Assessment of the lifetime of district heating pipes

ALBERTO VEGA

Department of Industrial and Material Science
Chalmers University of Technology
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Abstract

This thesis is concerned with the degradation and assessment of the lifetime of district heating pipes, where accelerated ageing is used to study the degradation in a short time frame.

The project was divided into four interrelated parts. In the first part, polyurethane foam obtained from district heating pipes was aged at an elevated temperature in two different environments, and the effects of the accelerated ageing on the physical properties and chemical structure were studied. In the second part, district heating pipes were aged using an accelerated method to examine directly the degradation of the polyurethane foam in the pipes. The adhesion strength and thermal conductivity were followed during the entire ageing process. The chemical structure of some polyurethane samples was also analysed to identify any sign of deterioration. In the third part, several naturally aged pipes were collected and their remaining adhesion strength measured, as well as their chemical structure to compare the natural and accelerated ageing. Finally, an alternative method for accelerated ageing was proposed, applying thermal and cyclic mechanical loads on the pipes at the same time and exposing the pipes to more realistic conditions than the traditional accelerated ageing.

The results confirmed that oxygen plays a central role in the activation of the degradation process, which is faster at higher temperatures. The adhesion strength and thermal conductivity measurements showed that the temperature of accelerated ageing should be chosen carefully to avoid the activation of degradation processes that are not relevant for the specific application. The studies of natural ageing presented evidence that some pipes have lost only approximately 20% of their initial adhesion strength after 30 years in service. These pipes could probably be used for a longer time. Finally, the combination of thermal and cyclic mechanical loads is a promising method of accelerated ageing because mechanical loads affected both the adhesion strength and the chemical structure of the tested pipes, leading to more rapid ageing. This methodology should be adopted in accelerated ageing testing to avoid overestimating the lifetime of DH pipes.

Keywords: District heating pipes, rigid polyurethane foam, mechanical performance, degradation mechanisms, natural ageing, artificial ageing, FTIR

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Acknowledgments

In 2012, some people at SP (now RISE) started an experiment for accelerated ageing of district heating pipes. We would heat the pipes to elevated temperatures and accelerate the diffusion of air into the polyurethane foam by increasing the ambient temperature. This was my first research experiment. I was fascinated by the experimental difficulties that we needed to solve in order to get everything in place, but I knew nothing about the degradation or accelerated ageing of polymers at that moment. We obtained some peculiar results and Nazdaneh thought that it was worth to investigate the real reason behind these results. In 2015, I got the opportunity to start my doctoral studies.

During five years, I have haft time to get some knowledge, but also to meet a lot of people that have supported me in many different ways. From conversations about how to handle big district heating pipes to academic discussions about degradation, lifetime prediction and radicals. I would not have enough space here to thank all of them.

First, I would like to thank my supervisors Nazdaneh and Ignacy. I know they spent many hours revising my work including experiments, articles and thesis. I have a big respect for them professionally, but I also appreciate them personally therefore I do not call them Dr. or Prof. here. It does not feel natural for me.

Thanks to my examiner at Chalmers University Prof. Antal Boldizar who always was concerned about my academic development.

This PhD work was carried out at RISE facilities in Gothenburg, where my colleagues helped me with all the tough work: cutting, carrying, and testing DH pipes. Special thanks to Anders Persson who never said "I don't have time" and made real many of my incomprehensible ideas.

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Finally, I would like to thank my family for understanding my situation during the last five years and for accepting that I could not spend time with them some days. Thanks for giving me the strength to complete my projects.

List of Publications

This thesis is based on the following publications:

[I] N. Yarahmadi, A. Vega, I. Jakubowicz, "Accelerated ageing and degradation characteristics of rigid polyurethane foam". Published in Polymer Degradation and Stability, 2017.

[II] A. Vega, N. Yarahmadi, I. Jakubowicz, "Determination of the long term performance of district heating pipes through accelerated ageing". Published in Polymer Degradation and Stability, 2018.

[III] A. Vega, N. Yarahmadi, I. Jakubowicz, "Determining the useful life of district heating pipes: Correlation between natural and accelerated ageing". Published in Polymer Degradation and Stability, 2020.

[IV] A. Vega, N. Yarahmadi, J. Sällström, I. Jakubowicz, "Effects of cyclic mechanical loads and thermal ageing on district heating pipes". Published in Polymer Degradation and Stability, 2020.

Contribution to the appended papers

PAPER I

The author planned the artificial ageing of polyurethane samples, and also carried out the mechanical tests and developed a methodology to analyse the results obtained from the infrared spectroscopy experiments. The author was involved in the revision of the submitted paper.

PAPER II

The author was responsible to maintain the accelerated ageing of district heating pipes ongoing during a period of two years, performing thermal and mechanical tests, and chemical analysis of the samples. The author wrote the first draft and was involved in the revision of the submitted paper.

PAPER III

The author was responsible to plan the tests of several naturally aged pipes collected from different locations. The author upgraded the the equipment used for the mechanical test, and carried out the tests and chemical analysis. The author wrote the first draft and was involved in the submission and revision of this paper.

PAPER IV

The author together with other colleagues planned a test set-up for combination of mechanical and thermal loads on district heating pipes. The author studied any change in the mechanical and chemical properties of the pipes. The author wrote the first draft and was involved in the submission and revision of this paper.

Acronyms

4GDH: Fourth-generation district heating

ATR: Attenuated total reflection

CFC: Chlorofluorocarbon

DH: District heating

E_a: Activation energy

FTIR: Fourier transform infrared spectroscopy

GHP: Guarded hot pipe

GC–MS: Gas chromatography with tandem mass spectrometry

HDPE: High-density polyethylene

IR: Infra-red

NCO: Isocyanate

PUR: Polyurethane

TPS: Transient plane source

Contents

Part I

Overview

CHAPTER 1

Introduction

A district heating (DH) system comprises a heating plant, a distribution network that transports heat to houses, schools, and offices in a city, and to consumer systems. The heat is produced or collected in a centralised plant, eliminating the use of individual boilers in each building. There are now four generations of DH pipes, each of which has been developed to provide a more energy-efficient system with better thermal and mechanical performance. The Romans used to circulate hot water for baths and to heat some of their buildings, and other civilisations have used similar techniques, but the steam distribution systems established in the United States in the late 1870s and later in Europe are recognised as the first generation of DH networks. The steam distribution system in New York is one of the largest DH systems in the world in terms of supply capacity, and it is still in use [1]. In Europe, DH technology took a different direction, with hot water systems using pipes in concrete ducts to transport pressurised hot water. This second generation was developed between the 1930s and 1970s, combining heat and power plants with a greater level of reliability and safety than the first generation. In the 1970s, a new design was introduced using insulated pipes, which were directly buried underground. This design is considered to be the third generation of

DH pipes, its primary motivation being to improve energy efficiency and to eliminate oil-dependence by using other energy sources, e.g. coal, biomass, and waste energy from other industrial activities. Now, the fourth-generation district heating (4GDH) is under development, where the main goal is to operate at lower temperatures, making use of heat from low-temperature sources. It will also be possible to implement lighter and cheaper materials in DH pipes, such as cross-linked polyethylene instead of steel. Fredriksen and Werner [2], [3] have described the history and development of district heating systems in more details, and Lund [4] has reviewed the introduction and transition to the fourth generation.

The third generation of DH pipes currently predominates and it is the focus of this work. The pipes consist of three bonded components: an external casing made of high-density polyethylene (HDPE), an intermediate insulating layer made of rigid polyurethane (PUR) foam, and an internal steel pipe, as shown in Figure 1.1. This type of DH pipe is called a pre-insulated pipe or a bonded pipe. Currently, the DH systems work at varying operating temperatures and these variations lead to axial movement of the steel pipe. The shear force generated between the PUR foam and the steel pipe can cause failure and in the worst scenario leakage in the joints between pipes. After many years of service, the mechanical and insulating properties of the pipes deteriorate.

In Sweden, there are about 424 DH systems with extensive networks of DH pipes, most of which may now be close to the end of their service life. However, no suitable method is available to assess the status of the DH pipes.
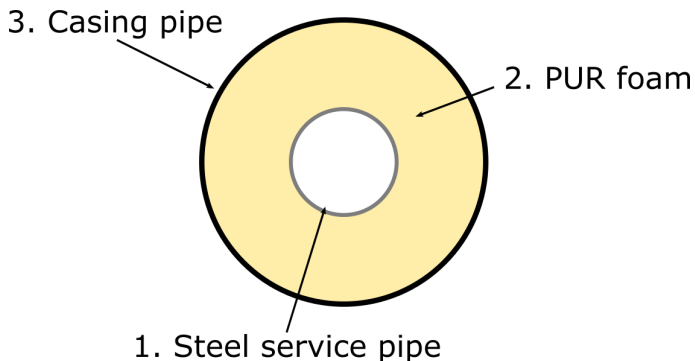

Figure 1.1: Sketch of DH pipes showing the three main components.

1.1 Purpose of this study

DH pipes are exposed to high temperatures, mechanical loads, and temperature variations, which affect the long-term performance of the pipes during their entire service life. According to the EN253 standard published in 2019, the minimum lifetime of a DH pipe used continuously at temperatures up to 120°C must be 30 years. If the operating temperature is lower than 115°C, the pipes may last for more than 50 years [5], but there is no reliable method to assess the actual status of DH pipes or to predict their remaining lifetime [6]–[8]. The purpose of this work was to better understand the degradation of DH pipes during their operating time and to develop various tools to determine the status of the DH pipes and their remaining lifetime.

1.2 Specific problems addressed

Many pipes in the current DH systems should be close to the end of their expected life according to the design criteria described in the EN253 standard [5]. Consequently, suitable maintenance strategies are needed. Currently, accelerated ageing at elevated temperatures is the standard test method used to predict the lifetime of DH pipes, using a linear Arrhenius relationship. However, this method can lead to an underestimation of the lifetime of the pipes because the method is too simple to describe the whole degradation process [9], [10], and the extrapolation to the service temperature of data obtained at high temperatures can be misleading due to irrelevant degradation processes activated by the excessively high temperatures. It is crucial to determine the appropriate conditions for the accelerated ageing of DH pipes to obtain useful data to predict their service lifetime.

The assessment of the status of the current DH networks is also an issue for energy companies and urban planners. It is necessary to design a tool that can easily be taken to the field to determine the remaining lifetime of the DH pipes.

1.3 Aims

To find a solution to the problems described above, it is necessary:

- to understand the degradation mechanisms of the critical components of the DH pipes at the service temperatures,

- to develop technical and theoretical tools to assess the status of the current and future DH pipes,

- to develop relevant accelerated ageing methods and lifetime prediction models.

1.4 Novelties of this thesis

In this work, the most relevant degradation mechanisms have been identified, and their effects on the general performance of DH pipes have been studied. The results have shown that the temperature for the ageing experiment must be chosen carefully to accelerate the degradation processes correctly. It has also been shown that a linear Arrhenius relationship is not sufficient to describe the rate of the degradation processes involved. A technical method has been developed to evaluate rapidly and easily in the laboratory or directly in the field, the mechanical properties related to the service performance of the DH pipes. New strategies for the accelerated ageing of DH pipes have been proposed, exposing the pipes to both thermal and mechanical loads, and Fourier transform infra-red (FTIR) spectroscopy has been used to detect the changes in the chemical structure of the PUR foam caused by the degradation.

1.5 Limitations

In this work, we have focused on pre-insulated DH pipes consisting of three components where an intermediate rigid PUR foam is bonded to an internal steel service pipe and an external casing pipe. Particular attention has been paid to the degradation of the PUR foam and the strength of the adhesion between the foam and the steel pipe. The adhesion plays an important role in restraining the free movement of the service pipe due to thermal expansion. Powerpipe Systems AB produced most of the single straight pipes tested in this work, using a traditional production method.

Twin or flexible pipes were outside the scope of this work, as well as the optimisation of the DH network, and the analysis of customers' heat demands and district cooling systems.

1.6 Structure

The project was divided into four parts. The degradation of the PUR foam from DH pipes was first studied to identify the most relevant processes activated by elevated temperature and different environments, viz., in the presence and absence of air. The results are summarised in Paper I. Second, the knowledge gained from the first part was applied to further studies of the ageing processes in DH pipes, where DH pipes were aged at different temperatures and their mechanical performance was studied during the ageing period. Changes in the chemical structure of PUR foam were shown using the FTIR technique by comparison with the results from the earlier work. Paper II summarises these results. Third, the effects of natural ageing in DH pipes were compared with those resulting from accelerated ageing in the laboratory. DH pipes from different locations were collected and brought to the laboratory for testing of the adhesion strength and for analysis of the chemical structure of the PUR foam. The results are summarised in Paper III. Finally, an experiment was designed to apply both thermal ageing and cyclic mechanical loads to DH pipes, so that the pipes were exposed to realistic operating conditions. The methodology and results are presented in Paper IV. Figure 1.2 summarises the structure of the project.
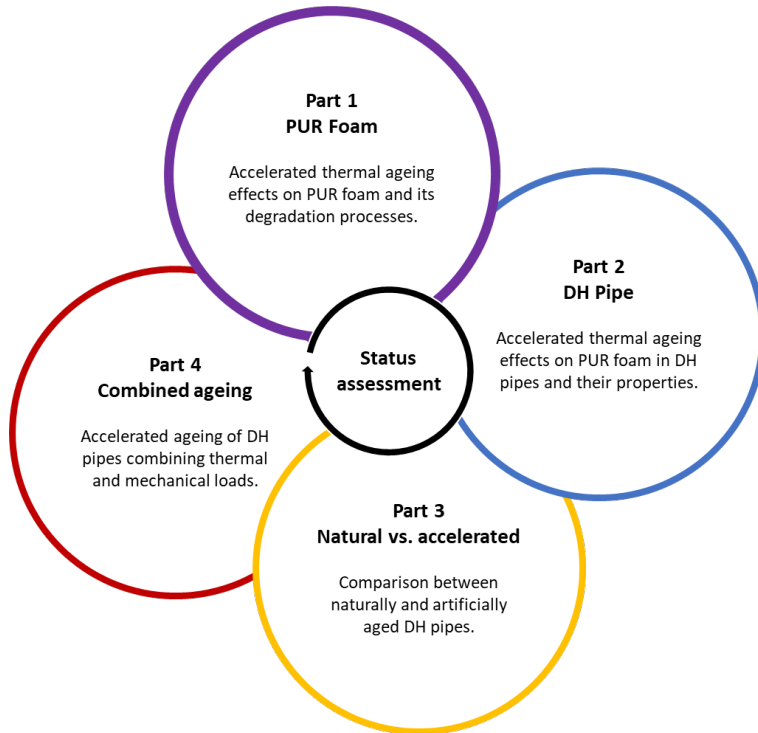
Figure 1.2: Structure of the project.

CHAPTER 2

District heating pipes

The third-generation DH pipes consist of three components, which adhere to each other forming a single unit, which supports both external and internal mechanical loads and improves the thermal performance of the network. During the last decades, a few changes have been made in the design of DH pipes, one of the most significant being the replacement of chlorofluorocarbons (CFCs) by cyclopentane as the blowing agent in the production of the pipes because of the adverse effect of CFCs on the stratospheric ozone layer. In recent years, an oxygen barrier has been introduced to stop the diffusion of air into the PUR foam and to retard its degradation. Another development is twin DH pipes where both supply and return flow pipes are placed within a single casing. Twin pipes can save space and costs, but they were outside the scope of this work. Persson [11] presents thermal models for both single and twin pipes.

There are two main techniques for the large-scale manufacture of pre-insulated DH pipes, discontinuous and continuous production. Traditionally, the pipes are produced one by one, where the PUR foam is injected between the steel and casing pipes. When the pipes are produced continuously, the foam is sprayed onto the surface of the steel pipe and the casing pipe is then

extruded directly onto the PUR foam. Kellner [12] describes both techniques in more detail. Most of the DH pipes tested in this project were produced by Powerpipe AB in Gothenburg using a traditional discontinuous method.

2.1 Thermal performance

Rigid PUR foam is a material designed to conduct as little heat as possible. It is a very versatile material used in many applications thanks to its excellent thermal and mechanical properties and its long-term stability. The foam is made by mixing two chemicals, polyol and diisocyanate, with a physical blowing agent, surfactant, and catalyst. Several reactions occur simultaneously, the most important being polymerisation and foaming reactions. The polymerisation is the result of a condensation reaction between polyol and isocyanate, and the blowing agent is responsible for expanding the polymer into a foam. The carbon dioxide formed in the reaction is involved in the foaming process [13]. Many chemical groups such as esters, ethers, and aromatic rings can be found in the foam structure. This makes it possible to customise the material to obtain the desired properties. The process is exothermic and this vaporises the blowing agent, cyclopentane, creating bubbles, which are trapped inside a honeycomb cell structure that is a vital part of the PUR foam, contributing to its thermal performance [14]. The thermal conductivity of the gas accounts for almost 50% of the thermal conductivity of the foam. Cyclopentane has a thermal conductivity of 0.013 W/mK at 25°C.

Rigid PUR foams for DH pipes consist mostly of closed cells with trapped insulating gas (cyclopentane and carbon dioxide). The cells have a diameter of 200 to 400 μm, with two principal structures: polymeric membranes forming the cell walls, and the intersection of several cells forming a polymer edge, as shown in Figure 2.1. PUR foams consist to 92–98% of closed cells containing insulating gas, and the rest is solid PUR polymer [15]. Depending on the production technique, the foam grows inside the pipe in all directions, affecting the cell size, elongation, and consequently also the foam properties [16].

According to the EN253 standard, the maximum initial thermal conductivity of the PUR foam should not exceed 0.029 W/(m K) at 50°C. It is usually measured using a guarded end apparatus [5]. Modern PUR foams often have values lower than 0.029 W/(m K), but this value may change slightly due to the migration of gases into or out of the foam. In the short-term, car-
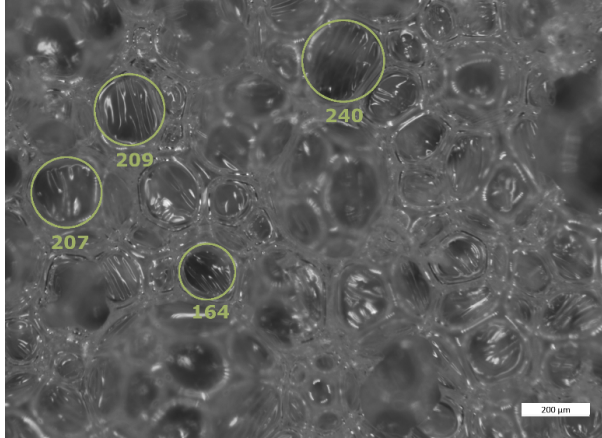
Figure 2.1: Photomicrograph of an unaged PUR sample showing four cells with diameters of 164, 207, 209 and 240 μm, respectively.

bon dioxide will diffuse out and be replaced by air. Air has a higher thermal conductivity than carbon dioxide, and consequently, the foam thermal conductivity will also increase. In the long-term, the blowing agent may diffuse very slowly out of the foam, which acts as a diffusion barrier. A casing pipe made of HDPE is a good barrier to the diffusion of both air and carbon dioxide. Because the pipes are buried in the ground, the soil acts as an insulator and the presence of air is limited.

An increase of about 10% in the thermal conductivity over a period of 30 years has been reported [11].

2.2 Mechanical performance

Because the pipes are installed underground, the casing pipe must support an external load and protect the insulation layer from moisture. Several failure mechanisms have been observed in the casing pipe, e.g. slow crack growth, rapid crack propagation, and thermal degradation, but these are outside the scope of this project. Nilsson studied some of these modes of failure [17].

Good adhesion of the PUR foam to both the casing and service pipes is essential for the functionality of the DH network. The foam is expected to

limit movement of the steel service pipe and to prevent damage to the network, especially at joints and bends. The adhesion between the PUR foam and the steel service pipe was the main focus of this work. This interface is exposed to the highest temperatures and will deteriorate faster than the other components, leading to an inadequate thermal and mechanical performance of the DH network. The minimum requirements of shear strength in both unaged and aged conditions are shown in Table 2.1.

Standardised axial and tangential shear strength tests are described in the EN253 standard, but we used a method designed at RISE, called the RISE plug method, which can be applied in the laboratory or directly in the field [18]. The RISE method is described in Chapter 3.

Table 2.1: Minimum shear strength requirement [5].

Test temperature [°C]	Shear strength [MPa]	
	Unaged	Aged
23 ± 2	0.12	45% of initial value and 0.12
140 ± 2	0.08	0.08

2.3 Failures and degradation mechanisms

Leakage and heat loss are the most common types of failure observed in DH systems. Leakage can start at the casing pipe or the steel service pipe. External leakage occurs when water finds its way through the casing pipe, e.g. at points between pipes or joints, and reaches the PUR foam, which is sensitive to hydrolytic degradation. Internal leakage occurs when the steel service pipe fails, and hot pressurised water reaches the PUR foam. This type of failure is severe and affects the system immediately due to heat loss and to a decrease in pressure. In both cases, the moisture increases the risk of degradation of the PUR foam and corrosion of the steel service pipe [17].

If no leakage or failure occurs, the DH pipe is expected to suffer only the natural ageing driven by the operating temperature, so that the components deteriorate and eventually become useless. The lifetime ends when essential features reach a critical level and the product must be replaced. The most sensitive component in a DH pipe is the PUR foam, which is susceptible to

degradation by both thermal and oxidation mechanisms. If the pipes are produced correctly, and the installation is carried out appropriately, the long-term thermo-oxidative process, in combination with mechanical loads, will determine the technical lifetime of the pipe.

A crucial factor is the stability of the PUR foam and the time–temperature limits under which the PUR foam can be used without any significant damage or loss. The degradation of a PUR foam is generally understood to occur in three phases. First, volatile material is released, after which the PUR foam structure and morphology deteriorate. Finally, the PUR foam network breaks down, as described by Chattopadhyay et al. [19].

In this work, we have studied the impact of physical and chemical phenomena on the degradation of DH pipes, especially on the PUR foam, evaluating both thermal and mechanical performance, and changes in the chemical structure.

CHAPTER 3

Experimental methods

The properties of polymers, like those of other materials, deteriorate with time under operating conditions. This phenomenon is known as ageing. Typically, the natural ageing of DH pipes takes several years, so that accelerated ageing methods are required to deteriorate the material within a reasonable time frame to estimate their service lifetime. It is well known that exposure to an elevated temperature accelerates the degradation process, but it is agreed that tests should be performed carefully to avoid degradation mechanisms that differ from those involved in natural ageing.

Many factors can affect the ageing of DH pipes, especially the natural ageing of the PUR foam. The temperature fluctuates depending on the season and on the working conditions of the network, and the composition and morphology of the insulating foam have been changed in the last decades.

In this chapter, the different test methods used to evaluate the DH pipes, considering the PUR foam as the weakest component, are explained and discussed.

3.1 Artificial ageing

Accelerated ageing is a laboratory test procedure, frequently used to hasten the thermal degradation of a polymeric material and to predict the service life using the Arrhenius relationship. The mechanisms involved in accelerated ageing tests should be similar to the mechanisms observed in natural ageing under operating conditions. Accelerated ageing involves the use of a temperature higher than the operating temperature and at the same time a property relevant for the satisfactory function of the product is studied until the property reaches a critical level. It is important to choose an appropriate temperature to induce the relevant degradation mechanism.

3.1.1 Rigid polyurethane

In the first part of the project, we studied the degradation of ELASTOPOR H 2130/79/OT PUR foam, prepared from polyether polyol, diisocyanate IsoP-MDI 92140 (BASF) and cyclopentane. The foam density was between 67 and 70 kg/m^3. This PUR foam is used to produce standard pipes by Powerpipe Systems AB. A block of PUR foam was also produced using the same commercial mixture under ideal conditions, to obtain a cell structure with a more uniform cell size and a more uniform density distribution than in ordinary foam. The dimensions of the block were 250 x 250 x 150 mm.

For this experiment, rectangular samples were cut from ordinary PUR foam (called o-PUR) obtained directly from DH pipes and from the ideal PUR block (called i-PUR), as shown in Figure 3.1. The samples were placed in ovens at 150 ± 2°C, in two different environments, air and nitrogen. The experimental design is shown in Table 3.1.

Figure 3.1: Rectangular PUR foam sample with dimensions 114 x 19 x 18 mm.

In the nitrogen environment, the samples were free to expand without any

restriction, but, in the air environment, the samples were divided into three groups. One group was placed in aluminium boxes to restrain the expansion, one group was placed in boxes that had holes to increase the amount of air that could diffuse into the samples, and one group was placed freely to allow expansion in the air environment. The i-PUR samples were aged only in the air environment. Figure 3.2 shows the test set-up.

Table 3.1: Experimental design for testing the ordinary and ideal PUR samples.

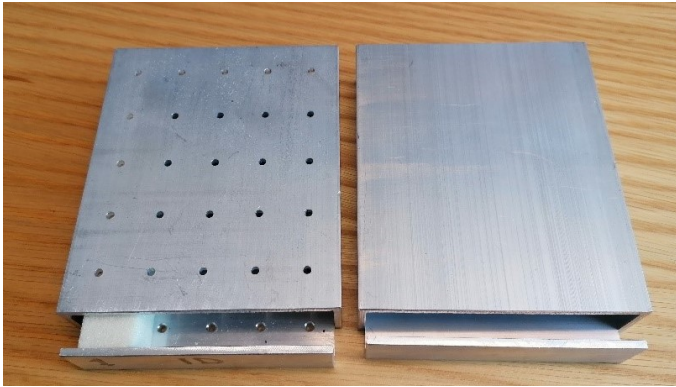|	o-PUR		i-PUR
	Air	**N$_2$**	**Air**
Free to expand	x	x	x
Box with holes	x		x
Box without hols	x		x

Figure 3.2: Aluminium boxes with and without holes for the ageing of PUR foam samples.

The total ageing time was eight weeks and samples were withdrawn for testing after 1, 2, 4, and 8 weeks to measure their size and to determine their weight.

A three-point bending test was performed with a universal testing machine to evaluate the force at break and how it was affected by the accelerated ageing, as shown in Figure 3.3. The chemical structure was analysed using FTIR, and the gas composition by gas chromatography with tandem mass

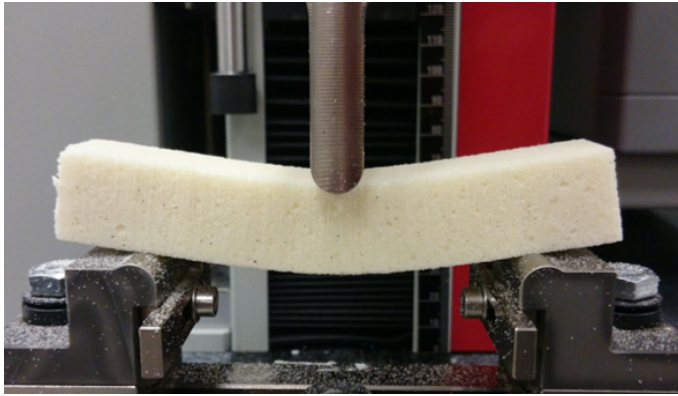spectrometry (GC–MS). Paper I describes the experiments in more detail.

Figure 3.3: Three-point bending test on a PUR foam sample.

3.1.2 DH pipes

The PUR foam in the DH pipes deteriorates more slowly than the o-PUR and i-PUR samples aged artificially in the laboratory where the entire material was exposed to the same high temperature. In DH pipes, only a thin layer nearest to the steel service pipe is exposed to this high temperature. The degradation of the PUR foam in the DH pipes was investigated, with special attention to the PUR surface in contact with the steel service pipe, which was exposed to the highest temperatures. Because the temperature gradient is distributed radially, the PUR foam close to the casing pipe is exposed to almost the same temperature as room temperature.

Several DH pipes were aged in a chamber with a controlled temperature of $23 \pm 2°C$. An electrical source was connected to the steel pipe and it was controlled to deliver the necessary power to achieve the desired ageing temperature.

In the first experiment, three DH pipes DN50/160 were placed in the chamber, and the desired ageing temperatures were 130, 150, and 170°C. Figure 3.4 shows the experimental set-up. The lowest temperature, 130°C, was chosen to be close to the highest temperature prevailing in a DH network. The highest temperature, 170°C, is recommended for accelerated ageing of DH pipes in the

EN253 standard. The temperature of 150°C was chosen to be intermediate between the highest and lowest temperatures. A reference pipe was kept at room temperature. Two properties were measured during the ageing time, adhesion strength and thermal conductivity, and two sensors were installed at distances of 5 and 30 mm from the steel service pipe in the radial direction to measure the thermal conductivity, as shown in Figure 2 in Paper II. Three thermocouple type K sensors were placed along each pipe to monitor the ageing temperature.
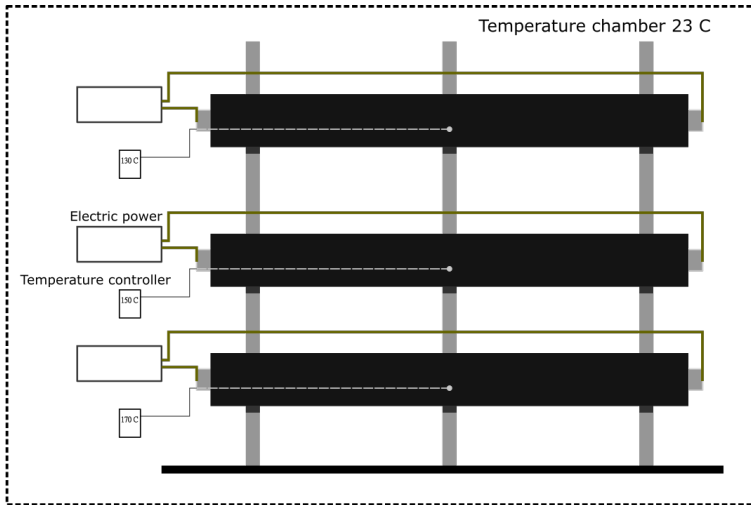

Figure 3.4: Sketch of DH pipes arranged in the temperature chamber in the first accelerated ageing experiment.

In the second experiment, the effects of both temperature and cyclic axial loads on the degradation of the PUR foam were studied. Two temperatures were chosen, 130 and 140°C. Ageing at 150°C and higher temperatures was excluded because of the results obtained in the first experiment and explained in Paper II. An axial load of up to 20 kN with a cycle time of one hour was applied to the steel pipe. Figure 3.5 shows the test rig for the cyclic axial loading. We hypothesised that the combination of a thermal and a mechanical load should further accelerate the degradation of the pipes. The adhesion strength was measured to determine the degradation level of the pipes. More details can be found in Chapter 4 and Paper IV.
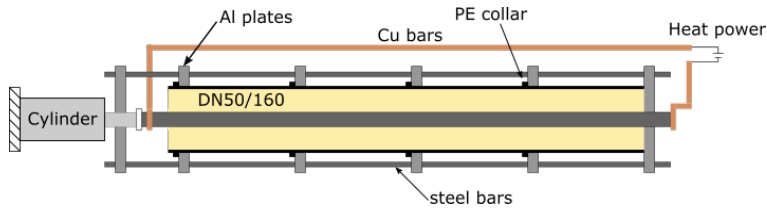
Figure 3.5: The test rig used to combine thermal and mechanical axial loads in the second ageing experiment [Figure 1 in Paper IV].

3.2 Natural ageing

DH pipes in use are exposed to temperature variations due to changing operating conditions and seasons. These temperature variations lead to motions of the steel pipe, which affect the adhesion strength between the PUR foam and the steel pipe. Other factors, such as inappropriate installation, cracking of the casing pipe or failure of the joints can also affect the performance of the DH pipes and lead to failure and a consequent need to replace the pipes. However, these factors were not investigated in the present work.

To verify the results obtained from the accelerated ageing, a comparison between the natural and artificial ageing of pipes is necessary.

Several pipes that had been in service for different periods were collected and sent to the RISE laboratory to test their adhesion strength and analyse their chemical structure, to compare the degradation associated with natural ageing with the degradation caused by accelerated ageing in the laboratory, although the naturally aged pipes differed in composition and manufacturing process. The results are presented and discussed in Paper III.

3.3 Evaluations

To evaluate the deterioration in properties caused by the accelerated ageing conditions, the adhesion strength, thermal conductivity, and chemical structure of PUR foam were determined.

3.3.1 Thermal conductivity

To measure the thermal conductivity, a transient plane source (TPS) technique developed by Gustafsson [20] was used instead of the guarded hot pipe (GHP) method described in the EN253 standard. The TPS technique is a standard method, but not for DH pipes [21].

Two sensors were installed before foaming on the steel pipe of four DH pipes that were later aged as described in Section 3.1.2. Figure 2 in Paper II shows the TPS sensors installed on the DH pipes. These sensors act both as a heat source and as a measuring device. These sensors act both as a heat source and as a measuring device. They send out a signal to heat a small area around the sensor, and, after a short time, they measure the response in the form of a change in the resistance. The total measuring time was about 10 min, making it a much faster method than the GHP technique. However, this method measures the thermal conductivity locally in only a small area. Two sensors were therefore placed at 5 and 30 mm from the service pipe radially, to obtain further information regarding the deterioration due to the temperature gradient through the PUR foam. The sensors were marked SenT_1 and SenT_2, where T corresponded to the ageing temperature (130, 150 or 170°C), and 1 and 2 to the distance of 5 mm and 30 mm, respectively.

3.3.2 Adhesion strength

Adhesion between the PUR foam and the steel service pipe is essential for the good functioning of DH pipes. If this adhesion is lost, the DH pipes can fail. To study this property, a method developed at RISE and called the RISE plug method was used. This method was first described by Sällström [18] and developed further in this project. The adhesion strength is determined with a cylindrical test sample still adhering to the service pipe, the torque required to remove the PUR cylinder from the steel service pipe being measured with a torque transducer, as shown in Figure 3.6. Full details about the test procedure are given in Paper II.

Where possible, three measurements were made at different positions around and along the pipe, and the average PUR adhesion strength was calculated. Compared with the standard axial shear strength test method, the plug method has some advantages and disadvantages. It is much faster and easier to implement, and many measurements can be performed in a small area, but the

torque is applied to a relatively small region resulting in larger scatter of the results due to local inhomogeneities.
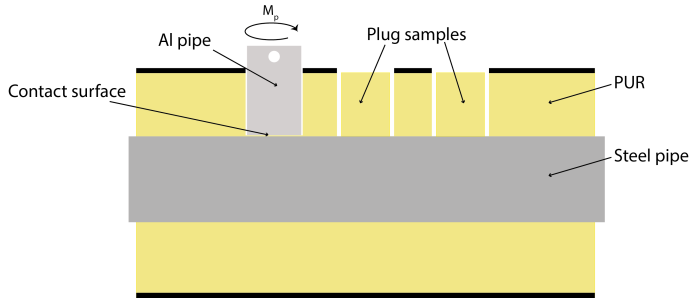

Figure 3.6: Sketch of the RISE plug method.

An electrical torque transducer was used to apply the torque with a constant angular velocity and to measure the maximum torque at break. This method was used to measure the adhesion strength of both artificially and naturally aged DH pipes and to obtain as much data as possible for comparison. The test rig was also modified so that measurements could be made directly on pipes that are still in service.

3.3.3 Infra-red spectroscopy

FTIR is a well-known technique used to identify chemical bonds in a molecule. It effectively produces a molecular fingerprint of the studied material, with a spectrum consisting of absorption peaks that correspond to the frequency of vibration of specific bonds in the material. In this project, an attenuated total reflection (ATR) technique was used, where the sample is placed on a small crystal such as zinc selenide, germanium, or a diamond with a high reflection index. ATR is a simple method based on internal reflect in the crystal, and the refractive index of the reference crystal must be higher than that of the test sample [22]. ATR provides a convenient technique for obtaining local IR spectra from PUR foam. The transmission technique was also considered, but the sample preparation was too time-consuming and did not deliver a better-quality spectrum.

A micro-ATR module with a single reflection diamond was used to study changes in the peaks of the PUR foam due to the different treatments and

to analyse PUR samples from all the DH pipes studied. At least three measurements were made on each sample. The main parameter settings were, in general, the averaging of 32 spectra with a resolution of 4 cm^{-1}. The background spectrum was refreshed every two hours.

Figure 3.7 shows the spectra of unaged and aged PUR samples. To make the changes easier to assess, the relevant peaks were normalised with respect to the reference peak at 1595 cm^{-1} corresponding to the vibration of C=C bond in the aromatic rings, which are thermally stable, was chosen. Particular attention was paid to the peaks at 1712 cm^{-1} for the C=O bond and 1512 cm^{-1} for the N-H bond in the urethane linkage, to indicate degradation of the PUR foam. Indexes of absorbance were obtained and plotted as a function of ageing time. This methodology was used in Papers I–IV.
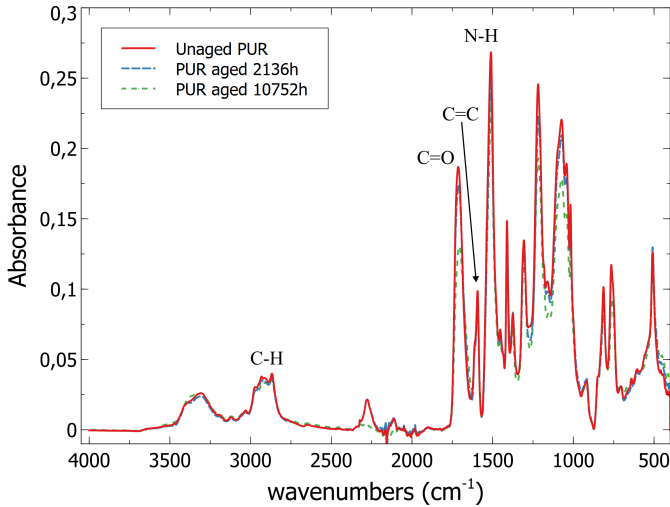

Figure 3.7: FTIR spectra of unaged and aged samples.

3.3.4 GC–MS analysis

The cell gases in the PUR foam must be analysed to investigate the deterioration in thermal insulating capacity. Olsson et al. studied both gas composition and diffusion in DH pipes [23]–[25]. We used a tandem GC–MS method to analyse the gases in the PUR foam. The critical step in this procedure was

to extract all the cell gases without altering their characteristics. To achieve this, the PUR samples were placed in a vial containing lead pellets and liquid nitrogen, and the foam cells were crushed by shaking the vial for a few minutes. The volatile compounds were then analysed. This test was performed only once to determine the gas composition in aged and unaged samples. The results are published in Paper I.

3.3.5 Accelerated thermal ageing in an oxygen-free atmosphere

We also subjected samples to accelerated ageing in an inert atmosphere to study the effect of oxygen on the degradation mechanism.

In the first experiment, cross-sectional discs were cut from a DH pipe and placed in a desiccator connected to a supply of nitrogen gas. The desiccator was placed in a chamber at 150°C, and after a certain ageing time the discs were removed from the oven. Three triangular pieces were cut from the PUR foam as shown in Figure 2a in Paper I. A load was applied on the triangle approximately 30 mm from the service pipe and the maximum force needed to separate the sample from the steel pipe was registered.

In the second experiment, a pipe with a length of 1 m was placed inside an aluminium cylinder, which was 10 cm greater in diameter and length than the tested pipe. The cylinder was first connected to a supply of nitrogen gas with a low flow to expel any remaining air from the cylinder and to create an inert atmosphere inside the cylinder and the pipe was then heated using the method described in Section 3.1.2. Figure 3.8 shows the test set-up. After 5, 10, 15, and 20 weeks, the adhesion strength was measured to determine the degree of degradation.
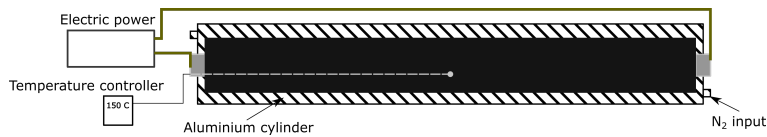

Figure 3.8: Sketch of the test set-up for accelerated ageing of a DH pipe in an inert environment.

CHAPTER **4**

Summary of the results

In this section, the results obtained from the different experiments, explained in Chapter 3, are presented and discussed.

4.1 Accelerated ageing of PUR

The effects of the presence and absence of air on the accelerated ageing of the PUR foam at 150°C were studied. An intense change in the colour of the samples when they were aged in air was the first observation made, as shown in Figure 4.1.

Ageing in an inert nitrogen environment led to no remarkable change except for a small decrease in the weight of the samples, probably due to loss of volatile components that diffused out from the PUR foam. In contrast, changes in the dimensions and weight were observed in addition to the discolouration of PUR samples aged in air. In the case of the PUR samples marked o-PUR and i-PUR, the measurements of weight and dimensions showed some differences in behaviour between the o-PUR and i-PUR samples at the beginning of the ageing. The i-PUR was produced in a more controlled manner, which probably gave it a more homogeneous PUR morphology, mak-

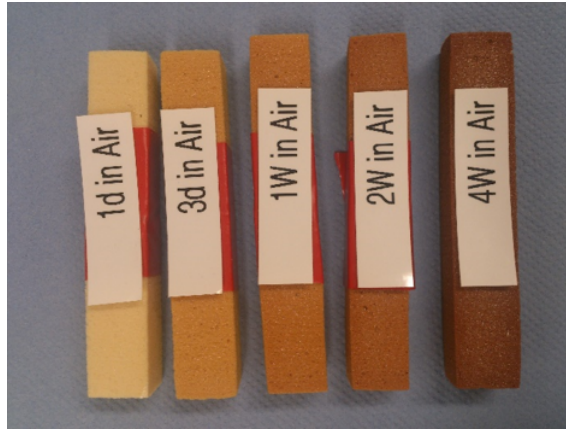ing its structure more stable, as explained by Kellner [26].

Figure 4.1: PUR samples aged at 150°C in air shows a progressive change in the colour with increasing ageing time.

The force needed to break the samples in a three-point bending test after different ageing times is shown in Figure 4.2. Each point is the average of five measurements and the values are normalised with respect to a reference value measured on unaged samples. The breaking force did not decrease with increasing ageing time regardless of the ageing condition. This breaking force is a measure of the cohesion strength of the PUR foam and is not related to the strength of the adhesion between the PUR foam and the steel pipe. To clarify this difference, a single-point bending test was performed on triangular PUR samples still attached to the steel pipe aged at 150°C in a nitrogen environment, as described in Section 3.3.5. Figure 4.3 shows that the force measured in the single-point bending test decreased by 40% after approximately 20 days and remained at this level after 90 days, whereas the breaking force measured by the three-point bending test decreased by only about 7% and remained at the same level for almost 60 days.

Regarding the accelerated ageing of PUR foam, we concluded that oxygen plays an essential role in the degradation of the foam. Samples aged in air showed significant changes in almost all properties, but not in the cohesion strength. On the other hand, samples aged in an inert environment presented insignificant changes. However, disc samples aged in nitrogen exhibited a

decrease in the adhesion strength. Consequently, a thermo-oxidative process did not cause this loss as the exposure was performed in an inert environment.
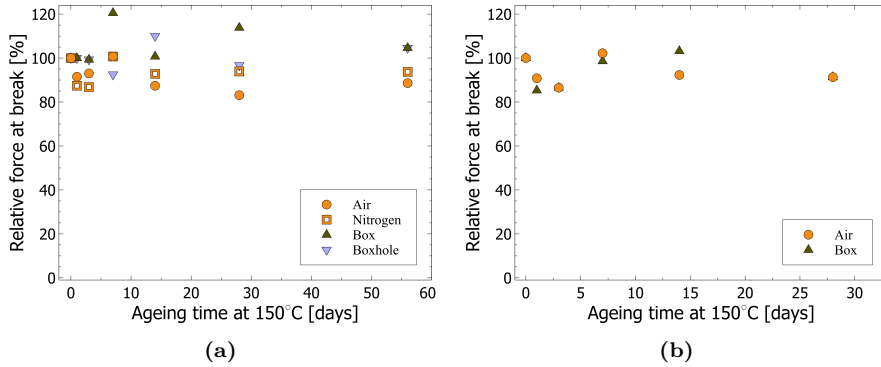

Figure 4.2: Relative force at break in a three-point bending test after different ageing times in different environments. (a) o-PUR foam and (b) i-PUR foam [Figure 8 in Paper I].
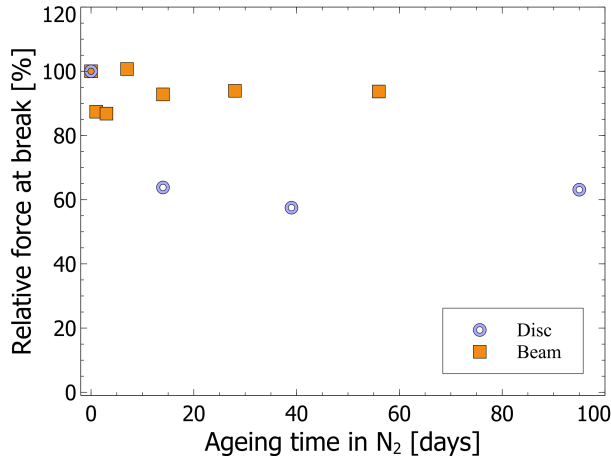

Figure 4.3: Comparison between the force at break measured in the single-point bending test and in the three-point bending test on PUR samples aged at 150°C in nitrogen [Figure 9 in Paper I].

Changes in the chemical structure of the PUR foam were studied using

the micro-ATR technique, focusing on the intensities of the absorbance peaks for the C=O bond at 1712 cm^{-1} and 1512 cm^{-1} (N–H bond), which are sensitive to oxidative degradation, as shown in Figure 4.4. These bonds are parts of the urethane linkage and any decrease in their absorbance is a sign of degradation of the PUR foam. Other peaks of interest, e.g. the C—H bond in CH$_2$ at 2975 cm^{-1}, the NCO group at 2277 cm^{-1} and the isocyanurate group at 1411 cm^{-1}, were also studied as an indication of degradation. The peak corresponding to the NCO group showed that extra isocyanate had been added during production to ensure that all the polyol had been consumed. The intensity of this peak decreased rapidly at the beginning of the ageing because isocyanate reacts with itself when heated. PUR foam with an excess of isocyanate also contains a significant amount of isocyanurate, which increases the thermal stability of the foam. Samples aged in nitrogen did not show any remarkable changes during the ageing, as shown in Paper I.
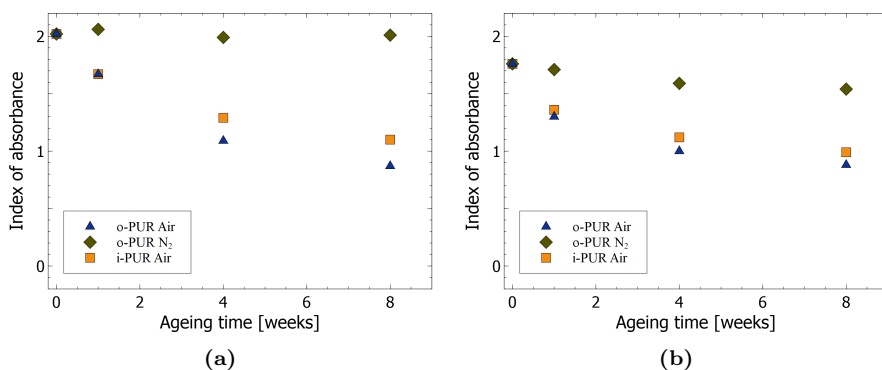

Figure 4.4: Index of absorbance of peaks (a) 1512 cm^{-1} for the N–H bond and (b) 1712 cm^{-1} for the C=O bond.

The gas analysis indicated not only that pentane and cyclopentane were released from the PUR foam but also that the loss increased with ageing time and the presence of air, as shown in Table 4.1. The amounts of pentane and cyclopentane in the sample aged for eight weeks in nitrogen were similar to those in the unaged sample, but the sample aged in air showed a decrease in the amounts of these substances. Other volatile compounds were also detected in the sample aged in air. The gas analysis was performed only once in the present project.

Table 4.1: Results of the GC–MS analysis.

Compound	Non-aged [mg/kg]	8w in N_2 [mg/kg]	8w in air [mg/kg]
Isopentane	138	150	133
Pentane	143	148	58
Cyclopentane	4804	5536	1819
2,2,4-trimethyl1-1,3-dioxolane	<5	<5	54
2-Ethyl-4-methyl-1,3-dioxolane	<5	<5	15
5-Dimethyl-1,4-dioxane or isomer	<5	<5	44
N,N-Dimethylbenzenemethanamine	452	497	<5
Sum of all compounds	5537	6331	2123

The results show that oxygen plays an essential role in the loss of volatile substances from the PUR foam because no remarkable effects were observed in the samples, although the force needed to break the samples was contrary to our expectations. It was also observed that the force needed to separate the PUR foam from the steel pipe decreased with ageing time, even in the absence of air. Because there was no loss of volatile substances in the presence of nitrogen, it can be concluded that the molecules were too large to diffuse from the foam. It is therefore probable that they were first oxidised to smaller molecules in oxygen or that the discolouration and loss of weight of the foam were accompanied by an opening up of the structure (without any loss of strength) permitting the larger molecules to diffuse out.

The next step was to study the accelerated ageing of DH pipes.

4.2 Accelerated ageing of DH pipes

Two ageing experiments were carried out. In the first experiment, three DH pipes were aged at 130, 150, and 170°C as explained in Section 3.1.2, the pipes being marked DHP130, DHP150 and DHP170. An additional pipe was kept at room temperature and marked DHP23. The adhesion strength was measured using the RISE plug method, as explained in Paper II. The absolute shear strength values were in the range of 0.02 to 0.95 MPa and the standard deviation was between 0.0 and 0.42 MPa. Figure 4.5 shows how the adhesion

strength changed during the total ageing time, more than two years, the results here being normalised with respect to the initial value. Each point is the average of three measurements. More information can be found in the Appendix. The values obtained with the RISE plug method are presented as relative measurements to make it easy to compare the changes in different pipes.
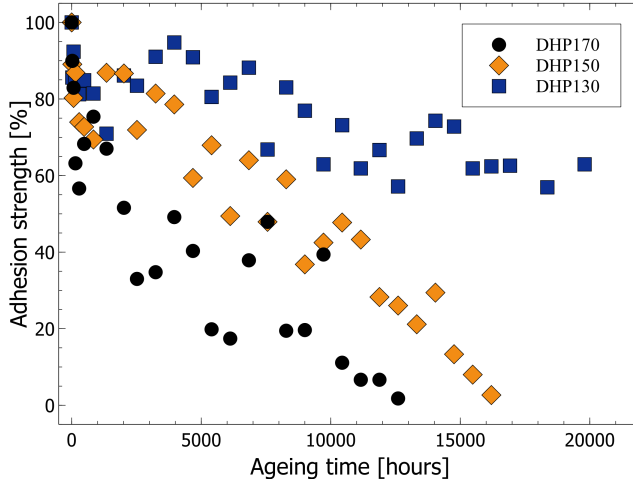

Figure 4.5: Adhesion strength measured using the RISE plug method on DHP170, DHP150, and DHP130 for more than two years [Figure 4a in Paper II].

During the initial stage, the predominant fracture mode was a cohesive fracture in the PUR sample itself, meaning that the strength of the adhesion between PUR foam and the steel pipe was still higher than the strength of the PUR sample. This stage lasted for different periods depending on the ageing temperature; the fracture mode eventually changed and become a purely adhesive failure at the contact surface between PUR foam and the steel pipe, as explained in Paper II. For DHP150 and DHP170, the adhesion strength decreased until it was entirely lost, but the process was different for DHP130. The adhesion strength decreased to approximately 60% of the original value 10 000 hours after the initial stage and then remained at a plateau value, as shown in Figure 4.5. The ageing of DHP130 was stopped after more than two years because it was not possible to take more test samples from the pipe.

The adhesion strength of the DHP23 pipe was measured only sporadically. It decreased to approximately 85% of the original value and it was used when comparing the natural and accelerated ageing, as explained in Section 4.3.

This experiment showed that elevated temperature itself affected the adhesion strength of the PUR foam. However, the trend of the results obtained for DHP130 was quite different from the results for DHP150 and DHP170. It was, therefore, not possible to apply a linear Arrhenius relationship to calculate the activation energy. According to the Arrhenius model, the adhesion strength of DHP130 should decrease to a critical level, following a similar trend as DHP150 and DHP170. This was not the case. It might be possible to use a non-Arrhenius model, defining different activation energy values, depending on the temperature, as reviewed by Celina [10].

The thermal conductivity (λ) was also measured to study the effect of ageing on this property. The measurements were made at the corresponding ageing temperatures and then at room temperature after a cooling period of at least 24 h. The results from two of the sensors placed close to the steel pipe, Sen150_1 and Sen170_1, showed significant effects of the elevated ageing temperature, especially when the measurements were performed at the corresponding ageing temperature, as presented in Paper II.

Meanwhile, the sensor placed in DHP130 behaved similarly to the sensor placed in the reference pipe kept at room temperature. The λ increased by 20—30% of the initial value and remained constant for a long time. The changes might be caused by the diffusion of carbon dioxide out of the PUR foam and diffusion of air into the foam. Here, it can be mentioned that the diffusion of gases in the DH pipe is likely retarded to a certain degree by the casing pipe. The cyclopentane is controlled mainly by the morphology of the PUR foam, as reported by Mangs [27]. This means that additional processes could cause the change of λ at the elevated temperatures besides the diffusion of gases. A possible cause might be alterations in the morphology, such as rupture of the cells due to thermo-oxidative degradation, causing losses of cyclopentane, as shown in Table 4.1.

Changes in the chemical structure of the analysed PUR foam samples confirmed the results obtained in Section 4.1. The decrease in the intensity of the peaks at 1712 cm^{-1} and 1512 cm^{-1} dshows the degradation of the urethane linkage, especially for pipes aged at 150 and 170°C, as show in Figure 4.6. A closer look at the FTIR spectra also revealed the appearance of a new

carbonyl band in the range from 1760 to 1790 cm^{-1}, which is an evidence of the oxidation process, as shown in Paper II.

The results raise the question of the choice of the ageing temperature. Ageing temperatures higher than 130°C caused significant alterations in the ageing instead of the acceleration of the degradation. This can underestimate the lifetime of the DH pipes. Nevertheless, an ageing temperature closer to the maximum operating temperature of a DH network, 130°C, could simulate the natural ageing more realistically, but the ageing time needed to obtain the desired results could be too long to be considered an accelerated method.
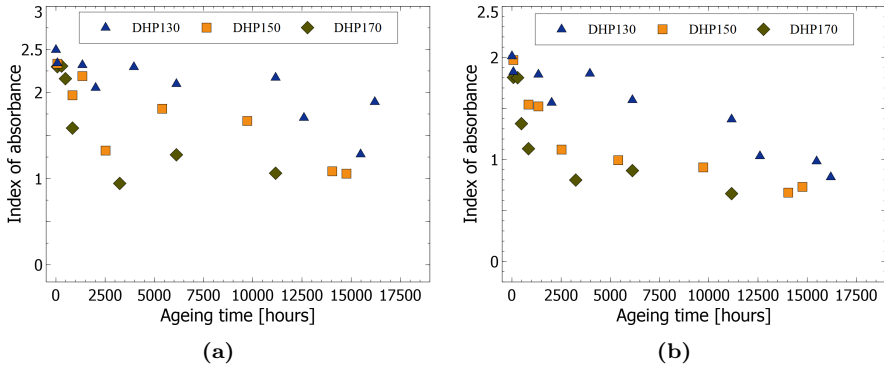

(a)   **(b)**

Figure 4.6: Index of absorbance of peaks corresponding to (a) the N-H bond at 1512 cm^{-1} and (b) the C=O bond at 1712 cm^{-1}.

4.3 Natural ageing of DH pipes

Accelerated ageing is an essential tool to predict the lifetime of DH pipes. But how accurately does this method simulate the ageing in normal operating conditions? This question was the driving force for the next part of this work.

Several DH pipes, that had been in service for more than 10 years, were collected and their mechanical and chemical properties studied. It was essential to have access to both the supply (S) and return (R) pipe. Because the R pipes had been exposed to a lower temperature, these pipes were used as a reference to compare the degradation between the S and R pipes.

Figure 4.7 compares the absolute values of the adhesion strength from the collected pipes. Three values from the pipe aged at 130°C (DHP130) in

the first experiment were added and in this case the adhesion strength from
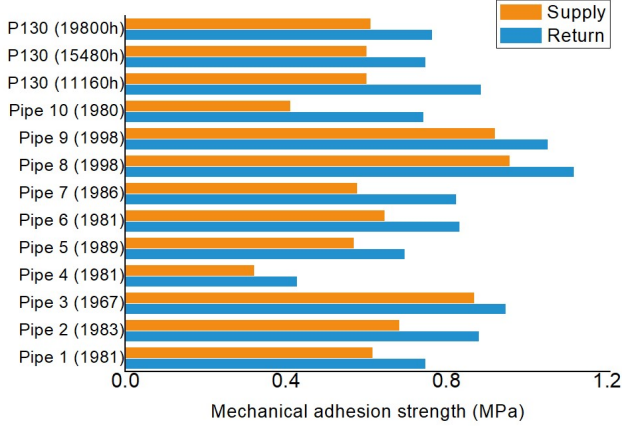DHP23 was used as the reference pipe for DHP130.

Figure 4.7: Adhesion strength measured on DH pipes aged naturally and DH pipes
aged in the laboratory at 130°C [Figure 3 in Paper III].

The adhesion strength of the R pipes, σ(R-pipe), was slightly higher than
the adhesion strength of the S pipes, σ(S-pipe), as expected. We calculated the
ratio σ(S-pipe)/σ(R-pipe) to compare the adhesion strength of the different
pipes. σ(S-pipe) was approximately 80% of σ(R-pipe).

DH pipes in service are exposed to temperature fluctuations in contrast
with the pipes aged in the laboratory, where the ageing temperature is held
constant. It was necessary to recalculate the variations of the annual tempera-
ture to some predetermined temperature intervals and then choose a common
reference operating temperature. For this matter, a 90-100°C interval was
chosen for the supply pipe based on the collected temperature data. The ac-
tivation energy (E_a) is needed to make this calculation. Unfortunately, there
is no reliable information about the values of E_a for the degradation of PUR
foam in DH pipes. Leuteritz et al. [7] suggested 95 kJ/mol for PUR foam.
Based on information found in the literature, we choose two values for the
acceleration factor (A_f), 2.0 and 2.5, corresponding to E_a equal to 70 and 103
kJ/mol, respectively, close to the reported values for polymer degradation in
the range of 90-100°C.

Using these values, we recalculated the service life of all collected DH pipes to a reference temperature of $95 \pm 5°C$ for the S-pipes and $55 \pm 5°C$ for the R pipes. The differences between the recalculated service time using A_f equal to 2.0 and 2.5 were quiet small, except for the values from DHP130, labelled Pipe 11, Pipe 12, and Pipe 13, as shown in 4.8. The calculations resulted in a service time of 26 and 56 years at 95°C for Pipe 13, depending on the A_f value used.
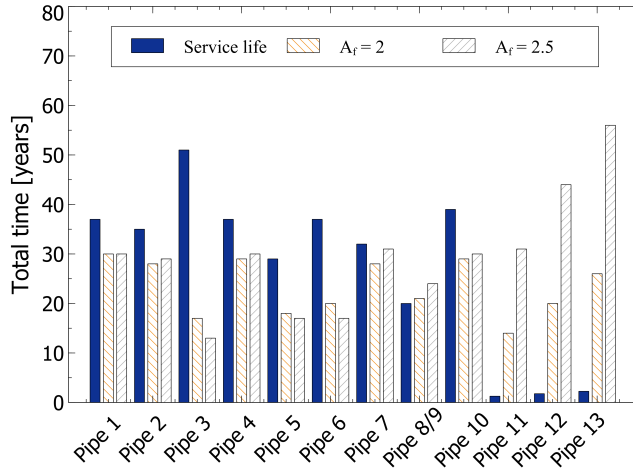

Figure 4.8: Real and recalculated service time at $95 \pm 5°C$ of supply pipes using $A_f = 2$ and $A_f = 2.5$ [Figure 6 in Paper III].

4.4 Comparison of accelerated and natural ageing

In Paper III, we recalculated the service time of the naturally aged DH pipes using two values for A_f, 2.0 and 2.5. We obtained a better fit of the results with $A_f = 2.5$. Therefore, we decided to use this value to compare how the adhesion strength of the different pipes changed.

We measured the adhesion strength and the changes in the chemical structure of both artificially and naturally aged DH pipes. The next step was to compare the results obtained and to use this data to predict the lifetime of DH pipes. Figure 4.9 shows a plot of the ratio $\sigma(\text{S-pipe})/\sigma(\text{R-pipe})$ and

the calculated service times with $A_f = 2.5$. Most of the points are located between 70% and 90% and independent of the recalculated time. Only one measurement was outside this range. The PUR foam of this pipe could be damaged due to leakage, but we did not receive enough information to confirm this. Three points from DHP130 were also added to Figure 4.9 and showed that the results from the accelerated ageing at 130°C were consistent with the results from the naturally aged DH pipes.
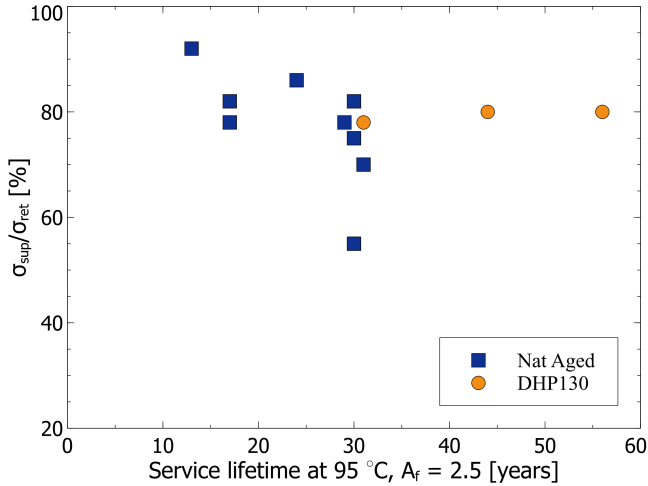

Figure 4.9: Adhesion strength ratio as a function of the calculated service time at 95°C using $A_f = 2.5$.

According to this result, the strength of the adhesion between the PUR foam and the steel pipe in a DH pipe that is operated continuously at 95°C for 56 years will decrease to 80%. It is noteworthy that other external factors can damage or alter the functionality of the DH pipes and end its service time earlier.

Changes in the chemical structures were also investigated, especially the intensity of the peaks located at 1512 and 1712 cm^{-1}. The absorbance of these peaks from the R pipes presented very small changes due to the low operating temperatures, as shown in Paper III. The results from the S pipes showed more remarkable changes. Some measurements from DHP130 were also added to the plot and using $A_f = 2.5$ we again obtained a better fit

of the results. Figure 4.10 suggests what can happen if the DH pipes are operated at 95°C for 56 years.
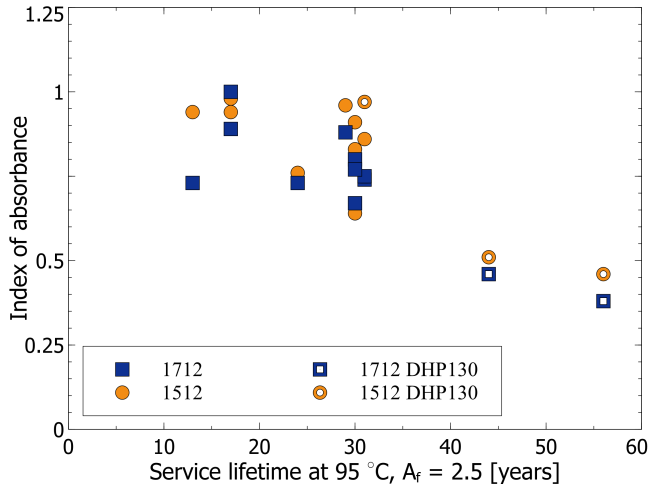

Figure 4.10: Index of absorbance from S pipes and three points from DHP130 for peaks at 1512 and 1712 cm^{-1}.

Accelerated ageing at 130°C caused a further degradation of PUR foam as indicated by the decrease of the index of absorbance. Meanwhile, the adhesion strength remained unchanged, as shown previously in Figure 4.9. This finding suggests that the IR analysis could be useful to find indications of degradation in an early stage before the loss of the adhesion strength.

4.5 Combination of thermal and mechanical loads

Another accelerated ageing experiment was designed to combine elevated temperatures with mechanical loads. This combination should be closer to the real operating conditions that a pipe is exposed to in a DH network. For this experiment, two temperatures, 130 and 140°C, were chosen. An axial load of 20 kN was applied directly to the steel pipe, as explained in Section 3.1.2 and in Paper IV. The pipes were marked P130, P130Load, P140, and P140Load.

Figure 4.11 shows how the adhesion strength of the pipes subjected to cyclic axial loads decreased faster than for pipes without a mechanical load. The

points represent the average of three measurements. The absolute value for the adhesion strength was between 0.13 and 0.88 MPa. The standard deviation was around 0.04 to 0.24 MPa. More information can be found in the Appendix.
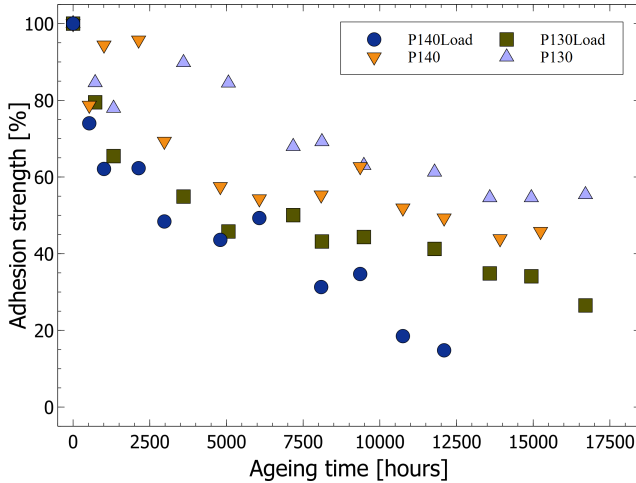

Figure 4.11: Adhesion strength measured on P140, P140Load, P130 and P130Load pipes over two years.

The adhesion strength of P140Load decreased to 15% after 12 096 hours. Similarly, the adhesion strength of P130Load decreased to 22% after 17 544 hours. Figure 4.11 shows a similar behaviour of the adhesion strength for P130 as the results presented in Figure 4.5 for DHP130. The adhesion strength decreased to approximately 60% and then entered a plateau after approximately 11 800 hours of ageing. The adhesion strength for P140 decreased also to approximately 55%, and then entered a shorter plateau after 8 088 hours. However, it seems that the adhesion strength decreased again after 12 000 hours. The 10°C difference could explain why P140 entered the plateau earlier than P130.

As previously, the FTIR analyses show a decrease in the intensity of the peaks located at 1512 and 1712 cm^{-1}. In this experiment, we sliced the plug samples obtained from the RISE plug test and analysed a 2 mm thick slice taken from the surface in contact with the steel pipe, and another slice from 20 mm above the steel pipe, as explained in Paper IV. Comparing the results

presented in Figure 4.12 and Figure 4.13, we observed an additional decrease of the index of absorbance in the pipes that were stressed mechanically.

The combination of thermal and mechanical loads can be an option to simulate and accelerate the degradation of DH pipes correctly. The applied mechanical stress seems to accelerate the chemical degradation of the PUR foam samples [28]–[30]. Nevertheless, this experiment should be repeated to confirm these results.
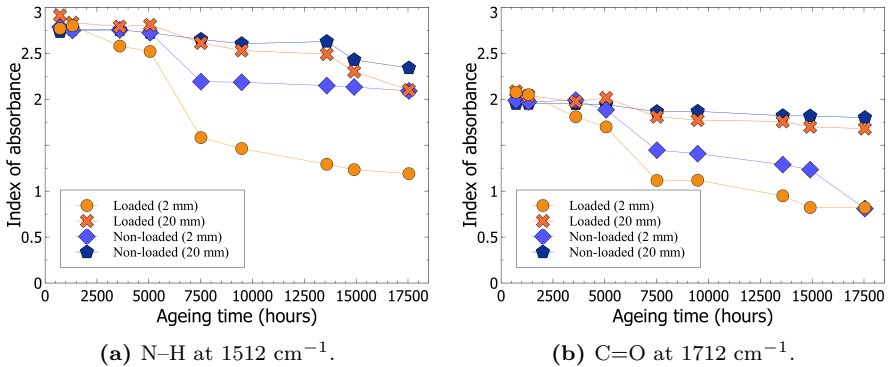

(a) N–H at 1512 cm^{-1}.   **(b)** C=O at 1712 cm^{-1}.

Figure 4.12: Index of absorbance for the peaks at 1512 cm^{-1} (a) and 1712 cm^{-1} (b) from P130 and P130Load [Figure 13 in Paper IV].

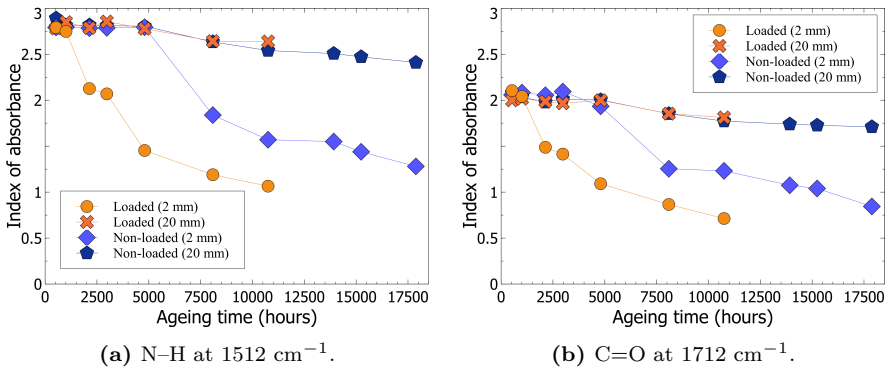**(a)** N–H at 1512 cm^{-1}.   **(b)** C=O at 1712 cm^{-1}.

Figure 4.13: Index of absorbance for the peaks at 1512 cm^{-1} (a) and 1712 cm^{-1} (b) from P140 and P140Load [Figure 14 in Paper IV].

CHAPTER 5

Concluding remarks

After the accelerated ageing of the PUR foam obtained from DH pipes, we found a correlation between the degradation and the changes in the chemical structure, using the FTIR technique to study how the absorbance of some relevant chemical bonds in the PUR foam changed due to the degradation. The results showed the urethane linkage to be prone to thermo-oxidation.

Accelerated ageing is an essential tool to assess service life. However, the ageing temperature is a difficult parameter and important to simulate the degradation correctly. Temperatures lower than 150°C for accelerated ageing showed the best results. The degradation process observed in the pipes aged in the laboratory at those temperatures was similar to the process observed in the pipes that had been in service for more than 30 years. However, accelerated ageing at those low temperatures results in a long test time, which is not practical as a laboratory method.

The combination of thermal and mechanical loads showed some potential to be considered a method for accelerated ageing of DH pipes. In addition, it is closer to the operating conditions of the current DH systems and can be relevant for the 4GDH networks. This methodology needs validation to determine the optimal parameters regarding the mechanical loads.

It seems that the lifetime of DH pipes has been underestimated by the existing standard methods. Some of the naturally aged DH pipes tested in this work had been in service for more than 30 years and the results indicated a decrease of only 20% in the adhesion strength. Apparently, these pipes could be in service for many years before their adhesion strength reaches a critical value. According to our calculation, using $A_f = 2.5$, the adhesion strength would remain at the same level for more than 50 years if the operating temperatures would be held between 90 and 100°C, which is normal in a DH network.

An objective of this work was to develop better methods to evaluate the properties of PUR foam. The RISE plug method was improved to measure the adhesion strength of DH pipes both in the laboratory and in the field. We noted, even so, there are some uncertainties in the measurements because small areas are tested, and they may contain inhomogeneities of the PUR foam. Further improvements of the RISE plug method regarding the number of measurements, uncertainty, and correlation with other test methods are needed.

FTIR, in ATR mode, was used to study the changes in the chemical structure. It was fast and handy to evaluate many PUR samples. Nevertheless, FTIR is mostly used for the identification of materials and is a qualitative method. The data normalisation made it possible to quantify the results. However, small changes in the index of absorption should be interpreted carefully. For that reason, we were most interested in the trend of the data.

The debate about the use of a linear Arrhenius relationship for the lifetime prediction of DH pipes is still open. In this project, we did not obtain the desired data to calculate the activation energy for this type of model. The adhesion strength of the pipes aged at temperatures lower than 150°C did not decrease to a critical value under a reasonable time. A non-Arrhenius approach can be interesting and probably future work.

The implementation of the 4GDH network in the near-future would introduce well-known and new materials for both the service pipe and insulation, such as cross-linked polyethylene, vacuum insulation, and expanded polystyrene. Scientists would need to understand better the degradation processes of these materials in relation to DH applications, especially when the operating temperatures will be lower than the current temperatures. However, the temperature variations will likely increase due to the use of renewable en-

ergy sources, e.g. wind, geothermal, or solar power. For this purpose, the combination of thermal and mechanical loads for accelerated ageing can be of great interest.

In this thesis, we have confirmed the effects of thermo-oxidative degradation under accelerated conditions. It involved heterogeneous degradation of the material due to different aspects that limited oxygen diffusion. In future work, the amount and rate of oxygen that diffuses into the PUR foam should be measured directly.

APPENDIX A

Appendix

The RISE plug method, used to measure the adhesion strength of the PUR foam in this project, is applied to a smaller area compared with the standard methods, and therefore it can catch inhomogeneities of the material, resulting on significant differences between the measurements. In this section, we present the measured torque needed to separate the PUR foam from the steel service pipe, instead of the relative values presented in Chapter 4.

Every point in the figures represents the average value of three measurements. The standard deviation is also added to the figures. Equation A.1 was used to calculate the standard deviation for all points in the figures.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \tag{A.1}$$

where $\bar{x}$ is the sample's mean and n is the size of the sample. Equation A.2 was used to calculate the adhesion strength. Where M_p is the measured maximum torque and d is the diameter of the plug.

$$\tau_{tan} = \frac{16 \ \times \ M_p}{\pi \ \times \ d^3} \tag{A.2}$$

Figure A.1, Figure A.2, and Figure A.3 show the average and standard deviation of the measured torque during the adhesion strength test for DHP170, DHP150 and DHP130, respectively, from the first accelerated ageing test. The measured torque was in the range of 0.1 to 3.7 Nm. Equation A.2 gives a shear strength between 0.02 and 0.95 MPa. Comparing the figures, we found that the standard deviation was high for many measurements made on DHP170. The highest standard deviation for DHP170 was registered at 3 960 hours, 1.61 Nm (0.41 MPa). A slightly higher value was registered at 6 120 hours, 1.63 Nm (0.42 MPa), for DHP150. The highest value for DHP130 was calculated at 7 560 hours, 0.64 Nm (0.16 MPa).

Figure A.4, Figure A.5, Figure A.6 and Figure A.7 show the average values and the corresponding standard deviation for P130, P130Load, P140 and P140Load, respectively, from the second accelerated ageing test. The nominal values for the measured torque were between 0.55 and 3.44 Nm (0.13 and 0.88 MPa). The highest standard deviation was registered at 2 136 hours, 0.95 Nm (0.24 MPa), for P140Load. The standard deviation values were lower in general compared with the values obtained in the first ageing test. A reason can be the introduction of an electrical torque transducer that apply the force with the same rate every time.
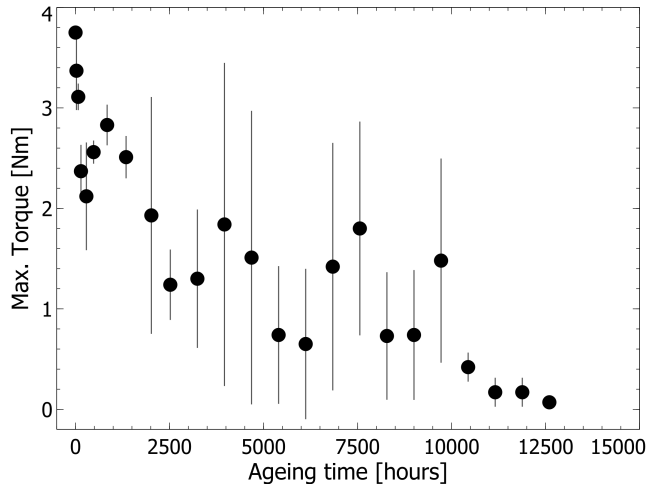

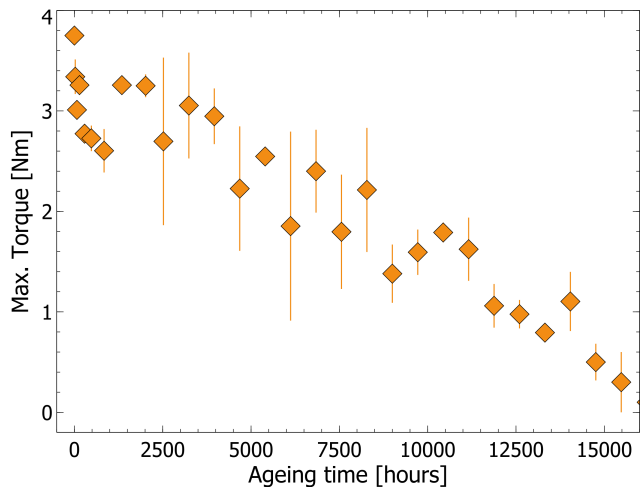**Figure A.1:** Average and standard deviation of the mechanical tests performed on DHP170.

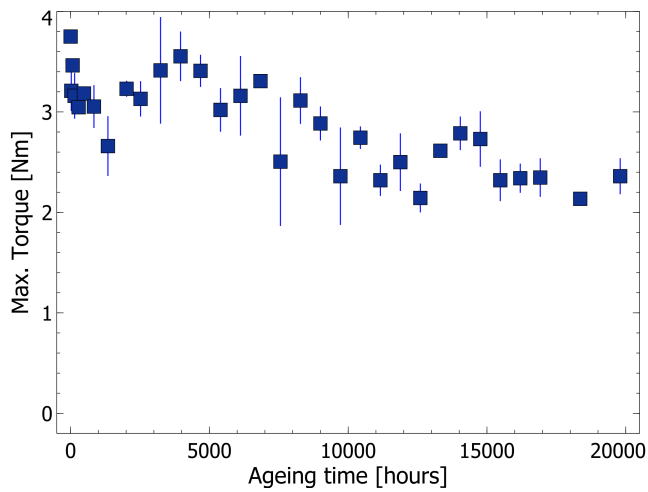**Figure A.2:** Average and standard deviation of the mechanical test performed on DHP150.

Figure A.3: Average and standard deviation of the mechanical test performed on DHP130.
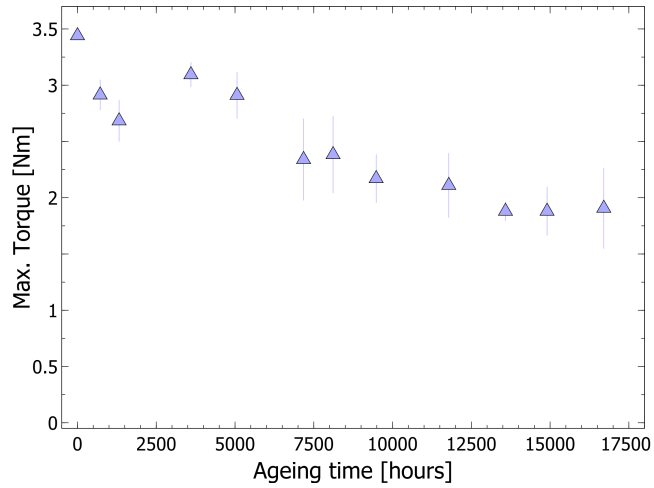
Figure A.4: Average and standard deviation of the mechanical tests performed on P130.
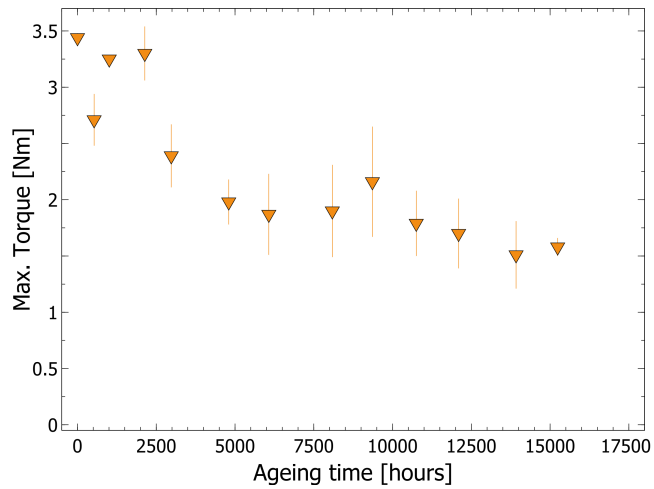

Figure A.5: Average and standard deviation of the mechanical tests performed on P140.
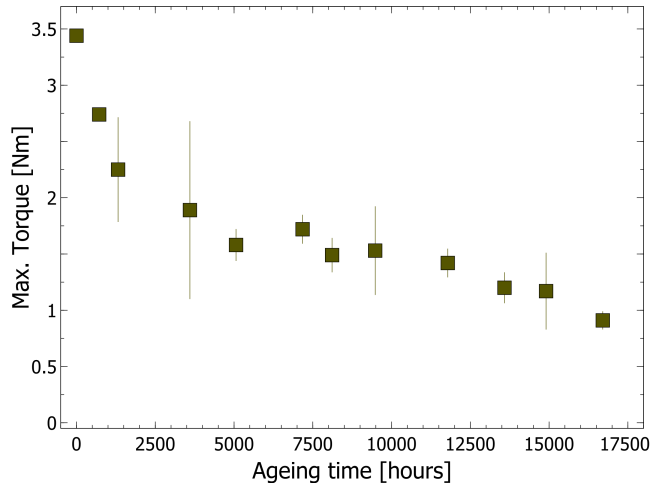
Figure A.6: Average and standard deviation of the mechanical tests performed on P130Load.
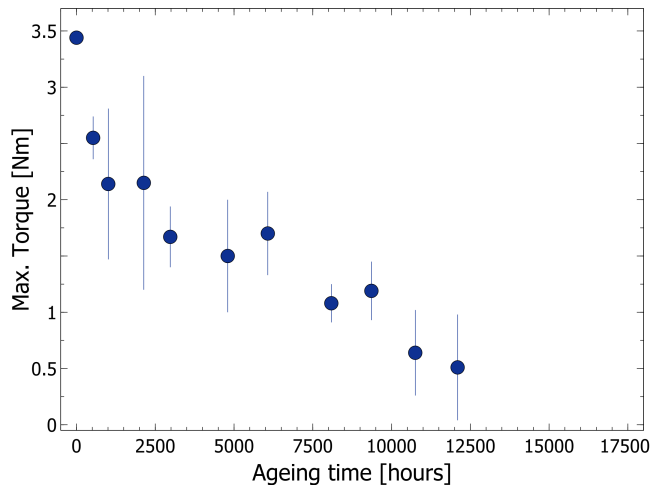

Figure A.7: Average and standard deviation of the mechanical tests performed on P140Load.

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