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Characteristics of drinking water polyethylene pipes tested with the purpose of quality certification
Historical data, trends and their potential consequences

Master's thesis in Master Program Infrastructure and Environmental engineering

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ABSTRACT

Every year, large investments are buried in the ground when repairing and extending drinking water networks. The most common pipe material is high-density polyethylene, HDPE. The HDPE-pipes used are classified after their believed strength after 50 years. Yet, the lifetime of new pipes is predicted to be above 100 years. To guarantee a good quality of used pipe different certifications are used, the difference between approved pipes can however be vast.

Test results from test performed in association with the *Nordic Poly Mark* certification between 2000 and 2012 was reviewed. Data regarding OIT, MFR, elongation at break and longitudinal reversion was then analyzed to find trends over time as well as correlation between different pipe characteristics.

Changes was observed in several characteristics, most notably was the changes in melt mass-flow rate, MFR. Significant differences in MFR-values was found for PE80 pipes and as they are produced by both high- and medium-density PE, this can be problematic in certain welds. For PE100 pipes, the MFR-values have declined and was around 0,25g/10min at 2012, which is a concerningly low value as butt fusion joints are ideally performed on pipes with MFR-values above 0,1-0,3g/10min (DVS Media GmbH, 2015; DVS, Technical Commitee, Working group "Joining of Plastics", 1995). Due to difficulties when welding pipes with differences in MFR-values and pipes with low MFR-values, it could be advised to renew the demands for new polyethylene pipes, for example add a lower limit for MFR-values to the certification criteria.

Apart from a data analysis, an OIT-analysis has been performed on a HDPE drinking water pipe that had been in use for nine years. The analysis was made to validate expected lifetime predictions as well as further deepen the understanding of the aging process of drinking water pipes.

The analysis showed an OIT-result that was 23% lower at the surface compared to the middle of the pipe wall. If a linear consumption of antioxidants at the surface of the pipe is assumed, the antioxidants will be depleted in roughly 50 years, which would lead to an accelerated deterioration of the pipe, which corresponds well with the literature study. After 50 years, the diffusion speed of antioxidants within the pipe wall is believed to play an important role in how fast the pipe will deteriorate.

Keywords: HDPE, polyethylene, drinking water pipe, lifetime, OIT-analysis

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SAMMANFATTNING

Varje år görs stora investeringar för att renovera och expandera dricksvattenledningsnätet. Det vanligaste rörmaterialet som används är högdensitetspolyeten, HDPE. Rören är klassificerade efter deras förmodade styrka efter 50 år men livslängden på nya HDPE-rör förutspås vara över 100 år.

Nordic Poly Mark är en kvalitetscertifiering som används för nya dricksvattenrör. Resultaten från tester gjorda i samband med certifieringen mellan 2000 och 2012 har granskats och dokumenterats. Information kring OIT, MFR, förlängning vid brott och längdutvidgning har undersökts och analyserats för att finna trender kring rörkvalitet och kopplingar mellan olika egenskaper hos rören.

Förändringar har observerats för flera egenskaper, mest anmärkningsvärt är förändringar rörande smältindex, *melt mass-flow rate* (MFR). Stora skillnader mellan olika PE80 rör noterades och kunde härledas till att dessa rör tillverkas av både medium- och högdensitets polyeten. Stora skillnader mellan olika rör kan vara problematiskt då det försämrar svetsegenskaperna. För PE100 rör så har MFR-värdena sjunkit och var under 2012 cirka 0,25g/10min. Rekommenderat värde för en stumsvets är mellan 0,1–0,3g/10min vilket kan göra allt för låga MFR-värden till ett problem (DVS Media GmbH, 2015; DVS, Technical Commitee, Working group "Joining of Plastics", 1995). På grund av svårigheter med att svetsa rör med olika MFR-värden eller låga MFR värden rekommenderas att *Nordic Poly Mark* certifieringen också ska ställa krav på ett mista tillåtna MFR-värde.

Utöver granskningen av gjorda tester genomfördes också OIT-analyser på ett HDPE-dricksvattenrör som varit i bruk i nio år. Analysen gjordes för att styrka livstidsprognoser samt för att ytterliga kunna fördjupa och förstå åldringsegenskaperna hos åldrande dricksvattenrör.

Analysen visade att OIT-värdarna för rörets insida var 23% lägre än i rörets mitt. Om en linjär åtgång av antioxidanter antas kommer rörets antioxidanter i ytskiktet att vara förbrukade efter cirka 50 år vilket överensstämmer bra med litteraturstudien och tidigare förväntningar. Efter 50 år förväntas antioxidanternas diffusionshastighet spela en stor roll för hur snabbt röret kommer oxidera och således också hur röret försvagas.

Nyckelord: HDPE, polyeten, dricksvattenrör, livslängd, OIT-analys

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PREFACE

This Master's thesis was prepared during the spring of 2017 at Chalmers university of Technology in cooperation with RISE technical research institute of Sweden. The work consists of two parts. One part focusing on characteristics of new high-density polyethylene (HDPE) drinking water pipes approved with the *Nordic Poly Mark* certification. The other part of the thesis investigate wear on used HDPE drinking water pipes using oxidation induction time. The project has been carried out through literature studies, lab tests, data gathering and statistical analysis of large data quantities.

Firstly, I would like to thank Annika Malm from RISE who has been the supervisor of this Master's project as well as Thomas Petterson from Chalmers who has been the examiner.

Furthermore, I would like to thank all the personal at *Pipe Centre, RISE* for their hospitality and kind words. Olle Persson deserves a special mention for his key role in my project, he has been a contributing with positive energy and a drive as well as well-founded knowledge in the area that have affected this project positively. I would also like to thank Kristian Thörnblom who helped with OIT-analysis as well as Chalmers MasterCard who financed the tests.

Lastly, I would also like to thank my partner Elin Tjäder as well as family and friends who has supporting me during this Master's Thesis.

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Emil d'Elia

1. INTRODUCTION

Drinking water utilities are essential in modern cities and are often taken for granted. For a lot of citizens, the drinking water distribution is only acknowledged when it fails or during short distribution abruption during maintenance or expansion of the system.

Large investments are made continuously to maintaining and expanding the drinking water network. In the United States during the twenty-first century the capital cost for water infrastructure has decreased while the maintenance cost is steadily increasing (Congressional Budget Office, 2015). The maintenance cost during 2014 was two times the annually capital cost and the trend shows that the gap will increase further. When large investments are made, it is crucial that the best materials, techniques and know how is used as this directly affect future maintenance costs. The cost for a new drinking water pipe is commonly around 640 EUR/m while the cost to repair a pipe failure was 6000 to 16000 EUR during 2007 to 2009 in Gothenburg (Malm, et al, 2015), however a single repair can exceed 500 000 SEK (52 000 EUR) (4S Ledningsnät, 2017) which future shows the importance of a rigid installation and the use of long lasting materials and joining methods. Future more, all pipe failures bares a potential risk to harm citizens while also being a disturbance for traffic and other systems within the city.

The most common drinking water network pipes used in Sweden as well as internationally are different kinds of polyethylene pipes. In Sweden, high density PE80 and PE100 is commonly used (Malm, et al., 2011).

In Sweden and neighboring countries, the certification *Nordic Poly Mark* is commonly used to guarantee a good quality for polyethylene pipes used in drinking water networks. The certification can be requested for purchased pipes in order to guarantee a certain quality (Nordic Poly Mark, 2017). However, the differences between certified pipes can be vast even though they both have been certified. In order to improve the quality of pipes even further it is believed that knowledge regarding the pipes need to be increased. A knowledge gap between manufacturers and client has been identified for example by the organization 4S (4S Ledningsnät, 2017), a knowledge gap and a lack of information exchange can lead to a halted development of new pipes and pipe materials.

This thesis is done in collaboration with "*Rörcentrum*", in English *"Pipe Centre"*. *"Pipe Centre"* is a part of RISE, Research institutes of Sweden; "*Pipe Centre*" is conducting tests and *Nordic Poly Mark* certification of pipes and plastic tubes. Furthermore, they are consulted in situations and investigations in need of a third part evaluation regarding pipe, pipe-joints etc. Entwined in the organization are also several researchers which support a high level of expertise within the organization.

1.1 Aim

The purpose of this thesis is to increase the knowledge regarding polyethylene pipes, as well as identify trends regarding the quality of produced pipes and to evaluate these in an academic and constructive way.

Furthermore, thermal oxidation properties will be tested on a pipe that have been installed for nine years to evaluate current lifetime predictions for drinking water polyethylene pipes. The test is also performed to assess the methodology of OIT-measurements and how they can be used to investigate oxidation properties of polyethylene drinking water pipes.

1.2 Delimitations

This report will focus on polyethylene pipes in polyethylene material PE80 and PE100. Only drinking water pipes have been investigated even though PE-pipes commonly are used for pressurized sewerage pipes as well.

The data investigated is limited by the database, the database contains data from roughly 900 PE-pipes tested for the certification Nordic Poly Mark or prior to 2004 KP-marking. The tests were performed by RISE (previously SP) during the period 2000 to 2012.

The OIT-analysis performed is limited by the number of test taken and the results are not conclusive. In order to receive conclusive results, several tests on multiple pipes over a long period of time would have to be conducted. The test is rather done to test the methodology and to get a hint of how if any noticeable oxidation has occurred.

2 THEORETICAL BACKGROUND

The annually replacement rate of drinking water distribution pipes in Gothenburg is 0,5%, corresponding to 8km/year (Malm, 2015). In the future, depending on the quality of the pipes used today, the replacement rate will have to be adjusted accordingly. The main material used for replacement and expansion of the drinking water network is polyethylene (PE)-pipes. However, some ductile iron pipes are also used, primarily in areas where there is contaminated soil or possibility of contaminated soil.

The budget for reinvestment and maintenances of the drinking water distribution network in Gothenburg during 2016 was 46 MSEK(5 MEUR) (Kretslopp och Vattennämnden, 2015), which corresponds to roughly 100 SEK (10 EUR) /year for each inhabitant. Due to a change of the budget for 2017 where investments, reinvestment cost and maintenance costs have been merged, and for 2017 the total budget for drinking water distribution within Gothenburg is 124,5 MSEK (13 MEUR).

The most common replacement method is pipe bursting, and for 2017, 37MSEK (4 MEUR) (Kretslopp och Vattennämnden, 2016) is budgeted to be spend on pipe bursting projects. For pipe bursting projects, high-density polyethylene, HDPE, is the primary pipe material used. The total budget during 2017 is assumed to be similar as the budget of 2016. Due to the big economical resources that are spent on drinking water infrastructure, it is of high importance to fully understand the effects and parameters that can affect the lifetime of the infrastructure. Of the total cost spent on drinking water distribution, only a small part is spent on the pipes. However, the pipe plays the most central role when it comes to lifetime and total life cycle cost of the projects.

High density polyethylene, commonly abbreviated as HDPE or PEH, is the dominant material for new drinking water distribution pipes (Janson, 2003). Previously, before 1980, some lower density PE was also used, mostly for pipes with a smaller diameter. PE with lower density is sometimes referred to as PEL or PEM, which refers to low and medium density. PEM pipes replaced most of the applications for PEL pipes in the middle of the 1970: s (Malm, et al, 2011).

In Sweden, PE-pipes has grown in popularity during the last decades, and is now the primary pipe material for pressurized drinking water networks. Few pipe failures have been seen and the majorities of leakage from PE-pipes comes from insufficient connections between pipes. The leaks are commonly a result of lacking montage (weak joints) or corrosion of metallic parts (Malm, et al, 2011).

2.1 Plastic

A plastic material is generally composed by a synthetic polymer mixed with different kinds of additives for example anti-oxidants stabilizers, softeners and fire retardant in order to form a functional material for the specific purpose (Klason & Kubát, 1987).

2.1.1 Polyethylene - PE

Polyethylene is a plastic material composed of polymers with few added substances. For PE-pipes, substances such as anti-oxidants and carbon black, are added to improve oxidation- and UV-resistance as well as to change the colour of the pipe (Klason & Kubát, 1987). Polyethylene is the most common plastic in the world as it can be modified and formed for

multiple uses. Common everyday uses are in plastic bags, packaging, plastic toys and utensils. (PlasticsEurope, 2017).

Polymers are composed of carbon and hydrogen connected in a chain like structure. The polymer is built up by numerus monomers which attach to each other and create longer polymer chains. The monomer is the smallest distinctive atom composition that forms the plastic. Polyethylene in composed of the simple monomer created from ethylene shown in *Figure 1* below (Janson, 2003). The ethylene can be produced by heating crude oil. The heat breaks longer hydrocarbon chains and separates the different organic compounds, this process is called cracking. Ethylene can also be extracted from natural gas.
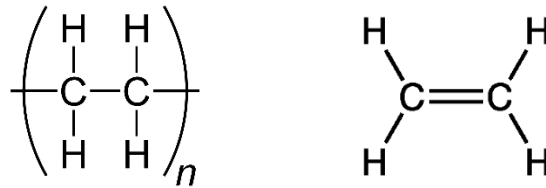

Figure 1: Polyethylene monomer and ethylene. "n" number of monomers are connected to form the polymer.

Through polymerization, the monomers are polymerized into longer carbon chains that form the final plastic material. Polymerization process can happen in multiple ways, the one described here is called *"free radical polymerization"*. The polymerization process is initiated by the addition of a catalyst. The structure of the polymer depends on the properties of the polymerization process, temperature and pressure. The original monomers composition affects the final polymer as well. Furthermore, different additives or catalysators can be added to control the process (Lepoutre, 2017). The polymerization process ends when a free radical takes an entire hydrogen atom from the polymer instead of just an electron. When the hydrogen is removed, a double bind is created between the carbon atoms and the polymerization process ends. This is called a termination reaction and ends the polymerization for that specific polymer (Kelley, 2017).

The molecular weight of the high-density polyethylene ranges from 10^3 to 10^4 g/mole. Compared to other polyethylene, the length of the polymer chain is distributed over a shorter span, which is connected to the molecular weight. At the same time, the branching of the polymers is limited, see comparison between HDPE and LDPE, low-density polyethylene, in *Figure 2* and *3*. This results in a material that is physical harder and more compact compared to materials composed of more branched polymers.

The high-density polyethylene, HDPE, which the investigated pipes are made of, is produced at a lower pressure and temperature and with an aluminium based catalyst. Low-density polyethylene, LDPE, which for example is used in plastic bags, is produced at a higher temperature and pressure (Lepoutre, 2017). After the polymerization of the ethylene to polyethylene, the material is cooled and formed into smaller resins at the size of roughly 5mm in diameter. Depending of the final use of the plastic, different additives can be added. Some of the most important additives in HDPE for pipe production are antioxidants and carbon black.
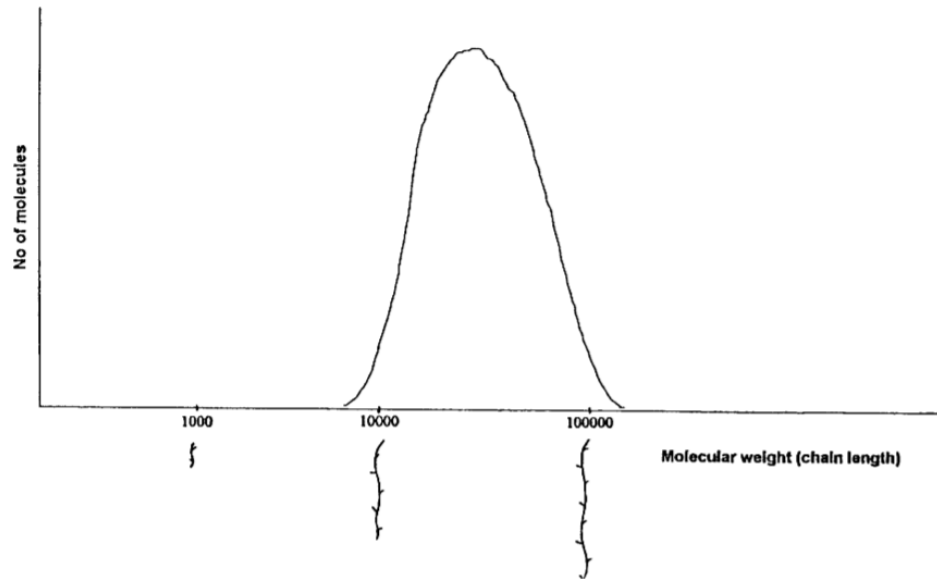
Figure 2: Molecular weight distribution and visualization of branching in, HDPE (Lepoutre, 2017).
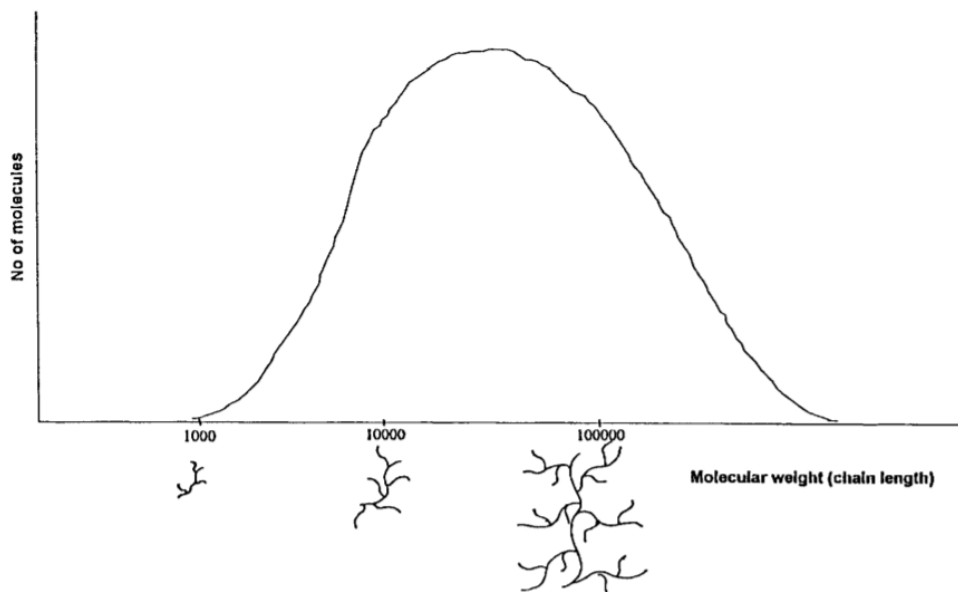

Figure 3: Molecular weight distribution and visualization of branching in, LDPE (Lepoutre, 2017)

2.1.2 Additives in Polyethylene Pipes

Adding antioxidants to the polymeric material is crucial to increase the resistance towards chemical reactions within the material. The use of antioxidants can increase the time to chemical embrittlement by far beyond 10 times (Tolinski, 2015). Commonly, a mixture of at least two different antioxidants are used, one primary and one secondary. The primary antioxidant is mainly added to the material to act as a buffer. It reacts with and neutralizes free radicals that otherwise would react with the amorphic part of the polymer. The secondary antioxidant is designed to more effectively react with oxidised parts of the polymer and by doing so reducing the risk of a chain reaction. Antioxidants account for approximately 0,2% of the total weight in the finished pipe material.

Common antioxidants for polyethylene pipes is different types of hindered phenol antioxidants as primary in combination with thioester or phosphite as secondary (Tolinski, 2015) The hindered phenol, as well as other primary antioxidants, donates an active hydrogen atom to a free radical and thus stabilizing it. When reacting with the free radical, the antioxidant becomes a less aggressive radical called hindered phenoxy. The newly created radical is not capable of reacting with the polymer chains. In this process, the antioxidant is consumed and part of the inbuilt protection against oxidation is degenerated (Tolinski, 2015).

The secondary antioxidant is supposed to react with the products created by autoxidation in the material and by doing so, halt the chain-process that otherwise would lead to continues oxidation of the polymer. However, the effects and characteristics of the secondary and primary antioxidants overlap with each other. Furthermore, other additives, for example carbon black, can have a positive effect of the oxidation properties of the material even though that might not be the primary purpose (Dgawan, et al, 2012).

In an oxidation process it is the surface of the material that will oxidise first since it is there that free radicals can become present. Thus, it is in the surface area of the material that anti-oxidants are primarily needed. Antioxidants are capable to diffuse in the material and by doing so increase the oxidation resistance of the surface areas. The diffusion of anti-oxidants is however slow and affected by the molecular size of the anti-oxidant (Roe, Bair, & Gieniwski, 1974). A common primary antioxidant is *Irganox 1010*, which has a molecular weight of 1178g/mole which according to Roe et. al.(1974) has a diffusion speed of $0,32*10^{-8}$cm^2/s at 67°C, which is equal to roughly 0,19mm/10 years at 10°C. As comparison, a smaller antioxidant with a molar weight of 358g/mole, such as *4,4'-Thiobis,* has a corresponding diffusion speed of 0,81mm/10years at 10°C. The diffusion speed for 10°C are calculated using the assumption that for every 10°C in temperature drop, the diffusion occurs 50% slower. This assumption is attested by a study done by J. Y. Moisan. However, the study was done at a higher temperature (Moisan, 1985).

In polyethylene pipes carbon black is commonly added to protect the material from harmful UV-light. The additive is primarily used to reduce the sensitivity of the pipes during outdoor storage and transportation. However, carbon can also affect the long-term oxidative properties of the pipes in both negative and positive ways. Polyethylene tested with and without 2,5 % added carbon black showed that the added carbon black increased the initial OIT-value (Oxidation Induction Time) with 5% (Wong & Hsuan, 2014).

2.1.3 Difference between PE80 and PE100 pipes

The pipes investigated in this report are PE80 and PE100. The plastic materials are tested according to the standard ISO TR 9080, meaning that the materials are classified to withstand a hoop stress of 8MPa for PE80 and 10MPa for PE100 at 20°C for 50 years. The value is referred to as "*minimal required stress*" or MRS-value (Zhang & Jar, 2016).

PE100 is a stronger material compared to PE80, but PE80 still has benefits in some areas. PE80 is a softer material which makes it possible to transport the pipe in coils, while also the number of joints that must be welded on site can be reduced. Joints are the weakest part of the drinking water distribution network, all joints that can be avoided leads to a better project economy as well a better result (Malm, et al, 2011). PE80 is commonly used for pipes with a smaller diameter, less than 90 mm, while PE100 often is used for pipes with a bigger diameter. The softer material also makes PE80 pipes more resistant towards stress cracking

and has a better slow crack growth resistance. The material used to produce PE80 pipes can be both high and medium density polyethylene while PE100 almost exclusively is produced by high density polyethylene.

High-density polyethylene gets a higher density as it has a higher crystallization ration compared to medium-density polyethylene. Crystalline polyethylene has a density of $1,0$kg/dm^3 while the amorphous part has a density of $0,85$kg/dm^3 (Griskey, 1995).

The higher strength of PE100 is acquired in two ways or a combination of the two. PE100 typically has a higher rate of crystallization, which leads to a more rigid material. Moreover, it gives the material a higher density, therefore PE100 and HDPE is sometimes used as synonyms even though the name refers to different characteristics of the material rather than differences in the material. A higher crystallization is accomplished by having longer and less branches molecules in the material, see *Figure 2* and *3*.

A high strength polyethylene, PE100, can also be acquired by using a bimodal molecular composition (Bilda, et al 2007). Bimodal material has been produced since the end of the twentieth-century and is now the dominating PE100 material. By using a mixture of two different molecular sizes, a material with better slow crack growth resistance is acquired. The finished pipes also get more flexible compared to traditional single modular PE100 material. The first molecule is similar to the polyethylene polymer used in monomolecular polyethylene. It gives the material a high density, high stiffness and a corresponding high hoop stress value. The second molecule used is a more branched molecule which "ties" the material together. It improves the notch stress resistance of the material while also making it more flexible (Bilda, et al 2007). In *Figure 4,* the distribution of molecular sizes within the material is visualized.
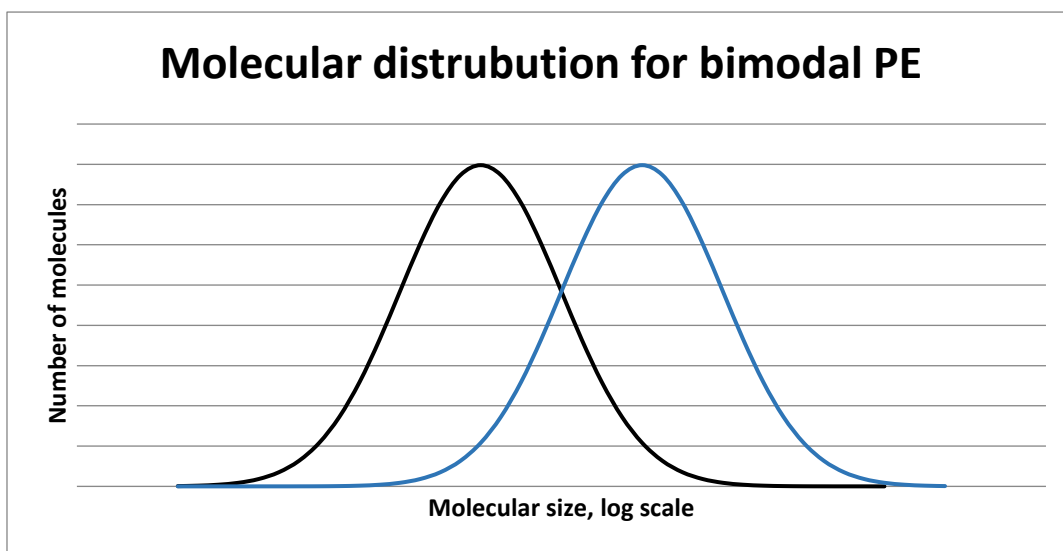

Figure 4: The black and blue line represents two different molecular distributions. A bimodal PE has two molecular distributions while a unimodal only has one (see Figure 2).

A PE100 pipe is manufactured by high-density polyethylene, HDPE. PE80 pipes can be manufactured by HDPE or MDPE. Since different polyethylene materials are used to manufacture PE80-pipes their characteristics can differ considerably compared to PE100 pipes which have a more consistent performance.

In Table 1, characteristics of PE80 and PE100 is presented. By evaluation of the numbers a numeric comparison of the materials can be made. PE80 is a softer material with a higher melt flow index and a weaker stress resistance. Apart from that, only minor differences can be seen between the materials. Worth noticing is that both PE80 and PE100 have a thermal expansion which cannot be ignored when designing larger drinking water networks.

Table 1: Characteristics of PE80 and PE100 pipes (Pipelife Sverige AB, 2017)

Properties	Unit	PE100	PE80
Density	Kg/m3	959	951
Melt Flow index	g/10 min	0,25	0,85
Modulus	MPa	1100	800
E50	MPa	1200	860
E0	MPa	210	160
Thermal expansion	mm/m/K	0,2	0,24
Thermal conductivity	W/m/K	0,4	0,36
Specific heat	g/K	1,8	1,9
Yield stress	MPa	25	19
MRS-value	MPa	10	8
Thermic stability (OIT, 210°C)	Min	>20	>20
Carbon black additives	%	>2	>2

Other plastics that are commonly used as pipe material is PP, polypropylene and PVC, polyvinyl chloride. However, PE is the primary plastic choice in pressurized systems, concerning both drinking water and pressurized sewerage systems.

2.2 Manufacturing of Pipes

To produce drinking water pipes from the raw material, the polyethylene resins are created for the intended purpose and a suitable amount of for example carbon black and antioxidants have been added to the plastic resins. The resins are melted in a chamber where temperature and other parameters are monitored and regulated to suit the end result. From the melting chamber, the melted plastic is extruded through a mould with the required dimensions of the pipe. The pipe is then cooled in a water bath to stabilize its form. The moulding process is continuous which means that the pipes can be made extremely long if it is practically possible. Pipes up 5km have been extruded in continuing and seamless section (Janson, 2003).

Extrusions speed is dependent on pipe diameter and SDR-value. The SDR-value stands for *Standard Dimension Ration* and is the outside diameter of the pipe divided by the thickness of the wall, common SDR-values are 11 and 17. The extrusion speed is also dependent on the specific pipes as well as material properties. Extrusion machines are commonly manufactured to be able to extrude a specific amount of material per time unit, for example 100 kg/hour. This means that smaller and thinner pipes can be extruded at a greater speed compared to larger and thicker pipes. Moreover, the molecular size and molecular size distribution in the material affects the melting properties of the plastic, and how easily it is to extrude. A plastic with a broader molecular distribution is more easily extruded compared to a plastic with a narrower molecular size distribution (Bilda, et al 2007).

2.3 Joint Methods

Polyethylene pipes are jointed using primarily three different techniques.

- Butt fusion
- Electrofusion
- Flanged joint

Preferably, pipes are joined using butt fusion, also referred to as heat fusion or heat welding. The joint is accomplished by placing the pipe ends that is to be joined towards a heated plate. The plate is heated to above 200°C causing the plastic to melt. Where after, the heated plate is removed and the pipes are forced together under pressure. As the plastic cools, the pipes merge together. If the joint is done properly, there will be no significant weak zones due to the joint (Janson, 2003).

Electrofusion is commonly used when joining pipes in situations where there are difficulties to accomplish a butt fusion due to for example lack of space. The electrofusion is done by positioning a plastic sleeve over the pipe endings that will be joined. Within the sleeve there is a metal resistance tread. The copper wire is then connected to an electrical voltage causing the sleeve and pipe to melt. As the material cool down the sleeve and the pipes weld together in a homogenous joint (Janson, 2003).

Flanged joints are commonly used when joining PE-pipes with objects of different materials, valves, flowmeters, water posts etc., as well as other types of pipes.

2.4 Predicted Lifetime of PE-pipes

Plastic pipes have a predictable aging cycle where the first two stages are dominated by physical properties of the pipe and then the third and last stage of the aging process happens as a result of chemical deterioration of the material. The regression curves can be seen in *Figure 5*. (Colin, et al, 2009)
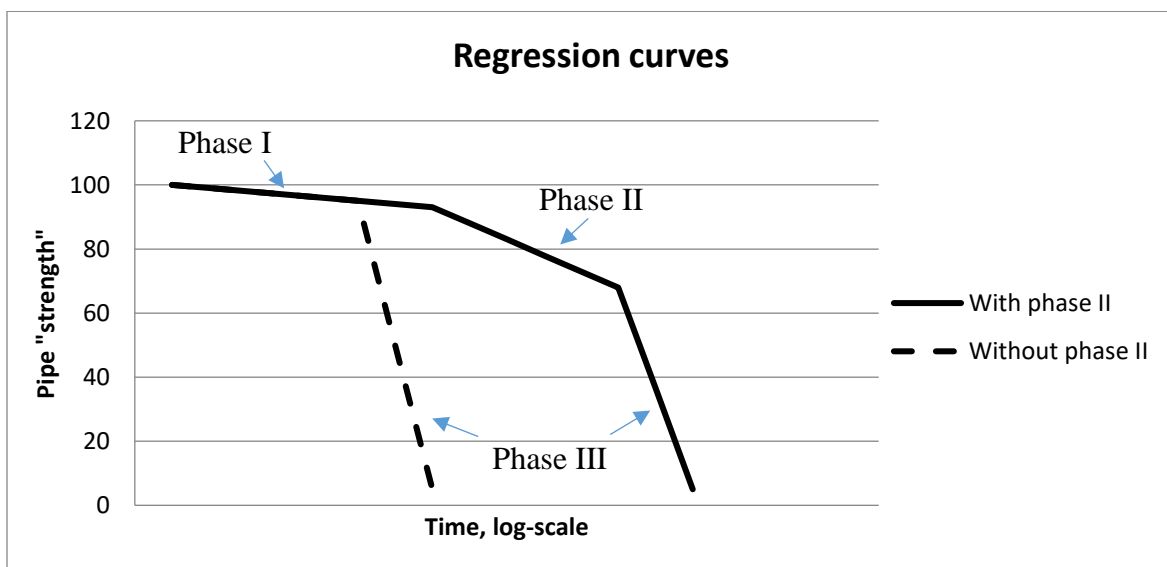

Figure 5: Regression curves for a drinking water polyethylene pipe.

During the first phase, only small changes to the material occur and the pipe is designed to stay within this phase for the guarantied lifetime of 50 years. Deformation caused by extensive stress to the pipe within this phase is generally recoverable (American Water Works Association, 2016). While in this phase, pipe overloads will result in ductile failure and overall the capacity of the pipe is good as it is designed with a safety factor of 1,25, except for its durability of 50 years (Malm, et al, 2011).

During the second phase, failure occur as a slower crack growth with a brittle characteristic on a macroscopic scale, Colin et al (2009) refers to this phase as "*The physical brittle regime*". Deformations caused to the pipes within this phase are most likely permanent in contrast to similar damages in phase 1. In the second phase, no significant chemical effects affect the material but rather physical stress contributes to the deterioration. Only small or no changes can be observed regarding the molecular weight of the polymer.

In the last, and third, phase a more rapid deterioration of the material occurs, Colin et al (2009) refer to the phase as "*The chemical brittle phase*". The phase occurs when the material starts to chemically deteriorate and the molecular weight of the polymer decreases. The molecular weight decreases due to chain scissoring performed by oxidation. The pipe could be considered to have surpassed its lifespan as the deterioration happens at a rapid speed once it has begun. If the pipe is exposed to a particularly harsh environment, the oxidation can start prematurely causing the pipe to skip phase two, see dotted line in *Figure 5*(Colin, et al, 2009).

Several studies regarding lifetime predictions of polyethylene drinking water pipes are found in literature. Several studies where pipes have undergone an accelerated aging process in hot water, 70-90°C, has been conducted, both under pressure and at different chlorine concentration etc. Different studies have predicted the lifetime of the pipes to be between approximately 30-200 years which is a massive range (Colin, et al, 2009; Hoáng & Lowe, 2008).

A study conducted by Hoáng and Lowe tested the relation between aging, temperature and the measured oxidation resistance (OIT-value) of the pipes. The study was done using oxidation analysis on pipes that had been artificially aged under pressure and in water at 80°C. The study showed promising results regarding the lifetime of plastic pipes using a combination of pressurized testing and chemical analyses (Hoáng & Lowe, 2008). They estimate the lifetime to between 150-200 years while in use in a drinking water network at a service temperature of 10°C.

Colin et. al. concluded that the lifetime for drinking water PE pipes where chlorine, concentration of 15mg/l, was used as a disinfectant could be less than 40 years (Colin, et al, 2009). Within the project, approximately 130 tests were conducted on polyethylene pipes that had been in operation for various times between 1 to 30 years. The pipes were collected from drinking water networks in southern France where chlorine was used as a disinfectant (2 samples was taken from non-chlorinated systems). The pipes were black polyethylene drinking water pipes, between 30 and 63mm in diameter and produced in accordance with the French standard NF EN 12201. The pipes were analyzed using OIT-measurements as well as other analysis. The plastic material in the studied pipes was however believed to be less resistant towards oxidation compared to newer pipes as the material development has continued.

As can be seen from reviewed studies, there are contradictions within the scientific field regarding the lifetime of PE-pipes. However, a common prediction is that the modern PE-pipes have a life-span of above hundred years (Malm, et al, 2011).

2.5 The Oxidation Process

In the following chapter, a deeper analysis has been made regarding the oxidation process and thus the third phase of pipe deterioration process mentioned in previous chapter. A common test to measure oxidation resistance of a material is by conducting an OIT-analysis, *Oxidation Induction Time*-analysis. The results give an indication of how well the anti-oxidants in the material works, a hinger value is better than a low.

Oxidation is a chemical reaction that involves a transfer of electron/-s from one atom/-s to another (Petrucci, 2007). A common electron taker is oxygen, which easily attracts electrons and therefore the process has been given the name oxidation. Firstly, the oxidation occurs at the end of the polymer chains where a double bound between two carbon atoms is reduced by one electron to a free radical such as oxygen. Oxidation can also cause a chain scissoring of longer molecules which leads to a higher melt flow index and a weaker material (Oluwoye, et al, 2015).

The oxidation process that takes place in polyethylene is initiated at the amorphous part, unstructured part, of the material thus making a more crystalized polyethylene less vulnerable to oxidation compared to a polyethylene with a lower degree of crystallization (Oluwoye, et al, 2015). This is one factor that makes high-density polyethylene a more suitable pipe material over low or medium-density polyethylene. Once the amorphous part has been oxidized and broken down into smaller polymer chains, the crystalline portion of the material can start to oxidize. The integrity and the stability of the material is decreasing even as the amorphous part oxidizes.

The chemical failure of the material occurs when the material enters phase III, see *Figure 5*. At this point, the polymers in the polyethylene have begun to break down as a result of oxidation. During oxidation, the longer polymer chain reacts with free radicals diffused into the material or free radicals in the direct vicinity of the pipe wall years (Colin, et al, 2009). Depending on the surrounding factors, the pipe will break in phase II or phase III. In strongly reactive environments the material will oxidize before it even reaches phase II of its aging process.

There is a correlation between oxidation of the material and the mechanical properties, however it is not a linear correlation as it depends on several factors; molecular weight, crystallinity ratio, antioxidants type and concentration, temperature, water pressure and chlorine concentration (Whelton & Dietrich, 2009). As can be seen in *Figure 6,* it is first when very low OIT-values are observed, that the strength of the material suffers significantly. The pipe with the lowest OIT-value is probably close to, or in phase III of its aging cycle.
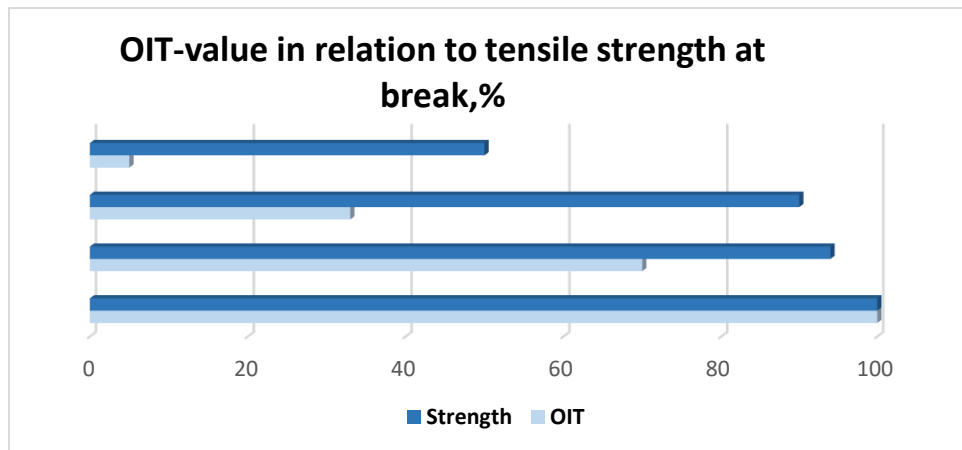
Figure 6: OIT in correlation to tensile strength at break compared to the initial value of 100%. Test performed on pipes that had been aged at 23-37℃ in water with high chlorine concentration. The OIT-analysis was performed at 200℃ and origin OIT-value of the pipe was 92min (Whelton & Dietrich, 2009)

Oxidation of the material drastically increases the risk of brittle failure (Colin, et al, 2009). To reduce the risk of oxidation, antioxidants are added to the pipe material. When conducting the OIT-test it is primarily the amount and effectiveness of the added antioxidants that is tested. This explains why the change in pipe strength is relatively stable as the OIT-value declines, as seen in *Figure 6*. Until the OIT-value of the pipe is highly reduced it is mainly antioxidants that is depleted. Once the antioxidants within in the material have been depleted, the last, and third, phase of its aging process starts and a more drastic decrease of strength occurs.

The oxidation of the pipe material is affected by several factors associated with drinking water distribution. It has been concluded that chlorine in the water can act as a catalyst for the chain reaction, leading to an increase of free radicals which in turn can react with the polyethylene (Mitroka, et al, 2013). However, studies have shown that the chlorine concentration was only responsible for a part of the degradation of the HDPE. Test performed on hot water PE-pipes using water at 70°C showed that low levels of chlorine, 1ppm, had an insignificant effect on the degeneration of the material. Other studies have shown that higher concentrations do have an effect. At chlorine concentrations of 25ppm and 100ppm, a clear degeneration of the pipe material could be seen. However, the difference between the degeneration of the material was small between the different concentrations, 25ppm and 100ppm (Montes, et al, 2012).

2.6 INSTA-CERT, EN 12201-2:2011 and *Nordic Poly Mark*
INSTA-CERT is a coalition between four certification bodies within the Nordic countries. The bodies are RISE certification, Sweden; Dancert A/S, Denmark; Norner AS, Norway and Inspecta Serifiointi, Finland. The organisation works with quality certifications for a variety of products. For plastic polyethylene pipes the certification is called *Nordic Poly Mark*.

The certification acknowledges that the product has the required properties to be used in the Nordic countries (Nordic Poly Mark, 2017). The requirements for the certification is in line with the international standard EN 12201-2:2011. The certification demands both mechanical and chemical testing of the material used in the pipes as well as on the finished product. Furthermore, it is required that certified companies have a structured and continuous quality control system for all produced products.

The testing methods described in this chapter are the ones conducted on the finished pipe to receive the *Nordic Poly Mark* certification.

2.6.1 Pressure Tests

When assessing the pipes for the *Nordic Poly Mark* certification, four different pressure tests are performed Two test are performed at 80°C in order to accelerate the aging of the pipes. One pressure test is performed at room temperature (20°C) for 100 hours and is done to test the max stress of the pipe. The last pressure test is performed at room temperature (20°C) for 2500 hours. The longer pressure test is seldom performed, which is why this test has not been evaluated in this project due to limitations in data availability. A summary of the parameters for pressure tests can be seen in *Table 2*

Table 2: Performed pressure test for the certification Nordic Poly Mark with time, temperature and pressure for PE80 and PE100.

	Circumferential hoop stress for various pipes and minimum temperature			
Pipe material	20°C for 100h	80°C for 165h	80°C for 1000h	20°C for 2500h
PE80	10 MPa	4,5 MPa	4 MPa	9,1 MPa
PE100	12 MPa	5,4 MPa	5 MPa	11,1 MPa

2.6.2 Elongation at Break

To see how much the material can be stretched before breaking, the *elongation at break* test is performed. The test is regulated by ISO 6259-1:2012 and is a part of the *Nordic Poly Mark* certification requirements. To pass the test, the elongation at break must exceed 350% (Swedish Standards Institute, 2011).

The test is performed by cutting or making "dog-bone" shaped forms from the pipe surface, as shown *in Figure 7*. The cut test piece is then placed in a machine that continuously stretches the piece until breakage. Depending on thickness of the pipe it is stretched at a continuous speed of 25, 50 or 100 mm/min.
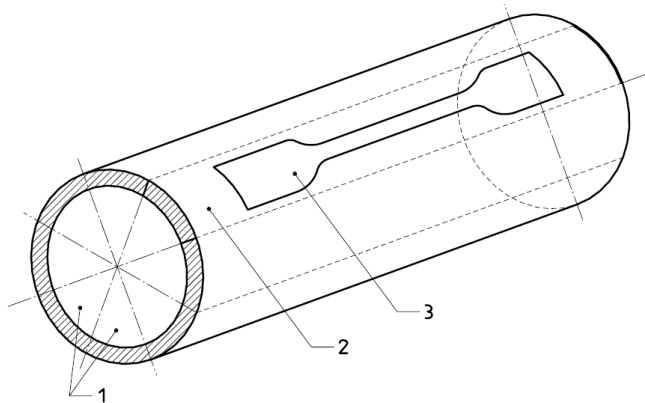

Figure 7: Principle of how the pipe is cut prior to testing elongation at break (International Organization for Standardization, 2012).

2.6.3 Melt Mass-Flow Rate, MFR

Melt flow rate, MFR, measures the liquidity, ease of flow, of a molten thermoplastic polymer. The result gives a good indicator on the molecular weight in the material, which can affect the physical properties of the pipe. The test is performed by collecting a small portion of the polymer that is placed in a barrel. The material is heated to a specific temperature, typically 190°C in accordance with ISO 1133-1 (European Committee for Standardization, 2007). The material is preheated for 5 minutes before a piston starts to apply pressure to the sample. The molten plastic is then forced through a gap, a few millimetres wide. The amount of plastics extruded gives the melt mass-flow rate of the material, *Figure 8* visualizes the methodology. Depending on the liquidity of the material, different forces and temperatures can be used. For polyethylene, a nominal load of 5 kg is commonly applied but depending on the result 0.325 kg, 2.16 kg or 21.6 kg can be used.
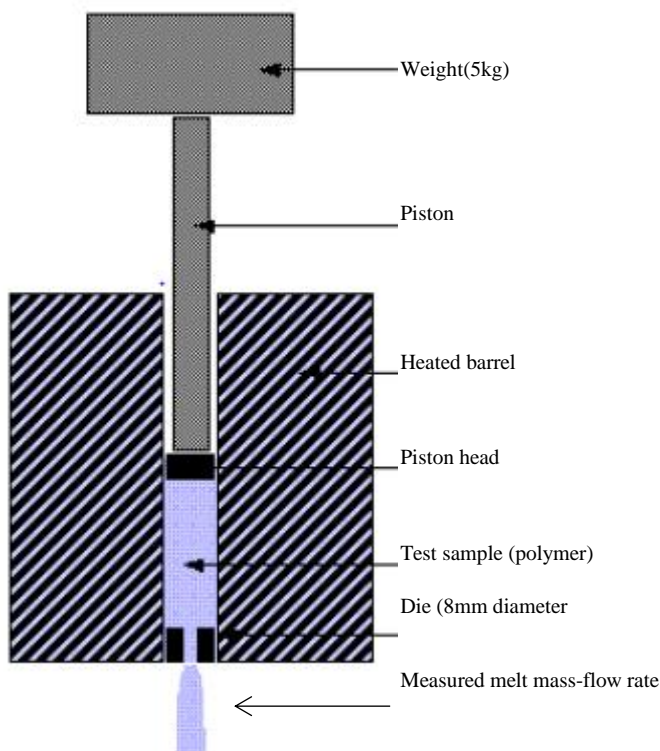
Weight(5kg)

Piston

Heated barrel

Piston head

Test sample (polymer)

Die (8mm diameter

Measured melt mass-flow rate

Figure 8: Principle figure of how MFR is tested.

Melt volume-flow rate is sometimes reported instead of melt mass-flow rate. Instead of evaluating the weight of the of the polymer, the volume is addressed. Melt volume-flow rate, MVR, is expressed in units of cubic meters per 10 min in while MFR is expressed as grams per 10 min (International Organization for Standardization, 2011). Sometimes MFR-value is referred to as melt flow index (MFI). Confusingly, MFR can also be used as an abbreviation of melt flow ratio. Melt flow ratio is a value obtained when dividing the melt flow-rate from different test with each other, for example MFR at 190°C and 2,16 kg, nominal load, divided by MFR at 190°C and 21,6kg, nominal load. As the standard EN 12201-2:2011 focuses of MFR, melt mass-flow rate, so will this report.

The MFR value is connected to the molecular weight in the material. Larger molecules result in a lower MFR value. Therefore, HDPE typically has lower MFR compared to MDPE and LDPE as high-density polyethylene generally has a higher molecular weight and a narrower

molecular weight distribution. Because of larger molecules and narrower distribution of molecular size, a material with a low MFR typically has higher density due to a higher crystallization rate and therefore also less amorphous molecular structure.

To reach the standards required by EN 12201-2:2011 that is needed for the *Nordic Poly Mark* certification, the MFR must not deviate more than 20% between the finished pipe and the raw material used. The MFR is tested in accordance with EN ISO 1133. Apart from the requirements, the melt flow-rate of a pipe material is also of importance in practical work, especially when considering the joining of two separate pipes, as the preferable joining techniques are butt-welding and electrofusion.

When butt-welding pipes, the MFR value should be taken into consideration. ISO TR 11647 claims that butt fusions can be made satisfactorily when the materials have an MFR between 0,3 - 1,3g/10min (190°C /5kg). Materials with a MFR value outside the specific range should be test welded before permanent installation (International Organization for Standardizartion, 1996). An older version of the German standard DVS 2207 -1 gives similar guidelines, the standard supports butt welding using material with a MFR within the range 0,3-1,7g/10min (190°C /5kg) (DVS, Technical Commitee, Working group "Joining of Plastics", 1995). However, in the most recent *DVS Technical Codes on Plastic Joining Technology* a significantly lower MFR-value of 0,1g/10min is mentioned as a problematically low MFR-value to acquire successful joints (DVS Media GmbH, 2015).

Furthermore, it is of importance that the difference between the MFR-values between joining material is not too large. It has been concluded that large differences can cause weak joints. In an article regarding failure analysis of a high-density butt weld joint Tariq et al(2012) concludes "*Large difference between the MFI of cylinder and dome section renders both materials very difficult to weld". (*Tariq, et al, 2012).

2.6.4 Oxidation Induction Time, OIT

There are two different kinds of OIT-testing methods, one isothermal and one dynamic. The *Nordic Poly Mark* certification uses isothermal test. The isothermal OIT test measures the time it takes for the material to start oxidising at a constant temperature. To get the certification, the OIT time must exceed 20min at 200°C. The dynamic test measures at what temperature the material start to oxidise in an environment where the temperature is constantly increasing, for example 10°C/min (Swedish Standards Institute, 2013). AWWA, American Water Works Association, demands a dynamic temperature above 230°C to pass the C901 standard commonly used for drinking water pipes in North America (American Water Works Association, 1997).

The OIT-test performed on *Nordic Poly Mark* certified pipes is explained by EN ISO 11357-6:2013. The test procedure is described as follows:

 "The specimen and a reference material are heated at a constant rate in an inert gaseous environment (a flow of nitrogen). When the specified temperature has been reached, the atmosphere is changed to oxygen or air maintained at the same flow rate. The specimen is then held at constant temperature until the oxidative reaction is displayed on the thermal curve. The isotherm OIT is the time interval between the initiation of oxygen or air flow and the onset of the oxidation reaction." (Swedish Standards Institute, 2013)

Throughout the test, the heat flow is monitored. When the oxidation reaction happens, it can be seen on the heat flow demand. The demand decrease as the temperature will increase due to the exothermic reaction occurring when the oxidation on the polymer takes place (Hoáng & Lowe, 2008).

Prior to the oxidation it is the antioxidants within the material that are used to bind the free radicals responsible for the oxidation (Viebke & Gedde, 1997). The testing parameters can be seen in EN 12201-2:2011 (Swedish Standards Institute, 2011). According to Olle Persson,[1] new pipes seldom fails the test; hence the testing is often done at a higher temperature (210-220C) in order to save time.

In a study concentrated on finding the oxidation effects from different additives in polyethylene, it was found that an initially higher OIT-value cannot be seen as a guarantee that the material is more resistant towards oxidation, see *Table 3* (Wong & Hsuan, 2014). OIT-measurements were performed on four polyethylene plastics with different amount of additives in form of carbon black and two antioxidants.

Table 3:OIT-value changes over time with different anti-oxidants added to the plastic (Wong & Hsuan, 2014)

Test sample	Concentration primary antioxidant, I-1010, Phenolic, ppm	Concentration secondary antioxidant, I-168, phosphite, ppm	Initial OIT, min	OIT after 1200 days in hot air environment
PE1	500	0	19,4	18
PE2	500	1000	33,3	18
PE3	1000	0	34,0	31
PE4	1000	1000	58,7	33

It appears as the primary antioxidants had the best effect for the long-term oxidation in the tested pipes. The added secondary antioxidant appears to have a limited effect on the long-term oxidation. However, as the test pieces were aged in an air environment at 85°C, the results cannot be directly translated towards the aging of drinking water pipes.

2.6.5 Longitudinal Reversion

The test measurers how much the pipe expands with rising temperatures as well as if any permanent changes can be observed due to the heating. The longitudinal expansion of the material is partly a consequence of internal stress in the pipe. During manufacturing, extrusion and the following cooling, a stress is built into the pipe. A higher extrusion speed leads to a faster cooling of the pipe material. A faster cooling process leads to a higher internal stress and that is shown as a higher result in the longitudinal reversion test.

Internal stress may also lead to a larger "*tow-in*", or "*barrelling*"-effect on extruded pipes. The "tow-in" is a consequence of internal stress causing the pipe ends to deform. The tip of the pipe bends inwards and the maximum diameter increases slightly a small distance from the pipe end, see *Figure 9* (Guevara-Morales & Leevers, 2012). An extensive barrelling of the pipe can lead to joint complications. The electrofusion sleeve used to join two pipes can be

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[1] Conversation/study visit RISE-facilities 2016-12-16

hard to install properly due to the increased diameter, furthermore the surface area is reduced. The reduced surface area between the pipe and the electrofusion sleeve leads to weaker joints.
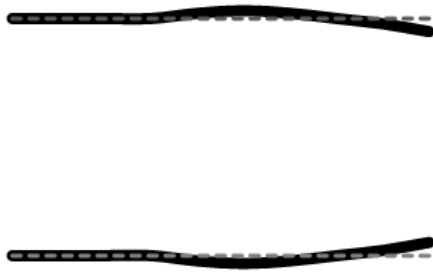

Figure 9: An exaggeration of the "tow-in" effect caused by internal stress.

The *Nordic Poly Mark* requires a maximum longitudinal reversion of 3%. The test is performed in accordance with ISO 2505. The pipe is cut into pieces of 200 ± 20mm, if the pipe diameter is 250mm or larger longer pipe sections may be cut. The test piece is then submerged into a liquid at a temperature of 110°C for 15 or 30 minutes, depending on wall thickness. Before and after testing, the test pieces are visually inspected and measured (International Organization for Standardization, 2005).

3 METHOD

3.1 Literature Study

Firstly, a literature study was conducted. The study started wide, first by learning about the general properties and usage of polyethylene pipes. Then a short review of different pipe materials and their benefits and differences was conducted. The study then narrowed down to look closer at the properties and structure of the polyethylene material. The material must be thoroughly understood to be able to draw valid conclusions and make suitable assumptions when the test phase of the project is initiated.

To draw rightful conclusions, a wide understanding of the material down to a molecular level was believed to be necessary. Further literature studies were focused on testing methods to understand how the molecular characteristics can be monitored and analyzed. The last part of the literature study was to investigate differences between different standards used, as this can put a light on what the *Nordic Poly Mark* certification is lacking or not. It could also lead to suggestions of further changes or modifications of the certification requirements.

3.2 Analysis Historic Data

Firstly, all data was collected in a manageable excel document. The data come from test conducted as quality controls of pipes certified or to be certified *Nordic Poly Mark* or prior to 2004 the *KP-marking* (A similar national, Swedish quality certification). Data regarding OIT-values (both at 200°C and 210°C), melt flow-rate, longitudinal reversion, elongation at break and pressure tests was documented, see *Table 4*. Furthermore, pipe information such as manufacturer, raw material, pipe quality (PE100, PE80, etc.), density, dimension, pressure class and date of testing were documented.

Table 4: Tested and documented parameters. Parameters unit and their required value to get the Nordic Poly Mark certification.

Parameter	unit	Required for NPM-certification
OIT	min	>20min
MFR	g/10min	Max 20% deviation from raw material
Longitudinal reversion	%	<3%
Elongation at break	%	>350%
Pressure test 1	*Passed* or *failed*	100h at 20°C at 10 (PE80) or 12,5 (PE100) MPa
Pressure test 2	*Passed* or *failed*	165h at 80°C at 4,5 (PE80) or 5,4 (PE100) MPa
Pressure test 3	*Passed* or *failed*	1000h at 80°C at 4 (PE80) or 5 (PE100) MPa

Trends with regards to time was investigated to see if we have had a positive development or if some quality aspects have declined during the period of testing.

Furthermore, trends and correlations between different parameters was investigated and discussed in an informative and analytic way. Firstly, a plot of how the specific characteristics of the pipes have changed over time was made. A trend line was added to the graph in order to ease the analysis of the result. The changes over time are also expressed as a percentage

change to more easily comprehend the significance of the potentially observed trends. The changes, or lack thereof, have then been discussed with regard to real life application and how it might affect the overall quality of newly installed drinking water distribution networks. Secondly, the study focused on correlations between different pipe characteristics.

To investigate the correlation between different pipe parameters is believed to increase the understanding of the materials, as well as lead to an interesting discussion.

A total of roughly 10 000 pages were reviewed in order to gather the used data. From the reviewed reports, data concerning 893 pipes was collected with a total of 9681 data entries.

Data was collected from pipes where at least one parameter has been tested until failure, for example OIT or MFR, whereas pressure tests are not tested to failure as the test is aborted after a specific time. This has decreased the number of pipes in the used excel sheet as some pipes only have been pressure tested (marked as *passed* or *failed*) and thus not providing any data that could be reviewed and analysed in the same way as absolute values can.

3.3 OIT-analysis of Naturally Aged Pipe

In an attempt to analyze the aging performance in real life circumstances, OIT-tests was performed on a drinking water polyethylene pipe that were installed in 2008 (9 years ago). The pipe was a 315 mm SDR11 drinking water pipe, classified as PEH in the municipality GIS-software. The pipe was assumed to be PE100 since larger diameters seldom are PE80. The pipe has laid in a clay dominated environment soil and supported a pressure accelerating station in on the central areas of the island *Hisingen*, Gothenburg. The pipe was collected during a scheduled maintenance work not related to the specific pipe. Three tests were performed on the pipe, one at the internal surface, one at the external surface and one at the middle of the pipe wall.

The goal of the tests was to evaluate if any noticeable oxidation has occurred after nearly10 years in service. The pipe was tested at 210°C so that the results could be compared the collected historic data.

3.3.1 OIT-measurements Methodology

Firstly, the initial pipe was cut in to thinner slices, roughly 3-5mm thick, using a band saw, see *Figure 10*. The test pieces were marked and controlled for visible damages that could affect the result.

Figure 10: The figure shows the slices as they have been cut from the pipe. The white dots mark the pipe slices from which the test pieces were taken.

Once thinner sheets of the original pipe had been produced a punch was used to take out cylinder formed samples from the pipe. The side of the cylinder that was to be tested was then cut off with a scalpel to produce thin sheets of material that was to be tested, the total weight for the test pieces was 15mg ±2mg. To cut the test pieces proved to be a tedious task as the margin of error for the final cut was only 0,11mm. The equipment used, as well as the sheets of pipe material, can be seen in *Figure 11*.

Figure 11: The three pieces from with the test pieces was taken. The side that is not to be analysed is marked with a red pen to assure it is the surface pieces that is tested. The die as well as the scalpel can also be seen in the figure.

Once the test samples had been prepared, the pieces were loaded into a carousel and placed in a differential scanning calorimetry (DSC) machine, see *Figure 12,* for OIT-analysis. The pieces are supposed to be placed with the surface of interest facing up, e.g. the inside wall of the pipe. If the pipe is placed with the wrong surface facing upwards, the result of the test will indicate a higher OIT-value than it should. The oven in which the pieces are heated is controlled prior to testing to assure that the right kind of empty reference container is used, see *Figure 13*. The weight of each test piece as well as the testing program was specified. The program used for all the test followed the characteristics in *Table 5*.

Figure 12: The figure shows the loaded carousel when it is places in the DSC-machine prior to testing.

Figure 13: The oven of the DSC-machine in which the pieces are heated. An empty aluminium bowl is placed in the oven as a reference so that the result will not be affected by the aluminium carrier.

Table 5: Specific values of performed OIT tests.

Parameter	Value
Starting temp	50°C
Temp acceleration	25°C/min
Max temp	210°C
Nitrogen flow	50ml/min
Oxygen flow	50ml/min
Time at max temp in nitrogen	3min
Test abortion time	70min
Test abortion energy	4,5mW

Once the tests had been performed in accordance with the set characteristics, the results had to be analysed. The DSC-machine generates an energy curve of each piece analysed and the energy consumed by the test is constant for a time after that the plastic has melted. When an oxidation of the polymer occurs, a drastic change in energy demand can be noted and as the oxidation process is a exotherm reaction, less heat must be added to the test chamber. To evaluate the created curve, two tangents was added to the graph. One tangent to the horizontal line created prior to oxidation of the material. The other tangent is placed at the steepest angel on the curve after oxidation. Where the two tangents cross, the OIT-time can be observed, the method in shown *Appendix* 1.

4 RESULTS AND DISCUSSION - DATA ANALYSIS

In the following chapters, the test results from when pipes were assessed for the *Nordic Poly Mark*, or prior to 2004 the *KP-mark* certification are discussed individually as well as in correlation to other test results. The idea is to give the reader a wide understanding of correlation between different parameters and how they affect each other.

The results are based on test data 2000 and 2012 from tests performed by *RISE, Pipe Centre*. Out of the 893 tested pipes, 431 was manufactured from PE100 and 414 from PE80. The remaining pipes had unclear markings such as PEH which can indicate both a PE100 and a PE80 material; these pipes are used for general analyses where no considerations are taken to pipe material.

During the investigated period, the amount of tested PE80 pipes increased slightly, while the increase of tested PE100 pipes was more drastic. As seen in *Figure 14,* more pipes have been tested during the latter part of the period. In *Figure 15,* the pressure classification and diameter of the tested pipes can be seen.
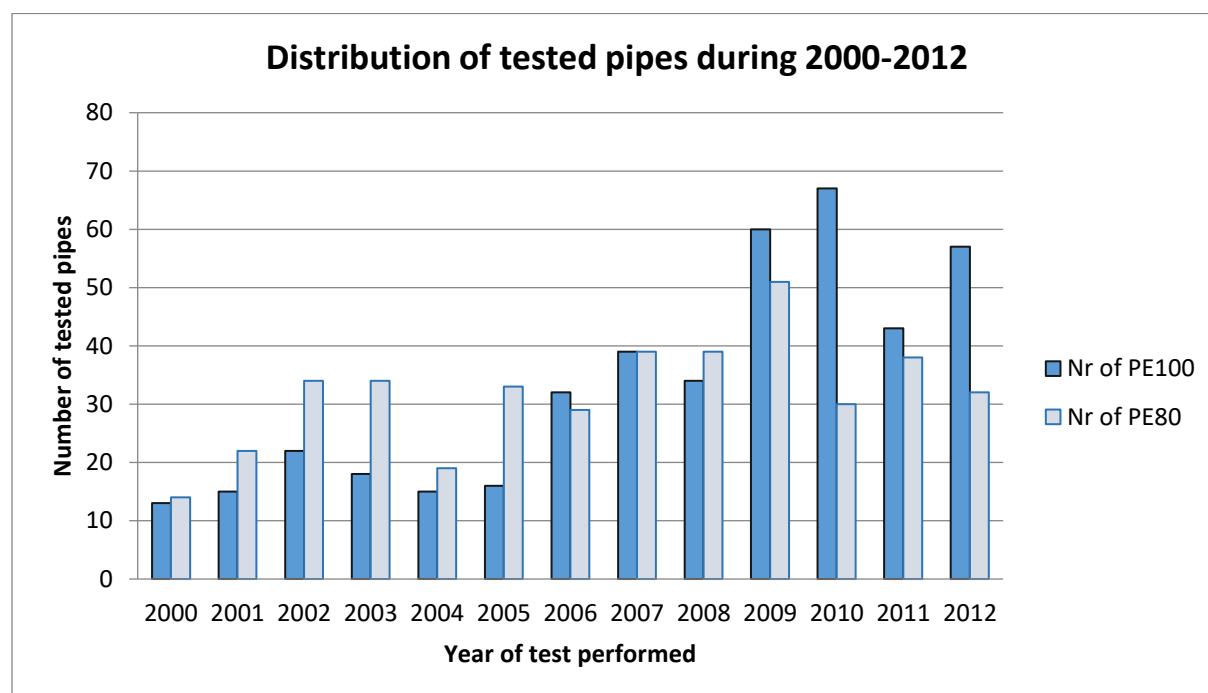

Figure 14: Diagram during which period the pipes was tested and whether they were PE80 or PE100 pipes.
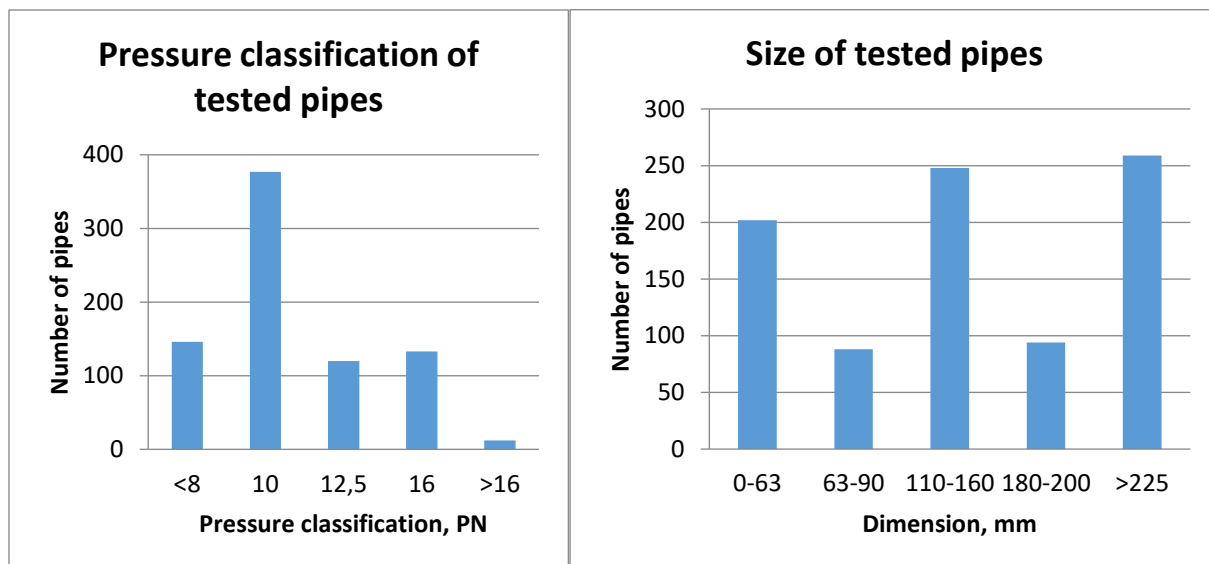
Figure 15: In the diagram to the left the pressure class of tested pipes can be seen and to the right the dimension of tested pipes.

4.1 Variations in OIT

The OIT-values has continuously been decreasing, however a reason for this might be due to the increase of test not driven to failure but rather was documented as ">60min". In *Figure 16* the blue full line represents the changes of OIT values over time excluding all values represented as ">60min", the dotted blue line shows the change where the documented result of ">60min" has been changed to 60min. The red line represents the changes of OIT values for PE80 materials.
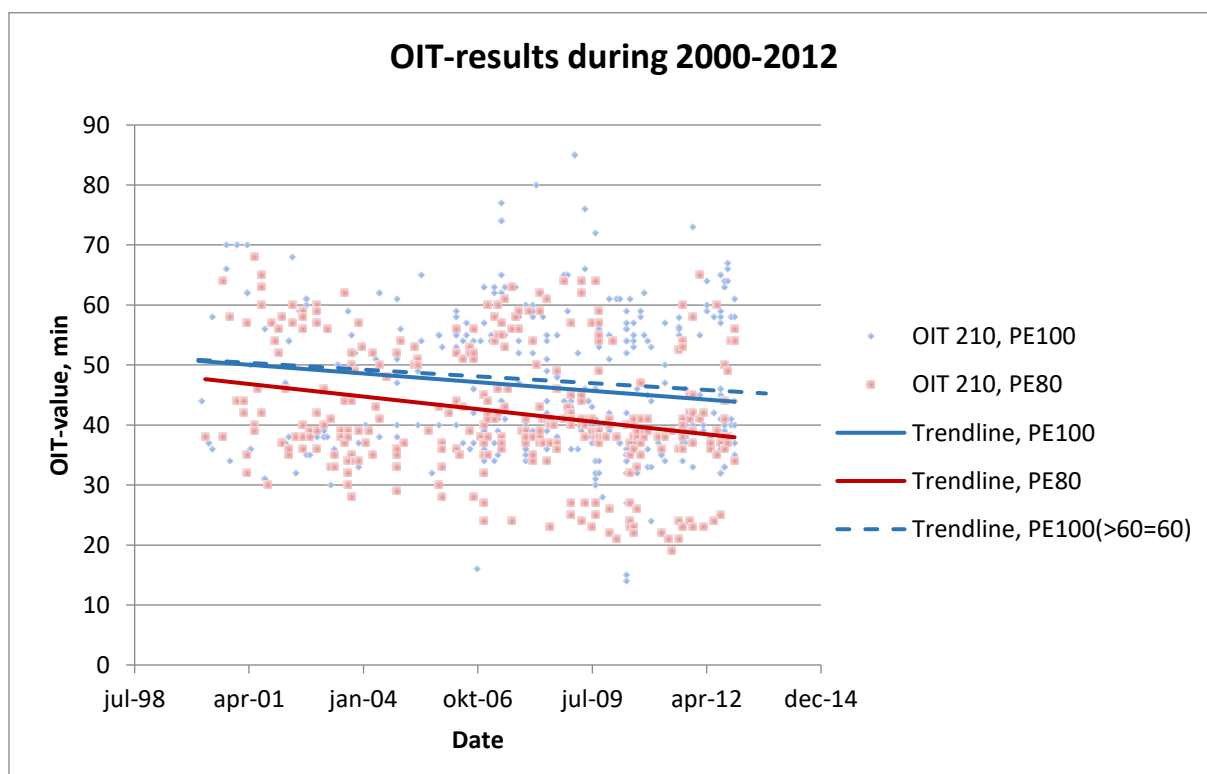

Figure 16: Variation of OIT-value over time

The difference between PE100 and PE80 are as expected, as higher density polymer generally is used for PE100. The crystallinity ration is predicted to be higher in the higher-grade polymer which also causes the material to have a natural better resistance towards thermal oxidation regardless of antioxidant additives. Something that must be remembered is that a higher OIT-value is not a guarantee that the material is better with regards to long-term oxidation, even though it is likely.

The decrease in OIT-value over time is somewhat unexpected and probably not a preferable change. If the polyethylene has larger molecules (higher end density of the material) which generally is a trend, a smaller amount of antioxidants has to be added. As the OIT-test primarily measures the performance of antioxidants, such a change could cause the test results to be worse while the long-term oxidation resistance has stayed the same or even improved.

Even though a negative trend can be observed, the test results are still far above the required quality of 20min at 200°C. Perhaps new and different ways of evaluating the oxidation resistance would be necessary to encourage a positive development with regards to thermal oxidation. As the test is performed today, a pass is almost guaranteed if a proper PE-material is used.

A correlation between dimension of pipe and OIT-values has been observed, see *Figure 17*. It is believed to be since lager pipes typically are thicker which leads to a longer cooling period during manufacturing. During manufacturing, a portion of the antioxidants in the material is depleted and the longer it takes to cool the pipe, the more antioxidants will be able to oxidize. A similar trend could not be observed when looking at pressure classification even though a higher-pressure class is acquired by having thicker pipe walls. It is believed that this correlation not could be found since smaller pipes commonly are classified at a higher pressure.

A possible way to reduce the thermal oxidation during manufacturing is by using nitrogen inside of the pipe during the cooling process. Since nitrogen contains no oxygen, the thermal oxidation cannot occur.
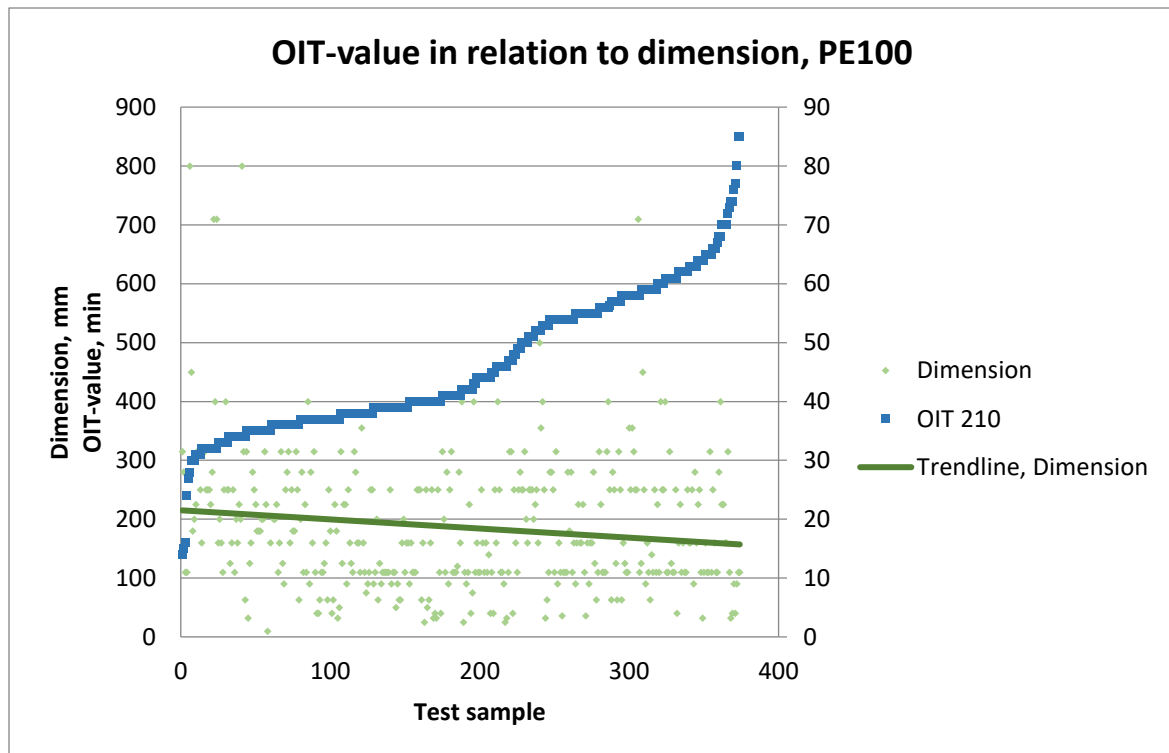
Figure 17: Diagram showing the correlation between diameter of pipe and OIT-value, the diameter of the pipe is shown to the left and the corresponding OIT-value to the right. Larger diameters pipe generally has a lower OIT-value.

A weak correlation was found between higher OIT-values and higher density. The data used for the investigation was done on both PE80 and PE100 and only comprehended 145 test samples out of which the majority was tested during the period 2000-2004. The correlation was expected as a higher density indicates a higher crystalline ration and thus makes the material more resistant towards oxidation.

4.2 Variations of Melt Flow-rate

The general trends concerning MFR-values are that PE100 has a declining trend while PE80 has an increasing. In 2000, the average MFR value for certified PE100 pipes was roughly 0,35g/10min in contrast to 0,25g/10min in the end of 2012. From a durability point of view, this can be considered a positive change as a larger molecular structure leads to a harder and less chemically reactive material.

Since the joining methods, butt fusion and electrofusion, relies on melting of the plastic to form the joint, a change in MFR can have negative effects for the joint strength. Several guidelines state that butt fusion is most suitable for materials with a MFR-value of above 0,3g/10min or a most recent source 0,1g/10min. Regardless of how low the MFR-value can be without harming the joint capability it is clear that a extremely low MFR-value is undesirable. Large differences in MFR-values has also been observed to cause weak joint both when using electrofusion sleeves and when using butt fusion. Large differences in MFR-values for PE80 can be seen in *Figure 18,* which contrasts with the results from PE100 pipes where the data points are a lot closer to each other. The large differences between MFR can be a potential problem for PE80.

Taking this into consideration, it might be good to be vigilant towards the MFR-values of new pipes. Low MFR-values can be a problem especially for PE100-pipes. Large differences between MFR-values for different pipes are likely to be more problematic for PE80 pipes. The *Nordic Poly Mark* certification has no requirements regarding MFR-value but rather that the change between raw material and finished pipe must not exceed 20%. With regards to current trend and how MFR can affect joint, it could be suggested to change the requirements regarding the MFR-values of new pipes.

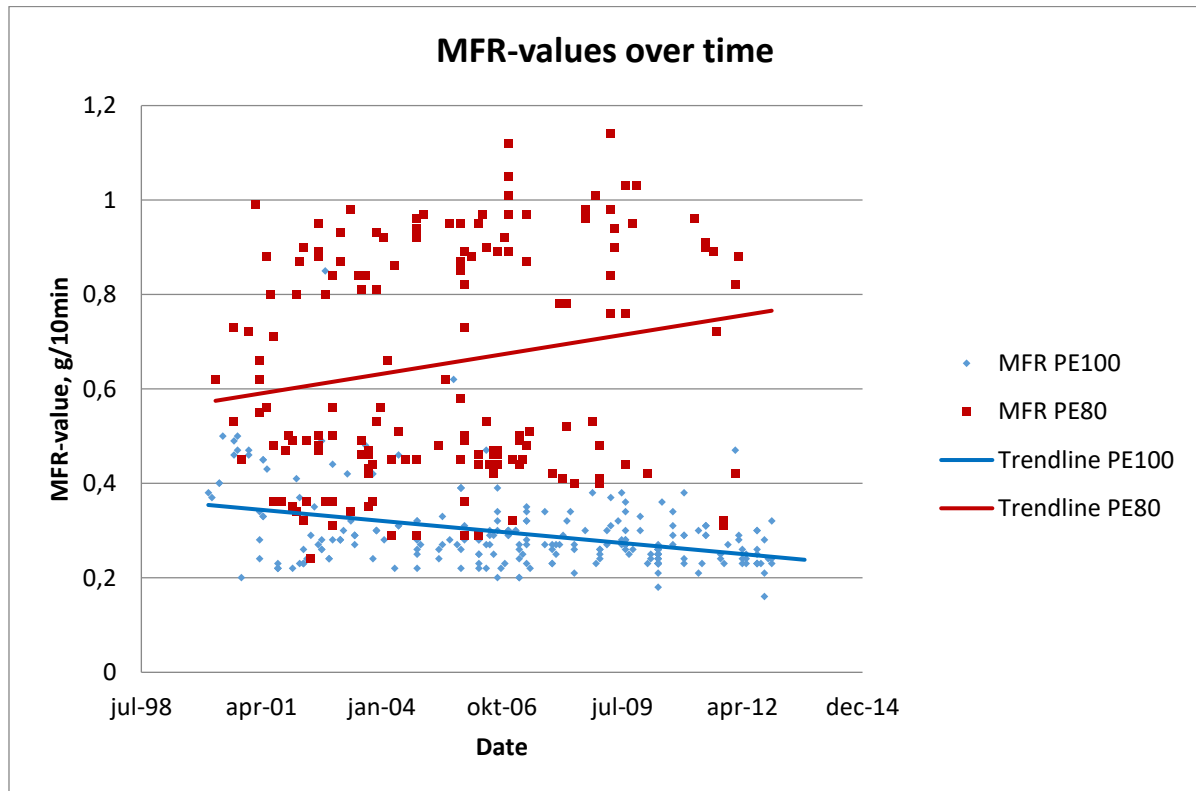The difference between PE80 and PE100 pipes has increased during the investigated period.

Figure 18: Changes in MFR-values over time for PE80 and PE100

The distribution for MFR-values for PE80 pipes is rather large compared to the distribution for PE100 pipes. The vast dispersion is a result of the raw material used to produce the pipes. A general trend is that PE80 material made from HDPE has a lower MFR-values compared to PE80 pipes made from HDPE. In *Figure 19*, it can clearly be seen that the distribution of MFR-values peaks at two different places. The first peak is believed to represent PE80 pipes made of HDPE while the second one represents pipe made from MDPE.
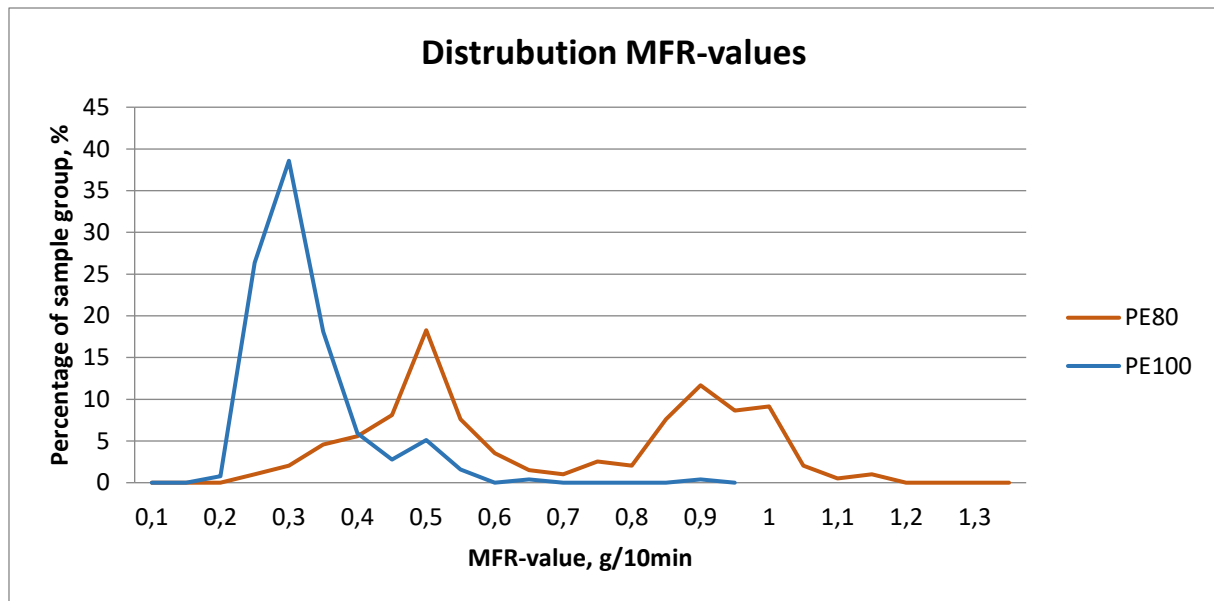
Figure 19: Distribution of MFR-values for PE80 and PE100. Three MFR-values above 2g/10min have been excluded from the figure.

When looking at the most common resins (raw material) used for the pipes, a lot of the PE80 pipes with a low MFR-value (0,3-0,6g/10min) are made from material such as HE3470 or GM 5010 T3, which by the manufacturer are classified as HDPE. In the same way, common materials used for PE80 pipes with a high MFR-value (0,8-1,1g/10min) are ME3440 and TUB 171, which are classified as MDPE. It has proven to be difficult to clearly find the difference between PE80 and PE100 pipes, as some PE80 pipes are made of very similar raw material as PE100 pipes, which can be problematic for certain kinds of jointing methods.

Since both butt fusion and electrofusion depends on the melting characteristics of the pipe to form the joint, it can be problematic that pipes marked in the same way can have noticeable different MFR-values. However, it is reasonable to believe that a successful joint can be accomplished between two very different PE80 pipes, but it could require a greater diligence from the operator. If the differences were to be unknown to the operator, the likelihood of a failed joint would probably increase. Hence it could be reasonable to further investigate in what way pipes should be categorized and marked in order to increase the quality of joints and drinking water distribution networks in general.

Density data is obtainable for 165 PE80 pipes prior to 2006. However, out of this sample size only one pipe had a density below $941kg/m^3$, hence it should be classified as MDPE according to common density classifications. The classification for MDPE appears to be fairly vague as several different manufactures classify their material as MDPE even though they have a higher density than $941kg/m^3$. Regardless the uncertainties concerning density-classification, the correlation between MFR-value and material density are undisputable, see *Figure* 20.
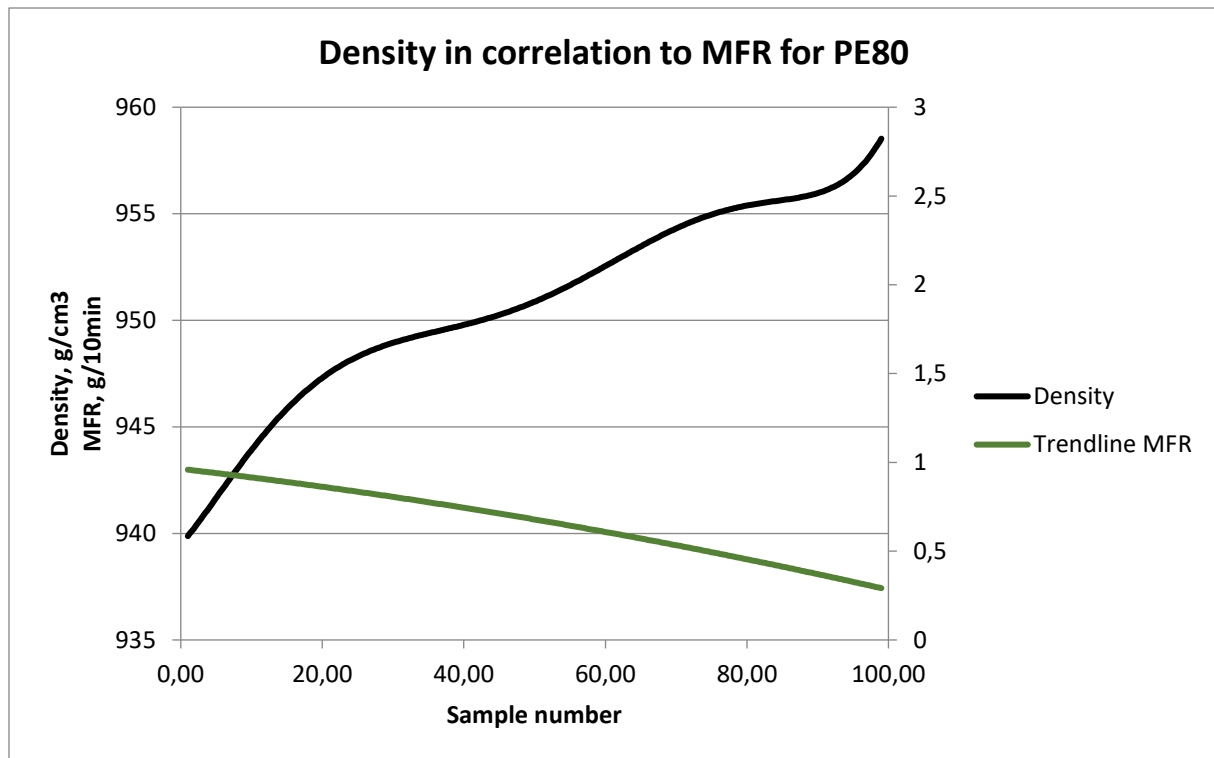
Figure 20: Correlation between density and MFR for PE80. The density of the pipes is shown on the left axis and corresponds to the black line while the MFR is shown on the right side and corresponds to the green line.

According to the trend shown in *Figure 18* and the distribution in *Figure 19,* it is likely to believe that more PE80 pipes are made from MDPE today compared to 15 years ago. The benefits with using MDPE for PE80 pipes rather than HDPE, is believed to primarily be a faster production rate due to the higher liquidity of the melted plastic.

A correlation between pipe dimension, pressure classification and MFR-value was also observed, see *Figure 21*. The difference can be due to a higher production rate for smaller diameters and thinner pipes. Smaller pipes are commonly extruded at a higher speed compared to larger pipes. The same goes for pipes with a lower pressure classification as their pipe walls are thinner. A higher extrusion rate is easier to accomplish if the molten plastic has a higher
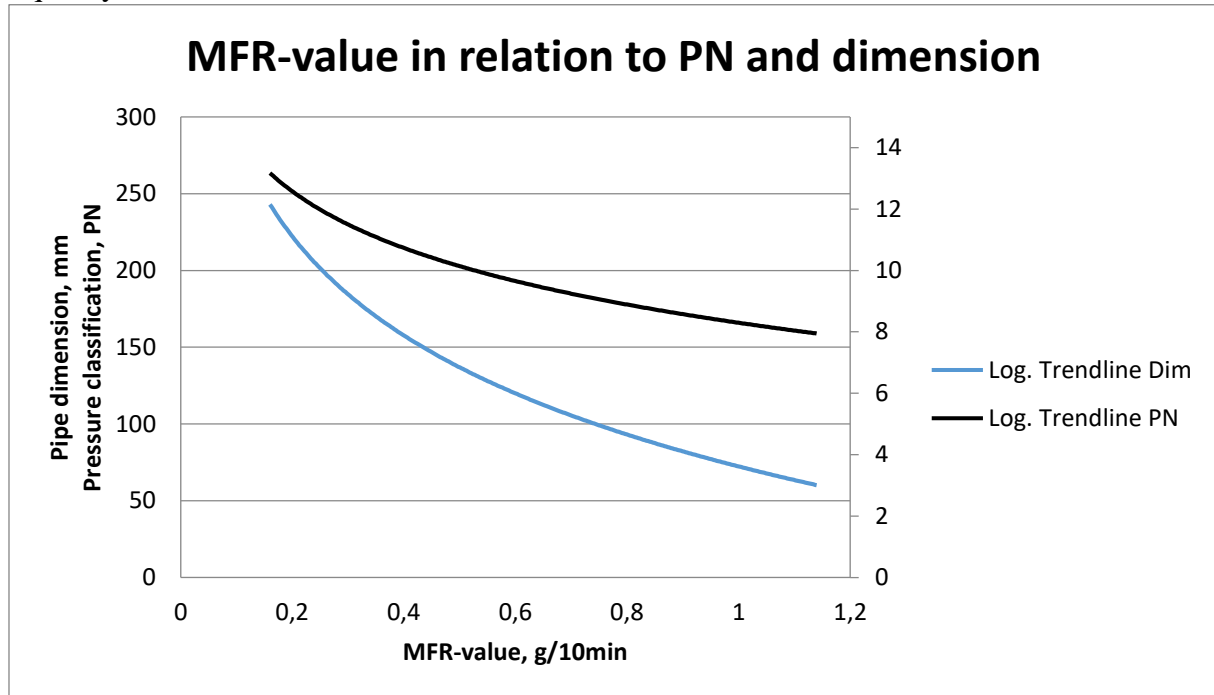
liquidity.

Figure 21: Correlation between PN, dimension and MFR. With increasing dimension as well as PN the MFR-value of the pipe declines. To make the trendline representative data from three pipes have been excluded due to MFR-values above 2,3g/10min.

4.3 Variations of Longitudinal Reversion

The longitudinal reversion is test that reveals the internal longitudinal stress within the material. A higher longitudinal reversion indicates a higher internal stress. Typically, a higher stress within the material is a consequence of higher extrusion rate at manufacturing. High internal stress can be problematic in several ways as it will increase the stress on installed pipes as a result of temperature changes. Furthermore, high internal stress can complicate joint due to the barrelling effect that can be caused by high internal stress.

Out of all tested pipes, 684 pipes had their longitudinal reversion tested, 314 PE100 pipes and 370 PE80 pipes. Over the period, the longitudinal reversion for PE80 pipes has increased slightly while the same value for PE100 has decreased, see *Figure 22*.
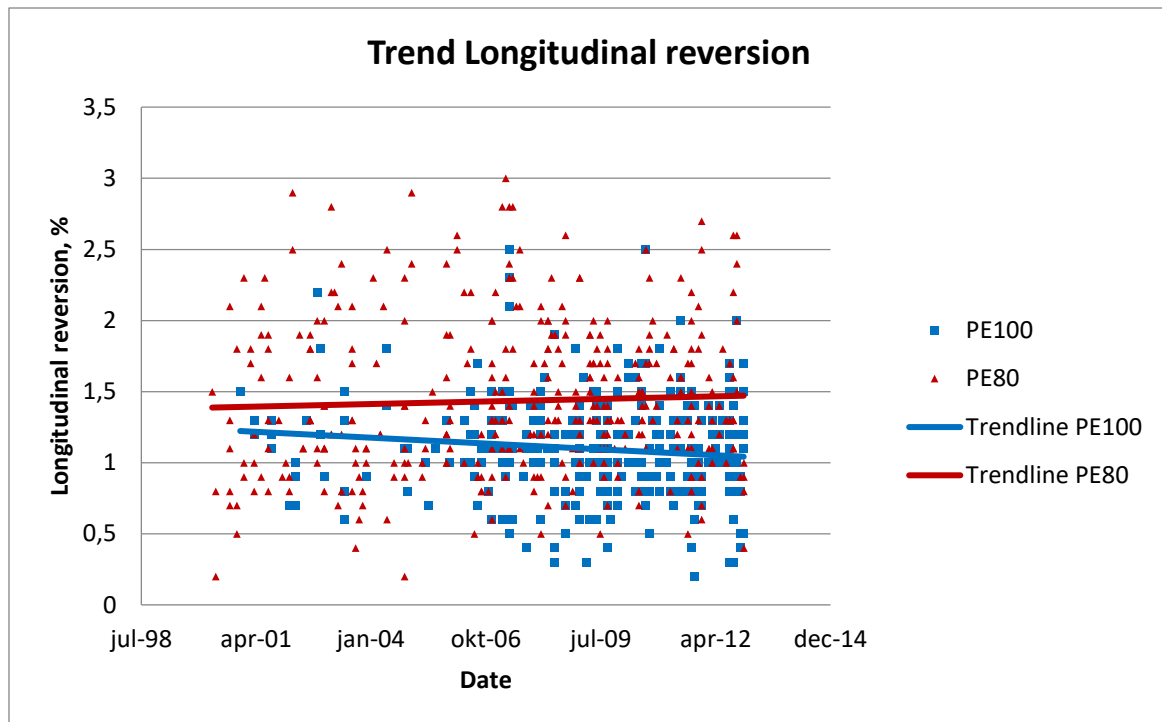
Figure 22: Changes in longitudinal reversion.

The longitudinal reversion appears to have a close relationship to the dimension of the pipes, see *Figure 23*. Smaller pipes generally have a greater longitudinal reversion compared to larger ones. The reason for higher values for smaller pipes is probably a result from a faster extrusion rate as manufacturing. Pipe extrusion machines have a specific capacity in terms of material extruded. This means that smaller pipes, with less material, can be extruder significantly faster compared to bigger pipes. Small pipes can occasionally be extruded at rates of above 1 m/s while larger pipes commonly are extruder at about 1 cm/s.

A high internal stress is luckily less of a problem in smaller pipes as these are commonly laid for shorter distances, for example as connection between main network and a private house. It could be advised that when using smaller dimension pipes over longer distances to control the longitudinal reversion value. Especially if using a PE80 pipe which tends to have a higher longitudinal reversion value.
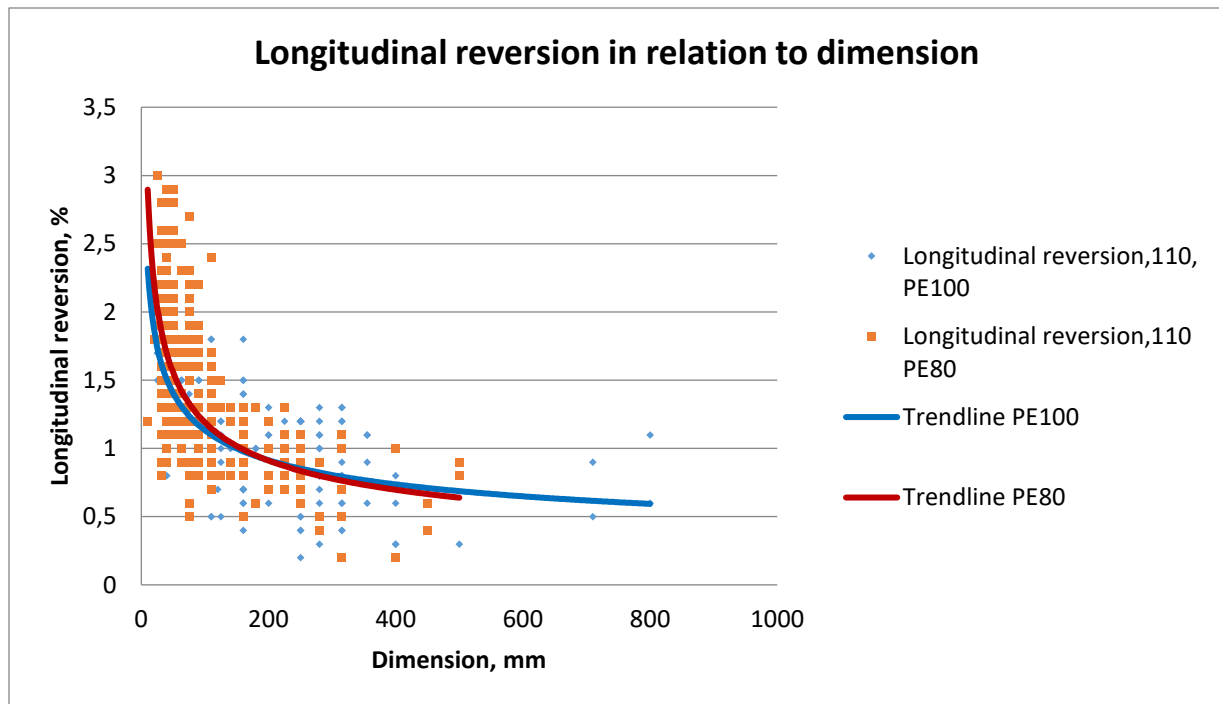
Figure 23: Correlation between dimension and longitudinal reversion.

4.4 Elongation at Break

The test for "elongation at break" is passed by most pipes. PE pipes typically have an elongation at break at around 600-700% compared to the required 350%. The "elongation at break" test was done on roughly 500 out of the 900 pipes in the database. Out of the 500 tested pipes, around half had a documented result marked as "bigger than a certain value" while the other half had the actual elongation at break documented. In the *Figure 24* only test where the actual elongation at break was documented is included.

The reason for that many tests are aborted prior to an actual break is that it increases the time to do the test significantly. Larger pipe diameter is tested with an elongation of 25mm/min which means that in order to make sure it passes it the test takes about 15 min, but in order to break the test piece it commonly takes more than double amount of time while also requiring a lot more attention from the test supervisor.

The results are quite clear and show few variations both when it comes to manufacturing date as well when it comes to material (PE80 and PE100), see *Figure 24*. Perhaps a trend can be seen when looking at elongation at break for PE80 pipes when comparing to pressure classification, but due to the limited amount of data, roughly 150 tests, the extreme values affect the trend too much to be able to say something about the general mass.
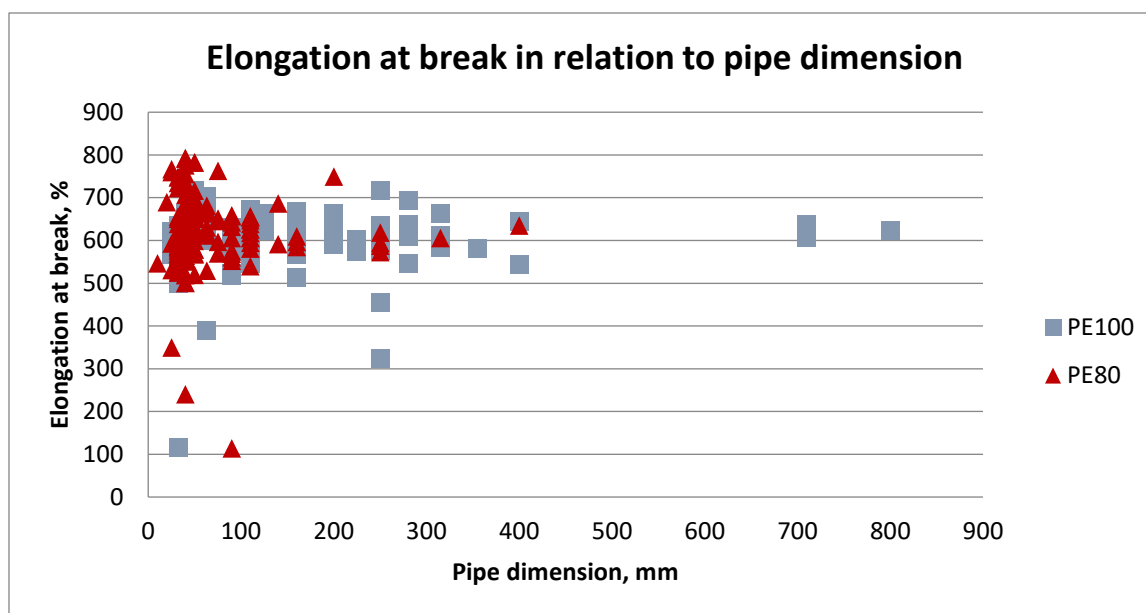
Figure 24: Elongation at break for PE100 and PE80

Since no clear differences can be seen between different diameters and pressure classifications, the test seems to be well performed and adjusted properly to fit different pipes even though the elongation happens at vastly different speeds for different pipes.

4.5 Pressure test

Out of all conducted test on the investigated pipes and a total of 1473 performed pressure tests only 2 pipes failed the test. The results are obviously good but since the pipes are not pressured until failure not much can be said about trends and differences between PE80 and PE100. The two tests that failed were both PE80 pipes with a small diameter and they failed at the 165h pressure test at 80°C.

4.6 Trends plastic quality PE100 and PE80

Overall, trends show what can be expected and that is that PE100 generally has a higher quality when it comes to durability, both mechanically and chemically. PE100 had an average OIT-value of 47.4 min compared to 42.3min for PE80. The difference equals roughly 11%.

MFR-values for PE100 is roughly 40% lower compared to PE80 pipes made from HDPE and 70% lower compared to PE80 pipes made from MDPE. The difference in MFR-values was anticipated as the value is an indication of the molecular size of the polymer which is an important difference between higher and medium density polyethylene. The difference between PE100 and HDPE PE80 pipes is not easily explained but it is believed that the bimolecular structure that is common for PE100 could play a role reducing its MFR-value.

No significant differences could be found regarding longitudinal reversion, elongation at break or results of pressure tests.

Over time it appears as the differences between PE80 and PE100 pipes have increased, even though the changes overall have been small. Both PE100 and PE80 pipes appears to have characteristics that manages to exceed the set requirements to obtain the *Nordic Poly Mark* certification.

5   RESULTS AND DISCUSSION - OIT-ANALYSIS NATURAL AGED PIPE

9 samples of the same pipe were taken, three from the internal surface, three from the middle of the pipe wall and three from the external surface. The oxidation induction time for each of the samples was tested, the results are presented in *Table 6,* along with the weight of the samples. For the plotted curves and the analysis of the curves see Appendix 1.

Table 6: Results OIT-analysis

Test sample	OIT value	Weight
Inside 1	45,97	14,3
Inside 2	46,18	16,3
Inside 3	39,82	13,0
Average inside	**43,99**	
Middle 1	56,74	14,4
Middle 2	57,63	15,7
Middle 3	56,93	16,1
Average Middle	**57,10**	
Outside 1	46,41	14,3
Outside 2	51,40	16,1
Outside 3	48,17	16,1
Average outside	**48,66**	

An average drop of 23% can be seen between the inner surface and the middle of the pipe wall. The difference between the outer surface and the middle of the pipe is 15%. The differences between the inner and the outer surface is 10%.

The assumption is that the OIT-value retrieved from the middle of the pipe wall corresponds roughly to the OIT-value of a new pipe. This is a conservative assumption as the initial OIT-value must have been the same or higher, since no antioxidants are added to the pipe after installation.

One of the three samples taken from the inside of the pipe shows a significant lower value. The reason for this can be irregularities in the pipe, for example a deviation in antioxidant concentration. The sample that showed a significantly lower value than the rest was also the test piece with the lowest weight, only 13.0 mg, in contrast to the two other pieces that had weight of 16.3 mg and 14.3 mg. The deviation in the value can be result of that the oxidation had not reached that far into the material of the sample. The larger pieces would then contain more material that has not been as affected as the surface of the pipe.

It could also be that the two other values show a too high values due to improperly placed samples in the oven, however, this is unlikely but cannot be discarded. If the surface of the

test piece that has not been exposed is placed upwards, the test will show a better resistance towards oxidation.

It is a clear difference between the oxidation that has occurred on the inside and the outside wall. This is believed to be a result of the stable surrounding that has been present around the outside of the pipe. The pipe laid in clay rich grounds with low, if any, noticeable permeability. This would result in few free radicals capable of reacting with the polyethylene. The inside of the pipe is under constant influence from flowing water and even though the reactiveness of the water is extremely low, the high flow contributes to the accelerated oxidation compared to the outside of the pipe. If further similar experiments are to be conducted, it is recommended to primarily concentrate on the OIT-value of the inside wall. The oxidation of the outside wall is believed to be entirely connected to the ground in which it is put. To test pipes installed in permeable soil with a variation in groundwater level could be interesting as permeable soil would likely lead to a faster oxidation of the outside pipe wall. It would also be interesting to test a new pipe in the same way as have been done in this project. It is likely that the inside of the pipe of new pipes has a slightly lower OIT-value, compared to the outside as the cooling of the pipes starts from the outside surface. Hence, the inside surface is at an elevated temperature for a longer period while also being in contact with free radicals in the air.

The change in pipe quality over the relatively short period of time is noticeable. If a linear degradation of the material would take place, the antioxidants in the inner surface would only last for 40 years. However, there is a natural diffusion mechanism in the pipe which allows some antioxidants from other regions within the pipe to diffuse to the outer surface and by doing so prolonging the lifetime of the pipe. However, the results as well as literature studies indicates that the diffusion of anti-oxidants are slower than the speed of the oxidation. Otherwise, no differences would be seen between the samples taken from different parts of the pipe. The diffusion of antioxidants in the material is highly dependent on molecular size of the antioxidant as well as the temperature of the medium.

The antioxidants in the tested pipe is unknown but it could be advised to use antioxidants with a smaller molecular size as this theoretically would increase the long-term resistance towards oxidation as the diffusion speed appears to be directly related to molecular size. It might not however increase the OIT-values tested on new pipes, as the test is performed at a very high temperature and at very limited amount of material. The high temperature liquifies the polymer which is believed to greatly increase the diffusion capabilities thus making diffusion speed more insignificant in the OIT-test compared to natural aging conditions. To properly evaluate the oxidation resistance of a plastic pipe material, it would have to be aged and then OIT-values should be tested at various depth from the inner surface and preferably also at different times.

The test results correspond well with the known degradation curve of polyethylene pipes. The result indicates that after roughly 50 years, the pipe would be more likely to degenerate because of oxidation on the inside wall since the antioxidants have been depleted in this region of the pipe. Physical changes to the polymer in the surface area would then become much more likely. The speed of the degradation of the polymer will be affected by the diffusion capabilities of the added antioxidants.

6   CONCLUSION

Overall few, if any, negative trends can be observed regarding high-density polyethylene drinking water pipes tested for the *Nordic Poly Mark* certification. However, changes have been observed in several characteristics. MFR-values has generally decreased for PE100 pipes while PE80 pipes appears to have a higher MFR-value today compared to in the early 21-century. The pipes tested had an overall high quality with only a very minor rate of failure which leads us to believe that pipes classified with the *Nordic Poly Mark* indeed is of high quality.

Furthermore, it was noted that pipes marked as PE80 are produced by both high and medium density PE which results in large differences in MFR-values. Large differences can be problematic in certain welds. New PE100 pipes appears to have MFR-values of around 0,25g/10min and the trend points towards lower values. Butt fusion joints are preferably performed on pipes with a MFR-value of above 0,3g/10min or at least above 0,1g/10min. Considering the difficulties of welding pipes with differences in MFR-values as well as pipes with very low MFR-values, it could be advised to renew the requirements for new polyethylene pipes. The suggestion would be to add a minimum and maximum MFR-value rather than only looking at changes between raw material and finished pipe.

The OIT-values has decreased during the studied period, but due to other changes such as lover MFR-values, which indicates larger molecular structure, the resistance towards thermal oxidation might not be negatively affected. Overall, the OIT-values in new pipes promote no concerns in that regard.

Regarding the nine-year-old tested pipe, a clear difference in OIT-results can be seen between the inside pipe wall and the middle of the pipe wall. The difference in OIT-values between the test zones was 23%, and if a linear degradation over time is assumed, the optimal lifetime of the pipe would equal roughly 50 years, which is in order with presented regression curves. After initial depletion of anti-oxidants in the surface of the pipe, the continuous regression of the pipe strength will likely be affected by the diffusion capabilities of the anti-oxidants used. Some changes in the testing procedure for OIT can be recommended to better account for diffusion issues with antioxidants. Now, pipes are only tested when they are completely new. As the testing method is designed today, it almost misses the target due to the complicity in how a polymer deteriorates over time. A suggestion would be to also test the pipes after aging, similarly to the pressure tests performed. It would be an easy procedure to test OIT in connection to the long term (1000h) pressure test in order to get a more comprehensive view on how well the antioxidants work to increase the long-term durability of the pipes. But, as stated earlier, there is little concern that the pipes used today are of poorer quality than promised. Yet, a different way of testing oxidation might be a possibility to further nourish improvement of the pipe material.

7 FUTURE STUDIES

In this project, it has been noted that the commonly performed OIT-analysis only shows a static situation with the goal of analysing a long-term behaviour. It would be interesting to see OIT-measurements performed on pipes aged in at 80°C for 1000 hours and compere these results with the initial OIT-values of the new pipes. This would probably give a better understanding of the real oxidation resistance in the pipes compared to test performed only at new pipes. Optimally these tests would also be compared to test done on pipes that has been in use to find how well the accelerated aging corresponds to the real-life situation.

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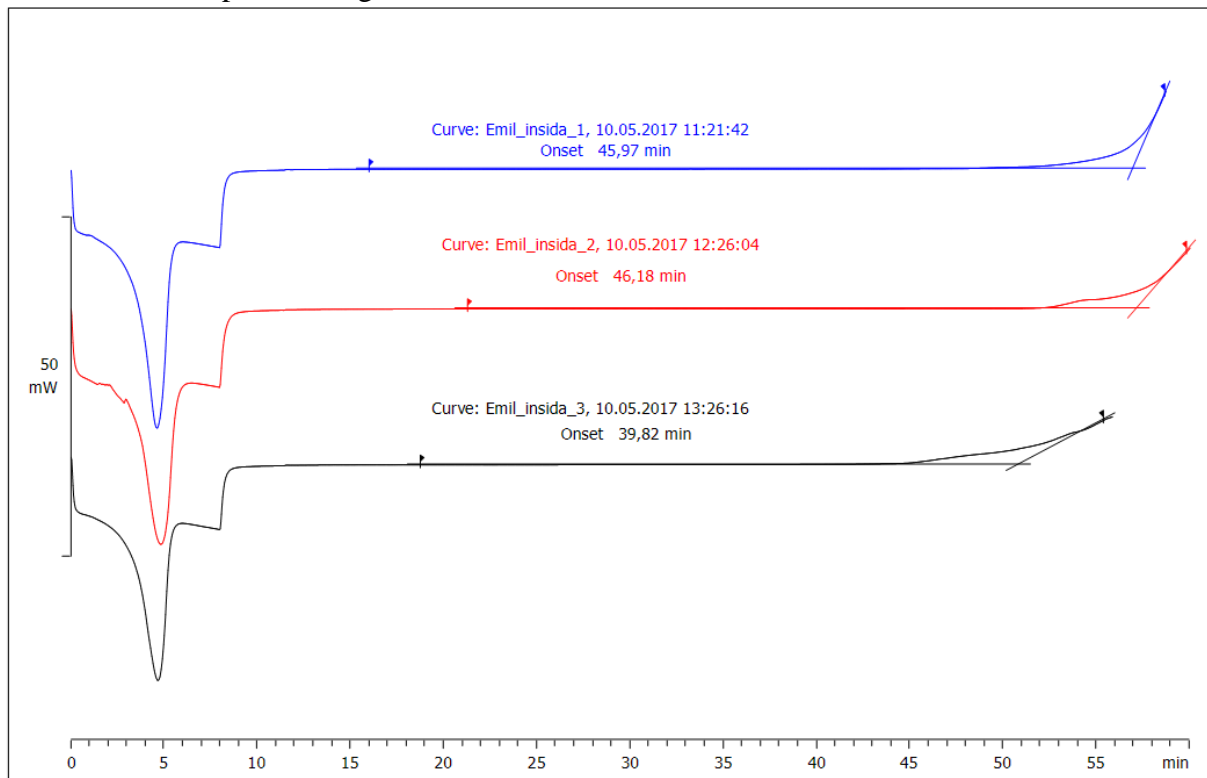International Organization for Standardization. (2005). *ISO 2505:2005(E).* Geneva: ISO copyright office.

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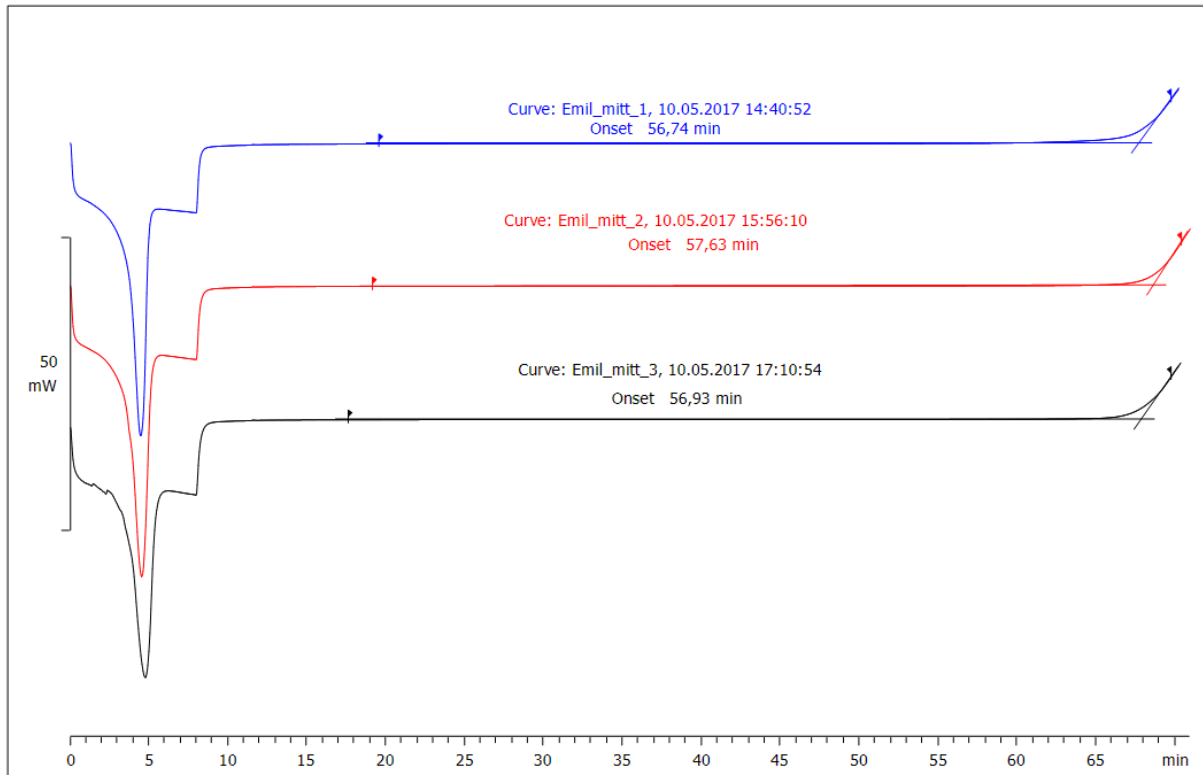
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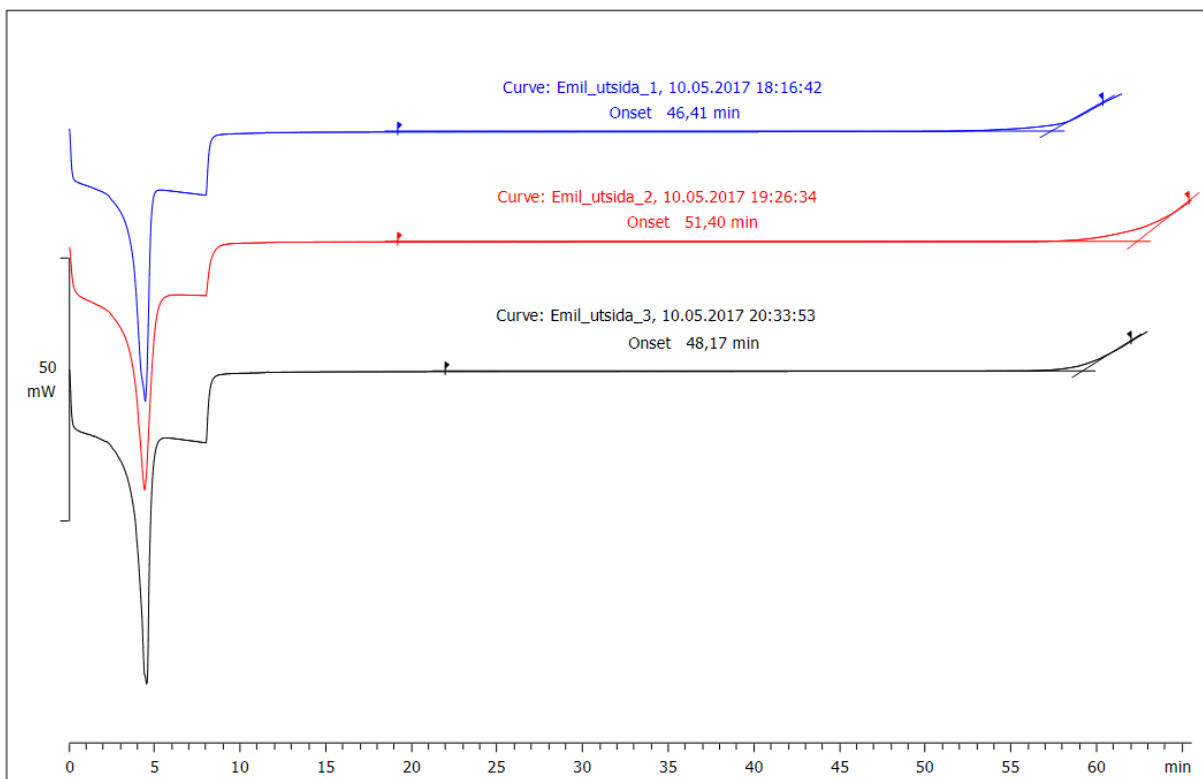
Appendix 1

OIT-curves with plotted tangent lines and OIT-times.

OIT-cures with plotted tangent lines and OIT-times for plastic taken from the inside of the pipe samples 1,2 and 3.

OIT-cures with plotted tangent lines and OIT-times for plastic taken from the middle of the pipe samples 1,2 and 3.

OIT-cures with plotted tangent lines and OIT-times for plastic taken from the outside of the pipe 1,2 and 3.