

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Degradation mechanisms and long-term performance of PUR
insulation in district heating pipes

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Cover:
District heating pipe after 12600 h exposed to accelerated ageing at 170 °C.

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ABSTRACT

District heating networks are used worldwide, especially in Scandinavian countries and also in many other countries, e.g. Germany, Russia, United States, South Korea and China. From an environmental point of view, district heating networks are a good alternative to more traditional building heating systems.

In 1970th, the third generation of district heating systems was established on the market, where pressurised hot water was used as a heat carrier. The heat is transported with help of pre-insulated pipes, which should have good mechanical and thermal performance in order to withstand both external and internal loads, and minimize the energy loss. These performances are normally evaluated in accordance with the European Standard EN 253. To estimate the lifetime of pipes, an accelerated thermal ageing is normally performed at higher temperatures than at normal operation.

The aim of the studies included in this thesis was to determine the parameters affecting the lifetime of district heating pipes during accelerated ageing tests. In the first part, the focus was on determining the most relevant degradation mechanisms in the insulation foam of district heating pipes. Physical and chemical properties were studied with different methods to establish the most significant degradation processes. After that, district heating pipes were subjected to accelerated ageing at three different temperatures. The results of ageing were obtained after various periods and interpreted using the key findings obtained.

It was confirmed that oxygen plays a main role in the activation of the degradation processes, being faster at higher temperatures. The most interesting results were found in the mechanical strength measurements, where the pipe aged at 130 °C behaved quite different in comparison with the pipes at 150 and 170 °C. These measurements are often used to evaluate the performance of the pipe and in the prediction of lifetime. The degradation pattern of pipes was further confirmed by the results collected from thermal conductivity measurements and analyses of the chemical structure.

Our investigation points out that accelerated ageing of pipes at too high temperatures may cause other degradation mechanisms rather than acceleration of the natural processes. This may lead to erroneous estimation of pipe lifetime, leading to incorrect assessment of the district heating networks.

Keywords: District heating pipe, rigid polyurethane foam, mechanical performance, thermal conductivity, long-term performance, degradation mechanisms

LIST OF APPENDED PAPERS

This thesis consists of an extended summary and the following appended papers, referred to by Paper A or Paper B in the text:

- Paper A** N. Yarahmadi, A. Vega, I. Jakubowicz. Accelerated ageing and degradation characteristics of rigid polyurethane foam. *Polymer Degradation and Stability* 138 (2017), 192-200
- Paper B** A. Vega, N. Yarahmadi, I. Jakubowicz. Determination of the long term performance of district heating pipes through accelerated ageing. *Polymer Degradation and Stability* Manuscript submitted for publication (2018)

Other publications related to this thesis, not included in the thesis:

- Publ. I** N. Yarahmadi, A. Vega, I. Jakubowicz. Determination of essential parameters influencing service life time of polyurethane insulation in district heating pipes. *Energy Procedia: 15th International Symposium on District Heating and Cooling, Seoul, South Korea*, 116 (2016), 320-323
- Publ. II** A. Vega, N. Yarahmadi, I. Jakubowicz. Degradation mechanisms in PUR foam of district heating pipes after accelerated ageing. *54th Nordic Polymer Days*. Stockholm, Sweden, 2017

CONTENTS

Abstract	i
List of appended papers	iii
Contents	v
1 Introduction	1
1.1 Purpose	1
1.2 Background	1
2 District heating systems	3
2.1 District heating pipes	3
2.1.1 Manufacturing of DHPs	4
2.1.2 Service pipe	5
2.1.3 Casing pipe	5
2.1.4 Insulating foam	6
2.1.5 PUR morphology and heat transport	7
2.2 Failures and degradation mechanisms	8
2.2.1 Failures of DHPs	8
2.2.2 PUR's degradation mechanisms	9
2.2.3 Service life prediction	9
3 Experimental	11
3.1 Accelerated ageing and material characterization	11
3.1.1 Ageing of PUR foam	11
3.2 Accelerated ageing of DHPs	12
3.3 Measurements	13
3.3.1 FTIR analysis	13
3.3.2 GC-MS analysis	13
3.3.3 Mechanical strength test	14
3.3.4 Thermal conductivity	14
3.4 Other tests	15
3.4.1 Adhesion strength test	15
3.4.2 Accelerated thermal ageing in nitrogen environment	15
4 Summary of results	16
4.1 Accelerated ageing of PUR foam	16
4.1.1 Accelerated thermal ageing and mechanical strength	16
4.1.2 FTIR analysis	16
4.1.3 Cell gas analysis	19
4.2 Accelerated thermal ageing of DHP	21
4.2.1 Mechanical strength	21
4.2.2 Thermal conductivity	23

4.2.3	FTIR analysis	25
4.2.4	Short DHP in N_2 environment	27
5	Conclusions	28
6	Further work	29
7	Acknowledgements	30
	References	31

1 Introduction

1.1 Purpose

The main goal of this project is to better understand the failure mechanisms of district heating pipes (DHPs) during service life to create a tool for improvement of maintenance strategy and lifetime prediction of the pre-insulated pipe.

The failure mechanisms for DHPs are closely connected to the performance of pipes, mainly the mechanical strength and thermal insulation. During service time, DHPs are often subjected to mechanical stresses from the surrounding environment but also from temperature variations depending on the season or heat demand in the cities. The thermal properties are affected by the material morphology which can change due to relative high operating temperature. The focus of the project is to analyse the degradation of the insulating foam by studying changes of physical and chemical characteristics. An accelerated ageing method, which is a well-known method for prediction of lifetime, has been used to study the long-term degradation of DHPs. An additional aim is to verify different methods that can be used to evaluate the performance of DHPs.

1.2 Background

Distribution heating (DH) systems have been developed during many centuries. The first examples were found in the antique Roma where distribution of hot water was used in thermal bath. Another distribution system used to transport hot water from geothermal points to a small town was used in France in the 14th century. However, it was at the end of the 19th century when the first district heating network was built in USA. This network relied on produced steam at a central point which was transported to different buildings in concrete ducts. Steam distribution became the most common district heating system in USA and in some countries in Europe [22]. However, engineers began to design a new DH technology that would use hot water instead of steam which was already considered not only dangerous, due to high temperature and pressure, but also an ineffective way to transport heat.

For many years, oil was the main fuel used for heat production. However, there were many countries that did not have access to oil or natural gas. This factor together with an increase in the oil price during the 1970s triggered the evolution of DH in Europe [16]. Denmark and Sweden developed a large district heating network using hot pressurized water which was heated by other energy sources than oil. This network needed a new and better piping technology.

This development resulted in a new transport medium called pre-insulated DHPs. This DHP has three components, an outer polyethylene (PE) pipe, a rigid polyurethane (PUR) foam and a steel service pipe. In such pipes, the hot water can be transported many kilometres, which subsequently relied on good insulation capacity of the pipe walls.

Energy efficiency is a big issue for sustainable development. DH system is a generally considered to be very attractive technology due to the flexibility related in heat sources and

the ability to combine heat and power generation in the same system. However, there are a couple of issues to be addressed. Firstly, in service, DHPs are subjected to external loads from the terrain and also due to internal temperature variations. Therefore, it is important to understand how the thermal and mechanical properties are affected during the technical lifetime of pipes. During recent decades, DHPs have been studied to determine their thermal and mechanical performance using different evaluation methods. Artificial thermal ageing methods have been used to accelerate the degradation mechanisms and to predict a relevant lifetime [7]. However, a big question is still unanswered: what is the well founded temperature for an accelerated thermal ageing test? Could an Arrhenius relationship be used to estimate the service lifetime including all the degradation mechanisms?

DHPs are required to have a service lifetime of around 30-50 years according to the European standard EN253 [6]. Obviously, assessing the performance of DHPs at service conditions is basically impossible. Accelerated ageing is necessary.

Another important aspect is the need to minimize energy loss during the heat transportation. For this purpose, the insulating foam plays a central role. Understanding the degradation mechanisms of the insulation rather important.

Further, based on such understanding, the evaluation method needs to be validate and such validation is a parallel task for this work.

2 District heating systems

Implementation of DH networks in high-density cities has helped our society to use the fossil fuels in more efficient ways. This also results in the reduction in CO₂ emission. DH systems comprise a network of pipes that transports heat with hot water or steam, heated at an energy centre, to other buildings in the same district. A heat interface unit is used locally in the buildings to control the hot water temperature. The water returns then to the centre for reuse. Heat production in a DH network can combine various energy sources e.g. waste heat from industries, biomass, geothermal sources, power stations, electric boilers or solar thermal arrays. Figure 2.1 shows a sketch of a district heating network. It has also been found that air quality actually improved in cities with DH systems [14, 18].

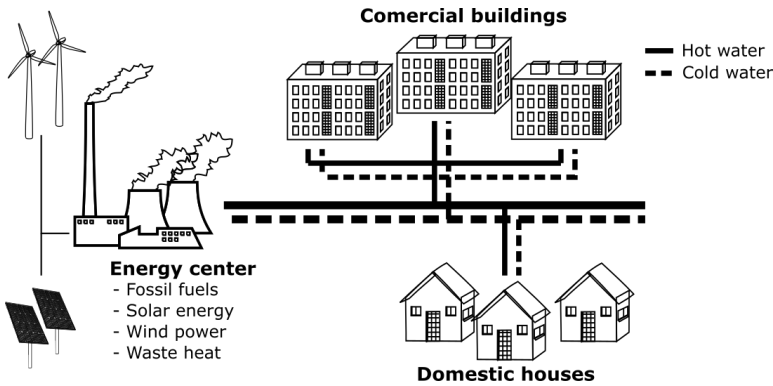


Figure 2.1: *Sketch of a district heating network.*

2.1 District heating pipes

DH networks have evolved together with the piping systems, integration of alarming systems and heat meters. The pre-insulated pipes used today were basically designed during the late 1960s and are considered the third generation. A pre-insulated pipe includes three important components: an inner service pipe made of steel for heat transport which is surrounded by a PUR foam for thermal insulation and the outer component being a casing pipe made of polyethylene for mechanical and water protection, as shown in figure 2.2. The three components are joined to each other and work as a unit so both thermal and mechanical loads are supported by the whole package.

During the last 50 years, few relevant changes have been done in the design of DHPs, but materials have been improved in some cases and new components, such as the oxygen barrier, were introduced.

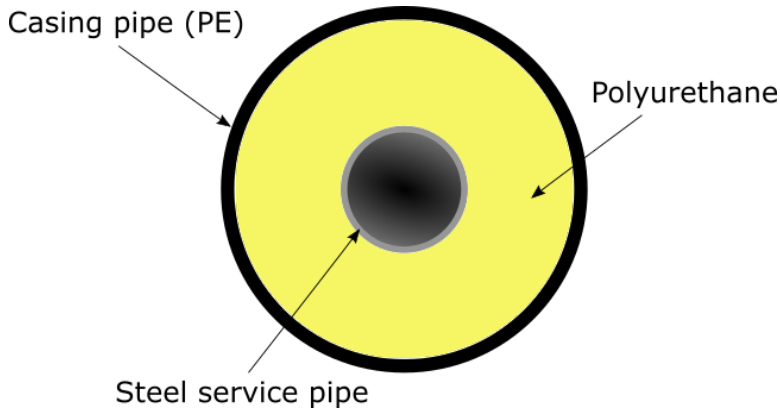


Figure 2.2: *Sketch of a district heating pipe.*

2.1.1 Manufacturing of DHPs

Two different techniques are used for large scale production of DHPs, designated as discontinuous and continuous production methods.

Discontinuous production

In discontinuous productions, the steel service pipe is first centred in the casing pipe by distance holders that are arranged around the steel pipe. At the pipe ends, the annular space between the inner pipe and the casing pipe is sealed off by end-caps. The foaming components are then injected into the annular gap to react and fill the cavity between the two pipes. There are several techniques to fill the gap cavity:

- Pour and rise technique
- Top filling technique
- Mid-point filling technique
- Lance withdrawal technique
- Pull-through technique

The three first techniques are very similar. The difference here is the insertion point of the foam material. However, it is important to control the time needed to fill the pipe completely before the system reaches the fibre time (the transition time from the liquid state to the solid state) so that the foam cells will not become elongated.

The two last techniques are a combination of the discontinuous production technique and a foam application of a continuous method [11]. The foam components are here applied directly and react very quickly. This ensures a good foam distribution.

Traditionally, DHPs have been manufactured by a discontinuous method. The main advantage of the discontinuous techniques is the relative low cost and work needed

to produce a large range of different pipe dimensions. The main disadvantage is the heterogeneous distribution of the foam material which results in variation of some physical properties in both length and radial directions, such as density and mechanical strength [11].

Continuous production

The continuous methods have two principal stages. In the first stage, the foaming material is applied directly on the steel pipe. In the second stage, a casing pipe is extruded around the foam. There are two continuous techniques:

- Continuous molding technique
- Continuous spray technique

The main advantage is the uniform foam distribution which ensures the same density and properties in the whole pipe. The production of the same dimensions is very fast and efficient. However, changing to a different pipe dimension involves rather higher costs. A further advantage is the possibility to add an oxygen barrier inside the casing pipe which will retard the degradation of PUR due to thermal oxidation

It should be stressed that in this project, only single DHPs produced with the discontinuous technique have been studied.

2.1.2 Service pipe

Steel pipes have normally been used as service pipes. In order to obtain a good adhesion between the foam and the service pipe, any trace of oil, grease or dirt should be removed from the pipe surface before the foam application according to the standard EN253 [6]. The adhesion of the foam to the service pipe is generally considered to be important and is one of the main issues investigated in this study.

Other materials than steel have also been used, motivated by specific combinations of working pressure and temperature. An example here is the fourth generation district heating and cooling pipes, where various polymer materials have been discussed to be used due to the low operational temperature.

2.1.3 Casing pipe

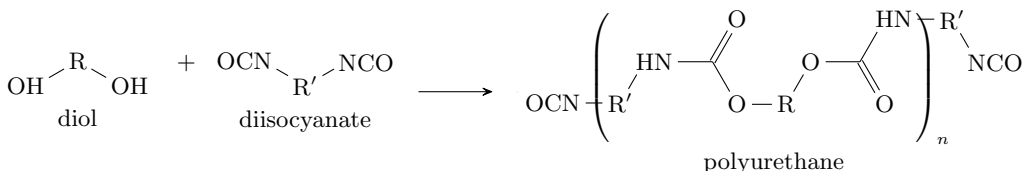
For the last 30 years, the casing pipe for DHPs has been made of high-density polyethylene (HDPE) which is one of the most widely used polymers for pipe applications. The function of the casing pipe is mainly to protect the piping system from mechanical loads and moisture. HDPE is known to be a rather good water barrier and perhaps more important shown to be rather good for protecting the whole package during production, transportation, installation and in service. During production of DHPs, the casing pipe should withstand relative high temperature and pressure without deformations.

There are also several failure mechanisms that have been observed for HDPE and should be taken into account for DH applications. Slow crack growth may appear due to stones pressed into the pipe by the surrounding environment. Also rapid crack propagation has

been observed during installation of DHP in cold conditions. Another failure mechanism is thermal oxidation, even though antioxidants are added to increase the casing pipe lifetime. There can be some parts where the insulation foam has lost almost all its capacity and high temperature can reach the casing pipe, accelerating the oxidation mechanism [17]. Carbon-black is also added to protect the casing pipe from degradation by ultraviolet radiation before place in ground.

2.1.4 Insulating foam

Rigid polyurethane (PUR) foam is the principal insulating material used in DHPs. PUR is known as a very versatile material that has been used in many different applications for thermal insulation, good mechanical performance and long-term stability. The production of PUR foam requires the three main components of a polyol, an isocyanate and a blowing agent. The blowing agent is usually added to the polyol together with other components such as activators and foam stabilizers. The reaction between the polyol and polyisocyanate results in a cross-linked material with urethane structures characterized by the urethane linkage between the repeating units. For PUR, polyols with functionality that exceed three are used. Also other components can be included e.g. catalysts, physical and/or blowing agents. The basic urethane reaction is:



Other groups can also be found in the structure such as ester, ether or aromatic rings. In the presence of certain activators, isocyanates can react to form materials with isocyanurate structures (PIR). This flexibility makes PUR interesting for producers to customize the insulation material to almost any special requirement.

The reaction between polyol and isocyanate is generally exothermic, known to reach up to 160 °C. Physical blowing agents are normally vaporized at this temperature and trapped in the cells formed. For DHPs, the polyurethane foam should have a high percentage of closed cells which would trap the vaporized blowing agent rather well. This will provide a good insulation. Different blowing agents have been used, chlorofluorocarbon (CFC) was used during many years, but it was banned due to concerns on ozon depleting effects and phase out in the 90's [21]. In order to replace CFC as the principal blowing agent, other systems such as the water blown systems were developed. Here, water is used as a blowing agent which reacts with isocyanate during foaming and generate carbon dioxide CO₂, which is trapped within the cells. This technique was used to obtain closed-cell structure foams with acceptable properties without using CFC.

Today, there are two principal foam systems which are used depending on the requirements and DHP manufacturing technique:

- Water blown systems
- Cyclopentane/water dual blowing systems

The results from both techniques are very similar. Water blown foams show a higher thermal conductivity due to the lower insulation property of CO₂ in comparison with cyclopentane or CFC. On the other hand, CO₂ has a lower molecular mass than cyclopentane and diffuses very fast out of the cell structure and the foam insulation performance decreases. In the second technique, a mixture of CO₂ and cyclopentane (CP) is found in the cells. CP has a lower thermal conductivity than CO₂ and is considered as rather environmental friendly [7]. However, liquid CP is flammable and has to be handled very carefully during DHP manufacture.

On the whole, the blowing process is quite complex and has many variables that need to be controlled simultaneously. In order to produce the cell size and orientation leading to favourable final foam properties.

2.1.5 PUR morphology and heat transport

PUR for DHPs is composed mostly of closed cells with trapped insulating gas. The cells are organized in a three dimensional mostly honeycomb structure and have a diameter between 200 and 400 μm as shown in figure 2.3. The most important cell parameters are:

- Cell wall thickness
- Cell size
- Arrangement
- Elongation
- Percentage of closed cells

The SEM, figure 2.3, shows that the cell structure is comprised of two principal structures: polymeric membranes that form the cell walls and the intersection of three cells, forming a polymer edge. The cell walls corresponds to 20 % of the volume, the rest of the foam is gas trapped in the cells [21]. Depending on the production technique used, the foam will reach the pipe end in different ways. This affects the cell size and elongation giving a variation on some properties when they are measured in parallel or perpendicular to the foaming direction [9].

The heat transport within the PUR foam can be divided into three mechanisms: heat transfer via the polymer matrix, via the gas and via thermal radiation. The total thermal conductivity of PUR, λ_{PUR} , can be described as:

$$\lambda_{PUR} = \lambda_m + \lambda_g + \lambda_r \quad (2.1)$$

which is the sum of the contribution from the polymer matrix, λ_m , gas within cells, λ_g and radiation, λ_r . The radiation is reduced by the many cells structure of the foam. Equation (2.1) is a simplified model of the heat transport and it is only valid under very specific conditions [2].

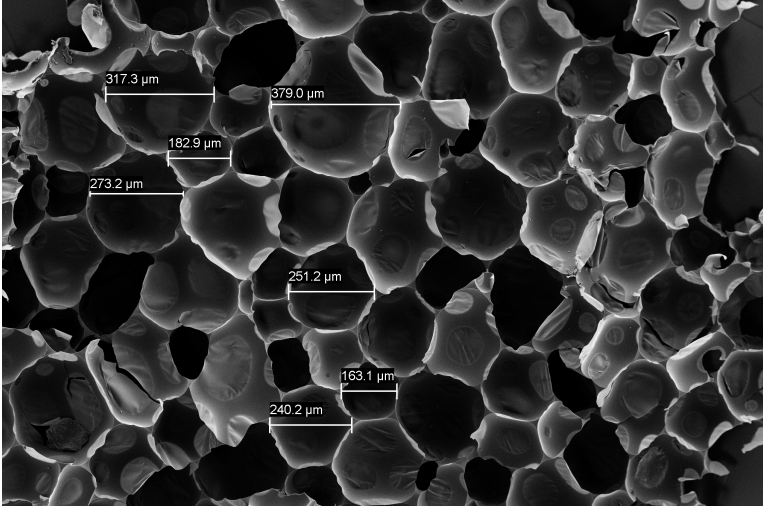


Figure 2.3: *Scanning electron microscope image of a cut from the surface of a PUR sample. The picture shows the honeycomb structure and the various cell sizes.*

The gas thermal conductivity represents almost 50 % of the total thermal conductivity. Gases with high molecular mass normally have low thermal conductivity which increases with temperature. Cell size also affects the PUR thermal conductivity. PUR with very small cells has a higher insulating capacity and the heat transfer via convection can be almost neglected.

In new pipes, PUR's thermal conductivity only depends on the cell size, but over time, air components diffuse into the foam and the cell gas out [19]. This gas composition change takes very long time and affects the total thermal conductivity.

2.2 Failures and degradation mechanisms

2.2.1 Failures of DHPs

Leakage and insufficient thermal performance are the most common failures observed in the DHPs. Leakages can come from inside the service pipe or from the casing pipe. The leaking of the service pipe is a serious failure and will affect the DH network almost immediately due to heat loose and reduction of pressure in the system. A leakage in the service pipe can lead to drift stops in the DH network.

Leaky casing pipe can be difficult to detect. Moisture ingress will affect the thermal performance of the insulation foam and finally cause service pipe corrosion. However, the energy performance of the system decreases very slowly due to the corrosion.

Normally, the weakest parts in a DH network are the joints. Welding joints are often used to make corners, branches or T-connections in the DH network. However, this technique increases the amount of pores in the steel pipe and the risk for crack initiation that can result in fractures. Studies have shown that a combination of steel quality and

workmanship can increase the amount of pores [17]. External mechanical loads from traffics, soil and temperature expansion can also cause crack in the service pipe that finally results in leakages.

PUR with a well ordered cell structure can be almost waterproof, reducing the water absorption during an immersion test to about 2 - 5 % by weight [17]. However, it is known that PUR used to fill the gap after welding has less ordered cell structure. Thus, the penetration of groundwater through the PUR is facilitated, if leakage through the casing pipe occurs, and reaches the service pipe within shorter time than expected. The moisture increases the risk for both degradation of PUR and for service pipe corrosion.

2.2.2 PUR's degradation mechanisms

Standard EN253 describes all requirements, quality and lifetime prediction that DH pipes must fulfil. In order to estimate the lifetime of the DHP based on changes of a certain property as a function of exposure time, the pipe can be exposed to an accelerated thermal ageing and calculated using Arrhenius relationship. The measured property can be mechanical strength using an axial or tangential method, which evaluates not only the PUR strength, but also the adhesion between PUR, casing pipe and service pipe [6].

Degradation's effects on the properties of DHPs and their performance are related mainly to two phenomena: poor thermal insulation and adhesion between the components. The interface between PUR and service pipe is very important for the correct operation of the district heating network. It ensures energy efficiency and resistance to mechanical loads.

PUR's degradation is a combination of both physical and chemical phenomena, and is not dominated by just one process [4]. First, it is important to determine the thermal stability of PUR. It means the time-temperature limit under which the PUR can be used without significant damage or loss of its essential properties.

In general, PUR's thermal degradation is understood to be divided into three steps. First step involves the release of volatile materials from PUR components. Next step is the degradation of mechanical and physical properties due to structural deterioration and morphological changes. Finally, the polyurethane network breaks down by thermo-oxidation. However, the decomposition depends on the structure of the foam material and exposure conditions [4].

2.2.3 Service life prediction

Life prediction of polymers is often based on accelerated ageing at elevated temperature. The material's performance is extrapolated to service conditions by measuring a direct or indirect property connected to a certain criteria for this property. The Arrhenius relationship has been used for many years assuming that an overall chemical process controls the degradation. The Arrhenius equation is described as:

$$k = A \times \exp\left(\frac{-E_a}{RT}\right) \text{ or } \ln(k) = \ln(A) + \frac{-E_a}{RT} \quad (2.2)$$

where k is the reaction rate coefficient, E_a is the activation energy, R the universal gas constant, T absolute temperature and A the pre-exponential factor. E_a is considered

constant independent on temperature. Equation 2.2 is often transformed to the time-temperature relationship and the test results are plotted in a logarithmic scale to obtain a straight line. This procedure simplifies the extrapolation to the operating temperature.

To calculate the service life of DHPs, a log-plot of degradation times ($1/k$) versus inverse temperature ($1/T$) is performed and expected to result in a straight line, allowing simple extrapolation to lower temperatures.

The main weakness in such assessment assuming a linear Arrhenius behaviour is often the limited availability of experimental data. Indeed, some studies have already shown that DHP's degradation mechanisms are complex and a linear Arrhenius relationship is insufficient to match the observed ageing data [13, 23]. For other polymeric materials, a non-Arrhenius curvature due to two competing processes has been proposed [3, 1].

3 Experimental

The experimental work was divided into three parts: influences of the environment on the degradation processes in rigid PUR foam, long-term accelerated ageing of DHP and evaluation of naturally aged DHP.

The careful material characterization is necessary to understand changes in the material's structure and properties in order to get a better idea of the material's functions and how the different degradation mechanisms are triggered. Normally, PUR's degradation takes several years. Therefore, it is very useful to implement accelerated ageing methods to obtain results within a reasonable time frame. Here, it is well known that the higher thermal acceleration, the less agreement is obtained with natural ageing effects. Consequently, comparisons between artificial ageing methods and natural ageing are needed in order to verify the validity of the accelerated ageing methods. It can become a difficult task because the operating temperature and the environment oscillate depending on the season and the network's working conditions. Another factor to take into account is that some natural aged DHPs, older than 30 years, can have insulation foams with different composition and morphology than the foams used nowadays.

The pipes tested in this study were manufactured by Powerpipe Systems AB using the discontinuous method with mid-point filling technique. The chosen dimension was DN50/160, which means a service steel pipe with a nominal diameter of 60.3 mm and a casing pipe with a nominal diameter of 160 mm.

3.1 Accelerated ageing and material characterization

3.1.1 Ageing of PUR foam

The main focus in the first part of the investigation was to study the foam insulation itself. For this propose, PUR foam was subjected to accelerated ageing and evaluated using both mechanical and chemical analyses.

PUR foam used in this study was taken from the standard pipes manufacture by Powepipe Systems AB. The foaming mixture was Elastopor® H 2130/79/OT, composed of polyether polyol, diisocyanate IsoPMDI 92140(BASF) and cyclopentane. Additional components were foam stabilizers and activator. The density of this foam was 67-70 kgm⁻³.

A foam cube was also produced using the same mixture, but under more ideal conditions, which means controlling the process to obtain a better cell structure with uniform cell sizes and density distribution. The cube's dimensions were 250 x 250 x 150 mm.

Accelerated thermal ageing methods are frequently used to create degradation of material in relatively short time, meant to correspond to that of natural ageing during many years. The test samples are here exposed to higher temperatures than the normal operating temperatures, in order to accelerate the degradation processes that occur during the real service life for a particular application. In the standardized ageing procedure, a particular property is studied during a period of time at elevated temperatures until

the property reaches an unacceptable level of deterioration. This level depends on the product application and the required performance. It is worth noting that it is critical to choose the correct temperatures in order to induce the intended mechanisms.

For such measurements, rectangular samples with dimension 100 x 20 x 18 mm were cut from both a standard pipe and from the ideal cube, as shown in Figure 3.1. First, the samples were exposed to accelerated ageing in air and in nitrogen respectively in heating chambers at 150 °C. In the nitrogen environment, the samples were placed without any restriction so they could expand freely. In the air environment, the samples were placed in aluminium boxes to restrain the expansion. Half of the boxes had holes to increment the amount of air around the samples. A certain number of samples were also placed freely to allow expansion in air.



Figure 3.1: *Rectangular sample with dimension 100 x 20 x 18 mm used for accelerated thermal aging of PUR.*

The samples were aged for 1, 2, 4 and 8 weeks in both environments at 150 °C. The samples were removed from the heating chamber at the given times for size and weight measurements. All samples, non-aged and aged, were also evaluated by measuring the mechanical properties using a three-point flexure test, according to the standard EN 178. The samples were loaded until break.

A non-aged sample and some aged samples, from both environments, were chosen to closer study of their chemical structure by Fourier Transform Infrared Spectroscopy (FTIR). The gas composition was also studied in order to identify cyclopentane changes by Headspace Gas Calorimetry - Mass Spectroscopy (GC-MS) analysis.

3.2 Accelerated ageing of DHPs

Three DHPs were placed in a temperature chamber and connected to an electricity source, which delivered the needed power to heat the service pipe to the desired elevated ageing temperatures as shown in figure 3.2. The chamber temperature was controlled to be 23 ± 2 °C. Three different temperatures were chosen for the ageing method to investigate the PUR degradation's behaviours and mechanisms. The lowest temperature was 130 °C, which is very close to the maximum operating temperature of district heating networks. The highest temperature was 170 °C which is specified as a possible ageing temperature in the standard EN253. 150 °C was chosen as a temperature between the lowest and highest temperatures. An identical fourth pipe was maintained at room temperature and was used as the reference measurements for both mechanical and thermal properties.

Two physical properties were followed during the ageing period to determine the

deterioration level of DHPs: mechanical strength and thermal conductivity. The pipes were instrumented with temperature sensors to control the temperature at ageing recorded at three different points along the pipe. Also, sensors for thermal conductivity measurements were installed at two radial distances from the steel service pipe, viz. 5 and 30 mm respectively.

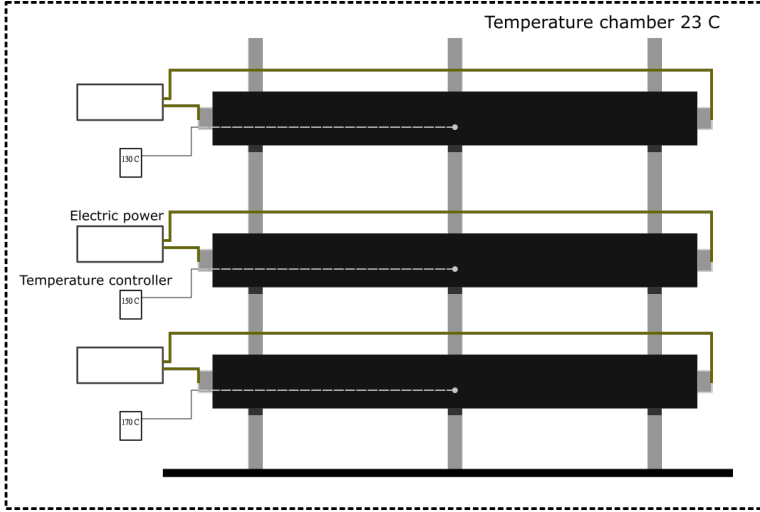


Figure 3.2: *The accelerated ageing arrangement in a temperature chamber.*

3.3 Measurements

3.3.1 FTIR analysis

FTIR was used to detect and follow changes in the chemical structure of the PUR foam caused by ageing. The attenuated total reflection (ATR) was the main method used in this study. The test samples were prepared by shaving some material from the PUR foam, obtaining very thin pieces.

First, a background was collected to ensure that the actual samples is all that is studied. Then, the test samples were placed on the diamond to be scanned 32 times. This generates an absorbance spectrum which can be compared with other spectra from samples aged during various periods of time.

3.3.2 GC-MS analysis

Analysis of the cell gases is of big importance to understand the deterioration of thermal performance. The critical step in the GC-MS analysis is to extract the cell gases without altering their characteristics. For this reason, the samples were placed in a vial containing lead pellets and liquid nitrogen. The cells were crushed by shaken the vial during a few

minutes and then analysed by GC-MS.

3.3.3 Mechanical strength test

In this study, the mechanical strength of DHPs was measured using a non-standard method called SP plug method, which was first described in [20]. The test sample was created by using a hole saw with a diameter of 27 mm. An aluminium pipe was then glued to the cylindrical test sample which was still attached to the service pipe. A torque was then applied manually as shown in Figure 3.3. The torque at break was recorded and the plug shear strength calculated using equation:

$$\tau_{tan} = \frac{16 \times M_p}{\pi \times d^3} \quad (3.1)$$

where M_p is the measured maximum torque and d is the plug's diameter. The mechanical test was performed after the DHPs were allowed to cool down to 23 °C. The remaining hole was sealed using a new polyurethane plug.

Three measurements were performed at different positions around and along the pipe every runtime from each pipe. This method is designed to test directly the adhesion strength between the PUR foam and the steel service pipe.

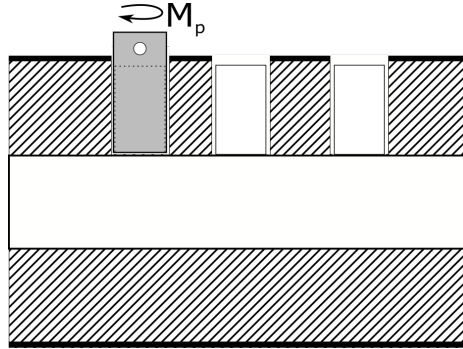


Figure 3.3: *Sketch of SP plug test arrangement.*

3.3.4 Thermal conductivity

A transient plane source (TPS) technique, developed by Gustafsson [8], was used in this project instead of the guarded hot pipe (GHP) method, which is commonly used to measure the thermal conductivity of DHPs. The TPS technique is a standard method described in [10].

The TPS sensor was programmed to send out a signal of 10 mW during 40 seconds. The response was measured by the sensor itself by measuring the changes of the resistance during some minutes. The total test time was about 10-15 minutes. The measurements were carried out first at the corresponding ageing temperature and then at room temperature 24 hours later. The reason to do so was to observe any structural change in the foam insulation.

3.4 Other tests

3.4.1 Adhesion strength test

The contact surface between PUR foam and the steel service pipe is affected by the thermo-oxidative degradation. but, what happens in an inert atmosphere?

Cross-section discs from a DHP were placed in a desiccator, which was connected to nitrogen gas and placed in a heating chamber at 150 °C. After specific period of ageing, the discs were removed from the oven, triangular pieces were cut out in the PUR, but still in contact with the steel pipe as shown in figure 3.4 and a load was applied on the triangle form approximately 30 mm from the service pipe. The maximum force at break was registered.

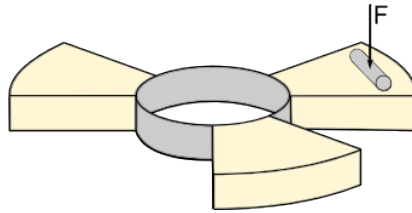


Figure 3.4: *Sketch of adhesion strength test of a cross-section of a pipe.*

3.4.2 Accelerated thermal ageing in nitrogen environment

A short DHP with a length of 1 m was especially manufactured for this test with the same material and properties as the other pipes. The pipe was placed into an aluminium cylinder, which was 10 cm bigger in diameter and length than the test pipe. The DHP was connected to an electrical source, similar to those used in the ageing method described above. The aluminium cylinder was connected to nitrogen gas with a low flow in order to push out the air remaining in the cylinder. Figure 3.5 shows a sketch of the arrangement.

Mechanical tests were carried out after 5, 10, 15 and 20 weeks to observe the degradation level of this pipe.

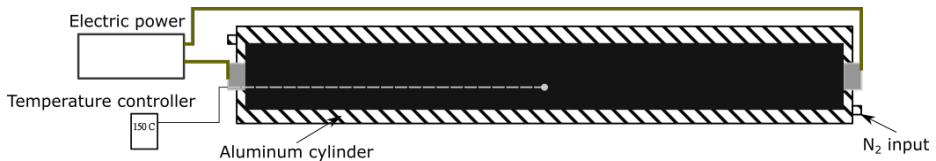


Figure 3.5: *Sketch of accelerated thermal ageing in N_2 environment.*

4 Summary of results

In this chapter, a summary of the most relevant results is presented. For more details and results please read **Paper A** and **Paper B** attached in this thesis.

4.1 Accelerated ageing of PUR foam

4.1.1 Accelerated thermal ageing and mechanical strength

At ageing in nitrogen, almost no changes were observed except for a small change in weight, probably due to some volatile components that disappear from the foam in the beginning.

In air, ordinary PUR (o-PUR) showed changes in all measured properties as shown in figures 4.1, 4.2 and 4.3. However, ideal PUR (i-PUR) showed similar changes but in a minor scale, except for the weight-loss which was very similar to o-PUR.

The biggest difference was in the degree of discolouration. The samples aged in nitrogen showed very small changes in colour, compared with the fact that ageing in air caused a strong yellowing, becoming dark brown after 28 days.

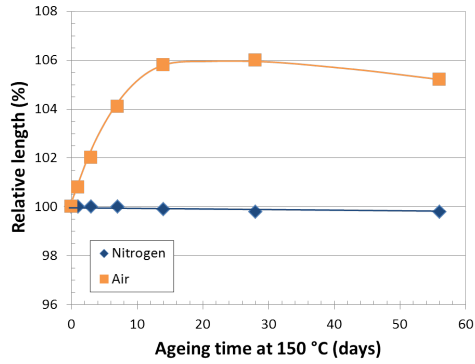
The three-point flexural test performed on all samples showed surprisingly no significant differences between samples, as shown in figure 4.4. It is worth to note that this mechanical test measured the strength of PUR itself (cohesion strength) while shear strength test methods, e.g. axial, tangential and SP plug method, measure the strength of the interface between the PUR foam and the steel pipe of the DHP (adhesion strength). In order to further clarify this difference, an adhesion test was performed on discs with triangular pieces and aged at 150 °C in nitrogen environment. The cohesion strength of PUR decreased by about 7 %, at the same time the adhesion strength decreased by approximately 40 %. Figure 4.5 shows two samples aged in nitrogen environment and in air during 8 weeks, and a diagram with the results obtained from the adhesion strength test on discs.

In addition to mechanical evaluation of the aged PUR samples, their chemical structure was studied to identify alterations due to degradation at ageing temperatures and the surrounding environment.

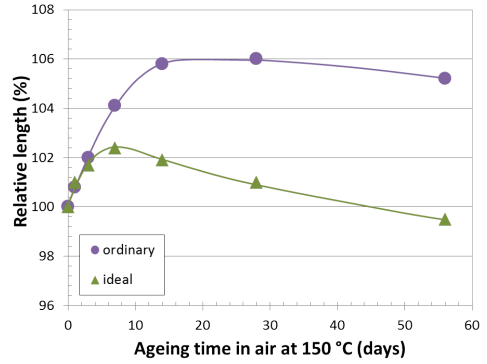
4.1.2 FTIR analysis

FTIR was used to identify the principal functional groups that were present in the polyurethane foam. Some of them stayed almost unchanged during ageing, others decreased and a few new peaks appeared.

It is known that an excess of isocyanate (NCO) is normally added during production to ensure the complete reaction with polyol. Foams with a large excess of NCO also have a significant portion of isocyanurate, which increases the thermal stability of the foam. However, some reactions may not be completed and could take place later when the pipe as heated.

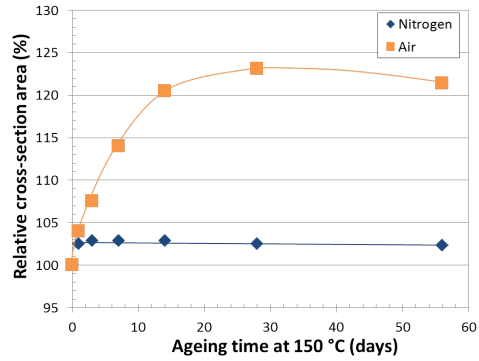


(a)

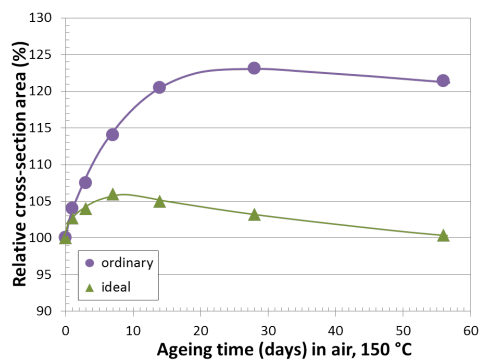


(b)

Figure 4.1: Measurements of length after ageing at 150 °C; (a) ordinary PUR aged in nitrogen and in air, and (b) comparison of ordinary and ideal PUR foam aged only in air.

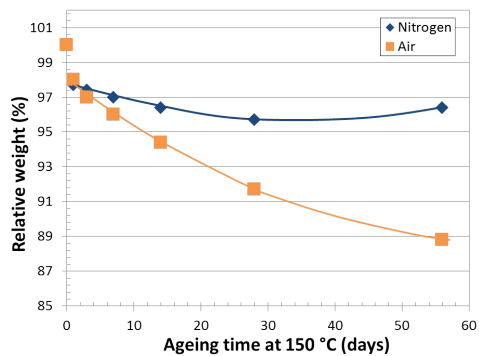


(a)

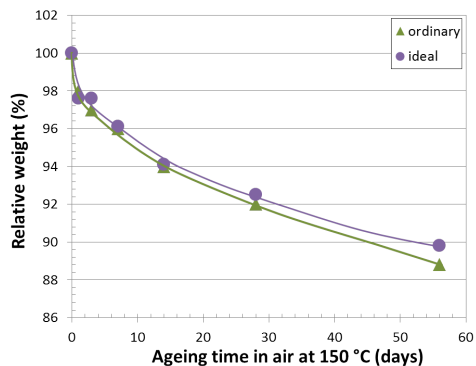


(b)

Figure 4.2: Measurements of cross-section area after ageing at 150 °C; (a) ordinary PUR aged in nitrogen and in air, and (b) comparison of ordinary and ideal PUR foam aged only in air.

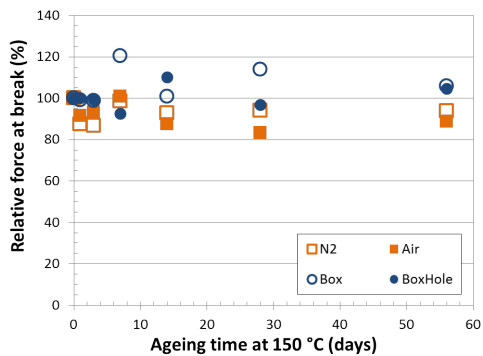


(a)

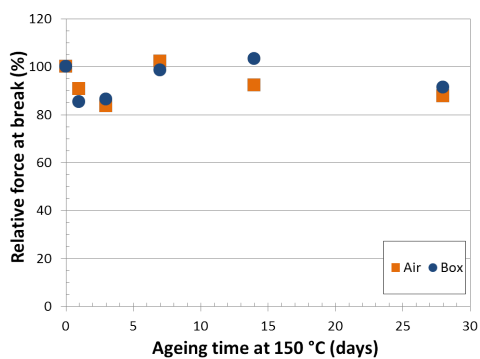


(b)

Figure 4.3: Measurements of weight after ageing at 150 °C; (a) ordinary PUR aged in nitrogen and in air, and (b) comparison of ordinary and ideal PUR foam aged only in air.



(a)



(b)

Figure 4.4: Measurements of relative force at break measured in a three-point bending test after ageing at 150 °C; (a) ordinary PUR aged in different conditions, and (b) ideal PUR aged in air and in boxes

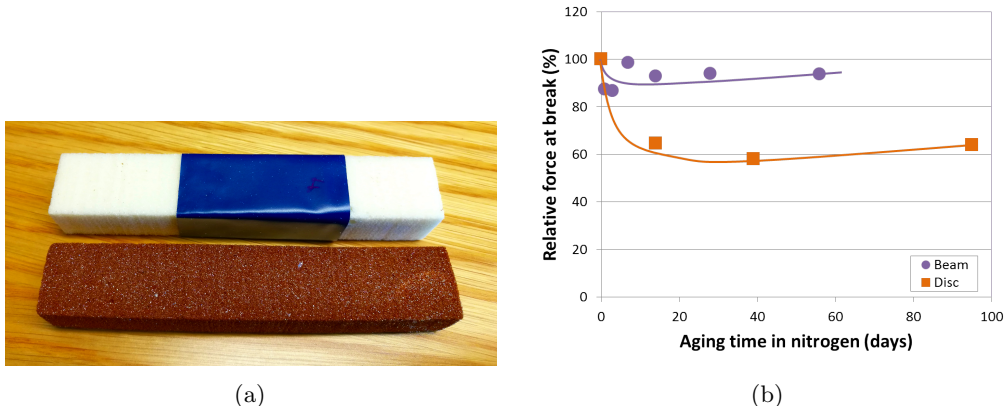


Figure 4.5: (a) Comparison between samples aged in N_2 and in air after 8w, and (b) mechanical strength for PUR samples and disc samples.

The peaks studied in the FTIR analysis were:

- 3302 cm^{-1} - stretching of N-H groups.
- $2975\text{-}2872\text{ cm}^{-1}$ - stretching vibration of C-H in methyl.
- 2277 cm^{-1} - unreacted NCO.
- 1765 cm^{-1} - lactones and peroxy acids.
- 1712 cm^{-1} - C=O stretching vibration in the urethane bond.
- 1595 cm^{-1} - aromatic C=C vibration
- 1411 cm^{-1} - isocyanurate rings

The spectra were complicated but it was possible to show changes in the chosen peaks intensity by normalization to the reference peak at 1595 cm^{-1} belonging to the aromatic ring, which is often used as an internal reference [15]. The relative concentrations were plotted versus the ageing time. The soft segments of PUR were found to degrade faster than the hard segments. Peaks corresponding to CH_2 groups and urethane linkage decreased, which was a clear indication of thermo-oxidative degradation process. Another indication of the oxidative degradation was the formation of a new carbonyl group around 1765 cm^{-1} as shown in figure 4.7. The concentration of the unreacted NCO decreased independent of the ageing environment.

These results are published in **Paper A** and summarized in figures 4.6 and 4.7.

4.1.3 Cell gas analysis

Our results in **Paper A** indicate that loss of pentane and cyclopentane does not occur through the gas exchange process only, because it does not occur in the nitrogen atmosphere. The amount of pentane and cyclopentane decreased however by about 40 % of the

original value in samples aged in air for 8 weeks at 150 °C. This indicates that the loss of pentane and cyclopentane was preceded by a significant oxidative degradation of the PUR material. Additionally, new volatile compounds were detected, as shown in Table 4.1.

Table 4.1: Results obtained in a 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
1,3-Dioxolane,2,2,4-trimethyl	<5	<5	54
1,3-Dioxolane,2-ethyl-4-methyl	<5	<5	15
1,4-Dioxane,2,5-dimethyl or isomer	<5	<5	44
Benzenemethanamine,N,N-dimethyl	452	497	<5
Sum of all compounds	5537	6331	2123

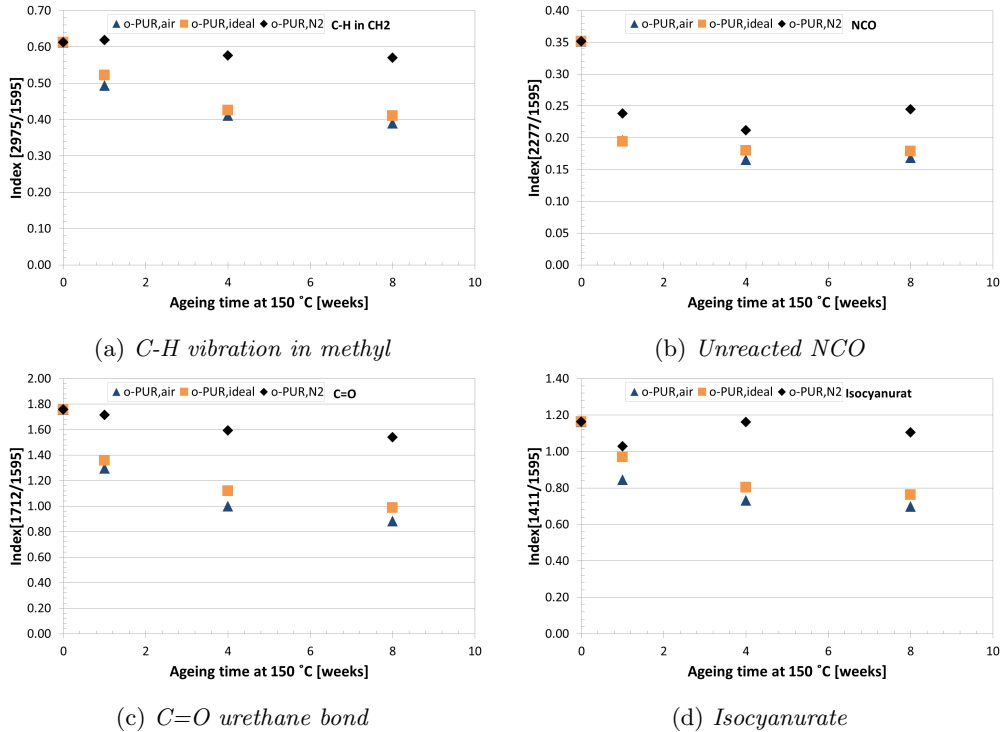


Figure 4.6: Change of concentration of various functional groups with ageing time at 150 °C.

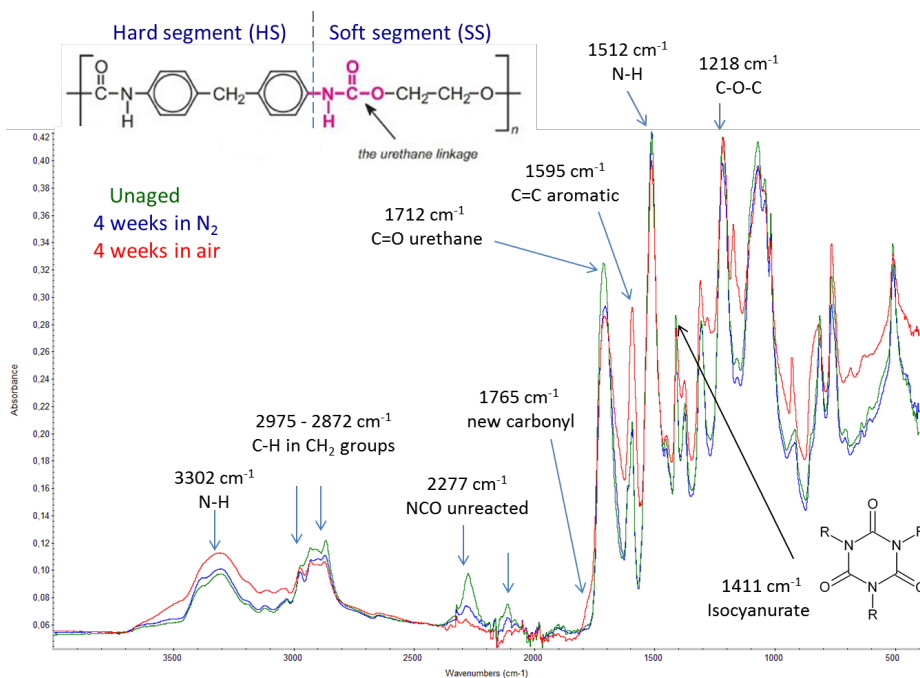


Figure 4.7: *FTIR spectra of the ordinary PUR foam.*

4.2 Accelerated thermal ageing of DHP

4.2.1 Mechanical strength

The contact interface between the PUR foam and the service steel pipe was evaluated using the SP Plug method. The measurements were performed after 24, 48, 72, 144, 192, 360, 504 and 720 hours. Thereafter, the test was carried out every 720 hours. On each test occasion, three measurements were carried out along the pipe. The change in mechanical strength seems to undergo three different stages. Firstly, it decreased very fast until a minimum was reached, where the dominant fracture mechanism was cohesion, which means that the PUR/steel contact interface was stronger than the foam's mechanical strength itself. After that, the mechanical strength increased to a local maximum. At this phase, a combination of cohesion and adhesion failure was registered. The first stage is commonly called the "induction" step and are shown in 4.8. After the maximum was reached, the shear strength decreased slowly, likely due to deterioration of the adhesion strength with time, depending on the ageing temperature. During the last stage, adhesion failure was the dominant fracture mechanism. The mechanical strength at the PUR/steel pipe contact interface became weaker than the foam strength itself. This last stage is called the rate-controlling step, as explained in **Paper B** and is shown in figure 4.8.

Using the data collected during the early stage of ageing processes, two activation

energies were calculated for the minimum and maximum points observed in figure 4.8. In figure 4.9 the natural logarithms of the ageing time are plotted versus $1/T$ according to the equation 2.2. The activation energies can be calculated from the slopes of the lines. In this case, the values obtained were 60.1 and 64.3 kJ/mol.

The mechanical strength for the pipes aged at 150 and 170 °C, decreased with almost a constant rate following a straight line until complete loss of adhesion. However, a different result was obtained for the pipe aged at 130 °C. The mechanical strength for DHP130 decreased linearly during 10000 hours, reaching 65-75 % of the original value. After this point, the strength remained more or less constant for 7000 hours, as shown in figure 4.10. It should be noted that the ageing at 130 °C was very close to the maximum operational temperature registered (120 °C). It was therefore concluded that accelerated ageing at commonly used high temperatures does not cause an acceleration of degradation processes at the steel/PUR interface, but rather a significant change in the degradation mechanism. The results obtained in this study can lead to a different and possible better understanding of how to design relevant ageing methods for DHPs.

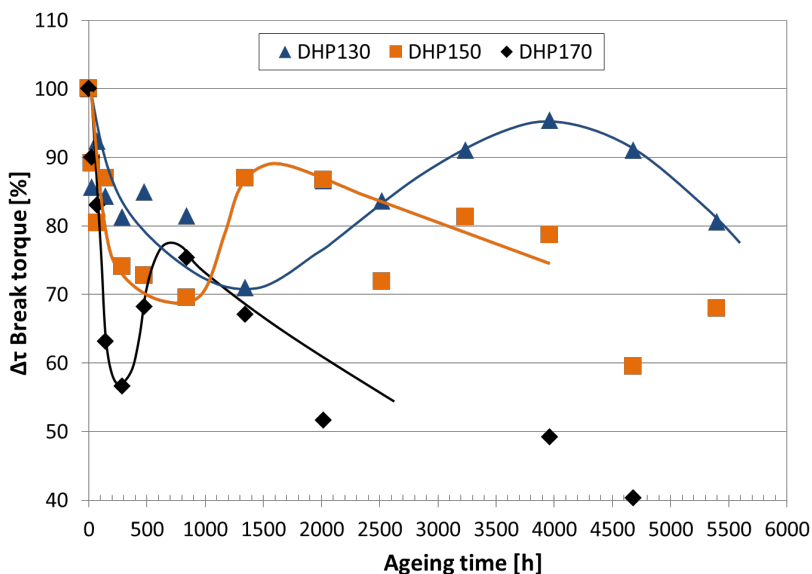


Figure 4.8: Measurements of the mechanical strength for the first 5500 h. Showing the first stages of the relative mechanical strength expressed in percent versus the ageing time in hours.

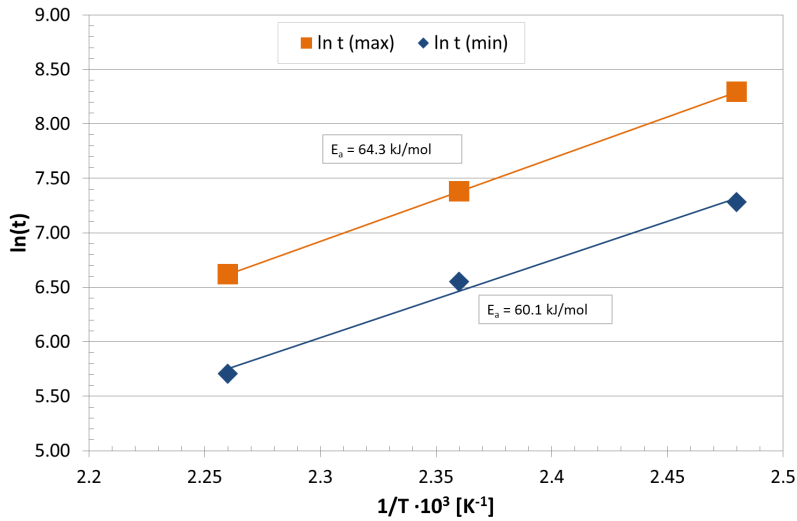


Figure 4.9: Activation energies for the process to reach minimum and maximum, respectively, in the early stages of the ageing test.

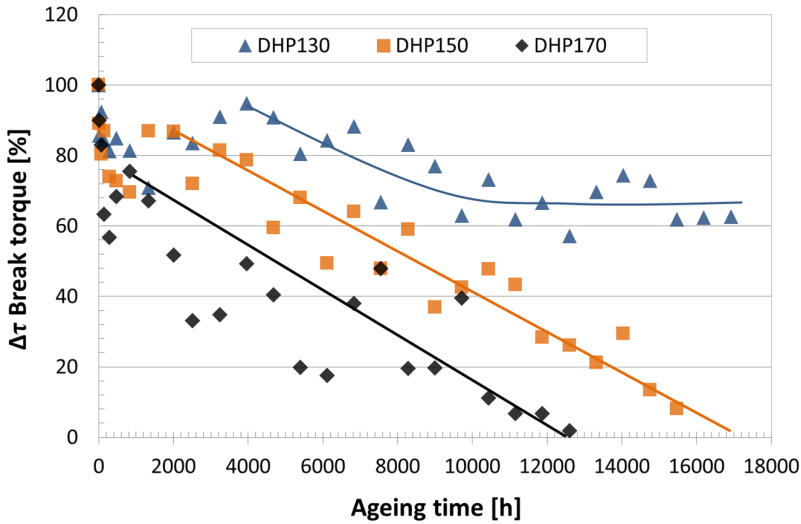


Figure 4.10: Relative mechanical strength expressed in percent versus the ageing time in hours.

4.2.2 Thermal conductivity

In new produced DHP, the gas mixture contains roughly equal parts of carbon dioxide (CO_2) and cyclo-pentane (CP). Normally, CO_2 diffuses fast and is replaced eventually

with air, which have much higher thermal conductivity, $\lambda_{25,air} = 0.027$, $\lambda_{25,CO_2} = 0.017$ and $\lambda_{25,CP} = 0.012$ W/(mK) [12]. Diffusion of CO_2 and its replacement with air made a change in the foam's λ values.

Figure 4.11 shows the λ values measured by the TPS sensors at 5 and 30 mm, respectively.

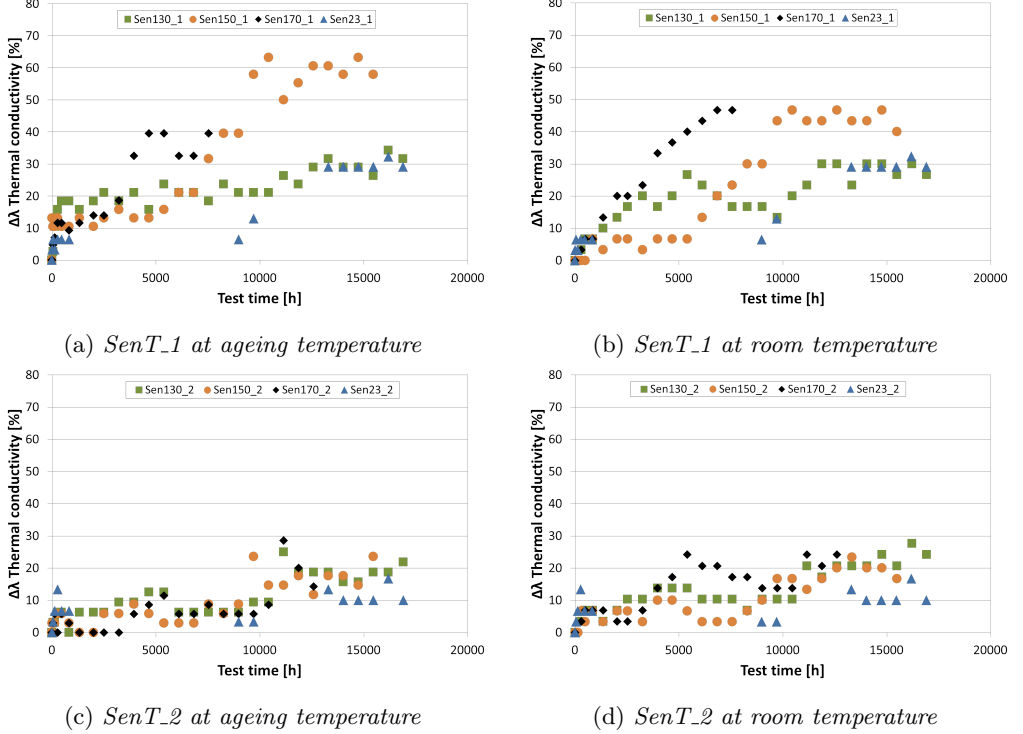


Figure 4.11: Measurements of λ values first at the corresponding ageing temperature and at room temperature 24h after ageing.

The changes in λ values were likely mainly due to the gas transport in the foam, which was affected by the HDPE casing pipe and the foam morphology [14]. The casing pipe was maintained at 23 °C for all DHPs. The results indicated that the gas exchange process was similar for all pipes as reflected in figure 4.11.

However, the measurements from the sensors at 5 mm from the steel pipe were significantly affected by the ageing temperature, especially at 150 and 170 °C, while ageing at 130 °C did not affect the values in the same way. The changes at higher temperatures could be caused by additional process besides gas diffusion, e.g. foam morphology alteration due to thermo-oxidative degradation, resulting in some losses of CP and deterioration of the insulation performance. In **Paper A**, it was observed that thermo-oxidative degradation of PUR at 150 °C resulted in losses of pentane and cyclopentane, which was not the case in the nitrogen atmosphere.

For the pipe aged at 130 °C, the λ values changed in a similar way as for the reference pipe. It means that CO₂ diffusion was the predominant process controlled by the HDPE casing pipe as gas barrier.

4.2.3 FTIR analysis

From figure 4.12, we can conclude that changes in the chemical structure went faster at 150 and 170 °C, confirming the results obtained in the mechanical strength test. The fast decrease of the peaks at 1712 and 1512 cm⁻¹ demonstrated the degradation of the urethane linkage by thermo-oxidative processes [5].

Additional to the peaks studied in figure 4.12, a closer look at the FTIR spectrum revealed new peaks in the range 1760-1790 cm⁻¹, shown in figure 4.13, indicating the formation of new carbonyl groups as a result of the oxidation processes [5].

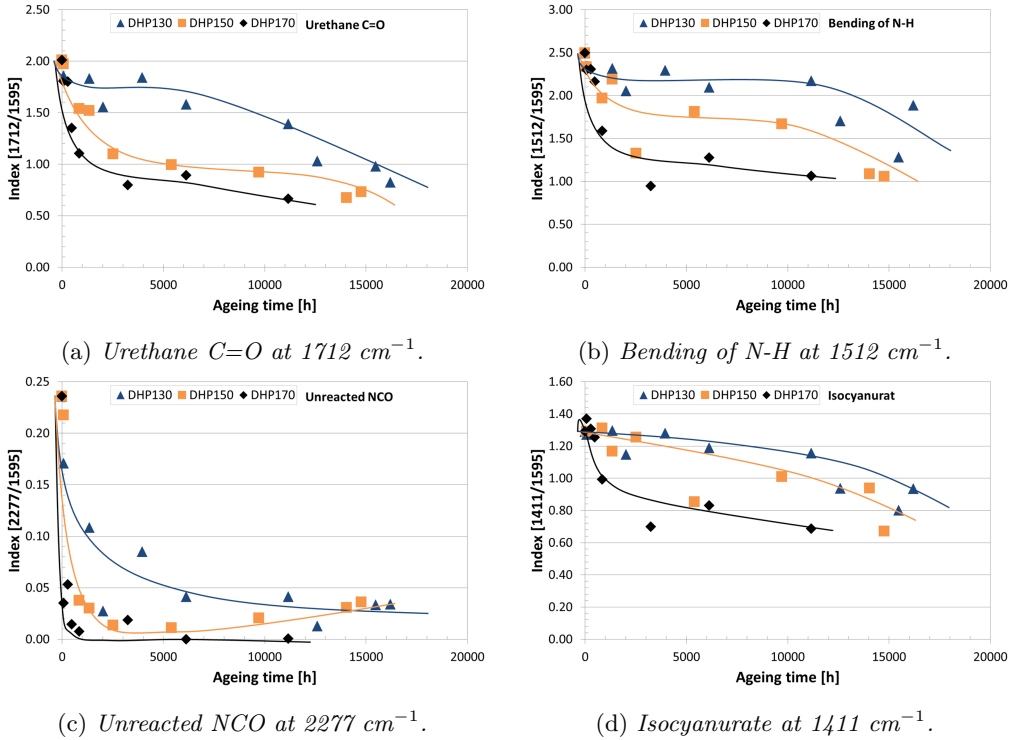


Figure 4.12: Change of concentration of various functional groups by FTIR with ageing time and temperature.

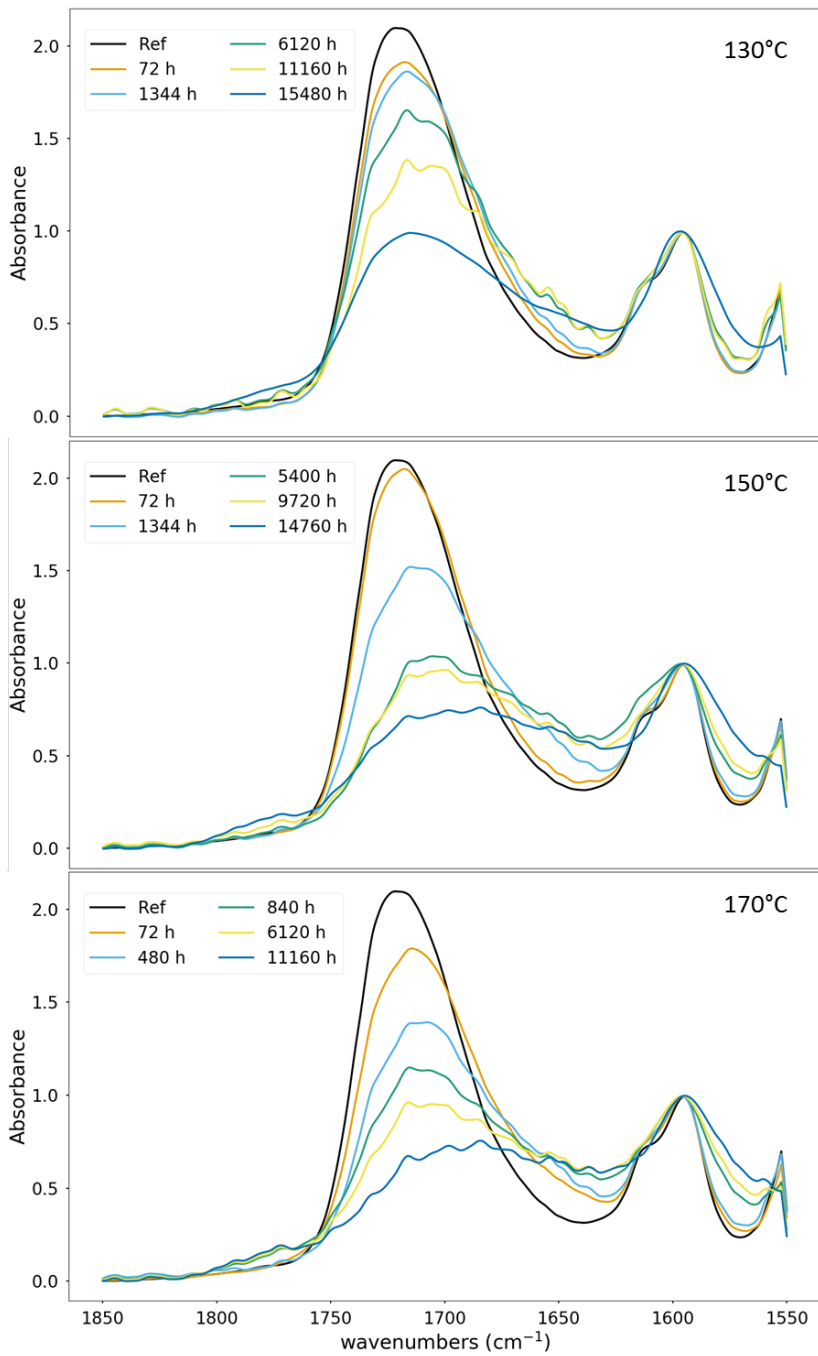


Figure 4.13: New carbonyl peaks formed as a result of oxidation processes. PUR samples collected from the accelerated aged DHP.

4.2.4 Short DHP in N_2 environment

The accelerated ageing test in a small scale gave interesting results and confirm the obtained results from the aged PUR foam in nitrogen atmosphere.

First, a visual observation revealed very little colour change as shown in figure 4.14. The mechanical test showed that the adhesion strength was not affected and was almost constant, in contrast with the DHP aged in air as shown in figure 4.15. This result confirmed the important effect of oxygen for the degradation mechanisms activation of the DHPs.



Figure 4.14: Samples from DHPs aged in air (upper row) and in N_2 environment (lower row) at $150\text{ }^{\circ}\text{C}$. The samples correspond to 840, 1680, 2520 and 3360 h of accelerated ageing time (from left to right).

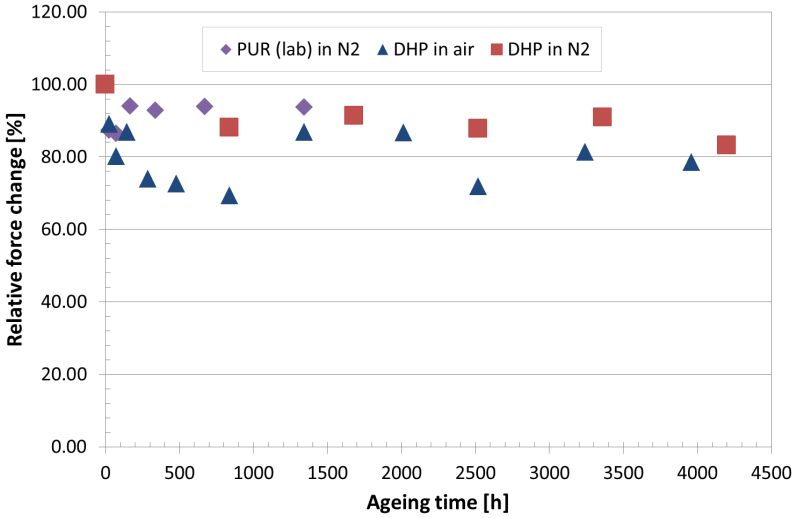


Figure 4.15: Comparison of the DHP mechanical strength aged in air and N_2 , respectively.

5 Conclusions

Regarding accelerated ageing of PUR foam, it was found that oxygen play an important role in the degradation mechanisms. Samples aged in an inert environment (N_2 gas) at 150 °C presented insignificant changes in colour, dimensions, weight or mechanical strength. However, a rapid decrease of the adhesion force between the PUR and steel service pipe (disc samples) was observed as shown in figure 4.5. This loss was not caused by a thermo-oxidative process.

On the other hand, samples aged in air presented significant changes in almost all measured properties, except the mechanical strength measured by a three-point flexural test as demonstrated in figure 4.4. Change of the chemical structure was detected by the FTIR analysis, revealing interesting results as the formation of new carbonyl groups together with degradation of the soft segment of the PUR foam, a clear evidence of thermo-oxidative degradation.

The GC-MS analysis indicated that the loss of pentane and cyclopentane was most likely to be the result of a significant oxidative degradation process, since it did not occur in the samples aged in nitrogen environment.

The mechanical strength underwent different phases during the ageing time. During the initiation step, it decreased very fast to a minimum point and then went up to reach a maximum. The change rate depended on the ageing temperature, being faster for higher temperatures. However, for ageing at 130 °C the relative mechanical strength remained unchanged for a long period after approximately 10000 h of ageing time as shown in figure 4.10. This result was important because it can mean that it is not possible to use temperatures higher than 130 °C for accelerated ageing of DHP, because it would result in alterations of the degradation mechanisms rather than the correct acceleration of the processes. It can also result in the underestimation of the DHP technical lifetime, which is an important issue for both pipe manufacturers and energy companies.

The ageing temperature had also an impact on the thermal conductivity. From the measurements, it was observed that the λ values changed due to thermo-oxidative degradation at the relative high ageing temperatures, resulting in loss of cyclopentane.

The changes of the PUR chemical structure were confirmed by the FTIR analyses of the PUR samples obtained from the mechanical tests. The thermo-oxidative degradation was found to be much faster at higher temperatures as plotted in figure 4.12. It was also possible to identify carbonyl peaks as shown in figure 4.13. This result confirms the thermo-oxidative degradation mechanism at high ageing temperatures.

Our investigation reveals the necessity of a revision to the European Standard EN 253, which is currently used to calculate the technical lifetime based on accelerated thermal ageing at temperatures higher than 150 °C. This has also been pointed out by other investigations as mentioned in this thesis.

6 Further work

In order to complete this work, measurements of oxygen diffusion in real-time into the pipes is needed. It has been mentioned in some papers that air replaces CO_2 in the PUR cells decreasing the thermal performance of DHPs as time goes. It has also been shown that oxygen is responsible for the thermo-oxidative processes, but it has not been measured directly so far.

It is also important to study the naturally aged DHPs to compare the degradation mechanisms found in the laboratory to the signs of degradation that arise during service life. This study will include both test of mechanical strength and analyses of chemical structure.

Finally, a single Arrhenius relationship seems to be unsuitable to describe the complexity of the degradation mechanisms of DHPs. In other fields, non-linear or deformed Arrhenius equations have been used instead to describe the observed deviations. It may be a good idea to use this type of relationship to obtain a better prediction of the technical lifetime. An improved model would be of great relevance for both involved industry and society.

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References

- [1] V. Aquilanti et al. Temperature dependence of chemical and biophysical rate processes: Phenomenological approach to deviations from Arrhenius law. *Chemical physics letters* 498 (2010), 209–213.
- [2] A. Biedermann et al. Analysis of Heat Transfer Mechanisms in Polyurethane Rigid Foam. *Journal of Cellular Plastics* 37 (2001), 467–483.
- [3] M Celina, K. T. Gillen, and R. a. Assink. Accelerated aging and lifetime prediction: Review of non-Arrhenius behaviour due to two competing processes. *Polymer Degradation and Stability* 90 (2005), 395–404.
- [4] D. Chattopadhyay and D. C. Webster. Thermal stability and flame retardancy of polyurethanes. *Progress in Polymer Science* 34.10 (2009), 1068–1133. ISSN: 00796700. DOI: 10.1016/j.progpolymsci.2009.06.002. URL: <http://www.sciencedirect.com/science/article/pii/S0079670009000550>.
- [5] A. Colin et al. Investigation of the thermo-oxidation mechanism of acrylic-urethane-silicone/aminosilane based topcoat. *Polymer degradation and stability* 114 (2015), 115–124.
- [6] *EN 253:2009 District heating pipes - Preinsulated bonded pipe systems for directly buried hot water networks*. Standard. CEN, 2009.
- [7] S. Frederiksen and S. Werner. *District heating and cooling*. 1st. Studentlitteratur AB, 2013.
- [8] S. E. Gustafsson. Transient plane source techniques for thermal conductivity and thermal diffusivity measurements of solid materials. *American Institute of Physics* 62.3 (1990), 797–804.
- [9] M. Hawkins, B. O’Toole, and D. Jackovich. Cell Morphology and Mechanical Properties of Rigid Polyurethane Foam. *Journal of Cellular Plastics* 41 (2004), 267–285.
- [10] *ISO 22007-2:2015 Plastics - Determination of thermal conductivity and thermal diffusivity - Part 2 Transient plane heat source (hot disc) method*. Standard. CEN, 2015.
- [11] J. Kellmer and R. Shen. *Production techniques for polyurethane pre-insulated pipes and foam systems suitable for the manufacture of high quality pipes applied in district heating*. Tech. rep. Shanghai, China, 2000.
- [12] C. Larsen, P. Tøgeskov, and A. Leuteritz. Analyses of diffusion rates through PE and impact on ageing. *Euroheat Power - English edition* 6 (2009).
- [13] A. Leuteritz et al. Accelerated ageing of plastic jacket pipes for district heating. *Polymer testing* 51 (2016), 142–147.
- [14] S. Mangs. “HFC-365mfc and cyclopentane as blowing agents in polyurethane insulation of district heating pipes”. Department of chemical engineering and environmental sciences. Licentiate Thesis. Chalmers University of technology, 2002.
- [15] M. Modesti and A. Lorenzetti. An experimental method for evaluating isocyanate conversion and trimer formation in polyisocyanate-polyurethane foams. *European Polymer Journal* 37 (2001), 949–954.

- [16] H. Mortensen and B. Overgaard. CHP development in Denmark. *Energy Policy* 20.12 (1992), 1198 –1206. ISSN: 0301-4215. DOI: [http://dx.doi.org/10.1016/0301-4215\(92\)90098-M](http://dx.doi.org/10.1016/0301-4215(92)90098-M). URL: <http://www.sciencedirect.com/science/article/pii/030142159290098M>.
- [17] S. Nilsson. “Durability of district heating pipes”. PhD thesis. Chalmers University of technology, 2002.
- [18] L Olsson, E Wetterlund, and M Söderström. Assessing the climate impact of district heating systems with combined heat and power production and industrial excess heat. *Resources, Conservation and Recycling* 96 (2015), 31 –39. ISSN: 0921-3449. DOI: <https://doi.org/10.1016/j.resconrec.2015.01.006>.
- [19] A. Ostrogorsky, L. Glicksman, and D. Reitz. Aging of polyurethane foams. *International Journal of Heat and Mass Transfer* 29 (1986), 1169 –1176.
- [20] J. H. Sällström, O. Ramnäs, and S. E. Sällberg. “Status assessments of district heating pipes”. *DHC13, 13th International symposium on district heating and cooling*. Copenhagen, Denmark, 2012.
- [21] M. Svanström. “Blowing agents in rigid polyurethane foam”. PhD thesis. Chalmers University of technology, 2002.
- [22] R. Whiltshire. *Advanced District Heating and Cooling (DHC) Systems*. Woodhead Publishing Series in Energy, 2016. ISBN: 978-1-78242-374-4.
- [23] N. Yarahmadi and J. H. Sällström. “Improved maintenance strategies for district heating pipe-lines”. *DHC14, 14th International symposium on district heating and cooling*. Stockholm, Sweden, 2014.