Characterisation and analysis of polyethylene pipes and polymers in water pressure pipe applications

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Characterisation and analysis of polyethylene pipes and polymers in water pressure pipe applications

A report submitted in the total fulfilment of the requirements for the award of Master of Philosophy of Loughborough University

January 2019

by

Sarvar Jahani

Project Supervisors: Mr. Barry Haworth
Dr. Simon Martin
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My last but not least gratitude goes to my husband Behsad for all his patience, support, concern and dedication.
Abstract

Lifetime prediction of plastic pipelines is a critical aspect of any long term asset management programme. From the existing literature, material degradation, mechanical damage, fatigue, inherent flaws, operational pressure changes or welding defects are the most common reasons for failure in plastic water mains pressure pipes. Thanks to project sponsors, the UK Water Industry Research (UKWIR) and the Engineering and Physical Science Research Council (EPSRC), this thesis will deliver some early stage research work needed to support any later development of a non-destructive or accelerated method to assist in predicting the lifetime expectancy and condition of polyethylene pipes used in the water pressure-pipe sector.

As a first stage of the study, different types of polyethylene pipes and polymers of different molecular structure, including high density polyethylene (HDPE) and medium density polyethylene (MDPE) sourced from commercial pipe manufacturers, were characterised using a range of analytical techniques. The purpose of carrying out this analytical programme was to compare some physical and chemical properties of the MDPE and HDPE polymer and pipe samples to obtain an overview of PE performance attributes such as surface homogeneity, through-thickness variations of crystallinity/density, endothermic melting temperatures and stability of polymer and pipe samples in N₂ and air atmospheres.

PE pipes and polymers generally indicate similar thermal performance across two heating/re-heat cycles in thermal analysis, but due to cooling rate variations during the extrusion process of PE pipes, the value of crystallinity measured by DSC varied through the pipe thickness: for example, the inner surface of both HDPE and MDPE pipes demonstrated higher values of crystallinity (about 50 %) in comparison to the outer layers. Weight loss data for HDPE/MDPE polymer and pipe samples were measured utilising TGA in N₂ and air atmospheres in order to obtain more information about the decomposition kinetics and the effect of reactive atmospheres on PE materials. The results showed that both HDPE/MDPE polymer and pipe samples underwent thermal degradation over a broader temperature range in N₂ atmosphere while, their mass loss in air took place at a lower temperature around 250 °C. An analysis of the atomic compositions of the surface and bulk of pipe samples using XPS was carried out in order
to reveal the presence and distribution of contaminants resulting from the manufacturing methods. The results show that there is no difference between the atomic composition of bulk of GPS and Radius (Two main polyethylene pipe manufacturers in UK located in Huntingdon and Alfreton in Derbyshire) samples.

Furthermore, the measured density values of PE polymer samples were compared with literature values. The density of HDPE polymer samples from both pipe manufacturers, with the range of $0.94 - 0.95 \text{ g cm}^{-3}$ were higher in comparison to MDPE polymer samples, which were within the range $0.93-0.94 \text{ g cm}^{-3}$. This is due to the difference in molecular structure between MDPE and HDPE, in molecular weight distribution and chain branching.

In the XRD analysis, the crystallinity of two HDPE/MDPE polymer samples and four HDPE/MDPE pipe samples (outer layers) were analysed to verify the values of crystallinity measured through DSC analysis. The results showed that the crystallinity of PE pipe and polymer samples range from 42 to 50 %, which corresponded well to the crystallinity values measured by DSC.

Considering FEM, some analysis was carried out using ANSYS workbench R16.2 in order to simulate the effect of mesh size, boundary conditions, pressure and axial notch length and also depth of notch on stress concentration under constant internal loading pressure inside PE pipes with a specific diameter. According to results, von Mises’ stress was predicted to increase with internal pressure, which is $10.97 \text{ MPa}$ at $24.8 \text{ bar}$ pressure for MDPE pipe with 2-metre length and changes to $20.67 \text{ MPa}$ at $24.8 \text{ bar}$ internal pressure for the same pipe. Furthermore, PE pipe material shows a highest degree of deformation in the deepest notch, as the value of von Mises strain was predicted to increase with the depth of the notch. It is about $0.01458 \text{ m/m}$ for the notch depth of $0.5 \text{ mm}$ and increases to $0.01835 \text{ m/m}$ for the notch depth of $3\text{ mm}$.
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Chapter 1

1. General Introduction

1.1 Introduction

Polyethylene (PE) pipes have been used for applications in water mains pressure pipes for more than 50 years. The first plastic pipes were installed in the mid-1930s, but their usage increased significantly in the 1950s. Among PE materials, high density polyethylene (HDPE) and medium density polyethylene pipes (MDPE) are used widely for the transportation of natural gas and water [1].

By the early 1980s, plastic materials accounted for about 40% of the UK pressure pipe markets, and the potential for accelerated growth increased significantly as ductile iron had a capacity to cause corrosion problems and when the introduction of medium density polyethylene (MDPE) coincided with the growth of interest in special rehabilitation techniques as PE pipes especially the new fracture resistant grades, hold many advantages in comparison to other types of pipe materials [2].

Ductility and easy manufacturing processes in various pressure classes and diameters are the main advantages of PE pipe materials. These properties usually result in reduced disruption in pipe installation and allow pipes to be easily laid and installed, including in-situ welding. Furthermore, PE pipes show high resistance to attack from most chemicals, which generally contributes to their life expectancy [3].

Lifetime is one of the main aspects which plays an important and critical role in the application of plastic pipes in water and gas distribution systems and has been researched previously in various studies [4]. Generally, PE pipes are installed with a design lifetime of at least 50 years. Hydrostatic pressure testing is one of the traditional methods which have frequently been applied in previous studies to assess the strength and life time of plastic pressure pipe materials [5]. Hydrostatic pressure tests have been undertaken in research studies in an internal and external environment and also at various pressure levels and different temperatures, since the specific material type,
environment and loading conditions are the main factors which control the lifetime of a plastic pipe [6] [7]. Polymers, additives, manufacturing processes and microbiological effects are some examples of material and external factors which have been researched extensively [8]. The effect of chlorinated water on the life time of PE has also been investigated in recent years. The life time of PE pipes exposed to non-chlorinated water are about 10-30 times longer than the same pipes exposed to chlorinated water [9]. Failure mechanisms in polyethylene pipes are another main subject that has been studied comprehensively previously. Regarding this, PE generally shows three types of failure, creep rupture, rapid crack propagation (RCP) and slow crack growth (SCG) [9].

According to previous study, mechanical failure often happens in badly installed pipes, when the applied mechanical stress is higher than the yield strength [10]. Rapid crack propagation usually occurs at lower stress conditions. The failure mode which is often characterised by stable growth of a crack, and with little macroscopic plastic deformation is called slow crack growth (SCG) [10]. In fact, SCG can be considered as a majority of the brittle failures in pressure pipe applications. This can also occur when a pipe undergoes hydrostatic loading for a considerably long period of time. In this case, chemical degradation of the polymer may also contribute to the failure. In some studies, various microscopical techniques have been used to examine the micro-deformation mechanisms contributing to SCG, under tensile loading for PE materials at 80 °C, in order to obtain more information about the micro-mechanisms of long term creep failure in these types of materials [11][12].

The effect of geometrical irregularities such as notches, defects, and flaws which generally act as local stress concentrations was also investigated previously in some research work [13]. Generally, the non-uniformity of geometry changes the lines of principal stress and cause stress and strain concentrations at the tip of the notch or defect [13]. Relating to this, numerical modelling has been reported previously, which is validated by standard analytical and experimental analysis [14].

Degradation performance of PE pipes was one of the main research areas studied previously [15]. Regarding various investigations, a type of oxidation called auto-oxidation which generally occurs in open air or in presence of oxygen and sometimes in
UV radiation, is a major type of degradation which occurs in PE pipes. Other types of degradation, such as chemical, environmental or physical degradation can also take place. Studies have also been carried out applying different methods to extrapolate the life time of polymeric materials regarding thermal stability [15]. There is also some research reporting the carbonyl content of the polymer after degradation [16][17]. According to these studies, there is a relationship between the carbonyl index and the ageing process. The carbonyl index generally increases with the degree of ageing of the PE pipe material. In fact, carbonyl index can be considered as an indicator for any changes in mechanical properties of the pipe material and is therefore applicable as a chemical marker in PE materials which are used in water distribution systems.

A number of research studies were carried out to obtain an overall overview about the lifetime of new and used PE pipes are also significant [18][19][20], but relatively few of them consider the chemical and physical characterisation of different grades of HDPE and MDPE polymers and pipes in detail.
1.2 Project Objectives

This project is designed to deliver the early stage of non-competitive research work needed to support the later development of a non-destructive method of determining the condition and life expectancy of PE pipes in service in the water industry.

In the first stage of this study, the physical and chemical behaviour of PE materials will be evaluated and characterised using different analytical and testing methods such as, DSC, OIT, TGA, XRD and XPS to obtain more information about the crystallinity, weight loss, oxidation induction time and temperature and surface contamination of MDPE and HDPE pipe and polymer samples, which are currently used extensively in the PE pressure pipe industry. Since these factors plays an important role in chemical and physical performance of PE pipes.

Furthermore, the prediction of stress and strain concentrations under constant loading pressure and temperature inside the pipe with the specific inside and outside diameter will be simulated and modelled using Finite Element Method (FEM), to assess the change of value of stress and von Mises’ strain at different internal pressures and also at different notch depths.
Chapter 2

2. Literature review

2.1 Polyethylene (PE)

2.1.1 Structure of Polyethylene

Polyethylene (PE) is one of the most commonly produced plastics in the world which can be used for a wide range of applications like bags, bottles and many other everyday use articles. It is also considered as the material of choice for use in pressure pipes for gas and drinking water applications.

The material polyethylene contains long chain molecules based on ethylene monomer C₂H₄. Ethylene is a hydrocarbon that is usually produced from ethane, which is a main constituent of natural gas or can be drawn from petroleum. Ethylene molecules consist of two methylene units (CH₂) connected to each other by a double bond between the carbon atoms (the mentioned structure is presented by this formula: (CH₂=CH₂) [21]. MDPE, and HDPE are actually branched copolymers, with other monomers connected to their main ethylene chains during polymerisation.

The degree of chain branching in a constant molecular weight is a typical index for material’s density and crystallinity. The density of the polymer decreases with increasing the ratio of branching, as the branch points cannot be absorbed into crystallites. The polymerisation process generally affects the number and length of the branches depending on pressure and catalyst applied in this process. Low density polyethylene (LDPE) is usually synthesised under the condition of high pressures and temperatures, using initiators that generally result in a softer material with short chain branching (see figure 2.1). On the other side, high density polyethylene (HDPE) is formed at lower temperatures and pressures conditions using the catalysts which result in the production of almost unbranched polymer, that is much harder and more crystalline than LDPE [22].
2.1.2 Properties

Molecular Weight

The size of the polymer molecule is indicated by molecular weight, which is the total of atomic weights of all the atoms that form the molecule. Molecular weight does have a great influence on the process- ability and physical and mechanical properties of the polyethylene. Molecular weight is continuously controlled in PE manufacturing process. Generally, the type of catalyst, conditions of polymerisation and type of applied process determine the amount of length variation. In fact, not all molecules grow to the same length during the PE production process [23]. Thus, the molecular weight can be described as an average value of molecular length. Figure 2.2 demonstrates typical molecular weight distribution of polyethylene in which

\[ M_n = \frac{\sum N_i M_i}{\sum N_i} \]  

(2.1)

\[ M_w = \frac{\sum N_i M_{i2}}{\sum N_i M_i} \]  

(2.2)

\( M_i \) is molecular weight of the chain and \( N_i \) is the number of chains [23].
$M_w$ is weight average molecular weight.

Polydispersity index which is generally used as a measure of the broadness of a molecular weight distribution is defined by the following equation [23]:

$$PD \text{ index} = \frac{M_w}{M_n}$$ \hspace{1cm} (2.3)

This figure also indicates the $M_w$ distribution difference between MDPE and HDPE. In a MDPE, the low $M_w$ fraction contains higher branching and the branching disappears with increasing $M_w$. Further to this figure, the unimodal materials have one single peak in their distribution in contrast to HDPE, which has two peaks in the $M_w$ distribution (MWD). This is due to its two stage polymerisation process. So that HDPE is designated as bimodal.

![Figure 2.2. Molecular weight distribution for unimodal MDPE and a bimodal HDPE [24].](image)

In fact, both short and long chain branching in two peak MWD give advantages. Short chain branches increase the processability and impact fracture toughness of the material as they do for MDPE and on the other hand, long chains at higher molecular weight fractions provide the tie molecules, which hold the crystalline sections
together by penetrating the amorphous regions (see figure 2.3).

Figure 2.3. Polyethylene molecular structure [23].

Crystallinity

Polyethylene is generally considered as a semi-crystalline polymer, which means that it consists of both highly ordered crystalline areas and of the amorphous regions, that are mingled together (see Figure 2.4).

Figure 2.4. Crystalline and amorphous region [23].
A single plate like (lamellar) crystal with a very thin thickness is generally produced. Figure 2.5 shows a schematic of PE chains, in which the chains are folded (see figure 2.5).

![Figure 2.5. Schematic of PE chain folding [23].](image)

In the PE pipe manufacturing process, which involves the use of extrusion PE granulates as the raw material. The granulates melt under high temperature and pressure and form a homogenous mixture with the help of an archimedian screw. The final crystallite that is commonly obtained after cooling and crystallisation process are spherulites of 10 µm diameter. These form by lamellae after nucleation at random points (see figure 2.6).

![Figure 2.6. Polymer crystalline spherulite [24].](image)
However, it should be mentioned that the spherulite formation in HDPE as a result of high molecular weight is usually supressed. Any form of order and also movements can be decreased with increasing the length of chain branches and entanglements. Decreasing of spherulite size can clearly been seen in extruded pipe grades, where the fast surface cooling decreases their development. But spherulites can be seen in the pipes with large wall thicknesses and higher diameters, as the difference in cooling rate of the outside surfaces, leaves the middle pipe wall section to reach ambient temperature at a slower rate, so that increased crystalline formation can happen in those areas [24].

Density

Density measurement gives an indication of the degree of crystallinity in PE. The degree of crystallinity is generally affected by the extent of branching in the polymer and the crystallisation conditions such as rate of cooling, application of stress etc. In fact, the amount of the crystallinity has a great influence on mechanical and ageing properties of material.

<table>
<thead>
<tr>
<th>Type of Polyethylene</th>
<th>Density (g cm$^{-3}$)</th>
<th>Type of branching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low density</td>
<td>0.910 - 0.925</td>
<td>Long branched</td>
</tr>
<tr>
<td>Medium density</td>
<td>0.926 - 0.940</td>
<td>Short Branched</td>
</tr>
<tr>
<td>High density</td>
<td>0.941 - 0.959</td>
<td>Linear</td>
</tr>
</tbody>
</table>

Table 2.1. Density values of LDPE in both long and short branched [23].

The increase of PE density makes a positive influence on several mechanical properties, but on the other side some properties are affected negatively. The required balance of properties should be achieved by optimising the density level together with co-monomer content and distribution. Typical mechanical properties of PE with different densities are shown in Table 2.2.
<table>
<thead>
<tr>
<th>Properties</th>
<th>MDPE</th>
<th>HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg m$^{-3}$)</td>
<td>926 - 940</td>
<td>941 - 959</td>
</tr>
<tr>
<td>Tensile Modulus (MPa)</td>
<td>750</td>
<td>1050</td>
</tr>
<tr>
<td>Stress at yield (MPa)</td>
<td>19</td>
<td>24</td>
</tr>
<tr>
<td>Strain at yield (%)</td>
<td>20</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 2.2. Typical mechanical properties of MDPE and HDPE [24].

The value of density gives an indication of the material strength. For example, HDPE pipe has a higher long-term strength or minimum required strength (MRS) than MDPE. But this gives no indication as to other long-term properties, such as slow crack growth, or resistance to rapid crack propagation. The relation between density or degree of crystallinity and mechanical properties are described in figure 2.7.

![Figure 2.7. The influence of density and crystallinity on the main properties of PE [25].](image)

Figure 2.7 shows that some properties such as tensile strength increases with density, due to increased degree of crystallinity [25]. The same is valid for creep resistance and Young's modulus. On the other, there are some properties that generally decreases with increasing density including permeability and slow crack growth resistance and ductility.
Chemical properties

Generally, PE is resistant to many acids, alkalis and salt solution. It has a moderate resistance to oils, fuels and organic solvents. Depending on its level of density, PE tends to swell in contact with some of the above-mentioned substances. This can lead to stress corrosion under pressure and stress conditions. In general, chemicals can affect plastics in two ways: chemical solvation or permeation and direct chemical attack [26]. Certain organic chemicals can be absorbed by PE through chemical solvation or permeation and cause swelling, softening or decrease of long–term strength of the material. In fact, gas, vapour or liquid molecules pass through the polymer without damaging the material itself. It can be said that the physical properties of the material might be affected in this process, but the polymer molecule structure is not chemically changed, degraded or destroyed [26].

In some cases, the polymer is not soluble, but it may contain a soluble ingredient that can be extracted from the polymer compound. In the permeation process, the permeating chemical usually transfers into a fluid on the other side of the pipe and can cause damage. Direct chemical attack happens when polymer molecules are exposed to a chemical. The chemical can cause a chemical alteration of molecules through chain scission, crosslinking, and oxidation or substitution reaction [27]. In contrast to solvation, direct chemical attack results in irreversible changes that cannot be restored by removal of the chemical. Direct chemical attack can sometimes cause a reduction of mechanical and physical properties. The rate of damage resulting from chemical attacks depends on different factors. Generally, the resistance of some plastics to a specific chemical decrease with an increase in concentration. For example, PE pipe can be applied to carry 70% sulphuric acid at 22.7°C but is not satisfactory for 95% sulfuric acid [28]. In fact, the resistance of some plastics to a specific chemical decrease by increasing temperature or stress. In some cases, combination of chemicals has a great influence on a thermoplastic material.
Flow properties

The distribution of the macromolecules of different chain lengths determines generally the rheological behaviour or flow characteristics of molten material. As noted before, the distribution of the lengths of the polymer chains depends on the catalyst and polymerisation conditions. High viscosity at lower shear rates is created by long macromolecules and low viscosity at higher shear rates is created by short macromolecules. Thus, a polyethylene with a wide macromolecular weight distribution shows a steep viscosity curve and polyethylene with a narrow molecular weight distribution shows a narrow viscosity curve (see figure 2.8) [29]. In fact, a polymer with a narrow molecular weight distribution (MWD) contains molecules that are nearly the same in molecular weight [29]. A polymer that contains a varied range of chain lengths, from short to long has a broad MWD. Polymers with this type of distribution have a better slow crack growth (SCG) and impact resistance in comparison to polymers with narrow molecular weight distribution [29].

![Viscosity curve of PE at different MWD](image)

Figure 2.8. Viscosity curve of PE at different MWD [29].

Some polymers have a bimodal shaped distribution curve. This type of distribution, as its name suggests, indicates a blend of two different polymer populations. These types of polymers are normally produced by two polymerization reactors in series of low and high molecular weights (LMW and HMW) which operate under different process conditions [29].
2.1.3 PE polymers for pressure pipe

Polyethylene (PE) as a pipe material has been used for more than 50 years in the field of water and gas distribution and sewage systems. This kind of pipe material was used initially in low pressure applications of up to 4 or 6 bars. Nowadays, they are being operated at pressure levels up to 10 bars for application in gas fields and 16 bars for application in water fields. PE pipes are lightweight and flexible which enables the application of new installation techniques. They can be designed with a smaller diameter, as they are hydraulically smoother than other materials. Butt fusion welding method is generally used as a joining method in PE pipe. This reduces the number of mechanical joints which are the main cause of leaks in pipes. A study that has been conducted by the Plastic Pipe Institute has indicated that a good longer-term field performance is generally achieved by PE pipes. PE pipes exhibit high resistance to stress increasing situations [30].

Durability is one of the main features that are principally required in PE pipes, as crack initiation and creep crack growth (CCG) are two common failure mechanisms that happen in pressurised pipes in long-term applications. Until the 1980s, both LDPE and HDPE were used for water application, but from this time modern pipe grades of HDPE with the minimum required strength (MRS) of about 10 MPa or MDPE with the MRS of 8 MPa have been used for applications in water distribution systems, and LDPE has been replaced completely by MDPE [31].

In fact, designations of MDPE and HDPE, classifies the materials for their specific MRS, and also nowadays normally serves as a distinction for their molecular structure as well. As described before, essential improvements in the field of raw materials of PE, especially in the bimodal molecular mass distribution and in implementation of short chain branches have taken place to increase the resistance of PE material against crack initiation and creep crack growth, but these improvements result sometimes in time consuming and expensive test procedures. In fact, the working strength of a material requires to be defined in relation to the various conditions in a successful design.

PE pressure pipe is generally available in diameters from ½ “through to 65 ”. In fact, PE pressure pipes are designated by their outside diameter. Depending on the type of PE pressure pipe, the outside diameter of PE pipe varies from 20 to 1600 mm. The maximum
operating pressure with a minimum service coefficient is generally designed for water and other pressure applications [32].

Thermal fusion joints are most common joining methods for PE pipes or fittings. Among them, butt fusion joint is a method which is widely used for joining individual lengths of PE pipe and fittings, as this technique produces a permanent, economical and flow efficient connection. In this joining method, PE pipes of the same outside diameter but with different specific wall thicknesses may be butt-fused to each other under special conditions. Saddle conventional, socket and electro-fusion and mechanical compression coupling are other joining methods that can be applied sometimes under special conditions. The tensile strength of PE is generally influenced by the same variables which can affect its stress/strain relationship, such as load duration, temperature and environment. In pressure pipe application, the stress which is generally increased by internal hydrostatic pressure is considered as a nominal stress. Regarding this factor, each material from which a PE pipe is made, needs to have an established long-term hydrostatic strength. The rate of PE pipe pressure is then based on this hydrostatic strength. Figure 2.9 compares the performance of PE in pipe applications with other types of materials [33]. According to this figure, PE materials has the lowest number of failures by application in the pipe industry in contrast to other types of materials such as iron and PVC. This indicates that PE materials has the highest performance in considering various types of failures such as corrosion, environmental ageing mechanisms, ductile failures etc.

![Figure 2.9. Performance of PE and other pipe materials in UK [33].](image-url)
2.2 Plastic water mains pressure pipe

2.2.1 Extrusion

Plastic pipes are generally produced using the extrusion. Prior to processing, PE pellets are stabilized for heat and also UV protection. Colour pigment is usually added to the pipe at the producer’s facility for this purpose. However, the choice of colour depends on the type of application of pipe purchasers. In terms of application in water mains pressure pipes, carbon black and dark blue are the most common pigments used for water, sewer and above-ground uses [34].

Heating, melting, mixing and material transfer to the die are actually the main functions of the extruder. Figure 2.10 shows a schematic of the extrusion process.

![Extrusion Diagram]

Figure 2.10. Extrusion.

One of the main factors that plays an important role on the performance of the extruder and on the quality of pipe is extruder screw design. There are different types of screw designs and each screw is designed for a specific type of material being extruded. Figure 2.11 shows a typical extrusion screw.
Figure 2.11. Schematic of extrusion screw [35].

Basically, extruder is used first for heating the raw material and then for forcing the resulting melted polymer through the pipe extrusion die. The barrel of the machine has a series of four to six heater bands. An instrumented thermocouple controls the temperature of each band individually. However, the shear energy generated by the screw and motor drive system is the major part of the heat supplied to the polymer during the manufacturing process [34]. This type of heat supply can also be controlled by applying cooling or heating to the various barrel zones on the extruder by a series of air or water cooling systems. This seems to be important, as the amount of heat absorbed by the polymer needs to be closely monitored. The temperature of the extruder melted polymer is usually between 200°C and 240 °C, and it is also under high pressure (140 to 280 Bar).

The molten polymer leaves the extruder and then goes through a screen pack which consists of one or more wire mesh screens, located against the breaker plate. The breaker plate is formed from a perforated solid steel plate. Screen packs avoid foreign contaminants from entering the pipe wall and assist in the development of a pressure gradient along the screw. This results in homogenisation of the polymer. However, many extruders are equipped with an automatic screen changer device to help in the changing of dirty screen packs [34]. The main function of the pipe extrusion die is to support and distribute the homogeneous polymer melt around a solid mandrel, that forms it into an annular shape for solid wall pipe. The production of a profile wall pipe involves extruding the molten polymer through a die which has a specific shaped profile. The spider die design (See figure 2.12) and the basket die design are two common types of die designs for solid wall pipe.
In the spider die, the melt stream is distributed around the mandrel over the torpedo which is supported by a ring of spider legs. Because of splitting the melt by the spider legs, the flow must be re-joined.

Reducing the annular area of the flow channel just after the spider legs generally prevent the flow line caused by mandrel supports. This is for building up in die pressure and also for forcing the melt streams to converge and consequently reducing the weld or spider lines. The melt moves after re-joining into the last section of the die, which is called the land. The land is the part of the die that has a constant cross-sectional area. It actually re-establishes a uniform flow and allows the final shaping of the melt and also allows the resin a specific amount of relaxation time.

Through sizing and cooling process, the dimensions of the pipe are determined. The pipe is kept in its proper dimensions by sizing operation during the cooling process. In the case of a solid wall pipe, the process is done by drawing the hot material from the die through a sizing sleeve and into a cooling tank. Vacuum and pressure techniques are two common used methods for sizing. In vacuum sizing (see figure 2.13), Molten extrudate is drawn by a sizing tube while its surface is cooled enough to maintain proper dimensions and a circular form. Pipe is then moved through a second vacuum tank or a series of spray or immersion cooling tanks after exiting the first vacuum sizing tank [35].
Generally, a positive pressure is maintained on the inside of the pipe in the pressure sizing system (see figure 2.14) by applying a plug attached to the die face or, on very small bore pipe. The pressure on the outside of the pipe remains at ambient and the melt is forced against the inside of the calibration sleeve with the same results as in the vacuum system.

However, the pipe must be cooled enough in order to maintain its circularity before exiting the cooling tank for both vacuum and pressure sizing technique. Different methods of cooling can generally be applied to remove the residual heat out of pipe. Depending on pipe size, two types of cooling including total immersion or spray
cooling might be applied. Regarding this, spray cooling is commonly used for large diameter pipes, while immersion method might be inconvenient for this purpose. Smaller diameter pipe is usually immersed in a water bath. Cooling water temperatures typically changes between 4° to 10°C. The total length of the cooling baths must be adequate to cool the pipe below 71°C to withstand subsequent handling operations. Providing the annealing zones in this process minimize the residual stresses, which are generated by the cooling process within the pipe wall, as long-term pipe performance is improved when the internal pipe wall stresses are reduced. These zones are defined as spaces between the cooling baths which allow the heat contained within the inner pipe wall to radiate outward and anneal the entire pipe wall [34].

In the last stage, the puller must provide the necessary force to pull the pipe through the entire cooling operation. It also helps in maintaining the adequate wall thickness control through providing a constant pulling rate. The pulling rate together with the extruder screw speed determine the wall thickness of the finished pipe. The wall thickness usually reduces by increasing the puller speed at a constant screw speed.

Figure 2.15. Schematic of pipe extrusion cooling process on HDPE pipe. (Photos taken from GPS pipe system-Huntingdon)
2.3 Degradation mechanisms of PE pipes

Slow and irreversible change of a materials chemical and physical structure is generally defined as an ageing mechanism. Due to this alteration, a materials physical, chemical and mechanical properties will change, which usually results in loss of the design and function of the material.

2.3.1 Chemical degradation

Chemical interactions with plastic pipes can be divided into various mechanisms. Various physical and mechanical properties of plastic pipes can be affected by decreasing molecular weight caused by decomposition. The most damaging effects were particularly with in-service pipes, when the degradation process remains undetected. Some of the most common degradation mechanisms are summarised in the following section.

Oxidative and thermal degradation

PE materials generally undergo significant changes over time when exposed to heat, light, or oxygen. These changes have a great influence on the service life and properties of the polymer. In this case, only addition of UV stabilisers and antioxidants can prevent or slow down the degradation mechanisms. The degradation of polymers can commonly be induced by heat, oxygen, light or even by weathering. Stress conditions and also exposure of PE materials to other reactive compounds accelerate or even deteriorate the degradation process. In fact, all polymers undergo some degradation during their service life. Degradation usually results in a steady decline of mechanical properties, because of change of molecular weight distribution and molecular weight of PE. However, embrittlement (chain hardening), softening (chain scission), colour changes and also cracking are some examples of the changes that can occur in the PE material due to degradation mechanisms [36]. Thermal degradation is defined as the degradation of the polymer in the absence of oxygen. PE materials are stable up to around 300°C, after this the thermal energies become high enough to break the covalent bonds in the polymer chain. Around 250 -450 kJ mol⁻¹ would be required as dissociation energy for breaking
the bonds in polyethylene (C–H: 320–420kJ mol⁻¹ and C–C: 260–400kJ mol⁻¹). Figure 2.16 shows the general mechanism of thermal degradation [37].

Figure 2.16. General mechanism of thermal degradation [37].

When polymer chains form radicals, oxidative degradation is generally initiated. This is either by hydrogen abstraction or by homolytic scission of a carbon-carbon bond. This can happen during manufacture processing or even during PE application by exposing to light or heat.

\[ R-H \rightarrow R^• + H^• \]

At the first step of propagation of thermal degradation, a free radical (R•) usually reacts with an oxygen molecule (O₂) in order to form a peroxy radical (ROO•*), which then abstracts a hydrogen atom from another polymer chain to form a hydroperoxide (ROOH). The hydroperoxide is then divided into two new free radicals, (RO•) + (•OH), which abstract hydrogens from other polymer chains. The process can be accelerated, as each initiating radical can generate two new free radicals. However, this depends on how the free radicals will undergo termination through recombination and disproportionation.
\[ R\cdot + O_2 \rightarrow ROO\cdot \]
\[ ROO\cdot + RH \rightarrow R\cdot + ROOH \]
\[ ROOH \rightarrow RO\cdot + \cdot OH \]
\[ RO\cdot + RH \rightarrow R\cdot + ROH \]
\[ \cdot OH + RH \rightarrow R\cdot + H_2O \]

Recombination of two radicals or disproportionation usually cause the termination of thermal degradation. The addition of stabilisers can accelerate these reactions. In fact, an increase of the molecular weight and crosslinking density are achieved by recombination of two chain radicals [36].

\[ R\cdot + R\cdot \rightarrow R-R \]
\[ 2 \text{ROO}\cdot \rightarrow \text{ROOR} + O_2 \]
\[ R\cdot + \text{ROO}\cdot \rightarrow \text{ROOR} \]
\[ R\cdot + \text{RO}\cdot \rightarrow \text{ROR} \]
\[ \text{HO}\cdot + \text{ROO}\cdot \rightarrow \text{ROH} + O_2 \]

But on the other hand, termination by chain scission, results in the decrease of the molecular weight which leads to softening of the polymer and reduction of the mechanical properties.

\[ R_n\cdot + R_m\cdot \rightarrow R_{n.2^-CH=CH_2} + R_m \]
\[ 2 \text{RCOO}\cdot \rightarrow \text{RC}=O + \text{ROH} + O_2 \]
Further to these two types of reactions, the type of polymer materials determines which of these termination steps will be predominant. In case of PE, crosslinking during ageing mechanism results in embrittlement [36].

Relating to this, it should also be stated that cross-linking normally occurs when a PE undergoes random chain scission and this randomness generally increases with decreasing the number of side branches. This is specially common when a degradation happens because of the high levels of radiation and oxidation and results in an increase of density, crystallinity, and consequently the brittleness of the sample [36].

**Antioxidants**

Although unsaturation and branching increase oxidation, straight chain saturated hydrocarbons and straight chain saturated PE polymers can oxidise at a measurable rate. In this case, a proper antioxidant addition is the only practical way for protecting PE against oxidation [38]. Figure 2.17 indicates the effect of antioxidants on the reduction of degradation rate.
Antioxidants have long been used to protect rubber and other polymers from oxidation. An antioxidant plays a key role in terminating the normal oxidative chain reaction by forming both non-radical species and radicals with very low reactivity. In one study, 0.02 % of 2,6-di-t-butyl 4-methyl phenol (DBPC) was used as a stabiliser and then the oxidation induction time and the rate of hydro peroxide formation in polyethylene were measured by infrared analysis [39]. According to the results, the oxidation induction period, for example, was higher than 10hr, compared to un-stabilised species. This means that 0.02 % DBPC gave only a 60-min. induction period in the formation of hydro-peroxide. Therefore, reaction occurs during the induction period even in the presence of antioxidant. Chain breaking and oxidation rate preventative are the two main types of antioxidants [39]. Figure 2.18 represents a series of chemical reactions that happen by polymer degradation in the presence of oxygen and how antioxidants work in stopping or reducing the rate of oxidation.
The type of stabiliser which is used for PE pipe materials depends generally on their condition of use. Primary (phenolics) and secondary antioxidants (phosphites, also known as processing stabilisers) which are shown in figure 2.18 play an important role in counteracting the effects of degradation during the production of plastics. In fact, chain breaking anti-oxidants, which are also called primary anti-oxidants work by either donating or accepting electrons. In contrast to chain breaking accepting anti-oxidants that oxidizes the radical, chain breaking donating anti-oxidants reduce the radical to its anion [36]. However, preventive anti-oxidants, which are also called secondary anti-oxidants prevent the hydroperoxide radicals from re-initiating the chain reaction. Because of this, the rate of oxidation will reduce.
2.3.2 Mechanical degradation

In mechanical degradation, irreversible deformations in PE material can result due to mechanical forces. This generally happens by placing under sufficient stress chemical bonds or intra and intermolecular forces between atom breaks. Environmental stress cracking and also fatigue related stress cracking are some examples of mechanical degradation that commonly occur as a result of static and dynamic loads on the material [40].

In environmental stress cracking (ESC), when PE material is exposed to stresses in the presence of various environmental / chemical agents (mainly vapours or fluids), environmental stress cracking may occur. ESC and SCG have many similarities. Some factors and conditions such as dependence of failure time on load and temperature and the type of failures that appear on the surface are generally similar between ESC and SCG. Therefore, it is supposed that they probably have a common molecular deformation mechanism. If so, it would be valuable to use ESC to evaluate the long-term behaviour of material, as the ESC process takes a much shorter time to carry out and complete than conventional SCG tests [52]. The effects of environmental agents which accelerate SCG have been investigated by many researchers. Some researchers believe that the environmental agent provokes the plasticisation of tie molecules and increases their disentanglement; thereby the stress cracking can be accelerated [41].

Figure 2.19. Lamellar structure of HDPE and how it yields in high stress condition [41].
Further to figure 2.19, when a high stress is applied to structure of HDPE, the linking chains remain entangled in the adjacent lamellae and result in breaking the lamellae into fragments which produce the yielding and also elongation. However, the linking chains have sufficient time to disentangle themselves slowly in case of applying the low pressure (see figure 2.20). Because of this, separation of lamellae occurs and consequently a smooth break in comparison to the previous yield/elongation ductile break can be generated.

Figure 2.20. Stress cracking in low stress condition [41].

Fatigue-related stress cracking

In the fatigue-related stress cracking, dynamic loading can significantly increase crack propagation rates. The failure of PE pipes consists of two modes: ductile and brittle. Ductile failure is generally associated with macroscopic yielding and the creep rate determines the time to failure. On the other hand, brittle failure is associated with crack growth, in which two processes occur simultaneously and the final failure usually depends on the rate of each process under specific loading conditions, temperature and notch depth [42].

The common example of ductile failure is the tensile test of plastic samples, thereby relatively high applied stresses are required, and failure takes place in a relatively short
time. The mechanism is related to the viscoelastic behaviour of PE materials and also refers to creep rupture. Nishimura and Shishich (1985) [43] found that the creep failure time in fatigue testing can be shortened by more than two orders of magnitude. Brown (1995) [44] found that the tension-compression mode of loading is probably due to buckling of the fibrils under the compressive load and due to the fastest failure in the fatigue test occurs when the loading is in tension-compression mode. Figure 2.21 shows that the disentanglement in PE result in stable crack extension. This is also referred to as static fatigue. However, dynamic fatigue is a similar mechanism.

Brittle failure, particularly in HDPE, usually occurs under low stress conditions and takes a long time to propagate through the materials thickness by SCG. Lustiger (1998) [45] found that SCG process can vary from hours to years at rates less than 0.1 ms$^{-1}$. The fatigue test is usually conducted at room temperature as fatigue loading can significantly increase the failure rate. In some aspects fatigue and SCG have similarities. For example, their fracture surfaces have a similar appearance. Furthermore, the fatigue crack growth indicates step propagation, which means that a craze is formed at the crack tip and raises the stress required for crack growth. Zhou et al. (1989) [46] carried out
fatigue and creep tests on PE and found that there is a linear relationship between the cycles to failure under a fatigue test and the time to failure under a constant load test. This suggests that fatigue test can be applied to predict the creep fracture of material.

2.4 Methods for determining the in-service life of polymer water pipes

2.4.1 Mechanical evaluation and testing methods

Generally, PE pipes show three different kinds of failure under pressure, as shown in figure 2.22.

![Figure 2.22. Different kinds of failures in PE pipe at different stress levels](image)

According to figure 2.22, depending on the stress level, the failure mechanisms of pressurized pipes can be divided into three characteristic regions. As the figure shows, region I appears at a relatively elevated level and at short times. This generally results to large deformation and consequently ductile failure of the PE pipes. Plastic pipe systems are commonly designed to operate below region I. However, a transition knee occurs with decreasing hoop stress and brittle failure appears in region II. The failure in this region is characterized by creep crack growth initiation, creep crack growth, and only small-scale crack tip plasticity. Considering this, it can be stated that this failure region determines the lifetime of long-term applications. The brittle failure happens in region III is nearly load-independent and is
usually caused by large scale material ageing and polymer degradation. Molecular structure and morphology of material such as molecular mass, molecular mass distribution, the concentration and length of short chain branches and also crystallinity have the great influence on the crack initiation and slow crack growth. Regarding this, the raw material would be able to achieve the significant increase in resistance of material to crack initiation and slow crack growth by considering the improvement in polymerization process of PE and controlling the variations of these materials parameters [47].

Regarding brittle failure that mainly happens in region II, several accelerated laboratory tests using fracture mechanics considerations have been developed. The Notched Pipe Test (NPT), the Pennsylvania Notch Test (PENT) and the Full Notch Creep Test (FNCT) are some examples of the most widely applied methods in the industry and also in the research area for determining the long-term performance of PE pipes. Further to these test methods, fatigue tests with cyclic loads are also used for accelerated characterisation of the resistance to crack initiation and SCG, and a number of studies prove the correlation of fatigue and SCG in high density PE as well as in medium density PE [48].

Hydrostatic stress rupture test

Hydrostatic stress rupture test is generally considered as an effective and traditional method for determining the real life of PE pipe materials. Generally, HDPE and MDPE pipes used for water or gas transport are under pressure continuously for the duration of their useful service and the pressure often fluctuates. Therefore, establishing the maximum load that such a pipe can withstand without deformation and damage over its' expected lifetime can play an important role in this aspect. Short – term tests such as the tensile or flexural tests could not be effective for estimating the durability and the design stress of pipes. That's why, the design stress and the useful service lifetime of PE pipes are commonly predicted by performing creep rupture tests at multiple temperatures [49]. In this kind of test, a section of PE pipe is filled with water or any other ageing liquid and then sealed. The water is under a certain pressure in order to give a specific hoop stress applied to the pipe. In other words, pipe is subjected to a certain hydrostatic pressure
(expressed as hoop stress) and the failure time is recorded. In this case, failure is defined as a continuous loss of pressure within the pipe. A log-log plot of pipe hoop stress versus failure time is typically constructed (See figure 2.23) and extrapolated to a desired lifetime.

![Log-log plot of pipe hoop stress versus failure time.](image)

Figure 2.23. Schematic of plot of pipe hoop stress versus failure time.

Analysis of the pipe creep rupture data of different kinds of PE pipes indicates that the failure time of these pipes is dependent only on the applied hoop stress and the yield stress of the pipe, as long as the failure mode is ductile. In fact, the failure time for ductile fracture at a specific hoop stress depends exponentially on the tensile yield stress of the pipe. This means that density or crystallinity are the main material properties, which generally contribute to the ductile failure of PE pipes [50]. This also indicates that ductile failure of PE pipes doesn’t depend on molecular weight, molecular weight distribution and also branching distribution.

In the pipe creep rupture data analysis, normalisation of ductile failure data at multiple temperatures shows a systematic improvement in performance with increasing temperature in the range between 20 °C and 80 °C. In other words, the level of performance can be improved by testing at higher temperatures (80 °C), which is mainly due to the large increase of crystallinity. The small increase in crystallinity will result in longer failure times in the ductile failure mode. Therefore, it has been proposed in the research study that testing at higher temperatures leads to some residual stress relaxation in the pipe. This consequently results to the better performance of the pipe. Since, residual stresses might accelerate the fracture process [50].
Brittle failure characterisation

Brittle failure is the most common type of failure. Slow and steady growth of a crack which is initiated in a defect or stress concentration area in the pipe is generally used for the characterisation of brittle failure [51]. Some external factors like rock impingement, and bending can also have a great influence on accelerating the SCG fracture in gas transport pipe. The occurrence of early brittle failure in creep rupture testing can decrease the effective design stress of the pipe and limit its durability. Creep rupture data at 80 °C for HDPE pipe are shown in figure 2.24 [52]. The knee or the transition from ductile failures at high stresses to brittle failures at low stresses can clearly be seen for both types of HDPE pipes in this figure. The knee for HDPE-D happens at much longer times in comparison to that of HDPE-A. This indicates that the HDPE-D pipe shows generally more resistance to SCG failure.

In the Pennsylvania Edge Notch Tensile (PENT) test, time to failure is generally used to categorise PEs regarding their resistance to SCG. In the PENT test, when a notched sample undergoes a constant load, and many stages of deformation usually occur. However, the ultimate failure time is usually recorded and reported in each case. For example, the failure time can be said to be composed of three sequential deformation regimes as a first approximation. These three regimes include a) fracture initiation procedure b) slow crack growth and c) post–yield tensile stretching [52]. However, it is widely recognised that brittle fracture (through the initiation and subsequent crack propagation mechanism) at low stresses is one of the most common modes of failure for pressure pipes. In most studies relating to analysis of pipe creep rupture fracture, no correlation between the brittle failures in pressurised pipes and the PENT failure times has been found [52].
2.4.2 Numerical methodology for lifetime estimation of HDPE pipes

Numerical modelling has become an important tool in fracture analysis since analytical method cannot solve the most of practical problem in this aspect. In the fracture field, stress intensity solution for hundreds of configurations have been published in the recent years and the majority of which were numerical models [53]. In the numerical studies, linear elastic fracture mechanics describe the slow crack propagation in a pipe material and a substantial part of the pipe failure time is estimated based on numerical modelling [54] [55]. Generally, it is necessary to estimate the stress intensity factor which is applied in fracture mechanic to predict the stress state near the tip of the crack. Therefore, finite element model of the structure with crack was suggested (see figure 2.26). The schematic of the geometry of the structure is shown in figure 2.25. Dimensions of the pipe are generally considered according to standard dimension ratio (SDR). The SDR is the ratio of the nominal outside diameter of a pipe to its nominal wall thickness d/s. 9, 11, 13.6, 17, 21 are typical pipe SDRs used in practice.

Figure 2.24. Pipe hoop stress versus failure time data for HDPE-A and HDPE-D at 80 °C [52].
Figure 2.25. Schematic of pressured pipe and geometry of the crack [54].

Figure 2.26. Finite element model of internally pressured pipe with crack [55].

Internal pressure loading

In a previous study, the lifetime of HDPE at 80 °C was evaluated using a specific FEM concept [53]. In some studies, a two-dimensional (2D) model of the pipe with a crack loaded by internal pressure was applied and then three – dimensional (3D) model was developed to verify the reliability of the results. However, an important dissimilarity was found by comparison of the stress intensity factors of these two different models (see figure 2.27). The relative crack length (a/s) are shown in figure 2.25.
The main difference between the 2D representation of the pressure pipe and the more realistic 3D pipe geometry can explain these different results, as the crack width in 2D models with plane strain conditions is going to be infinite. This can result in a much higher value of stress intensity factor in comparison to a 3D model with a finite length of the crack. The crack geometry has therefore a great influence on the value of stress intensity factor.

The shape of the crack (in 3D calculation) could be numerically estimated using a special algorithm, which generally ensures constant stress intensity factor (SIF) along the crack front. This condition corresponds with performance of the real crack. For a specific crack length the ratio $b/a$ is considered in order to obtain constant stress intensity factor along the crack front [54].

SIF values could be estimated in different distributed points along the crack front except the points which are close to the free surface (See figure 2.28 For given crack length a the ratio $b/a$).
Further to all mentioned points relating to FEM calculations, the performance of creep crack in internal and external pressure loading conditions could be analysed. From the practical point of view and regarding research works, the effect of soil embedding of the pipe also plays a key role in the modelling of life time of the pipe. A 3D model was generally used for the estimation of stress intensity factor of the pressured pipe with additional external pressure resulting from soil embedding. Soil embedding can therefore be considered as an external pressure which can change the stress state in the pipe significantly. Regarding previous studies, the tangential stress would be negative if the internal pressure is smaller than external one. This means that the crack stops growing in this situation [56].
2.5 Summary

Among different types of plastic materials, PE is widely applied in water mains pressure distribution systems. Many different research projects have been carried out on different aspects of PE pipe performances and properties. Literature on this type of material with different additives and grades has been investigated in terms of mechanical, chemical and physical aspects for the evaluation of life expectancy and ageing mechanisms. In addition, different modes of destructive testing methods have also been reviewed for determination of failure time, slow and rapid crack growth behaviour in PE pipes.

Hydrostatic pressure test is for example one of the most conventional and relevant destructive testing methods which is commonly applied for monitoring mechanical properties of material and their resistance to creep rupture and slow crack growth at different temperatures and pressures.

By considering analytical evaluation methods, various research works have been completed for characterising the degradation performance of PE and for improving the Polyethylene compounds by adding antioxidants in order to prevent or at least reduce the oxidation rate in PE pipe when it is exposed to oxidative agents. Some methods have also been designed to represent the antioxidant depletion and thermo-oxidative degradation behaviour of PE pipe.
Chapter 3

3. Materials and Methods

3.1 Polymers and pipes used in the research

PE polymers pellets of different compounds and grades and also PE pipe samples with different thicknesses obtained from both GPS and Radius PE pipe manufacturers have been analysed and studied in this work. The details and characteristics of analysed pellets and pipe samples from GPS and Radius pipe systems are shown in table 3.1 and table 3.2 respectively.

<table>
<thead>
<tr>
<th>PE pellet</th>
<th>PE pipe</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE (SABIC HDPE Vestolen A6060R, Black compound, MRS 10 MPa)</td>
<td>HDPE (black compound, Ø 125mm)</td>
<td>GPEH1</td>
</tr>
<tr>
<td>HDPE (Total HDPE dark blue compound MRS 10MPa, light blue compound MRS 8MPa)</td>
<td>HDPE (dark blue compound, Ø 125mm)</td>
<td>GPEH2</td>
</tr>
<tr>
<td>MDPE (Total, light blue compound, MRS 8MPa)</td>
<td>MDPE (light blue compound, Ø 63 mm)</td>
<td>GPEM3</td>
</tr>
<tr>
<td>MDPE (supplier: Total, Yellow compound, MRS 8MPa)</td>
<td>MDPE (yellow compound, Ø 90 mm)</td>
<td>GPEM4</td>
</tr>
</tbody>
</table>

Table 3.1. List of polyethylene polymers and pipes from GPS pipe systems

<table>
<thead>
<tr>
<th>PE pellet</th>
<th>PE pipe</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE (Lyondellbasell, Black compound, MRS 10MPa)</td>
<td>N/A</td>
<td>RPEH1</td>
</tr>
<tr>
<td>HDPE (Lyondellbasell, Dark blue compound, MRS 10MPa)</td>
<td>HDPE (dark blue compound, Ø 125mm)</td>
<td>RPEH2</td>
</tr>
<tr>
<td>MDPE ( Ineos, Eltex PC 002-50 R968 Light blue compound )</td>
<td>MDPE (light blue compound, Ø 63 mm)</td>
<td>RPEM3</td>
</tr>
</tbody>
</table>

Table 3.2. List of PE pellets and pipes from Radius pipe systems
3.2 Physical testing methods

In this part, some physical testing methods and conditions considered in this study are explained.

3.2.1 Density measurement

The immersion technique following BS 2782-6 was generally applied for density measurement of MDPE/HDPE pellets and pipes. According to this method, the mass of the specimen was measured first in the air (for most of samples about 0.85487 g) and then the sample was immersed into the immersion liquid (distilled water). It should also be noted that due to the lower density in comparison to water, the polyethylene samples must be weighted down. The uncorrected mass of specimen in the immersion liquid was recorded using a balance with about 4 digit accuracy and the value of the density of sample was calculated using the following equation:

\[ \rho_{S, t} = \frac{m_{S,A} \rho_{IL}}{m_{S,A} - m_{S,IL}} \]  \hspace{1cm} (3.1)

Where:

- \( m_{S,A} \) is the mass, in grams, of the specimen in air
- \( m_{S,IL} \) is the mass, in grams, of specimens in the immersion liquid
- \( \rho \) is the density of the immersion liquid, expressed in grams per cubic centimetre

The value of density was measured 5 times for each sample and at the end of the test the average value of density was calculated for each MDPE/HDPE polymer sample.
3.2.2 Crystallinity of pipe samples through thickness

DSC is the most commonly accurate and relatively simple method for determining the crystallinity percentage of a polymer.

Melting temperatures and enthalpies (heats of fusion), crystallisation temperatures and enthalpies glass transition temperatures (Tg), oxidative-induction time (OIT), degree of crystallinity, reaction temperatures and enthalpies, cross-linking reactions (curing) and specific heat capacity are the main examples of thermal characteristics, which can typically be detected by using DSC.

DSC is generally based on measuring the enthalpy of fusion when for example the semi-crystalline polymer undergoes the phase change. During the phase change, heat is either released (solidification case) or absorbed in the case of melting.

The experimental apparatus generally consists of two aluminium pans in separate, identical ovens (see figure 3.1), one of them containing the investigated material and the other one kept and considered as a reference. Both sample and reference are heated at the same rate from a single heating source in a heat flux DSC system. The specimen reaches its melting point by increasing the temperature.

Figure 3.1. Schematic of heat flux DSC [57].
Because of the heat capacity of the sample ($c_p$), the reference pan (usually an empty pan) generally heats faster than the sample pan during heating of the DSC measuring cell. For example, the reference temperature in figure 3.2 ($T_R$, green) increases faster than the sample temperature ($T_P$, red). The two curves demonstrate parallel behaviour during heating at a constant heating rate – until a sample change happens. In this case, the sample starts to melt at $t_1$. The temperature of the sample does not change during melting. The temperature of the reference side remains unaffected and continues showing a linear increase. on completing the melting process, the sample temperature also begins to increase again and, beginning with the point in time $t_2$, again exhibits a linear increase [58].

Figure 3.2. Schematic of DSC-thermal process [58].
The differential signal ($\Delta T$) of the two temperature curves is demonstrated in the lower part of the image. Calculation of the differences generates a peak (blue) in the middle section of the curve, which commonly represents the endothermic melting process. This generated peak might be shifted upward or downward in the graph during the calculation process. This generally depends on subtracting or adding the reference temperature from the sample temperature or on the sample temperature during this calculation, the generated peak may point upward or downward in the graphs. The peak area is correlated with the heat content of the transition (enthalpy in J/g) [58].

In the whole process of differential scanning calorimetry, only a small amount of energy would be enough for melting the crystalline phase. So that, the enthalpy of fusion can be measured for the specific mass that the specimen has. The percentage of crystallinity can finally be determined by comparing that energy to a 100 % crystalline specimen.

In the experiment, DSC 2920 – (TA instrument) was employed to characterise the thermal behaviour of polyethylene pipes through thickness. Thin films were cut vertically through the wall of three HDPE/MDPE samples from both GPS and Radius pipe manufacturers (black, yellow and blue compounds samples with 6 -11 mm thickness. The samples were then punched in to discs using a standard hole punch. The recommended mass of the samples by ISO 11357-3 (10 mg) weighed and then sealed into aluminium pans and loaded in to the apparatus with an empty aluminium pan as a reference. The test was carried out in two heating cycles with the heating rate of 10 °C min$^{-1}$ to 200°C onwards and protective gas - Nitrogen (50 mL min$^{-1}$). Heating and cooling cycles were recorded and then imported in to the TA universal analysis software. The software calculated both the enthalpy of fusion ($\Delta H_f$) and the peak melt temperature ($T_m$). The crystallinity of the sample was then determined using the following equation [58]:

\[
\text{Crystallinity (\%)} = \frac{\Delta H_f^{\text{obs}}}{\Delta H_f^\circ} \times 100
\]  

(3.2)

$\Delta H_f^\circ$ is the heat of fusion of 100 % crystalline polymer and is 293 J g$^{-1}$ for polyethylene [58].

$\Delta H_f$ is the enthalpy of fusion
3.2.3 Oxidation Induction Time (OIT)

PE is generally subjected to elevated temperatures and high shear forces when processed in the presence of oxygen from the atmosphere. This factor has a great influence on the formation of radicals on the polymer chain from which subsequent degradation reactions can occur [59]. These radicals result in degradation of the polymer by causing chain scission or crosslinking reactions. Oxidative induction time is widely used for characterisation and determining of thermal oxidative resistance of PE materials. In general, there is a linear relationship between the concentration of phenolic antioxidant and the observed OIT in PE [60]. In fact, the OIT testing provides more information about the level of anti-oxidants which usually remain in the pipe material but is also a suitable method for monitoring depletion degree of antioxidants from the pipe surface [59].

Measuring the oxidation induction time in this experiment was carried out by using a Differential Scanning Calorimeter (DSC) 2920. Thin strip of material of different PE pipes and pellets were prepared in our workshop and weighed. The sample of 10 mg was then located in an open aluminum pan and heated under nitrogen atmosphere with the flow rate of 60 mL min$^{-1}$ usually from room temperature up to 200 °C min$^{-1}$ at a constant rate of 20 °C /min. The gas was then switched to oxygen after 10 minutes. The test termination is dependent upon the appearance of an exothermic peak. The intercept of extended baseline and the tangent exothermic slope was determined as Oxidation Induction Time (see figure 3.3). The test was repeated 3 times for each sample and the average was recorded as OIT (time).

![Figure 3.3. Schematic of OIT (time) graph [60.]](image)
3.2.4 Oxidation Induction Temperature

The two methods of calculating oxidation induction have their own advantages and disadvantages. In the first method OIT (time) as described in figure 3.3, after reaching the required temperature for the first time at $t_1$, the atmosphere is switched to oxygen and the temperature remains constant until an exothermal signal (oxidation) can be recognised.

In the second method OIT (temp), as shown in figure 3.4, the sample is heated up continuously under an oxygen gas flow. The temperature was constantly raised with a specific heating rate and finally $OIT_{temp}$ was determined as the onset of the decomposition signal.

![Figure 3.4. Schematic of OIT (temp) graph [60].](image)

In the experiment, PE pipe and polymer samples were weighed (10 mg) and then heated up to 200 °C at a heating rate of 20 °C min⁻¹ and an oxygen flow rate (60 mL min⁻¹) using a Differential Scanning Calorimeter (DSC) 2920. The termination of OIT (time) test depends on the appearance of an exothermic peak. The interception of extended baseline and the tangent exothermic slope was determined as Oxidation Induction temperature. Figure 3.5 shows an example of an OIT (temperature) graph. In practice, the main advantage of the OIT (temp) method was that it is not required to change the gas during the analysis.
3.2.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis technique (TGA) is a common thermal analysis which generally determines weight loss of materials which appear due to decomposition, oxidation or loss of volatiles (such as moisture) as a function of temperature or time [60]. Investigation of degradation mechanisms, and reaction kinetics and determination of organic contents in an analysed sample are some examples of common application areas of TGA. It is an especially applicable technique for studying the properties of polymeric materials, including thermoplastics, thermosets or elastomers [61].

A TGA consists of a sample pan that is supported by very precise and accurate balance. The pan is heated or cooled in the furnace during the experiment. The mass of the sample is monitored during the experiment. A purge gas controls the sample environment. This gas could be inert or reactive gas that flows over the sample and exits through an exhaust. The thermogravimetric data is compiled into a plot of mass or percentage of initial mass on the y axis versus temperature and time on the x-axis (see figure 3.6). This plot is referred to as a TGA curve [62].
Figure 3.6. Schematic of weight loss in independence of time in TGA analysis [62].

In the experiment, the weight of material was measured as a function of temperature with a constant heating rate.

Figure 3.7 shows a typical TGA graph which indicates weight loss occurring for one of HDPE pipe sample in N₂ atmosphere and figure 3.8 illustrates the schematic of TGA instrument. The mass change of samples during the test is generally compensated by electromagnetically or electro mechanically compensating balance.

Figure 3.7. Typical TGA curve in N₂ atmosphere for one of the HDPE pipe samples.
A TA Instruments Q 5000 IR was used for thermo-gravimetric testing. The PE pipe and polymer samples were first prepared and weighed. About 10 - 15 mg of sample was placed in a platinum pan and was heated under nitrogen (50 mL min \(^{-1}\)) and air atmospheres with a constant heating rate of 10 °C min\(^{-1}\). It is important that the scales of the balance should be justified before starting the test. At the end of test, the resulted graphs from N\(_2\) and air atmosphere were analysed using TA Instruments analytical software.

### 3.2.6 Melt Flow Index (MFI)

The melt flow index indicates the fluidity or melt viscosity of a plastic under specified conditions of temperature and applied force. Generally, change in molecular weight or branch content result in changes of the melt viscosity and melt flow index. A high melt flow index demonstrates a low viscosity which indicates low molecular weight or low branching or crosslinking content and on the other hand low melt flow index indicates a high viscosity which results from high molecular weight, high branch content or crosslinking [63].

In this experiment, the melt flow index of different compounds of PE polymers and pipes after sample preparation was determined by MFI using an extrusion plastometer- model MP600 controller. As figure 3.9 shows, about 5 grams of PE polymer (or pipe samples) was extruded by an applied specific weight ( 5 kg). The process involved making three cuts of the extrudate at timed intervals when it exits the extrusion die under 5 kg test load.
at 190°C temperature. The cuts were then weighed to determine the average mass and this value is extrapolated to the mass that would be extruded in 10 minutes—the MFR. The test was repeated three times for each sample.

![Figure 3.9. Schematic of a MFI measuring device.](image)

### 3.3 Analytical testing methods

In this part, analytical testing methods and experimental conditions used for PE pipe and polymer samples are described.

#### 3.3.1 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique. It is a special form of photoemission in which the energy of emitted photoelectrons is analysed by an electron spectrometer and the data are generally depicted as a graph of intensity versus electron energy [64].

The kinetic energy of the electron ($E_k$) is the experimental quantity and is measured by the spectrometer. But it cannot be considered as an intrinsic material property as it is dependent upon the photon energy of the applied X-rays. The binding energy of the electron ($E_b$) is the parameter that characterises the electron clearly in terms of its
element and atomic energy level. The relationship between the parameters included in an XPS experiment is as follows [64]:

\[ E_B = h\nu - E_k - W \]  

(3.3)

Where \( h\nu \) is the photon energy, \( E_k \) is the kinetic energy of the electron, and \( W \) is the spectrometer work function (see figure 3.10). A photoelectron spectrum in XPS can reproduce the electronic structure of an element due to production and featuring of all electrons with the binding energy which is less than the photon energy [64]. In terms of surface analysis, X-ray photoelectron spectroscopy (XPS) is applied for determination of quantitative atomic composition and chemistry.

The XPS instrument used in this study was a K- Alpha Thermo-scientific surface analysis machine with the detection limits of 0.1-1 atom % and an analysis depth up to 10 nm. The main purpose of applying XPS for bulk of pipe samples was to identify any difference in atomic composition between the bulk and surface of MDPE/HDPE pipe samples. Figure 3.11 shows some prepared PE pipe bulk samples analysed by XPS characterisation method.
3.3.2 X-Ray diffraction

X-ray diffraction as its name suggests is a diffraction of X-rays on regular structures such as crystals or quasi-crystals. In fact, X-ray crystallography is generally applied for analysing or identification of atomic and molecular structure of a crystal, in which the crystalline atoms commonly result in to a beam of incident X-rays to diffract into many specific directions [65]. In fact, X-rays are scattered from the periodic repeating electron density of a crystalline material to give sharp diffraction peaks at angles that satisfy the Bragg relationship. Both types of materials including amorphous and crystalline materials diffract X-rays and electron, but for amorphous materials the diffraction is a much more diffuse, low frequency halo (the so called “amorphous halo”). Generally, some information about the statistical arrangement of atoms in neighbourhood of another atom can be obtained through the analysis of the diffraction peaks from amorphous material. A superposition of both diffuse and sharp scattering generally happens in polymers that are never completely crystalline [66].

A cathode ray tube generates X-rays. They generally produce monochromatic radiation, collimated to concentrate, and directed toward the sample. When conditions correspond to Bragg’s Law ($n \lambda = 2d \sin \Theta$), the interaction of the inclined rays with the sample produces diffracted ray. As figure 3.12 shows, $\lambda$ is the x-ray wavelength, $\Theta$ is the angle between the x-ray beam and these atomic planes and $n$ is related to the order of diffraction. Details about the crystal structure can be obtained by considering the...
condition for maximum intensity contained in Bragg’s law. Figure 3.13 shows an example of x-ray spectrum in a semi crystalline polymer, in which the intensity of X-ray diffraction is shown at different diffraction angle (° 2 θ).

![Bragg's reflection](image)

Figure 3.12. Schematic of Bragg’s reflection [65].

![X-ray spectrum example](image)

Figure 3.13. An example of partially crystalline polymer x-ray spectrum [65].

In the experiment the structure of PE pipes and polymers was studied using X-ray diffraction. The tests were carried out at room temperature using a Bruker D2 Phaser Bench top X-ray diffractometer using CuKα radiation (λ=1.5406 Å). Small solid samples were scanned from 1 to 50° in 0.05 ° increments and the crystallinity of samples was calculated. A detector is scanned around the sample along a circle in order to collect all the diffracted X-ray beams.

3.3.3 FTIR- Attenuated total reflection spectroscopy (ATR)

Many substances can be characterised and identified by attenuated total reflection spectroscopy (ATR). ATR as an analytical technique can obtain spectra from different
ranges of solids, liquids and gases. ATR generally works by measuring the changes that happen to a totally internally reflected infrared beam, when the beam contacts with a sample (see figure 3.14). A high reflective index of an infrared beam is directed in to an optically dense crystal and an evanescent wave which extends beyond the crystals surface into the sample can be generated [65]. In ATR, there must be a good contact between the sample and crystal surface. Evanescent waves may be attenuated or altered in the areas of the infrared spectrum, where the samples absorb energy [65]. The attenuated energy from each evanescent wave is returned to the IR beam and then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer.

In this experiment, the surface of PE polymers and pipes was examined using a Shimadzu FTIR – 8400S fitted with a Specac Golden Gate ATRMkII. The spectroscopy was running at a resolution of 0.85 cm\(^{-1}\) and peak to peak S/N ratio of 20.000 to 1. IR spectra for the materials were analysed from 4000 to 600 cm\(^{-1}\). Prior to each scan a background scan was run to ensure consistency. Software connected to the spectrometer was used to evaluate the peaks of interest. All spectra compared to establish differences in sample composition. This would also show any difference in ageing mechanisms.

![Figure 3.14. Schematic of Attenuated Total Reflectance (ATR) [65].](image)

**3.4 Summary of applied experiments for HDPE /MDPE pipes and polymers**

Tables 3.3 and 3.4 show the summary of analysis and testing methods carried out in this study for HDPE and MDPE polymer and pipe samples from both GPS and Radius pipe manufacturers.
Table 3.3. An overview of the applied experiments for PE polymer samples.

<table>
<thead>
<tr>
<th>PE polymer</th>
<th>Density</th>
<th>XPS</th>
<th>DSC</th>
<th>OIT (time)</th>
<th>OIT(temperature)</th>
<th>FTIR</th>
<th>TGA</th>
<th>XRD</th>
<th>MFI</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPEH1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>GPEH2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>GPEM3</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GPEM4</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>RPEH1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPEH2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPEM3</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4. An overview of the applied experiments for PE pipe samples.

<table>
<thead>
<tr>
<th>PE pipe</th>
<th>XPS</th>
<th>DSC</th>
<th>OIT (time)</th>
<th>OIT(temperature) through thickness</th>
<th>TGA</th>
<th>MFI</th>
<th>XRD</th>
<th>FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPEH1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>GPEH2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>GPEM3</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>GPEM4</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>RPEH2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPEM3</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 4

4. Results and Discussion

In this chapter, the results of the above mentioned physical and analytical tests of selected PE polymer and pipe samples will be discussed and the samples analysed according to their specific properties.

4.1 Physical testing methods

In this section the results of physical testing methods are described in detail together with appropriate graphs and available data.

4.1.1 Density measurement

The density of PE polymers from both GPS and Radius pipe suppliers was measured using the immersion testing method (see table 4.1 and 4.2). The density value of each polymer was measured three times and the average values have been plotted together with the density value of PE polymers in the literature and the graph is illustrated in figure 4.1.

<table>
<thead>
<tr>
<th>GPS polymer samples</th>
<th>Density (g cm$^{-3}$)</th>
<th>Radius polymer samples</th>
<th>Density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPEH1</td>
<td>0.953</td>
<td>RPEH1</td>
<td>0.955</td>
</tr>
<tr>
<td>GPEH2</td>
<td>0.951</td>
<td>RPEH2</td>
<td>0.950</td>
</tr>
<tr>
<td>GPEM3</td>
<td>0.943</td>
<td>RPEM3</td>
<td>0.940</td>
</tr>
<tr>
<td>GPEM4</td>
<td>0.940</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1. Average error values of density measured for HDPE/MDPE polymers.
Figure 4.1 clearly shows that the density of HDPE polymer samples from both pipe manufacturers are within the range of 0.94 - 0.95 g cm\(^{-3}\) and are higher than MDPE polymer samples within the range of 0.93-0.94 g cm\(^{-3}\). This significant variation of density is generally related to the basic difference of molecular structure between MDPE and HDPE in molecular weight distribution, chain branching and crystallinity. MDPE polymer is less dense, as MDPE has higher degree of side branching in contrast to HDPE polymer and branched chains cannot readily undergo chain folding to form crystals and this resulted to a lower density for MDPE polymer, as it is effectively a co-polymer with many short side-chains. The error bars show the standard deviation of the density as measured using the immersion technique. However, the measured value of density for all polymer samples was compared to the value of density given in the literature (table 4.2) and most of the calculated values of density by the immersion method correspond the literature value regarding safety data sheets of the polymers (Appendices1.2 and 1.3).

<table>
<thead>
<tr>
<th>GPS polymer samples</th>
<th>Density (g cm(^{-3}))</th>
<th>Radius polymer samples</th>
<th>Density (gr/cm(^{3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPEH1</td>
<td>0.959</td>
<td>RPEH1</td>
<td>0.959</td>
</tr>
<tr>
<td>GPEH2</td>
<td>0.95</td>
<td>RPEH2</td>
<td>0.95</td>
</tr>
<tr>
<td>GPEM3</td>
<td>0.94</td>
<td>RPEM3</td>
<td>0.943</td>
</tr>
<tr>
<td>GPEM4</td>
<td>0.94</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2. Literature values of density for different HDPE/MDPE polymers.
By considering the measured density values for HDPE and MDPE polymer samples from both GPS and Radius pipe manufacturers and comparing with literature values, it can be concluded that the immersion technique could be considered as reliable and accurate method for measuring density, as in comparison to other methods, the number of errors in carrying out the experiment was too low. In fact, air bubbles and inaccuracy of balance are two main factors contributed in errors in measuring density by this method.

### 4.1.2 Melting temperature & crystallinity

Melting temperature and crystallinity data for PE polymer and exterior surface of pipe samples from GPS and Radius PE pipe manufacturers were measured by DSC. The obtained results from different polymer compounds and pipes were compared to each other, as differences in physical properties can be seen during processing for some thermoplastic materials. However, the melting points or glass transitions may not show any significant changes as illustrated in test results. However, crystallisation can sometimes reveal subtle differences in material properties during processing such as...
cooling rate. PE pipe generally passes through a water-cooled sizing sleeve, in which pipe is expanded by internal pressure or external vacuum which is followed by a train of water baths or spray [67]. During this process, solidification happens because of crystallisation. Rapid cooling rate leads to lower crystallinity in comparison to slow cooling rate.

The peak temperatures in the two DSC heating cycles were considered as melting temperature and according to this, crystallinity percent was also calculated using the standard equation (see section 3.2.2). The values of crystallinity and melting temperature of GPS PE (exterior surface) of pipe and polymer samples and Radius PE pipe and polymer samples in second heating cycle are shown in table 4.3 and 4.4 and DSC graphs of these analysed PE polymers with different compounds are illustrated in figure 4.2 and 4.3.

<table>
<thead>
<tr>
<th>sample</th>
<th>Type</th>
<th>Thermal characteristics</th>
<th>Crystallinity (%)</th>
<th>Melting temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPEH 1</td>
<td>polymer</td>
<td>41.5</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pipe</td>
<td>55.2</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>GPEH 2</td>
<td>polymer</td>
<td>41</td>
<td>133</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pipe</td>
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<td>134</td>
<td></td>
</tr>
<tr>
<td>GPEM 3</td>
<td>polymer</td>
<td>41.5</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pipe</td>
<td>55.3</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>GPEM 4</td>
<td>polymer</td>
<td>40.1</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pipe</td>
<td>51.1</td>
<td>129</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3. Crystallinity and melting temperature of analysed GPS HDPE and MDPE pipe and polymer samples.
Table 4.4. Crystallinity and melting temperature of analysed Radius HDPE and MDPE pipe and polymer samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Crystallinity (%)</th>
<th>Melting temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPEH1</td>
<td>polymer</td>
<td>45.1</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>pipe</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>RPEM2</td>
<td>polymer</td>
<td>40.8</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>pipe</td>
<td>55.2</td>
<td>135</td>
</tr>
<tr>
<td>RPEM3</td>
<td>polymer</td>
<td>40.4</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>pipe</td>
<td>42.3</td>
<td>128</td>
</tr>
</tbody>
</table>

By considering the melting point and crystallinity of PE polymer and pipes with different compounds, 10 to 15 % increase in crystallinity between polymer and pipe samples can be seen. This is generally related to the processing of PE pellets and pipes. PE pipe fitting and fabrication through extrusion and injection moulding can be carried out at different pressures and heating or cooling conditions. As stated before, because of cooling which occurs with various rates during the pipe extrusion process, the crystallinity of pipes samples generally indicates a slight difference [67]. However, the melting temperature of polymer prior and after processing remains still the same (between 129 -135 °C).

Figure 4.2. DSC overlay of GPS - PE polymers (Black, light and dark blue compounds).
Figure 4.2 shows the DSC overlay of GPS HDPE black and dark blue compounds and MDPE light blue compound over two heating cycles. The DSC graph relating to GPS MDPE polymer sample with yellow compound is shown in figure 4.3. The illustrated graphs generated with the values of melting temperatures and crystallinity shown in table 4.3.

![DSC graph](image)

Figure 4.3. Dual heat DSC of GPEM4 (PE polymer – yellow compound).

According to figure 4.3, thermal properties such as melting temperature and crystallinity of GPS-MDPE over two heating cycles shows a slight decrease of melting temperature (128 °C) and crystallinity (40%) in comparison to figure 4.2. This supports the values shown in table 4.3 and the slight difference between the value of crystallinity of MDPE and HDPE polymer samples as described before is related to their different molecular structures.

Crystallinity and melting temperature of each PE polymer and pipe samples from Radius pipe system have also been measured (See table 4.4). The melting temperature of samples remains relatively constant (between 128-135 °C), but a 10 to 15 % increase in crystallinity of HDPE and MDPE pipe samples can be observed again. However, the external surface of GPS and Radius HDPE and MDPE pipe samples were analysed in this experiment. It might be useful to repeat the test again for various
parts of pipe samples, since the rate of cooling in the extrusion varies from the outer surface into the inner surface of the pipe respectively, which generally results in changing the crystallinity in various parts of the pipe.

Figure 4.4. (a) Dual heat DSC of RPEH1  (b) Dual heat DSC of RPEH2

Figure 4.4. shows the thermal properties of HDPE and MDPE radius polymer samples, which correspond the data in table 4.4. However, most of the illustrated figures relating to DSC thermal analysis of HDPE and MDPE pipe and polymer samples show that DSC is an ideal technique for the identification and quantification of polymer and pipes, as DSC is the most commonly used and has also been proven to be a very accurate and relatively simple method to measure the value of crystallinity percentage of a polymer. As stated before, It is generally based on measuring the enthalpy of fusion when the semi-crystalline polymer undergoes phase change [68]. Furthermore, DSC measurements are usually carried out at heating rates of 10 to 20 °C /min. This is a good compromise between accuracy, resolution, sensitivity and actual measurement time [69]. However, a slight difference between the melting point and crystallinity between MDPE and HDPE of both PE pipe manufacturers can be seen. That is because of the difference in chemical structure and properties of HDPE and MDPE and manufacturing process. Generally, HDPE has stronger intermolecular forces and higher tensile strength in comparison to MDPE. This is because of its lower degree of branching and also indicates that the higher the density and crystallinity, the higher the peak temperature and the larger the melting peak overall [70].
4.1.3 Crystallinity of pipe samples through thickness

All the samples of MDPE and HDPE pipes were prepared and were studied using DSC in two heating cycles. The thermographs were analysed to obtain more information about the melting temperature and crystallinity of extruded pipe samples through thickness of the wall, since the cooling rate varies significantly in different parts of pipe during the fabrication [71]. The melt temperature was calculated by finding the minimum of the heat flow curve at the crystalline melting peak. From this peak, the crystallinity of pipe samples was calculated, and the results are shown in figure 4.5. This figure shows the crystallinity profiles through the thickness of the pipes for both MDPE and HDPE materials with different compounds. As the figure indicates, the crystallinity is highest at the inner surface. The value of crystallinity is about 59%, 54 % for the outer and 44 % for the inner surface of HDPE pipe (black compound), MDPE (blue compound) and MDPE (yellow compound) and shows the difference with the value of crystallinity (see table 4.5) in the outer surface of the pipe samples.

<table>
<thead>
<tr>
<th>Distance from the outer surface (mm)</th>
<th>GPEM4 Crystallinity (%)</th>
<th>GPEM3 Crystallinity (%)</th>
<th>GPEH1 Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>45</td>
<td>50</td>
<td>56</td>
</tr>
<tr>
<td>1</td>
<td>42</td>
<td>50</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
<td>43</td>
<td>50</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>44</td>
<td>50</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>51</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>42</td>
<td>51</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>44</td>
<td>54</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 4.5. Percentage of crystallinity (%) through thickness of the pipe wall for HDPE and MDPE pipe samples with different compounds.
In fact, crystallinity for some analysed samples is the highest at the inner surface. This is because of the way in which the extrusion process of PE pipes happens. Since, cooling is applied to the outer surface of the pipe during extrusion process and because of the diffusion of this cooling through the pipe, the inner surface of the pipe has higher crystallinity. In this case, the crystallisation process is retarded on the outer surface because of rapid cooling, but it can continue through the pipe wall, since the cooling diffuses through the pipe wall thickness [71].

4.1.4 Oxidation Induction Time and Temperature

Oxidation induction time and temperature are initially carried out to assess the level of stabilisation of material such as PE pipe by determining time and temperature of oxidative decomposition. Generally, we would expect materials to be stable when they are exposed to air, but the fact is that materials particularly PE, are susceptible to oxidation over the long term. As a result, PE manufacturers usually add stabiliser in order to make polyethylene more resistant to oxidative degeneration [72]. The measured Oxidation Induction Time (OIT) of GPS and Radius pipe and polymer
samples are shown in table 4.6 and illustrated in a form of correlated OIT time and temperature graphs figures 4.6 and 4.7 for both MDPE and HDPE pipe and polymer samples. OIT (time) as stated before, is generally defined as the time between the gas change from nitrogen to oxygen and the first observed exothermic peak.

From overall point of view, the obtained results for OIT (temperature) showed a good correlation to those reported by doing OIT time tests and it can be applied exclusively in the research area instead of traditional OIT time method for characterisation of degradation behaviour of PE pipes.

<table>
<thead>
<tr>
<th>GPS pipe and polymer</th>
<th>OIT (time) [min]</th>
<th>OIT (tem) [°C]</th>
<th>Radius pipe and polymer</th>
<th>OIT (time) [min]</th>
<th>OIT (tem) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPEH1 pipe</td>
<td>41.84</td>
<td>260</td>
<td>RPEH1 pipe</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>GPEH1 Polymer</td>
<td>45.84</td>
<td>261</td>
<td>RPEH1 Polymer</td>
<td>30</td>
<td>254</td>
</tr>
<tr>
<td>GPEH2 pipe</td>
<td>30.5</td>
<td>255</td>
<td>RPEH2 pipe</td>
<td>52</td>
<td>262</td>
</tr>
<tr>
<td>GPEH2 Polymer</td>
<td>38.17</td>
<td>256</td>
<td>RPEH2 Polymer</td>
<td>64</td>
<td>261</td>
</tr>
<tr>
<td>GPEH3 pipe</td>
<td>50.28</td>
<td>260</td>
<td>RPEH3 pipe</td>
<td>30</td>
<td>254</td>
</tr>
<tr>
<td>GPEH3 Polymer</td>
<td>54.31</td>
<td>264</td>
<td>RPEH3 Polymer</td>
<td>32</td>
<td>261</td>
</tr>
<tr>
<td>GPEH4 pipe</td>
<td>33.27</td>
<td>260</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GPEH4 Polymer</td>
<td>44.51</td>
<td>263</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6. OIT time and temperature of MDPE and HDPE polymer and pipe samples
Results show that the OIT time and temperature for all HDPE and MDPE polymer samples is higher than the same samples in the form of pipes (see figures 4.6 and 4.7). This indicates that HDPE/MDPE pipe samples show lower resistance to oxidation induction than polymer samples. This similarity can be seen in both GPS and Radius pipe samples, which may be expected to result in lower mechanical durability and slow crack growth resistance [73]. But in case of GPEH2 which HDPE with dark blue compound is and also with about 30 min OIT (time) for pipe and 38 min for polymer, there are still some unanswered questions that can be cleared by doing more tests and analysis. Although the test was carried out for all samples in the same condition, this type of HDPE showed relatively lower oxidation induction time and temperature in comparison to other test samples. But the difference is not too high. This occurrence is probably related to the additives which were used as stabiliser in this type of HDPE. Therefore, more analytical experiments might be required to obtain more information about the formulation of applied additives in HDPE with dark blue compound. The OIT time showed good correlation with OIT temperature in most analysed samples. In fact, all PE pipe materials showed similar trends in OIT (time) and temperature. The OIT time of HDPE and MDPE pipe samples ranged from 30 to 64 minutes and the temperature for these samples varies from 255 -260 °C. In comparison, the range of OIT time of HDPE and MDPE polymer samples was between 30 -50 minutes and temperature is between 254-263 °C.
The OIT temperature for both types of PE polymers and pipes showed the best correlation with OIT time. However, the OIT temperature method does not show if oxidation has happened, it is only considered as a reliable method for determining the temperature at which, the remaining material starts to degrade. Despite a slight experimental uncertainty, overall both types of materials showed similar trends.

4.1.5 OIT of pipe samples through - thickness

Figure 4.8 shows the OIT (time) profile through thickness of HDPE and MDPE samples with different compounds details shown in table 4.7.

<table>
<thead>
<tr>
<th>Distance from the outer surface (mm)</th>
<th>GPEM4</th>
<th>GPEM3</th>
<th>GPEH1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33,27</td>
<td>50,28</td>
<td>41,84</td>
</tr>
<tr>
<td>1</td>
<td>61,42</td>
<td>53,14</td>
<td>50,20</td>
</tr>
<tr>
<td>2</td>
<td>56</td>
<td>55</td>
<td>53,10</td>
</tr>
<tr>
<td>3</td>
<td>54</td>
<td>60,35</td>
<td>50,25</td>
</tr>
</tbody>
</table>

Table 4.7. OIT time (min) through the thickness (mm) of the pipe wall for three different MDPE and HDPE pipe samples.
For all three samples, oxidation induction time is lower at the outer surface. For example, it can be seen clearly for MDPE pipe with blue compound from GPS pipe manufacturer (GPEM3), OIT is about 60 minutes for the sample 3 mm from the surface and about 50 minutes for the outer surface. Several reasons can contribute to this. Firstly, the outer surface would have been exposed to more UV than the inner surface of the pipe and so anti-oxidant consumption would have already started [74]. However, this is not valid completely for other two HDPE and MDPE samples as the figure shows. There is generally not strong evidence of different oxidation resistance through thickness for these two samples, it remains relatively constant. They all show a trend of lower OIT at the surface except GPEM4.

Figure 4.8. OIT through thickness for MDPE/HDPE pipe samples.
4.1.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to determine thermal stability of the PE pipes and polymers by monitoring their weight change as a function of temperature. The measurements were carried out for both MDPE/HDPE pipe and polymer samples in air and nitrogen atmospheres and the weight was recorded as a function of increasing temperature to get more information about the decomposition kinetics and the effect of reactive atmospheres on materials. The results of 1%, 2% and 99% weight loss of samples in both N₂ and air atmospheres are illustrated in the following figures.

![Graph](image.png)

**Figure 4.9.** 1% weight loss temperature of PE polymer samples in N₂/air atmospheres.
As figures 4.9 and 4.10 indicate, both HDPE/MDPE polymer and pipe samples start to undergo thermal degradation with about 1% weight loss at 340-350 °C temperature range in N\textsubscript{2} atmosphere while, their mass loss of 1% in air atmosphere takes place at lower temperature which is around 250 °C. In general, it can be stated that, both types of materials including pipes and polymers start to decompose at higher temperature in N\textsubscript{2} atmosphere than in air. In fact, the test was carried out in N\textsubscript{2} atmosphere to indicate the role of changing the atmosphere in slowing down the oxidation process, as the nitrogen atmosphere isolate the effects of thermal degradation and avoid any misleading oxidation reactions [75]. PE generally degrades under a nitrogen atmosphere in a single, smooth step. However, the degradation curve contains some irregularities in air atmosphere (See figure 4.11).
Figure 4.11. TGA curve of HDPE pipe sample in a) air and b) N\(_2\) atmosphere

Figures 4.12 and 4.13 compare the temperature at which different values of weight loss occurs for both HDPE pipe and polymer sample (black compound) in the above mentioned atmospheres.

Figure 4.12. Comparison of weight loss % vs temperature in N\(_2\) and air for GPEH1 pipe sample.
As the figures demonstrate, the decomposition temperature for polymer is about 270°C and for pipe is about 251 °C which relatively corresponds the OIT temperatures 261 °C for pipe and 259°C for polymer. For most of analysed samples the temperature in which the sample starts to decompose verifies the OIT temperature as well (See table 4.8).

<table>
<thead>
<tr>
<th>GPS and Radius pipe samples</th>
<th>OIT- temperature [°C]</th>
<th>Decomposition temperature [°C] [ 1% weight loss]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPEH1</td>
<td>261</td>
<td>270</td>
</tr>
<tr>
<td>RPEH2</td>
<td>260</td>
<td>268</td>
</tr>
<tr>
<td>GPEH2</td>
<td>256</td>
<td>263</td>
</tr>
<tr>
<td>RPEM3</td>
<td>261</td>
<td>264</td>
</tr>
<tr>
<td>GPEM3</td>
<td>264</td>
<td>261</td>
</tr>
<tr>
<td>GPEM4</td>
<td>263</td>
<td>267</td>
</tr>
</tbody>
</table>

Table 4.8. Comparison of OIT temperature and decomposition temperature of PE pipes in air
Figure 4.14 shows the relationship between the OIT –temperature and the measured decomposition temperature by TGA for PE pipe samples in which the decomposition of sample in air atmosphere occurs. The comparison suggests that OIT temperature studies would be reliable for measuring the thermal and degradation behaviour of PE pipe and polymer samples.

![Graph showing correlation between OIT temperature and decomposition temperature](image)

Figure 4.14. Correlated OIT (temp) and decomposition temperature (in air atmosphere) for HDPE/MDPE pipe samples

4.1.7 Melt Flow Index (MFI)

Melt Flow Index (MFI) or flow ability of polymer samples have been measured in this study. The results of Melt Flow Index of GPS and Radius polymer samples are shown in tables 4.9 and 4.10 and the variation of melt density between HDPE and MDPE polymer samples for both GPs and Radius polymer and pipe samples are illustrated in figures 4.15 and 4.16.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Radius samples</th>
<th>Melt Flow Index(g/10min)</th>
<th>GPS samples</th>
<th>Melt Flow Index(g/10min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE pipe</td>
<td>RPEH2, RPEM3</td>
<td>0.3, 0.6</td>
<td>GPEH 1, GPEH 2, GPEM 3, GPEM 4</td>
<td>0.3, 0.3, 0.9, 0.8</td>
</tr>
</tbody>
</table>

Table 4.9. Melt flow Index of GPS and Radius PE pipe samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Radius samples</th>
<th>Melt Flow Index(g/10min)</th>
<th>GPS samples</th>
<th>Melt Flow Index(g/10min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE polymer</td>
<td>RPEH1, RPEH2, RPEM3</td>
<td>0.3, 0.3, 0.9</td>
<td>GPEH 1, GPEH 2, GPEM 3, GPEM 4</td>
<td>0.3, 0.3, 0.9, 0.9</td>
</tr>
</tbody>
</table>

Table 4.10 Melt flow Index of GPS and Radius PE polymer samples

According to testing results, MDPE polymer samples with yellow and light blue compounds illustrated the highest value of melt flow rate (0.9 g / 10 min) in comparison to HDPE polymers with dark blue and black compounds (0.3 g /10 min). This significant variation of rheological performance is generally related to the basic difference of molecular structure between MDPE and HDPE in molecular weight distribution and chain branching. High molecular weight polymer resists flow and has a lower MFI in comparison to short chain length polymer. A larger melt index denotes lower melt viscosity. However, this value of MFI for PE polymers can be influenced sometimes by the pressure, the degree of shear working, and degradation or oxidation experienced by polymer [76].
The MFI of pipe samples was also measured at the same conditions to obtain more information about the change of PE chemical structure during the processing. Regarding melt flow index values of GPS and Radius pipe samples which ranges from 0.3 to 0.6 g/10min for Radius and 0.2 to 0.8 g/10min for GPS pipe samples (See Appendix 2.4), no enormous difference can be seen between the rheological behaviour of polymers before and after processing. However, these measured values for HDPE and MDPE polymer samples correspond and are also comparable to those in the materials safety data sheets attached in Appendices 1.2 and 1.3, particularly for GPS polymer samples. According the attached data, The MFI of HDPE polymer samples from GPS pipe manufacturer is about 0.3 g/10 min and for MDPE polymer samples from the same pipe manufacturer is 0.9 g/10 min, while it is about 0.8 g/10 min for MDPE polymer samples from Radius pipe manufacturer and is about 0.2 g/10 min for HDPE polymer samples. This shows that the manufacturing processing has not changed molecular structure significantly.
4.2 Analytical testing methods

The results of analytical testing methods considered for HDPE/MDPE polymer and pipe samples are described in this section.

4.2.1 X-Ray Photoelectron Spectroscopy (XPS)

XPS was used to measure the atomic concentration and homogeneity of outer and inner surfaces of PE pipe samples with different compounds. The XPS spectra of each sample revealed the presence of carbon (C), oxygen (O) and silicon (Si). The atomic concentrations of these elements on the outer and inner surface of analysed samples from GPS and Radius PE pipe manufacturers are presented in tables 4.11 and 4.12 respectively.
### Table 4.11. Atomic composition of inner and outer surface of GPS PE pipes.

<table>
<thead>
<tr>
<th>sample</th>
<th>Surface</th>
<th>Atomic concentration (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₁</td>
<td>O₂</td>
</tr>
<tr>
<td>GPEH 1</td>
<td>Outer</td>
<td>89.7</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>86.64</td>
<td>9.67</td>
</tr>
<tr>
<td>GPEH 2</td>
<td>Outer</td>
<td>82.7</td>
<td>10.85</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>73.74</td>
<td>12.85</td>
</tr>
<tr>
<td>GPEM 3</td>
<td>Outer</td>
<td>80.14</td>
<td>13.08</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>77.14</td>
<td>15.72</td>
</tr>
<tr>
<td>GPEM 4</td>
<td>Outer</td>
<td>83.57</td>
<td>10.49</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>82.8</td>
<td>12.3</td>
</tr>
</tbody>
</table>

### Table 4.12. Atomic composition of inner and outer surface of Radius PE pipes.

<table>
<thead>
<tr>
<th>sample</th>
<th>Type</th>
<th>Atomic concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₁</td>
</tr>
<tr>
<td>RPEH2</td>
<td>Outer</td>
<td>91.71</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>81.80</td>
</tr>
<tr>
<td>RPEM3</td>
<td>Outer</td>
<td>80.52</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>81.49</td>
</tr>
</tbody>
</table>
Figure 4.17 shows the high-resolution scan of O1 spectrum in outer surface of HDPE / MDPE pipe samples. By considering the atomic composition of inner and outer surface of GPS pipe samples, carbon concentration in comparison to inner surface increased in outer surface of analysed samples. The highest carbon and oxygen concentrations in surface area are generally related to the adhesion or chemical reaction on the surface [77]. The oxygen concentration is also higher on the inner surface. This suggests oxidation may have occurred on the inner surface. Samples that have been exposed to the atmosphere will usually have a detectable quantity of silicon contamination.

However, regarding XPS spectrum of analysed Radius PE pipe samples, it can be concluded that there is not a high difference in atomic concentration and composition between Radius and GPS test pipe samples.

**X-Ray Photoelectron Spectroscopy (XPS) - bulk properties**

In this type of XPS analysis, some bulk samples from the HDPE and MDPE pipes were prepared and atomic concentration and homogeneity were compared to the analysed surface of the pipes. Figures 4.18 and 4.19 demonstrate the high-resolution scan of O and C composition.
The XPS experiment in this thesis consisted of repeated measurements of c 1s and o 1s high resolution narrow scan spectra and a survey spectrum from the same PE material. The objective of the analysis was to investigate the chemical composition differences in the surface of PE pipe samples.

By comparing atomic composition of bulk of GPS and Radius pipe samples; there is no evidence of different atomic composition in bulk and surface of PE pipes. However, some high-resolution scans from the c 1s and o 1s compositions have been made during the analysis in order to get a better overview about difference of bulk properties of MDPE and HDPE pipe samples.

![Figure 4.18. High resolutions scan of o1s spectrum in the bulk of MDPE and HDPE samples.](image)

Figure 4.18. High resolutions scan of o1s spectrum in the bulk of MDPE and HDPE samples.
As stated before, figures 4.18 and 4.19 show XPS high resolutions scan of c1s and o1s binding energy measured on the bulk of GPS/Radius pipe samples. Regarding figure 4.18, the appearance of o 1s spectrum peak takes place for all samples in the specific energy range which is in the broad feature centred at 532 eV binding energy. In fact, Oxygen will always be present on samples exposed to the atmosphere, either due to adventitious contamination, oxidation or water. The raw data was fitted with one component or chemical state. By considering figure 4.17, the appearance of c 1s spectrum peak happens for all pipe samples at about 283 eV binding energy. Because of overlapping of some O1s components, all moiety generations and modifications observed in C1s XPS spectra do not directly fit with the O1s XPS spectra. In fact, Carboxyl groups are formed on the PE surfaces through the bond scission by the irradiation of o2 monomer ions. An increase of the irradiation levels generally leads to an increase of oxygenated compounds.

4.2.2 X-Ray diffraction

In the XRD analysis, the crystallinity of two HDPE/MDPE polymer samples and four HDPE /MDPE pipe samples (outer layers) were analysed and calculated using specific software for the verification of value of crystallinity measured through DSC thermal
analysis. The general PE X-Ray spectrum for most samples has a broad amorphous peak, even if the polymer had crystallinity, it therefore can be illustrated as sharp peaks on the top of large amorphous peak. The spectrum is the sum of crystalline peaks and an amorphous peak. As mentioned before, computer software has determined the true area of the crystalline peaks and the amorphous peak (see figure 4.20) using mathematical deconvolution of the peaks. The percentage of the polymer that is crystalline has been determined from equation described in chapter 3.3.2 and is reported in table 4.13.

<table>
<thead>
<tr>
<th>GPS and Radius pipe /polymer samples</th>
<th>Crystallinity (%) through DSC</th>
<th>Crystallinity (%) through XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPEH2</td>
<td>50.1</td>
<td>53.64</td>
</tr>
<tr>
<td>RPEH2</td>
<td>55.2</td>
<td>57.3</td>
</tr>
<tr>
<td>GPEM3</td>
<td>55.3</td>
<td>53.8</td>
</tr>
<tr>
<td>GPEM4</td>
<td>51.1</td>
<td>46.4</td>
</tr>
<tr>
<td>GPEH2 (Polymer)</td>
<td>41.07</td>
<td>37.55</td>
</tr>
<tr>
<td>GPEM4 (Polymer)</td>
<td>40.06</td>
<td>43.72</td>
</tr>
</tbody>
</table>

Table 4.13. Value of crystallinity (%) measured for HDPE/MDPE pipe and polymer samples by DSC and XRD.
Figure 4.20. XRD diffraction pattern for GPEH2 pipe sample.

Figure 4.20 shows a typical XRD diffraction pattern for a GPEH2 pipe sample. On this graph, amorphous/crystalline areas can be defined, with the crystalline peak typically located between 20° and 22° in 2θ and amorphous peak is placed between 13 and 26°. However, this diffraction pattern may change depending on the structure of the polymer chain (degree of order), the physical treatment of the polymer (e.g., tensile pull), the thermal history of the polymer (e.g., above T_m, it becomes amorphous while if it is cooled slowly it will crystallise) or the molecular weight of the polymer [78].

By considering the crystallinity value of analysed pipe sample, no evidence of significant difference between the values of crystallinity measured by using these two methods can be seen. However, there is slight change in the value of crystallinity. But it should be mentioned that the greatest possible source of error is generally related to the preferred orientation of the polymer, when XRD is applied for determination the value of crystallinity of polymeric materials. This is commonly due to the failure to observe large sections of the Debye ring in the XRD instrument. Therefore, essential peak intensity is generally missed and consequently the relative intensities of the crystalline peaks could be
misrepresented [78]. It can be concluded that DSC is as good as XRD in terms of measuring the crystallinity and also is an easier and more convenient method.

4.2.3 Attenuated total reflection -FTIR spectroscopy (ATR-FTIR)

The surface of PE polymer and pipe samples was examined by ATR-FTIR in order to assess and identify the chemical compounds, contaminants and or number of vinyl groups (C=C) in polyethylene polymers. Typical ATR-FTIR spectra of GPEM3 (GPS polyethylene -light blue compound) polymer and pipe sample are shown in figures 4.21 and 4.22.

Figure 4.21. FTIR spectra of GPS-MDPE pipe sample (GPEM3)

Figure 4.22. FTIR spectra of GPS-MDPE polymer sample (GPEM3)
In figures 4.21 and 4.22, the presence of two peaks between 2800 and 3200 wave number (cm\(^{-1}\)) and also 20 % of transmission identifies the stretching of C-H group which corresponds with the literature values. Between 1400 – 1600 of wave number (cm\(^{-1}\)) some deformation in C-H group occurs and the reason for this is not entirely clear, hence more experimental analysis will be required to obtain some information about the chemical structure of PE polymer.

By considering both graphs, there is not a great difference between the chemical compounds and structure of GPS MDPE pipe and polymer samples. As the stretching of C-H group (2800-3200 cm\(^{-1}\)) and deformation of C-H group (1400-1600 cm\(^{-1}\)) happens relatively at the same wave range and length.

However, some small peaks in ATR-FTIR spectra of both GPS polymer and pipe samples can be seen which generally appears between 2000 and 2400 cm\(^{-1}\) of wave number and also at higher transmission (between 90-100 %). This could be contributed to a small concentration of some contaminants or fillers.

### 4.3 Summary and conclusions

Different methods of analysis carried out on the samples have been described and the applied methodologies were also stated. Two different types of anti-oxidant concentration analysis were explained in this study. The OIT time was used to determine the anti-oxidant concentration first. The reasons for applying OIT temperature method in the second stage was that the OIT temperature method generally has no error caused by gas change. This method also produces thermographs that are easier to analyse and the time needed to perform the test is less in comparison to OIT time method. Any differences to standards for these methods are explained and stated. According to OIT time and temperature results, Radius and GPS MDPE and HDPE polymer and pipe samples show different OIT time and temperature and in some cases unstable thermal reactions, which seem to be critical in terms of pipe life time and ageing process. Overall, the range of OIT (time) of HDPE/MDPE polymers and pipes was about 40 to 50 minutes and the range of OIT (temp) was about 255 -265 °C.
Further to XPS, FTIR and MFI analysis, it can clearly be seen that GPS and radius PE polymer and pipe samples have relatively similar performance in Melt Flow Index measurement, FTIR-ATR spectroscopy or even at XPS surface analysis measurement (for pipe samples).

In terms of crystalline melting temperature (°C) and crystallinity (%), PE pipes and polymers generally indicate similar thermal performance across two heating/re-heat cycles of thermal analysis. Typical PE crystallinity was around 40-50 %, but due to cooling rate variations during the extrusion process of PE pipes, the value of crystallinity varied through pipe thickness: the inner surface of PE pipe demonstrated higher values of crystallinity (about 50 %) in comparison to outer layers (42-45 %). Weight loss data for HDPE/MDPE polymer and pipe samples has been examined utilising TGA in N₂ and air atmospheres to obtain more information about the decomposition kinetics and the effect of reactive atmospheres on materials. The results show that both HDPE/MDPE polymer and pipe samples start to undergo thermal degradation with about 1 % weight loss at 340-350 °C temperature range in N₂ atmosphere while, their mass loss of 1 % in air atmosphere takes place at lower temperature which is around 250 °C. Since, N₂ atmosphere generally isolate the effect of thermal decomposition and also avoid the occurrence of any early oxidation.

These fundamental analyses have been carried out to obtain a ‘baseline’ analytical footprint of the characteristics of the PE materials currently used in water pressure pipe products. More analytical and mechanical testing will be required to be undertaken in the future research works for different grades of PE materials, to identify the antioxidant types and concentrations, together with molecular weight distribution and structural branching, in order to correlate to slow or rapid crack propagation under different conditions, for PE pipe samples.
Chapter 5

5. Numerical modelling

5.1 Overview of Finite Element Theory

Finite Element Method (FEM) is one most commonly used computational methods. The majority of FE analyses are conducted using two-dimensional analysis under plane stress or strain conditions. Newman and Armen (1975) were the first to conduct a two dimensional finite element analysis of a crack growth process in PE material [79]. FEM was traditionally a branch of solid mechanics but nowadays it is commonly used for multi physics problems. FEM can be applied in different areas such as thermal analysis, dynamics, electrical analysis, structural analysis and biomaterials.

FEM applies a complex system of points called nodes which make a mesh. This mesh is generally programmed to describe the material and structural properties that indicate how the structure will react to specific loading conditions. Depending on the anticipated stress level of a area, nodes are usually assigned at a certain density throughout the material. Areas which will receive large amounts of stress usually have a higher node density than those which experience little or no stress [80]. The mesh elements extend from each node in the mesh, which act as a spider to the adjacent nodes. This web of vectors is what carries the material properties to the object. Figure 5.1 illustrates a schematic of nodes and elements.

![Figure 5.1. Schematic of nodes, element nodes and elements [80].](image-url)
Irregular geometries and boundary conditions can easily be taken into consideration in FEM. But this method has some limitations. For example, it is based on continuum mechanics principles, hence some rupture phenomena which are generally characterised by a continuum or dis-continuum transition cannot be completely described by this method. Furthermore, proper choice of element size and hardware problems could be considered as other limitation of FEM. The last one considers boundary difficulties.

The results of structural analysis using FEM represent only the approximation of the actual structural behaviour. Thereby, the committed failures will be decreased, when the structure is discretised perfectly. Time required for computing increases significantly with increasing the number of elements, or reduced mesh size.

The input data in FEM analysis usually includes definitions of nodes, the networking of node elements, definition of element properties and constitutive equations, determination of boundary conditions, the type of analysis geometrically linear (or nonlinear), the applied displacement boundary conditions, the type and size of the load and determination of load steps.

Figure 5.2 represents the interplay between the material, design, geometry and manufacturing process and ultimate resistance to slow crack growth [81].

Figure 5.2. Interplay between the materials, design, and geometry slow crack growth [81].
5.2 ANSYS Model Setup & Optimization

The selected parameters applied in the construction of all the ANSYS FE models for this project are provided in Appendix 3.1 and 3.2. However, it is necessary that the chosen modelling and meshing procedures are verified before utilizing the stress data obtained from the models. In this project, ANSYS workbench R16.2 - Academic Research Mechanical for statistical structure has been applied for following purposes:

- Simulation of the effect of mesh size and boundary conditions on stress concentration under constant internal loading pressure inside PE pipes with a specific diameter.
- The influence of pipes length on stress concentration inside the un-notched pipe.
- The effect of pressure on stress distribution
- The effect of axial notch length and also depth of notch as main factors on the change of stress concentration inside the notched pipe.

5.2.1 Effect of Internal Pressure

Definition of Barlow’s formula:

Barlow's formula defines a pipe’s cylinder internal pressure in relation to its dimensions and the strength of its material. In fact, Barlow's formula is generally applied to determine the internal pressure at minimum yield which a pipe can withstand. The formula is described using the following equation for a thin wall [82]:

\[ P = \frac{2\sigma t}{D} \]  \hspace{1cm} (5.1)

Where \( P \) = Pressure, \( \sigma \) = Allowable stress, \( t \) = Wall thickness and \( D \) is outside diameter
In the frame of this project, stress and strain behaviour of HDPE and MDPE pipe with specific pipe dimensions, were designed using Siemens- NX 10 software are investigated in different conditions of internal pressures, mesh size and boundary conditions. At the first stage of this study, the HDPE pipe sample with dark blue compound with its specific mechanical properties was designed in Siemens NX 10 with the Standard Dimension Ratio 11 (SDR 11); in which the ratio of pipe outside diameter (mm) to pipe wall thickness (mm) is 11. Various pipe length ranging from 0.5 – 2 m are considered in this study in order to obtain more information about the relation of the length of the pipe and maximum principal stress, von Mises’ stress and strain, under specific internal loading conditions.

5.2.2 Von Mises’ stress

Von Mises’ stress, which is a part of a plasticity theory, is generally evaluated in most numerical modelling methods by designers to determine whether an isotropic or ductile material will yield when it is subjected to the specific loading condition. This type of stress can be generally formulated considering von Mises stress or equivalent tensile stress $\sigma_v$. In this case, a material generally starts to yield when its value of von Mises’ stress reaches a critical value of yield strength $\sigma_y$. So that, von Mises’ stress is generally applied to predict yielding of materials under any loading conditions. In fact, the details about the stress tensor are generally required to get more information about the stress situation in a component. This generally contains six different stress values, as they are relatively the same as the shear stress. The shear stresses as zero or three normal stresses (main stresses) describe the stress condition in the system by transforming the stress tensor in
a coordinate system [83].

The elements of the vector of main stress or of the stress tensor can only be converted into a scalar which should meet two conditions: firstly, the stress condition should be comprehensively described as possible; secondly, failure relevant information should be illustrated in any case.

The general stress condition can be defined using the following formula:

\[
\sigma_v = \sqrt{\frac{1}{2} \left[ (\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2 + 6(\tau_{xy}^2 + \tau_{xz}^2 + \tau_{yz}^2) \right]} \quad (5.2)
\]

Another form:

\[
\sigma_v = \sqrt{\frac{1}{2} \left[ (\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2 + 6(\tau_{xy}^2 + \tau_{xz}^2 + \tau_{yz}^2) \right]} \quad (5.3)
\]

In the condition of main stress:

\[
\sigma_v = \sqrt{\frac{1}{2} \left[ (\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2 \right]} \quad (5.4)
\]

Where \(\sigma_x, \sigma_y, \) and \(\sigma_z\) are the main stress factors.

In plane stress condition:

\[
\sigma_v = (\sigma_x^2 - \sigma_x \sigma_y + \sigma_y^2 + 3\tau_{xy}^2)^{1/2} \quad (5.5)
\]
Figure 5.4 illustrates a comparison of Tresca criterion to Von Mises criterion. Figure 5.4 (b) is a failure map, in which the dashed lines indicate the Tresca failure surface. Tresca criterion is generally known as maximum shear stress theory. According to this criterion, yielding starts when the maximum shear stress in the material $\tau_{\text{max}}$ equals the maximum value of shear stress at yielding in a simple tension test $\tau_y$.

\[
\tau_{\text{max}} = \tau_y \tag{5.6}
\]

Where:

\[
\tau_{\text{max}} = \frac{\sigma_{\text{max}} - \sigma_{\text{min}}}{2} \tag{5.7}
\]

$\sigma_{\text{max}}$ and $\sigma_{\text{min}}$ are the maximum and minimum values of principal stresses. In fact, the Tresca criterion together with the Von Mises criterion are two main criteria applied for ductile materials.
5.2.3 Principal stress

It is always possible to find three common orthogonal planes that have one common intersection and are also so oriented that the value of shear stress is zero.

$$\tau_{12} = \tau_{23} = \tau_{31} = 0$$

In this case, only the normal components of stress remain [106].

$$\begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & \sigma_{22} & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & \sigma_{33}
\end{bmatrix} \rightarrow \begin{bmatrix}
\sigma_{11} & 0 & 0 \\
0 & \sigma_{22} & 0 \\
0 & 0 & \sigma_{33}
\end{bmatrix}$$

These three planes without any shear stress are described as principal planes of stress and they intersect each other along three mutually perpendicular lines of the main axes. The stress components, acting in the direction of these three axes are generally principal stresses, $\sigma_{11}$, $\sigma_{22}$ and $\sigma_{33}$. Normally, $\sigma_{11} \gg \sigma_{22} \gg \sigma_{33}$. This corresponds to the maximum, intermediate and minimum values of principal stress. In other words, the principal stresses are normal stresses which influence the surfaces without any shear stresses [84]. The main stress axes coincide with the principal axes of stress ellipsoids.

Figure 5.5. Components of the stress tensor [84].
5.2.4 Von Mises’ strain

In continuum mechanics, Strain generally describes the deformation of a body because of action of an external force. Deformation may appear as a length or angular change. Different equivalent variations may be applied for the expression of a strain field generally depending on whether it is defined with respect to the initial or the final configuration of the body or not.

A deformation can happen by applying various factors including external loads or changing temperature, moisture content or chemical reactions. In a continuous body, a deformation field commonly results from a stress field which is induced by applied forces or even by changing the temperature field inside the body. There are various equations such as Hooke’s law for linear elastic materials which express the relation between stresses and induced strains [85].

The von Mises yield criterion is applicable for the analysis of plastic deformation of ductile materials, as the onset of yield for these materials does not depend on the hydrostatic component of the stress tensor. The equivalent von Mises strain equation is used to estimate the corresponding equivalent strain commonly at the onset of plastic yielding and beyond.

\[ \varepsilon^e = \frac{\sqrt{2}}{3} \left[ \sqrt{2(\varepsilon_1 - \varepsilon_2)^2 + (\varepsilon_2 - \varepsilon_3)^2 + (\varepsilon_3 - \varepsilon_1)^2} \right] \]  

(5.8)

In the case of multi-axial stress and strain, the state at any point in three-dimensional solid element can be resolved using the von Mises stress-strain equation. This can then be related to the tensile test stress and strain response for modelling the elastic –plastic stress-strain curve behaviour of a ductile material. Generally, the linear elastic region can be modelled by Hooke’s law, in which stress (\( \sigma \)) and strain (\( \varepsilon \)) are related by Young’s Modulus (E) and the plastic strain hardening region can be modelled by a time Independent nonlinear stress –strain relationship.
5.3 Material properties

5.3.1 HDPE: mechanical properties

The general mechanical properties of HDPE are shown in table 5.1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength</td>
<td>26</td>
<td>[MPa]</td>
</tr>
<tr>
<td>Elongation at yield stress</td>
<td>10</td>
<td>%</td>
</tr>
<tr>
<td>Modulus of Elasticity (Young’s Modulus)</td>
<td>1100</td>
<td>[MPa]</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>0.96</td>
<td>g cm$^{-3}$</td>
</tr>
</tbody>
</table>

Table 5.1. Mechanical properties of HDPE (See Appendix 1.2, HDPE safety data sheet).

Room temperature (21 °C) was considered in the analysis process. A series of FE models were generated with mesh size of 0.003 m, 0.004 m and software default mesh size (defined mesh size by ANSYS software) by considering variation of element numbers. In fact, the default size function for mechanics application is generally designed to capture the geometry accurately, while minimizing the number of elements in the model. Figure 5.6 shows stress distribution of coarsest and finest mesh model.
Figure 5.6. a) Coarsest (software default resolution) and b) finest considering mesh resolution (0.004 m) applied for HDPE pipe length with 0.5 m.

As stated before, three different mesh sizes of 0.003, 0.004 m and the software default mesh size were considered for HDPE pipe materials with various lengths ranging from 0.5 - 2 m at the first stage of analysis process and the value of von Mises’ stress, von Mises’ strain and maximum principal stress have been calculated relating to appropriate internal pressure ranging from 12 to 24.8 bar. The results for the HDPE pipe with 2 m length are shown in table 5.2 to 5.4, (Variables: length of pipe and internal pressure). The rest of the results relating to the HDPE pipes with 0.5, 1 and 1.5 m length are shown in appendix 3.1.
As the tables show, variations in the value of stress are small for these three mesh sizes and also for the specific pipe length. According to the data shown in the tables, the value of equivalent von Mises' stress ranges from 11.28 MPa to 23.31 MPa for the 2 m length HDPE pipe for 2508 number of elements (software default mesh resolution). This value changes for the same pipe length in 0.004 mesh resolution and 137000 number of elements from 10.63 MPa to 20.46 MPa and its range for 0.003 mesh resolution with 330165 number of elements is from 9.77 MPa to 15.74 MPa (for the internal pressure range 15 - 24.8 bar). From the overall result, it can be concluded that the maximum principal stress and also the value of von Mises’ stress increase with increasing of
constant loading pressure. Overall, the value of Von Mises stress decreases with increasing the number of element nodes (See figure 5.7). It can also be said that the value of stress increases with internal pressure which generally corresponds to Barlow’s theory. In fact, smaller mesh size can improve the accuracy of results but at the same time there are some other factors that should be considered. For example, stress concentration can happen underneath concentrated forces at certain locations of the model or it can happen at a support point or at a re-entrant corner. By continuing the mesh size reduction for such cases, the stresses are only going to get higher. However, in regions where there are higher variations of stress, it is advisable to use a finer mesh. Overall, it can be concluded that finer mesh provides more accuracy, it also can slow down the analysis.

Figure 5.7. Relationship of number of element nodes and von Mises’ stress at the specific pipe length.
Figure 5.8. Relationship of internal pressure and equivalent von Mises' stress for 2-m HDPE pipe (SDR-11) at the software default mesh resolution.

Figure 5.8 shows the relationship between the von Mises' stress and number of element nodes for the HDPE pipe with the specific length (2 m). As this figure shows, the value of equivalent von Mises' stress increases from 11.28 MPa at 12 bar of internal pressure to 23.31 MPa at 24.8 bar of pressure. In fact, when a pipe is subjected to an internal pressure varying gradually (increased in steps), the corresponding maximum von Mises stress values are generally noted from the analysis results. The iterative procedure is usually continued till Von Mises stress nears yield strength values and failure according to grade of deformation happens.

Figure 5.9. Maximum principal stress distribution for the pipe with 0.5 m length at 24.8 bar pressure.
Figure 5.10. Maximum principal stress distribution for the pipe with 2 m length at 24.8 bar pressure and software default mesh size.

Figures 5.9 and 5.10 show a comparison of maximum principal stress distribution at 24.8 bar internal pressure for HDPE pipes with 2 m and 0.5 m length at the software default mesh size, in order to indicate the influence of material geometry on mesh elements and nodes on stress distribution. The graph that indicates the relation between pipe length and maximum principal stress at different values of internal pressure without considering the effect of mesh size is illustrated in figure 5.11 to show that the value of maximum principal stress decreases with increasing of pipe length.

Figure 5.11. Relationship between the pipe length for HDPE (HDPE) pipe sample and maximum principal stress at 24.8 bar internal pressure and software default mesh size.
According to figure 5.11 the value of maximum principal stress decreases with increasing the length of the HDPE at 24.8 bar internal pressure. As it is about 28.1 MPa for 2 m pipe and it increases to 33 MPa for the pipe with 0.5 m length. This generally refers to stress concentration in different pipe dimensions under specific internal loading pressure. Since, the stress concentration for the pipe with 0.5 m length totally differs from the pipe with 2 m length.

5.3.2 HDPE: Mechanical properties

The general mechanical properties of MDPE are shown in table 5.5.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength</td>
<td>20</td>
<td>[MPa]</td>
</tr>
<tr>
<td>Elongation at yield stress</td>
<td>10</td>
<td>%</td>
</tr>
<tr>
<td>(Young’s Modulus) [MPa]</td>
<td>900</td>
<td>[MPa]</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>0.95</td>
<td>g cm⁻³</td>
</tr>
</tbody>
</table>

Table 5.5. Mechanical properties of MDPE (see MDPE safety data sheet in appendix 1.3).

Room temperature (21 °C) was considered in the analysis process. A series of FE models (with the same dimension as the HDPE) were generated with mesh size of 0.003 m, 0.004 m and software default for considering variation of element numbers. Like HDPE pipe, MDPE pipes were also analysed at various lengths ranging from 0.5 to 2 m at the first stage of analysis process and again the value of von Mises’ stress, von Mises’ strain and maximum principal stress have been simulated relating to appropriate internal pressures ranging from 12 to 24.8 bar, and also by considering the pipe condition which was fixed from two sides for the three different mesh sizes. The results for 2 m length MDPE are shown in tables 5.6 to 5.8 and the rest are shown in appendix 3.2.
<table>
<thead>
<tr>
<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>6.65</td>
<td>10.63</td>
<td>0.00751</td>
</tr>
<tr>
<td>15</td>
<td>7.73</td>
<td>13.29</td>
<td>0.00910</td>
</tr>
<tr>
<td>20</td>
<td>10.31</td>
<td>17.72</td>
<td>0.01392</td>
</tr>
<tr>
<td>24.8</td>
<td>12.43</td>
<td>20.03</td>
<td>0.01662</td>
</tr>
</tbody>
</table>

Table 5.6. MDPE pipe -2 m length - Mesh resolution: 0.003m– Number of elements (330660).

<table>
<thead>
<tr>
<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>6.78</td>
<td>11.87</td>
<td>0.01052</td>
</tr>
<tr>
<td>15</td>
<td>7.97</td>
<td>15.88</td>
<td>0.01167</td>
</tr>
<tr>
<td>20</td>
<td>10.31</td>
<td>19.92</td>
<td>0.01790</td>
</tr>
<tr>
<td>24.8</td>
<td>14.79</td>
<td>21.93</td>
<td>0.02035</td>
</tr>
</tbody>
</table>

Table 5.7. MDPE pipe -2 m length - Mesh resolution: 0.004m– Number of elements (138096).

<table>
<thead>
<tr>
<th>Internal Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>10.97</td>
<td>16.98</td>
<td>0.01161</td>
</tr>
<tr>
<td>15</td>
<td>13.71</td>
<td>21.22</td>
<td>0.01451</td>
</tr>
<tr>
<td>20</td>
<td>18.28</td>
<td>25.30</td>
<td>0.01935</td>
</tr>
<tr>
<td>24.8</td>
<td>20.67</td>
<td>26.82</td>
<td>0.02399</td>
</tr>
</tbody>
</table>

Table 5.8. MDPE pipe -2 m length - Mesh resolution: software default – Number of elements (2508).

From an overall point of view, it can be seen that the value of maximum principal stress ranges from 16.98 MPa to about 30.09 MPa for the MDPE pipe with 2 m length in software default mesh resolution and 2508 elements, while it changes from 11.87 MPa to 21.93 MPa for 0.004 mesh resolution and from 10.63 MPa to 20.03 MPa for 0.003 mesh resolution for the pressure range 12 -24.8 bar. As data show, the value of von Mises’ stress decreases with increasing the number of mesh elements, which is 12.43 MPa at 24.8 bar for 0.003 mesh resolution and it increases to 20.67 MPa at the same internal pressure for software default mesh resolution (See figure 5.12). The same is valid for the value of von Mises’ strain, which also indicates a high decrease for all four
pressure ranges in various mesh sizes. (About 0.02399 m/m at 24.8 bar pressure for software default mesh size and decreases to 0.016622 for 0.003 m mesh resolution). From the overall point of view, it can be said that the value of stress and strain increases with internal pressure which generally corresponds the Barlow's theory.

Figure 5.12. Relationship of number of element nodes and von Mises’ stress at the specific pipe length (2 m) and 0.003 m (mesh resolution).

Figure 5.13 illustrates the relationship between internal pressure of MDPE pipe with 2-meter length and von Mises’ stress considering software default mesh size with 2508 elements.
As figure 5.13 shows, the equivalent von Mises’ stress increases with increasing internal pressure, increasing from 10.97 MPa at 12 bar to 20.67 MPa at 24.8 bar pressure. The comparison result of maximum principal stress, stress and von Mises’ strain of HDPE and MDPE are presented in the Figure 5.14 and 5.15 respectively. The results show HDPE pipe sample has relatively higher resistance to stress at applied internal pressure than MDPE pipe sample, but the strain value von Mises shows a small increment for MDPE pipe sample, which is for example about 0.00751 m/m for MDPE pipe with 2 metre length at 12 bar internal pressure and 0.003 mesh resolution and it increases to 0.01662 m/m at 24.8 bar pressure for the same condition, while the value of von Mises’ strain for HDPE pipe sample with 2 metre length and the same mesh resolution at 12 bar pressure is 0.00692 m/m and is 0.01432 m/m at 24.8 bar pressure. That is because of the difference in crystalline structure of HDPE and MDPE materials, as high-density polyethylene has a greater proportion of crystalline regions that medium density polyethylene. HDPE (HDPE) with fewer branches than MDPE (MDPE) has a greater proportion of crystals, which can result in to greater density and greater strength. MDPE has commonly higher flexibility but less strength due to the lower crystalline constant than HDPE [86].
Figure 5.14. Von Mises’ stress versus von Mises’ strain for HDPE (HDPE) pipe sample with 2 m length in 0.003m mesh resolution.

Figure 5.15. Von Mises’ stress versus von Mises’ strain for MDPE (MDPE) pipe sample with 2 m length at various internal pressure.
5.4 The effect of sharp notch depth on stress and strain behaviour

In this part of the research, HDPE -SDR 11 pipe sample with 2 m length was considered for analysing the effects of notch depth on the stress and strain concentrations due to the defect.

Using NX (Siemens) CAD software version 6.0, sharp notches with various depths ranging from 0.5 mm – 3 mm (as a function of pipe size and thickness which is about 20% of pipe wall thickness) were designed on a HDPE pipe -2 m length sample at 24.8 bar pressure. Figure 5.16 shows a schematic of the axial sharp notch on the pipe sample.

![Figure 5.16. Schematic of axial sharp notch.](image)

In fact, defects in pressurised pipes are proposed to cause failure in PE pipes under loading by slow crack growth, which plays an important role in prediction of pipe life time. First, as stated above, sharp notches with various depths ranging from 0.5 mm to 3 mm were chosen in this study and the calculated values of stress and von Mises’ strain and maximum principal stress for a 2 m HDPE (SDR 11) pipe at 24.8 bar pressure and default mesh size are shown in table 5.9.
As seen in table 5.9, stress and von Mises’ strain together with the maximum value of principal stress increase with increasing notch depth, e.g. maximum principal stress for the notch with 0.5 mm depth is about 16.43 MPa and is about 25.16 for the notch with 3 mm depth. In fact, the deformation behaviour is very sensitive to the depth of the notch. Figure 5.17 shows stress distribution the parts of a pipe of 2 m length at 24.8 bar pressure near the notch area (at default mesh size). The figure indicates how the mesh structure changes in different areas considering the stress concentration. For example, in the areas with high stress concentration the mesh nodes and lines would be tighter than the area with relatively low stress level.

<table>
<thead>
<tr>
<th>Notch depth (mm)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent von Mises’ strain (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>15.05</td>
<td>16.43</td>
<td>0.01458</td>
</tr>
<tr>
<td>1</td>
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<td>21.30</td>
<td>0.01560</td>
</tr>
<tr>
<td>2</td>
<td>19.24</td>
<td>22.34</td>
<td>0.01620</td>
</tr>
<tr>
<td>3</td>
<td>23.30</td>
<td>25.16</td>
<td>0.01835</td>
</tr>
</tbody>
</table>

Table 5.9. Stress and strain value at the base of the notch for different notch depths

Figure 5.17. Section of the HDPE pipe with the notch.

Figures 5.18 and 5.19 show the relationship of maximum principal stress and equivalent von Mises’ strain for the studied pipe with the sharp notch.
In figure 5.18 (default mesh size), strain values increase with increment of maximum principal stress in various notch depths. There is a linear relationship between the maximum principal stress and strain values for different notch depths. The value of maximum principal stress is 16.43 MPa at 0.5 mm notch depth, while it reaches to 25.16 MPa at 3 mm notch depth. The same performance can be seen for the von Mises’ strain values. It is 0.01428 m/m for 0.5 mm notch depth and increases to 0.01835 m/m for 3 mm notch depth. Overall, notch depth has a strong effect on the variation of strain and stress behaviour. The deformation generally reaches its highest value at the notch depth of 3 mm.
According to figure 5.19, the value of von Mises’ stress increases with notch depth, from 15.05 MPa for the 0.5 mm notch depth to 23.30 MPa for the notch depth of 3 mm. Overall, the depth of an external notch in a pressurised PE pipe significantly effects its lifetime, which is generally terminated by slow crack growth [87]. For the analysis and prediction of stress and strain concentration in a pressurised PE pipe under notch condition, various areas with different distances from the notch base must be taken into account [108]. Relating to this, pipe sample was divided in three sections with the help of the software CAD section considering the distance from the base of a notch of 3 mm depth and the value of stress calculated depending on the distance to the notch base.
As figure 5.20 illustrates, the value of stress increases closer to the base of the notch for a 2 m HDPE pipe with a 3 mm notch depth. It is about 12 MPa at 10 mm remote from the notch base and reaches to 20 MPa at the notch tip. This corresponds to theory, in which the stresses at crack tip are higher than stresses in the areas which are further from the notch tip.

**5.5 Summary**

In this chapter, the basic information about the appropriate length, stress and strain behaviour of HDPE and MDPE pipe samples (SDR11) with different lengths have been characterised in different conditions. At the first stage of FEM analysis, the relationship between PE pipe length and the value of maximum stress at different internal pressures was calculated in order to obtain the minimum length (2 m) for more accurate data and the pipe sample with the appropriate length was chosen for further study which generally related to investigation the effect of mesh size on stress concentration. As the numerical modelling calculated, the value of stress and von Mises' strain together with maximum principal stress increase with decreasing the number of mesh elements. A large number of elements gives more accurate results. In the next stage of this study, the effect of
pressure on the maximum principal stress and stress and von Mises’ strain of HDPE and MDPE pipes was investigated considering Barlow equation. Further to the various internal pressures applied in this study, von Mises’ stress was predicted by FEM to increase with internal pressure, which generally corresponds to Barlow formula. Finally, the effect of notch size was simulated to predict the degree of stress concentration. Regarding notch depth and its effect on the deformation behaviour of material, it can be said that PE pipe material shows the highest degree of deformation in the deepest notch, as the value of von Mises’ strain was predicted to increase with the depth of the notch. Stress intensity and concentration in areas near to notch base, it was also simulated and it confirmed that the stress reaches its highest in the notch base and also decreases with increasing distance from the notch tip. However, the analysis of sharp notch geometry has indicated that the notch effect in fracture mechanics is sensitive to structure geometry, scale effects and loading mode.
Chapter 6

6. Conclusions and further research

6.1 Conclusions

In this thesis, methods have been presented for physical and analytical characterisation of HDPE and MDPE polymer and pipe samples suitable for application in the water mains pressure pipe industry. The major contributions of this work are presented in Chapters 3, 4 and 5. In Chapter 3, the theory of applied analytical and characterisation testing methods have been explained in detail and results and data interpretations have been presented in Chapter 4.

According to results, the range of OIT (time) of HDPE/MDPE polymers and pipes was about 40 to 50 minutes and typical PE crystallinity was around 40-50 %. In terms of crystallinity through the pipe surface, the inner surface of PE pipe demonstrated higher values of crystallinity (at about 50 %) in comparison to outer layers (at 42-45 %). Furthermore, TGA in N₂ and air atmospheres for both HDPE/MDPE polymer and pipe samples start to undergo thermal degradation with about 1 % weight loss at a higher temperature range (340 - 350 °C) in N₂ atmosphere than in air atmosphere (about 250 °C), which relatively corresponds to OIT (temperature) results.

Regarding MFI testing results, MDPE polymer samples (yellow and light blue compounds) illustrated highest values of melt flow index in comparison to HDPE (dark blue and black compounds). By considering the values of melt flow index of GPS and Radius pipe samples, it can be concluded that there is no significant difference between the rheological behaviour of polymers before and after processing.

According to FTIR-ATR graphs for MDPE / HDPE pipe and polymer samples, there is not a great difference between the chemical compounds and structure of the GPS and Radius MDPE and HDPE pipe and polymer samples, as the stretching of C-H group
(2800-3200 cm\(^{-1}\)) and deformation of C-H group (1400-1600 cm\(^{-1}\)) occur relatively at the same wave range and also at the peaks with relatively the same height.

By comparing atomic composition of surface of GPS and Radius pipe samples in XPS analysis, carbon concentration in comparison to inner surface increased in outer surface of analysed samples. In addition, samples that have been exposed to the atmosphere have generally a detectable quantity of silicon contamination. By comparing atomic composition of bulk of GPS and Radius pipe samples; no evidence of different atomic composition can be seen in bulk, inner and outer surface of PE pipe samples.

The results of XRD analysis indicate that the value of PE sample crystallinity measured by this method corresponds to the values measured by DSC testing method. No evidence of huge differences between the values of crystallinity measured by applying these two methods can be seen. This generally provides evidence of consistency.

In Chapter 5, the prediction of stress and strain in HDPE and MDPE pipe samples with specific pipe lengths and also specific pipe thickness under constant internal pressures ranging from 12 bar to 24.8 bar have been carried out in the first stage of this study. Different mesh resolutions and element sizes were used in order to obtain an overview about the implication of elements resolution, size and pipe length on predicted value of stress and strain (Von Mises) for different conditions of internal pressure. As results show, maximum principal stress and also the value of von Mises’ stress increase with increasing of constant pressure, while the expected stress value decreases with increasing number of element nodes (finer mesh size) for both HDPE and MDPE pipe samples with the specific geometry (SDR11) and 2 m pipe length.

The compared results of maximum principal stress, stress and von Mises’ strain of HDPE and MDPE indicate that HDPE pipe sample has a higher resistance to stress at applied internal pressure than MDPE pipe sample, but the strain value von Mises shows a small increment for MDPE pipe sample. This is due to the difference in elastic modulus, attributed to PE crystallinity.

In the second stage of numerical modelling, the influence of notch depth on stress concentration and value of stress and von Mises’ strain for HDPE pipe sample with
specific length and thickness was investigated for a specific mesh size. In addition to this, the effect of distance from the base of notch on stress concentration has also been reviewed. The results of strain values show an increase with increment of maximum principal stress in various notch depths. Overall, notch depth has relatively strong effect on the variation of strain and stress behaviour. The deformation generally reached its highest value at the largest notch depth studied (3 mm). The value of stress increases towards to the notch tip. This corresponds to theory, in which the stresses in front of the crack tip are higher than stresses in the areas distant from the notch tip.

6.2 Further work

By considering all the research carried out in previous years on various aspects of PE polymers and pipe and also in this study, further analytical testing methods will be developed in the near future to identify the role of antioxidant depletion in plastic pipes degradation behaviour. As PE materials are generally subject to oxidation, they are commonly manufactured with antioxidants to prevent excessive long-term deterioration to pipe material.

Some further investigations might be required to understand how the antioxidant level in PE material can influence the degradation mechanism and oxidation induction time, particularly in long periods of time.

Regarding DSC analysis and crystallinity, more analytical experiments need to be developed to investigate the internal structure and morphology of extruded HDPE and MDPE pipes with various compounds, since the internal structure and molecular orientation and crystallinity might be influenced in the fabrication process. It also might be required to do more investigation on the influence of draw force, screw speed, melt temperature or even melt stress on the molecular orientation of PE.

In terms of mechanical and analytical testing, more investigation will be required to be undertaken in the future research work for different grades of PE materials in order to identify the antioxidant types and concentrations, together with molecular weight distribution and structural branching for correlation of slow or rapid crack propagation
under different conditions. Further to numerical modelling, the effect of distance to the notch tip was investigated in this research and it has been found that the stress concentration reaches its highest level in the area near to notch tip, but it will be required to focus more in the next research works on the effective distance which corresponds to the effective value of stress. Further to this, creep behaviour of HDPE and MDPE pipe material in the condition of long-term pressure testing, in which strain will increase with time might be considered more in the future research works.
Reference


[52] R. K.Krishnaswamy,” Analysis of ductile and brittle failures from creep rupture
testing of high-density polyethylene (HDPE) pipes”, Polymer science, 2005, p. 11664-11672.


Appendix

Appendix 1

Appendix 1.1 Project Sponsors

**EPSRC** is the main UK government agency for funding research and training in engineering and the physical sciences, investing more than £800 million a year in a broad range of subjects - from mathematics to materials science, and from information technology to structural engineering.

EPSRC supports excellent, long term research and high quality postgraduate training in order to contribute to the economic competitiveness of the UK and the quality of life of its people.

**UKWIR** was set up by the UK water industry in 1993 to provide a framework for the procurement of a common research programme for UK water operators on 'one voice' issues. UKWIR's members comprise 21 water and sewerage undertakers in England and Wales, Scotland and Northern Ireland.

Over the last 15 years, UKWIR subscribers have contributed some £50m with a further £30m of research coming from UKWIR collaborators, resulting in over 750 reports delivered to members. Work is often carried out in collaboration with government departments and regulators including the Department for Environment, Food and Rural Affairs; the Drinking Water Inspectorate and the Environment Agency. Some work is also done in collaboration with research organisations internationally. The majority of work is put out to open tender to a wide range of companies, academic institutions and other organisations in the UK and overseas. Project management is undertaken by both the water industry's R&D departments and by individuals employed by UKWIR.
Appendix 1.2 Material Data Sheets - GPS PE polymers

**Polyethylene MDPE 3802 YCF**

**Medium Density Polyethylene PIPES & FITTINGS Protocol in Europe**

**Description**

MDPE 3802 YCF is a high performance low-iron based yellow compound, with a MRS 8 MPa - PE 80 classification and primarily intended for gas pipe applications.

MDPE 3802 YCF key characteristics are:

- A superior resistance to slow crack growth ensuring safe and long-term network operation
- An optimal balance of flexibility and mechanical strength that allows easy coiling, handling and installing of pipes
- An optimized formulation of additives and finely dispersed pigments providing outstanding long-term stability in service

Designation ISO 1872-PE, E/M-ACIHL 40-T012

**Characteristics**

<table>
<thead>
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<th>Property</th>
<th>Method</th>
<th>Unit</th>
<th>Typical value (*)</th>
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</thead>
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<tr>
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<tr>
<td>Water content (**)</td>
<td>EN 12118</td>
<td>ppm</td>
<td>≤ 300</td>
</tr>
</tbody>
</table>

(*) Data not intended for specification purposes
(**) Measured at the stage of compound manufacturing

**Processing**

MDPE 3802 YCF can be processed under the following recommended conditions. Adjustments may be useful depending upon the pipe/fitting dimensions, appearance and/or the type of processing equipment used.

Extrusion melt temperature: 190-220°C
Injection melt temperature: 200-260°C

**Compliance with regulations**

MDPE 3802 YCF is formulated to comply with the regulations applying to gas pipe systems in most countries. A Product Stewardship certificate giving the conformity to various regulations or statements on absence of certain chemicals is available on request.

It is recommended to contact your local sales representative to obtain specific information and individual certificates regarding compliance to regulations.

**Handling and storage**

MDPE 3802 YCF should be stored at ambient temperature and at atmospheric pressure in its original packaging (plastic or cardboard boxes) or in bags made of appropriate material (aluminum, stainless steel, etc.).

The product should be stored in dry, well-ventilated areas, and it is recommended to avoid prolonged storage under extreme temperatures, direct sunlight or other sources of radiation.

It is advisable to convert the product within 6 months after delivery; provided appropriate storage conditions are used.

Please refer to the Safety Data Sheet for further information.

Information contained in this publication is true and accurate at the time of publication and/or the best of our knowledge. The nominal values stated herein are obtained using laboratory test specimens. Before using any of the products mentioned herein, customers and other users should take all care in determining the suitability of such product for the intended use. Unless specifically indicated, the products mentioned herein are not suitable for applications in the pharmaceutical or medical sector. The Company, TOTAL Petrochemicals, does not accept any liability whatsoever arising from the use of this information or the use, application or processing of any product described herein. No information contained in this publication can be considered as a suggestion to infringe patents. The Company disclaims any liability that may be claimed for infringement or alleged infringement of patents.
# SABIC® Vestolen A 6060R 10000

**High density polyethylene for Pipe extrusion**

**Description.**
SABIC® Vestolen A 6060R 10000 (black) is a grade which has a high density (class MFI: 10-PE 100) and a unimodal distribution of the molecular mass. Due to an improved profile of properties the material offers additional security when used for gas and drinking water piping. The material is further characterised by a significantly higher resistance to long-term loading and has a very high resistance to rapid crack propagation. Owing to a special stabilisation package, good organoleptic properties are ensured with grade 6060R 10000. This material meets international standards for use in gas, drinking water and waste water piping.

## Typical data

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<tr>
<th>Properties</th>
<th>Units Si</th>
<th>Values</th>
<th>Test methods</th>
</tr>
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<td>g/10 min</td>
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<td>ISO 1133</td>
</tr>
<tr>
<td>at 190 °C and 5 kg</td>
<td>%</td>
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<td>stress at yield</td>
<td>%</td>
<td>9</td>
<td>ISO 527-2</td>
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<td>strain at yield</td>
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<td>ISO 527-2</td>
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<td>Kj/litre</td>
<td>8.2</td>
<td>ISO 17095/A</td>
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<tr>
<td>at 30 °C</td>
<td>-</td>
<td>69</td>
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<td>at 1.80 MPa (HDT/A)</td>
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<td>at 0.45 MPa (HDT/B)</td>
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<td>melting point</td>
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<td>DSC 53765</td>
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**Internet links:**
SABIC Europe, [TC6.0M PE626](http://www.sabic.com)

call: TC6.0M PE626 [Europe]

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Revision: 09/2018
SABIC® Vestolen A 6060R 10000
High density polyethylene for Pipe extrusion.

General Information:
These products are produced in a Gruve Halata plant, which is operated as a cascade. A particular characteristic of the SABIC® Vestolen A 6060R 10000 is their bimodal molecular weight distribution, which allows to gain high elongation to break. Moreover, besides the production of PE 100 it is possible to produce PE 80 with the same distribution.
SABIC® Vestolen A 6060R 10000 has been designed for the high requirements of pressure pipes. Depending on their specific grades they are suited for the extrusion of:
- pressure pipes for water, gas and sewage
- high pressure pipes and containers
- network

Health, Safety and Food Contact regulations. Detailed information is provided in the relevant Material Safety Data Sheet and/or Standard and the declaration, available on the internet (www.SABIC.com). Additional specific information can be requested via your local SABIC Office.

Quality: SABIC Europe is fully certified in accordance with the internationally accepted quality standard ISO 9001:2000. The SABIC Europe policy is to supply materials that meet performance specifications and needs and to keep up its reputation as a pre-eminent, reliable supplier of e.g. polyethylene.

Storage and Handling: Polyethylene resins (in pelletised or powder form) should be stored in such a way that it prevents exposure to direct sunlight and heat. This may lead to quality degradation. The storage location should be dry, dust free and the ambient temperature should not exceed 50°C. Not compliaance with these precautions may result in degradation of the product which can result in lower machinability and inadequate product performance. It is also advisable to protect polyethylene resins (in pelletised or powder form) within 6 months after delivery, this because of excessive aging of polyethylene cap end lead to a deterioration in quality.

Environment and recycling: The environmental aspects of any packaging material do not only apply to1s in use but also to the material after it has been used. SABIC Europe has made a commitment to an environmentally efficient packaging material. The less specific energy consumption and insignificant emissions to air and water designate polyethylene as the ecological alternative in comparison with the traditional packaging materials. Recycling polyethylene material is supported by SABIC Europe. Every recycling mill can benefit on increased value while a social infrastructure for substitute recycling and selling of packaging is fostered. Whenever the total recycling of packaging (i.e. integration with existing economy) is carried out, polyethylene needs to be linked to a simple molecular structure and the amount of additives is considered to be a troubleless task.

Internet site: SABIC Europe.com
email: TECSAM RECS@SABIC.com

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Appendix 1.3 Material Data Sheets - Radius PE polymers
# Hostalen CRP 100 blue

Polyethylene, High Density

## Product Description

`Hostalen CRP 100 blue` is a high density polyethylene (HDPE), blue coloured similar RAL 5005 with high melt viscosity for extrusion, injection and compression moulding. The product is classified as PE 100 and provides excellent stress crack resistance properties (ESCR) combined with very good long term hydrostatic strength. It is not intended for medical and pharmaceutical applications.

## Product Characteristics

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<td>Test Method used</td>
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<td>Typical Customer Applications</td>
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## Mechanical

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<td>kJ/m²</td>
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Hardness
Shore hardness (Shore D (3 sec))

ISO 868
52

Thermal
Vicat softening temperature (VST/B/50 K/h (50 N))
ISO 306
74
°C

Oxidation induction time (OIT) (210°C)
ISO 11357-S / EN 728
30
min

Additional Properties
Processing:
Recommended melt temperatures: 190-220 °C.
Recommended injection moulding temperatures: 200-230 °C.

Notes
Typical properties; not to be construed as specifications.

Further Information
Conveying:
Conveying equipment should be designed to prevent production and accumulation of fines and dust particles that may be contained to a small extent in polymer materials. These particles can under certain conditions pose an explosion hazard. We recommend the conveying system used is equipped with adequate filters, is operated and maintained so that no leak develops and adequate electrical grounding exists at all times.

Health and Safety:
Special requirements apply to certain applications such as food contact end-use and direct medical use. For specific information on regulatory compliance contact your local representative.

Workers should be protected from the possibility of skin or eye contact with molten polymer. Safety glasses are suggested as a minimum precaution to prevent mechanical or thermal injury to the eyes.

Molten polymer may be degraded if it is exposed to air during any of the processing and off-line operations. The products of degradation have an unpleasant odour. In higher concentrations they may cause irritation of the mucus membranes. Fabrication areas should be ventilated to carry away fumes or vapours. Legislation on the control of emissions and pollution prevention must be observed. If the principles of sound manufacturing practice are adhered to and the place of work is well ventilated, no health hazards in processing the material have been reported.

The material will burn when supplied with excess heat and oxygen. It should be handled and stored away from contact with direct flames and/or ignition sources. In burning the material generates considerable heat and may generate dense black smoke. Minor fires can be extinguished by water. Developed fires should be extinguished by heavy foams forming an aqueous or polymeric film. For further information about safety in handling and processing please refer to the Material Safety Data Sheet (MSDS).

Storage:
The material is packed in 25 kg bags or in bulk containers protecting it from contamination.

Storage times of natural materials longer than 6 months may have a negative influence on the quality of the final product (for example the brightness). It is generally recommended to convert all materials latest within 6 months from the date of delivery.

The material is subjected to degradation by ultra-violet radiation or by high storage temperatures. Therefore the material must be protected from direct sunlight, temperatures above 40°C and high atmospheric humidity during storage.

Further unfavourable storage conditions are large fluctuations in ambient temperature and high atmospheric humidity. These conditions may lead to moisture condensing inside the packaging. Under these circumstances, it is recommended to dry the material before use. Unfavourable storage conditions may also intensify the material’s slight characteristic odour.

Due the hygroscopic character of the carbon black pigments, black coloured materials may pick...
up moisture even under appropriate storage conditions. If this is the case it is recommended to
dry the material before processing. After a storage period of more than 3 months drying of such
material is recommended as standard practice.

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LEP, Lucterol, Lutfene, Lupolen, Luporol, Lupotech, Luposan, Lusitex, Metacore, Microthene, 
Mydoden, MPQDL, Neprene, Petorethane, Pexar, Polymag, Pristene, Proflex, Pro-fex, 
Puncilous, Pureper, Reflex, SAA100, SAA131, Sequel, Softaire, Spherione, Spheritone, Starflex, 
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Ideal, Integrate, Kadtron, Lucterol, Luporen, Lupotech, Metacore, Microthene, Mydoden, MPQDL, Neprene, 
Petorethane, Pexar, Polymag, Pristene, Pro-fex, Puncilous, Pureper, Reflex, SAA100, SAA131, Sequel, Softaire, Spheritone, 
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Release Date: 23 Aug 2013
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Duocap, Duoprim, Explore & Experiment, Filmex, Fleatherene, Fueling the power to win, Get in touch
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Linkal, Luperlox, Lupalox, Lupusdax, Lupotech, Metodene, Micohonene, Mopal, MP0101, Nerolites,
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Petrolithene, Pexar, Polymeg, Prolene, Pro-flex, Prolinol, Proulax, Sequel, Softex, Spherenene, Spheronene,
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Office.

Release Date: 23 Aug 2013

**Hostalen CRP 100 black**

Polyethylene, High Density

**Product Description**

Hostalen CRP 100 black is a high density polyethylene (HDPE), black coloured similar RAL 8017 with high melt viscosity for extrusion, injection and compression moulding. The product is classified as PE 100 and provides excellent stress crack resistance properties (ESCR) combined with very good long term hydrostatic strength.

It is not intended for medical and pharmaceutical applications.

**Product Characteristics**

**Status**
Commercial: Active

**Test Method used**
ISO

**Availability**
Europe, Asia-Pacific

**Processing Methods**
Extrusion Pipe Sheet and Semi Finished Products

**Features**

**Typical Customer Applications**
Drinking Water Pipe, Gas Pipe, Industrial, Soil & Wastage Pipe

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<thead>
<tr>
<th>Typical Properties</th>
<th>Method</th>
<th>Value</th>
<th>Unit</th>
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<td>Density</td>
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<td>0.939</td>
<td>g/cm³</td>
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<td>Melt Flow Rate (MFR)</td>
<td>ISO 1133</td>
<td>5.4</td>
<td>g/10 min</td>
</tr>
<tr>
<td>(190°C/2.16 kg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(190°C/5.0 kg)</td>
<td></td>
<td>0.23</td>
<td>g/10 min</td>
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<td><strong>Mechanical</strong></td>
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<td></td>
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<tr>
<td>Tensile Modulus (23°C, v = 1 mm/min, Sustained)</td>
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<td>Tensile Stress at Yield (23°C, v = 50 mm/min)</td>
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<td>ISO 899-1</td>
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<tr>
<td>Mean: [Test stress in MPa]</td>
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<td>Creep Modulus 1000h</td>
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<td>MPa</td>
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<tr>
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<tr>
<td>Maximum elongation TD</td>
<td>EN 838</td>
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<tr>
<td>MTS classification</td>
<td>ISO/TR 9000</td>
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<td>MPa</td>
</tr>
<tr>
<td>PNCT (4.0 MPa, 2% Antidegrad N 100, 80°C)</td>
<td>ISO 16770</td>
<td>≥ 1000</td>
<td>h</td>
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</tbody>
</table>
Flexural creep modulus

(4 point loading method, 1 min-value) 1200 MPa
(4 point loading method, 24 h-value) 560 MPa
(4 point loading method, 2000 h-value) 330 MPa

Impact

Charpy notched impact strength
(23 °C) ISO 179 26 kJ/m²
(-30 °C) 13 kJ/m²

Hardness

Shore hardness (Shore D (3 sec)) ISO 858 63

Thermal

Vulcan softening temperature (VST/8/10 K/h (56 N)) ISO 306 74 °C
Oxidation induction time (OIT) (210°C) ISO 11357-6/EN 728 30 min

Additional Information

Carbon black content ISO 6964 2.25 %
Odor threshold EN 1622/EN 1420 < 2

Additional Properties

Processing:
Recommended melt temperatures: 190-220 °C.
Recommended injection moulding temperatures: 200-280 °C.

Notes
Typical properties; not to be construed as specifications.

Further Information

Conveying
Conveying equipment should be designed to prevent the production and accumulation of fines and dust particles that may be contained to a small extent in polymer materials. These particles can under certain conditions pose an explosion hazard. We recommend the conveying system used is equipped with adequate filters, is operated and maintained so that no leak develops and adequate electrical grounding exists at all times.

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Storage:
The material is packed in 25 kg bags or in bulk containers protecting it from contamination. Storage times of natural materials longer than 6 months may have a negative influence on the quality of the final product. It is generally recommended to store all materials within 6 months from the date of delivery.

The material is subjected to degradation by ultra-violet radiation or by high storage temperatures. Therefore the material must be protected from direct sunlight, temperatures above 40°C and high atmospheric humidity during storage.

Further unfavourable storage conditions are large fluctuations in ambient temperature and high atmospheric humidity. These conditions may lead to moisture condensing inside the packaging. Under these circumstances, it is recommended to dry the material before use. Unfavourable storage conditions may also intensify the material's slight characteristic odour.

Due to the hydroscopic character of the carbon black pigments, black-coloured materials may pick up moisture even under appropriate storage conditions. If this is the case it is recommended to dry the material before processing. After a storage period of more than 3 months, drying of such material is recommended as standard practice.

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Use the following short links to get directly to the properties of interest in this datasheet:
- Rheological properties
- Mechanical properties
- Thermal properties
- Other properties

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<th>Properties</th>
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<tr>
<td>ISO Data</td>
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<tr>
<td>Melt flow index, KF1</td>
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<tr>
<td>Tensile modulus</td>
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<td>Yield stress</td>
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<td>%</td>
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<td>Thermal properties</td>
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<td>ISO Data</td>
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<tr>
<td>Visc. softening temperature A</td>
<td>111</td>
<td>°C</td>
<td>ISO 308</td>
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<td>Other properties</td>
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<td>ISO Data</td>
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<tr>
<td>Density</td>
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<td>Characteristics</td>
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<td>Other Extrusion</td>
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Appendix 2- Chapter 4
Results and Discussions

Appendix 2.1 Thermal analysis
DSC - Melting temperature & crystallinity

Crystallinity (%) = \( \frac{\Delta H_f (obs)}{\Delta H_f^*} \times 100 \)

\( \Delta H_f^* \) is the heat of fusion of 100 % crystalline polymer and is about 293 J g\(^{-1}\) for polyethylene

Thermal properties of analysed Radius MDPE and HDPE pipe and polymer samples.

Dual heat of GPS – HDPE pipe sample (GPEH1)- black compound

Melting point = 132°C (Second heating cycle)

Crystallinity = 55.2 (Second heating cycle)
Second heat of GPS–MDPE pipe sample (GPEM3) - Light blue compound

Melting point = 131°C    Crystallinity = 55.3 % (Second heating cycle)

Second heat of GPS-MDPE pipe sample (GPEM4) - yellow compound

Melting point = 128°C    Crystallinity = 51.1 % (Average)
Second heat of Radius MDPE pipe sample (RPEM3) - light blue compound

Melting point = 129 °C  Crystallinity = 41.01 %

Second heat of Radius HDPE pipe sample (RPEH2) - Dark blue compound

Melting point = 135°C  Crystallinity = 55.2 %
Appendix 3–Chapter 5
Numerical Modelling

Appendix 3.1 HDPE pipe sample

Sample 1:
Pipe length: 0.5 m
Boundary condition: 2-fixed support

<table>
<thead>
<tr>
<th>Internal Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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<tr>
<td>12</td>
<td>10.02</td>
<td>16.18</td>
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<td>11.65</td>
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<tr>
<td>20</td>
<td>12.52</td>
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<tr>
<td>24.8</td>
<td>14.32</td>
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<td>0.00810</td>
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A: Mesh size: 0.003 (Resolution) – Number of elements /nodes: 82665

<table>
<thead>
<tr>
<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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<td>20</td>
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B: Mesh size: 0.004 m (Resolution), Element numbers (34250)

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<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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</thead>
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<td>12</td>
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C: Mesh size: Software default (Resolution), element Numbers:
Sample 2:
Pipe length: 1 m
Boundary condition: 2-fixed support

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<tr>
<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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A: Mesh size: 0.003 (Resolution) – **Number of elements:** 165330

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<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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B: Mesh size: 0.004 m (Resolution), **Element numbers (68500)**

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<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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C: Mesh size: Software default (Resolution), **element Numbers:** 1454
Sample 3:
Pipe length: 1.5 m
Boundary condition: 2-fixed support

<table>
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<tr>
<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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</tbody>
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A: Mesh size: 0.003 (Resolution) – **Number of elements: 247500**

<table>
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<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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</thead>
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B: Mesh size: 0.004 m (Resolution), **Element numbers (102750)**

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<th>Equivalent Von Mises’ strain (m/m)</th>
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C: Mesh size: Software default (Resolution), **element Numbers: 1870**

Appendix 3.2 MDPE
Sample 1:
Pipe length: 0.5 m
Boundary condition: 2-fixed support

<table>
<thead>
<tr>
<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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</thead>
<tbody>
<tr>
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A: Mesh size: 0.003 (Resolution) – **Number of elements**: 82665

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<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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<tr>
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B: Mesh size: 0.004 m (Resolution), **Element numbers** (34250)

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<th>Internal Pressure (Bar)</th>
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C: Mesh size: Software default (Resolution), **element Numbers**: 1287
Sample 2:
Pipe length: 1 m
Boundary condition: 2-fixed support

<table>
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<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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<tr>
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<tr>
<td>15</td>
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<td>0.0081</td>
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<tr>
<td>20</td>
<td>10.30</td>
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A: Mesh size: 0.003 (Resolution) – **Number of elements: 165330**

<table>
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<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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B: Mesh size: 0.004 m (Resolution), **Element numbers (68500)**

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<th>Internal Pressure (Bar)</th>
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<th>Equivalent Von Mises’ strain (m/m)</th>
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<td>28.25</td>
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C: Mesh size: Software default (Resolution), **element Numbers: 1454**
Sample 3:
Pipe length: 1.5 m
Boundary condition: 2-fixed support

<table>
<thead>
<tr>
<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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<td>0.0081</td>
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A: Mesh size: 0.003 (Resolution) – **Number of elements:** 247500

<table>
<thead>
<tr>
<th>Pressure (Bar)</th>
<th>Equivalent von Mises’ stress (MPa)</th>
<th>Maximum principal stress (MPa)</th>
<th>Equivalent Von Mises’ strain (m/m)</th>
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<tr>
<td>12</td>
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B: Mesh size: 0.004 m (Resolution), **Element numbers** (103572)

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<th>Equivalent Von Mises’ strain (m/m)</th>
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C: Mesh size: Software default (Resolution), **element Numbers:** 1870