of conformational changes, making them more prone to brittle failure [37, 46]. Physical ageing causes a decrease in the elongation at break [66–69] and the impact-breaking energy [21, 46, 70] and eventually leads to an increase of the ductile-to-brittle transition temperature [45]. Physical ageing should therefore be taken into account for predicting (ongoing) embrittlement of uPVC pipes.

As mentioned above, the level of gelation also has a distinct influence on the ductility of uPVC. The level of gelation of a PVC pipe is a measure for the extent of primary particle breakdown and fusion after production [71]. When the level of gelation is insufficient, poorly fused primary particles act as crack initiation sites [72], which can cause brittle failure [19]. The level of gelation does not change after production and is therefore a measure of the initial product quality [10]. Hence, this chapter focuses primarily on physical ageing, as the main interest is on the time dependent embrittlement during service life and not on the quality of the pipes during installation. In Chapter 5 the focus will be on the level of gelation and finding a way to determine this property using a non-destructive, in-situ test method.

The goal of this chapter is to investigate whether embrittlement of uPVC pipes caused by physical ageing can be predicted using the ageing kinetics of the yield stress. As a first step, it is shown that the ductile-to-brittle transition can be related to the process of physical ageing by assuming a certain critical thermodynamic state. This relationship is used to propose a yield stress criterion for embrittlement of uPVC. Next, experimental evidence is obtained which shows that this criterion holds for uPVC. Then a method is proposed for predicting embrittlement of uPVC pipes in

operation using this yield stress criterion. Finally, some possible issues of the practical implementation of this method are discussed.

3.2 Theoretical background

3.2.1 Embrittlement upon physical ageing

Physical ageing can cause a ductile-to-brittle transition to occur during impact testing, whereas none of the measurement conditions change other than the (thermal) history of the specimen; such was shown for polycarbonate (PC) in [73]. The ageing process originates from the fact that glassy polymers are not in thermodynamic equilibrium but continuously strive towards it [37]. Although polymers are in a glassy state below their glass transition temperature, $T_g \sim 80^\circ\text{C}$ for uPVC, there is still some molecular mobility. Conformational changes can still take place which allow a change in the thermodynamic state of the polymer towards its thermodynamic equilibrium. The kinetics of the ageing process is determined by the molecular mobility and therefore the temperature influences the ageing rate. At elevated temperatures (but still below T_g) physical ageing progresses faster and consequently shortens the time scale required to reach the equilibrium [37]. The thermodynamic state of a uPVC pipe depends therefore on its thermal history. As a result of the conformational changes, the density increases causing an increase in the interactions between the polymer chains. These interactions in turn cause a decrease in molecular mobility and thus an increase in the resistance against plastic deformation, which is observed as a significant increase in the yield stress [39, 40].

Figure 3.3 A schematic illustration of the influence of physical ageing on the intrinsic deformation behaviour of a glassy polymer like uPVC in compression. Solid line: before annealing below T_g , dashed line: after annealing below T_g .

The influence of physical ageing on the intrinsic deformation behaviour is shown schematically in Figure 3.3. The solid and dashed lines represent the true stress-

strain response before and after an annealing treatment respectively. An annealing treatment (defined here as a heat treatment at a temperature relatively close to but below T_g) accelerates the process of physical ageing. The figure shows that the yield stress increases as a result of the annealing treatment, whereas the effect of the annealing treatment disappears as soon as strain hardening occurs. This effect results in an increase in the yield drop, also referred to as strain softening. The interplay of the amount of softening and the subsequent (strain) hardening taking place determines the amount of localisation of plastic deformation when a glassy polymer is subjected to a tensile load. Depending on the interplay, the plastic deformation zone (at a stress concentrator) will grow to macroscopic scale or will grow further on a local scale. In the first case, failure after macroscopic growth of the plastic deformation zone is characterised as ductile failure. In the second case, a hydrostatic stress builds up, because the plastic deformation in the deformation zone is constrained by its surrounding material. The polymer can relieve the increasing stress only by voiding, which occurs when the hydrostatic stress in the plastic zone surpasses a critical value (a critical hydrostatic stress) [74]. Upon further deformation, the voids grow and coalesce, forming highly orientated fibrils, which will form a craze [75]. Eventually, the craze fibrils break, and a crack is formed which can propagate until complete failure. Although the plastic strain within the fibril of a craze can be very high, the region of plastic deformation is strongly localised. Therefore, this type of failure is perceived as brittle failure on a macroscopic scale. This phenomenon as a result of a change in intrinsic properties (caused by physical ageing in this case) is referred to as strain localisation [41–44].

The value of the critical hydrostatic stress at which a craze is formed (and subsequently at which brittle failure occurs) is barely influenced by physical ageing as shown for PC [74, 76], poly(methyl methacrylate) [76] and polystyrene [77]. The ductile-to-brittle transition can be related to the process of physical ageing by determining the critical thermodynamic state at which the deformation localises to such an extent that the critical hydrostatic stress is reached. The critical thermodynamic state will have a corresponding (critical) yield stress. This critical tensile yield stress can therefore be used as a tool for predicting embrittlement. In the next section a critical tensile yield stress criterion for uPVC is proposed.

3.2.2 Yield stress criterion for uPVC

Experimental evidence for the existence of a critical tensile yield stress has been given by Visser et al. for PC [45]. They analysed impact data of Legrand [73] and yield stress data of Klompen et al. [63] on PC to show that a ductile-to-brittle transition for those PC tensile bars indeed occurred at a certain thermodynamic state with a constant yield stress. It should be borne in mind that the development of the hydrostatic stress in the plastic deformation zone during impact loading depends

on the deformation behaviour of the material surrounding the plastic zone. The deformation behaviour of the surrounding material in turn depends on the loading conditions [78], for instance, on the deformation field imposed by an impactor, on the presence of a notch in the specimen, and on the applied strain rate. The critical tensile yield stress is therefore not a material parameter, but merely a tool for predicting embrittlement for the testing conditions and type of test used.

A yield stress criterion for uPVC was formulated by Visser et al. [45] which is based on a similar criterion proposed before for PC [78]; a ductile-to-brittle transition will occur when the yield stress σ_y of uPVC specimens surpasses a critical tensile yield stress σ_{cr} . The critical tensile yield stress σ_{cr} is independent of test temperature, strain rate and thermodynamic state. In mathematical terms, the yield stress criterion means that the material will fail in a macroscopically brittle way (due to localisation) if:

$$\sigma_y(T, t_a, T_a) \geq \sigma_{cr} \quad (3.1)$$

with T the temperature during testing, t_a the annealing time and T_a the annealing temperature. This criterion holds if the influence of annealing on the ductile-to-brittle transition temperature can be accurately predicted by the yield stress, taking into account the influence of temperature and physical ageing [45]. Therefore, to validate the criterion the influence of annealing on the ductile-to-brittle transition temperature ($T_{d \rightarrow b}$) has to be determined. Next, the choice for the type of test to determine $T_{d \rightarrow b}$ as employed in the present work is described and founded.

In previous work [45] a puncture test was used to characterise $T_{d \rightarrow b}$. The disadvantages of this type of test are that (i) the specimens are relatively large, such that a large length of pipe material is required for a full characterisation and (ii) the strain field is rather complex with a combination of compression, shear and tensile strains [45, 79]. Besides these disadvantages, the observation of Mandell et al. [80] that the plane strain fracture toughness (K_{Ic}) of uPVC pipes is not significantly influenced by annealing was taken into account. As opposed to starting from a sharp notch, with the aim to reduce plasticity at the notch tip, it is better to use blunt/unnotched specimens to promote plasticity leading to crack initiation, as physical ageing has a strong influence on this plastic behaviour. From these considerations a tensile impact test using a rectangular shaped tensile bar with a circular hole at its centre (as also used by Weller et al. [65]) was chosen as the preferred testing geometry. In comparison with the puncture test specimens [45], about nine times more tensile impact specimens can be produced per metre of manufactured uPVC pipe (diameter of 110 mm). Furthermore, the strain applied is predominantly in tension and the specimens are relatively easy to manufacture with the use of milling (for the geometry and the hole), which is convenient as impact testing mostly requires a large number of specimens (about 124 specimens were impacted in this work).

Once the influence of physical ageing on $T_{d \rightarrow b}$ is characterised using tensile impact testing, the validity of the critical yield stress criterion which was proposed above can be checked. As mentioned, the advantage of the tensile impact test geometry is that the stresses and strains are predominantly in tension, thus comparable to standard tensile tests which were used to determine the influence of ageing on the yield stress. However, the strain field is somewhat more complex around the hole and the (local) strain rate can be determined only with the use of advanced optical strain measurements or numerical calculations. Here the global strain rate (impactor speed divided by gauge length) is used to calculate the yield stress at a certain temperature (and after a certain annealing treatment). Although this global strain rate is not equal to the highest local strain rate, it does have the same order of magnitude (up to the yield point). It is assumed here that this simplification is allowed, as the quantitative increase in yield stress as a function of temperature and physical ageing are barely influenced by the chosen strain rate [81].

Furthermore, it can be argued that the local strain rate will depend on the degree of ageing as a severely aged specimen will display more strain localisation; its local strain rate can be expected to be higher at the location where yield starts to occur, when compared to the strain rate of a more homogeneously deforming unaged specimen. However, the interest here is on the onset of failure and thus on the point of yielding. As localisation is a post-yield effect, this relationship between local strain rate and the ageing state is neglected here with the assumption that up to yielding no localisation occurs and the (local) strain rate is equal to the global strain rate.

As the impact velocity for all tests is quite high, not only the α -relaxation, which is related to the glass transition, but also the β -relaxation, which is presumably related to the local twisting motions of small-scale macromolecular segments [82, 83], contributes to the yield stress of the specimens [45, 84–87]. The contributions of both the α -relaxation and β -relaxation on the yield stress can be characterised quantitatively using the Ree-Eyring relation [88]. This relation is a modification of the Eyring rate equation [89], where the contributions of the two relaxation mechanisms are added independently. The Ree-Eyring relation used here was adopted from [45]:

$$\sigma_y(T, \dot{\epsilon}) = \sum_{x=\alpha, \beta} \frac{RT}{\nu_x^*} \cdot \sinh^{-1} \left[\frac{\dot{\epsilon}}{\dot{\epsilon}_{0,x}} \cdot \exp \left(\frac{\Delta U_x}{RT} \right) \right], \quad (3.2)$$

where σ_y is the yield stress, R the universal gas constant, T the test temperature, ν_x^* the activation volume, $\dot{\epsilon}$ the strain rate, $\dot{\epsilon}_{0,x}$ a pre-exponential factor and ΔU_x the activation energy. The subscript x of the parameters is equal to α or β , which refers to the respective relaxation mechanism.

The yield stress of PC and uPVC can be accurately described using constant values of the activation energies and the activation volumes for both relaxation mechanisms and thus do not change upon annealing [45, 90, 91]. Furthermore, the factor $\dot{\epsilon}_{0,\beta}$

(related to the β -relaxation) was found to be unaffected by physical ageing for PC [90, 91] and PVC [45]. The presumed local twisting motions of small-scale macromolecular segments related to the β -relaxation in PVC are in equilibrium at the annealing temperature applied in this work (60 °C) and therefore do not change upon annealing [45]. The only parameter which changes upon annealing is $\dot{\epsilon}_{0,\alpha}$. Therefore, this parameter depends on the (annealing) time (t_a) and annealing temperature (T_a) in order to incorporate the influence of physical ageing on the deformation kinetics [63]. The ageing model, identical to that presented in [40], is described by:

$$\dot{\epsilon}_{0,\alpha} = b_0 \cdot \left(\frac{t_{\text{eff}}(t_a, T_a) + t_{\text{ini}}}{t_0} \right)^{b_1}, \quad (3.3)$$

where b_0 and b_1 are constants, $t_0 = 1$ s and t_{ini} is the initial age. It is well known that the kinetics of physical ageing is influenced by temperature [39], but also by the presence of stress [40]. The average temperature of uPVC pipes in operation is ~ 10 °C. At this temperature, physical ageing progresses very slowly and its effects can be measured only at experimentally unacceptably long time scales [45]. To predict the increase in the yield stress for this (reference) temperature, the effective ageing time t_{eff} is introduced. In the present study the specimens are aged only at a constant (annealing) temperature. Therefore, a simplified relation for the effective time as presented in [40] can be used here:

$$t_{\text{eff}}(t_a, T_a) = t_a \exp \left[\frac{\Delta U_a}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T_a} \right) \right], \quad (3.4)$$

where ΔU_a is the ageing activation energy and T_{ref} the reference temperature.

In the remainder of this chapter, the yield stress criterion for uPVC (Equation 3.1) will be validated and will subsequently be applied for predicting embrittlement of uPVC pipes in operation. As a first step, the influence of annealing on $T_{d \rightarrow b}$ will be characterised using tensile impact tests. Then the yield stress criterion is applied, which enables the prediction of $T_{d \rightarrow b}$ based on the influence of test temperature and physical ageing on the yield stress. After the criterion has been validated, it is applied to predict embrittlement of uPVC pipes in operation.

3.3 Experimental

3.3.1 Materials and specimen preparation

Two types of experiments were performed with two different materials. The first series of experiments were tensile impact tests performed on specimens which were taken from a newly produced uPVC water pipe (pipe 8 in Table A.1 in Appendix A).

The pipe, having a diameter of 110 mm and a wall thickness of 2.7 mm, was characterised previously by Visser et al. who determined the deformation and the ageing kinetics [45]. The model parameters of the pipe are summarised in Table 3.1. Tensile impact specimens were produced by cutting 70 mm long semi-cylindrical segments from the water pipe with a bandsaw. These segments were pressed at a compressive stress of ~ 1 MPa into flat plates at 100 °C (~ 15 °C above T_g) for 25 minutes. Rectangular bars were milled from the plates with the length direction parallel to the axial (length) direction of the pipe, see Figure 3.4. The production of the tensile impact specimens was completed by milling a hole ($\varnothing 4$ mm) at the centre of the bars and milling holes ($\varnothing 6$ mm) at each end of the bars.

Figure 3.4 A test specimen for the tensile impact test. The holes ($\varnothing 6$ mm) on both ends of the specimen were used for clamping. The thickness of the bar is 2.7 mm.

The thermal pressing procedure erased all prior effects of physical ageing. Ohta et al. [92] have shown that a heat treatment above T_g can change the crystalline structure of PVC, which can in turn change the ageing kinetics of the material [93]. However, as the pressing procedure has been carried out just above T_g for a relatively short time, its influence on the ageing kinetics is assumed to be negligible here.

Table 3.1 The values for the parameters in Equations 3.2 to 3.4 for the α and β relaxation mechanisms in the uPVC water pipe taken from Visser et al. [45].

	α	β	
$\dot{\epsilon}_{0,x}$	$1.88 \cdot 10^{38}$	$2.21 \cdot 10^9$	$[s^{-1}]$
ν_x^*	$1.29 \cdot 10^{-3} \dagger$	$8.39 \cdot 10^{-4}$	$[m^3/mol]$
ΔU_x	$2.97 \cdot 10^5$	$5.86 \cdot 10^4$	$[J/mol]$
$\Delta U_{a,x}$	$2.38 \cdot 10^5$		$[J/mol]$
b_0	$7.39 \cdot 10^{41} \ddagger$		$[s^{-1}]$
b_1	-0.45		$[-]$

$\dagger$ includes the pressure dependence on the yield stress of PVC [94].

$\ddagger$ The value of b_0 is determined for $T_{ref} = 25$ °C.

The second series of experiments were uniaxial tensile tests performed on specimens which were taken from an excavated uPVC gas pipe (pipe 6 in Table A.1 in

Appendix A). The pipe was taken from the Dutch gas distribution network and was first subjected to a saw test. Subsequently, the tensile specimens were extracted from the pipe section that was unaffected by the saw test. The pipe has a diameter of 110 mm and a wall thickness of 2.9 mm. Bars having dimensions $70 \times 10 \times 2.9 \text{ mm}^3$ were sawed from the pipe with the length direction parallel to the axial direction of the pipe. The bars still have the curvature of the pipe, because the pipe was not pressed into a flat plate prior to the production of the specimens. The tensile fixtures used were custom made to have a clamping surface that matches the specimens curvature. As the specimens were not pressed (and hence not rejuvenated), the thermodynamic state of the bars and the state of the specimens for the saw test is the same. After sawing the bars, a gauge section having dimensions $30 \times 5 \times 2.9 \text{ mm}^3$ was milled into the bars.

For both the tensile impact as the uniaxial tensile tests, the specimens were annealed at 60°C ($\sim 15^\circ\text{C}$ below T_g) for various annealing times. As mentioned, one set used for the uniaxial tensile test did not receive an annealing treatment at all. The sets of specimens and annealing times are shown in Table 3.2.

Table 3.2 *Annealing treatments of various sets of specimens. Each set contains tensile impact specimens taken from the newly produced uPVC water pipe and contains uniaxial tensile specimens taken from the excavated uPVC gas pipe.*

Set	Annealing time (at 60°C)
1 (as-received)	-
2	$1 \cdot 10^4 \text{ s}$
3	$3 \cdot 10^4 \text{ s}$
4	$1 \cdot 10^5 \text{ s}$
5	$3 \cdot 10^5 \text{ s}$
6	$1 \cdot 10^6 \text{ s}$
7 (severely aged)	$3 \cdot 10^6 \text{ s}$

3.3.2 Test methods

Instrumented tensile impact tests were carried out on a Dynatup impact machine. The machine was equipped with a tensile impact fixture which has been developed in-house. A simplified front view of the fixture is given in Figure 3.5. The impactor with a mass of about 5 kg falls and its arms hit the movable crosshead with an average velocity of 3.7 m/s , corresponding to an (excess) kinetic energy of 35 J and a global engineering strain rate of 122 s^{-1} (i.e. impact velocity divided by initial clamp distance). Air bearings were employed to reduce energy loss caused by friction between the impactor and the guiding rails of the impact machine. The force during

impact loading was measured using a precompressed 7.5 kN Kistler (type 9001A) force cell connected to a Kistler Type 5011A charge amplifier. The displacement was measured using a Meterdrive ZAM 301 linear encoder and checked with the force signal by integrating the displacement twice over a period of time. The tensile impact tests were carried out at various temperatures between $-20\text{ }^{\circ}\text{C}$ and $80\text{ }^{\circ}\text{C}$. An additional device was employed for controlling the temperature of the specimen around the centre hole within a range of $\pm 1.1\text{ }^{\circ}\text{C}$ around the testing temperature.

Figure 3.5 Front view of the fixture used for the tensile impact test.

Uniaxial tensile tests were carried out on a Zwick 1445 universal tensile testing machine equipped with an AST 2.5 kN force cell and a temperature controlled chamber. All tensile tests were carried out at a constant engineering strain rate of 10^{-3} s^{-1} and at a fixed temperature of $20 \pm 0.1\text{ }^{\circ}\text{C}$. The value of the yield stress was calculated using the local maximum in the force signal and the average of the initial cross-sectional surface areas measured at three locations along the gauge section.

3.4 Impact test results

3.4.1 Types of failure

The failures observed during impact testing can be divided into three types: brittle, semi-ductile and ductile failure. Force-displacement curves and photographs of the fractured specimens are given in Figure 3.6 for each type of failure.

For brittle failures, the force increases from the start of the impact loading to a maximum value of $\sim 1.5\text{ kN}$, after which the force suddenly drops to zero directly

Figure 3.6 Force-displacement curves (*left*) and photographs of fractured specimens (set 7 in Table 3.2) (*right*) taken from the uPVC water pipe. Each specimen was photographed from different views labelled (a), (b) and (c). **Top to bottom:** brittle failure at $-10\text{ }^{\circ}\text{C}$, semi-ductile failure at $50\text{ }^{\circ}\text{C}$ and ductile failure at $70\text{ }^{\circ}\text{C}$.

upon failure, as shown in Figure 3.6 top left. The photographs of a specimen fractured at $-10\text{ }^{\circ}\text{C}$ show no signs of macroscopic plastic deformation but instead show an irregular fracture surface, Figure 3.6 top right. The occurrence of an abrupt force drop and the absence of macroscopic plastic deformation is categorised here as brittle failure.

For semi-ductile failure, stress whitening bands are visible which diminish in

radial direction from the hole, Figure 3.6 middle right. These bands indicate that macroscopic plastic deformation took place during impact loading. As shown in view (a), no plastic deformation was observed at the side edge of the specimen. Stress whitening over the partial cross section shows that the material deformed plastically to some extent before failure. This effect caused a small increase of the displacement at the force drop of the semi-ductile failed specimens in comparison with the displacement at the force drop in brittle failure events, Figure 3.6 middle left. The occurrence of an abrupt force drop and macroscopic plastic deformation over the partial cross section is categorised here as semi-ductile failure.

Extensive stress whitening was observed in the photographs of the specimens which failed in a ductile way, Figure 3.6 bottom right. The photographs from views (a) and (b) show that the plastic deformation zone extended over the complete cross section of the specimen. The extension of the plastic deformation zone complies with a more or less smooth decrease after the point of maximum force up to the point of fracture as a function of the displacement, Figure 3.6 bottom left. The occurrence of plastic deformation over the complete cross section of the specimen and smooth decrease of the force after the point of maximum force is categorised here as ductile failure. In the next section, the absorbed energy and the plastic extension will be determined from the obtained force-displacement curves and will be used to differentiate quantitatively between the types of failure observed.

3.4.2 Characterisation of force-displacement curves

During the tensile impact tests, the kinetic energy supplied by the impactor is (i) stored as elastic energy in the specimen, (ii) dissipated in the form of plastic deformation of the specimen, (iii) used to create surface area in the failure process, (iv) stored as elastic energy in the set up and (v) dissipated by the set-up (friction). The energy absorbed by the specimen during impact loading is equal to the total area under the force-displacement curve. Regardless of the type of failure, all specimens followed a similar path up to the point where the force reaches its maximum value $F_{\max}$, as was shown in Figure 3.6*. Only the part of the curves after $F_{\max}$ has a link with the failure behaviour as this contributes to the observed plasticity. Therefore, the part of the force-displacement curves after $F_{\max}$ is of interest in determining the influence of annealing on the amount of plasticity. Two parameters are proposed to be used here to distinguish the failure type from the force-displacement measurement, without having to revert to (the more subjective) image analysis. The first parameter

*The maximum force $F_{\max}$ decreases as the temperature increases. This causes a decrease in the area of the force-displacement curve up to $F_{\max}$. In parallel, the displacement at the point of $F_{\max}$ increases with temperature and causes an increase in the area. These two effects partially compensate each other. In fact, the area underneath the force-displacement curve up to $F_{\max}$ is hardly influenced by the test temperature and thus is hardly influenced by type of failure.

is the energy absorbed after $F_{\max}$ was reached; given by:

$$E_{t_{F_{\max}} \leq t \leq t_f} = \int_{s(t_{F_{\max}})}^{s(t_f)} F(s) ds, \quad (3.5)$$

where F is the measured force and s is the measured displacement. The integration bounds are defined in Figure 3.7.

The second parameter that is proposed as a measure for the ductility of the specimen is the plastic extension of a specimen ($s_{t_{F_{\max}} \leq t \leq t_f}$). This plastic extension is defined as the extension that is observed for the specimen between the times $t_{F_{\max}}$ and t_f (also shown in Figure 3.7):

$$s_{t_{F_{\max}} \leq t \leq t_f} = s(t_f) - s(t_{F_{\max}}). \quad (3.6)$$

Figure 3.7 A typical force-displacement curve of a specimen taken from the uPVC water pipe which failed in a ductile way. The time $t_{F_{\max}}$ is the time when the force reaches a maximum value $F_{\max}$. The time t_f is the time when the force reaches zero. The absorbed energy after maximum force, referred to as the plastic energy or $E_{t_{F_{\max}} \leq t \leq t_f}$ throughout the rest of this work, is defined as the surface area of the grey area. The plastic extension, $s_{t_{F_{\max}} \leq t \leq t_f}$, is indicated by the black arrow.

The histograms of all results for both the plastic energy and the plastic extension are given in Figure 3.8 for each type of failure. The histograms both show that the population of ductile failure data clearly is separated from the populations of semi-ductile and brittle failure data. The latter two populations cannot be distinguished clearly.

In the next section both failure parameters ($E_{t_{F_{\max}} \leq t \leq t_f}$ and $s_{t_{F_{\max}} \leq t \leq t_f}$) proposed in this subsection will be employed to characterise $T_{d \rightarrow b}$.

Figure 3.8 Histograms of the plastic energy $E_{t_{Fmax} \leq t \leq t_f}$ (left) and plastic extension $s_{t_{Fmax} \leq t \leq t_f}$ (right) for each type of failure. The plastic energy and plastic extension were calculated using Equations 3.5 and 3.6 respectively, and using the initial cross-sectional surface area measured at the centre hole of the specimen. The histograms were obtained from 124 tensile impact tests on specimens taken from the uPVC water pipe.

3.5 Ductile-to-brittle transition analysis

The plastic energy $E_{t_{Fmax} \leq t \leq t_f}$ and plastic extension $s_{t_{Fmax} \leq t \leq t_f}$ for severely aged specimens (set 7 in Table 3.2) are shown as a function of test temperature in Figure 3.9. Between -20°C and 50°C , the plastic energy and plastic extension are relatively small and almost independent of test temperature. The specimens failed in a brittle or semi-ductile way within this temperature range. In contrast, the specimens which fractured at 60°C and 70°C failed in a ductile way. This change in type of failure correlates with the onset of a steep increase in the plastic energy and plastic extension. The data shows that there is a transition from brittle (and semi-ductile) failure to ductile failure at $\sim 55^\circ\text{C}$.

The plastic energy and plastic extension as a function of temperature exhibit essentially the same characteristics as shown in Figure 3.9 and can thus both be used to determine the ductile-to-brittle transition. The onset temperature of ductile failure is the same for both properties. However, the scatter in the brittle/semi-ductile region is larger for the plastic energy than for the plastic extension. Therefore, the plastic extension is used as a measure for the ductility in the following analyses.

The influence of physical ageing on $T_{d \rightarrow b}$ has been studied to validate the yield stress criterion defined by Equation 3.1. The increase in $T_{d \rightarrow b}$ as a function of the annealing time has been determined from tensile impact tests on specimens taken from the uPVC water pipe. A graphical/mathematical methodology as presented in Figure 3.10 and in the next paragraph is employed to determine $T_{d \rightarrow b}$ of each set of specimens defined in Table 3.2.

The plastic extension versus the test temperature for severely aged specimens is

Figure 3.9 The plastic energy (*left*) and plastic extension (*right*) versus test temperature determined from tensile impact tests performed on severely aged specimens taken from the uPVC water pipe. The vertical dashed line separates brittle and semi-ductile failure events from ductile failure events.

shown in Figure 3.10 left. As shown before, a steep increase in the plastic extension with increasing test temperature correlates with the change in type of failure from brittle (and semi-ductile) to ductile. The temperature at the onset of this steep increase in the extension is defined as $T_{d \rightarrow b}$ and has been determined graphically using linear fit functions. In Figure 3.10 left, the dashed line was determined by a least squares fit of a linear function on the rejuvenated and severely aged specimens that failed in a brittle and a semi-ductile way and was assumed to be independent of physical ageing. The increase in the plastic extension for severely aged specimens, which failed in a ductile way, was fitted using a linear function (solid line). The linear function describes the data well ($R^2 = 0.95$) which shows that the extension increases with temperature in a linear fashion for range of temperatures investigated. The temperature at the intersection of the solid line with the dashed line defines the $T_{d \rightarrow b}$ of the severely aged specimens and was found to be 50.8 ± 4.5 °C (95% confidence intervals). The $T_{d \rightarrow b}$ of the rejuvenated specimens was determined by the solid line that was fitted using the slope of the solid line of the severely aged specimens. The obtained fit is of sufficient quality ($R^2 = 0.93$) to justify the assumption of a slope that is independent of physical ageing for the wide range of annealing times investigated. The temperature at the intersection of the solid line of the rejuvenated specimens with the dashed line was found to be 45.5 ± 2.0 °C (95% confidence intervals). Hence, a difference of ~ 5 °C in the average $T_{d \rightarrow b}$ between the rejuvenated and severely aged specimens was found. Visser et al. found a similar difference in $T_{d \rightarrow b}$ (~ 4 °C) [45]. They took specimens from the same uPVC water pipe and applied the same thermal history to their specimens, but used a puncture test instead of a tensile impact test, resulting in a different loading geometry.

The $T_{d \rightarrow b}$ as a function of the annealing time was determined for another batch of specimens taken from the uPVC water pipe. The specimens received annealing

Figure 3.10 The plastic extension versus the test temperature determined from tensile impact tests performed on specimens taken from the uPVC water pipe. **Left:** rejuvenated and severely aged specimens (set 1 and 7 in Table 3.2). The $T_{d \rightarrow b}$ of the rejuvenated and severely aged specimens are defined as the temperatures at the intersections of the parallel solid lines with the dashed line and are indicated by the arrows. The $T_{d \rightarrow b}$ shifts to higher test temperature as a result of the annealing treatment below T_g . **Right:** sets of specimens which were annealed according to Table 3.2. The nine specimens within a set have had the same thermal history. The error bars represent one standard deviation determined from the nine measurements. The dashed line is taken from the left figure. For each set of specimens a solid line is fitted which has the same slope as the solid lines in the left figure. The intersections of the parallel solid lines with the dashed line define $T_{d \rightarrow b}$ for the sets of specimens.

treatments according to Table 3.2 (sets 1-7). Figure 3.10 right shows the plastic extension for various annealing times. The average test temperature between the sets was about 60 °C and varied maximally 3.3 °C. The temperature variation within each set varied less; only 1.1 °C. The solid lines were fitted to the markers using the slope from the line describing the severely aged specimens in Figure 3.10 left. Referring to the proper fit of the rejuvenated and severely aged experimental data using this same slope, this assumption seems to be viable. The $T_{d \rightarrow b}$ of the sets of specimens were determined from the intersections between the solid lines and the dashed line in Figure 3.10 right. The $T_{d \rightarrow b}$ for increasing annealing times are given in Figure 3.11 left. The 68% confidence intervals were determined from the variation in the plastic extension and temperature in Figure 3.10 right. The $T_{d \rightarrow b}$ clearly increases by as much as 7.7 °C, with increasing annealing time. As the average test temperature between the sets is greater than the temperature variation within each set, the former of the two contributes most to the variation in average $T_{d \rightarrow b}$ in Figure 3.11 left.

Note that the $T_{d \rightarrow b}$ of the rejuvenated specimens (45.5 ± 2.0 °C) in Figure 3.10 left which did not receive an annealing treatment is greater than that of the specimens which were annealed for $1 \cdot 10^4$ s and $3 \cdot 10^4$ s shown in Figure 3.11 left. The rejuvenated specimens have been extracted from the circumferential direction instead of the extrusion direction of the original pipe. As also observed by others [21, 69], impact loading of specimens taken from in the circumferential direction the original

uPVC pipe exhibit a more brittle failure behaviour and a greater $T_{d \rightarrow b}$ than when specimens would be loaded in the extrusion direction of the pipe. The rejuvenated specimens were therefore not taken into account for determining the $T_{d \rightarrow b}$ as a function of the annealing time.

The influence of the annealing time on $T_{d \rightarrow b}$ can be calculated by assuming that the yield stress criterion for uPVC (Equation 3.1) holds and using Equations 3.2 to 3.4 and the parameters in Table 3.1. As a first step, the specimens annealed for $2.8 \cdot 10^6$ s that show a $T_{d \rightarrow b}$ of 49 °C, were chosen as a reference (see Figure 3.11 left). The yield stress for these specimens at the transition conditions has been calculated to be 74 MPa. The value of the yield stress is assigned as the critical tensile yield stress. The choice of another annealing time (and $T_{d \rightarrow b}$) is assumed to lead to a similar value of the critical tensile yield stress. Remember that the critical tensile yield stress is not a material parameter, but merely a value that enables the modelling of the increase in $T_{d \rightarrow b}$ resulting from annealing treatments below T_g for the loading conditions as applied by the tensile impact setup.

Figure 3.11 *Left:* markers: the experimentally determined $T_{d \rightarrow b}$ of specimens taken from the uPVC water pipe which were annealed at 60 °C for various annealing times. The error bars represent 68% confidence intervals taking into account the variation in temperature and plastic extension. Solid line: the calculated $T_{d \rightarrow b}$ versus the annealing time determined using the calculated critical tensile yield stress, Equations 3.2 to 3.4 and the parameters in Table 3.1. *Right:* the yield stress versus the test temperature for annealing times $9.0 \cdot 10^3$ s, $2.8 \cdot 10^5$ s and $2.8 \cdot 10^6$ s. The critical tensile yield stress was determined from the reference point indicated in Figure 3.11 left. The vertical dashed lines indicate $T_{d \rightarrow b}$ for the three annealing times.

The methodology for calculating $T_{d \rightarrow b}$ as a function of the annealing time from the critical tensile yield stress is outlined in Figure 3.11 right. The calculated temperature independent critical tensile yield stress is shown as the horizontal dashed line. The three solid lines are the yield stress versus test temperature for annealing times of $9.0 \cdot 10^3$ s, $2.8 \cdot 10^5$ s and $2.8 \cdot 10^6$ s respectively. The $T_{d \rightarrow b}$ for these annealing times have been determined by calculating the test temperatures at which the yield stress

is equal to the critical tensile yield stress. The $T_{d \rightarrow b}$ for these annealing times are indicated by vertical lines in Figure 3.11 right. The $T_{d \rightarrow b}$ for a range of annealing times from 10^3 s to 10^8 s were calculated using the methodology explained above and is given by the solid line in Figure 3.11 left. Although there is significant variation in the determined $T_{d \rightarrow b}$, clearly the trend in the experimentally obtained values complies with the model results.

Instead of calculating $T_{d \rightarrow b}$ using a critical tensile yield stress, the reverse route can also be followed. The yield stress at transition conditions was calculated for each of the different annealing times (in Figure 3.11 left) and is shown as function of the annealing time in Figure 3.12. The calculated values of critical tensile yield stress all fall within a range of 4 MPa, which is only 5% of the average value of 74 MPa. Furthermore, the critical tensile yield stress as a function of the annealing time is nearly constant. These results shows that uPVC exhibits a ductile-to-brittle transition when the yield stress of the material surpasses a critical tensile yield stress value that is independent of the thermodynamic state and justifies the assumption that other (reference) points in Figure 3.11 left will lead to similar values of the critical tensile yield stress.

Figure 3.12 The critical tensile yield stress for various annealing times. The critical tensile yield stress was calculated for each annealing time and experimentally determined $T_{d \rightarrow b}$ in Figure 3.11 left and using Equations 3.2 to 3.4 and the parameters in Table 3.1.

The results presented in this section indicate that the concept of a critical tensile yield stress, as proposed by Engels et al. [78], also holds quantitatively for tensile impact tests on uPVC. The kinetics of $T_{d \rightarrow b}$ with physical ageing can be described quantitatively with the use of a descriptive model for the deformation kinetics which incorporates the ageing kinetics. This means that it is possible to calculate $T_{d \rightarrow b}$ of a uPVC pipe once its yield stress at a certain deformation rate is known (for example from a micro-hardness test). It should, however, be emphasised that this value of $T_{d \rightarrow b}$ is specific for the loading conditions applied during tensile impact testing. For puncture tests much lower $T_{d \rightarrow b}$ values were found [45] and the value

of $T_{d \rightarrow b}$ found in practice can be different again. In the next section an approach is proposed that uses the link between failure behaviour and deformation kinetics to predict the embrittlement of pipes in practical applications.

3.6 Predicting embrittlement in practice

The saw test that was mentioned in the introduction of this chapter was developed by Weller et al. [65]. The loading case applied in this test corresponds closely to loading cases that typically take place in the field. This saw test can therefore be employed to determine to which extent ageing has progressed that the failure behaviour of a pipe is such that it is unacceptable to keep it in service in the field. This (critical) thermodynamic state can then be used as a limiting value that can be employed in combination with the existing model for deformation and ageing kinetics to predict the residual service lifetime of uPVC pipes. Before this procedure is presented, first some experiments that show the influence of physical ageing on the outcome of the saw tests are presented.

Saw tests were performed on two pipe segments which were cut from the excavated uPVC gas pipe. One segment was annealed at 60 °C for $2.8 \cdot 10^6$ s and labelled as 'severely aged'. The other segment did not receive an annealing treatment and was labelled as 'as-received'. Each segment was sawed at two different test temperatures and two different saw speeds. The resulting saw cuts were photographed and are shown in Figure 3.13. Two types of saw cuts can be observed: straight and irregular. A straight saw cut corresponds to ductile behaviour, whereas an irregular saw cut corresponds to brittle failure, as described in the introduction. Sawing slowly resulted in straight saw cuts irrespective of the range of test temperatures and degrees of physical ageing investigated. Therefore, the annealing treatment did not influence the failure behaviour of the pipe when sawing was done slowly. However, fast sawing the as-received segment at 20 °C resulted in a straight saw cut, whereas sawing the severely aged segment at the same conditions resulted in an irregular saw cut. This clearly illustrates that physical ageing can indeed influence the failure behaviour of pipes with this type of test.

For the determination of a critical thermodynamic state, a decision should first be made on which outcome of the saw test is still acceptable. If brittle fracture for fast saw speeds at 5 °C are still allowed, it will give a different limiting value than if this is not allowed. Once this decision has been made the critical thermodynamic state can be found by performing saw tests on not only specimens annealed at two different annealing times as shown in Figure 3.13, but on many specimens which were annealed for different (intermediate) times. Then a replacement criterion must be defined for determining the critical thermodynamic state at which the failure behaviour in saw tests becomes unacceptable. Subsequently, a tensile test

Figure 3.13 Photographs of saw cuts made by sawing as-received and severely aged ($2.8 \cdot 10^6$ s at 60 °C) pipe segments taken from the excavated uPVC gas pipe. Sawing was done at 5 °C and 20 °C and for two different saw speeds: slow and fast. The saw tests were performed at Kiwa Technology, the Netherlands.

should be performed on a specimen which must be in the same thermodynamic state. The critical thermodynamic state can then be quantified using the yield stress determined from the tensile test. Once the critical tensile yield stress has been determined, the residual lifetime of the pipe follows from the ageing kinetics of the yield stress and the value of the yield stress belonging to the present thermodynamic state of a pipe. The value of the current yield stress can be determined from a non-destructive measurement on a pipe, such as the micro-hardness measurement approach explained in Chapter 2.

A major drawback of the saw test is that a lot of material is required for each test. As the length of the excavated pipe available for this study was limited, saw tests results on specimens that received intermediate annealing times were not available. However, the yield stress was determined for a range of annealing times (listed in Table 3.2) using uniaxial tensile tests on specimens taken from the excavated pipe, such that the difference in thermodynamic state was quantified. The values of the yield stresses are plotted against the effective time in Figure 3.14. The effective time was calculated for a reference temperature of 10 °C using Equation 3.4. An ageing activation energy of 238 kJ/mol was assumed for this pipe (Table 3.1). The specimens that are in the same thermodynamic state as the segments cut for the saw tests are labelled 'as-received' and 'severely aged'. The annealing treatment applied to the segments for the saw tests caused the yield stress of the segments to increase by approximately 10%. Apparently, such an increase in yield stress corresponds to a sufficiently large increase in strain localisation that failure behaviour at 20 °C is changed as shown in Figure 3.13.

The residual lifetime of a pipe can be determined with the use of the ageing kinetics

shown in Figure 3.14 combined with a decision on the limiting thermodynamic state and the value of the (current) yield stress of a pipe. This is illustrated in Figure 3.14 by the following example. Assume that a yield stress ($\sigma_{y,mh}$) of 56 MPa is determined from a micro-hardness measurement on a specific sample taken from practice. Also assume that the limiting thermodynamic state corresponds to a (limiting) yield stress σ_{lim} of 60 MPa. According to the data in Figure 3.14, this difference of 4 MPa means that the gas pipe will have to be replaced within $4 \cdot 10^5$ years when the pipe is in service at a constant temperature of 10°C .

Figure 3.14 The yield stress versus the effective time for a strain rate of 10^{-3} s^{-1} and at a test temperature of 20°C . The yield stress was determined from tensile tests performed on tensile bars taken from the excavated uPVC gas pipe. The tensile bars were annealed according to the annealing times given in Table 3.2. The yield stress corresponding to the thermodynamic states of the sawed pipe segments in Figure 3.13 are labelled 'as-received' and 'severely aged'. The master curve (solid line) was determined for a reference temperature of 10°C using Equations 3.2 to 3.4. Using a non-linear least squares fitting routine, the best fit was found with the constants $b_0 = 1.36 \cdot 10^{44} \text{ s}^{-1}$, $b_1 = -0.60$ and initial age $t_{ini} = 5.9 \cdot 10^{10} \text{ s}$. The residual lifetime follows from the yield stress, $\sigma_{y,mh}$ and the limiting yield stress σ_{lim} .

In practice there are some factors which can limit the applicability of the proposed procedure. The most important limitations are discussed in the next section.

3.7 Discussion

The approach to determining the residual lifetime that was presented above assumes that all uPVC pipes have the same ageing kinetics and the same limiting tensile yield stress. However, Visser et al. noticed that the ageing rate[†] varies amongst uPVC pipes [40, 45]. The consequence of variations in the ageing rate on the residual lifetime is shown in Figure 3.15.

[†]defined here as the slope of the yield stress curve plotted on a logarithmic (annealing) time scale.

Figure 3.15 Master curves of the yield stress for three uPVC pipes having various rates of physical ageing. The master curves were determined for a strain rate of 10^{-3} s^{-1} , a test temperature of 20°C and a reference temperature of 10°C . The upper and lower horizontal dashed lines represent a hypothetical limiting yield stress σ_{lim} of 60 MPa and a hypothetical measured yield stress $\sigma_{y,mh}$ of 54 MPa respectively. The horizontal arrows indicate the corresponding residual lifetimes. The residual lifetime of the three uPVC pipes is, respectively, $3.2 \cdot 10^8$, $1.8 \cdot 10^6$ and 129 years for increasing ageing rate.

Here three master curves of different uPVC pipes are shown. These master curves were determined by shifting the yield stress data using Equation 3.4 to the average ageing temperature in practice (10°C). The master curves are described using Equations 3.2 to 3.4. The values of the parameters b_0 , b_1 and the ageing rates of the three pipes are given in Table 3.3. Clearly, each of the pipes has a distinctly different ageing rate. Figure 3.15 shows that a (hypothetical) limiting tensile yield stress σ_{lim} is reached at an earlier time, when the ageing rate of the pipe is higher. Consequently, in this example, the residual lifetime differs from about 300 million years to 129 years, assuming that all uPVC pipes in Figure 3.15 have the same limiting yield stress value. To conclude, if the ageing rate is sufficiently high, physical ageing could cause embrittlement of the pipe during service. As a consequence, the ageing rate must be taken into account for accurate determination of the residual lifetime. A study on the origin of the variation in the ageing rate is presented in Chapter 4 of this thesis.

Physical ageing is not the only factor that can result in a reduction in ductility. Apart from physical ageing, the most important other factor that influences $T_{d \rightarrow b}$ of uPVC gas pipes is the level of gelation [19]. The level of gelation (level of primary particle structure breakdown [71]) is expected to influence the limiting tensile yield stress and thus to influence the residual lifetime. As the level of gelation varies amongst uPVC pipes [95], it must be taken into account for accurate determination of the residual lifetime of uPVC pipes in service.

Meijering studied the influence of the level of gelation on $T_{d \rightarrow b}$ using puncture tests and found a minimum in $T_{d \rightarrow b}$ for $\sim 70\%$ level of gelation [19]. The expected influence

Table 3.3 The ageing parameters and ageing rates of the three master curves in Figure 3.15. The ageing rates were determined from the respective slopes of the master curves.

Pipe No.	b_0 [s ⁻¹]	b_1 [-]	Ageing rate [MPa/decade]
1*	$1.40 \cdot 10^{45}$	-0.94	3.75
2†	$3.46 \cdot 10^{43}$	-0.50	2.17
3‡	$1.95 \cdot 10^{41}$	-0.27	1.40

* yield stress data and corresponding parameters taken from [40].

† yield stress data and corresponding parameters taken from [45].

‡ yield stress data and corresponding parameters taken from unpublished results of Visser et al.

of the level of gelation on the limiting tensile yield stress is illustrated in Figure 3.16 left. The points 1 to 4 indicate the levels of gelation of specimens punctured by Meijering. For a low level of gelation (points 1 and 2), the relatively high number of poorly fused primary particles act as stress concentrators, which cause voids during impact loading [72]. The poor adhesion between the primary particles causes these voids to interconnect at lower loading and energy levels and will thus lead to poor impact properties [18]. As a result, the limiting yield stress can be expected to be relatively low. For an increasing level of gelation (point 3), the number of flaws decreases, and stronger adhesion between the primary particles causes increased plastic deformation. Increased plastic deformation will in turn lead to improved impact properties and a higher limiting yield stress. Several authors found an optimum in the impact properties with increasing level of gelation [16, 71, 96]. The decrease in impact properties after this optimum is expected to cause a decrease in the limiting yield stress as well (point 4). The origin of the decrease in impact properties after the maximum is under debate. Terselius et al. suggest that for high levels of gelation the small number of poorly fused primary particles are unable to block propagating cracks, leading to a decrease in impact properties [97]. In contrast, Summers suggests a lubricant inversion mechanism, where the lubricants become the discontinuous phase, which act as stress concentrators in the matrix causing a decrease in impact properties [98].

The ageing kinetics of the yield stress is insensitive to the level of gelation [99], in contrast to $T_{d \rightarrow b}$. The expected influence of the level of gelation on the residual lifetime can be illustrated using a single master curve as shown in Figure 3.16 right. It is shown that only uPVC pipes having very low levels of gelation (point 1) are expected to have a marked influence on the critical yield stress and on the residual lifetime. The sensitivity of the limiting yield stress on the level of gelation has not been experimentally determined yet. Therefore, at this point no quantitative predictions can be made using Figure 3.16.

Figure 3.16 Illustration of the expected influence of the level of gelation on the limiting yield stress and the residual lifetime. The horizontal dashed lines indicate hypothetical values of the limiting yield stress for four different levels of gelation. **Left:** the expected trend of the level of gelation versus the critical tensile yield stress based on the results of instrumented puncture tests performed by Meijering [19]. **Right:** the yield stress versus the annealing time for fixed annealing temperature and ageing rate. The horizontal arrows indicate the residual lifetimes.

Saw tests on uPVC pipes having various levels of gelation (but the same formulation[‡]) should be undertaken to confirm and to quantify the dependence illustrated in Figure 3.16 left. Furthermore, it would be helpful to have a technique available that can give information on the level of gelation, complementary to the information on the present yield stress. This would make it possible to take gelation effects into account as well. Chapter 5 of this thesis deals with finding a method which can measure the level of gelation in a non-destructive way.

3.8 Conclusions

Tensile impact tests were performed to determine the influence of isothermal annealing on the ductile-to-brittle transition temperature $T_{d \rightarrow b}$. An increase of 7.7 °C in $T_{d \rightarrow b}$ was found for the range of annealing times investigated. A yield stress criterion was applied, which implies that a ductile-to-brittle transition occurs when the tensile yield stress of uPVC surpasses a critical, temperature and time independent, value. The criterion enabled an accurate prediction of $T_{d \rightarrow b}$ with annealing time which shows that the proposed criterion holds for uPVC. Subsequently, a method was proposed for predicting the residual lifetime with the use of the relations given in this chapter and a limiting thermodynamic state (which directly relates to a limiting yield stress). For accurate prediction of the residual

[‡]Influence of molecular weight [78] and additives on the critical tensile yield stress are considered to be of less importance than physical ageing and gelation, but cannot be fully ruled out. A characterisation of these influences is, however, beyond the scope of this chapter.

lifetime of uPVC pipes in distribution networks, variations in the ageing rate and the level of gelation amongst uPVC pipes must be taken into account.

Chapter 4

The variation of physical ageing kinetics of uPVC pipes

4.1 Introduction

Unplasticised poly(vinyl chloride) (uPVC) pipes in the Dutch gas and water distribution networks physically age as explained in Chapter 1. This phenomenon is caused by the fact that glassy polymers, like PVC, are not in a state of thermodynamic equilibrium below the glass transition temperature T_g , but continuously strive towards it [37, 46]. Physical ageing causes a gradual increase in the yield stress over time [39] which can eventually lead to brittle failure behaviour of uPVC pipes upon impact loading events [45]. Physical ageing is an important factor that limits the lifetime of uPVC pipes as the occurrence of brittle failures in PVC distribution networks is highly undesirable [9].

Visser et al. observed a significant difference in the rate at which the yield stress increases as a function of time due to physical ageing, using the comparison of an old, excavated uPVC gas pipe against a new, unused uPVC water pipe [40, 45]. The influence of differences in the ageing behaviour on the residual lifetime for these pipes is shown in Figure 4.1. The yield stress is given as a function of the effective time at the reference temperature of 10 °C, which is the typical temperature during service. The rate at which the yield stress increases with the logarithm of time is denoted as the ageing rate, $\dot{\sigma}_y$, and is expressed in MPa/decade. The ageing rates of the two pipes investigated by Visser et al. are 3.75 MPa/decade and 1.88 MPa/decade respectively*.

The residual lifetime of each pipe was calculated using (i) an exemplary value of the limiting tensile yield stress σ_{lim} at which the failure behaviour of uPVC pipes becomes

*For long effective times, the master curves are expected to level off when the PVC approaches its equilibrium thermodynamic state [100]. This effect has not been observed within the investigated ranges of annealing temperatures and annealing times.

Figure 4.1 Master curves of the yield stress for two uPVC pipes [pipes 2 (3.75 MPa/decade) and 8 (1.88 MPa/decade)] having different ageing rates $\dot{\sigma}_y \left(\frac{d\sigma_y}{d\log(t)} \right)$ reproduced from Visser et al. [40, 45]. The arrow indicates the residual lifetime of pipe 2 for exemplary values of limiting tensile yield stress σ_{lim} and the yield stress $\sigma_{y,mh}$.

unacceptable (as defined in Chapter 2 and discussed in Chapter 3) and (ii) the present value of the yield stress $\sigma_{y,mh}$ which can be determined from in-situ micro-hardness measurements (see also Chapter 2). The residual lifetime is defined as the effective time it takes to reach the limiting tensile yield stress σ_{lim} according to the ageing behaviour of the PVC pipe from the current yield stress value $\sigma_{y,mh}$. In this (fictive) example the residual lifetime of pipe 2 is 130 years and is indicated by the arrow in Figure 4.1. The residual lifetime of pipe 8 is $1.7 \cdot 10^8$ years. This is a somewhat extreme example, but clearly the ageing behaviour has a pronounced influence on the predicted residual lifetimes. The variation of the ageing rate must therefore be taken into account for accurate implementation of the lifetime assessment model at hand. Consequently, the ageing rate of each uPVC pipe in the distribution network that is investigated with the micro-hardness approach (see Chapter 2) should be known. If the exact value for a particular uPVC pipe segment is unknown, it should be determined, preferably in situ and non-destructively. The development of any approach to obtain these values should be based on the origin of the variation in the ageing rates. The research described in this chapter concentrates on possible reasons for the observed variation in ageing rates amongst various uPVC pipes.

Physical ageing of glassy polymers like PVC occurs spontaneously at ambient conditions. It is accelerated by, for example, elevated temperatures and/or under the influence of an applied stress [37]. The variations in ageing rates observed may be the result of differences in composition, micro structure, extrusion conditions, service conditions, etc. In this chapter the possible causes for differences in ageing rates of a number of selected uPVC pipes are investigated systematically according to the stages in the lifetime of the uPVC pipes: polymerisation, processing and service life. So far, no systematic study is available in literature about variations in ageing

rates in line with these stages in the lifetime of uPVC pipes.

The structure of this chapter is as follows. Firstly, relevant material related properties that potentially influence the ageing rate are discussed in Section 4.2. Note that in this chapter the word "property" is used in a rather broad sense. It includes material properties, but also the presence of additives, the service conditions, the process conditions, etc., i.e. all aspects that may influence in some way the physical ageing rate of uPVC pipes. The selected properties have been determined for a broad range of uPVC pipes. The experimental conditions are described in Section 4.3. The measurement results and the discussion of the correlations between the properties and the ageing rate are discussed in Section 4.4, followed by the conclusions.

4.2 Possible factors influencing the ageing rate

Physical ageing arises from the fact that amorphous polymers below T_g are not in a thermodynamic equilibrium state. The "distance" to equilibrium serves as the driving force of the physical ageing process. As such, amorphous polymers below T_g continuously strive towards the equilibrium state. Although the molecular mobility below T_g is low, it is sufficient to allow small conformational changes of the polymer chains towards their thermodynamically more favoured positions [37, 46]. The resultant changes can be monitored using several material properties such as the yield stress [39, 40, 63, 101], the density [37], the enthalpy [67, 93, 102], creep compliance [46] or even the fluorescence intensity of dyes [103]. Although the kinetics of the ageing process have been studied extensively [37, 38], the exact specific molecular processes that take place during physical ageing are still unknown [37, 38, 104–108]. It is reasonable to assume that the ageing rate is influenced by mobility on a sub-molecular scale, that is to say the ability of the polymer chains to locally change their conformation. The molecular mobility in turn depends on the chain flexibility and on the interactions between the polymer chains and their physical/chemical environment [105]. Possible causes for variations in chain flexibility and chain interactions occurring during the lifetime stages of uPVC pipes related to a number of uPVC properties have been collected in Table 4.1. The background of the potential influence of these properties on the ageing rate is discussed below.

4.2.1 Stage 1: Polymerisation

The first stage is the polymerisation of uPVC from vinyl chloride (or chloro-ethene). The conditions during polymerisation control the chain structure and chain length distribution of PVC, which in turn influences the chain flexibility and the formation of crystallites. The characterisation of the polymerisation stage in terms of properties

Table 4.1 Properties of uPVC pipes which have been tested.

Stage	Class of properties	Property No.	Property description	Technique
polymerisation	<u>chain structure</u>	1	double carbon bond concentration	^1H NMR ¹
		2	isotactic triad concentration	^{13}C NMR
		3	heterotactic triad concentration	^{13}C NMR
		4	syndiotactic triad concentration	^{13}C NMR
	<u>crystallinity</u>	5	K-value (molecular weight)	viscometry
		6	crystalline fraction	DSC ²
processing	<u>processing conditions</u>	7	level of gelation	DSC
		8	processing temperature	DSC
	<u>stabilisers</u>	9	stearic acid concentration	GC-MS ³
		10	palmitic acid concentration	GC-MS
		11	tridecanoic acid concentration	GC-MS
		12	lead concentration	ICP-OES ⁴
		13	zinc concentration	ICP-OES
		14	sulphate (SO_4^{2-}) concentration	CE ⁵
	<u>lubricants</u>	15	relative hydroxyl group (OH) concentration	IR ⁶
		16	presence of PE wax	PVT-GC-MS ⁷
	<u>processing aids</u>	17	relative carbonyl group (C=O) concentration	IR
	<u>fillers</u>	18	chalk (CaCO_3) concentration	IR, X-Ray diffraction
		19	silicon dioxide (SiO_2) presence	X-Ray diffraction
	<u>pigments</u>	20	titanium dioxide (TiO_2) presence	X-Ray diffraction
	<u>geometry</u>	21	diameter	
		22	wall thickness	
service	<u>other</u>	23	chloride (Cl^-) concentration	CE
		24,25,26	melt enthalpies of additives	DSC
	<u>inorganic compounds</u>	27	lead sulphide (PbS) presence	X-Ray diffraction
molecular mobility	<u>service conditions</u>	28	excavated/unused	
		29	year of production	
		30	β -relaxation loss angle	DMA ⁸
		31	β -relaxation temperature	DMA
		32	glass transition temperature	DSC

¹Nuclear magnetic resonance spectroscopy²Differential scanning calorimetry³Gas chromatography–mass spectrometry⁴Inductively coupled plasma – optical emission spectrometry⁵Capillary electrophoresis⁶Infrared spectroscopy⁷Programmable temperature vaporising – gas chromatography – mass spectrometry⁸Dynamic mechanical analysis

that may affect the ageing rate was focused on (i) the occurrence of double bonds in the main PVC chain structure, (ii) the tacticity in the main PVC chain structure, (iii) the K-value (a measure for the chain length) and (iv) the crystalline fraction.

Double bonds are defects in the (regular) chain structure which can be formed during polymerisation by intermolecular H-abstraction, β -scission reactions [109] and during degradation of the polymer by means of dehydrochlorination [58]. The double bond inhibits local changes in conformation of the main chain which in turn

may decrease the ageing rate, as the carbon atoms connected by a double bond are not able to rotate around that bond. The concentration of double bonds can be determined using ^1H NMR [110]. Another property characterising the chain structure is tacticity, representing the regularity of chloride atoms along the PVC chains. Tacticity influences the ability of the PVC to form crystallites [111]. The presence of crystallites constrains the ageing process, especially in the vicinity of crystals, as shown for PVC [93] and polyethylene terephthalate (PET) [112]. It can be attributed to a decrease of the molecular mobility of chains in the amorphous phase that extend into the crystallites (also referred to as the rigid amorphous phase). Variations in tacticity may have an effect on crystallinity and consequently on the ageing rate. The tacticity of uPVC pipe materials was characterised from the syndiotactic-, isotactic- and heterotactic triad concentrations, which can be determined using ^{13}C nuclear magnetic resonance (NMR) [113]. The influence of crystallites on the physical ageing process relates to the crystalline fraction and the crystal morphology (size, shape) [93, 114]. A common technique to study crystalline morphology in PVC is X-ray diffraction [115]. However, quantifying differences in crystallinity in commercial PVC using this technique is difficult as (i) its crystalline fraction is low (usually 5–10%), (ii) the diffraction peaks are very broad owing to the small crystallite size (about 2–4 nm) and (iii) the presence of a mesomorphous phase in PVC makes it difficult to separate diffraction peaks of the crystallites from the background caused by the amorphous phase [115–118]. Here, as a start, only the crystalline fractions of PVC pipe materials were determined experimentally. The differential scanning calorimetry (DSC) method was chosen to determine the crystalline fraction as it is more sensitive to small variations in crystalline fraction than X-ray diffraction [118].

The length distribution of the uPVC chains was characterised by viscometry [119]. It is expressed in terms of the *K*-value, which is a measure for the average molecular weight of PVC [120]. The *K*-value is merely used to characterise the uPVC, as it is known that commercial extrusion companies have experimented with various *K*-values in the early days of uPVC pipe manufacturing. The effect of the value of *K* on the ageing rate is expected to be small, as indicated by published measurements on PC [63].

4.2.2 Stage 2: Processing

The second stage is the processing stage in which the polymerised PVC powder is mixed with additives and subsequently extruded into the shape of a pipe. During this temperature-dependent process entanglement[†] of PVC chains from different PVC particles occurs such that an interfacial network builds up during pipe production. The degree of interfacial entanglement is called the level of gelation. It has a marked influence on the mechanical properties of PVC pipes [16, 71, 122–124]. Both the

[†]Entanglement means the topological restriction of molecular motion by other chains [121].

processing temperature and the gelation level will be characterised using DSC [125–128]. The influence of the level of gelation on the mechanical properties is further discussed in Chapter 5.

Several additives are mixed with the PVC powder during processing for a variety of purposes, for example (i) to reduce friction during processing of PVC to prevent excessive heating, (ii) to improve thermal stability, (iii) to facilitate the gelation process and (iv) to increase volume/cost ratio) [58]. Apart from the general information about the employed formulations in textbooks, the typical additives that were used in uPVC pipes from 1950 to 1975 were provided by one of the Dutch PVC pipe manufacturers and are summarised in Table 4.2.

Table 4.2 Commonly used additives for uPVC pipes in the Dutch gas and water distribution networks from 1950 to 1975.

Type of additive	Compound name
stabilisers	tribasic lead sulphate
	lead stearate
	dibasic lead stearate
	lead phosphite
	dibasic lead phosphite
lubricants	glycerol monostearate
	polyethylene wax
	calcium stearate
fillers	calcium carbonate

Lead stabilisers are the oldest and most commonly used thermal stabilisers for uPVC pipe applications. Over time lead in stabilisers has been replaced by other compounds (e.g. calcium-zinc mixtures) because of environmental concerns with lead. The degradation of PVC already begins at 100 °C by the loss of labile chloride groups as HCl with the creation of a double bond [58]. This reaction causes the adjacent chloride to become labile; the chloride is also eliminated from the polymer chain through the release of HCl. This process repeats itself, eventually creating a series of conjugated polyene sequences leading to undesired physical properties of the PVC. The main function of a lead stabiliser is to substitute labile chlorides with stable ligands (e.g. lead chloride), mitigating the degradation process of the PVC during processing [129]. The most widely employed lead stabiliser for uPVC processing is tribasic lead sulphate [58] and is expected in old uPVC pipes taken from the distribution networks. Other commonly used lead stabilisers for uPVC pipe applications are (dibasic) lead stearate and (dibasic) lead phosphite, see also Table 4.2. Lubricants are added to PVC materials to reduce the tendency of PVC to stick to the metal of the processing equipment and to reduce friction between the primary PVC

particles improving the flow of the rubbery PVC melt during processing. Which of the two features dominates depends on the polarity of the lubricant and the metal surface of the extruder and the amount of lubricant added [58]. Commonly used lubricants are glycerol monostearate, polyethylene wax (PE wax) and calcium stearate (Table 4.2).

Fillers are traditionally used to increase volume/cost ratio. The most widely used filler for uPVC pipe applications is calcium carbonate (chalk) [58]. Other additives used in PVC pipes not mentioned in Table 4.2 are processing aids and pigments [58]. Processing aids are typically acrylate compounds which adhere to the PVC grains, facilitating the transmission of elongational and shearing forces to the PVC powder and promoting the breakdown and the homogenisation of the PVC melt. Pigments are typically added for colour and increase the resistance against weathering [58]. The presence of plasticisers (e.g. phthalate esters) is not expected in uPVC pipe applications as plasticisers are usually added to obtain flexible PVC products.

The determination of the relation between additives present and the physical ageing rate of uPVC pipes requires knowledge of the type and concentration of all additives added to the individual uPVC pipes. The list of commonly used additives, as given in Table 4.2, and information from textbooks will probably not be sufficient to cover the effects of all possible additives employed over time, nor will it cover their effects on the physical ageing rate or the effect of mutual interactions of the additives on the physical ageing rate. Nevertheless, a selection of uPVC pipes was analysed for the presence of various additives to see if a relationship between the presence/concentration of the additive and the physical ageing rate can be discovered.

As a first step, DSC and InfraRed spectroscopy (IR) was employed to obtain a general view of the compounds present in the uPVC pipes investigated. The DSC method has the advantage that also the level of gelation and the processing temperature can be determined in a single run. For determination of inorganic components such as fillers and pigments, X-ray diffraction is used first. In general these techniques suggest the family to which the additives belong, but are not always sufficient for identification and quantification of the specific compounds shown in Table 4.2 [58]. Therefore, in some cases compounds present in the PVC pipes investigated are separated from the PVC employing dedicated separation procedures and a number of other techniques were employed to characterise the specific compounds.

A number of additives in Table 4.2 are stearates consisting of metal ion(s) and fatty acids. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) is used to identify and determine the concentration of the metal ions. For fatty acids, the Gas Chromatography-Mass Spectrometry (GC-MS) method is employed, because it is able to determine accurately the amount of fatty acids and, combined with MS, substances can be identified simultaneously [58].

Stabilising salts, such as tribasic lead sulphate, consist of metal ions and molecular

ions. The Capillary Electrophoresis (CE) method is used to quantify molecular ions, as this technique uses an electrical potential difference to separate and identify charged molecules. The presence of lubricants was investigated employing Programmable Temperature Vaporising GC-MS (PTV-GC-MS).

A complete list of compounds (stabilisers, lubricants, processing aids, fillers and pigments) identified in this study is summarised in Table 4.1. Besides the compound analysis the dimensional properties of the uPVC pipes selected (diameter and wall thickness) were also determined.

4.2.3 Stage 3: Service

The third stage is service, in which the pipes are stored, installed and transport gas and water to the households. Compounds (e.g. PbS) may be formed during service as a result of chemical reactions of the pipe material with components in the soil. Also information regarding the year of production and installation are recorded if known.

4.2.4 Resulting molecular mobility

The presence of additives can have an effect on the thermal and mechanical properties of uPVC. If the additives modify the chain mobility on a molecular and/or a submolecular scale, relaxation processes in uPVC may be affected. The magnitude of the α -relaxation peak – related to the glass transition – and the β -relaxation peak can change in height or temperature depending on the type and amount of additive supplied. Sometimes the effects of the additive may be opposite depending on the additive concentration. A well-known example is the plasticiser dioctyl phthalate (DOP). The addition of 10 wt.% DOP increases the enthalpy relaxation rate of PVC specimens by 30% [102], presumably due to an increase in the mobility of the chain backbone segments caused by the plasticiser. Simultaneously, the application of DOP shifts the α -relaxation peak of PVC towards lower temperatures, implying an increase of segmental mobility (plasticisation effect) [130]. In addition, DOP causes a suppression of the β -relaxation, implying a reduction in molecular mobility (anti-plasticisation effect) [130, 131].

The characterisation of the relaxation processes is useful for two reasons. Firstly, an investigation can be made as to whether the variation in the ageing rate is related to (anti-) plasticisation effects. Secondly, the characterisation may lead to other ways to determine the ageing rates of uPVC pipes if changes in the ageing rate and the relaxation processes are related. Hence, the β -relaxation peak of PVC pipes was characterised employing Dynamic Mechanical Analysis (DMA). The glass transition temperature was determined using DSC.

4.3 Experimental

4.3.1 Materials

A broad range of uPVC pipes was investigated in this study (pipes 1 to 13 in Table A.1 in Appendix A). Excavated pipes (samples 1-7) were taken from different locations in the Dutch gas and water distribution network. Unused pipes 8-13 were added to determine whether the compounds found originate from the processing of the pipes or from external factors during service (e.g. influence of the soil). Pipes (samples 10-13) have the same composition, but only differ in level of gelation. The diameter and the thickness of the pipes are shown in Table 4.4. The year of production of the pipes was collected from the suppliers or read from the pipe segment itself.

4.3.2 Ageing rate

The ageing rates of the used and unused uPVC pipes were determined on the basis of a number of uniaxial tensile tests performed on artificially aged specimens. The tensile specimens were produced by cutting 70 mm long semi-cylindrical segments from the PVC pipes with a band saw. The segments were pressed at a compressive stress of ~ 1 MPa into flat plates at 100 °C (about 15 °C above T_g) for 25 minutes. This operation erased the thermodynamic history of the material. Rectangular bars were milled from the plates with the length direction parallel to the axial direction of the pipe. A gauge section with a length of 30 mm and a width of 5 mm was milled into the bars. The tensile test specimens were isothermally annealed at 60 °C for various times. Tensile tests were carried out on a Zwick Z5.0 universal testing machine at ambient temperature and a Zwick Z1445 universal testing machine, equipped with a temperature controlled chamber, at 20 ± 0.2 °C at a constant strain rate of 10^{-3} s^{-1} . At these test conditions, only the α -relaxation contributed to the yield stress [45]. The engineering stress was determined from the average of the initial cross-sectional surface areas measured at three locations along the gauge section. The yield stress was determined from the (first) local maximum in the force recording. Three experiments were carried out for each annealing treatment. The ageing rate was determined from the slope of the yield stress curve plotted on a logarithmic annealing time scale using a linear function.

4.3.3 Determining properties related to stage 1: Polymerisation

The polymerisation conditions have a large influence on the uPVC polymer chains formed, on possible defects occurring in the chains and on the fraction and properties of the crystals formed.

Several techniques were employed for characterisation of this stage. In all cases the additives were removed from the PVC before the experiments by the following procedure. Firstly, a pipe specimen was dissolved into tetrahydrofuran (THF). The undissolved additives were removed by centrifuging the solution. Then methanol was added to the clear solution, causing the PVC to precipitate. The PVC was subsequently filtered off and dried in a vacuum oven. The dried PVC was dissolved in THF- d_8 by annealing the mixture for at least two hours at 45 °C. The concentration of the PVC in the various solutions varied between 40 and 55 mg/l.

The double carbon bond concentrations were determined from the prepared solutions using ^1H (proton) NMR [110]. The ^1H NMR spectra were obtained at room temperature by employing a Bruker Ascend spectrometer operating at 400 MHz. The spectral width was 8224 Hz and 5000 scans per solution were performed.

The syndiotactic-, isotactic- and heterotactic triad concentrations of the PVC pipes were determined using ^{13}C NMR [113, 132–134]. Inverse gated decoupled ^{13}C NMR spectra were obtained at room temperature from the PVC solutions using the same spectrometer as in the ^1H NMR experiments. The resonance peaks of THF do not overlap with the PVC peaks from which the tacticity was determined [135, 136]. The spectral width was 24038 Hz and a relaxation time of 2 s was applied. A total of 10240 scans per solution were performed to acquire a sufficient signal to noise ratio.

The average molecular weight was determined by viscometry according to standard ISO 1628-2:1998, employing the PVC solutions. The molecular weight of PVC is expressed by the K -value which is related to the relative viscosity through the Fikentscher equation [119].

4.3.4 Determining properties related to stage 2: Processing

The manufacturing of uPVC pipes by extrusion requires polymerised uPVC (see stage 1) to be mixed with a number of additives, such as stabilisers, lubricants, fillers and pigments. Characterisation of this stage requires the application of a large number of analyses techniques.

The crystalline fraction, level of gelation, the processing temperature T_p , the melt enthalpies of additives present and the glass transition temperature were all determined using DSC. Three specimens were taken over the full wall thickness of each PVC pipe. The specimens were preheated to 50 °C under a nitrogen flow using a Perkin Elmer DSC 7. Subsequently, the heat flow was measured from 50 °C to about 250 °C at a rate of 10 °C/min. All properties were determined from the first run.

The concentrations of fatty acids were determined employing GC-MS. The PVC specimens were firstly dissolved in THF and the PVC was precipitated using pentane and filtered. Subsequently, the filtrates were treated with trimethylsulfonium

hydroxide (TMSH) for transesterification to methyl esters, so that the fatty acids became volatile. The compounds in the extracts were then separated and analysed using a HP 6890 and a HP 5972 gas chromatograph spectrometer. The detection limits of these devices is about 0.1 ppm ($1 \cdot 10^{-5}$ % w/w).

The concentrations of lead and zinc in the uPVC pipes were determined using a Perkin Elmer Optima DV 7000 ICP optical emission spectrometer. The destruction of the PVC specimens was carried out using concentrated nitric acid. After destruction, the acid mixture is diluted with water to a solution of 25 ml. The solution was then analysed for lead and zinc (detection limits of about 0.1 ppm).

The concentrations of different anions (SO_4^{2-} , Cl^-) were determined using a HP3D capillary electrophoresis system (detection limits of about 0.1 ppm). The extraction procedure corresponds to the procedure for analysing fatty acids, except that the precipitation of the PVC is carried out with water.

The concentration of the filler chalk and the relative concentrations of carbonyl groups and hydroxyl groups, attributed to processing aids and lubricants respectively, were determined using IR. Specimens, taken from the pipes, were pressed at 200 °C for 2-3 s into films of about 40 µm thickness. Infrared spectra of the films were determined at 20-23 °C using a Perkin Elmer Paragon 1000 mid infrared spectrometer having a resolution of 4 cm^{-1} . For each film, 16 scans were performed and the transmission was averaged for each wave number.

The presence of PE wax was determined using PTV-GC-MS. The PVC specimens were heated from 40 °C to 600 °C (16 °C/s) under a helium flow using an Atas Optic 2 PTV injector. The released components were brought with the helium to a HP 5890 II plus and a HP 5972 gas chromatograph spectrometers for separation and analysis (detection limits of about 0.1 ppm).

The presence of minerals was investigated with XRD. A PANalytical diffractometer was used equipped with a PW1830 standalone generator with Co radiation and an Fe incident beam filter. Measurements were conducted from 5° 2θ to 100° 2θ with a step size of 0.05° 2θ and a time per step of 1 s. Four measurements were performed on each PVC specimen to compensate for possible temperature and pressure variations. Phase analysis on the summed diffractograms was carried out with PANalytical HighScore phase identification software.

4.3.5 Determining properties related to stage 3: Service

The year of production/installation was supplied by the network service providers (if known) or is printed on the pipe itself in the case of newer pipes. Information on PbS formation is obtained by visual inspection of the pipe segments.

4.3.6 Determining properties related to molecular mobility

The molecular mobility in the used and unused uPVC pipes is characterised through the glass temperature as measured by DSC, see above, and the β -relaxation behaviour. The β -relaxation peaks of the uPVC materials were determined using an Anton Paar MCR501 rheometer equipped with an SRF-12 solid torsion bar fixture. The loss angle was determined during a temperature sweep from 60 °C to –120 °C at a cooling rate of 12 °C/min for a 0.1% strain amplitude at a frequency of 1 Hz. Rectangular specimens were milled from plates that were pressed according to the same procedure used for manufacturing the uniaxial tensile bars. The rectangular specimens have a length of 50 mm and a width of 12 mm. The thicknesses of the specimens were approximately equal to the original wall thicknesses of the pipes.

Detailed information regarding the various measurements performed and the processing of the measurement data to obtain the values of the relevant properties mentioned in Table 4.1 can be found in Appendix B.

4.4 Results and discussion

4.4.1 Ageing rates

The ageing rates of the uPVC pipes studied here are given in Figure 4.2. The ageing rates of the two pipes shown in Figure 4.1 in the introduction of this chapter (pipes 2 and 8) are also included. Most pipes in this study have an ageing rate of approximately 2.5 MPa/decade. The ageing rates of pipes 1, 2 and 3 are higher and pipe 1 has the highest ageing rate of 4.2 MPa/decade. Pipe 7 has the lowest ageing rate of 1.1 MPa/decade. So, the ageing rates of the pipes in this study differ considerably, up to a factor of almost four.

Throughout the rest of this section the experimental results of the properties investigated are checked for a linear correlation with the ageing rate. Besides this correlation check a multi-variable analysis was carried out. No striking additional observations were found by the multi-variable analysis. Therefore, the description of the multi-variable analysis and the results are presented in Appendix C.

4.4.2 Properties related to stage 1: Polymerisation

Various analysis techniques were applied to characterise certain aspects and properties of the polymerisation stage of the PVC material used for pipe manufacturing. The results of the analyses are given in Table 4.3. Properties related to the PVC chain structure can be found in columns 1 to 5 and the degree of crystallinity can be found in column 6.

Figure 4.2 The ageing rates of the uPVC pipes. The error bars indicate 95% confidence intervals.
[†]Unused uPVC pipes 10-13 have the same formulation and were processed on the same extruder, but have strong differences in the level of gelation.

Influence of chain structure

The conditions during polymerisation control the chain structure of PVC. The PVC chains of the uPVC pipes investigated do not seem to vary much in their chain structure and number of defects occurring, but only in their average length. The concentrations of chain defects in the form of double carbon bonds are very low (column 1). The variations in tacticity as characterised by the isotactic, heterotactic and syndiotactic triad concentrations are also small (columns 2-4). The largest variations occur in the average PVC chain length as given by the K -value in column 5: the K -value is mostly between 64 and 68, except for pipes 3 and 4, where the K -value is 72 or greater. The correlations between these properties and the ageing rates are very low, as observed from the R^2 values indicated by the bars shown at the bottom of Table 4.3. These values indicate how well the specific property correlates with the ageing rate using a linear regression function. Apparently, the sporadic occurrence of local non-rotatable chain parts, i.e. double carbon bonds and/or small variations in triad concentrations, do not seem to affect the ageing rate, nor does the observed variation in chain length. The absence of a clear correlation between the K -value and the ageing rate ($R^2 = 0.04$) is in line with the results found earlier for PC [63].

Influence of crystallinity

The crystalline fractions of the uPVC pipes vary considerably, by between 8% and 19%. These values are in the same order of magnitude as found in [118]. The crystalline fractions hardly correlate to the ageing rate for the uPVC pipes selected in this work as the R^2 is very small, see Table 4.3. The minor effect of crystalline fraction on the ageing rate is supported by Tsitsilianis et al. who found no clear correlation between the crystalline fraction and the enthalpy relaxation rate for PVC [93]. They

Table 4.3

The experimental results of the properties 1 to 17 as listed in Table 4.1. For the cases in which a property of a pipe is measured multiple times, the average value is shown in the table. Pipes 1-7 are excavated uPVC pipes and pipes 8-13 are unused uPVC pipes. The ageing rates are given in the second column with the 95% confidence intervals between brackets. The bars shown at the bottom are R^2 values which indicate how well a property correlates with the ageing rate for a linear regression function. The unused uPVC pipes 10-13 have different levels of gelation but the same formulation and have been processed on the same extruder. The '-' sign indicates that the measurements have not been performed. The zeros in columns 11, 13, 15 and 16 indicate that for these measurements the compound was not observed.

Pipe No.	Property Unit	No.	Polymerisation					Processing										
			chain structure					cyst	conditions			stabilisers				lubricants	aid	
			1	2	3	4	5		6	7	8	9	10	11	12			13
MPa/decade	[%]	[%]	[%]	[%]	[-]	[%]	[%]	[°C]	[%w/w]	[%w/w]	[%w/w]	[%w/w]	[%w/w]	[%w/w]	[%w/w]	[-]	[-]	[-]
	ageing rate (95% C)																	
	double carbon bond concentration																	
	isotactic triad concentration																	
	heterotactic triad concentration																	
	syndiotactic triad concentration																	
	K-value (molecular weight)																	
	crystalline fraction																	
	level of gelation																	
	processing temperature																	
	stearic acid concentration																	
	palmitic acid concentration																	
	tridecanoic acid concentration																	
	lead concentration																	
	zinc concentration																	
	sulphate (SO ₄ ²⁻) concentration																	
	relative hydroxyl group (OH) concentration																	
	presence of PE wax																	
	relative carbonyl group (C=O) concentration																	
1	4.17 (± 0.72)	-	18.26	48.78	32.96	66	9.2	52	184	-	-	-	-	-	-	0.083	-	0.513
2	3.75 (± 0.24)	2.2	18.81	48.63	32.56	67	7.9	45	182	0.074	0.042	0	0.847	0	0.002	0.080	0	0.581
3	3.14 (± 0.78)	-	18.68	48.43	32.90	72	18.4	60	180	0.184	0.090	0.013	0.823	0	0.001	0.205	0	1.000
4	2.52 (± 0.35)	-	19.20	48.65	32.15	73	18.3	74	191	0.120	0.077	0.009	0.921	0	0.004	0.212	0	0.888
5	2.28 (± 0.25)	2.4	18.81	48.63	32.56	68	18.6	79	188	-	-	-	-	-	-	0	-	0.172
6	2.17 (± 0.21)	-	18.36	48.84	32.80	68	13.5	69	180	-	-	-	-	-	-	0	-	0.320
7	1.05 (± 0.09)	1.9	17.64	48.92	33.44	66	6.9	63	182	0.147	0.069	0.008	0.357	0	0.002	0	1	0.170
8	1.88 (± 0.35)	-	18.51	48.70	32.79	65	18.4	71	186	0.083	0.048	0	0.178	0.040	0.002	0.770	1	0.178
9	1.86 (± 0.31)	2.1	18.13	48.94	32.94	68	18.1	80	185	-	-	-	-	-	-	1.000	-	0.185
10	2.25 (± 0.52)	1.6	-	-	-	64	13.7	19	162	-	-	-	-	-	-	0	-	0.178
11	2.50 (± 0.36)	2.5	18.76	48.46	32.78	66	11.9	48	177	-	-	-	-	-	-	0	-	0.143
12	2.22 (± 0.47)	1.8	-	-	-	65	12.9	73	183	-	-	-	-	-	-	0	-	0.109
13	2.24 (± 0.38)	-	-	-	-	65	13.8	91	196	-	-	-	-	-	-	0	-	0.157
Stage Class			Polymerisation					cyst	conditions			stabilisers				lubricants	aid	
			chain structure															

R^2 [%]

Pipe No.	Property	Unit	No.
	ageing rate (95% CI)		18
	chalk (CaCO_3) concentration	[wt.%]	19
	silicon dioxide (SiO_2) presence	[-]	20
	titanium dioxide (TiO_2) presence	[-]	21
	diameter	[mm]	22
	wall thickness	[mm]	23
	chloride (Cl^-) concentration	[%w/w]	24
	melt enthalpy 1	[J/g]	25
	melt enthalpy 2	[J/g]	26
	melt enthalpy 3	[J/g]	27
	lead sulphide (PbS) presence	[-]	28
	excavated [I]/unused [O]	[-]	29
	year of production	[year]	30
	β -relaxation loss angle	[-]	31
	β -relaxation temperature	[°C]	32
	glass transition temperature	[°C]	32

[illegible]

also suggested that knowledge of the crystalline fraction itself is not sufficient to explain the ageing behaviour of uPVC, and variations in the ageing process may originate as well from variations in the size, shape and perfection of the crystallites.

A higher degree of regularity of the polymer PVC chains promotes the formation of crystallites [111]. A clear correlation between the syndiotactic triad concentration and the crystalline fraction is not observed ($R^2 = 0.21$ determined from Table 4.3). This is in line with the results in [111]. The differences in tacticity determined are too small (around 0.3% on the content of 32%) to affect the crystalline fraction. The variations in the crystalline fraction of the uPVC pipes may thus predominantly originate from the processing stage [137].

Conclusion on the effect of the polymerisation stage

It is concluded from the above results and observations that the properties related to the polymerisation stage, i.e. the chain structure, average chain length and crystallinity, do not contribute significantly to the variation in the ageing rates of the pipes.

4.4.3 Properties related to stage 2: Processing

The extrusion process of uPVC pipes requires a number of additives to be mixed with the uPVC powder to facilitate the manufacturing process and obtain uPVC pipes of sufficient quality. Although it is known to a certain extent which additives have been used (see Table 4.2), a broad range of analysis techniques has been applied to characterise the uPVC pipes. The results of the measurements on the various material properties can be found in Table 4.3, columns 7 to 17 and Table 4.4, columns 18 to 26.

Processing conditions

The extrusion process of PVC pipes is temperature dependent and the process temperature has a marked influence on the level of gelation. This level varies between 45 and 79 for the excavated pipes (see column 7, pipes 1-7). The last four unused pipes, pipes 10-13, have the same formulation and were processed on the same extruder with different process temperatures to induce different levels of gelation. The correlation between the level of gelation and the process temperature is very strong: $R^2 = 0.97$ for pipes 10-13 [97]. In general, the processing conditions have a marked influence on the mechanical properties of PVC pipes [16, 71, 122–124], but the level of gelation has no significant influence on the ageing rate, as observed from the low values of R^2 in the bottom of Table 4.3, see columns 7 and 8.

Stabilisers

The presence of various stabilisers can be deduced from the relative concentrations presented in columns 9-14 of Table 4.3. For the pipes tested for lead and zinc, pipes 2-4 and 7 contain a substantial amount of lead (0.4-0.9% w/w) and pipe 8 contains zinc and a smaller amount of lead. Except for pipe 8 the infrared spectra of all pipes show a peak at 1534 cm^{-1} attributed to the COO^- -group of lead stearate [138]. In view of these observations, pipes 2-4 and 7 possibly contain lead stearate as a stabiliser, whereas pipe 8 could contain zinc stearate or calcium/zinc stearate mixture as a stabiliser. Furthermore, a small amount of SO_4^{2-} shows that (tribasic) lead sulphate is present in the PVC pipes investigated. Lastly, phosphite has not been observed in the CE experiments showing that stabilisers such as (dibasic) lead phosphite are not present in the PVC materials. Of the stabiliser properties investigated only the concentration of lead shows a correlation with the ageing rate. The ageing rate increases with increasing concentration of lead compounds, as shown in Figure 4.3. Apparently, the lead compounds present decrease the molecular interactions between PVC chains causing the ageing rate to increase.

A clear correlation was not found between the ageing rate and the possible compounds which are bound to lead. There might be one or more unidentified lead compounds which are responsible for the correlation, or the observed trend in Figure 4.3 might be disturbed by lead compounds which do not influence the ageing rates. A multi-variable analysis (see Appendix C) has shown that compounds which may be bound to lead (stearic acid, palmitic acid, tridecanoic acid, sulphate, chloride and sulphide) do not cause deviations from the observed correlation.

Figure 4.3 Ageing rate versus the concentration of lead. The dashed line is a guide to the eye. The vertical error bars represent 95% confidence intervals. The numbers indicate the pipes according to Table 4.3.

Plasticisers

As expected, none of the uPVC pipes investigated contain phthalate esters utilised for plasticisation of PVC. The absence of phthalate esters indicates that these substances do not cause anti-plasticisation effects, which might explain that the variation in the maximum loss angle for the β -relaxation is small (about 12%, as will be presented in 4.4.5) in comparison with a 22% decrease upon addition of 5 wt.% DOP in [131].

Lubricants

The relative concentration of hydroxyl (-OH) groups and the possible presence of PE wax is shown in columns 15 and 16 respectively of Table 4.3. The hydroxyl groups identified in the IR spectra of the PVC materials might indicate the presence of fatty alcohols such as glycerol monostearate, which is used as a lubricant. Molecular compounds having hydroxyl groups do not seem to influence the ageing rate ($R^2 = 0.05$), but further research is required to confirm the relation between the presence of fatty alcohols and the ageing rate.

In the PTV-GC-MS experiments a number of peaks of hydrocarbons were observed for pipes 7 and 8, see column 16. Some of these substances are also released during pyrolysis of polyethylene (PE), showing that these pipes may contain PE wax as a lubricant [139]. The ageing rate versus the presence of PE wax is shown in Figure 4.4, ($R^2 = 0.75$). The correlation suggests that the presence of PE wax hinders the molecular motion of the PVC chains and decreases the ageing rate. However, too little data points are available to make a firm statement.

Figure 4.4 Ageing rate versus the presence of PE wax. The dashed line is a guide to the eye. The vertical error bars represent 95% confidence intervals. The numbers indicate the pipes according to Table 4.3.

Processing aids

The relative carbonyl (C=O) group concentration can be found in column 17 of Table 4.3. The highest relative concentrations are found for excavated pipes 3 and 4, manufactured in the 1960s (see column 29 of Table 4.4). These pipes are also characterised by a relatively high *K*-value (see column 5 of Table 4.3). This observation suggests that the carbonyl groups can be attributed to a significant amount of processing aid required for extrusion of these pipes [58] and not to phthalate esters for plasticisation [140]. The concentration of carbonyl group does not influence the ageing rate ($R^2 = 0.32$) substantially as shown in Table 4.3. The presence of carbonyl groups, determined by employing IR, only suggests the family of additives: in this case processing aids. Here processing aids do not seem to significantly contribute to the variation in the ageing rate.

Fillers and pigments

Fillers are traditionally added to uPVC to increase the volume/cost ratio. Two types of fillers were observed – chalk and SiO₂; the concentrations of both fillers are shown in columns 18 and 19 respectively of Table 4.4. The ageing rate versus the chalk concentration is given in Figure 4.5. The dashed line drawn through the data points of pipes 8-13 suggests a decreasing trend of the ageing rate with the chalk concentration. The observed decrease suggests that particles of CaCO₃ may hinder the molecular motion of chains that surround these filler particles. Indeed, a large decrease up to a factor 14 in the ageing rate has been observed for nano-size fillers [103]. However, in the current uPVC samples the typical widths of the XRD peaks corresponding to chalk reflections indicate that the chalk crystals dimensions are typically a micrometre or larger [141]. It is unlikely that such large particles may have a significant influence on the overall ageing rate, given the typical dimensions of the segmental chain parts involved with physical ageing. Another reason may be that CaCO₃ particles do not strongly adhere to the PVC chains [142]. Hindrance of molecular motion responsible for physical ageing by CaCO₃ particles may therefore be rather limited.

Silicon dioxide (SiO₂) is found in used and unused pipes as a filler or reinforcing agent in the PVC materials [58]. Only in unused pipe 10 was titanium dioxide (TiO₂) observed, see column 20 of Table 4.4. It has no clear correlation with the ageing rate. The TiO₂ is a white substance and is used as a pigment for colour stability of PVC pipes which have to cope with outdoor conditions (e.g. during outdoor storage). The TiO₂ inhibits degradation of the PVC by absorbing ultra-violet radiation [58].

Figure 4.5 Ageing rate versus the concentration of chalk (CaCO_3). The dashed line is a guide to the eye.

Other compounds

In column 23 the relative concentrations of Cl^- are given. The presence of chloride is indicative of degradation of PVC during processing. For this reason stabilisers are added that substitute labile chloride with stable ligands mitigating dehydrochlorination. An increase in the concentration of chloride with increasing processing temperatures is observed. Possibly the PVC degrades more at higher temperatures by dehydrochlorination, causing a higher concentration of chloride in the specimens. However, no clear correlation between the chloride concentration and the ageing rate has been observed. Finally, in columns 24-26 of Table 4.4 the melt enthalpies observed within specific temperature ranges of the DSC measurements of the uPVC samples are given. It is unknown to what compound/material the melt enthalpies relate. Nevertheless, no clear relationships between the height of the various melt enthalpies and the physical ageing rate were observed. Further research is required to elucidate the background of these enthalpy peaks.

Geometry

The dimensions of the used and unused uPVC pipes are provided in columns 21 and 22 of Table 4.4. The diameter varies between 50 mm and 160 mm and the wall thickness varies between 2.2 mm and 4.5 mm. No correlation between the pipe dimensions and the physical ageing rate exists as observed from the R^2 data.

Conclusion on the effect of the processing stage

Despite the many analyses performed on the presence of a large number of additives a solid explanation to the origin of the variation in ageing rates cannot be given. It seems that the composition of the uPVC pipes is not completely defined by the list of

typical ingredients, as shown in Table 4.2. In many analysis results of IR, NMR, DSC and XRD some of the peaks observed cannot be explained. The data presented in Tables 4.3 and 4.4 indicates that the physical ageing rate is correlated to some extent with the lead concentration and the presence of PE wax.

4.4.4 Properties related to stage 3: Service

Service-related properties, i.e. the year of production, the state of the material (excavated versus unused) and the presence of lead sulphide at the outside of the pipe, are shown in Table 4.4, columns 27 to 29.

Year of production

An interesting observation is the behaviour of the ageing rate as a function of the year of production, as shown in Figure 4.6. The ageing rate of the uPVC pipes investigated increases as a function of the year of production up to approximately 1978-1980. Then the ageing rate suddenly drops and remains nearly constant, regardless of the year of production. It is difficult to explain in this way why the ageing rate increases as a function of the year of production up to the end of the 1970s. It is known that the process conditions and the types and concentrations of various additives used have changed somewhat over the years, but this type of smooth behaviour seems rather coincidental. The transition around the end of the 1970s might be related to the end of the production of uPVC pipes for natural gas transport applications. All (unused) uPVC pipes produced from 1981 onwards (pipes 8-13) are meant for water transport networks. Possibly different formulations have been applied since, leading to different responses as a function of the ageing time.

Figure 4.6 Ageing rate versus year of production.

Lead sulphide

The presence of hydrogen sulphide (H_2S) was observed only for excavated pipes 3 and 8. These pipes also have a very thin brown outer layer. Sulphate-reducing bacteria can be present in some types of soil. These bacteria convert sulphate in the soil into H_2S . Subsequently, the H_2S reacts with the lead stabiliser in the outer layer of the PVC pipe. In this process lead sulphide (PbS) is created, which turns the outer layer of the pipe brown. The absence of a clear correlation between the ageing rate and compound PbS shows that the physical/chemical changes of the PVC materials as a result of interactions between the lead stabiliser(s) with the surrounding soil do not seem to affect the ageing rate.

Conclusion on the effect of the service stage

It is concluded that the properties related to service do not clarify the variation in ageing rate of the pipes considered, although the year of production does suggest differences in the behaviour between uPVC pipes produced for gas transport applications that were typically manufactured before 1980 and those for water transport applications manufactured after 1980.

4.4.5 Molecular mobility

The β -relaxation temperature

The β -relaxation (or secondary relaxation) peaks for several unused and excavated uPVC pipes, characterised with DMA, are shown in Figure 4.7 left. The storage modulus data in the same temperature interval are shown in Figure 4.7 right. The peaks in the loss angle are attributed to molecular motion of chain segments. For PVC, it is not known exactly which chain segments cause the β -relaxation [143, 144] as the PVC chains have no flexible side groups. The relatively large chloride atoms cause substantial steric hindrance. Hence, it is thought that the process arises primarily from local main-chain motion [143].

The peak in the loss angle shows a small variation in height in Figure 4.7 left as well as a variation in peak temperature. It is known that small amounts of plasticisers (up to 10% w/w) can suppress the β -relaxation, leading to a smaller peak as well as lower peak temperatures for increasing plasticiser content [130, 131, 145]. However, the peak temperatures measured here do not decrease consistently in line with a decrease in the peak height. Moreover, no significant amount of plasticiser was found in the uPVC pipe material investigated here. Therefore, the variation in peak temperature is not considered to be related to anti-plasticisation for these pipes.

Figure 4.7 The loss angle (*left*) and storage modulus (*right*) versus temperature for PVC pipes having different ageing rates. The numbers indicate the pipes according to Table 4.3.

The locations of the maxima of the peaks, T_β , are shown in Figure 4.8 along with the corresponding data of the ageing rate of the uPVC pipes investigated. An interesting relation is observed, where the increase of the β -relaxation temperature is accompanied by a decrease in the ageing rate.

Figure 4.8 The ageing rate versus β -relaxation temperature for excavated and unused PVC pipes. The vertical error bars represent 95% confidence intervals. The horizontal error bars represent the uncertainty in T_β caused by measurement noise and the shape of the loss angle versus temperature curves. The dashed line represents the best ordinary least squares fit of a linear function.

Changes in the β -relaxation temperatures of the uPVC pipes may be associated with changes in the energy barriers that must be overcome by chain segments of the uPVC molecules to change their conformation locally. The activation energy of the β -relaxation for uPVC is determined from T_β and the applied strain rate during the

DMA measurements following the approach of Porter et al. [146] and others [83, 147]

$$f = 2\pi f_0 \exp\left(\frac{-H_\beta}{RT_\beta}\right), \quad (4.1)$$

where f is the frequency at which the strain is applied during the DMA experiments, H_β the activation energy and R the gas constant. Assuming the β -relaxation arises mainly from main-chain motion the angular frequency $2\pi f_0$ of only the skeletal modes of motion is taken into account and is calculated from the reference temperature θ_1 using

$$f_0 = \frac{k\theta_1}{h}, \quad (4.2)$$

where k is Boltzmann's constant and h is Planck's constant. For PVC, $\theta_1 = 368$ K [148]. The reference temperature θ_1 corresponds to the frequency of molecular vibrations in the direction of the polymer chain [148]. The reference temperature is thus basically determined by the stiffness of the main chain. The chain structure of PVC in the pipes investigated is quite similar, as shown by the triad concentrations in columns 2-4 of Table 4.3. It is reasonable to assume a constant value for θ_1 for all PVC materials investigated in this study. Then, according to Equation 4.2, the angular frequency $2\pi f_0$ is $4.82 \cdot 10^{13}$ 1/s. The frequency at which the strain is applied is 1 Hz for all measurements. The calculated activation energies H_β are given in Table 4.5 for pipes 2, 8 and 12. Similar values for the activation energy of the β -transition of PVC have been found using DMA, 64.8 kJ/mol [147] and dielectric measurements, 56.9 kJ/mol [149] and 57.9 kJ/mol [150]. Furthermore, the activation energy of pipe 8 is close to the value determined by Visser et al. from the deformation kinetics of this pipe employing tensile testing, 58.6 kJ/mol [45]. The value of θ_1 seems to be reasonable for the PVC pipes, because the determined activation energy of pipe 8 is in good agreement with the literature values. The activation energy H_β increases slightly with increasing temperature T_β as shown in Table 4.5. Therefore, more thermal energy is required for local chain motion as the height of energy barriers increases with the value of T_β .

The ageing activation energies ΔU_a of the pipes were determined from Visser et al. [40, 45] and Drenth et al. [99]. They are listed in the last column of Table 4.5. The ageing rate $\dot{\sigma}_y$ decreases with increasing ΔU_a , as expected. This relation suggests that, at a certain annealing temperature below T_g , the number of chain parts that have enough thermal energy to overcome energy barriers decreases with increasing activation energy ΔU_a . Hence, the ageing rate becomes lower when less chain parts are thermally activated. Furthermore, the ageing activation energy increases with increasing H_β . This relation may indicate that the same factors that restrain the molecular movement of β -relaxation also restrain the molecular movement

Table 4.5 The β -relaxation temperature T_β , the activation energy of the β -relaxation H_β , the ageing rate $\dot{\sigma}_y$ and the ageing activation energy ΔU_a for unused and excavated uPVC pipes.

Pipe No.	T_β [°C]	H_β [kJ/mol]	$\dot{\sigma}_y$ [MPa/decade]	ΔU_a [kJ/mol]
2	-55.6	57.0	3.75	115*
12	-48.2	58.9	2.22	194 [†]
8	-45.4	59.7	1.88	238 [‡]

* from Visser et al. [40].

[†] from Drenth et al. [99].[‡] from Visser et al. [45].

responsible for the ageing process, and may explain the strong correlation observed in Figure 4.8. It must be pointed out, however, that ΔU_a is a factor two to four higher than H_β . This significant difference suggests that ageing is caused by similar chain parts, but which have a more extended type of motion and/or include a larger number of chain parts than for the β -relaxation to occur.

The β -relaxation temperature has also been determined using the loss modulus instead of the loss angle. The values of H_β obtained from the loss modulus correlate with ΔU_a in a similar way as observed from the loss angle and led to the same conclusions.

The relationship between creep and relaxation

The correlation between the ageing rate and T_β may also be explained from the results of Struik [46]. He performed a large series of creep and relaxation experiments on various amorphous materials including uPVC. It was shown that physical ageing led to a significant reduction in the creep and relaxation rates. The effects of physical ageing for uPVC were observed only within the temperature range from the β -transition temperature to the glass transition temperature with a certain maximum within this range. At the limits of the range the ageing rate declined. At and above the glass transition temperature the amorphous material is in thermodynamic equilibrium and physical ageing does not occur. On the low temperature side of the temperature range the movement of chain segments becomes increasingly difficult at lower temperatures. Hence, the material ages at a slower pace. Below the β -transition temperature ageing ceases completely even though the material is far from thermodynamic equilibrium. Now, consider two uPVC pipes, where for the second one the movements of chain segments are restricted more in some way. For this pipe the corresponding β -relaxation temperature occurs at a higher temperature. If it is also assumed that the maximum shifts accordingly, the ageing rates decreases for all temperatures within the range from the β -transition temperature up to the

temperature where the effect of physical ageing is at its maximum. In this way the shift of the β -transition temperature has an effect on the kinetics of the physical ageing process as a whole, as also observed in Table 4.5 and Figure 4.8.

The relationship between β -transition temperature and crystallinity

The β -transition temperature is sensitive to segmental chain movements. These movements are restricted by the presence of the crystalline phase in the uPVC microstructure. However, the crystalline fraction does not correlate with T_β ($R^2 = 0.27$). The minor influence of the crystalline fraction on secondary relaxation peaks of polymers, the β -peak of PVC [143, 151] and PET [152] and the γ -peak of polycarbonate (PC) [153], support these results.

Although PVC exhibits a broad melt endotherm indicating a broad range of crystallite perfection, two types of crystallites are believed to exist in PVC [36, 115]: (i) smaller, less perfect, low-order crystallites which may have a nematic structure and (ii) larger, more perfect, high-order crystallites which have an orthorhombic lattice structure. The influences of changes in both types of crystallinity on T_β and the ageing rate are discussed below.

Changes in low-order crystallites in PVC were studied using DSC [154]. Annealing above T_g causes a melt peak that shifts to higher temperature with increasing annealing time. This effect shows that the perfection of the crystallites increases with annealing time [154]. Harrell and Chartoff showed that this type of annealing treatment increased T_β only marginally (about 2 °C) [147]. Moreover, Kalwak et al. observed no significant effect on T_β [155]. Furthermore, the data of Tsitsilianis et al. showed a small (14%) increase in the rate of enthalpy relaxation.

In this thesis the influence of the shape of the endotherms in the DSC measurements on the ageing rate was studied for pipes 10-13 to characterise differences in crystalline morphology[‡]. No relationship was found between the differences in the endotherm shapes and the ageing rates. Apparently, changes in the perfection of low-order crystallites have a minor influence on T_β and the ageing rate. Therefore, is it unlikely that changes in perfection of low-order crystallites cause the variation in the ageing rate and T_β of uPVC pipes.

Changes in high-order crystallites cannot be studied by annealing [92, 93, 111, 154], due to thermal degradation [92], but can be influenced by changes in chain structure [36]. Regular syndiotactic and isotactic chain segments fit into the orthorhombic lattice [36] and thus contribute to the crystallinity of high order in PVC. Harrell and Chartoff showed that a more crystallisable PVC grade increased

[‡]Pipes 10-13 were selected because the PVC materials have the same composition, but have undergone significantly different thermal histories.

T_β by about 5 °C [147]. Although these observations show that variation in high-order crystallinity influences T_β , differences in T_β found by Harrell and Chartoff were smaller than those found in this study (about 12.6 °C). Though, high-order crystallinity may have an effect on the ageing rate, it is not expected to be dominant.

Alternative approaches for determination of the ageing rates

The relationship between T_β and the ageing rate is observed for a broad range of pipes. An alternative to determining the ageing rate from tensile tests, as explained in Section 4.3.2, would be to measure T_β from DMA measurements and derive the ageing rate from Figure 4.8. In such case a single test would be required instead of several tests as is necessary in tensile testing; the new method would be quicker and require less material. Further research should be carried out to ascertain the accuracy of the alternative approach. Another alternative to determine the ageing rate would be to perform tensile tests at strain rates at which the β -relaxation contributes to the yield stress [156]. In this way H_β is computed and this value can be related to T_β through Equation 4.1 and the ageing rate follows from Figure 4.8. However, the resulting physical ageing rates are very sensitive to small variations in H_β . The relative differences between the H_β values for samples 2, 8 and 12 shown in Table 4.5 are small, whereas the ageing rates and ageing activation energies span a much wider range.

Conclusion on the measurements of molecular mobility

The ageing rates observed in the excavated and unused uPVC pipes correlate well with the temperature at which the β -transition has a maximum, as determined from DMA measurements. A higher β -relaxation temperature corresponds with a lower ageing rate. Apparently, the factors that restrain the molecular movement of the β -relaxation also restrict the molecular movement responsible for the ageing process. However, the correlation observed does not explain the origin of the differences in ageing rates observed among the uPVC pipes investigated.

4.5 Conclusions

The ageing rates of a broad range of uPVC pipes, both excavated and unused, have been determined using uniaxial tensile experiments. A large variation in ageing rates has been observed among the pipes studied. Possible causes for differences in ageing rates were investigated systematically according to the stages in the lifetime of the uPVC pipes: polymerisation, processing and service life. Each stage was characterised by a number of material and/or process related properties.

It has been shown that the variation in the ageing rate does not originate from the polymerisation stage, suggesting that the polymer chain structure among all uPVC pipes investigated was rather similar. Various analysis and measuring techniques were employed to characterise the processing conditions and the additives supplied during the uPVC pipe extrusion and the resulting levels of gelation of the uPVC pipes manufactured. Variations in the processing temperatures and the levels of gelation were observed, but these did not correlate with the ageing rates of the respective uPVC pipes. On the basis of a list of typical additives expected, including stabilisers, lubricants, fillers, processing aids, etc., no solid explanation as to the origin of the variation in the ageing rates can be given. A strong correlation between the presence and the concentrations of the various additives and the ageing rates does not appear. Nevertheless, some results indicate a weaker correlation with the ageing rate, such as the lead concentration and the presence of PE wax. Further research is required to elucidate the influence of composition of the uPVC pipes on the ageing rate. Two approaches are suggested: (i) research that focuses on retrieving the exact composition of the pipe material and (ii) a parametric study in which concentration of the additives is systematically changed, subsequently determining the effect these changes have on the ageing rate.

A possible hint is the year of production of the uPVC pipes. A considerably larger spread in ageing rates and uPVC pipe characteristics is observed for those pipes manufactured before 1980. It is known that a considerable variation in processing conditions and compositions occurred over the years, especially in the early days of uPVC pipe manufacturing. Since 1980 uPVC pipes have been mostly produced for water distribution purposes; the pipes investigated showed considerable less spread in ageing rates. Additional work on the relation between the ageing rate and molecular mobility from a study on the β -relaxation peak has indicated that this peak correlates with the ageing rate. A higher β -relaxation temperature corresponds with a lower ageing rate suggesting relations in the molecular movements responsible for the β -transition and physical ageing. The observed correlation could be employed to quickly determine the ageing rate from DMA analyses.

Chapter 5

Non-destructive determination of the level of gelation

5.1 Introduction

The occurrence of brittle failure is the main limit for the service life of unplasticised poly(vinyl chloride) (uPVC) pipes in the Dutch gas and water distribution networks. Unwanted brittle failure events can be prevented by locating and subsequently replacing brittle uPVC pipes. A non-destructive inspection method for locating suspected uPVC pipes can thus be a useful tool for the development of replacement strategies. In Chapter 3 it was shown that physical ageing can result in embrittlement of uPVC pipes and a method to determine the residual lifetime was presented. This method is still incomplete as the level of gelation is not taken into account, whereas it is considered to be an important factor influencing the failure behaviour of uPVC pipes [10]. Unfortunately, there are no devices available which are able to determine the level of gelation in a non-destructive way. Therefore, the focus of this chapter will be on screening of available techniques for their applicability for (in-situ) non-destructive evaluation of uPVC on the level of gelation.

Before the screening process can commence, it is important to have some insight into the background of the gelation process, which is typical for PVC. After polymerisation, PVC has the form of a powder, as do most of the polymers. The distinct difference of PVC is that it is not compounded into granules first but directly used as a powder in injection moulding machines and extruders. The reason for this is that PVC degrades at a lower temperature (~ 200 °C) than that at which the crystallites in the material are fully melted (265 °C). Therefore, an intermediate compounding step would induce extra thermal degradation and is commonly not used for PVC. Instead, PVC is processed directly from the powder and below its crystalline melting temperature (a common processing temperature range is 180-200 °C) using the combined action of temperature and high shear

rates. Lubricants and thermal stabilisers are mixed with the PVC powder to reduce thermal degradation during processing. Another preventive measure to reduce thermal degradation is that PVC pipes are commonly produced using counter-rotating twin-screw extruders, which ensure a low distribution of residence time of PVC material inside the extruder. The degree to which PVC powder is processed into a homogeneous material in a product is called gelation or fusion and is illustrated in Figure 5.1. Unprocessed PVC powder consists of grains having typically a size of 200 μm . During processing, the grains are progressively broken down into primary particles under the influence of temperature, pressure and shear. The primary particles have a typical size of 1 μm and are shown schematically in Figure 5.1 (a). The polymer chains located inside the primary particles are tightly bound by crystallites (called primary crystallites). As the temperature increases during processing, some of the primary crystallites melt. This leads to an increase of the molecular mobility that allows the polymer chains to diffuse across the boundaries of neighbouring particles, as shown in Figure 5.1 (b). After cooling, PVC recrystallises, resulting in a molecular network between the particles tied by secondary crystallites, as shown in Figure 5.1 (c). As a result, a homogeneous material is formed in which the additives are distributed homogeneously [157]. However, residual grains and primary particles can still be identified when fusion is incomplete [157–159]. The degree to which the powder grains have been broken down and to what extent the molecular network between the primary particles has formed is defined as the level of gelation. The level of gelation is determined only by the processing conditions, and does not change with the age of the PVC pipe. Therefore, the level of gelation influences only the initial quality of the pipe [10]. Since the first research on gelation of PVC in the early eighties, manufacturers have been keen to monitor this property for newly produced batches of pipes. The level of gelation of older pipes does vary strongly, which underlines the necessity of taking the level of gelation into account for the determination of the residual lifetime of pipes that are currently in service.

Experimental data of the influence of the level of gelation on the impact resistance is shown in Figure 5.2. For a low level of gelation the many poorly fused primary particles act as stress concentrators, which cause voiding during impact loading [72]. The poor adhesion between the primary particles causes these voids to interconnect at lower loading and energy levels and will thus lead to poor impact properties [18] and a higher ductile-to-brittle transition temperature. For an increased level of gelation, the number of flaws decreases, and stronger adhesion between the primary particles causes increased plastic deformation. Increased plastic deformation will in turn lead to improved impact properties and thus a lower transition temperature. Several authors found an optimum in the impact properties with increasing level of gelation [16, 71, 96]. The origin of the decrease in impact properties after the optimum is still under debate. Terselius et al. suggest that for high levels of gelation the low number of poorly fused primary particles are unable to block propagating cracks leading to a decrease in impact properties [97]. Summers suggests a lubricant

Figure 5.1 Physical working model of the gelation process according to Summers [160].

inversion mechanism where the lubricants become the discontinuous phase and act as stress concentrators in the matrix causing a decrease in impact properties [98].

The level of gelation should thus have an optimal value to achieve maximum impact resistance and prevent brittle failure as much as possible. As mentioned before, the extrusion process was not always fully under control in the early years of PVC pipe production. Consequently, uPVC pipes with a wide range of gelation levels were installed in the past [10]. The pipes that have an insufficient or a too high level of gelation may undergo brittle failure when impacted and should therefore be replaced (or should never have been installed).

Figure 5.2 The level of gelation versus the brittle-to-ductile transition temperature for puncture (impact) tests reproduced from [19].

Before the main task of screening for a proper technique for non-destructive evaluation of the level of gelation can be carried out, the boundary conditions should be clear. These boundary conditions can originate from the processing conditions as

well as from practical considerations. The first notable boundary condition is caused by the fact that during processing the shear rate of the PVC material increases towards the die wall [161]. Consequently, the outsides of the pipe wall have a higher level of gelation, whereas the level of gelation can be poor in the middle of the pipe wall (along its thickness) [20, 127, 162]. Poor processing conditions are therefore more critical for pipes having a large wall thickness, such as used for water distribution purposes, than for relatively thin-walled gas pipes. Secondly and more importantly, because the outer and inner wall of the pipe usually have a high level of gelation, it is difficult to determine the level of gelation in the middle of the pipe wall from measurements carried out on the surface of a pipe. This aspect complicates non-destructive determination of the level of gelation.

Another complication arising from processing is the variation in the length and circumferential direction of the pipe [163]. Non-homogeneous heating of the polymer, and therefore non-stable conveyance of the polymer in the screw channel and in the extrusion die, may lead to local variations in the level of gelation [164] (especially expected to occur in the early years of PVC pipe production). Since the location of the severest defect and of the severest impact load in service are not known, the area of the pipe which has the lowest level of gelation should be quantified rather than measuring some average value. Ideally, measurements at different locations are carried out to locate critical points inside the pipe.

Measurements on the outer surface of a pipe require excavation activities, which make these measurements nearly as costly as replacement of the pipe. Currently, autonomous robots to carry out measurements from the inside of the pipe are in development [48–50]. The extra requirements for in-situ measurements are that the technique is suitable for carrying out measurements on the inner surface of the pipe wall (single-sided) and that the measurement device can be made robust and small enough to fit into uPVC pipes (minimal inner diameter of about 60 mm).

The aforementioned requirements are taken into account for the screening process described in the rest of this chapter. In Section 5.2, the suitability of several methods is evaluated based on these requirements and the physical model of the gelation process given in Figure 5.1. Two potentially suitable methods have been selected for further evaluation using experiments and are described in Sections 5.3 and 5.4. The experimental procedure and results are described in Section 5.5. The (experimental) evaluations of the methods considered are discussed in Section 5.6.

5.2 Screening of test methods

In this section, the suitability of a number of methods is evaluated based on the requirements specified in Section 5.1. Taking into account the characteristics of gelation as outlined in Section 5.1 a number of techniques have been selected

for screening; they are listed and categorised according to their physical working principle in Table 5.1. The symbols used in Table 5.1 are defined in Table 5.2. The methods listed in Table 5.1 have been evaluated using both literature and preliminary experiments.

Thermal methods

Differential Scanning Calorimetry (DSC) is a widely used method to determine the level of gelation. DSC is capable of determining the amount of energy required to melt crystalline regions and can detect how many primary crystallites have melted during extrusion and how many crystallites recrystallised upon cooling. Only small specimens are required for DSC, which makes it possible to determine the level of gelation across the wall thickness of the pipe. As differences in the gelation level occur mainly in the middle of the pipe, a rather thick layer of material (about a half of the wall thickness) would, in practice, have to be removed from the inner wall to distinguish between poorly and properly processed pipes. This method is therefore destructive and not suited for practical implementation.

Thermography is a non-destructive, single-sided technique in which the surface temperature of an object can be measured using compact thermal infrared cameras. Although primary particles can still be identified in incompletely fused uPVC materials [158, 159], the internal grain porosity has been eliminated at an early stage in the gelation process [168, 177]. Because residual particle boundaries have intimate contact, local changes in thermal conduction in the material and subsequently in surface temperature are not expected and therefore this technique is not considered to be a viable candidate.

The thermal methods shown in Table 5.1 are thus not suited for determining the level of gelation and will be not evaluated experimentally.

Electric and magnetic methods

As PVC is an electrical insulator, non-destructive methods based on electric currents and magnetic fields, such as eddy-current testing cannot be applied to PVC pipes.

Electric fields of alternating direction are, however, able to induce several mechanisms of polarisation inside PVC materials which can be studied using dielectric spectroscopy [168]. At low frequencies (0.1 Hz-10 Hz) changes in dielectric properties of PVC were observed only at the initial stages of the gelation process, possibly caused by interfacial polarisation as a result of air inclusions [168]. As internal porosity is absent even for the lowest levels of gelation found in uPVC pipes [159], interfacial polarisation effects are not expected. Hence, low frequency dielectric spectroscopy is not capable of detecting differences in the gelation level.

Table 5.1 An overview of evaluated methods for determining the level of gelation of uPVC pipes in a non-destructive way.

Category	Method	Sensitivity	Non-destructive	Single-sided	Inside pipes	Ref.
Thermal	calorimetry	+	-	n/a	n/a	[125–128]
	thermography	-	+	+	+	[165, 166]
Electric/magnetic	electric/magnetic testing	-	+	+	+	[167]
	electric dynamic	-	+	-	+	[168]
	NMR*) spectroscopy	-	+	+	+	[169, 170]
Acoustic	ultrasonic testing	-	+	+	+	[171]
Optical	optical profilometry	+/-?	+	+	+	[172]
	visual inspection	-	+	+	+	[173, 174]
	optical microscopy	+/-	-	-	+	[125]
		+/-	-	+	+	[175]
		+/-	-	n/a	n/a	[176]
	electron microscopy	+/-	-	-	-	[124, 159, 177]
		+/-	-	n/a	-	[176, 177]
	optical depth profiling	+?	+	+	+	[178]
Mechanical	quasi-static	+	-	n/a	n/a	[71, 97, 125, 160, 179]
		+	-	n/a	n/a	[71, 97, 177, 180]
		+/-	-	+	+	[181]
		-	-	n/a	n/a	[158]
	dynamic mechanical profilometry	+/-	+	+	-	[159]
Electromagnetic	X-ray crystallography	+/-	+/-	+	+	[137, 159]
	radiography	-	+	+	+	[182]
Chemical	solvent testing	+/-	-	n/a	-	[97, 163, 180, 183]
		+/-?	+/-	+	+	[124, 125, 159, 184]
		+/-	-	n/a	+	

*) Nuclear Magnetic Resonance.

† method evaluated experimentally in this study.

Table 5.2 *The definitions of the symbols used in Table 5.1.*

For the sensitivity	Symbol
quantitative test results and high resolution over a wide range of levels of gelation	+
qualitative test results and/or limited resolution	+/-
the method is not sensitive to the level of gelation	-
For the destructive character of the test	
non-destructive	+
causes damage at local scale	+/-
destructive [†]	-
For the side(s) where the probe(s) should be located	
single-sided	+
double-sided	-
not applicable for this method	n/a
For the suitability inside a pipe	
robust and may fit into uPVC pipes	+
does not fit into uPVC pipes	-
not applicable for this method	n/a

[†] extraction of a specimen and heating above T_g are regarded as destructive operations.

At higher frequencies (10 Hz-10 MHz), molecular relaxation as a result of the rotation of Cl-C bonds in PVC can be detected [168] (similar to a dynamic mechanical tests [83]). The level of gelation is, however, not expected to influence this relaxation mechanism [158]. Preliminary experiments carried out as part of the present study indeed confirmed this: also at higher frequencies dielectric spectroscopy is not suitable.

In industry, non-destructive, single-sided and compact nuclear magnetic resonance (NMR) devices are widely used for determining changes in material properties from the relaxation behaviour of nuclear spins [169, 170]. Preliminary measurements were carried out using an NMR depth profiling device that is capable of determining the relaxation behaviour of spins in the centre of uPVC specimens where variations in gelation levels are most pronounced. Unfortunately, differences in relaxation behaviour for different gelation levels and over the thickness of the specimens were not observed. Relaxation-based NMR is thus not suitable to determine the level of gelation.

Apparently, the level of gelation has no significant influence on molecular relaxation effects resulting from dipoles and nuclear spins. It is concluded that further development of a non-destructive method based on electric and magnetic fields may not be useful.

Acoustic methods

Ultrasonic testing is a non-destructive method based on the propagation of sound waves through an object with frequencies between 20 kHz and 800 MHz. There is a strong link between ultrasonic and dielectric measurements and the latter technique is commonly used to find out whether ultrasonic waves are sensitive for the property under study [185]. The conducted dielectric experiments noted before have shown that dielectric properties are not influenced by the level of gelation. Based on this result it is expected that linear and non-linear ultrasonic techniques are not useful to determine the level of gelation.

Optical methods

Optical profilometry is a form of non-destructive testing in which incident light rays (from a compact laser device) are reflected from the surface of an object to determine surface roughness of the object [186]. Rabinovitch and Harshbarger have shown a relationship between the level of gelation and the surface roughness for PVC specimens produced at different temperatures [60]. At low processing temperatures, primary particles of the size of 1-2 μm can be distinguished at the surface and contribute to the surface roughness of the inner wall of a uPVC pipe. For increasing processing temperatures, the particles are more fused together and a nearly continuous melt is formed, resulting in a relatively smooth surface. It may still be possible to distinguish particles on the surface in the case of low processing temperatures, despite the fact that the level of gelation at the pipe surface is generally higher than at the centre of the wall [20, 127, 162]. Surface roughness measurements using laser reflections may therefore be useful for determining the level of gelation from the inside of pipes. Preliminary measurements have been carried out for a controlled set of specimens with identical composition, processed at the same extruder but at different processing temperatures. The observations of Rabinovitch and Harshbarger [60] are confirmed for this specific set of specimens. However, application of the technique to a variety of pipes revealed that, unfortunately, not only processing temperature, but also other processing variables, such as the screw speed [60, 96] and the surface of the die [60], influence the surface roughness. Therefore, the practical relevance of surface roughness measurements is limited.

The variety of microscopy methods listed in Table 4.1 can be used to observe residual grain boundaries and primary particles and thus can give direct information about the level of gelation. Generally, microscopy methods do not fit inside a pipe; they require specimens extracted from a pipe and are therefore destructive. Further development would be required if application in practice is pursued. Despite this disadvantage, the results of differential interference contrast microscopy experiments on PVC are particularly interesting to mention. A decrease in the magnitude of

fluctuations in the refractive index of PVC has been observed for increasing levels of gelation [125]. The precise reason for these fluctuations is not entirely clear [125]. It is reasonable to assume that light rays from an incoming laser beam are scattered as a result of the fluctuations, leading to attenuation of the beam as it travels inside the PVC material. A decrease in the attenuation of the beam with increasing levels of gelation would then be expected. MacDonald et al. observed differences in the attenuation of a laser beam in non-destructive, single-sided Raman depth-profiling experiments on PE (co)polymers [178]. The observed differences in attenuation were attributed to differences in optical scattering in the bulk of the polymers. Hence, Raman depth profiling may also be a suitable technique to determine the level of gelation of uPVC pipes.

Several Raman depth-profiling experiments are conducted and presented in the following sections of this chapter. It is known that the penetration depth is of the order of only several micrometres but, as mentioned earlier, for low processing temperatures, primary particles may still be identified at the pipe surface indicating incomplete fusion [60].

Mechanical methods

In mechanical testing, a quasi-static or a dynamic mechanical excitation is applied and the mechanical response is measured. Quasi-static tensile tests applied to PVC specimens show that the load-extension curves can be superimposed, the only difference being that break occurs earlier for decreasing level of gelation [123]. Consequently, tensile properties which can be determined by applying only a relatively small amount of strain (e.g. Young's modulus and yield stress) cannot be used to determine the level of gelation, ruling out "non-destructive" mechanical testing.

A dynamic mechanical excitation is used in Dynamic Mechanical Analysis (DMA), which can be used to non-destructively (at low strains and temperatures below T_g) study different molecular relaxation mechanisms of PVC in a similar way as in dielectric spectroscopy [83]. During preliminary measurements carried out below T_g differences in the storage and loss moduli with the level of gelation were not observed, see also Chapter 4. These results confirm the findings of Uitenham and Geil [158] and are in line with the results of the preliminarily dielectric measurements mentioned earlier. It is concluded from the results from tensile test and DMA that mechanical methods based on low strains and temperatures below T_g are not suited to determine the gelation level.

In contrast, differences in the level of gelation are clearly observed in measurements performed above T_g at high strains (e.g. in capillary rheometry tests and in indentation tests above T_g). However, the nature of these measurements is such that they cannot be developed for non-destructive, in-situ test methods.

So far, only macro-mechanical methods have been evaluated. A non-destructive, single-sided micro-mechanical method is Atomic Force Microscopy (AFM). With AFM a cantilever, typically with a length of about 1 mm, with a sharp tip at its end can be used to differentiate between additives and the rigid PVC based on the difference in their stiffness. This provides evidence of residual primary particles and can be related to the level of gelation [159]. However, an AFM is a precision device and is, in general, not robust enough for practical application inside a uPVC pipe.

It is concluded that none of the mechanical methods shown in Table 5.1 are suitable for the envisaged application and have been dropped in the screening process.

Electromagnetic methods

X-ray diffraction is used to identify regular atomic and molecular structures using X-rays. The crystallinity in PVC has been studied extensively using X-ray diffraction methods [116–118, 137, 187, 188]. Changes in the total crystalline fraction have been observed for increasing processing temperature and thus with increasing level of gelation [137]. However, the crystalline fraction and the gelation level do not correlate well, because one can be influenced without affecting the other. For example, by annealing PVC materials above T_g the crystalline fraction can be increased [93], whereas the level of gelation does not change upon annealing [127, 159]. The observation that the total crystalline fraction does not follow a monotonic trend with processing temperature [137] further complicates the correlation. For these reasons, determining the gelation level from the crystalline fraction is not straight forward and X-ray diffraction is excluded as a solution in the present study.

Radiographic testing is a non-destructive imaging method using X-rays. Backscatter computed tomography, which does not require a film on the opposing side of an object as in conventional X-Ray imaging [182], has recently become available commercially. Another advantage is that it can penetrate the material and scan the bulk with the lowest levels of gelation as well. However, the resolution of such systems is not yet high enough (about 2 mm) to observe individual grains and primary particles and therefore needs to evolve before it can be considered as a suitable technique.

Of the electromagnetic methods considered in Table 5.1, X-Ray tomography may be a suitable technique if its resolution can be increased.

Chemical methods

The chemical methods evaluated here are based on swelling and disintegration of PVC specimens using compatible solvents [159, 184]. The destructive character of these methods make them in principle unsuitable for non-destructive determination of the level of gelation.

A commonly used method for gelation measurements is the methylene chloride (or dichloromethane) temperature (MCT) test. In this test, a pipe part is chamfered to expose the inner wall. The chamfered part is submerged in methylene chloride (MC) and subsequently dried. By inspecting chamfered parts for attack after being submerged at different temperatures, the level of gelation can be determined over the thickness and the circumferential direction of the pipe. The inner and outer side of the pipe wall may have a higher level of gelation than the pipe interior, as mentioned before.

An interesting, less destructive variant of the MCT test was developed in house. A small concavity is milled in a uPVC pipe wall from the pipe inside and is exposed to methylene chloride locally. The key issue of the technique is to minimise the required depth of the concavity to recognise a pipe with an unwanted level of gelation. Depending on the minimum concavity depth the local reduction of wall thickness may be small enough for the method to be considered as non-destructive. The method is referred to as the micro methylene chloride (microMC) test and investigated in the next sections.

The screening procedure has led to selecting the Raman depth profiling method and the microMC method for in-depth experimental investigation as described in more detail in the next section.

5.3 Experimental approaches

The two selected methods, Raman depth profiling and the microMC method, have been investigated experimentally to further evaluate whether they fit the requirements drawn up in the introduction. The approaches followed are outlined and discussed in more detail in the following subsections.

5.3.1 Raman depth profiling

For increasing levels of gelation, a decrease in the attenuation of a laser beam which travels inside the PVC material is expected, as was already argued in Section 5.2. In Raman depth profiling, a laser beam is focused on a small material volume below the surface of a specimen. A small fraction of the light rays in the incident beam will lose energy due to Raman scattering*. The Raman scattered light rays are detected using a detector situated at the same side of the specimen as the laser source, enabling single-sided inspection. The intensity of these rays can be determined at different depths below the surface by employing the confocal optics configuration. The rate

*Approximately one in ten million of the incoming photons will scatter inelastically, transferring a part of its energy to the atoms.

at which the Raman intensity decreases with the depth is taken as a measure for the attenuation of the laser beam and may be used to determine the level of gelation.

A complicating factor in the analysis of Raman measurements is the attenuation of the beam due to the surface roughness [178, 189]. The surface roughness of a uPVC pipe is influenced by processing variables, such as the screw speed and the surface of the die, as mentioned before. The influence of the surface roughness must be minimised as the typical penetration depth of Raman measurements is only a few micrometres. Here, an immersion oil with a refractive index comparable to that of uPVC has been selected in favour of mechanical means to polish the pipe surfaces. In the latter case the additional treatment might have undesirable effects on the subsurface region investigated with the Raman measurements.

Lastly, because additives can influence the fluctuations in the refractive index [125], Raman depth profiling experiments were initially carried out on pipes having the same formulation.

5.3.2 MicroMC method

The level of gelation may be determined by the microMC test i.e. exposing a small portion of the pipe wall to methylene chloride. The microMC test is described schematically in Figure 5.3. Firstly, a cylindrical concavity is milled down to a certain depth in the pipe wall on the inside of the pipe. This exposes part of the pipe interior material (Figure 5.3 a). Secondly, the milled surface is submerged into MC at a specified temperature for a specified time (Figure 5.3 b). Finally, the specimen is dried and the bottom of the concavity is inspected for signs of attack using a light microscope (Figure 5.3 c). The sensitivity of the method for different gelation levels was assessed using different concavity depths and test temperatures.

Figure 5.3 Systematic description of the microMC test. (a) a cylindrical concavity milled into the inner wall surface of a PVC pipe. (b) exposing the milled surface to MC (c) light microscopy inspection of the exposed concavity (not to scale).

5.4 Experimental

5.4.1 Materials

Specimens were taken from four unused uPVC pipes and two excavated uPVC pipes (pipes 10 to 15 in Table A.1 in Appendix A). The unused pipes are composed of the same PVC materials used by Meijering [19]. The pipes have the same composition and were processed on the same extruder, but at different temperatures. The excavated pipes were taken from the Dutch water distribution network. The diameters and wall thicknesses of the pipes are given in the third and fourth column of Table 5.3 respectively.

Table 5.3 *The dimensions and levels of gelation as determined by the MCT test and the Macklow-Smith rheological procedure [71] of the unused and excavated uPVC pipes used in this study.*

Type	No.	Diameter [mm]	Thickness [mm]	Level of gelation	
				MCT	Macklow-Smith [71]
unused	10	50	2.3	under	19%
unused	11	50	2.3	intermediate	48%
unused	12	50	2.3	good	73%
unused	13	50	2.3	over	91%
excavated	14	320	8.1	under [†]	-
excavated	15	600	18	under [†]	-

[†] Not assessed according to ISO 9852:2007. Only determined on small pieces of the pipe.

The gelation level of the pipes was determined using the MCT method in accordance with ISO 9852:2007. After the pipes were chamfered, the pipes were submerged into methylene chloride at temperatures of 5 °C, 10 °C and 15 °C for 30 minutes. After submerging, the pipes were dried and subsequently inspected visually for signs of attack. The level of gelation is classified as 'under', 'poor', 'good' or 'over' based on the combination of the occurrence of attack and the test temperature. The levels of gelation from the MCT test are given in the fifth column of Table 5.3. The last column shows the gelation levels in terms of percentages for the unused pipes. These pipes were characterised using the Macklow-Smith rheological approach by Benjamin [71].

5.4.2 Raman depth profiling

Raman depth profiling experiments were carried out using a confocal Witec alpha 300R microscope equipped with a Nikon 100X 1.25NA objective, where NA is the numerical aperture of the objective. A Cargille 4108 LDF immersion oil having a refractive index of 1.518 was used to match the refractive index of PVC, which

is 1.540 according to [125]. Raman spectra were determined using excitation wavelengths of 633 nm and 785 nm and maximal laser powers of 4 mW and 32 mW, respectively. After each measurement, the specimen surface was checked for thermal degradation using a common light microscope. A piezoelectric stage was used to position the specimen relative to the microscope, such that the Raman spectra could be determined at different depths below the specimen's surface. The reference position of the surface of the specimen was determined from the position at which the intensity of the Rayleigh peak was at a maximum. After each measurement abnormally high narrow peaks in the spectra (possibly due to stray light and cosmic rays) were removed. The characteristic peak of PVC at 1425 cm^{-1} (C-H bending vibration [190]) was used to determine the intensity of Raman light rays as a function of the depth since this peak does not overlap with peaks from additives present in uPVC. The height of the peak was determined after removing the background signal assuming linear baselines. The dimensions of the sample volume at the focus point in air can be approximated using the equations [191]

$$d = \frac{1.22\lambda}{\text{NA}}, \quad (5.1)$$

and

$$L = \frac{4\lambda}{\text{NA}^2}, \quad (5.2)$$

where d is the width of the beam at the focus point, $L/2$ is the distance from the focus point at half of the intensity at the focal point and λ is the excitation wavelength. For $\lambda=785\text{ nm}$ ($\text{NA}=1.25$) the values are: $d = 0.8\text{ }\mu\text{m}$ and $L = 1.9\text{ }\mu\text{m}$. For $\lambda=633\text{ nm}$ the values decrease to: $d = 0.6\text{ }\mu\text{m}$ and $L = 1.6\text{ }\mu\text{m}$. The spatial resolution of the set-up is similar in this case for both wavelengths used.

5.4.3 MicroMC test

The specimens taken from the unused pipes (pipes 1-4) were sawn to dimensions of roughly $70 \times 30 \times 2.7\text{ mm}^3$. For the ease of further specimen preparation, the curvature of the original pipe was eliminated by pressing the specimens at a compressive stress of $\sim 1\text{ MPa}$ at $100\text{ }^\circ\text{C}$ ($\sim 15\text{ }^\circ\text{C}$ above T_g) for 25 minutes. Cylindrical concavities with depths from 0.1 mm to 1.2 mm (thus up to a depth equal to approximately half of the wall thickness) were milled on the side that was originally the inner surface of the pipe. The diameter of each concavity was 4 mm. Large variations in gelation levels along the length direction of the uPVC pipes were not expected. Hence, the depth of the concavities was varied along this direction. Possible variations in the circumferential direction were taken into account by milling several concavities of the same depth in this direction, as shown in Figure 5.4.

Figure 5.4 A test specimen used for the microMC test. Each of the columns C1 to C4 consists of five concavities with differences in depths. The orientation of the test specimen in the uPVC pipe is indicated.

The specimens were submerged in MC such that all concavities were filled at 5 °C and 10 °C for 30 minutes. The top of the MC filled glass containing specimen was sealed with parafilm to prevent excessive evaporation of MC. The specimen was dried after submersion and the concavities were inspected for signs of attack using a Leica M125 stereo microscope. The specimens submerged at 5 °C and 10 °C were reused for a measurement at 15 °C and 20 °C respectively. The chemical attack at the lower temperature was assumed to be negligible in comparison with the attack at the higher temperature and the use of fresh specimens would not give different results.

5.5 Results

In Section 5.2, the Raman depth profiling method and the microMC test were selected for experimental evaluation. The experimental details were described in Sections 5.3 and 5.4. The results of the experiments are shown in this section.

5.5.1 Raman Depth Profiling

In Raman depth profiling, a laser beam is focused below the surface of a specimen. The amount of (back)scattered rays (and thus the attenuation of the signal detected by the sensor) from this focal point is expected to decrease with increasing level of gelation. A typical depth profile of the intensity of Raman scattered light rays for PVC is shown in Figure 5.5. The decrease in the measured intensity with increasing depth is attributed to optical scattering of light rays travelling inside the bulk of the specimen. The influence of surface roughness has been eliminated by adequate refractive index matching. The variations in the curve are probably due to local inhomogeneities inside the material (e.g. crystals and additives) which interfere slightly with the light beam.

Figure 5.5 The intensity of the band characteristic of uPVC at 1425 cm^{-1} for pipe 1 determined using an excitation wavelength of 758 nm and a laser power of 32 mW. The depth indicates the distance from the specimen surface.

The depth profiles for pipes 1-4 that differ only in the level of gelation, are given in Figure 5.6, which shows only little differences in the depth profiles. Apparently, the optical scattering behaviour of these materials is not significantly different at these depths. A possible explanation is that differences in fluctuations in refractive index as a result of differences in level of gelation at the surface are too small to be detected, even though poorly fused primary particles were observed at the surface for these pipes at low processing temperatures in the preliminary experiments. A practical consequence is that Raman depth profiling experiments carried out from the inside of pipes are not sensitive enough and thus seem to be an unsuitable way to determine the level of gelation.

Figure 5.6 The averaged depth profiles for pipes 1-4 using an excitation wavelength of 758 nm and laser power of 32 mW. For each pipe, three measurements were carried out at different locations on the inner surface of the pipe wall. The legend indicates the pipe numbers and the level of gelation.

An extra specimen was prepared from pipe 5 (with low level of gelation), to confirm

this conclusion. The surface to be evaluated is the fracture surface through the thickness ($= 8.1$ mm) of a pipe section. The level of gelation varies strongly along this surface (as is shown later in Figure 5.11 (left)), which should be detected by a suitable technique. Six series of depth profiling measurements were carried out on the fracture surface at a distance of about 1 mm from each other, as shown in Figure 5.7 left. Each series contains two parallel rows of ten measurements with a spacing of $2\text{ }\mu\text{m}$ between each measurement. The spacing between the rows is also $2\text{ }\mu\text{m}$. Then, the profiles of each series were averaged. The averaged depth profiles are shown in Figure 5.7 right.

Figure 5.7 *Left: a schematic view of the positions of depth profiling measurements carried out through the thickness of pipe 5. Positions 1 and 6 are about 1 mm from the outer and the inner surface of the pipe wall respectively. For each position, twenty measurements were carried out as shown in the zoom in. Right: the averaged depth profiles determined from the six different positions along the wall thickness. The 20 measurements were averaged for each position. An excitation wavelength of 633 nm and a laser power of 4 mW were applied.*

Differences in the depth profiles along the wall thickness of the pipe were not observed. This means that differences in optical scattering as a result of differences in the level of gelation are too small to be detected using the Raman depth profiling method, even at locations in the middle of the wall where differences in gelation levels are most pronounced. The use of the intensity of other band characteristics of the PVC led to very similar results. Consequently, the conducted depth profiling measurements in this study show conclusively that Raman depth profiling is not an appropriate technique for determining the level of gelation of uPVC pipes.

5.5.2 MicroMC method

The level of gelation of uPVC pipes may be assessed by exposing small concavities made in the inner wall of pipes to MC and subsequently inspect them for attack. An overview of the microMC experiments for pipes 1-4 is shown in Figure 5.8. Variations in the occurrence of attack between the different columns (and thus in

the circumferential direction, see also Figure 5.4) were not observed for these pipes. Therefore, for each temperature only a single column with concavities is shown.

Figure 5.8 Photographs of cylindrical concavities are shown for pipes 1-4. The levels of gelation of the pipes as indicated in the top row were determined using the MCT test. For each temperature, the concavities of only column C1 are shown. The numbers indicate the depth of the concavities in millimetres. The concavities have depths up to 50% of the wall thickness of the original pipes (=2.3 mm).

For the under-gelated pipe 1, attack was observed for each depth at 5 °C, and was observed even at the inner surface itself. For pipe 2, which was gelated up to an intermediate level, the attack initiates at low depths and increases with increasing depth. For pipe 3, a pipe with a good level of gelation, attack was not observed for submersion at 15 °C, whereas for 20 °C attack initiated and increased with increased depth. For the over-gelated pipe 4, attack was not observed for the ranges of depths and temperatures investigated. So, significant differences in the occurrence and the extent of attack were observed for these pipes.

The depth at which attack initiates is influenced by the test temperature. This effect is highlighted for pipe 2 in Figure 5.9. The two photographs on the left show that at 5 °C, attack starts to occur at a depth of 0.4 mm, whereas at 10 °C, attack is observed already at a depth of 0.2 mm as shown in the top right photograph (and increases with increasing depth as shown in the bottom right photograph). The disintegration process of the PVC material is accelerated by increasing the temperature, which explains the initiation of attack at lower depths for higher temperatures.

For pipes 3 and 4 the first signs of differences between the initiation of attack are observed at 20 °C as shown in detail in Figure 5.10. For pipe 3, an attacked surface is observed at a depth of 0.4 mm, whereas for pipe 4 no attacked surface is observed at this and larger depths. So, for pipes having low levels of gelation, poorly fused material is located closer to the surface than for pipes having high levels of gelation, as expected. Thus, by carrying out measurements using the correct depths,

Figure 5.9 Photographs of concavities for pipe 2 for 5 °C and 10 °C. The numbers indicate the depth in millimetres.

temperatures and presumably also the exposure time which is not varied here, uPVC pipes having a wide range in levels of gelation can be distinguished from each other using the microMC method.

Figure 5.10 Photographs of concavities for pipes 3 and 4 tested at 20 °C. The numbers at the bottom right of each photograph indicate the depth in millimetres.

Remarkably, for pipe 1, attack was observed on the side of the specimen that was originally the inner surface of the pipe, but it was not observed on the outer surface of the pipe. This phenomenon is possibly a result of a post-extrusion step which is applied to reduce the effects of die-swell. After extrusion the hot PVC material is pulled through a calibration ring. This causes a friction force between, and thus a shear stress at, the PVC material (mostly at the outer surface) and the calibration

ring wall. This process may increase the level of gelation at the outside of the pipe wall. Consequently, the level of gelation is no longer symmetrical, but higher on the outside.

Figure 5.11 Results of MCT test on pipe 5 (*left*) and pipe 6 (*right*). The specimens were subjected to MC for 30 minutes at the temperature indicated above each of the photographs.

The microMC test was further validated by performing measurements on two excavated pipes with a relatively large wall thickness used for water distribution. The large wall thickness may result in strong variations in the level of gelation through the thickness after extrusion. The results of the regular MCT test are shown in Figure 5.11. Pipe 5 is classified as having an insufficient level of gelation as chemical attack is observed even at 5 °C. However, there is still a significant surface area on the chamfered edge located near the original pipes' outer and inner wall which does not show signs of chemical attack. Pipe 6 clearly has an even lower level of gelation, as the inner pipe wall surface was also attacked by the MC at 5 °C. The images of pipe 6 show that this pipe has an asymmetric profile of the level of gelation along its wall thickness. The calibration procedure that is used in the extrusion line could be the underlying reason for this observation as argued before.

The results of the microMC tests conducted on pipe 5 are shown in Figure 5.12. These images show that the attack starts to become visible somewhere between a depth of 0.8 mm and 1.6 mm when the measurement is carried out at 10 °C. A lower depth can be used if the measurement is carried out at 20 °C; the first signs of attack can be observed at the bottom surface of the 0.8 mm deep concavity. This means that a concavity of only about 10% of the wall thickness is required to determine whether or not the level of gelation is too low. A further experimental study is required to optimise the microMC procedure and to find the depth at which a pipe with an excessively high level of gelation can be distinguished from a pipe with an optimal level of gelation.

Figure 5.12 Photographs of concavities in pipe 5 at different depths after exposure to MC at 10 °C (*left*) and 20 °C (*right*) for 30 minutes.

5.6 Discussion

The presented results from the Raman and microMC experiments show that only the microMC method enables the determination of the level of gelation on a more or less non-destructive way. The microMC experiments have shown that a layer of material of about 0.4 mm has to be removed from the inner wall to distinguish between the levels of gelation for pipes in service. The method therefore seems more suitable for thick-walled water distribution pipes than for thinner walled gas distribution pipes. The microMC experiments show that the critical depth at which attack initiates depends on the concavity depth and the test temperature and, presumably, on the exposure time. Further research on the effect of test temperature and exposure time is required to optimise the approach and limit the required concavity depth as much as possible.

Based on the results on pipes 1-4 the following procedure can be used in practice. Firstly, a measurement should be carried out at 10 °C on a concavity of 0.2 mm deep to distinguish between under, intermediate and higher levels of gelation. If attack is observed on the inner pipe wall surface, the level of gelation is poor. If attack is observed only at the bottom of the concavity the pipe has an intermediate level of gelation. If attack is not observed the pipe has either an optimal or an excessively high level of gelation. A second measurement can be carried out at 20 °C on a concavity of 0.4 mm deep to differentiate between these levels. If attack starts to occur at the bottom of the concavity, the pipe has the optimal level of gelation and if no attack is observed the level of gelation is too high. So only one measurement is required to recognise whether a pipe has an insufficient level of gelation and an additional measurement is required to confirm whether the level of gelation is

optimal. Additional research is required to optimise this procedure for the situation found in practice. The depth of the concavity could, for example, be decreased by exploring higher test temperatures.

The major drawback of the microMC test is that it requires the use of the potentially harmful chemical methylene chloride inside the pipe. Water distribution operators in particular will be very reluctant to allow such measurements in their water distribution networks. Therefore, extra care should be taken with the (chemical) safety of the developed microMC device. Another drawback of the microMC method is that the level of gelation of the pipe is determined only locally. Therefore, more measurements should be carried out to locate critical areas of the pipe. The measurements should be done mostly in the circumferential direction, as variations in the level of gelation are more common in that direction than in the pipe length direction.

Furthermore, it should be noted that the conditions at which attack initiates are influenced by the K -value [180]. As most of the pipes produced after the mid-1960s have a K -value of 65, particular caution should be observed for pipes installed before this period.

For practical implementation of the microMC method, future research should focus on (i) the extent to which the removal of material has an influence on the mechanical performance of pipes in service, (ii) ways to automate the method (potentially using image recognition technology) and (iii) the influence of the test temperature in order to minimise the required depth that should be milled away from the pipe inner surface.

5.7 Conclusions

In this chapter a systemic study has been carried out to screen for methods to determine non-destructively the level of gelation of a uPVC pipe in gas and water distribution networks while the pipe is in service. No technique was found that was able to determine the level of gelation in a non-destructive fashion, through the thickness of the pipe wall and from the pipe inside. The main limitation is the fact that the level of gelation is lowest in the interior of the pipe wall, making a non-destructive method challenging. X-ray tomography was identified in the screening process as a viable option for the future if the resolution of the method can be sufficiently improved and the size of the device itself can be reduced drastically.

The level of gelation of thick-walled uPVC (water) distribution pipes can be determined with the newly developed microMC method, which is a modified version of the commonly applied MC method. Small concavities milled from the pipe inside readily show signs of attack related to the concavity depth, test temperature and the local level of gelation of the pipe. Measurements on water distribution pipes taken

out of service confirm the capabilities of the method. The microMC test seems more appropriate to thick-walled water distribution pipes, where the relative influence of the presence of local concavities is smaller than for thin-walled gas distribution pipes and also the expected variation in level of gelation is much larger.

A significant hurdle that should be overcome to implement the microMC method in practice is to develop a device that can be safely applied in water distribution networks.

Chapter 6

Residual lifetime assessment in practice

6.1 Introduction

The objective of the research project described in this thesis is to improve and extend the available residual lifetime assessment method for uPVC gas pipes, as formulated in Chapter 1. With the new knowledge and understanding obtained in Chapters 2 to 5 a significant step towards a more practical application of the method has been made. Before finalising the thesis, it is appropriate to take a critical look at the practical applicability of the developed and validated theoretical framework.

Each of the subsequent chapters contributed to answering this question. The characterisation of the current condition of a uPVC pipe in terms of the degree of physical ageing and the level of gelation was based on the material's hardness (Chapter 2) and the material's susceptibility to swelling and disintegration by solvents (Chapter 5). The critical/limiting strength of a uPVC pipe, defining the condition at which the uPVC pipe should be replaced, was studied through dedicated impact tests at a range of temperatures in Chapter 3. Physical ageing led to changes in the fracture behaviour as observed by an increase of the ductile-to-brittle temperature. The residual lifetime of a uPVC pipe follows from the time it takes for the material to reach the critical condition from its current condition, which depends strongly on the ageing rates. An in-depth analysis was carried out to investigate the causes of the observed differences in ageing rates among the uPVC pipes investigated in Chapter 4.

Both physical ageing and the level of gelation have a distinct influence on the ductility of a uPVC pipe, and thereby on the pipe's (residual) lifetime. Where the state of physical ageing changes during the lifetime of the pipe, the level of gelation remains constant as it is solely determined by the production process (extrusion). The influence of both processes on the ductile-to-brittle transition temperature and

the yield stress at which the pipe becomes too brittle is shown schematically in Figure 6.1 (left and right, respectively). At installation the ductile-to-brittle transition temperature depends largely on the level of gelation. To some extent the cooling rate after melt processing also plays a role, as this determines the initial degree of physical ageing after production. During the service life of the pipe this transition temperature increases, resulting in a progressively more brittle pipe. The mechanism depicted on the right side of Figure 6.1 is of greater importance for the residual lifetime method. It shows that the yield stress at which the transition to brittle failure behaviour occurs, as for example observed during a saw test, is influenced by the level of gelation (initial quality of the pipe). This implies that (i) physical ageing should be monitored in time and (ii) the level of gelation should be known for accurate residual lifetime predictions. It is important to note that the level of gelation does not influence the physical ageing process itself; only the limiting tensile yield stress is influenced and not the rate at which the yield stress of the material changes over time (i.e. the ageing rate). The physical ageing rate does, however, vary from pipe to pipe, and this variation should be taken into account when the ambition is to predict the residual lifetime quantitatively for each uPVC pipe. The goal of this chapter is to describe and discuss the current status of the developed lifetime assessment method and also how it can be adopted in practice. First, the ideal system is described, after which the deficiencies between the ideal and the current method are discussed along with propositions for improvements.

Figure 6.1 Interrelation between the influence of the level of gelation and physical ageing on the ductile-to-brittle temperature (**left**) and on the maximum accepted tensile yield stress σ_{lim} (**right**). The horizontal arrows in the right graph indicate the residual lifetime of two pipes for exemplary values of σ_{lim} and the yield stress $\sigma_{y,mh}$ (determined using in-situ micro-hardness measurements).

6.2 The ideal residual lifetime assessment method

Ideally, the residual lifetime assessment method for uPVC gas and water pipes is based on a full characterisation of all components in the transportation and distribution networks. Relevant information comprises not only the level of gelation and the extent of physical ageing, but also data on, for example, the roundness of the pipe and the presence of cracks. The ideal method is capable of determining the information in a non-destructive fashion. It performs measurements and analyses in situ, while providing a sufficiently detailed spatial resolution of all important pipe parameters, and it does so accurately and sufficiently fast.

6.3 Current status

In this thesis a robust method to determine the hardness or microhardness of a uPVC pipe, and thereby the yield stress of the uPVC pipe, has been developed. Although the proposed method is not an off-the-shelf solution, it does have the potential to be developed for in-situ field applications. Both the micro-hardness tester and the confocal microscope used in the lab may be scaled down to devices which are small and robust enough for field application inside uPVC pipes. Beside carrying out measurements, the gas and water distribution network service providers also need to decide on a limiting hardness and/or tensile yield stress value at which the pipes become too brittle to keep them in service. In Chapter 3 a procedure involving the saw test, as developed at Kiwa Technology, was proposed. An additional challenge, as discussed above in Figure 6.1 right, is that this limiting value of the tensile yield stress is also related to the level of gelation of the pipe under study. Either the lowest value encountered for this limiting yield stress can be used (conservative approach) or multiple limiting values could be decided upon, depending on the level of gelation. Having a limiting value as a function of the level of gelation means that the level of gelation is required as an input to the method. The microMCT test as proposed in Chapter 5 could in that case be employed to obtain information on the level of gelation.

6.3.1 *Decision for replacement*

Once the limiting value of the tensile yield stress has been decided upon, a series of measurements will give a mean value of the hardness (and thus the yield stress) of a uPVC pipe. This information will help the network service providers to decide whether or not the pipe should be replaced. The measurements presented in Chapter 2 do, however, show that there is always some variation in the hardness values found using micro-hardness testing on uPVC and that this variation can be

reduced substantially by reducing the surface roughness of the pipe material. This means that if the tensile yield stress of the pipe is near the limiting value, more measurements are required to determine with confidence whether the tensile yield stress is above or below the limiting value. How rapidly the required sample size increases when the limiting value is approached depends on the desired confidence level C and (inner) surface roughness of the pipe. The influence of both aspects on the minimal sample size are illustrated for two pipes having a different surface roughness. In the case of a smooth pipe with a hardness value that differs from the limiting value by up to around 2%, a reasonable number of measurements (about 20) will suffice to determine with high confidence (99%) whether the smooth pipe has to be replaced. For the rough pipe about 80 measurements are required. For an automated system, this number of measurements is still regarded as being feasible, assuming the measurement procedure takes no more than about one minute. It will require an accurate timing between the hardness test and the confocal measurement procedure, as is also discussed in Chapter 2. As an alternative for performing more measurements, the inner surface of the pipe can also be polished to reduce the scatter on the hardness results. This will increase the complexity of the tool, but could be combined with the preparations for the microMCT as some milling is required for this test.

Figure 6.2 The minimal sample size versus the distance from the limiting tensile yield stress for pipes having different inner surface roughness and for different confidence levels C . For the smooth pipe $R_a = 0.19 \mu\text{m}$ and for the rough pipe $R_a = 0.37 \mu\text{m}$. The vertical dashed line at 0% indicates the case in which the tensile yield stress of a pipe equals the limiting value. The minimal sample size was determined using Equation 2.8 and the standard deviation S (for the smooth pipe, $0.0012 \text{ 1}/\mu\text{m}^2$, for the rough pipe, $0.0024 \text{ 1}/\mu\text{m}^2$).

6.3.2 Estimating the residual lifetime

Where the tensile yield stress is below the limiting value the pipe does not have to be replaced immediately. The network company can determine the residual lifetime of

the pipe using the ageing kinetics of the pipe, and the value of limiting tensile yield stress (see Chapter 2). However, it is not possible to extract the ageing rate from one series of measurements on a pipe. Therefore, the residual lifetime cannot be directly calculated from the difference between the yield stress determined from the hardness test and the limiting tensile yield stress at which the pipe becomes too brittle. This deficiency can be dealt with in three ways, which can all be followed in parallel to develop the ideal system in the future:

- i* A conservative approach is followed; the residual lifetime is calculated using the highest ageing rate found for uPVC pipes. The downside of this approach is that most of the pipes will be replaced well before reaching their actual end of life, i.e. their ageing rates were overestimated.
- ii* The data of each of the measurements are stored in a database and the measurements are repeated periodically (e.g. every five years). Over time a dataset will be built up from which the development of the yield stress and thus the ageing rate will become clear. The estimated residual lifetime will be updated with the most recent information on the ageing rates obtained.
- iii* The residual lifetime assessment method is extended with a measurement from which the ageing rate can be determined directly. As shown in Chapter 4, the β -transition temperature has a direct relation with the ageing rate. Instead of using a DMTA, it might be possible to characterise the damping behaviour of uPVC in a non-destructive way, with ultrasonic or dielectric techniques for example. This will require additional research efforts, as these techniques have already been evaluated in their common (linear) form which were found to be inappropriate for such a goal in Chapter 4.

6.4 How to proceed

At the time of writing a research programme initiated by Kiwa Technology is being carried out, in which several excavated pipes are tested according to the methods developed in this thesis. The results of the testing and analyses will be compared with characterisation data obtained by Kiwa Technology using several destructive testing methods. The value of the developed methods for field application will emerge from the outcomes of this research programme. At this stage the execution of the research programme according to the developed methods is already a positive step towards routine lifetime assessment of uPVC pipes for transportation and distribution networks.

Chapter 7

Conclusions and Recommendations

The development of methods for determining the current condition and the residual lifetime of uPVC pipes in the gas and water distribution networks has been the main theme in this thesis. Up-to-date knowledge and understanding of the current and future state of the distribution networks is vital for safe and efficient condition based asset management by the gas and water distribution companies. Failures in the uPVC pipe networks do not occur frequently; they are induced mostly by impact loading events from (third party) excavation activities. The occurrence of brittle failure should be avoided, so as to limit the risks of (fatal) incidents. Two main factors have been known to increase the chances of brittle failure. Firstly, the occurrence of physical ageing leading to an increase of the strength and hardness of the uPVC pipes over time, but concomitantly to a decrease of its toughness. Secondly, a non-optimised level of gelation, where the level of the gelation is a measure for the homogeneity of the pipe material after extrusion, remaining constant over time. The crucial factors in characterising the current and future condition of uPVC pipes are the determination of (i) the current strength and/or hardness of a uPVC pipe, (ii) the maximum allowable tensile yield stress avoiding brittle failure, (iii) the development of the yield stress in the course of time due to physical ageing and (iv) the level of gelation. These topics have been investigated in depth in this thesis in Chapters 2 to 5. The most important conclusions and recommendations regarding the research are given below.

7.1 Conclusions

A new micro-Vickers hardness-based approach has been presented which can be employed to non-destructively determine changes in the thermodynamic state of uPVC pipe materials for gas and water distribution networks. The hardness measurements were carried out on non-polished specimen surfaces to replicate future use by in-situ pipe inspection systems. The hardness measurements were

characterised by considerable scatter in the hardness (H_δ) values that influences the accuracy of the determination of the residual lifetime. Nevertheless, the number of hardness measurements required for the desired degree of precision could be estimated with the help of statistical analysis; practically realistic numbers have been obtained. The sensitivity of the new approach to determine the hardness and to follow hardness changes over time in relation to physical ageing is similar to the approach used in a previous study. However, the current approach is simpler and more robust, being one step closer to practical implementation.

The failure behaviour of uPVC pipes is shown to be strongly dependent on the temperature and the degree of physical ageing at a constant level of gelation. Severely aged uPVC pipes showed a higher ductile-to-brittle transition temperature upon impact testing than younger uPVC pipes. The change in the ductile-to-brittle transition temperature could be predicted quantitatively from the ageing behaviour. The underlying criterion was that the transition occurred if a certain critical tensile yield stress level is reached upon impact testing that is independent of time and temperature. Practical tests, such as the pipe saw test, can be employed to determine the relevant value of the limiting tensile yield stress for prediction of the residual lifetime of uPVC pipes.

The prediction of the residual lifetime of a uPVC pipe depends strongly on the development of the yield stress over time, i.e. the ageing kinetics. A large variation in ageing rates was observed for a broad range of excavated and unused gas and water distribution uPVC pipes. An in-depth study of the origin of the differences in ageing rates was conducted according to the various stages in the lifetime of uPVC pipes: polymerisation, processing and service life. Properties related to the polymerisation stage of uPVC (chain structure, chain length and crystallinity) are not related to the variations in ageing rates observed. These variations seem to originate from the processing stage, where various additives, such as stabilisers, lubricants and fillers, are mixed with the uPVC powder. However, the correlation between the ageing rate and the presence of lead and PE wax, for example, is not very strong. Regarding the service stage, the physical/chemical changes of the PVC materials as a result of interactions between components in the surrounding soil and the lead stabilisers are not primarily responsible for the variation in ageing rates. Further results regarding the service stage seem to imply that the variation in ageing rates of pipes produced before 1980 is greater than after that year. In the early years of uPVC pipe production considerable variation in the processing conditions and compositions occurred, possibly explaining the observed differences. After 1980, uPVC pipes were produced mainly for water distribution. In addition, an interesting relationship between the ageing rate and the temperature at the maximum loss angle of the β -relaxation has been observed. A higher β -relaxation temperature corresponds with a lower ageing rate. It suggests that molecular movements responsible for the β -relaxation and the physical ageing rate are related. The relationship also makes it

possible to determine the ageing rate more quickly than by using uniaxial tensile experiments, as commonly performed up to now.

The level of gelation of uPVC pipes is another crucial factor in the determination of the condition of a uPVC pipe. A systemic study of potential useful methods of determining the level of gelation in a uPVC pipe was unsuccessful. No technique currently exists that is able to determine the level of gelation non-destructively, through the thickness of the pipe wall and from the inside of the pipe. The main limitation is the presence of regions with low levels of gelation in the interior of the pipe wall. A possible alternative is the newly proposed micro Methylene Chloride (microMC) test, which is a modified version of the commonly applied Methylene Chloride Temperature (MCT) test. The level of gelation of a uPVC pipe is determined on the basis of chemical attack within a small concavity milled into the inside of a pipe wall. As such, it seems more appropriate for the determination of the level of gelation in relatively thick-walled water distribution pipes than in thin-walled gas distribution pipes.

The results of this research provide a large step towards the realisation of residual lifetime assessment of uPVC pipes in practice. Additional research is required for the implementation of the residual lifetime assessment method. The recommendations for additional research are given in the next section.

7.2 Recommendations

In this thesis, it was shown that physical ageing increases the hardness (and yield stress) and causes embrittlement as shown in Chapters 2 and 3 respectively. However, the relation between hardness and embrittlement has only been shown for a few PVC pipe materials. For practical implementation of the residual lifetime method, it is recommended to confirm the relation for a large set of uPVC pipes taken from the distribution networks. On the basis of this result it can be decided to prepare the micro-Vickers hardness-based approach for in-situ pipe inspections.

In the hardness approach presented, the reference level for determining the indent depth and hardness H_δ is assessed from the topology data of the surface region close to the indent. It has been shown that the reference level is particularly sensitive to the surface roughness present. It is recommended to determine the surface region of the indent prior to and after the hardness measurement and subtract the measurement data. It is expected that this procedure strongly reduces the variation in hardness values and makes the approach more suitable to determine the residual lifetime. Further aspects worth consideration are miniaturisation of the device, reduction in the recovery and measurement time, influence of the applied load, and reduction in the number of measurements by proper preparation of the inner wall (see Chapter 2).

The expected influence of the level of gelation on the limiting tensile yield stress has been shown qualitatively in Chapter 3. Only uPVC pipes having very low levels of gelation are expected to have a marked influence on the limiting yield stress and the residual lifetime. Saw tests on uPVC pipes having large differences in levels of gelation should be performed to confirm this expectation.

The variation in ageing rates of uPVC pipes could be attributed to the processing stage; the concentration of lead, PE wax and chalk strongly affects the ageing rate. Further research is required so as to determine exactly which lead component influences the ageing rate. Furthermore, the underlying mechanisms for the molecular interactions between these additives and the PVC polymer are unknown and should be elaborated on.

It is not yet possible to determine the ageing rate without having to dig up the pipe and determine the location of the maximum of the β -relaxation peak in a DMA experiment. A practical recommendation to still determine the ageing rate non-destructively and without excavation activities is to perform several measurements of the hardness of the pipe over time. In the course of time, more data will become available and the ageing rate and residual lifetime can be adjusted.

The level of gelation can be assessed virtually non-destructively employing the newly developed microMC method presented in Chapter 5. However, the potential of the method was shown only for a small number of pipes. The microMC experiments should be performed on a large collection of excavated PVC pipes to assess whether the method yields reliable results in practice. Based on this result, the microMC method can be prepared for employment inside buried uPVC pipes.

Lastly, for determining the yield stress and the level of gelation of uPVC pipes in service, it is recommended to combine the hardness method and the microMC method. Firstly, polish a part of the inner wall surface and carry out hardness measurements on the polished surface to determine the yield stress. Secondly, apply the microMC method to the polished surface area of the inner wall to determine the gelation level. The network operator can then determine the residual lifetime from the limiting tensile yield stress and the ageing kinetics of the yield stress. The limiting tensile yield stress follows from the level of gelation and the ageing kinetics follows from the hardness measurement data.

Appendix A

Table with pipes

Table A.1 *The ageing rate and dimensions of excavated and unused uPVC pipes in this thesis. The ageing rates are given in the second column with the 95%-confidence intervals in brackets.*

Pipe No.	Ageing Rate (95% CI)	Diameter	Thickness
[-]	[MPa/decade]	[mm]	[mm]
1	4.17 (± 0.72)	110	2.9
2	3.75 (± 0.24)	160	4.1
3	3.14 (± 0.78)	83	3.0
4	2.52 (± 0.35)	110	3.0
5	2.78 (± 0.25)	160	4.2
6	2.17 (± 0.21)	110	2.9
7	1.05 (± 0.09)	60	2.2
8	1.88 (± 0.35)	110	2.7
9	1.86 (± 0.31)	110	3.0
10	2.25 (± 0.52)	50	2.3
11	2.50 (± 0.36)	50	2.3
12	2.22 (± 0.47)	50	2.3
13	2.24 (± 0.38)	50	2.3
14	-	320	8.1
15	-	600	18

Appendix B

Details of experimental analysis

In this appendix, a detailed description is given in which way the values of the material properties of the PVC pipes were determined using the experimental techniques described in Section 4.3. The ageing rate and values of all other material properties are summarised in Figure 4.2 and Table 4.3 respectively.

B.1 Properties related to polymerisation

A typical ^{13}C NMR spectrum of PVC dissolved in THF- d_8 is displayed in Figure B.1 left. The peaks at ~ 25 ppm and ~ 67 ppm have been attributed to the solvent THF- d_8 [135], and the peaks at ~ 45 ppm and ~ 57 ppm to PVC [136]. Figure B.1 right shows a section of the spectrum in the region of carbon atoms in the $-\text{CHCl}-$ part of the PVC polymer chain [113, 134]. The concentration of each type of triad* was calculated from the relative areas of the carbon peaks [113]. The maximum variation in the triad concentrations in the PVC pipes is about 8%.

A typical ^1H NMR spectrum of PVC is shown in Figure B.2 left. The number of carbon double bonds $N_{\text{C}=\text{C}}$ per 1000 monomer units is determined by [110]

$$N_{\text{C}=\text{C}} = \frac{A_s}{A_{\text{CHCl}}} \cdot 1000, \quad (\text{B.1})$$

where A_s is the area of the group of hydrogen resonance peaks between 5.6 ppm and 6.0 ppm which are assigned to the hydrogen atoms in the chain parts denoted in the legend in Figure B.2 right. Carbon double bonds are located in these chain parts and thus the area A_s is directly related to the concentration of carbon double bonds. The area A_{CHCl} is assigned to hydrogen atoms in the $-\text{CHCl}-$ part of the polymer chain. The double carbon bond concentration in the PVC pipes investigated is about 2-3 double bonds per 1000 monomer units.

*A triad is a segment of the polymer chain consisting of three monomer units.

Figure B.1 (left) An ^{13}C -NMR spectrum of PVC isolated for pipe 1. (right) a section of the spectrum showing resonance peaks of carbons in the $-\text{CHCl}-$ part of the polymer chain [113, 134]. The groups of carbon peaks located at 56.5, 57.3 and 58.4 ppm are attributed to the isotactic, heterotactic and syndiotactic triads of the PVC chains respectively [113].

The K value (molecular weight) of most pipes is about 67. Excavated pipes 3 and 4 have a higher K value (73-74). These pipes were installed in 1967 and 1961 respectively. Around this period, a PVC powder having a higher K value was used in processing.

Figure B.2 An ^1H spectrum of PVC which was isolated from pipe 4. (Left) the peaks at 1.8 ppm, 2.7 ppm and 3.6 ppm are of THF-d_8 [135]. (Right) a section of the spectrum showing resonance peaks related to the hydrogen atoms in the $-\text{CHCl}-$ chain parts. The hydrogen atoms in the chain parts responsible for the group of peaks located between 5.6 ppm and 6.0 ppm are underlined in the legend [109, 192].

B.2 Properties related to processing

The crystalline fraction, the level of gelation, the processing temperature, the relative concentrations of additives and the glass transition temperature were determined using DSC. In Figure B.3 left two typical DSC measurements are shown in which the quantities of interest are labelled. The level of gelation G was determined according to the equation

$$G(\%) = \frac{\Delta H_A}{\Delta H_A + \Delta H_B} \cdot 100\%, \quad (\text{B.2})$$

where ΔH_A and ΔH_B are the melt enthalpies of the secondary and primary crystallites, respectively [126]. The processing temperature T_p is defined as the temperature at which the primary crystallites start to melt and is a measure for the maximum temperature the material endured during extrusion [125]. The level of gelation increases with increasing processing temperature [125, 126], which is also observed here and shown in Figure B.3 right.

Figure B.3 The heat flow versus the temperature for (left) pipes 1 and 13 and (right) for pipes 10-13. The endotherms H_1 , H_2 and H_3 were observed in the temperature ranges 99-105 °C, 106-110 °C and 112-120 °C respectively.

The level of gelation of pipes 10-13 corresponds with the level of gelation specified by the manufacturer. The crystalline fraction in PVC pipes is defined as the sum of the enthalpies of the endotherms H_A and H_B divided by the enthalpy H_{cr} for the crystalline phase [115, 118]. A value of H_{cr} equal to 3 kJ/mol is selected, adopted from [115, 118]. The endotherms H_1 , H_2 and H_3 are a consequence of the melting of (molecular) additives in the PVC pipes. The enthalpies of all endotherms were determined using linear baselines. The glass transition temperature T_g is determined from the corresponding jump in the heat flow.

The concentrations of various fatty acids were determined using GC-MS. A chromatogram of a TMSH treated filtrate of pipe 3 is given in Figure B.4. The arrows

indicate the identified methyl esters. The other peaks in the chromatograms correspond to substances which were formed during the pretreatment, substances which could not be identified and electronic disturbances from the gas chromatograph spectrometers.

Figure B.4 A GC-MS chromatogram of the compounds, treated with TMSH, in the filtrate of pipe 3. The arrows indicate the peaks at 15.88, 17.98 and 19.91 minutes and are attributed to tridecanoic acid methyl ester, palmitic acid methyl ester and stearic acid methyl ester respectively.

The presence of polyethylene wax was determined using PTV-GC-MS. Chromatograms of pipe 7 and pure PVC are shown in Figure B.5. The peaks indicated by the black filled arrows are attributed to the presence of (small) hydrocarbons, which may be caused by pyrolysis of lubricants like polyethylene. The peaks indicated by the white filled arrows are attributed to degradation products of black deposits (possibly bitumen) located on the outer surface of this pipe. The other peaks were assigned to degradation products resulting from the pyrolysis of the PVC. Peaks attributed to phthalate esters (plasticisers) were not observed.

The concentrations of chalk, carbonyl groups and hydroxyl groups in PVC pipes were determined using infrared spectroscopy. Figure B.6 shows infrared spectra of pure PVC and two PVC pipes. The peaks with the highest absorbance are attributed to PVC chains. The presence of additives is shown in Figure B.7. The peaks at the wave numbers 712, 848, 876, 1796, and 2514 cm^{-1} were attributed to CaCO_3 [193], a mineral filler found only in PVC water pipes. The peak at 1736 cm^{-1} is caused by absorption of carbonyl (C=O) groups [27, 194] and was observed in almost all PVC pipes. The carbonyl groups may be attributed to processing aids [58]. The broad peak at $3100\text{--}3700\text{ cm}^{-1}$ is caused by hydroxyl groups (OH) [195]. It was only present in relatively new unused PVC pipes and may be attributed to lubricant and/or stabilisers like glycerol monostearate. The peak at 2850 cm^{-1} is more intense for the PVC pipes than for pure PVC. This phenomenon might be attributed to polymeric additives like stearate compounds [196] and polyethylene waxes.

Figure B.5 PTV-GC-MS chromatograms of pipe 7 and pure PVC. The black filled arrows at the peaks at retention times 3.03, 4.11, 4.24, 6.07 and 8.18 minutes are attributed to small amounts of pentane, butene, hexane, heptane and octane respectively. The white filled arrows indicate the peaks at 21.32, 28.59, 29.54, 30.47, 33.67 minutes were attributed to degradation products [lauric acid and hydrocarbons ($C_{24}H_{50}$ and $C_{26}H_{54}$)] of black deposits (bitumen) located on the outer surface of this pipe.

Figure B.6 Infrared spectra of pipes 4 and 8 and of pure PVC.

Figure B.8 shows peaks at 1536 and 1570 cm^{-1} which are attributed to carboxylate salts containing carboxylate ions (COO^-) [138, 194, 196–198]. The peak at 1468 cm^{-1} is attributed to vibrations of methylene bridges ($-\text{CH}_2-$) in carboxylate salts [196]. Carboxylate salts are commonly used as stabilisers in PVC pipes. The presence of carboxylate salts was observed for all PVC pipes and was added in relatively small amounts. To summarise, the presence of processing aids and stabilisers were observed for all PVC pipes. At first sight, large differences in the applied formulation of the PVC pipes were not observed.

The weight percentage of chalk in the PVC pipes was determined by comparing the absorbance ratios A_{876}/A_{695} and A_{1795}/A_{695} with the same ratios for PVC pipes

Figure B.7 Infrared spectrum of pipes 4 and 8 after subtraction of the spectrum of pure PVC such that the PVC absorbance peak at 836 cm^{-1} disappears [199]. The arrows indicate the presence of carbonyl (C=O) groups, hydroxyl groups (OH) and chalk (CaCO_3). The spectrum of pipe 4 is shifted vertically for clarity.

Figure B.8 *Left:* infrared spectra of pipes 4, 8 and 9. *Right:* a zoom-in of the left figure. Linear baselines were applied for determining the peak height of the carbonyl group. A linear baseline is shown for pipe 8.

with known contents of CaCO_3 [†]. The PVC peak at 695 cm^{-1} was taken as a reference [147] and all peak heights were determined using linear baselines. The absorbance ratio A_{1736}/A_{695} was taken as a measure for the concentration of carbonyl groups. Figure B.8 left shows that the carbonyl peak and the peaks of carboxylate salts overlap. Therefore, a linear baseline was applied for determining the height of the carbonyl peak as shown in Figure B.8 right. The concentration of hydroxyl was taken as the peak area in the range $3086\text{--}3730\text{ cm}^{-1}$ divided by the PVC peak height at 695 cm^{-1} .

The presence of minerals was investigated by X-ray diffraction phase analysis. Figure B.9 shows relatively small and broad peaks at $20^\circ 2\theta$, $28^\circ 2\theta$ and $46^\circ 2\theta$

[†] A_w is the value of the absorbance at wave number w in cm^{-1} .

Figure B.9 X-ray spectra of excavated pipes (1-7) and of unused pipes 8, 9 and 10.

which are attributed to reflections of the PVC crystallites. The small height and the relatively large width of the peaks show that the PVC crystallites are relatively small and that the crystalline fraction in the PVC pipes is relatively low. The broad peak at $8^\circ 2\theta$ is attributed to clusters of packed crystallites [116, 187]. The sharp peaks are attributed to small concentrations of chalk (CaCO_3), titanium dioxide (TiO_2 , a pigment [58]), silicon dioxide (SiO_2 , a filler [58]) and lead sulphide (PbS). The X-ray diffraction phase analysis confirms the presence of chalk determined by infrared spectroscopy.

B.3 Properties related to molecular mobility

The molecular mobility as a function of temperature was determined by characterising the β -relaxation peak using DMA. The maximum loss angle and the temperature at maximum loss angle were determined by spline approximation procedures.

Appendix C

Multi-variable analysis

A multi-variable analysis is included to aid the investigation of the background of the potential influence of all properties shown in Table 4.1. For simplicity, only linear regression models were used. Other models involving squared terms, power-law terms and cross terms were considered, but these models did not yield useful information. Furthermore, it was only sensible to incorporate not more than two properties in a multi-variable model, because of the limited number of investigated pipes. The general form of a linear regression model having two properties x_{i1} and x_{i2} is given by [200]

$$\dot{\sigma}_{y,i} = c_0 + c_1 x_{i1} + c_2 x_{i2} + \epsilon_i, \quad (\text{C.1})$$

where $\dot{\sigma}_{y,i}$ are the experimentally determined ageing rates, c_0 , c_1 and c_2 the regression coefficients and ϵ_i the error. The index i indicates the pipe number. It should be noted that the two properties in the model must be independent of each other to avoid collinearity between both properties.

The multi-variable analysis was conducted by applying the following steps: (i) Determine which of the pairs of properties are independent. The criterion for a pair of properties regarded as independent is if the coefficient of determination R^2 from a linear fit between the two properties is less than 0.10. (ii) Incorporate two independent properties in Equation C.1 and determine the adjusted coefficient of determination R^2_{adj} . (iii) Repeat step (ii) for all pairs of independent properties.

The R^2_{adj} is defined as [200]

$$R^2_{\text{adj}} = 1 - (1 - R^2) \frac{n - 1}{n - p - 1}, \quad (\text{C.2})$$

where R^2 is coefficient of determination, p the number of properties (in this study

$p=2$) and n the number of pipes included into the regression model*.

It is important to note that, because of limited resources, certain properties were not determined for all pipes. As a result, the number of data points for fitting the regression coefficients c_j is reduced if one of the properties in the model contains fewer data points. The reduction in the number of data points can cause an increase in the R^2_{adj} value. This effect has been taken into account by considering only those models for which a reasonable number of data points is available.

*The R^2_{adj} adjusts for the number of properties p in a combination relative to the number of data points n . Unlike R^2 , R^2_{adj} increases only when a new property is included if the new property improves the R^2 more than would be expected by chance.

Table C.1 *The R^2_{adj} values for pairs of independent properties ($R^2 \leq 0.10$). The R^2 values for linear regression between the ageing rate and a single property are shown in the bottom row.*

Property description	Property No.		Stage														
	1	2	Polymerisation					Processing									
			chain structure	cryst.	conditions	stabilisers	lubricants	aid									
Class	3	4							5	6	7	8	9	10	11	12	13
double carbon bond concentration	1	-				0.40	0.02	0.05	0.08	0.06		0.19		0.01			
isotactic triad concentration	2	-				0.09	-0.05	0.53				0.35		-0.02			
heterotactic triad concentration	3		-			0.44			-0.30	-0.30				-0.05			
syndiotactic triad concentration	4			-		-0.32	-0.05					-0.14		-0.32		0.43	
K-value (molecular weight)	5				-	0.04	-0.15							-0.09			
crystalline fraction	6						-0.15	-0.90		-0.96	0.17			-0.95		0.52	0.31
level of gelation	7							-		-0.23				-0.04		0.29	
processing temperature	8								-	-0.92	-0.93	0.28	-0.79	-0.14	0.59	0.20	
stearic acid concentration	9								-		0.37				0.67		
palmitic acid concentration	10													-0.97	-0.91	0.78	
tridecanoic acid concentration	11									-				-0.98			
lead concentration	12										-			0.37			
zinc concentration	13											-		-0.79			
sulphate (SO ₄ ²⁻) concentration	14												-	-0.94	0.65	0.02	
relative hydroxyl group (OH) concentration	15													-		0.23	
presence of PE wax	16														-		
relative carbonyl group (C=O) concentration	17																-
chalk (CaCO ₃) concentration	18																
silicon dioxide (SiO ₂) presence	19																
titanium dioxide (TiO ₂) presence	20																
diameter	21																
wall thickness	22																
chloride (Cl ⁻) concentration	23																
melt enthalpy 1	24																
melt enthalpy 2	25																
melt enthalpy 3	26																
lead sulphide (PbS) presence	27																
excavated/unused	28																
year of production	29																
β -relaxation loss angle	30																
β -relaxation temperature	31																
glass transition temperature	32																
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R^2 [%]

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60

40

20

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Table C.2 The R^2_{adj} values for pairs of independent properties ($R^2 \leq 0.10$). The R^2 values for linear regression between the ageing rate and a single property are shown in the bottom row.

Property description	Property No.		18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
	Stage	Class	Processing										Service		Molecular mobility		
			fillers	pig.	geometry		other compounds	comp.	conditions								
double carbon bond concentration	1	0.13		-0.08	0.12				0.14			-0.08	-0.07				0.03
isotactic triad concentration	2	0.11		-0.00	0.35	0.07	0.25		0.11			0.00	0.09				0.03
heterotactic triad concentration	3	0.06		-0.18					0.05	-0.11		-0.17	-0.02				0.96
syndiotactic triad concentration	4	-0.32			0.03				-0.34	-0.36	-0.36	-0.81	-0.36	0.41			0.85
K-value (molecular weight)	5	-0.25		-0.21							-0.08				-0.04	0.80	-0.35
crystalline fraction	6	-0.22		-0.21	0.11	0.07	-0.83	-0.01	-0.12	-0.12	-0.20	-0.02	-0.02	0.50	0.34		-0.09
level of gelation	7	0.09	-0.12		0.20			0.08	-0.03	-0.03	-0.12	-0.12	0.09	0.21	0.08		0.00
processing temperature	8	0.02			0.07			-0.03	-0.16	-0.14	-0.27	-0.04	0.14	0.14	-0.12	0.79	-0.12
stearic acid concentration	9			-0.94			-0.82		-0.94	-0.90					-0.61	0.37	
palmitic acid concentration	10			-0.99			-0.88	-0.99	-0.99	-0.96					-0.57	0.48	
tridecanoic acid concentration	11			-0.99			-0.89	-0.99	-0.99	-0.96					-0.61	0.46	
lead concentration	12		0.80	0.16			0.63		0.16	0.17							
zinc concentration	13		-0.82	-0.82	0.38		-0.61	-0.82	-0.82		-0.65						
sulphate (SO ₄ ²⁻) concentration	14	-0.78	-0.82	-0.99	0.22			-0.66	-0.99	-0.95	-0.20	-0.78	0.03		0.30	0.89	-0.95
relative hydroxyl group (OH) concentration	15		-0.20	-0.17			-0.81	-0.01		-0.09	-0.20				0.30		-0.07
presence of PE wax	16		0.91	0.51			0.80		0.51	0.52							
relative carbonyl group (C=O) concentration	17		0.20	0.16			0.26			0.23					0.32	0.73	
chalk (CaCO ₃) concentration	18	-	-0.02	-0.05	0.16		-0.60					-0.27	-0.10	0.07	-0.34	0.76	
silicon dioxide (SiO ₂) presence	19			-0.27						-0.23	-0.27			0.07	-0.34	0.76	
titanium dioxide (TiO ₂) presence	20						-0.89			-0.23	-0.27			0.14	0.78		
diameter	21				-		0.17			-0.23	-0.27			0.40	0.11		
wall thickness	22						0.72		0.07	0.00	0.00	-0.07		0.39	0.27		0.03
chloride (Cl ⁻) concentration	23							-0.57	-0.89	-0.83			-0.60			0.98	
melt enthalpy 1	24														0.61		
melt enthalpy 2	25										-0.26			0.32	-0.01	0.83	
melt enthalpy 3	26													0.81			
lead sulphide (PbS) presence	27														-0.28	0.75	
excavated/unused	28														0.67		
year of production	29																
β -relaxation loss angle	30														-	0.89	0.33
β -relaxation temperature	31																
glass transition temperature	32																-
R^2 [%]			<div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div><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