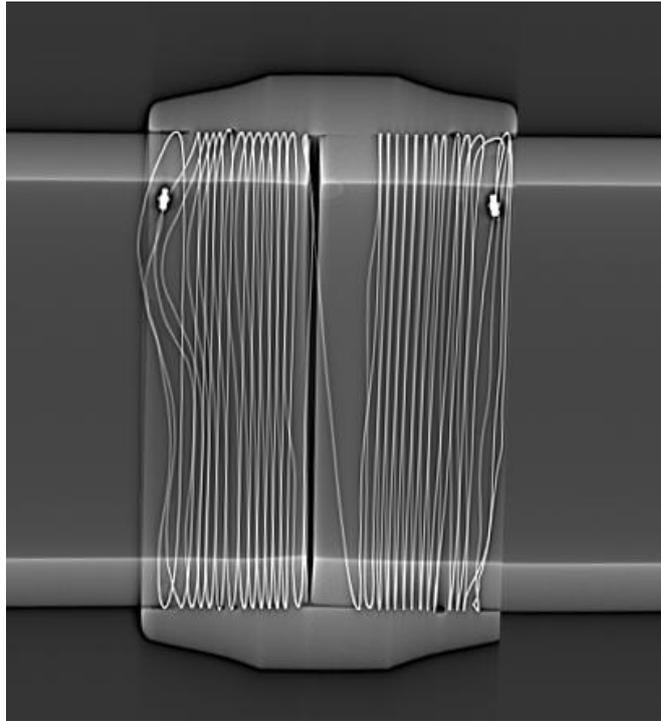


CHALMERS



Surface analysis of polyethylene pipes and failure characterization of electrofusion joints

Master of Science Thesis in the Master Degree Programme, Materials and Nanotechnology

LUKAS BOGE
EMIL HJÄRTFORS

Department of Chemical and Biological Engineering
Division of Applied Chemistry: Polymer Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
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Technical report no. 380
Department of Chemical and Biological Engineering
Division of Applied Chemistry: Polymer Technology
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone + 46 (0)31-772 1000

This work was carried out at:
SP Pipe Centre - Technical Research Institute of Sweden
Gibraltargatan 35
400 22 Göteborg
Sweden

Cover:
X-ray computed tomography image of an electrofusion joint.

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EMIL HJÄRTFORS

Department of Chemical and Biological Engineering

Division of Polymer Technology

Chalmers University of Technology

ABSTRACT

Electrofusion welding is today a common method for joining polyethylene pipes for water and gas distribution. Before welding, scraping of a 0.2 mm outer layer of the polyethylene pipe surface is needed to get an approved joint. The explanation for this procedure is investigated in this study. Today the characterization of the strength of electrofusion joints is done in a subjective way, and a more objective methodology will be investigated. The aim of this thesis is to increase the knowledge and understanding regarding these two aspects of the electrofusion method.

Two PE-pipes from Wavin, with a 10 months difference in manufacturing date, and a jacketed Profuse pipe from Uponor were analyzed. The outer diameter of the pipes was 280 mm. A total of eleven electrofusion joints were made with different surface treatments of the pipes. Evaluation of the joints were done according to peel decohesion test, ISO 13954.

The contact angle was found to be significantly higher for surfaces that could be welded. This difference can be explained by the presence of oxidized polymer at the pipe surface and was only seen by ESCA. FTIR-ATR analyses of pipe surfaces showed none or very small absorption in the carbonyl region, which was inconsistent with the ESCA results. Only scraped Wavin pipes and Profuse pipes resulted in approved joints. Cleaning with either ethanol or heptane could not replace the scraping of Wavin pipes.

Another type of peel decohesion test, similar to EN 12814-4, in combination with normalized peel energy calculations seems to give a more objective evaluation of electrofusion joints. X-ray computed tomography and microwave scanning were performed on one joint, where the latter showed to be a good candidate for characterizing the quality of electrofusion joints.

Keywords: electrofusion, electrofusion joints, polyethylene pipes, oxidation.

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1. Introduction

During the past 50 years the main choice for water and gas distribution has become pipes made of polyethylene (PE). PE-pipes have several advantages over traditional pipe engineering materials, such as steel, due to the combination of having a low price, being non-toxic and corrosion resistant, resulting in lifetimes up to 100 years or more (O'Connor, 2011). Pipes with large diameters, as for civic main distribution of water, have the disadvantage that many joints are required due to the fact that it is only possible to distribute the pipes in lengths of 6 or 12 meters. A water pipe of a couple of kilometers will thus result in hundreds of joints and it is obvious that the welding process is of great importance. Today there are two main welding techniques for joining PE-pipes called butt-fusion and electrofusion, where the latter has become more and more popular. (Huo et al., 2003, Janson, 1996)

This report will focus on two problematic aspects of the electrofusion method of joining PE-pipes based on literature research and own experiments. This work is carried out at SP Technical Research Institute of Sweden in Göteborg and Borås.

1.1. Background

A major drawback with electrofusion joining is the need for scraping off a 0.2 mm outer layer of the PE-pipe surface at the location for the weld. The reason for this procedure is said to remove an oxide layer, dirt, grease, and any possible degraded polymer which can restrict molecular diffusion across the welding interface. The scraping is time consuming and would preferably be avoided in order to rationalize the welding process. The surface of the scraped pipe and electrofusion couplers shall also be wiped with i.e. alcohol to keep the surfaces clean from dust and contaminations. If these two steps are neglected or not well performed, the result may be a brittle joint which can easily fail (Bowman, 1997, Allen et al., 1997). However, there are directly weldable PE-pipes on the market today from a couple of producers where no scraping precautions are needed. The directly weldable PE-pipes, such as Uponor's Profuse pipes, are coextruded with a thin layer of polypropylene. The polypropylene layer is peeled away prior welding. (Uponor, 2010, Varmedal, 2002)

Another possibility is that additives in the plastic diffuse to the pipe surface during storage which can affect the strength of the joint. This theory can be of relevance if the pipes are stored for long time prior welding. However, diffusion of additives cannot be the reason why a scraped pipe surface is said to be perishable, since the diffusivity is low in the plastic material.

The large number of joints makes adequate testing for characterizing the joints strength crucial. Peel decohesion testing of specimens from the joint is an important method for analyzing the behavior of the joint under load until failure. The problem is that the ISO standard used today (ISO 13954) is hard to adapt in reality. It does not give an objective measurement due to the fact that the analysis is very individual. There is a strong need for a better method to characterize and quantify the brittleness/ductility of failed samples. It is of great importance when it comes to who is responsible for a failed joint, the manufacturer or the company who made the joints on site?

1.2. Question formulation 1

Why does the outer surface layer of PE-pipes have to be scraped away before electrofusion, while jacketed Profuse pipe can be welded without being scraped? What is the difference between weldable and unweldable pipe surfaces?

1.3. Question formulation 2

How can the quality of electrofusion joints be quantified in a more objective way?

1.4. Limitations

To be able to investigate as many joint combinations as possible during this project, only one joint of each pipe combination will be investigated. The dimension of all pipes and coupler is 280 mm, SDR 11/17, no other dimensions are under study. Three different pipes from two manufactures are welded with couplers from only one manufacturer. The pipes are random samples and will probably stand as representative ones. No studies of how pipes surfaces change during artificial ageing (heat, UV) will be done. A total of 11 joints are investigated. Approval of joints will only be done according to ISO 13954, where 8 samples from each joint are examined. Peel tested samples will not be investigated by the method 'Quantified Surface Ductility', due to lack of image analyzer. In order to save time the test pieces for EN 12814-4 will be slightly modified, thus joint toughness cannot be calculated.

2. Theory

The following chapters are an attempt to summarize the field of electrofusion welding based on a literature research in article databases, Plastic Pipes Conference articles, internet, contact with pipe manufactures and people skilled in the art. The two major welding techniques will be described, different properties that influence the joining process and different methods used for characterizing the strength of electrofusion joints will be explained.

2.1. Polyethylene pipes

Over the past 50 years different polyethylene materials have been developed and used to achieve best possible properties. The different types of polyethylene that have been used were first categorized by their difference in density; Low Density Poly Ethylene (LDPE), medium (MDPE) and high (HDPE). In the early 1990s a new generation of HDPE material was developed which had a bimodal molecular weight distribution, see Figure 1 (INEOS, 2007). The advantage of bimodal HDPE was the higher hydrostatic pressure strength and better long-term properties, such as increased slow crack growth resistance (Brömstrup, 2007). In 1996, an ISO standard was developed which categorized the different types of pipes based on their long term hydrostatic strength. (INEOS, 2007). According to this classification the minimum required strength (MRS) after 50 years of service life for water at 20 °C is 8.0 MPa for PE80 and 10 MPa for PE100 (O'Connor, 2011).

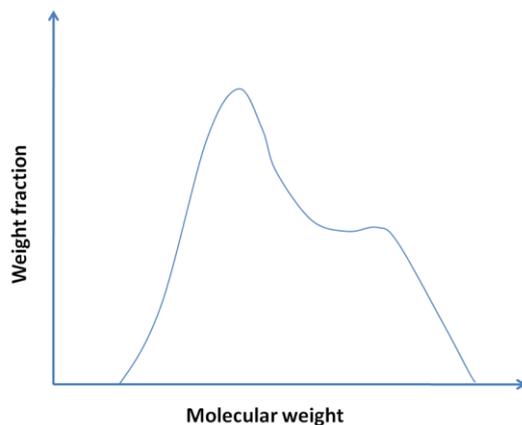


Figure 1. Bimodal weight distribution, characterized by having two peaks.

Pipes are also defined by their Standard Dimensional Ratio (SDR), which is defined as the ratio between the outside diameter and the wall thickness, thus a SDR11 pipe has a thicker wall than a SDR17 pipe.

2.2. Butt-fusion welding

In butt-fusion welding two pipe ends are joined together in a dedicated butt-fusion machine. The pipe ends are first planed and thereafter heated up by pushing the ends against a flat hot plate. When the pipe ends is melted the hot plate is removed and the pipe ends are pushed together and allowed to cool. (Chipperfield, 2008)

2.3. Electrofusion welding

Electrofusion welding is a common technique to weld PE-pipes and other polymeric materials, such as polypropylene (PP). It involves a coupler, which the two pipe ends can slide into. Some couplers also have an internal stop to prevent the pipe ends from meeting. Within the coupler-wall, is a coil of resistive heating wire which is connected to a terminal at each end. When an electric current passes through the resisting heating wire the surrounding polymer melts. Molten polymer that attempts to escape from the fusion zone cools down, in the internal or external cold zone, and inhibits further melt flow. Thus, the cold zones maintain the molten polymer in the fusion zone where a melt pressure is build up. Weld indicators are attached on the coupler to give the operator a visual indication that sufficient melt pressure has been generated. If the weld indicator protrudes it is an indication that the weld process was carried out successfully. The advantage of electrofusion compared to butt fusion is that the electrofusion process is more practical and can be carried out even if the space is very limited.

In order to obtain a joint with good strength it is important to follow a certain preparation procedure. Firstly, approximately 0.2 mm of the pipe surface is scraped off and prior to welding the surface is cleaned with a lint-free cloth soaked with ethanol or isopropanol. Thereby no contamination is allowed to affect the strength of the joint. The pipes and coupler should then be properly aligned and clamped to avoid relative moment. Thereafter, electricity is connected to the terminals and depending on the pipe size and ambient temperature, different fusion times is used. The fusion process can be divided into three stages:

1. Initial heating and coupler expansion
2. Heat soaking to create joint
3. Joint cooling

The first two stages are commonly termed as the fusion time. In Figure 2 a cross section of an electrofusion joint can be seen. The two terminals are highlighted as well as the fusion zones and the internal and external cold zones.

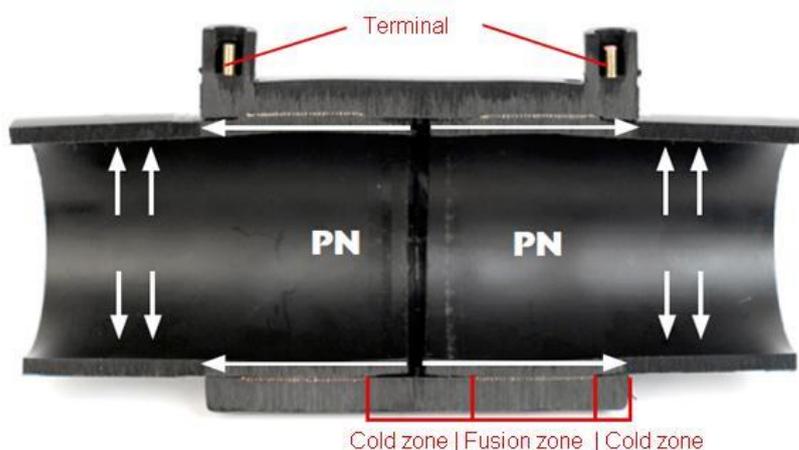


Figure 2. Cross section of an electrofusion joint. Picture used with permission from Nordiska Plaströrgruppen.

Electrofusion couplers can be found in a wide variety of sizes, normally from 16 mm to 500 mm but there are also larger couplers, up to 800 mm now available. (Chipperfield, 2008)

2.4. Properties that influence the joint quality

There are several factors influencing, or which may influence, the electrofusion process and in turn the strength of the joint. The procedure of scraping and cleaning, and the hypothesis about migration of additives to the pipe surface have been briefly described earlier. The following part will describe in more detail which different material properties of the plastic that can affect the joint. Regardless how well characterized and understood a material is, in the end humans make the joints and the craftsmanship will of course influence the quality of the joint. Joints made in ideal laboratory conditions may not perform in the same way as joints made out in the field. The reality is sometimes much warmer or colder, wetter, dustier and muddier.

2.4.1. Scraping and contamination of pipes

The influence of scraping procedures has been studied quite well. In one article the authors wanted to see the effect on the joint when they introduced different flaws: unscraped pipe, sand and talc contamination. The flawed joints were then compared with a joint produced with scraped pipes. The unscraped and sand contaminated joints surprisingly passed the peel decohesion test, while the talc contaminated failed in a brittle manner. Despite their results the authors do not want to conclude that scraping is unnecessary since their joints were done in an ideal laboratory environment (Troughton et al., 2006). Also welding fresh extruded pipe seems to give a more ductile behavior of the joints than stored pipes (Allen et al., 1997).

Vanspeybroeck evaluated different scraping, cleaning and contamination procedures. Scraped pipes contaminated with butter or vaseline gave a mixed brittle/ductile behavior of joints. Pipes only subjected to cleaning did fail in a brittle manner. They also scraped the inner surface of the coupler with abrasive paper, but it did not give a ductile joint until the pipe itself was scraped. Scraping off only 0.05 mm, instead of the recommended 0.2 mm, of the outer pipe surface resulted in ductile joints. (Vanspeybroeck, 2006)

In one study, extracts from the surface of brittle failures were analyzed by FTIR and some contaminations were found. They found that siloxane can be a reason for poor joint adhesion. Also contaminations such as glycol, ammonium salts, silicates and iron oxide were found in brittle joints. (Scholten and Wolters, 2011)

If water is present on the pipe or coupler during welding, it may be trapped inside the fusion zone and expand during the fusion cycle, leading to void formation. To avoid this problem it is important to wipe the scraped pipe surface and coupler with a dust free cloth, soaked in a suitable solvent and then let it evaporate prior to welding (Nordiska Plaströrsguppen, 2009).

Overscraping can increase the gap between the pipe and the coupler, especially for pipes with small diameters. If the gap is too large (>0.5 mm) there is a risk that no contact at all is formed between coupler and pipe after welding, with catastrophic result. Too long fusion times can give material degradation and too short; a brittle and weak joint (Bowman, 1997). The influence of a shorter fusion time than specified have also been investigated by Troughton et al. Electrofusion joints were done using a 38 % reduction of the recommended fusion time. The result of five produced joints was surprisingly, since they all failed in a ductile mode in a peel decohesion test (Troughton et al., 2006). This indicates that the recommended fusion times may be longer than needed in order to compensate for improper scraping and misalignment for pipes.

2.4.2. Oxidation of polyethylene surfaces

It has been suggested that the problematic oxide layer is formed during the extrusion process. The oxidation will mostly occur in the amorphous regions. (Moore et al., 1989, Vanspeybroeck, 2006).

The oxidation process, a chain process, is initiated and propagated by formation of free radicals. A radical is formed by removal of hydrogen from the polyethylene chain. This can be caused by mechanical shear, thermal decomposition or UV degradation (Whelan, 1994). When HDPE is thermally oxidized, the main oxidation products have been found to be ketone, carboxylic acid, ester and lactone specimens (Yang et al., 2006). Carbonyl containing degradation products as well as vinyl groups has been found when HDPE has been photo oxidized (Hoekstra et al., 1995).

2.4.3. Antioxidants

If oxidation is the primary factor influencing the quality of an electrofusion joint, the presence of antioxidants and their migration in the plastic is of great interest. The most common antioxidant system used in PE-pipes is a combination of primary antioxidants, such as hindered phenols, and some secondary antioxidant i.e. phosphites or thioesters. The division into the two groups is due to their different stabilizing action (Gedde et al., 1994). The antioxidant content in the plastic is typically in the order of 0.1 weight % (Allen et al., 1997).

It has been shown that antioxidant concentration of a medium density PE-pipe is almost twice as high in the center of the wall compared to the surface of the inner and outer wall. The antioxidant concentration was measured indirectly by oxidation induction time (OIT) measurements. They also conclude that loss of antioxidant is very rapid if the pipe is exposed to elevated temperature (Karlsson et al., 1992). Based on migration experiments from aged linear and branched polyethylene plaques, it is stated that the migration of antioxidant is controlled by a boundary loss process. The oxidation induction time for aged samples (oxygen free water, 90 °C up to 244 days) decreased to ¼ of the value for an unexposed plaque, indicating a large loss of antioxidant efficiency (Lundbäck et al., 2006).

Profuse pipes with their protective polypropylene layer have shown to withstand outdoor aging in the Arizona desert and produce electrofusion joints with good quality. Unprotected pipes, exposed to the same environment, that were not scraped prior to welding resulted in a joint with bad quality. One side of the pipe was not exposed to the sun and a clear difference could be seen when samples from the joint was tested. Samples that were taken from the non exposed side performed better than the samples that were taken from the sun exposed side. Based on the low oxidation induction time values, the authors speculate that the sun-light had damaged the polymer and that chain scission might have occurred. A low oxidation induction time value implies that large amounts of stabilizers have been consumed. (Huang et al., 2010)

It seems like the concentration of antioxidant is lowest at the pipe surface, were it is probably most needed in order to avoid oxidation and degradation of the polyethylene. Migration of antioxidants to the surface itself seems unlikely to influence the quality of the joint. This is because of the slow diffusivity due to their large molecular size and low segmental flexibility (Lundbäck et al., 2006). Oxidation of the pipe surface is a competing phenomenon with the rate of oxidation reaction versus the rate of consumption/migration of stabilizers to the pipe surface. At the surface oxidation reactions can be faster (Allen, 2011).

2.4.4. Fillers

Carbon black is a widely used filler in rubber and plastics, and is the main difference in filler content between the pipes used in this study. The multi-functional black pigment provides both thermal and photo oxidative stabilization. It is known to interact with other stabilizers, either synergistically or antagonistically. Adding up to 2 weight percent of carbon black in polyethylene has shown to provide protection against outdoor weathering of up to 30 years. It is manufactured by incomplete combustion of organic substances (usually oil or gas) and depending on the manufacturing process the size of the particles can be varied. (Allen et al., 1998)

In order to be used in PE-pipes for water supply the carbon black has to meet the quality standards, where the average (primary) particle size of the carbon black should be in the range of 10 to 25 nm (ISO 4427, 2007, EN 12201, 2003).

2.4.5. Molecular weight

The longest polymer chains contribute most to the mechanical properties and a reduction of their length is therefore undesirable. Ageing and degradation of polymers always include a reduction of the molecular weight. This is revealed by Gedde et al. on MDPE-pipes (ID 28 mm, wall thickness 2.2 mm, exposed inside to 80 °C pressurized water) by size exclusion chromatography. The molecular weight for samples taken at the inner wall surface showed a dramatic decrease to about 30 % of the initial value. Chain scission is believed to mainly occur in the amorphous polymer phase. (Gedde et al., 1994)

It can be the case that low molecular weight products could migrate onto the surface and create a "greasy" layer which in turn could affect the weldability in a negative way. This liquid-like layer of material is showed on aged plaques made of branched polyethylene by Lundbäck et al. It is most probably a thin layer of highly branched low molecular oligomeric species (Lundbäck et al., 2006). How such a layer could influence the joint is not known, but cleaning the surface with alcohol or an organic solvent would probably remove it (Allen, 2011).

2.4.6. Morphology

HDPE is semi-crystalline, made up of crystalline and amorphous regions, with a crystallinity between 40 and 80 % (Polymers A Property Database, 2011). There is not much work done in the field on how the morphology of conventional PE-pipes influences the strength of electrofusion joints, most papers describes work with highly oriented materials. The crystalline morphology of conventional HDPE-pipes is spherulitic with mostly a banded appearance (Huang et al., 2008). A slight orientation of the polymer chains in the extrusion direction can be observed at the pipe's outer surface (Trifonova et al., 1997). The orientation of macromolecules seems not to influence the failure mode of HDPE-pipes, which is seen in work regarding slow crack growth resistance of different PE-resins used for water pipe extrusion. The article describes only results from short term hydrostatic tests of pipes, not the effect on electrofusion joining (Peres and Schön, 2007)

During pipe extrusion the pipes are cooled externally by water and internally by air which create a density gradient across the pipe wall thickness. Lowest degree of crystallinity is found on the outside of the pipe and the highest degree of crystallinity is found in the middle of the pipe wall. The degree of crystallinity at the inside of the pipe is slightly lower than in the middle. The density distribution follows the same pattern, since density and degree of crystallinity is directly proportional. (Eyerer and Gettewert, 2010)

2.5. Characterization of electrofusion joints

In order to evaluate the quality of an electrofusion joint several methods can be used. The joints or pieces cut out from the joints can be subjected to various long-term or short-term tests. In this work the focus will be on short-term tests where pieces have been cut out from joints and tested in various tensile type tests. One problem with these tests is their non-quantitative and subjective nature (Bowman, 1992). A novel mechanical testing method of electrofusion joints is under development by Exova, and can be a candidate to replace the peel decohesion test (Murphy and Lowe, 2010). Peel decohesion test, ISO 13954 (1997), is used by SP Technical Research Institute of Sweden to evaluate electrofusion joints. In this work a modified EN 12814-4 (1999), which will be called double peel decohesion test, will also be used.

By examining the fracture surface and by using the data obtained from the peel test it has been suggested that quantified surface ductility and normalized peel energy can be used to evaluate electrofusion joints more objectively (Bowman, 1992).

2.5.1. Peel decohesion test (ISO 13954)

A total of eight test samples are cut out from the joint, four samples from each side of the coupler. The chosen samples shall include the parts where the maximum and minimum gap between the pipe and coupler is found. The peel test samples are then cut out with a band saw in order to obtain the dimensions seen in Figure 3.

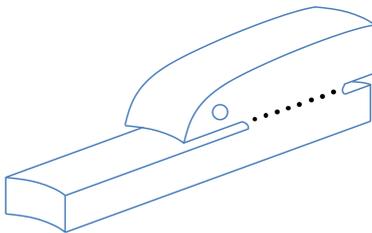


Figure 3. Illustration of a peel test sample.

The test setup data output can be seen in Figure 4. The sample is mounted into a vice and a shackle is attached prior testing. The test piece is peeled at a rate of 25 mm/min and the force is measured against the displacement and produces a load/displacement curve.

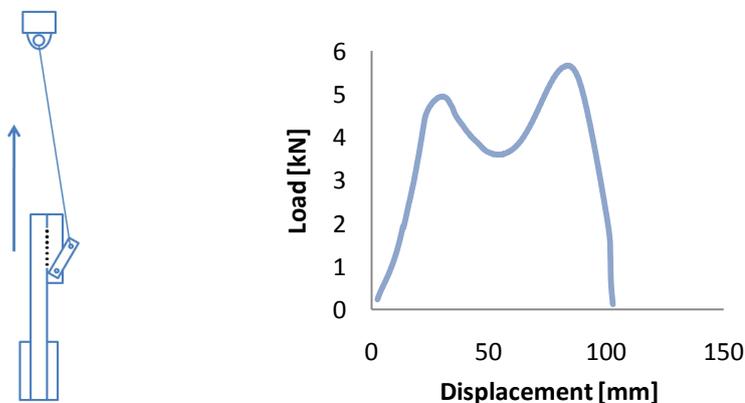


Figure 4. Illustration of the setup for peel decohesion test ISO 13954 and a typical load/displacement curve obtained during the test.

After failure has occurred the sample is characterized according to the standard by measuring the length of the fusion zone and the total brittle length at the interface between pipe and coupler. The amount of brittleness is then calculated by:

$$\text{Amount of brittleness}(\%) = \frac{\text{Total brittle length}}{\text{Fusion zone length}} * 100 \quad 1$$

If all eight test samples of a joint are lower than or equal to 33 % brittle, the joint is approved.

2.5.2. Double peel decohesion test (EN 12814-4)

Since most ductile failures of peel test ISO 13954 occurs in either the coupler or the pipe, less detailed information is given about the actual strength of the joint. In order to obtain this information a similar peel decohesion test, EN 12814-4, can be used.

The samples are chosen following the same procedure as in ISO 13954 but the dimensions of the specimens differ, as can be seen in Figure 5. In this standard rectangular test specimens with flat parallel surfaces are cut out. A 5 mm wide and deep groove is cut into the joint line at both sides of the pieces. The samples are then mounted in tensile machine using two shackles.

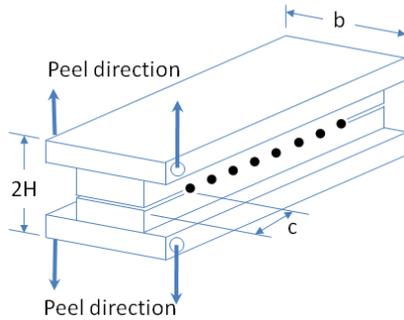


Figure 5. Dimension of the test piece according to EN12814-4.

After failure occurs the samples are characterized by calculating the joint toughness of the joint by:

$$K = \frac{F_w \cdot c}{(0.5bH^2)^{\frac{3}{2}}} \left(3.46 + 2.38 \frac{H}{c} \right) \quad 2$$

where F_w is the maximum force obtained during the test, c is the distance from the centre of the loading pin to the start of the joint, b and H are defined as in Figure 5.

2.5.3. Quantified Surface Ductility

Bowman (1992) suggest dividing different areas of the fracture surface, a_i , to be measured and assigned a ductility index, d_i , ranging from 1 (most brittle) to 5 (most ductile) depending on specific characteristics. The total ductility factor and the amount of ductility are then calculated by:

$$D_T = \sum_{i=0}^5 d_i a_i \quad 3$$

$$\% \text{ ductility} = D_T * \frac{5}{100} \quad 4$$

However, the author points out that the validity of the different ductility indexes were merely educated guesses and should be further evaluated before implementation.

2.5.4. Normalized peel energy

By using the data obtained during a peel test, the force and the displacement, Bowman (1992) propose calculating the measured energy to peel (area below the load/displacement curve), E_P , by:

$$E_P = \int_0^{x_f} P(x) dx \quad 5$$

Where $P(x)$ is the force, x the displacement and x_f is the displacement at failure. Since the sample widths (W) and the fusion zone lengths (L) varies the normalized peel energy, E_N , is calculated by:

$$E_N = \frac{E_P}{W(L-n\phi_w)} \quad 6$$

Where n is the number of wires and ϕ_w the diameter of the wires in the fusion zone. These are removed from the fusion zone length since the wires do not contribute to the energy absorption process.

2.6. Fractography

To be able to characterize the fracture surface from different peel tests, fractography can be adapted. Fractography is the science of examine fracture surfaces in the failure analysis of broken parts. The fracture appearance can give valuable clues about the cause of fracture. The analysis can be done at different scales, macroscopic (i.e. by ocular investigation) and microscopic (i.e. with an optical microscope or scanning electron microscope). Fractography has been used for decades in failure investigations of metals but as a result of the increased use of plastic pipes the concepts is more and more adapted onto plastic materials. An analysis can identify the fracture origin, direction of crack propagation, failure mechanism, material defects among other relevant information. The failure mechanism can be either brittle or ductile, or a mixture, depending on the appearance. (American Society of Metals, 2003, Parrington, 2002)

2.6.1. Ductile fractures

Ductile failures on a macro scale involve gross plastic deformation characteristics. These are material tearing, yielding, plastic flow, necking and shear which all results in change in shape and distortions (American Society of Metals, 2003). A model commonly used to describe what is happening on a molecular scale in a plastic deformation is the stretching of tie molecules in-between the crystalline lamellar regions, as can be seen in Figure 6. When the tie molecules cannot be stretched out any more, the lamellae breaks up into smaller regions as they become pulled apart (Lustiger and Markham, 1983).

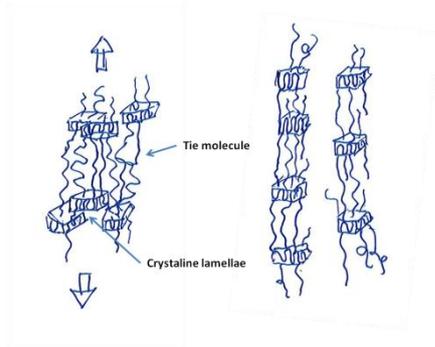


Figure 6. Illustration of plastic deformation on a molecular scale. As the sample is stretched the tie molecules between the crystalline lamellar regions is pulled apart and the lamellae breaks up into smaller parts.

Figure 7 shows typical pictures of ductile fractures of failed peel decohesion test pieces. A too high service temperature, usually above the glass transition temperature, can also induce ductile failures (Parrington, 2002). The energy required for a ductile fracture is much larger than for a brittle fracture due to that the plastic deformation takes place over a much larger material volume (American Society of Metals, 2003).



Figure 7. Typical ductile failures from peel decohesion test showing plastic deformation. Top view to the left and side view to the right.

2.6.2. Brittle fractures

Brittle fractures normally occur below the yield stress of the material and are associated with unexpected short term failures of plastics. Failures exhibit little or no gross plastic deformation. After a period of low stress the tie molecules starts to untangle and eventually

the strength of the remaining tie molecules are not sufficient to keep the crystal lamellae intact (Lustiger and Markham, 1983). The result is a brittle failure as illustrated in Figure 8 below.

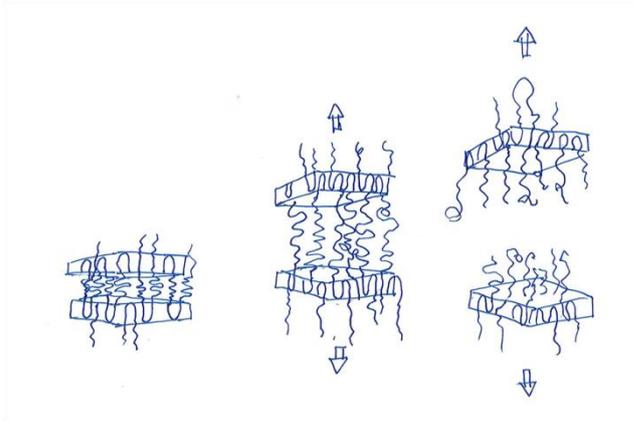


Figure 8. A brittle failure resulting of stretching out and unfolding of tie molecules.

On a macroscopic scale the fracture surface appear quite flat due to no change in shape or deformation of the material (American Society of Metals, 2003). The surface may have several characteristic features divided into different zones, depending on the appearance (Parrington, 2002). Two distinct commonly appearing areas are present during brittle failures of black polyethylene, dark black and gray brittle, see Figure 9.



Figure 9. Typical brittle failures from peel decohesion tests. Notice the different surface appearance, dark black and gray.

3. Experimental

In order to get information about why scraping of pipes is necessary and how it comes that Profuse pipe is said to be directly weldable several experiments were carried out. Methods used in previous work for investigation of pipe surfaces will be used for characterization of pipe and coupler. These are FTIR, DSC, OIT and SEM. Also analyzes suggested by the authors of this report will be used; ESCA, GC-MS and contact angle measurements. The evaluation of the different joints produced will be made according to ISO 13954, modified EN 12814-4, X-ray computed tomography and with a novel microwave scanning technique.

3.1. Materials

In this study two different kinds of pipes have been analyzed and joined together by electrofusion. Two black 280 mm pipes SDR11 were obtained from Wavin (former KWH) and uncolored jacketed Profuse 280 mm pipe SDR17 from Uponor. The two Wavin pipes had different manufacturing dates, one pipe was produced in April 2010 (referred to as “old pipe”) and the other produced in the end of February 2011 (referred to as “new pipe”). All pipes are made of bimodal high density PE100-material from Borealis, Borstar® HE3490-LS for Wavin pipes and 3493 LS for Profuse-pipe. Selected material data can be found in Table 1. Plastitalia S.P.A couplers of 280 mm were used, made of black PE100, approved for both SDR11 and 17. The couplers were produced in February 2010. Pictures of pipes and coupler can be seen in Figure 10.

Table 1. Material data for the different PE100 resins used in black Wavin-pipe.

	Borstar® HE3490-LS ⁽¹⁾ (Black Wavin)	3493 LS (Uponor Profuse)
Density	959 kg/m ³	950 kg/ m ³ ⁽²⁾
Melt flow rate (190° C, 5 kg)	0,25 g/10 min	0,3 g/10 min ⁽²⁾
Color additive	≥2 w% carbon black	0,1-2,5 w% ⁽³⁾ (unknown pigment)
Thermal stability (OIT 200° C)	≥20 min	>20 min ⁽⁴⁾

¹ (Borealis, 2005), ²(Uponor, 2010), ³(Uponor, 2005), ⁴ (Harget, 2002)



Figure 10. Materials used for electrofusion welding. Wavin pipe (left), jacketed Profuse pipe (middle) and electrofusion coupler (right).

3.2. Electrofusion welding

Pipes with different surface preparations were joined together with couplers by electrofusion. A total of 11 joints were made in order to evaluate if it was possible to weld pipes that had:

- Not been scraped, only cleaned with ethanol.
- Not been scraped, only cleaned with a non-polar solvent (heptane).
- Been scraped and aged outdoors for 6 days.

These joints were then compared to joints that were welded by following the prescribed instructions, i.e. by scraping and cleaning with ethanol. The circumference and ovality (the difference between the largest and smallest outer diameter) were measured in order to evaluate if the tolerances were fulfilled (Nordiska Plaströrsgruppen, 2009). In Table 2 the different surface preparations made on each pipe, are shown. To minimize the influence of the coupler, pipes with two different surface preparations were put into each coupler.

Table 2. Overview of the different configurations and surface preparations made.

Joint	Preparation left pipe in coupler	Preparation right pipe in coupler
1-2	Old pipe: Scraped and weathered outdoors 6 days (25/2-3/3) Cleaned with approved lint-free towels soaked with ethanol	Profuse pipe: Polypropylene layer peeled off and surface is cleaned with approved lint-free towels soaked with ethanol
3-4	Old pipe: Scraped Cleaned with approved lint-free towels soaked with ethanol	Old pipe: Cleaned with approved lint-free towels soaked with ethanol
5-6	Old pipe try 1: Cleaned with heptane	Old pipe try 1: Cleaned with water
7	PE80 pipe: Scraped Cleaned with approved lint-free towels soaked with ethanol	PE80 pipe: Cleaned with approved lint-free towels soaked with ethanol
8-9	Old pipe try 2: Cleaned with heptane	Old pipe try 2: Cleaned with water
10-11	New pipe: Cleaned with heptane	New pipe: Cleaned with approved lint-free towels soaked with ethanol

Scraping of the pipes were made with a RTC 315 (Ritmo America LLC), see Figure 11.

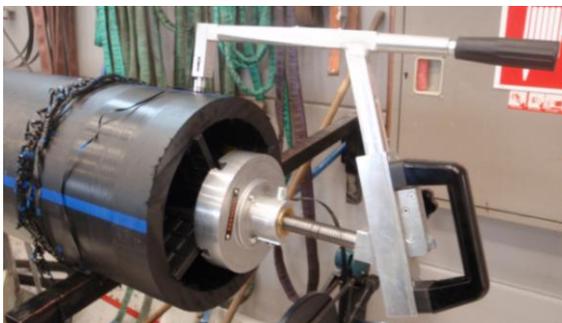


Figure 11. Picture showing the scraping process.

After the fusion program was completed the joints remained at rest for an hour to cool. The joints were then ocularly evaluated and changes prior the welding were noted.

3.3. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy is a common method to investigate oxidation of polymeric materials. Chemical bonds interact with the infrared radiation and the amount of absorbed radiation at different wavelengths gives information about the functional groups in the sample. The carbonyl absorption occurs at approximately 1700 cm^{-1} and depending on the wavenumber it is possible to state what kind of carbonyl is observed; e.g. 1740 (ester), 1728 (aldehyde), 1715 (ketone) and 1705 cm^{-1} (carboxylic acid) (Karlsson et al., 1992). A Thermo Nicolet 6700 (Thermo Electron Corporation) with a Smart Orbit diamond Attenuated Total Reflectance (ATR) attachment was used for the measurements. The diamond crystal used had destructive interference around $1900\text{-}2600\text{ cm}^{-1}$. The FTIR-ATR spectra were collected in absorbance mode and recorded during 200 scans at 4 cm^{-1} resolution. The obtained FTIR-ATR spectrums were analyzed in the software OMNIC v.7.1a.

Pieces of the different pipes were cleaned with ethanol and samples were either cut out from the surface by a scalpel or by using a microtome (Leica SM 2500). Following samples were evaluated:

- Samples from the outer surface of the old, new, Profuse pipe and coupler.
- Samples taken at 12 spots evenly distributed around the circumference of the old pipe in order to see if the oxidation differ.
- Depth profile of the old and Profuse pipe by microtoming $30\text{ }\mu\text{m}$ thick films from the surface to the depth of $210\text{ }\mu\text{m}$ (approximately the scraping depth).

3.4. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to determine the degree of crystallinity of the pipes. In DSC a sample is heated at constant rate and the heat released/uptaken by the sample is measured against an empty reference pan. Phase transitions are seen in the heat flow versus temperature plots as endothermic/exothermic peaks (Smart and Moore, 2005). By integrating the peaks, the enthalpy for the different phase transitions can be calculated. Crystallinity was calculated assuming the heat of fusion for 100 % crystalline HDPE to be 290 J/g (Polymers A Property Database, 2011). The integration interval was placed in line with the baseline, which practically meant that the left limit was placed at $50\text{-}60\text{ }^{\circ}\text{C}$ and the right at $10\text{-}15\text{ }^{\circ}\text{C}$ above the peak melting temperature. A schematic picture of a DSC-curve can be seen in Figure 12. To measure the crystallinity and melting temperature of the samples, the melting peak during the first heating cycle was used, since it contains the thermal history.

A Mettler Toledo DSC1 robot with a GC100 gas control system were used for the analysis and programmed as following: the sample was first kept at $25\text{ }^{\circ}\text{C}$ in 5 minutes followed by heating to $165\text{ }^{\circ}\text{C}$ with the rate of $20\text{ }^{\circ}\text{C}/\text{min}$. Isotherm at $165\text{ }^{\circ}\text{C}$ in 2 min, then cooled to $50\text{ }^{\circ}\text{C}$ with $-20\text{ }^{\circ}\text{C}/\text{min}$. Isotherm $50\text{ }^{\circ}\text{C}$ 2 min and then heated again with the same rate to $165\text{ }^{\circ}\text{C}$. Nitrogen atmosphere ($50\text{ ml}/\text{min}$) was used during the whole cycle.

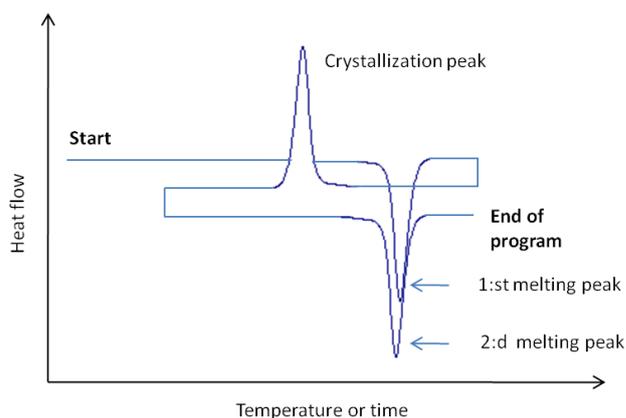


Figure 12. A schematic DSC-curve for a polyethylene sample. The sample is first heated above the melting temperature and then cooled below its crystallization point, followed by another temperature increase over the melting temperature.

Microtomed samples were analyzed and due to the small amount of sample (2-3 mg) a 20 μ l aluminum pan were used instead of a standard 40 μ l pan. The crystallinity at different depth was measured of old, new and Profuse pipe and at the fusion zone on the electrofusion coupler.

3.5. Electron Spectroscopy for Chemical Analysis

Electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS) is a technique to get both qualitative and quantitative chemical information of an approximately 4-5 nm thin layer of the sample surface. An X-ray beam is focused onto the sample and the electrons that are photo emitted from the sample are detected and analyzed by measuring their kinetic energy.

Samples from the outer surface and bulk of all pipes and electrofusion coupler were prepared by microtoming into thin sheets. All outer pipe surfaces and coupler were cleaned with ethanol in order to minimize the impact from possible fingerprints and to mimic the procedure performed prior to welding of the pipes. For the analysis a Quantum 2000 scanning ESCA microprobe from Physical Electronics was used with an Al K α (1486.6 eV) X-ray source and a beam size of 100 μ m. The analyzed area was about 500 x 500 μ m and the take-off angle was 45 $^\circ$ with respect to the sample surface. Two spots on each sample were analyzed.

3.6. Oxidation Induction Time

The oxidation induction time is a measurement of the stability of a sample and gives an indirect measurement of the level of effective antioxidants present. A sample is kept in oxygen atmosphere under constant temperature in a DSC apparatus until an exothermic oxidation peak is present. The oxidation induction time value is the time from the start of the isotherm until the oxidation peak occur (Huang et al., 2010, Gedde et al., 1994).

How to measure the oxidation induction time from a curve can be seen in Figure 13.

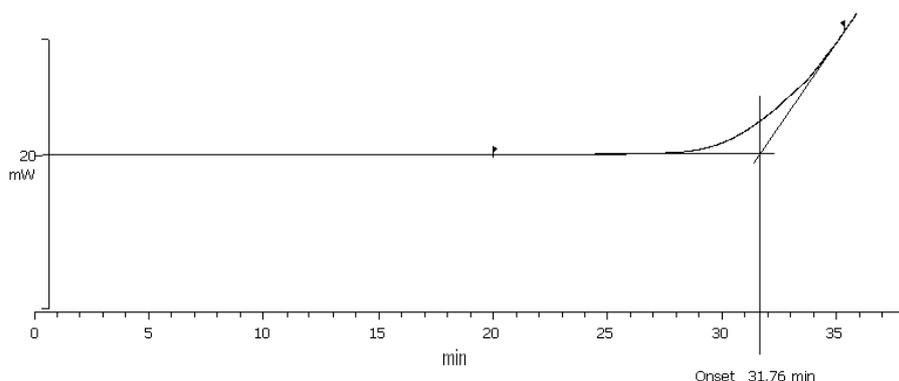


Figure 13. A typical curve showing how to measure the oxidation induction time, in this case after 32 minutes isotherm at 210 °C an exothermic oxidation takes place.

For the oxidation induction time measurement a Mettler Toledo DSC823^e robot with a TSO 800GC1 gas control system was used in the following way: sample was first heated from 50 to 210 °C with 20 °C/min and kept at 210 °C for 3 min in nitrogen (80 cm³/min) atmosphere. Then oxygen atmosphere (80 cm³/min) at 210 °C until the exothermic oxidation occurs. Samples were cut with a microtome to a thickness of 50 µm and punched into discs with 5 mm in diameter. The weight of each sample was around 1 mg.

3.7. Gas Chromatography - Mass Spectrometry

Gas chromatography - mass spectrometry (GC-MS) was used in order to detect the possibility of migration and depletion of low molecular compounds at the surface. The gas chromatography column separates the compounds, based on boiling point and interaction with the column material, while the mass spectrometer ionizes the compound and form ions that is detected and quantified.

The surface of a piece of pipe was scraped with a knife and the scrapings were collected and put into a vial with dichloromethane. A sample weight of approximately 100 mg was used. The samples were then subjected to ultrasonication for one hour followed by injection into the GC-MS machine. The analyses were performed with an Agilent system consisting of a 6890 gas chromatograph and a 5975 mass spectrometer. A non polar column, BPX-5 (95 % methyl polysilphenylene/siloxane phase, 5 % phenyl), was utilized. The columns had an inner diameter of 0.22 mm and a length of 25 m with a 0.25 µm film thickness. The injector temperature was 300 °C and the GC oven temperature was initially held at 35 °C for 3 minutes, then ramped at 15 °C/min to 210 °C, then ramped at 8 °C/min to 300 °C, with a final hold of 30 minutes.

3.8. Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a commonly used technique for mapping the surface topography of polymers and for investigating the semi-crystalline morphology. The sample is bombarded with an electron beam during scanning. This can result in charge build up during scanning of poor conducting materials such as polymers. Therefore sputtering with a thin layer of gold is needed, especially when high vacuum system is used. (Smart and Moore, 2005)

A ZEISS SUPRA 40 scanning electron microscope system was used in order to investigating the topography on fracture surfaces and to reveal the semi-crystalline structure of pipes. Test pieces were cut with a scalpel and punched to disks with a diameter of 5 mm. To reveal the lamellar structure the samples were subjected to etching prior imaging. The etching was done for 3 hours with permanganate in a solution of concentrated phosphoric and sulfuric acid, following the procedures in Shahin et al. (1999). All samples were sputtered with gold for 40 seconds prior imaging with an Agar Sputter Coater model no. 109.

3.9. Peel decohesion test (ISO 13954)

Samples were tested and evaluated according to ISO 13954 as described in section 2.5.1, and peeled at a rate of 25 mm/min in an Instron 1195 with a 100kN load cell.

3.10. Double peel decohesion test (EN 12814-4)

Several samples from peel decohesion test had failed in the pipe and were therefore tested by double peel decohesion test in order to separate the coupler from the pipe. Some additional samples were cut out from the joints. Grooves were cut out and two additional holes were drilled. Note that the samples were not sawn perfectly planar and rectangular as stated in the standard, see Figure 14. The samples were mounted with two shackles in an INSTRON 1195 with a 100 kN load cell and peeled at 25mm/min.



Figure 14. Test sample for double decohesion test with side grooves, which have previously failed in the pipe in peel decohesion test.

3.11. Contact angle measurements

A contact angle measurement is a simple and extremely surface sensitive method to investigate the surface properties i.e. the hydrophilicity/polarity. Different hydrophilicity may be related to surface oxidation, degradation or migration of different substances. Figure 15 is an illustration of how a water droplet acts on a hydrophobic surface (left) and on a hydrophilic surface (right) and how the contact angle θ is defined.

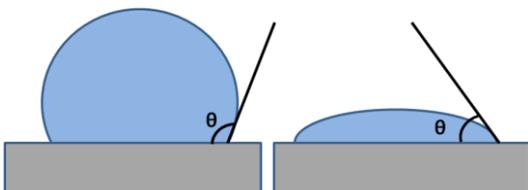


Figure 15. A water droplet on a hydrophobic surface (left) with large contact angle θ and on a hydrophilic surface (right) showing a low contact angle.

Contact angle was measured with deionized water and a KRÜSS DSA 100 apparatus on all pipes outer surfaces, scraped surfaces, scraped and aged surfaces and on electrofusion coupler. Each contact angle was measured as a mean value during 3 seconds with a sampling interval of 0.2 seconds of 5 μl droplets. Measurements were performed on 6 droplets placed on each surface and in turn summarized into a mean value. The software used for the measurement was Drop Shape Analysis v. 1.90.0.14.

3.12. X-ray Computed Tomography

In order to investigate if X-ray computed tomography (CT) could be used for detection of faults, one electrofusion joint was sent to SP Trätek Skellefteå for scanning. The electrofusion joint (joint 7 in Table 2) was fused with one scraped and ethanol cleaned pipe, and one only cleaned with ethanol. This should result in one ductile and one brittle side of the joint to investigate. There were also some faults in the alignment of pipes.

The CT used was a Siemens Somatom Emotion Duo. A CT scanner uses an X-ray beam in form of a cone and the photons that pass through the material are detected and counted. CT gives an image of density differences within the material (Oja, 2011). The joint were scanned in two directions; parallel and perpendicular to the pipe direction. Images were taken with a 1 mm wide X-ray beam (130 kV) with a distance of 1 mm between each scan. After scanning, the image was compared with peel tested samples cut from the actual joint.

3.13. Microwave scanning

A novel non destructing testing (NDT) method for evaluation of electrofusion joints have been developed by Evisive Inc. based on a microwave technique. A probe (see Figure 16) consisting of a microwave transmitter and two receivers is moved over the surface. Energy is reflected at every interface where the materials have different dielectric constants. Due to that the receivers are offset 1/4 of a wavelength from each other it give rise to an interference pattern. The interference pattern is measured as a voltage difference and gives an image of the pipe and coupler (Murphy and Lowe, 2010). The technique shows good results in identifying common faults with electrofusion joints such as contamination, misalignment and melts flow into cold zones. One electrofusion joint was scanned by Evisive staff on site at SP Pipe Centre in Göteborg. The joint was the same as investigated by X-ray computed tomography.

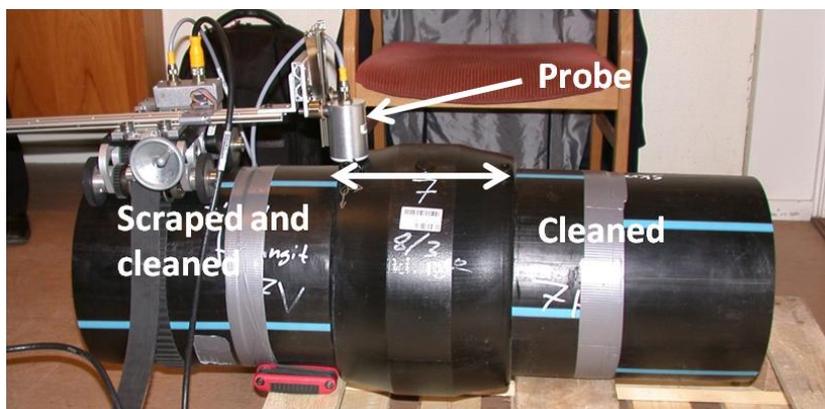


Figure 16. Microwave scanning of an electrofusion joint. The probe is moving back and forth over the coupler and simultaneously moved around.

4. Results

The results from the previously explained experiments will be shown in the following chapter. Most valuable results were obtained from the ESCA analysis, described in section 4.5, showing large variation in surface oxidation.

4.1. Electrofusion welding

All pipe and coupler configurations were successfully fused together without any complications during the welding process. However, the subsequent visual inspection of the joints showed several defects. Figure 17 shows examples where melt flow have leaked out (left) and heating wires have been pushed out and become exposed (right).



Figure 17. Pictures showing defects such as melt flow and exposed heating wires. These defects might suggest something is wrong with the joints.

In some joints the weld indicators did not protrude at all, implying not enough melt pressure was obtained in the fusion zone. According to Nordiska Plaströrgruppen (2009) these kinds of defects would indicate that there might be something wrong with the joints. Despite the leaked out melt flow and exposed heating wires the joints can still be approved after evaluation with peel decohesion test.

4.2. Fourier Transform Infrared Spectroscopy

Although FTIR has been commonly used to observe surface oxidation of PE-pipes, our analyses showed no, or for a few cases only very small, carbonyl absorption. This was the case for the old pipe, new pipe, Profuse pipe and coupler. No major difference in carbonyl absorption could be observed when comparing spectra of samples taken around the whole circumference of the old pipe. In Figure 18 a selection of spectra from a depth profile experiment of the old pipe is shown. A small carbonyl peak is observed at the outer surface of the old pipe but is not present at the depth of 30 and 210 μm .

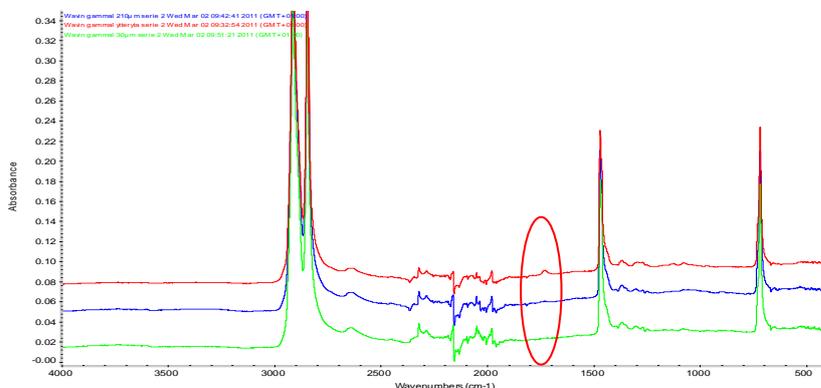


Figure 18. FTIR spectra at the surface (top), 30 μm and 210 μm (bottom). One of few cases where carbonyl absorption could be seen. Interference at 1900-2600 cm^{-1} is caused by the diamond crystal.

4.3. Differential Scanning Calorimetry

The results from the differential scanning calorimetry are collected in Table 3. The old pipe shows lowest crystallinity at the outer pipe surface with an increase towards the middle, then a small decrease at the inner pipe surface. The trend for new and Profuse pipe is approximately the same with the difference that the highest crystallinity is found at the inner pipe surface. The crystallinity at the fusion zone on the electrofusion coupler is somewhat higher than at pipe outer surfaces.

Table 3. Results from the crystallinity measurements of all pipes and electrofusion coupler.

% Crystallinity	Old pipe	New pipe	Profuse	Coupler
Surface (0-20 μm)	54.2	53.6	56.3	61.1 ¹
Scraped (~200 μm)	57.4	51.1	56.2	-
Middle pipe wall	69.6	61.9	61.5	-
Inside pipe surface	66.6	64.2	69.0	-

¹Sample were cut with scalpel due to the rifled surface

The crystallinities stated above are approximated to be in the order of ± 1 % due to how the integration limits are placed in the curves, see Figure 19.

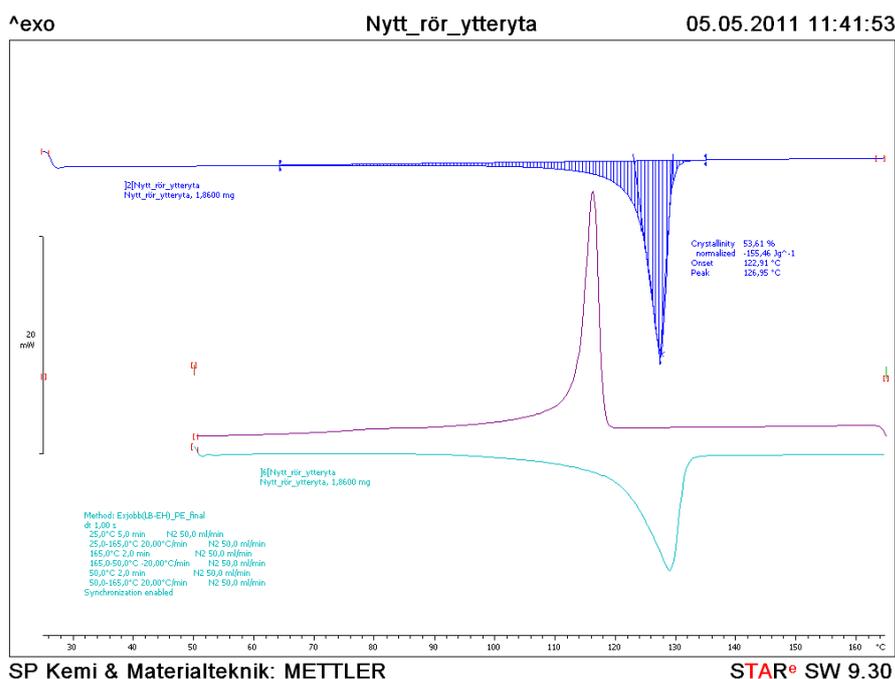


Figure 19. A typical DSC curve, with the segments separated, from a run of the outer 20 μm surface of a new pipe. The upper (filled) peak corresponds to the first melting and is used to calculate the crystallinity. The peak is quite broad due to that different sizes of crystallites have different melting temperatures.

The melting temperature of the first melting cycle varied between 126-131 $^{\circ}\text{C}$ for all samples.

4.4. Oxidation Induction Time

The results from the oxidation induction time measurements on old, new, and Profuse pipe and coupler can be seen in Figure 20. The outer surface samples show the lowest stability of all investigated pipes. For both old and new pipe the oxidation induction time increased from surface to the middle of the pipe wall.

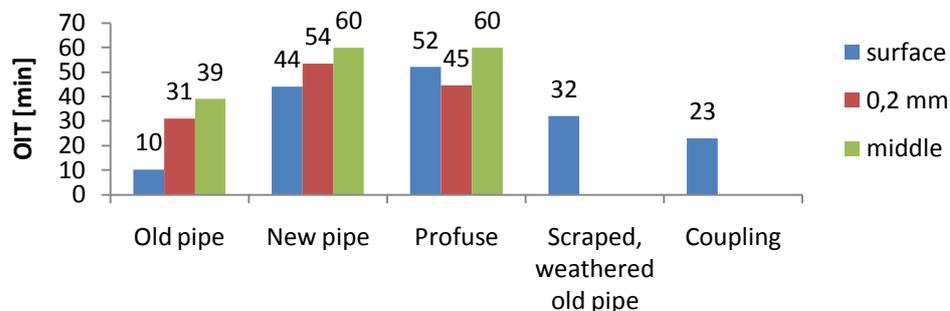


Figure 20. Results from the oxidation induction time measurements for the three pipes and coupler.

The old pipes circumference was divided into 4 sides named I, II, III and IV, oxidation induction time were measured at each of these sides. Differences can give an indication of the storage conditions e.g. material degradation due to sun exposure. The mean oxidation induction time at the surface was 10 minutes, with a small variation around the pipe surface as can be seen in Figure 21. For the new pipe and Profuse pipe the surface oxidation induction time were 4 to 5 times higher than for the old pipe.

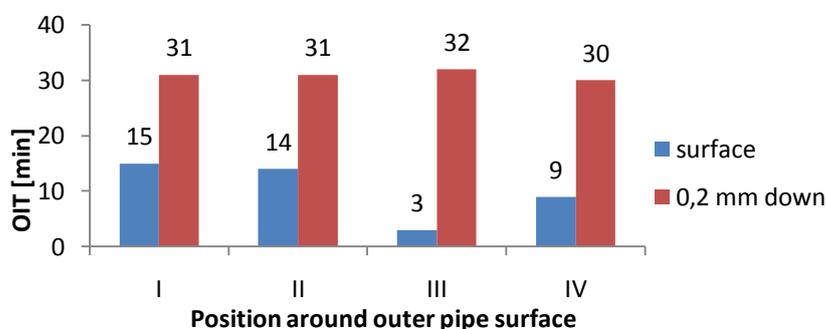


Figure 21. Oxidation induction time around old pipe at outer surface and 0.2 mm down.

4.5. Electron Spectroscopy for Chemical Analysis

Mean values from the ESCA analyses can be seen in Table 4. The results from the two spots being analyzed on each sample were consistent in all cases. The analysis shows that the outer surface of old and new pipe are oxidized. On the other hand, the surface of the jacketed Profuse pipe contain close to 0 % oxygen. The oxygen concentration in the bulk samples were always zero or close to zero. The surface of the electrofusion coupler at the fusion zone was also oxidized, but not as much as the surface of new and old pipe. Some traces of other elements can be found on the surface samples, especially silicon on new and old pipe. These small fractions of other elements are probably due to contaminations of the samples or insufficient cleaning.

Table 4. Results from the ESCA-analysis of pipes and coupler. All values are in % of atomic concentration.

Element/orbital	C/1s	O/1s	Na/1s	Si/2p	N/1s	S/2p
Surface old pipe	87.4	11.2	0.1	1.3	-	-
Bulk old pipe	100.0	-	-	-	-	-
Surface new pipe	88.4	8.7	-	2.0	0.9	-
Bulk new pipe	99.9	0.1	-	-	-	-
Surface Profuse	99.8	0.2	-	-	-	-
Bulk Profuse	99.9	0.1	-	-	-	-
Surface coupler	95.5	3.5	0.6	-	-	0.4
Bulk coupler	99.7	0.3	-	-	-	-

The C/1s peak was resolved into components peaks at different binding energies for all samples. For the Profuse and bulk samples the carbon peak is only due to the C-C band at 283.5 eV. Figure 22 shows a spectrum from a wide-scan (left) and the corresponding high-resolution spectra for the strong carbon peak at 283.5 eV, resolved into four component peaks around 283.5, 284.8, 286.4 and 287.5 eV.

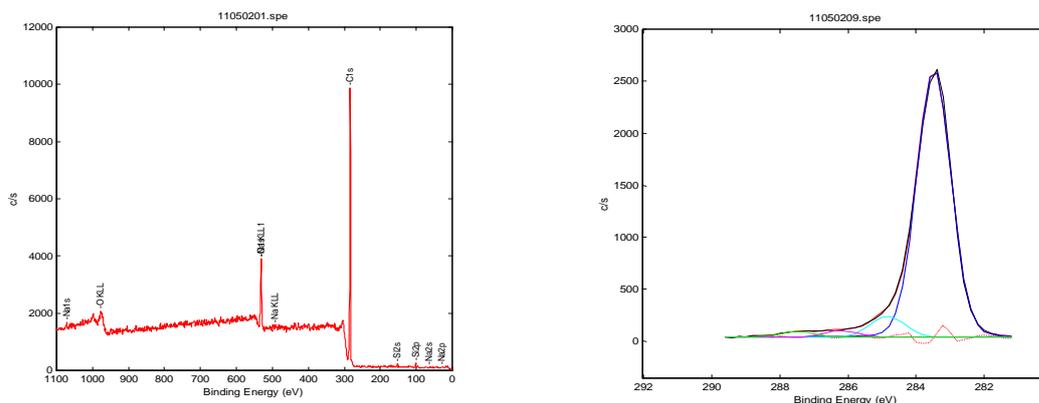


Figure 22. ESCA spectrum for a wide-scan (left) and for a high-resolution scan over the C/1s region at the outer surface of old pipe.

The results from the high resolution scan and its corresponding bonds in atomic percent can be found in Table 5. Surface of old pipe, which contains most oxygen, have lowest value of C-C bonds and in turn highest content of C-O, C=O and C(=O)O bonds and vice versa for Profuse pipe. Chemical shifts adapted from Beamson and Briggs (1992).

Table 5. Distribution of different carbon bonds according to the high-resolution scan over the C/1s region for new and old pipe and electrofusion coupler.

Bond	C-C %	C-O %	C=O %	C(=O)O %
Surface old pipe	88.5	7.5	2.2	1.8
Surface new pipe	93.9	4.4	1.0	0.7
Surface coupler	97.6	2.4	-	-

4.6. Gas Chromatography - Mass Spectrometry

The GC-MS tests showed the presence of aliphatic hydrocarbons in all samples, ranging from tetradecane (C₁₄H₃₀) to hexacosane (C₂₆H₅₄). No oxidation products or other oxygen-containing compounds were found. At the untreated surface squalene was found, however it is very likely a contaminant from a fingerprint (Weyermann et al., 2011).

In Figure 23 the chromatogram of the bulk sample of the old pipe is shown, where the largest peaks were identified.

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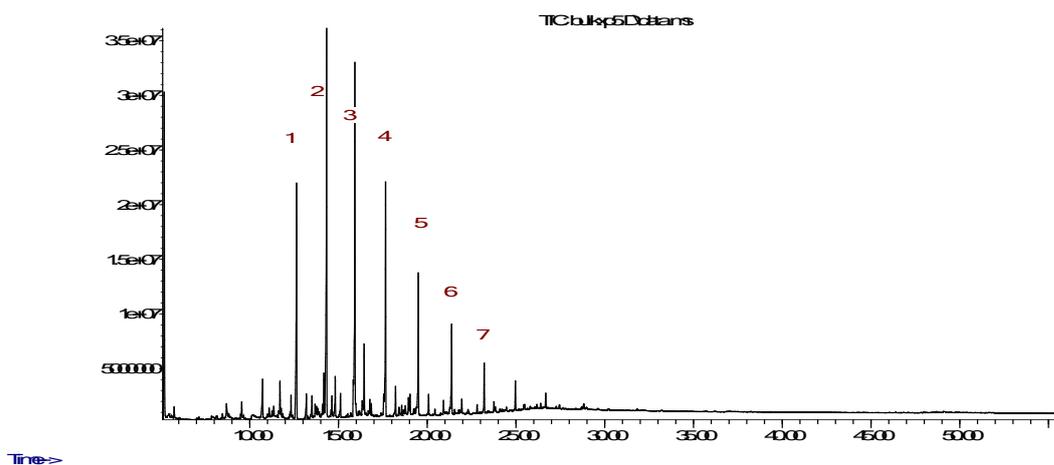


Figure 23. Chromatogram of the bulk sample of the old pipe. According to mass spectrometry the seven largest peaks corresponds to; 1: tetradecane, 2: hexadecane, 3: octadecane, 4: eicosane, 5: docosane, 6: tetracosane, 7: hexacosane.

In order to evaluate a depletion of shorter aliphatic hydrocarbons at the surface the amount of the specific substances found in the bulk was set to 100%. The amount of substance found at the heptane washed surface can be compared to the amount in the bulk, highlighted in Table 6. Unfortunately it is not possible to compare this data with the untreated surface since this sample was not tested at the same time.

Table 6. Results from GC-MS of bulk, heptane washed and untreated surface.

Nr	Substance	Bulk [%]	Heptane washed surface [%]	Untreated surface [%]
1	Tetradecane	100	25	10
2	Hexadecane	100	30	10
3	Octadecane	100	55	40
4	Eicosane	100	100	90
5	Docosane	100	110	119
6	Tetracosane	100	140	160
7	Hexacosane	100	160	250

4.7. Scanning Electron Microscopy

Images of the lamellar profile of outer surface for old pipe and Profuse pipe are shown in Figure 24. The lamellae structure is built up by randomly banded spherulites. The banded spherulites in Profuse seems to be more “thread-like” (upper right) and more elongated than those at surface (upper left) and bulk (down left) for old pipe. There is no difference in crystal morphology between the outer surface of old pipe and bulk, as can be seen in upper and down images to the left in Figure 24.

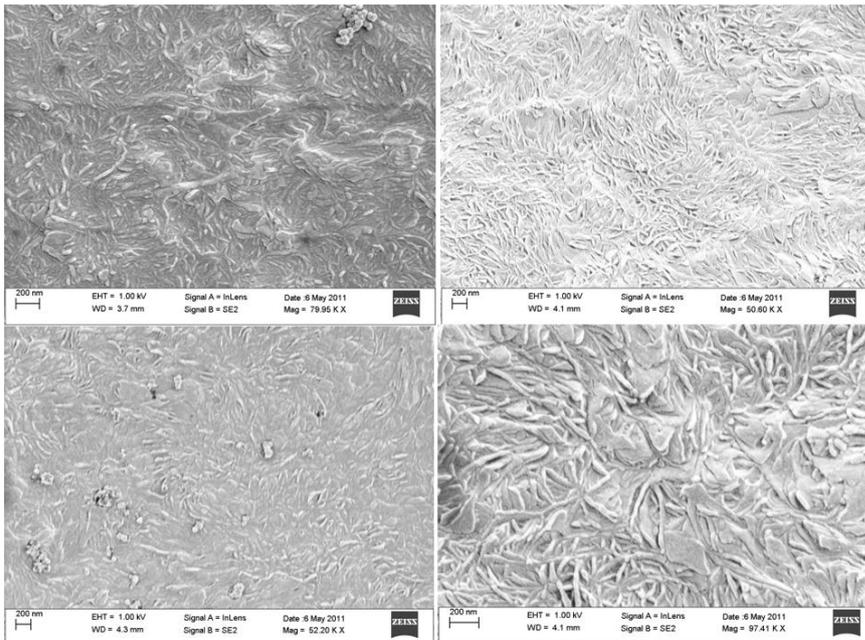


Figure 24. Crystal morphologies revealed after removal of amorphous regions by etchant. The lamellae structure consists of randomly oriented banded spherulites.

In order to reveal if there is any difference in topography of the two kinds of brittle failures present at peel testing pieces of electrofused joint, dark black surface and gray surface, SEM imaging were carried out. The result can be seen in Figure 25. The image to the left shows a dark black brittle fracture surface with no signs of plastic deformation present. Plastic deformation can easily be seen in the right hand side image of a gray brittle fracture.

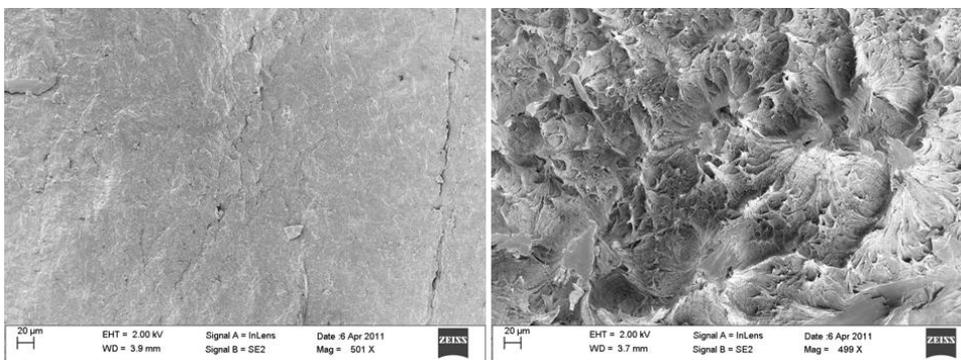


Figure 25. SEM images of the two kinds of brittle fractures, dark black to the left at and gray to the right. The magnification is close to 500 x. Notice the difference in plastic deformation.

4.8. Peel decohesion test (ISO 13954)

All samples were successfully tested according to ISO 13954. The number of passed and failed samples of every joint can be seen in Figure 26. In order for a joint to be approved all test samples have to pass, thus only three of the tested joints have passed. Two of these joints, scraped and Profuse, were made according to prescribed instructions while the joint scraped and weathered were not. Cleaning only, with water, ethanol or heptane, did not result in an approved joint.

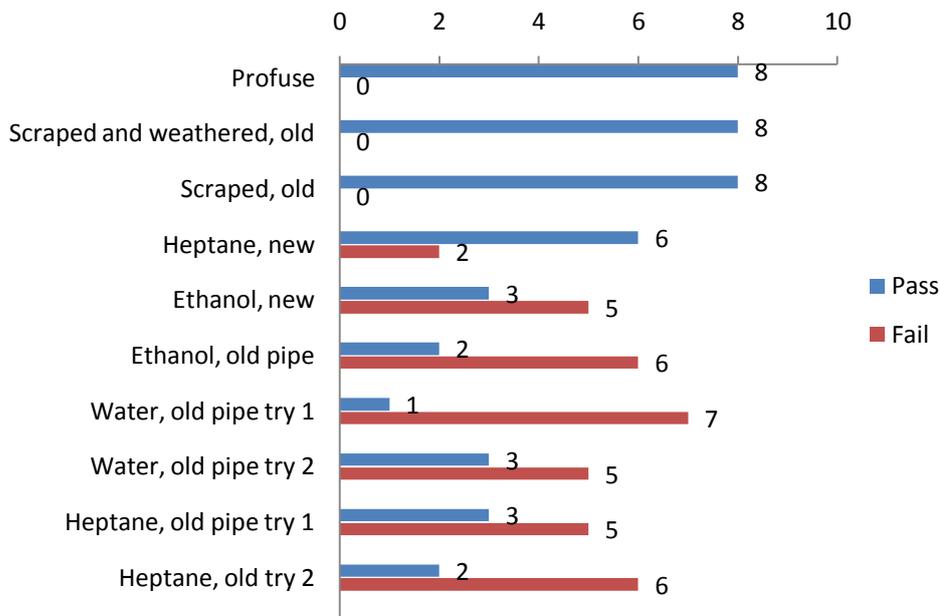


Figure 26. Number of passed and failed samples per joint according to peel decohesion test ISO 13954.

Although the cleaning does not seem to have a substantial effect on welding of the old pipe, cleaning the new pipe with heptane was slightly better than cleaning with ethanol, but not enough to produce an approved joint.

In Figure 27 the number of passed and failed test samples per side of the old pipe, for the not approved joints, is shown. Side II of the pipe seems to be slightly worse than the others.

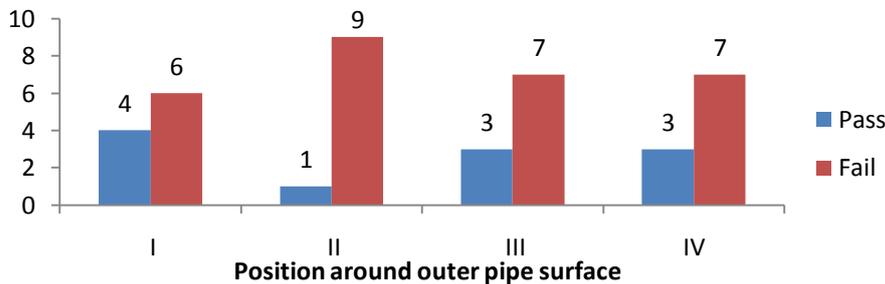


Figure 27. Number of passed and failed peel-test samples per side for the old pipe.

In Figure 28 four peel decohesion test samples are shown. The first sample has failed in the pipe while the second failed in the coupler. The third sample failed in both pipe and coupler while the last sample failed in pipe, joint interface and finally in the coupler. These samples are classified as ductile since the joint is stronger than the pipe and/or coupler.

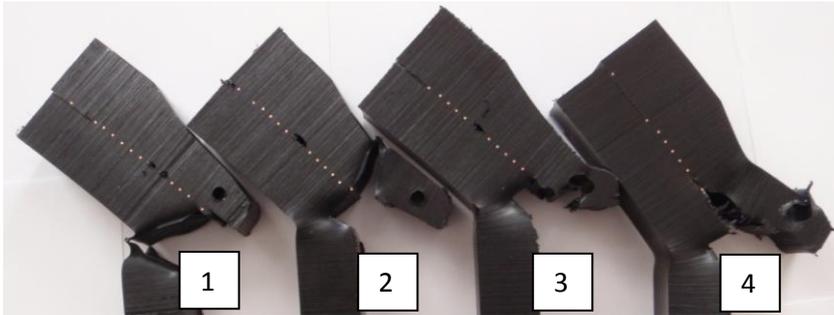


Figure 28. Peel decohesion samples with different failing modes in pipe/coupler/joint interface.

In Figure 29 typical peel decohesion tested samples are shown. First sample is characterized 0 % brittle, the second one as 70 % brittle and the last two ones 100 % brittle. Almost no wire imprints are present at sample 4, indicating extremely low strength at the fusion interface.

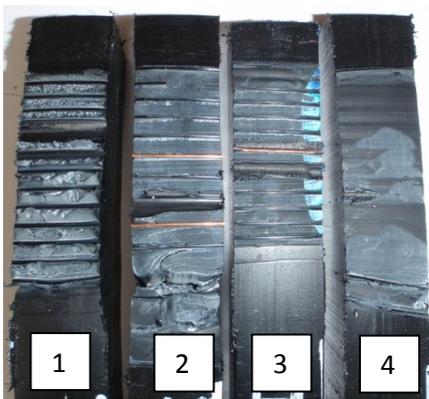


Figure 29. Typical failures in fusion interface with increasing brittleness from left to right.

Figure 30 shows four typical graphs obtained during peel decohesion test. From the appearance of the graphs it is possible to get an indication of the failure mode. A typical brittle failure drops fast after reaching the peak load (found at 30-45 mm), thus brittle failures results in low positions. A typical ductile failure has a smoother and more extended curve. During the tests three different kinds of ductile failures could be observed; separation of pipe and couple or failure in either the pipe and/or the coupling. The ductile failures in pipe and/or coupling commonly lead to a second peak.

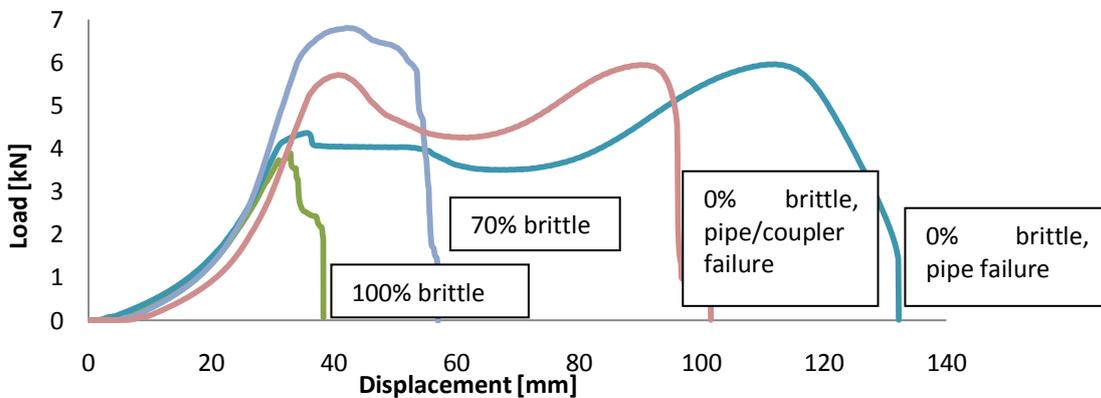


Figure 30. Example of load/position curves obtained from a peel test (ISO 13954). From the figure several types of failure mode can be seen

4.9. Double peel decohesion test (EN 12814-4)

Figure 31 shows the load/displacement graphs obtained from double peel decohesion test. Compared to the load/displacement curves obtained from peel decohesion test, these curves show a more distinctive difference between the different kinds of failures. Apart from the peel decohesion test there is also a larger difference between the peak load of brittle and ductile samples.

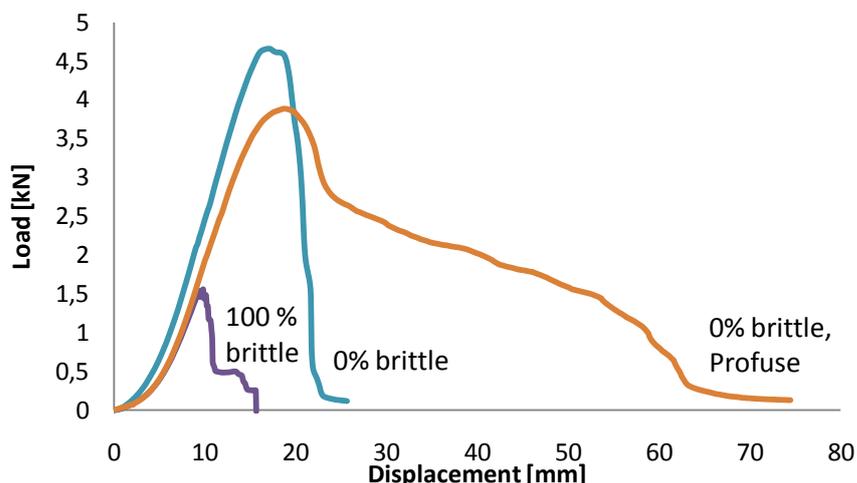


Figure 31. Example of load/displacement curve obtained from a double peel test (EN 12814-4).

4.10. Contact angle measurements

The contact angles for old pipe can be seen in Figure 32. The untreated pipe surface shows lowest contact angle indicating to be most hydrophilic. The contact angle increased after cleaning with heptane. Heptane cleaned surfaces showed higher contact angle than surfaces cleaned with ethanol. All three scraped surfaces have roughly the same contact angle and are thus more hydrophobic than the untreated pipe surface. Cleaning of a scraped pipe surface seems to decrease the contact angle, except when cleaning the outdoor aged sample with ethanol.

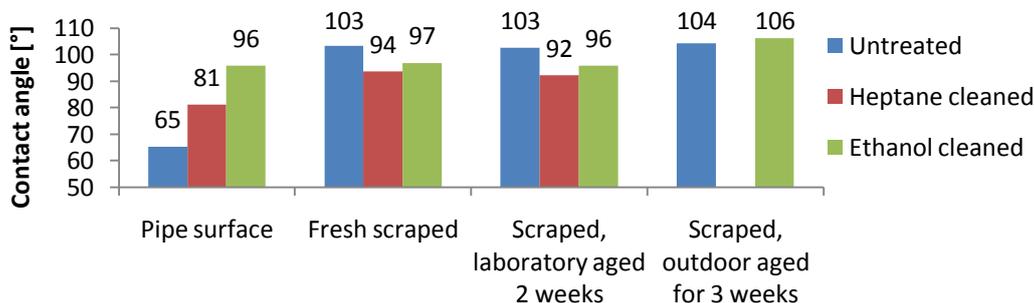


Figure 32. Results from the contact angle measurements on old pipe.

The results for new pipe show the same trend as the old pipe, with the difference that the untreated pipe surface is a bit more hydrophobic. The fresh Profuse outer surface (PP-jacket peeled away instantly) acts super hydrophobic i.e. water droplets do not wet the surface at all, and the contact angle was thereby set to 180°.

Data for new pipe and Profuse pipe is stated in Figure 33 below.

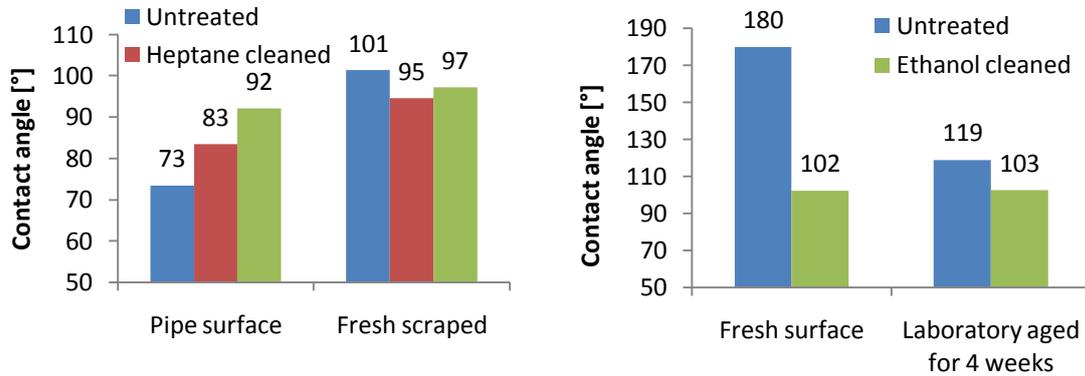


Figure 33. Contact angles for new pipe (left) and Profuse pipe (right).

Due to the rifled inner surface of the electrofusion coupler it was impossible to measure contact angle properly. Some tries indicated a contact angle of approximately 75° of an untreated surface.

4.11. X-ray Computed Tomography

Problems during the X-ray computed tomography scans occurred due to interference with the heating wires that caused large artifacts in some of the images. These artifacts can be seen as white areas at the joint interface as seen in Figure 35. Figure 34 below shows a slice of the joint parallel to pipe axis. All heating wires are present in the picture but no artifacts are seen. Voids are present at the fusion zone at both pipe sides. The voids were also seen at the same sites when the joint were sawed into pieces for investigation. Some misalignment of the pipes in the coupler is evident in the image.

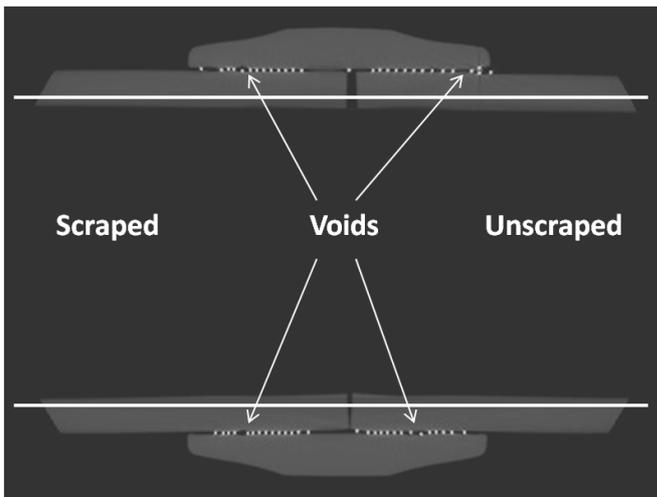


Figure 34. X-ray computed tomography image taken parallel to pipe axis.

Figure 35 shows images from the CT-scans perpendicular to the pipe axis. Again, voids were present at both the pipe ends.

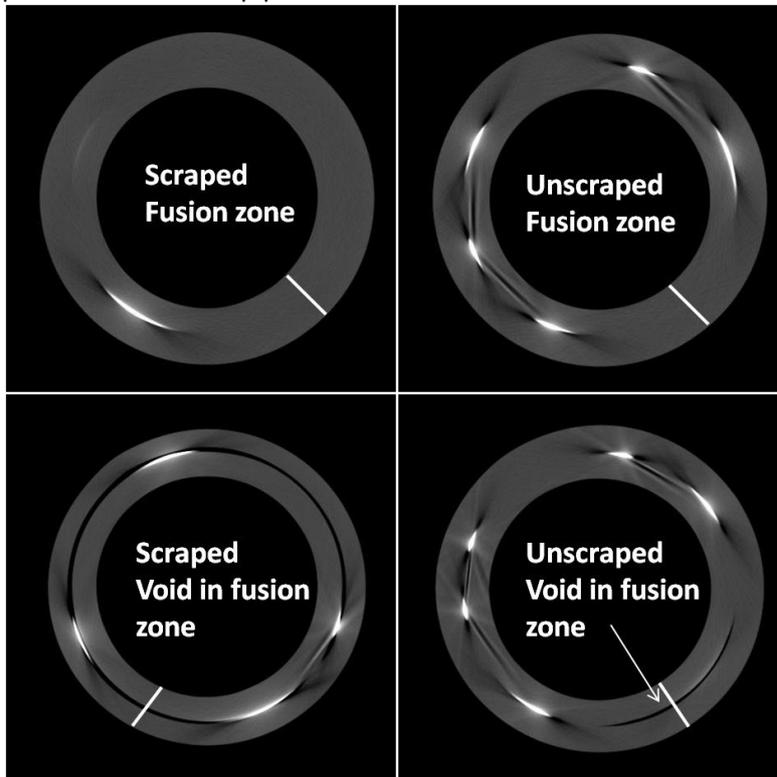


Figure 35. X-ray computed tomography images taken perpendicular to pipe axis.

Density profiles, see Figure 36, were plotted at positions marked as white lines in Figure 35 above. The gray value (which is proportional to density) drops drastically close to the value for air (1000) in the profiles over a void. This drop was not present in profiles over a consistent fusion zone indicating fusion between pipe and coupler.

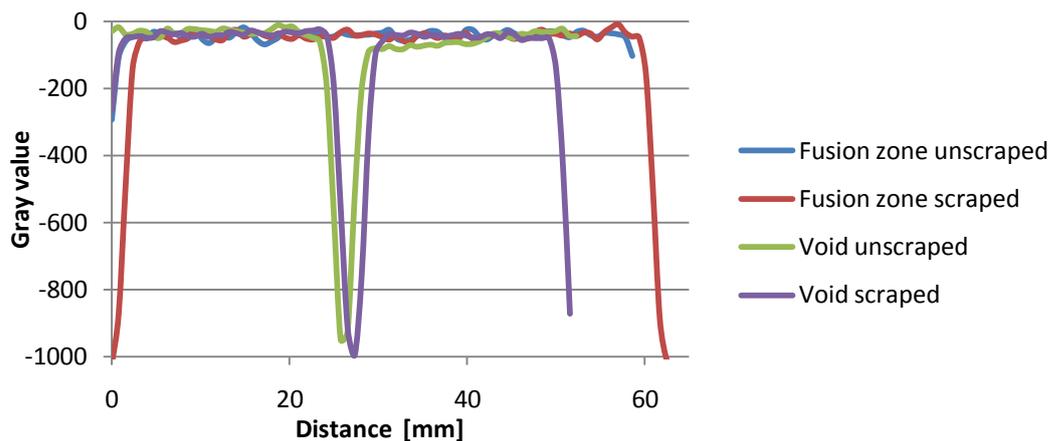


Figure 36. Density profiles over a cross-section at the fusion zone for scraped and unscraped side. The fusion interface is located around 26 mm.

A whole series of images were taken with CT over the joint and analyzed with the software ImageJ.

4.12. Microwave scanning

The image from the Evisive Inc. microwave scan can be seen in Figure 37. The image was analyzed by Ken Murphy, Exova. Murphy concludes that the signal from the fusion zones is mostly consistent except at the marked area at the unscrapped side of the joint. The fact that the cold zone in the middle is not straight could be an indication of melt flow, due to misalignment during production of the joint. Vertical lines can be found in the cold zone which are due to external features on the coupling. The final conclusion is that there may be a fault with this joint. Some degree of brittleness should be observed at the marked area at the unscrapped side in a peel test. (Murphy, 2011)

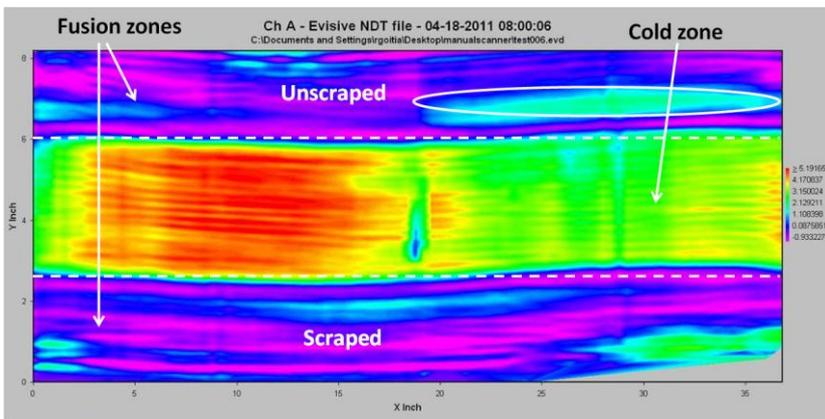


Figure 37. Microwave scan of the investigated electrofusion joint. The two fusion zones can easily be distinguished from the cold zone in the middle.

Test pieces for peel decohesion test were cut as in Figure 38 and analyzed according to peel decohesion test. The result was as expected, ductile behavior at the scraped side and brittle behavior on the unscrapped side. Notable is that samples with a similar pattern behave different in peel decohesion test, especially for pieces “1” and “4”.

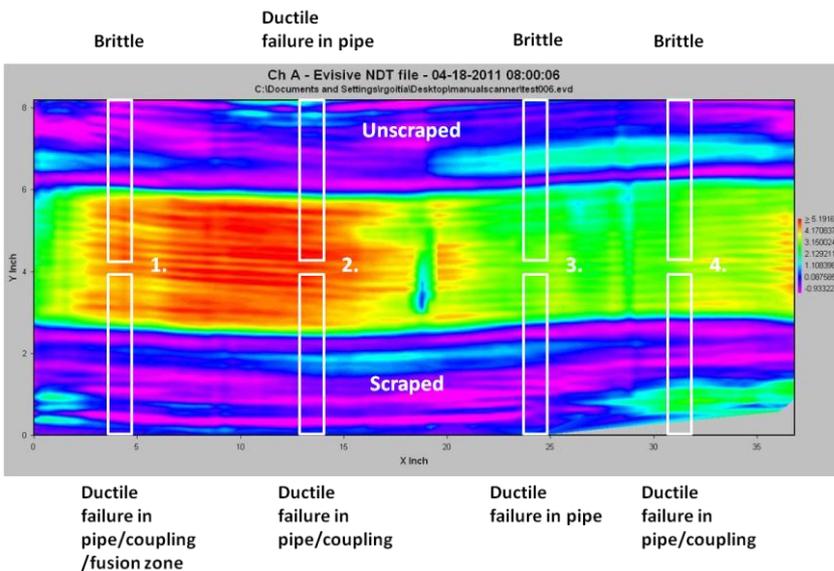


Figure 38. Results from peel tested samples, cut at marked positions, around the coupling.

5. Discussion

The following chapter will discuss the results according to the two question formulations.

5.1. Question formulation 1

The result from the electrofusion welding of the black pipes from Wavin (old and new pipe) shows that scraping is necessary in order to obtain an approved joint. None of the cleaning preparations with either ethanol or heptane could replace the scraping process. Only Profuse pipe was possible to weld without scraping. Our results from welding of outdoor aged scraped pipes indicate that good joints with high ductility can be made, despite re-scraping recommendations (Nordiska Plaströrsgruppen, 2009). However, the pipes were aged for only 6 days during February in Sweden. They were not subjected to as high temperatures and UV radiation as would be expected during a summer week. Brittle failures of the unscraped old pipe were quite evenly distributed along the pipe circumference. Quarter II had the largest amount of brittle failures even though oxidation induction time had its lowest value at quarter III. Surprisingly, no correlation between oxidation induction time and brittle failures were found as described in previous work by Huang et al. (2010).

All eight peel decohesion specimens have to fail ductile in order to approve a joint. Surprisingly the unscraped and cleaned pipes always showed one, two or three ductile pieces. No explanation for this observation has been found, but it may be due to differences in oxidation around the pipe circumference or possible migration of unknown species.

It is evident that there is a difference between the surfaces that were weldable (scraped pipes and Profuse pipe) and those who were not weldable (unscraped pipes). The ESCA analysis shows that the outer surface of Wavin pipes are oxidized which is not the case for scraped ones and Profuse pipes. This is consistent with the results from contact angle of untreated surfaces and oxidation induction time measurements. The difference in contact angle between the outer surface of Wavin pipes and scraped ones can be explained by the presence of an oxide layer, which gives a more hydrophilic outer surface. Cleaning with ethanol and heptane seems to affect the contact angle for unscraped pipes significantly. After ethanol cleaning all surfaces, scraped and unscraped ones, obtained approximately the same contact angle. This behavior was unexpected and might be due to traces of non volatile species in the cleaning liquids. The very low oxidation induction time for the outer surface of old Wavin pipe suggests that it may have been subjected to degradation. The degradation may be due to chain scission and oxidation as discussed by Huang et al. (2010). The new Wavin pipe is almost as oxidized as the old one but have a significantly higher oxidation induction time. The difference may be related to the outdoor storage for almost a year in exposure of weather and UV radiation. Despite the high oxidation induction time for new Wavin pipe, it is not weldable without scraping. This indicates a high concentration of stabilizers even if the outer surface is oxidized. No significant carbonyl peaks could be observed in the FTIR analysis of pipes and coupler, contrary to ESCA results. The absence of a carbonyl peak can be due to carbon black, which is known to absorb IR radiation, or an extremely thin oxide layer.

A difference in oxidation was observed between coupler and pipes. This may be related to the manufacturing processes; the pipes are extruded while the coupler is injection molded. Immediately after the extrusion die, when the polymer resin is at very high temperature, the material is in contact with air. The pipe is then externally cooled with water which also contains oxygen to some extent. This is not the case for injection molded parts. After injection

the part is allowed to cool in oxygen-free environment in the mold and thus lower oxidation levels are expected. The small difference in oxygen content at the surface between the old and new pipe implies that the major oxidation occur in the extrusion process and not during storage. Thereby it should be possible to scrape the pipes in advance and not necessarily in connection with the welding. If the oxidation could be avoided in the extrusion process it may result in directly weldable pipes were no scraping precautions is needed. To achieve this, introducing an inert atmosphere (e.g. nitrogen) or change of the cooling procedures can be of interest. Inert atmosphere is most likely to avoid oxidation at places were the material is hot i.e. immediately after extrusion. It may also help to change the cooling medium to a liquid (or gas) which does not contain as much oxygen as water.

Aliphatic alkanes, C₁₄-C₂₆, were found at the surfaces and in the bulk of the old Wavin pipe by GC-MS. Unfortunately, it is not possible to conclude anything about the amount in the bulk compared to the untreated surface since all samples were not run at the same time. Any possible migration of low molecular species could not be verified.

No major difference in crystallinity and crystal morphology was detected by DSC and SEM of the different pipes. The lamellae structure is built up randomly by banded spherulites as shown previously in literature (Huang et al., 2008).

5.2. Question formulation 2

The peel decohesion test, ISO 13954, is hard to adapt since some parts of the standard is not clearly defined. A big disadvantage is the lack of pictures of typical brittle and ductile failures. It is also unclear how to deal with voids, wire imprints and melt flow in the fusion zone and how the brittle fracture length is defined. The ISO 13954 standard does not deal with how to handle failures that not take place in the fusion zone e.g. failures in the pipe. These samples are commonly characterized as ductile since it implies a strong joint. Surprisingly, one peel decohesion specimen that first failed ductile (in the pipe) was then tested in double peel test and failed brittle. This result indicates the fact that a brittle joint can be strong enough to pass a peel decohesion test.

In literature it is suggested that this peel test might not be a good evaluation method, since failures in this short-term test does not imply failures in long term test. The test poorly mimics in-service failures, which are more likely to start in the internal cold zone and propagate outwards the fusion zone. This is also shown by FEM-analysis by (Troughton et al., 2006). Joints that have been in service for a long time (up to twenty years) without implications have shown brittle behavior in peel tests.

Double peel test, EN 12814-4, seems to be a more adequate method to evaluate electrofusion joints. During this test only the weld zone is subjected to stress and the failure is then more likely to happen in the fusion interface. Therefore, the data obtained from this test, e.g. the load and displacement, gives more information of the actual joint strength than ISO 13954. The difference in normalized peel energy between a brittle and ductile sample is also more significant, see Figure 31. One drawback with double peel test is the more time consuming sample preparation. We suggest using a simpler test piece where the wall thickness of the pipe and coupler remain unchanged, compare Figure 5 and Figure 14. A problem when using normalized peel energy is to define a suitable threshold for joint approval. This threshold also needs to be defined for, or adaptable to, different pipe dimensions and couplers, which can be a challenge.

A combination of double peel test and 'Quantified Surface Ductility' can be another approach for a more objective way to evaluate electrofusion joints. Image analyzing software would be suitable to use for measuring different fracture areas. However, more work is needed to be done regarding the ductility index and the different fracture surfaces. We have shown large difference in ductility at the micro scale of dissimilar brittle areas by SEM. This has to be taken into account when defining the ductility indexes.

Of the two non destructing test methods used in this study, X-ray computed tomography and microwave technique, the latter seem to be the most promising. Microwave scans of our joint showed some differences between the two pipe sides. Strangely, samples with similar microwave pattern turned out to behave completely different in peel decohesion test. Microwave images give hints about interesting areas for cutting peel decohesion test pieces and thus minimize the probability to miss brittle areas. The technique can only today be used as a compliment to peel decohesion tests. If it will be possible to discriminate between brittle and ductile areas, there is work ongoing in this topic, the technique can be very useful for non destructive investigation of electrofusion joint on site.

The X-ray computed tomography scans revealed interesting details about the investigated joint, but cannot distinguish brittle and ductile areas. CT images gave a good overview of voids in fusion zone, pipe alignment and movement of the heating wires. The artifacts caused by the wires, when scanned perpendicular to the pipe axis, makes analyzes of the images more complicated. Since the method does not provide any information regarding the joint strength, X-ray computed tomography is not a suitable candidate for non destructing test assessment of electrofusion joints.

6. Conclusions

The difference found in this study between a weldable and an unweldable pipe surface is a thin oxidation layer in the latter case. This means that only scraped Wavin pipes and Profuse pipes can be joined by electrofusion properly. Cleaning the pipe surfaces with ethanol or heptane cannot replace scraping. No correlation between oxidation induction time and weldability was found. ESCA can be used to detect and quantify oxidation of PE-pipe and coupler surfaces. On the other hand, FTIR-ATR was not sensitive enough to give any valuable information regarding surface oxidation. Contact angle measurements give a good indication of the oxidation level on untreated and scraped pipe surfaces.

The peel decohesion test, ISO 13954, should be revised in order to be fully utilized in practice. The standard today needs several clarifications. The test poorly mimics the in-service conditions and may either be modified or replaced. A double peel decohesion test, EN 12814-4, has several advantages over the peel decohesion test. Double peel decohesion test and normalized peel energy calculations with a suitable approval threshold gives a more objective approach and should be subjected to further considerations.

Of the two non-destructive techniques only microwave scanning can give information about the quality of electrofusion joints.

7. Future work

It would be interesting to investigate when the oxidation of the pipe occur, during the extrusion process or during storage. The level of oxidation at different spots in the production line could be analyzed by ESCA and thereby conclude where the major oxidation occur. If the main oxidation occurs during the extrusion process, how can it be avoided in the production?

In order to understand how fast and under which conditions the oxidation occurs during storage conditions, artificial and natural weathering of pipes can be done. Temperature and UV radiation are important parameters.

A suitable threshold for joint approval when using normalized peel energy for different pipe dimensions and classifications can be developed. This can then be used for quantifying the strength of electrofusion joint in a more objective way.

More work regarding the correlation between contact angle and ESCA results can be done. If contact angle correlate well with the oxidation level found by ESCA, it can be used as a much faster and cheaper method to investigate oxidation.

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Surface analysis of polyethylene pipes and failure characterization of electrofusion joints

LUKAS BOGE
EMIL HJÄRTFORS

Department of Chemical and Biological Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2011