Relationship between Short-Term and Long-Term Creep, and the Molecular Structure of Polyethylene

by

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Abstract

Polyethylene has been studied from many different perspectives; a final application property perspective, in which the response of the material to loads is the topic; a micromechanical point of view, in which the macroscopic state of the material is related to its microstructure, e.g., Alvarado (2007), and a chemical point of view in which the molecular structure and the processes that create polyethylene are investigated. This thesis focuses on the mechanical behavior of polyethylene observed from testing and relates the mechanical behavior to the molecular structure of the material.

High density polyethylene is a material used in civil engineering applications such as pipes and containers. There are two general modes of failure for polyethylene: ductile failure that happens at relatively large stresses (up to 200MPa) and in short amount of time, and brittle failure that occurs when a much lower stress is sustained over a long period of time (Cheng 2008). Other than these two modes of failure, excessive deformation of the material that is usually caused by creep is also to be avoided. This thesis studies the relationship between short-term and long-term creep of polyethylene and its molecular structure.

In this work three types of mechanical tests were performed on six samples of polyethylene. The existing models that prescribe the constitutive behavior of the material were then critically evaluated against the observed data. Furthermore the molecular properties of the samples that had been obtained from previous research by Cheng (2008) were compared against the mechanical behavior observed from testing in order to assess what molecular properties are important in determining the mechanical behavior of polyethylene. This information can also help polyethylene designers to produce longer lasting material, or a material that has high stiffness, by knowing what molecular properties to control and optimize.

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1.0 Introduction

Synthetic plymers have been increasingly used in engineering applications ever since they were invented in 1862. Today, considerable research in structural engineering involves polymers, e.g. Fiber Reinforced Polymers, FRP, strengthening of concrete, structures and polyethylene pipes in the ground. This range of application is partly due to the fact that, unlike steel, polymers do not corrode.

In the construction industry polymers may be safe when it comes to corrosion but when they are subjected to a constant load they keep deforming with time. Hence there are long-term concerns regarding the use of polymers in infrastructure. Moreover, since the invention of plastics is relatively recent, there are not many long-term observations available and there is much uncertainty regarding long-term material behavior.

Polyethylene is used mostly in pipes, many of which are installed in highly populated areas. Therefore, there are huge costs associated with failure of these pipes. Failure may not occur for many years. This fact is known from such tests as environmental stress cracking, in which the failure mechanism is accelerated. Given that many of the pipes have been installed relatively recently there are growing concerns about the long term performance and reliability of this part of the infrastructure.

A good assessment of the long term behavior of polyethylene is important in planning. It is also valuable to know how the pipe manufacturer can produce longer lasting pipes from knowing the relationship between molecular properties of polyethylene and its long term performance. This thesis attempts to address both problems.

From a civil engineering perspective one of the biggest concerns regarding the use of polyethylene is creep. Most construction materials are used in their elastic region of behavior at service loads, which means that imposed deformations can be recovered once the load is taken off. Elastic region refers to a region in the stress-strain curve in which the stress or strain is fully recoverable. For many materials it can be assumed that if the material is in the elastic region then plastic deformation can be neglected in the design. In polyethylene a large portion of strain can be recovered at loads below the yield point. However some creep or plastic deformation is observed at almost any load.

1.1 Objectives

This thesis has the following objectives:

1. Evaluation of existing models for the constitutive modeling of polyethylene.
2. Prediction of long term behavior of a given sample of polyethylene, based on short-term testing.
3. Relating molecular properties of the material to visco-elastic behavior and creep.

To achieve these objectives, both experimental and theoretical work was undertaken.

1.1.1 Evaluation of Existing Models for Polyethylene

A review of existing models has been done in this thesis. The emphasis is on assessment of the model ability to predict long-term behavior of polyethylene. Experimental data are usually obtained from relatively short tests. Therefore, it needs to be acknowledged that the models, calibrated based on these short-term tests, may not be able to predict long term behavior of polyethylene.

1.1.2 Prediction of Long-Term Behavior

The expected life span of a pipe network can be up to fifty years. Civil engineers are particularly interested in knowing how reliable materials are after several years of service. The material properties change with time. This process is referred to as aging of the material. Since short term creep tests do not include any aging effects they do not incorporate these effects.

One of the main focuses of this research is to find out a way to assess the long term behavior of a given sample of polyethylene not only from performing a short-term creep test but also from studying molecular properties of the polyethylene.

1.1.3 Relating Molecular Properties to Visco-elastic Behavior and Creep

Different polyethylenes exhibit the same type of creep behavior. However the creep function parameters can vary by a factor of 2 for different polyethylenes.

There are many quantities that are used to specify the molecular structure of polyethylene. Distribution of molecular weight is one of them. Polyethylene is made of chains of carbon. Not all chains have the same length. The lengths of these chains vary for a given sample. This varying length of chains can be described by a distribution. Molecular weight distribution, MWD, is a key property for polyethylene. It is hard to measure or manufacture MWD with great precision. Nevertheless manufacturers of polyethylene do have some control over MWD. One of the objectives of this research is to provide information about long term behavior of a polyethylene sample knowing its MWD.

Another important molecular property of polyethylene is crystallinity. Polyethylene is a two-phase material having a crystalline phase and an amorphous phase. Crystallinity of the polyethylene refers to the percent of the crystalline phase over the total mass. The long term behavior of polyethylene can be correlated with MWD, crystallinity, and other molecular properties. This thesis attempts to find out which molecular properties are relevant to creep. The thesis tries to answer the following questions:

1. Which molecular properties influence short-term behavior of polyethylene?
2. Which molecular properties influence long-term behavior of polyethylene?
3. How can a manufacturer produce longer lasting material without jeopardizing its short-term properties?
4. What is the relation among these molecular properties?

More information regarding the molecular structure of polyethylene is available in Chapter 2.

1.2 Contents of the Thesis

The contents of the thesis are divided into 8 chapters:

Chapter 1 gives the problem statement and the objectives of the research.

Chapter 2 provides background information that was used as the foundation for this work. The information can be categorized into:

- General macroscopic behavior of polyethylene
- Information about molecular structure of polyethylene

Chapter 3 provides a full description of the experimental program. It also discusses the accuracy of the results and sources of error.

Chapter 4 presents the obtained data and discusses the results.

Chapter 5 evaluates the existing models based on the obtained data.

Chapter 6 provides studies on the influence of molecular properties on short-term and long-term behavior of polyethylene.

Chapter 7 presents the conclusions based the finding of the research.

Finally, Chapter 8 lists the recommendations for future work.

2.0 Background

According to the Plastic Pipe Institute, PPI, polyethylene was invented in 1933 in England by the Imperial Chemical Company (2006). In 1939 polyethylene was first commercialized to insulate telephone cables. Today, there are three methods for producing polyethylene: gas-phase, solution, and slurry ploymerization.

Polyethylene can be studied from two different perspectives:

1. A study of the response of the material to a given load. The scientist may only focus on the behavior of the material not paying attention to what causes it to behave the way it does.

2. The other perspective is to try to understand explain why polyethylene behaves the way it does. The advantage of this approach is that it allows for the scientist to make predictions based on knowing the structure of the material without having to run a series of tests.

This chapter considers the micro structure of polyethylene in section 2.1. It also describes the observed general behavior and theories that explain them in section 2.2.

2.1 Molecular Structure of Polyethylene

Basic information and definitions related to the molecular structure of polymers are provided in this section in order to have a better understanding of what happens on the micro scale when polyethylene is subjected to loads, and also to assess how some of the quantities, defined in this section, govern the behavior of the six polyethylenes chosen for the experiments.

Polyethylene is a polymer having ethylene, C_2H_4, as its repeating monomer unit. The general structure of polyethylene is comprised of carbon chains each carbon carrying 2 hydrogen atoms. The length of the chains is variable in any given polyethylene sample. Figure 2.1 shows a schematic configuration of a polymeric chain for polyethylene.

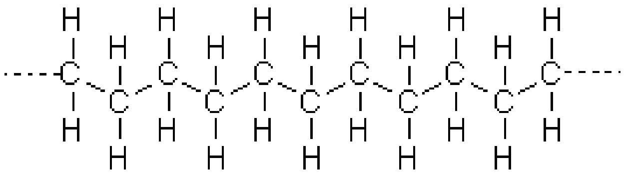


Figure 2.1 – Polymeric Chain for Polyethylene

High-Density Polyethylene, HDPE, is a two-phase material. The two phases are the amorphous phase and the crystalline phase. What distinguishes the crystalline phase from the amorphous phase is that in crystals the carbon chains are packed together in an organized fashion as opposed to forming a random shape which is the case for the amorphous phase. The crystallinity in the HDPE samples under study varied from 50% to 60%. According to Cheng (2008), when polyethylene is subjected to a load each phase behaves differently. The crystalline lamellae provide high yield stress while the amorphous phase provides flexibility and hence a recoverable elastic response. Figure 2.2 shows a schematic representation of the two phases in polyethylene. The parallel lines at the centre of the figure represent the crystalline phase and the random configuration at the two sides represents the amorphous phase.

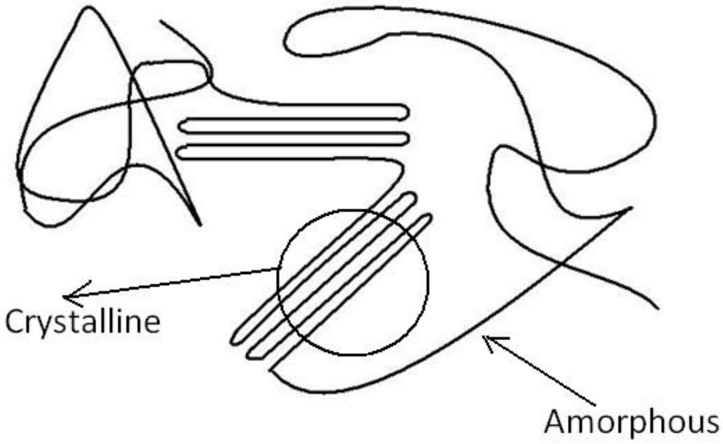


Figure 2.2 - Crystalline and Amorphous Phase

Even though much research has been done on polyethylene, according to Mills (2005), some details of crystalline polymer are unknown to this date. Therefore usually the polymer is developed empirically and the study of its microstructure follows later. In other words often times polyethylene is designed by trial and error before its mechanical properties are studied.

2.1.1 Chemical Bonding in Polymers

What gives polyethylene its uniform resistance to load is the covalent bonds between carbon molecules. Covalent bond is a chemical bond in which the electrons are shared between the atoms. The angular relations between atoms in a polymer determine the strength of the covalent bond. To create a polymeric chain each central atom needs to have at least two bonds with other atoms. However, two carbon atoms can have double or triple bonds.

Van Der Waals forces are responsible for the cohesive properties of polymer. These forces come from interactions of different molecules. According to Daniel (1989), there are two mechanisms that are in play when it comes to Van Der Waals forces: one is the mass attraction and the other is the momentary electron fluctuation. The strength of the Van Der Waals force relative to a covalent bond is usually about 1%. However, there are several factors that can help increase this value to 10%. Some of these factors are as follows:

- Proximity of molecules
- Increase in molecule size
- Multiple bonds between carbon atoms

Hearle (1982) described two general modes of deformation in polymer crystals:

1. Within chains of the polymer. This mode of deformation can be caused by:
    - Stretching of covalent chains: This stretching is strongly resisted and therefore does not account for much of deformation
    - Change of angle between adjacent covalent bonds, which is more easily accommodated that the previous mode
    - Rotation of one bond with respect to the next adjacent bond, which is easier than the two above modes.
2. Between chains
    - Refers to deformations that are perpendicular to the chains. This type of deformation happens with much less resistance than the ones within the chains.

2.1.2 Molecular Weight

Clegg and Collyer (1993) described the dependency of properties of polymers on the size of the molecules. Polyethylene is made of polymeric chains. Molecular weight distribution, MWD, of a material cannot be measured using one constant since each material consists of many different chains. A probability or distribution function can be used to quantify molecular weight. Figures 2.3 and 2.4 show a couple of the possible shapes the distribution function may have. Molecular weight distribution in Figure 2.3 is known as a unimodal distribution and MWD in Figure 2.4 is known as a bimodal distribution, having two peaks in its probability function.

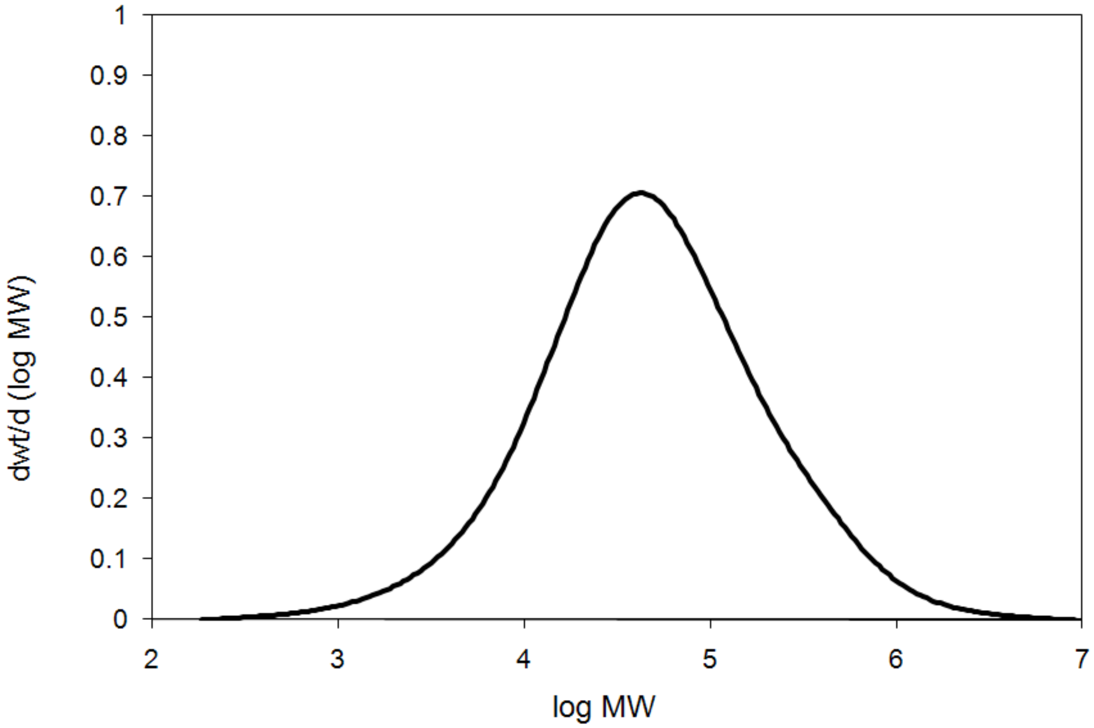


Figure 2.3 – Unimodal Molecular Weight distribution

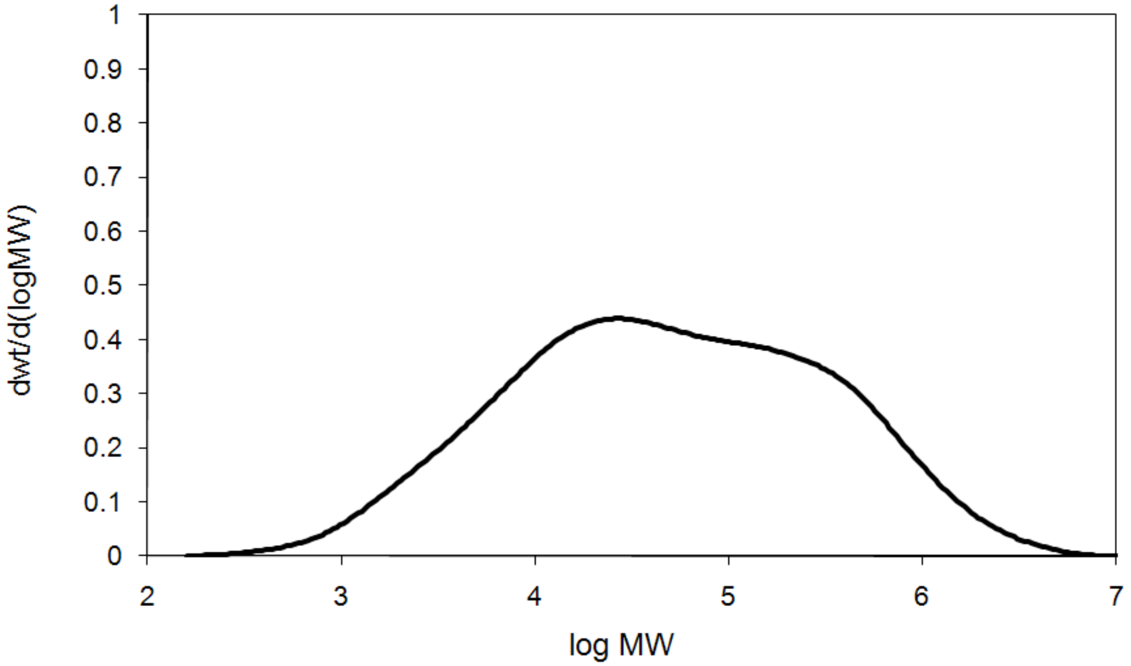


Figure 2.4 – Bimodal Molecular Weight Distribution

It can be concluded from Figures 2.3 and 2.4 that a molecular weight distribution can sometimes be approximated using a Gaussian distribution, but in general, it can be skew-symmetric and have a non-conforming shape.

Several quantities such as M_n, M_w and M_z are defined, in Equations 2.1, 2.2, and 2.3, to assign a number to a distribution. Here N_i refers to the number of chains having a mass equal to M_i.

- Number Average Molecular Weight Mn:

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\sum_i w_i}{\sum_i \frac{w_i}{M_i}} \tag{2.1}$$

- Weight Average Molecular Weight Mw:

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\sum_i w_i M_i}{\sum_i w_i} \tag{2.2}$$

- Z-Average Molecular Weight:

$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i} \tag{2.3}$$

2.1.3 Cross-linking and Branching of Polymers

When long chains form large three-dimensional networks atomic bonds form between primary chains. This phenomenon is referred to as cross-linking of polymers. It needs to be noted that the mechanism behind cross linking is very different from what causes crystallinity in polymers and in fact cross-linking always occurs in the amorphous phase of the polymer.

A polymer can have a number of secondary chains attached to a principal chain. These secondary branches will require the polymer to occupy more space since having branches will reduce the compactness. This phenomenon is referred to as branching in polymers. According to Cheng (2008), branching can occur between comonomers in the case of Short Chain Branching, SCB, or can be formed from side reactions during polymerization.

2.1.4 Crystallization and Lamellar Crystals

Crystallization refers to the process of chains folding into a plate-like structure referred to as a lamella. The thickness of a lamella is in the order of 10 nanometers. According to Daniels (1989), the length and the width of a lamella is usually about the same and much greater than the lamellar thickness. It needs to be mentioned that crystallinity in polyethylene is far from perfect and there are usually many defects in the general structure of the crystals. The samples of polyethylene in this study have crystalinity ranging between 50% and 60%.

2.1.5 Tensile Properties

Polymers that are not cross-linked usually neck when subjected to excessive tensile load. The term yield stress refers to the value at which the polymer starts to neck. The yield stress for polyethylene is highly sensitive to temperature when compared with almost all other structural materials. This value will depend on the rate of loading as well as on the magnitude of the stress. The response of stress to a controlled strain is usually not linear, but recoverable up to a limit. In semi-crystalline polymers the crystalline portion has much more rigidity than the amorphous phase.

The chains in a lamella cannot straighten up to accommodate strain as they are already straight. The chains in the amorphous phase can. When tension is applied to a sample the chains in the amorphous phase are responsible for the large portion of the elastic response. Plastic deformation occurs when crystals begin to slip against each other.

2.2 Macroscopic Behavior of Polyethylene

The response of polyethylene to stress is significantly time dependent. This response is usually divided in two portions. One is the elastic response which takes into account the change in strain due to a sudden increase or decrease in stress. The other portion of response, that is the remainder, is referred to as creep. Krishnaswamy et al. (1992) described how materials that exhibit both responses are further categorized into two groups: visco-elastic materials and visco-plastic materials. The difference between the two is clearly shown in Figure 2.5. Figure 2.5 corresponds to strains caused by a constant load applied at time zero and taken off at time t*. As shown in the figure, there is a delay in the recovered strain for visco-elastic material which indicates that portion of non-elastic strain or creep is not permanent. On the other hand, all of the non-elastic responses for visco-plastic materials are permanent and for that reason there is no delay in recovery of strain. Viscoplastic models are most suitable for high-temperature creep while visco-elastic models best describe ductile polymers.

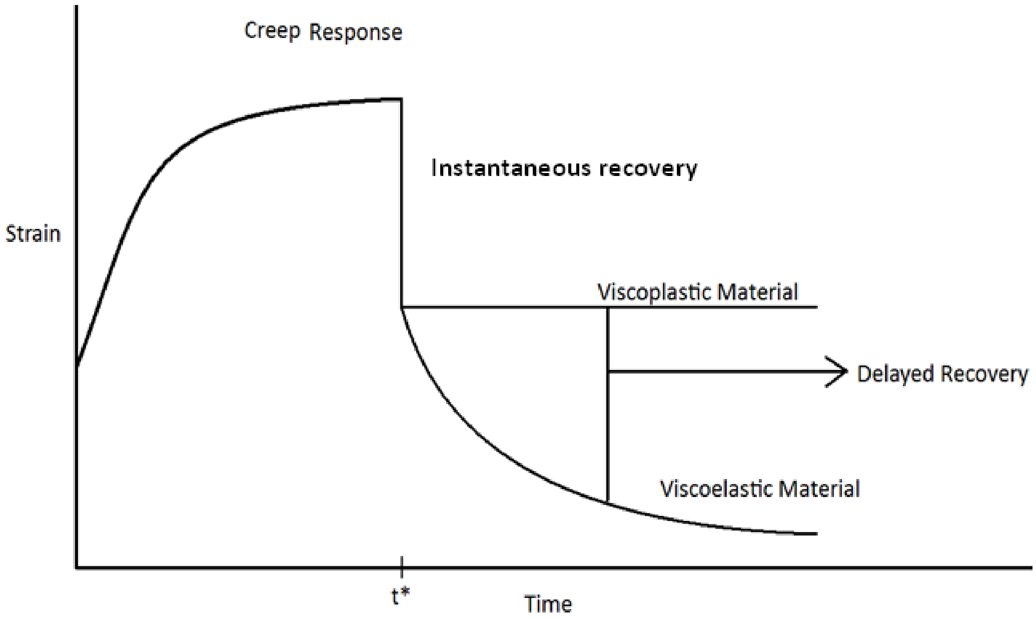


Figure 2.5 - Response of Visco-elastic and Visco-plastic Material to Step Loading – from Krishnaswamy et al. (1992)

2.2.1 Requirements for Constitutive Modeling

Once information on material behavior is known, a constitutive model can be evaluated to see if it conforms to the material response. Before examining existing models, it is necessary to know what is mathematically required to formulate a relationship between stress, strain and time.

Lockett (1972) described how it can be assumed that if the history of strain, ε, along with the information on how the material behaves during its lifetime and at any point, X, is given, then stress, σ, can be found as a function of time:

$$\sigma(X,t) = \underset{\tau=-\infty}{\overset{t}{F}}\{\varepsilon(X,\tau)\} \tag{2.4}$$

In Equation 2.4, F describes a functional, τ is referred to as the relaxation time, and t is the time at which stress and strain are examined. In this relationship “functional” suggests that the stress component can only be found when the strain history is known as opposed to simply knowing the value of strain. Here ε and σ can represent any of the tensor components. For linear, homogeneous, and continuous behavior the relationship can be reduced to:

$$\sigma(t) = \int_{-\infty}^{t} \zeta(t,\tau)\frac{d\varepsilon}{dt}(\tau)d\tau \tag{2.5}$$

$\zeta(t,\tau)$ is called the material response function that is, in general, dependent on time as the material can age. Assuming there is no aging, the relationship is further reduced to:

$$\sigma(t) = \int_{-\infty}^{t} \phi(t-\tau)\frac{d\varepsilon}{dt}(\tau)d\tau \tag{2.6}$$

Here ϕ is the stress relaxation function. An assumption can be made that changes in strain at a given time will have a direct effect only on the stress at times close to the time where the change in strain occurred. This assumption is called the assumption of fading memory. Using this assumption the stress relaxation function can be written as:

$$\phi(t) = \phi_\infty + \int_0^\infty R(\tau) e^{\frac{-t}{\tau}} d\tau \tag{2.7}$$

R here is called the relaxation spectrum. When the stress relaxation function was defined we made the assumption that if strain as a function of time is known then stress can be found. The relationship seen in Equation 2.7 can also be defined so that if stress as a function of time is known then the strain can be found:

$$\varepsilon(t) = \int_{-\infty}^{t} \psi(t-\tau) \frac{d\sigma}{dt}(\tau) d\tau \tag{2.8}$$

In Equation 2.8, ψ is the creep or compliance function. The above formulations can be extended to 3D by using multiple relaxation functions, for example:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} \phi_{ijkl}(t-\tau) \frac{d\varepsilon_{kl}}{dt}(\tau) d\tau \tag{2.9}$$

ϕ_{ijkl} are stress relaxation functions for the 3D model.

2.2.2 Linear Visco-Elastic Models

Hook's elastic model is represented with a simple spring. This model implies that there is a one-to-one relationship between stress and strain and that the strain history has no impact on the stress. Therefore according to this model if a stress is kept constant the strains will remain constant forever. Isaac Newton modeled fluids by assuming that there is a linear relationship between shear stress and the time-rate of shear strain. In his model shear stress is equal to viscosity times the time-rate of shear strain. Therefore according to this model when a fluid is subjected to a constant shear stress the shear strain will grow at a constant rate forever. This model is usually represented with a dashpot.

Most materials exhibit both elastic and viscous behavior. The elastic behavior is modeled using a spring and the viscous behavior using a dashpot. (Ferry et al. 1970). There are many ways to assemble springs and dashpots to model material behavior. Maxwell fluid is one element that is assembled employing one spring and one dashpot. In this thesis Maxwell fluid is shown in Figure 2.6. This element will exhibit an instantaneous response to a shock in stress and it is also capable of unlimited deformation under finite stress. Here ε refers to strain, E refers to modulus of elasticity, and η refers to viscosity of the dashpot. Equation 2.10 shows the governing differential equation for Maxwell fluid.

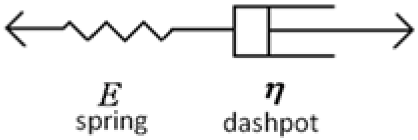


Figure 2.6 – Maxwell Fluid

$$\epsilon_{\mathrm{total}} = \epsilon_{\mathrm{Spring}} + \epsilon_{\mathrm{Dashpot}} \quad \text{Therefore: } \frac{d\epsilon_{\mathrm{total}}}{dt} = \frac{d\sigma/dt}{E} + \frac{\sigma}{\eta} \tag{2.10}$$

Kelvin solid is another way to assemble one dashpot and one spring in parallel as shown in Figure 2.7. In this element the strain is the same for the dashpot and spring and sum of the two stresses is equal to the applied stress:

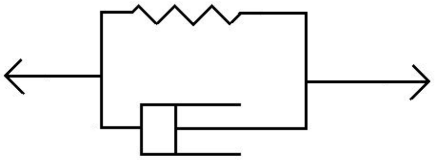


Figure 2.7 – Kelvin Solid

$$\sigma_{total} = \sigma_s + \sigma_d = E\varepsilon + \eta\frac{d\varepsilon}{dt} \tag{2.11}$$

If multiple Kelvin elements are assembled together with a spring, as shown in Figure 2.8, the governing equation will be:

$$\varepsilon(t) = \int_0^t \left\{ \frac{1}{E_0} + \sum_{i=1}^{N} \frac{1}{E_i}\left\{1 - \exp\left(-\frac{t-\tau}{\tau_i}\right)\right\}\right\} \dot{\sigma}(\tau)\,d\tau \tag{2.12}$$

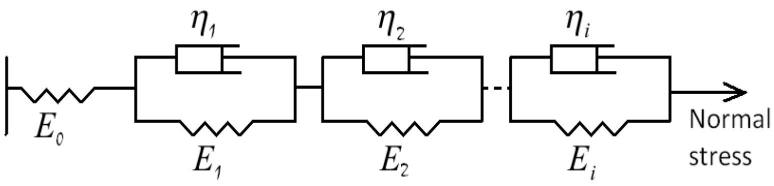


Figure 2.8 - Multi-Kelvin Model

τ in this formulation is referred to as relaxation time and is defines as:

$$\tau_i = \frac{\eta_i}{E_i} \tag{2.13}$$

2.2.3 Non-Linear Visco-elastic Behavior

Compliance function was introduced in section 2.2.1. For a simple creep test, in which a constant tensile stress is applied to the specimen, the compliance function can be found by dividing the values of strain, as a function time, by the constant stress that is applied. Figure 2.9 shows a typical compliance curve.

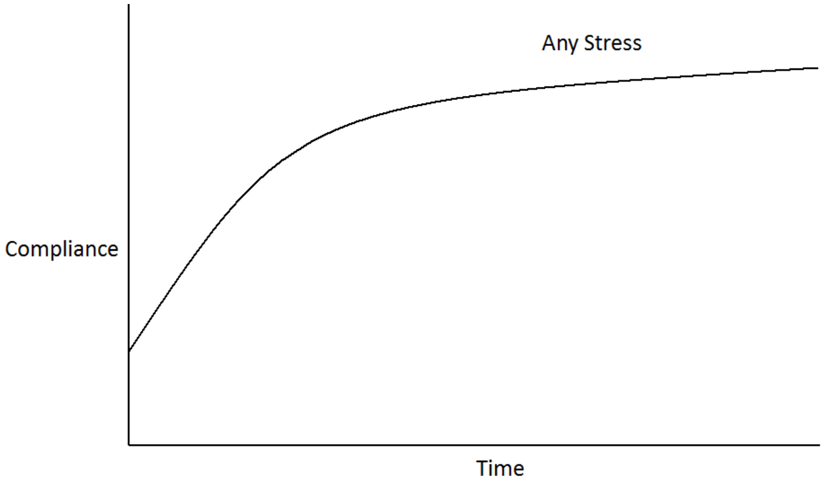


Figure 2.9 - Typical Compliance Curve

Linear visco-elastic materials are those that can be modeled with one compliance function. For many materials however one compliance function is not sufficient to obtain strain as a function of time for any given constant stress because the compliance function itself is dependent on the stress level. In other words the compliance curve is a function of stress. Materials with such property are said to exhibit non-linear behavior. Figure 2.10 shows schematically how compliance can be a function of stress. In this figure the constant stress is increased from A to B to C.

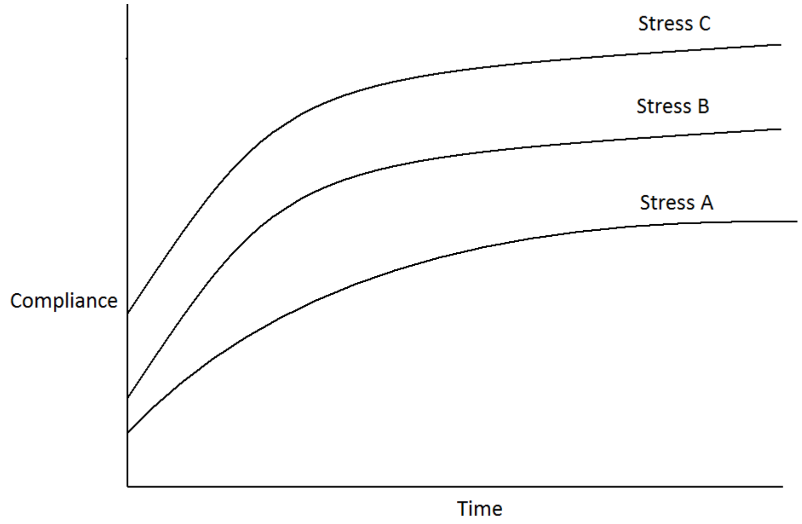


Figure 2.10 - Compliance as Function of Stress.

When different compliance curves that represent the same material's response at different stresses have the same shape they are said to be separable. Mathematically this statement means that strain at a given time for a given constant stress can be found by multiplying functions "h" and "f" in:

Strain = h(Stress) x f(time)

However, if the shape of the compliance curves representing the same material at different stress levels changes from one stress to another, then the two variables, stress and time, cannot be separated and strain can only be represented in the general from using function "g":

Strain = g(Stress, Time)

Many experiments have been conducted on polyethylene and it has been concluded that polyethylene exhibits non-linear behavior. There have been several formulations proposed for constitutive modeling of non-linear polyethylene, among which are: the adaptive springs model developed by Drozdov and Kalamkarov (1996), nonlinear time-dependent formulation proposed by Schapery (1969), Krishnashwamy et al.(1992), and Zhang and Moore (1997).

2.3 Failure of Polyethylene

Ductile and brittle failure both can occur in polyethylene. Some conditions can result in crack propagation and catastrophic failure while others can cause ductile yielding. It is important to mention the two modes of failure are competitive processes and occurrence of one means that the other will not occur (Hearle, 1982). Ductile failure happens in short time-intervals and at high stress (Cheng, 2008). Figure 2.11, taken from Cheng (2008), shows the steps involved in ductile yielding of polyethylene. At small strains, lower than 0.05 and before material yielding, the stresses are mainly taken by the crystalline phase. After yielding, which occurs at a strain around 0.05, and before strain hardening, which occurs at a strain around 1.5, the stress grows at a much slower rate. The deformations in this region is due to a combination of amorphous phase rearranging itself and crystal lamellae slipping against each other. At strain around 1.5 a phenomenon referred to as strain hardening starts to happen. When strain hardening happens the amorphous phase is stretched to its full length and further deformations are accommodated by breakage of crystals, and unfolding of lamellae. As strain is increased beyond strain hardening, polyethylene eventually breaks in two pieces.

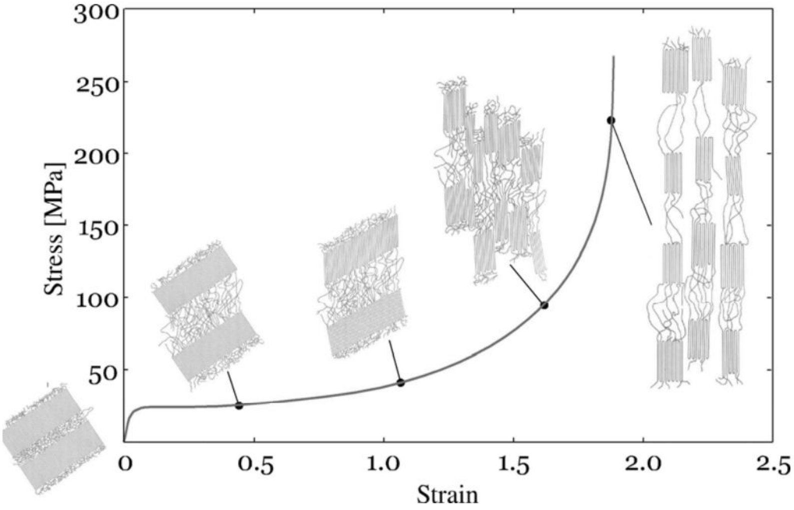


Figure 2.11 – Stretching of Polyethylene – From Cheng (2008)

Brittle failure in polyethylene occurs when the material experiences low stress for a long period of time. During this process the amorphous phase gets stretched causing the inter-lamellar links to gradually untangle and eventually fail in a sudden way. Figure 2.12, taken from Cheng (2008), demonstrates this process.

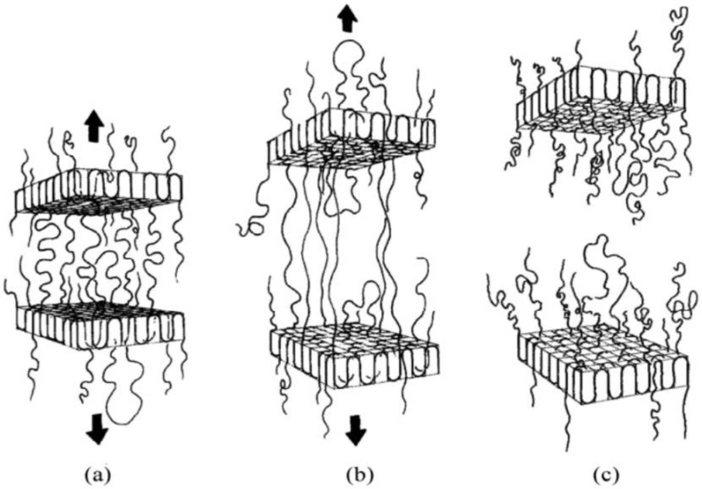


Figure 2.12 - Brittle Failure: (a) lamellae start to pull away, (b) amorphous phase stretched tight, (c) clean break of lamellae. – From Joy (2008)

3.0 Experimental Program

Six polyethylenes were chosen for the experiment: PE1, PE4, PE7, PE8, PE9, and PE10. The six polyethylenes covered a wide range of environmental stress cracking resistance (ESCR), which was measured and analyzed in previous work by Cheng (2008). Detailed information on the molecular properties of the six polyethylenes is given in Chapter 6.

ESCR is a failure mode that is related to long-term behavior of PE. It occurs when polyethylene is exposed to certain chemicals and is under stress. ESCR for the polyethylene samples vary from 4 hours to more than 3000 hours. The measurements were obtained by Cheng (2008). The failure mechanism is believed to be chain entanglements unraveling. The failure is not due to a chemical reaction, and is purely mechanical. The function of exposure to the chemical is to speed up the unraveling of the chains. Failure is sudden and brittle.

The following tests on six polyethylenes were done in order to assess the long term behavior of a given polyethylene having certain molecular properties:

1. Strain-rate controlled tests.
2. Short-Term creep tests.
3. Longer-Term creep test.

The tests were performed to get a general idea of how polyethylene behaves and also to see how different molecular properties influence mechanical properties.

The strain-rate controlled tests were performed because they are standard tests that are performed to get the basic mechanical behavior of any material. Short term creep tests were performed at different stress levels for all six polyethylenes. The duration of the tests was eight hours. After observing the short term creep behavior of the six polyethylenes, three of them were chosen for longer creep tests. The duration of these tests varied from 4 to 14 days.

3.1 Specimens

All tests that were carried out in this research were uniaxial tension tests. When most materials are tested in tension, they are shaped into dogbones as shown in Figure 3.1 and then subjected to tension along their length. The dogbones used for this research were all made according to American Standards for testing and Materials' (ASTM) D-638-03 (2007). The shape facilitates a gradually varying cross sectional area. Therefore:

1. There is no significant stress concentration anywhere along the dogbone.
2. The centre of the dogbone carries the highest stress and has the highest probability of failure.

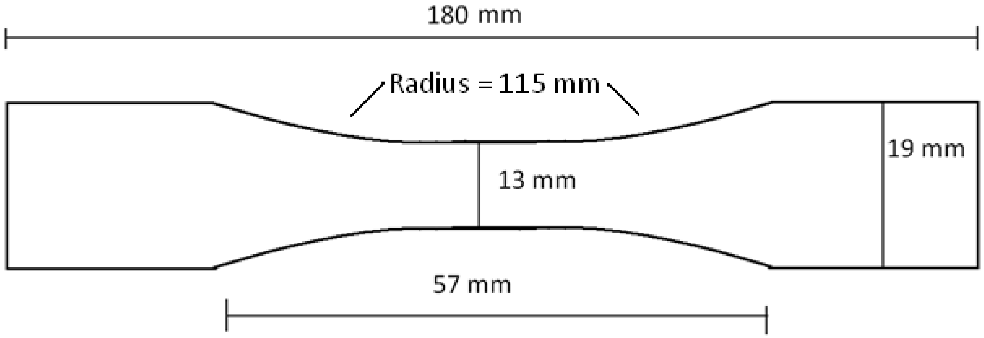


Figure 3.1 – Typical Dogbone Dimensions

The dogbones used in this experiment were 19 mm wide at the ends, 13 mm wide at the centre, and 180 mm long. The thickness varied between 5 to 6 mm. All dogbones were made in-house. They were all made from polyethylene resins. The raw material is shown in Figure 3.2.

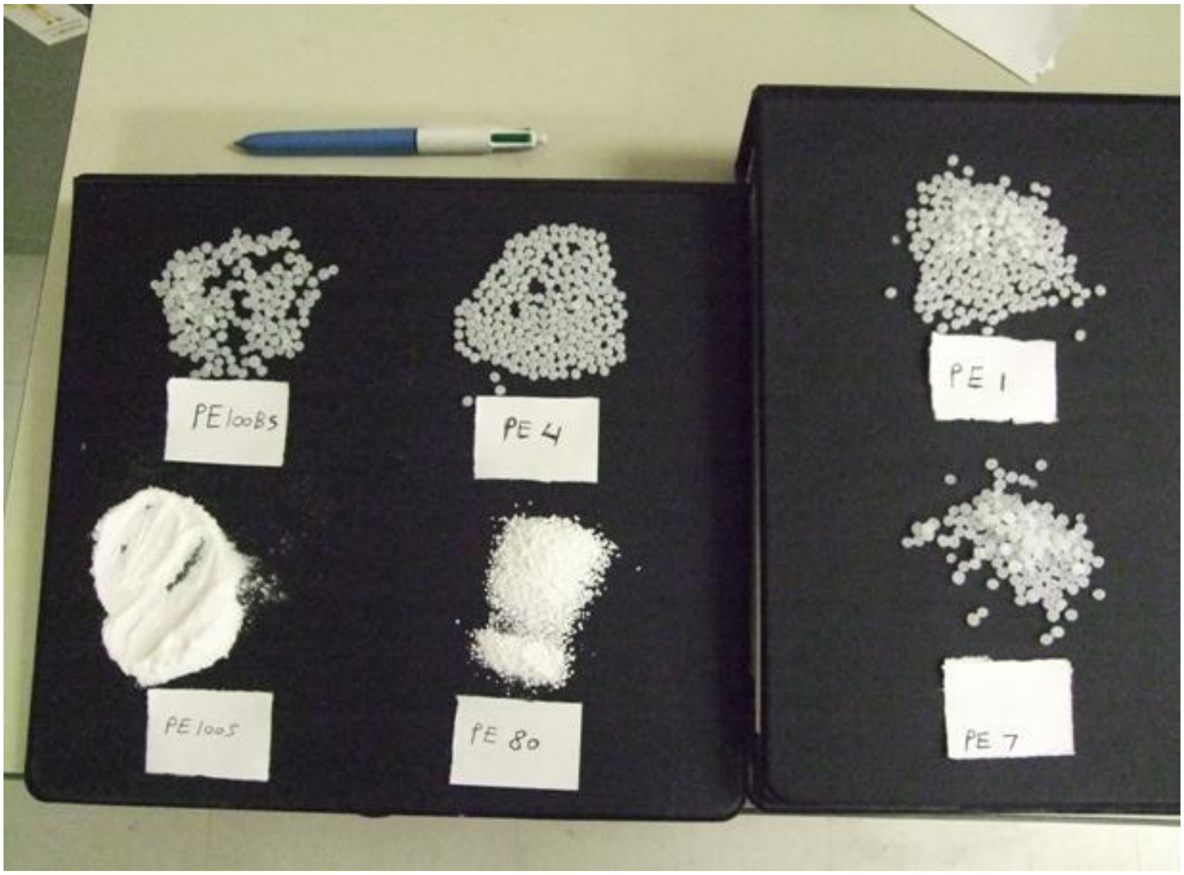


Figure 3.2 - Polyethylene Pellets

To prepare the dogbones, the pellets shown in Figure 3.2 were melted between two metal plates, 180 mm by 180 mm, and a metal frame, thickness 6 mm, at 190°C and compressed at an initial stress of 7.6MPa. Figure 3.3 shows the metal plate. 190°C was maintained for 3 minutes, then heating was stopped, but compression maintained until the system reached room temperature.

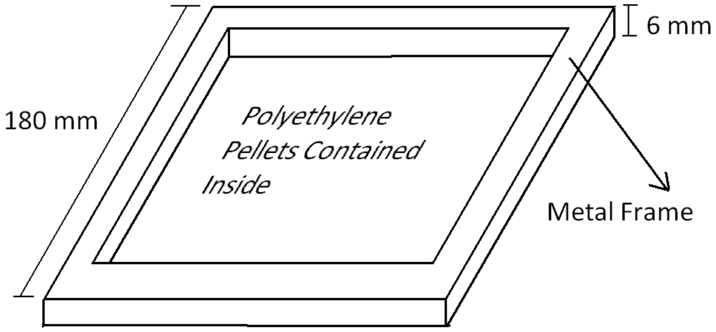


Figure 3.3 – Metal Frame used for Melting the Pellets

A few observations are worth mentioning:

1. The void ratio of the loose polyethylene resin before melt, defined as volume of air in the resins over volume of polyethylene, varies roughly between 40% and 100%. Therefore when poured into the mold one needs to take into account the reduction in volume as polymer is melted. Raw materials with larger pellets had lower void ratios. It is suspected that it is so because the large pellets were shaped like disks as opposed to the smaller ones that were shaped as spheres.
2. When melted polymer is under compression it will start to flow out of the box until all excessive mass has gone out of the mold and compression will then be carried by the frame between the plates. In conclusion it can be said that as long as the controlled pressure of 7.6 is being gradually reduced there is small leakage of polymer and the technician can assume significant portion of compression is taken by the polymer. At the beginning of the project, a few times not enough material was placed between the two metal plates. As a result compression would not drop from the controlled value of 7.6MPa since it was being carried by the frame containing the polymer. Those plates were not used for testing.
3. As molten polymer cools, its viscosity is dramatically reduced and it will be harder for it to leak out of the mold, and eventually will stop.

After the plates were cooled to room temperature an average shrinkage of 2.7 mm per 182 mm was observed. Some plates shrank more than others. Table 3.1 provides the shrinkage for all resins.

Table 3.1 – Shrinkage in polyethylene plates

Number	**1**	**2**	**3**	**4**	**5**	**6**
Name	PE1	PE4	PE7	PE8	PE9	PE10
Shrinkage (mm)	2.8	2.9	2.4	2.5	2.7	2.7
Shrinkage (%)	1.538	1.593	1.319	1.374	1.484	1.484

To shape the dogbones, the polyethylene plates were cut using a machine saw into 19 mm wide strips. The strips were then worked into dogbones using a milling machine and a standard dogbone guide for cutting. Since the material shrank and it was cooled under compression in a mold it is known that there are residual stresses. These residual stresses would tend to deform the strips when they are cut away from the plate as the cutting creates free surfaces.

There were no visible changes in geometry when the strips were cut. In other words, the strips remained straight after the cut. Therefore residual stresses were not large enough to deform the strips in a visible way.

It needs to be noted that the polyethylene samples that were created in this research were expected to be anisotropic because cooling starts at the edges and also because the material was cooled under uniaxial compression normal to the plate.

There is no way to directly measure how much error is introduced from varying cooling rate inside the plate, however since the same procedure is used for all plates there should be very little error in a relative comparison of the results.

3.2 Strain Controlled Tests – Test 1

Strain controlled test uses a controlled strain on the specimen and measures the stress that is caused by the imposed strain. Each material exhibits a different response and a different curve is generated for each material. The curves obtained from this test also vary with the rate of strain or displacement. For this study, a strain rate of 7 mm per minute, suggested in the ASTAM Standard D638-03, and a clip gauge of 2 inches were used. Figure 3.4 shows the schematic setup, and the MTS machine used for the test. The load cells measured the load that was imposed on the dogbone. The stresses were calculated based on the total load and knowing the cross sectional area of the dogbone.

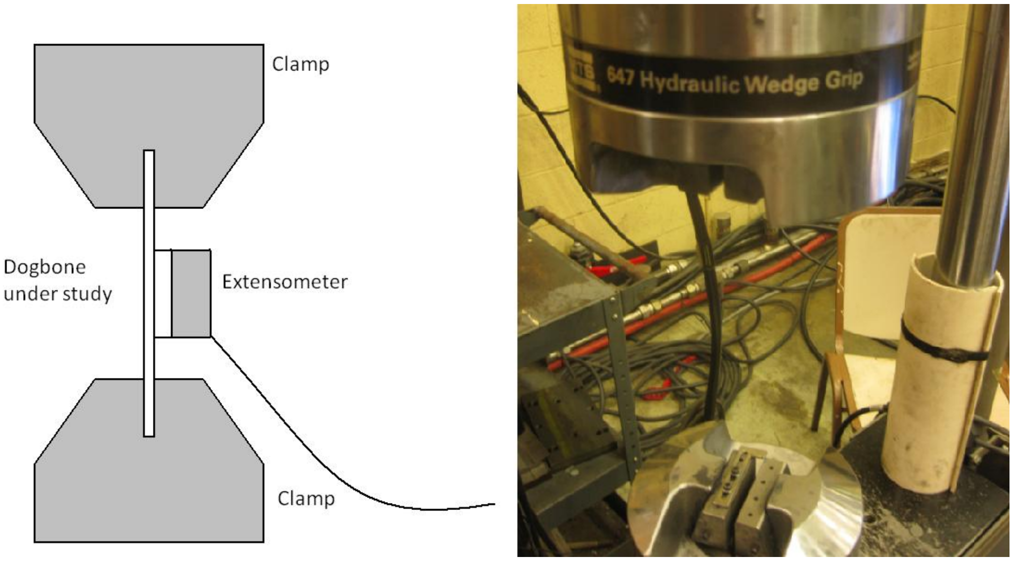


Figure 3.4 – Schematic Setup and MTS Machine used for Test 1

3.3 Eight Hour Creep Tests - Test 2

Creep test refers to a test in which a constant engineering stress is applied to the specimen and the resulting strain is measured at the centre of the specimen as a function of time. Engineering stress refers to a stress that is defined as the applied force divided by the cross section of the original shape. It ignores the changes in geometry which occur under stress. Engineering strain is a good measure when the strains are small. The strains that are presented in this thesis do not exceed 6%, and therefore using engineering strain is appropriate.

To create a constant stress in the specimens, an assembly of a lever arm and two clamps was used as shown in Figure 3.5. The photo of the setup is taken from Liu (2007) who used the same frame. The load was magnified through the lever arm by a factor of 10 and then applied to the dogbone. The dogbone was fixed at the end using two grips. To measure the strain an extensometer of gauge length equal to 2.54 mm was attached to the dogbone at the centre using rubber bands

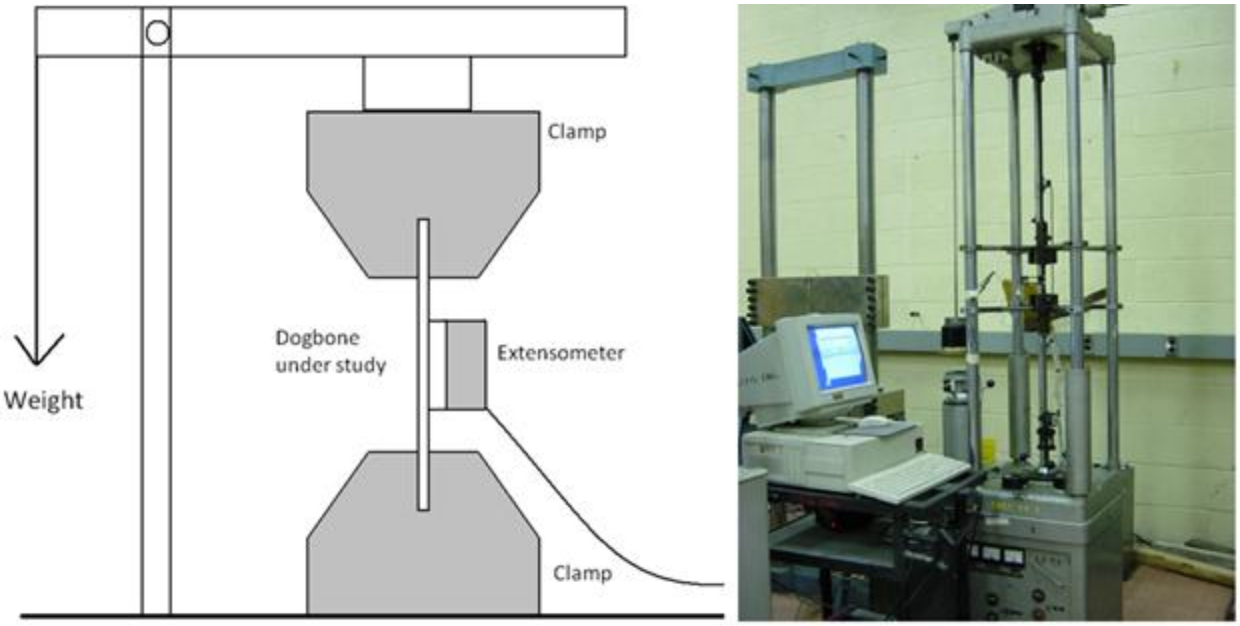


Figure 3.5 – Setup for Test 2

All 6 polyethylene samples were tested at 5 different loads of: 2, 4, 6, 8, and 10MPA for at least 8 hours and the results are presented in Chapter 4.

3.4 Long Term Tests – Test 3

From the 8 hour creep tests, it was observed that among all stress levels some materials shared consistently higher strains than others. Due to time constrains not all polyethylenes could be tested long term. Therefore 3 out 6 were chosen for long term tests so that there were one “good”, one “medium”, and one “bad”. Section 4.3 presents the measured long-term data and discusses the findings.

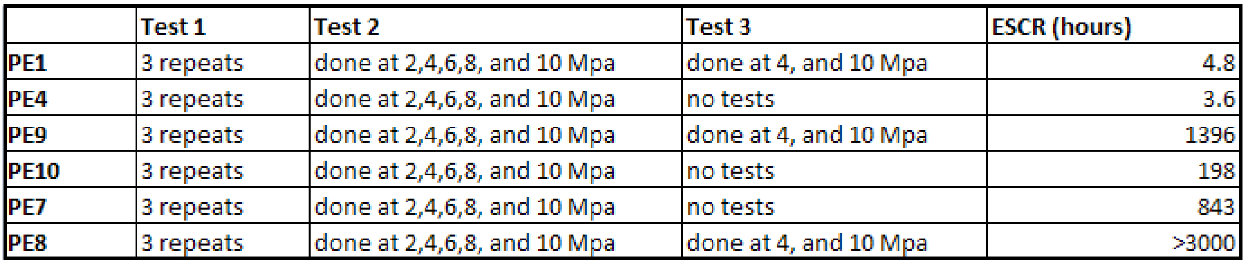
3.5 Summary of Tests Performed

This section summarizes the tests performed for the chosen polyethylenes. Test 1 was performed for all polyethylenes three times and short term creep test was done for all six polyethylenes at 2,4,6,8 and 10MPa. Test 3, which is the long-term creep test, was done for PE1, PE8 and PE9 at 4MPa and 10MPa. Only three resins were chosen for the long-term test, test 3, due to time constraints. To choose the three samples out of six the following methodology was used:

It had been found from short-term creep tests and also from their ESCR value that PE1 and PE4 had very similar properties. Hence they were grouped together as one type of PE, and only PE1 was considered for the long-term test. From the four remaining polyethylenes, PE7, PE10, and PE8 were grouped together since they had similar short-term creep properties and relatively large ESCR. From this group PE8 was chosen for the long-term test, because it was the least stiff material. PE9 was not grouped with any other polyethylenes because it has short-term creep properties similar to PE1 and PE4, but unlike those two it has a much larger ESCR, equal to 1396 hours. For this reason PE9 was also chosen for the longer-term test.

Table 3.2 summarizes the test performed on the samples along with their respected ESCR values obtained by Cheng (2008). Repeats in Table 3.2 refer to independent replicates.

Table 3.2 – Tests performed on Polyethylenes



	Test 1	Test 2	Test 3	ESCR (hours)
PE1	3 repeats	done at 2,4,6,8, and 10 Mpa	done at 4, and 10 Mpa	4.8
PE4	3 repeats	done at 2,4,6,8, and 10 Mpa	no tests	3.6
PE9	3 repeats	done at 2,4,6,8, and 10 Mpa	done at 4, and 10 Mpa	1396
PE10	3 repeats	done at 2,4,6,8, and 10 Mpa	no tests	198
PE7	3 repeats	done at 2,4,6,8, and 10 Mpa	no tests	843
PE8	3 repeats	done at 2,4,6,8, and 10 Mpa	done at 4, and 10 Mpa	>3000

4.0 Tensile Tests Results

As discussed in Chapter 3 three types of tests were performed. The obtained results are discussed in this chapter.

4.1 Stress-Strain Tests – Test 1

Figures 4.1 to 4.6 provide the stress-strain curves obtained from pulling the sample at a rate of 7 mm per minute as ASTM D638-03 suggests. All graphs except 4.3 show good repeatability. Several observations are worth noting:

- Maximum stress that the materials can withstand varies between 20MPa and 25MPa
- Maximum stress is achieved at around 10% strain for all samples

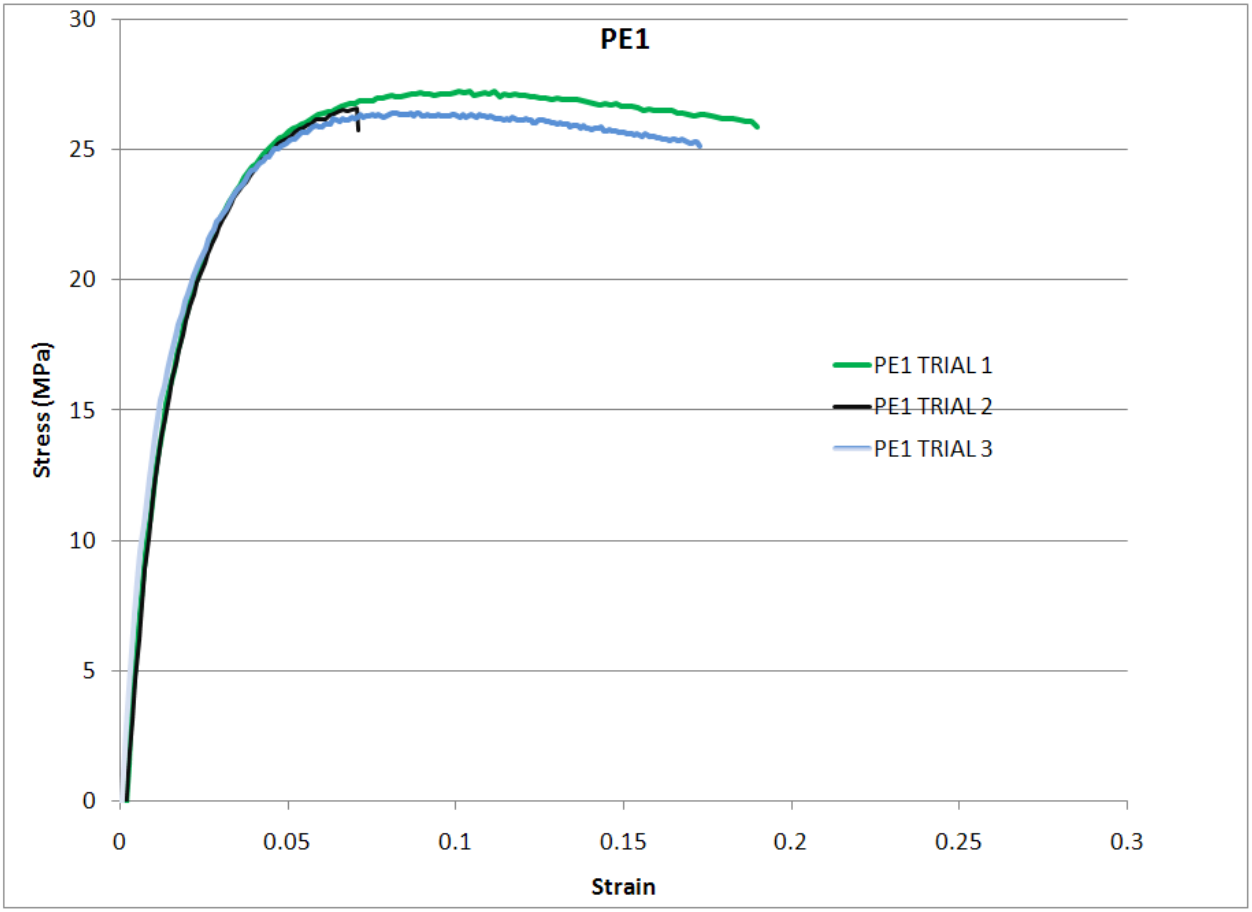


Figure 4.1 – Strain-Controlled Tests for PE1

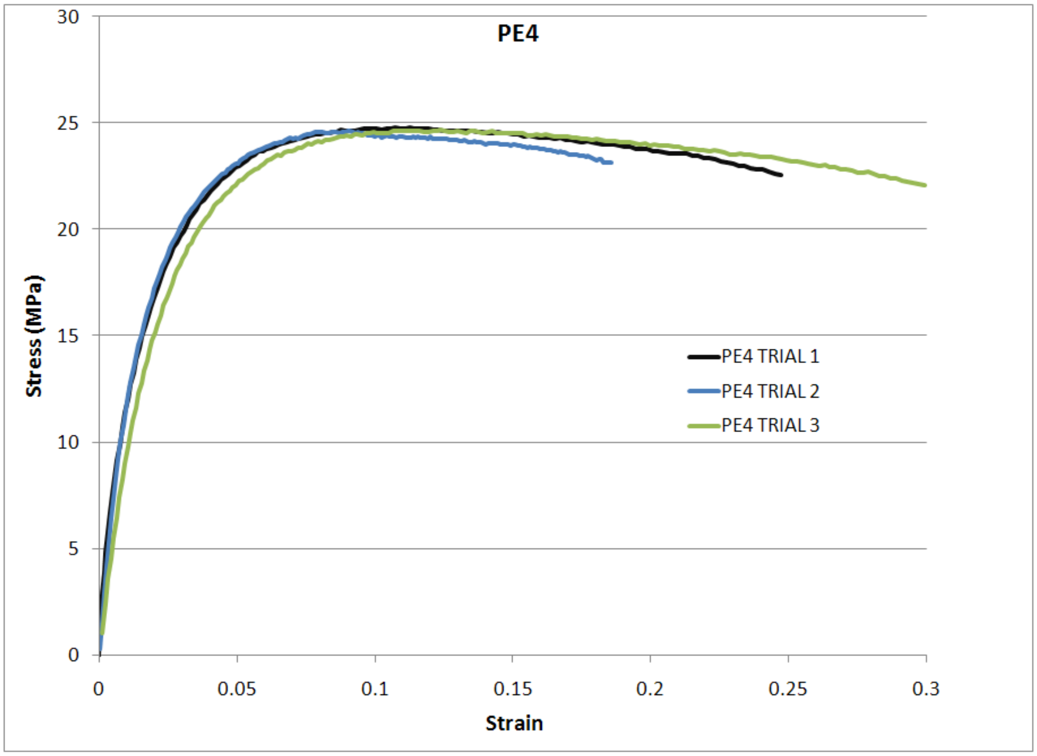


Figure 4.2 – Strain-Controlled Tests for PE4

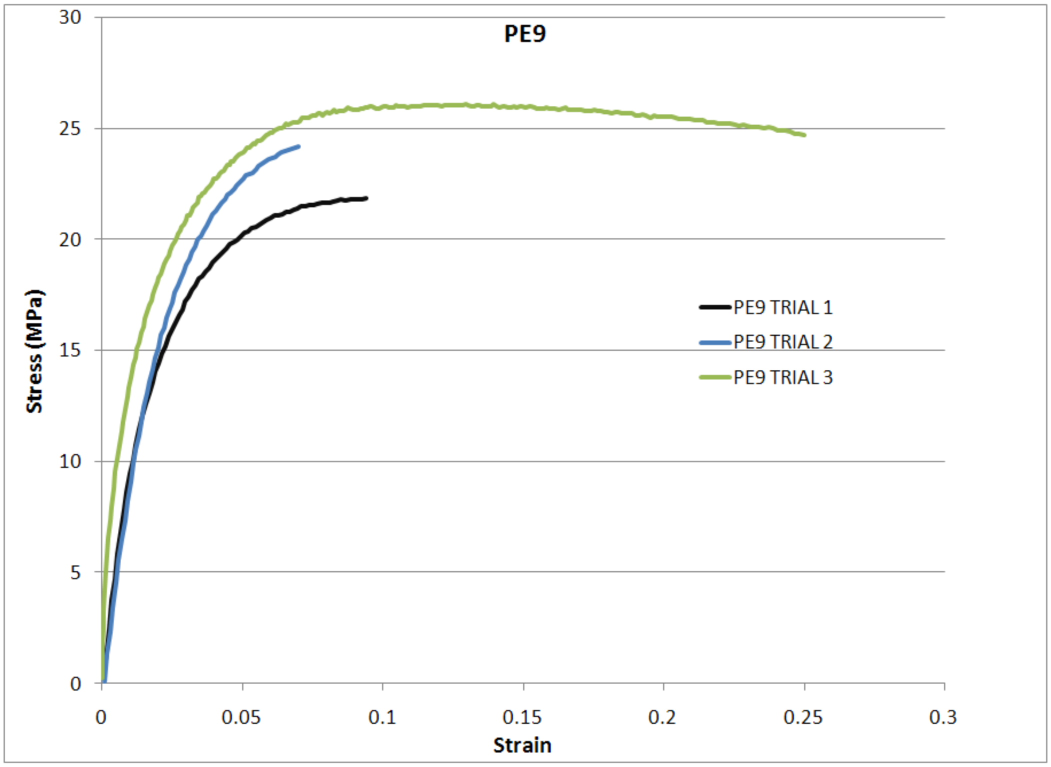


Figure 4.3 – Strain-Controlled Tests for PE9

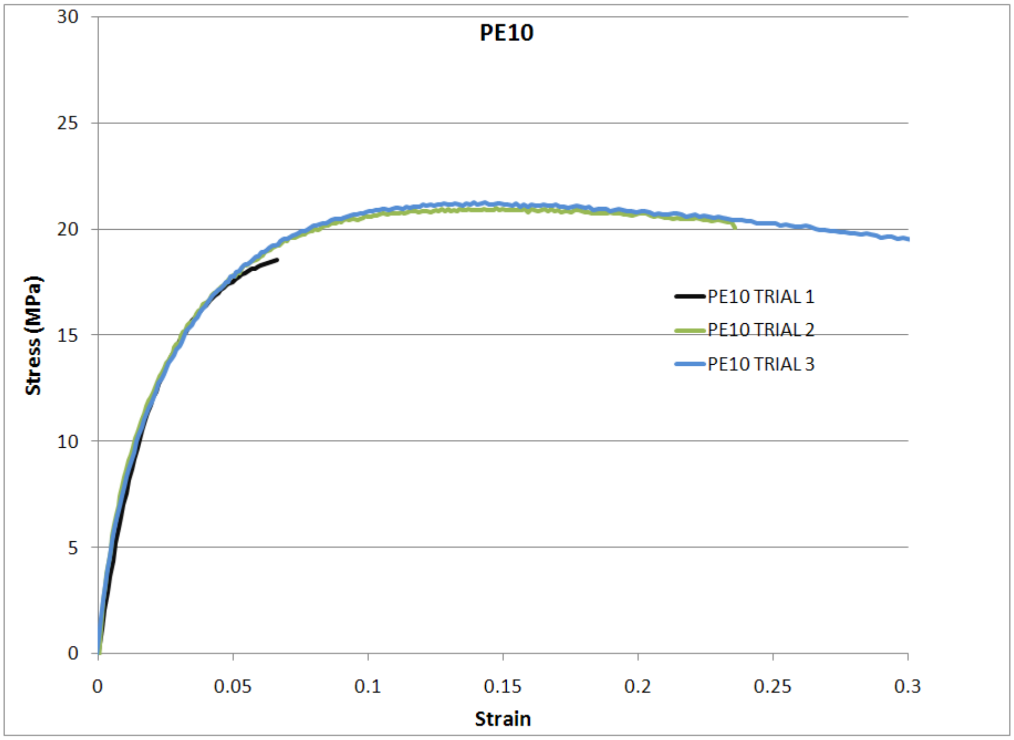


Figure 4.4 – Strain-Controlled Tests for PE10

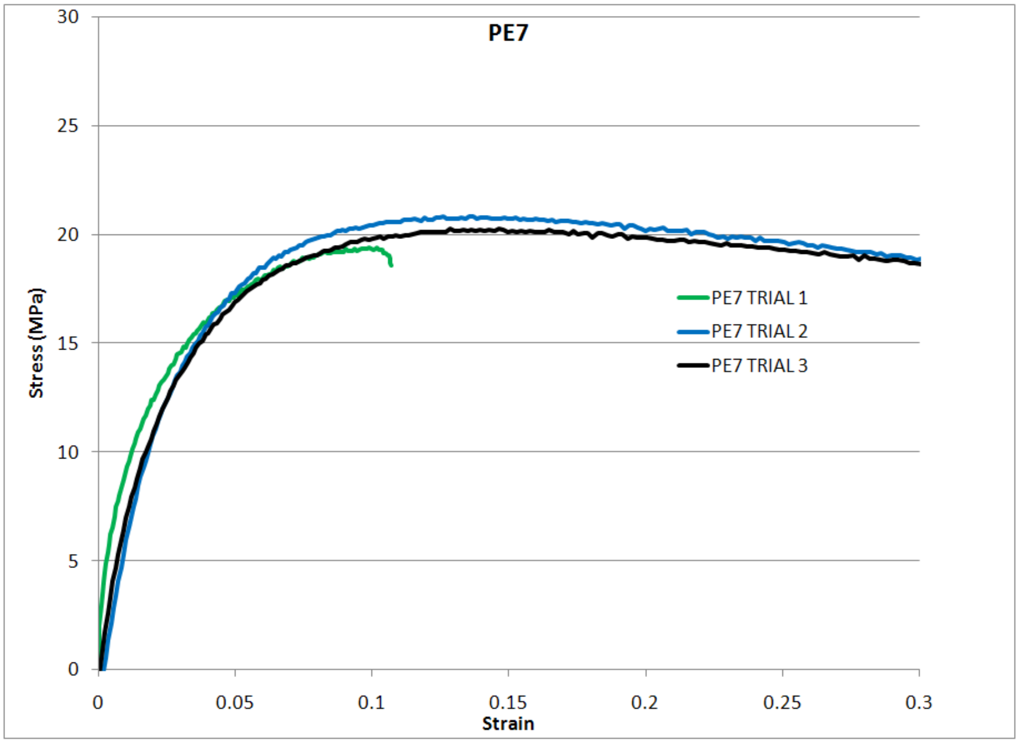


Figure 4.5 – Strain-Controlled Tests for PE7

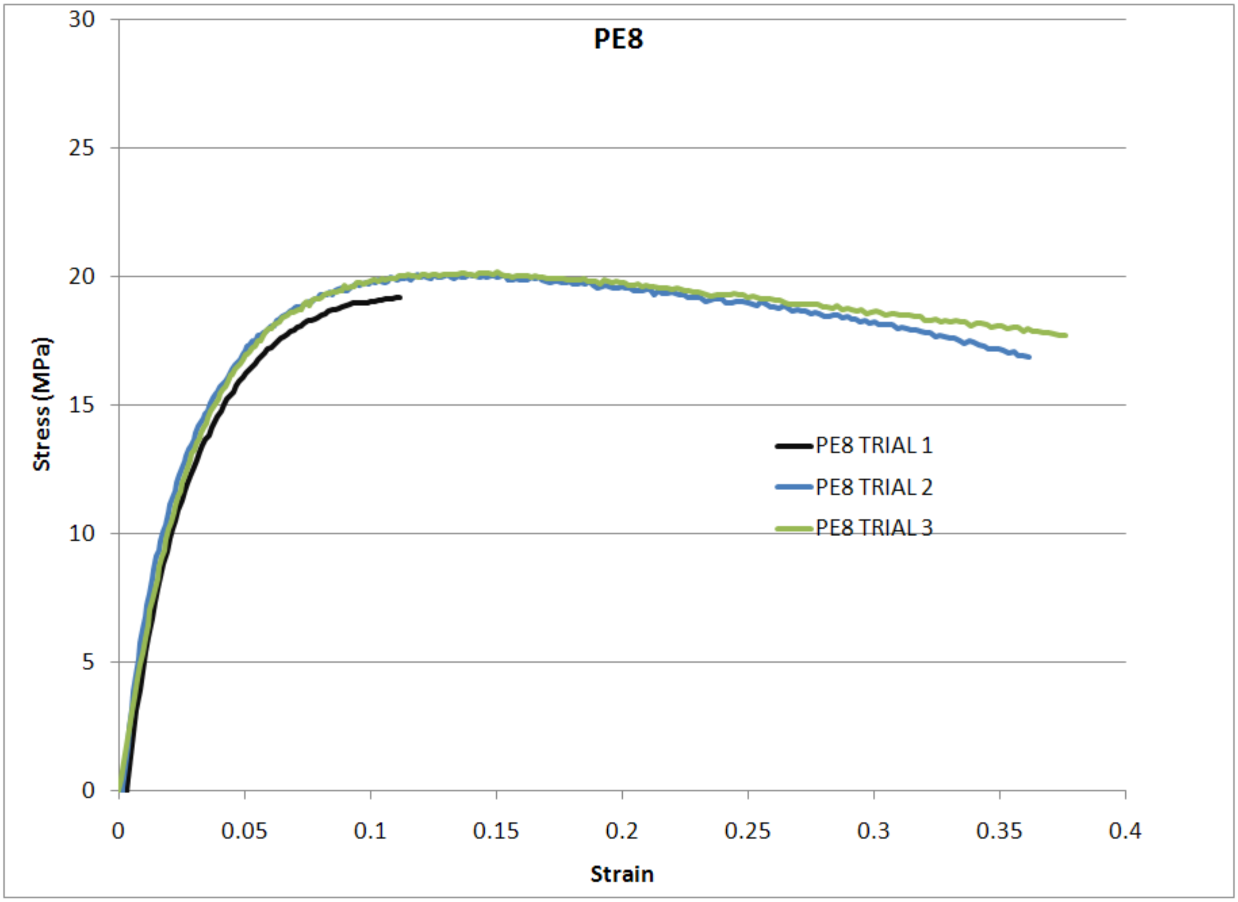


Figure 4.6 – Strain-Controlled Tests for PE8

To compare the 6 resins on one graph, Figure 4.7 is provided. This figure shows one stress-strain curve from each PE. As it can be seen on Figure 4.7 PE1, PE4, and PE9 have similar curves and can be grouped as stiffer materials: Group 1, having good short-term performance. PE7, PE8, and PE10 on the other hand can be grouped as softer materials, having lower stiffness and lower yield stress: Group 2, having poor short-term performance. It can be seen that the highest stiffness and yield stress are observed for PE1 and these values are decreasing for PE4, 9, 10, 7, and 8, respectively.

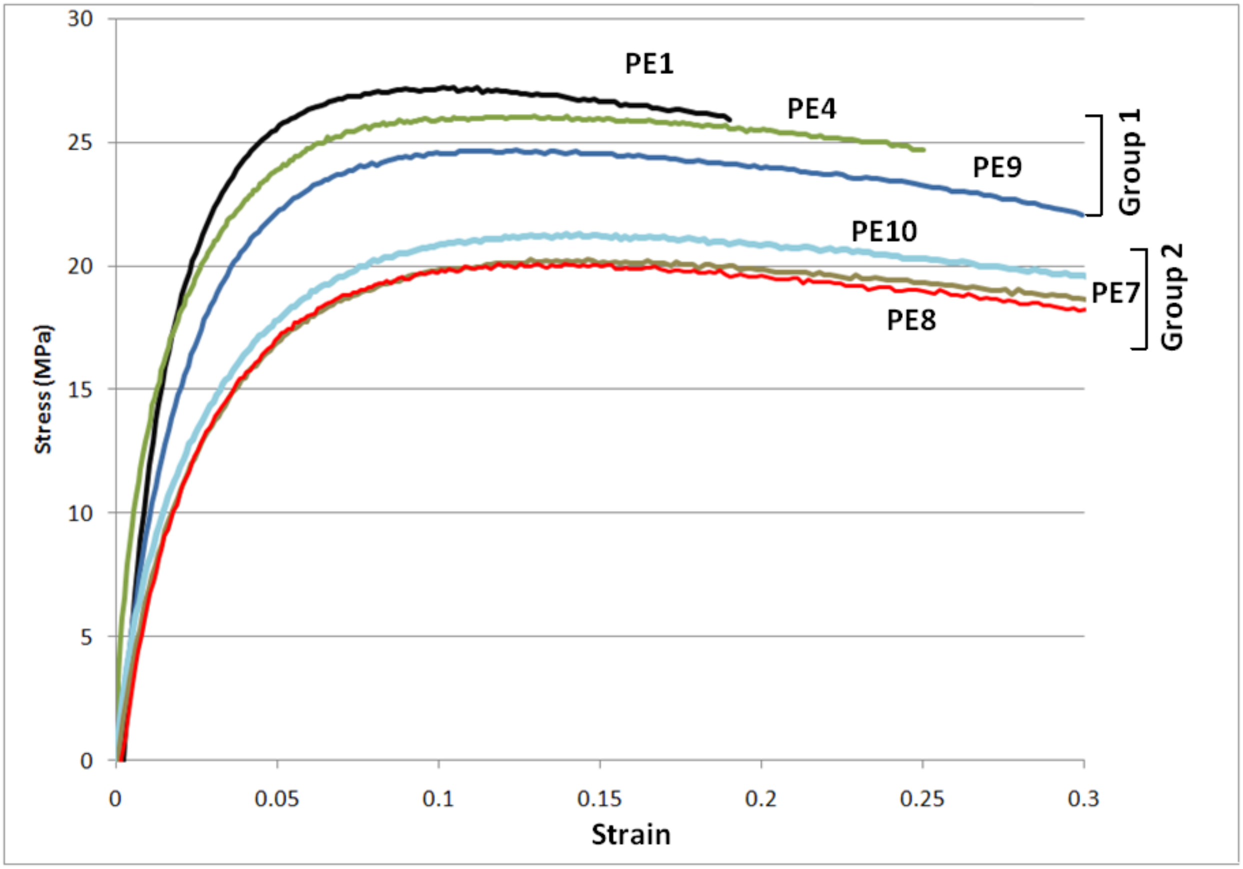


Figure 4.7– Strain-Controlled Tests for all 6 samples

4.2 Eight Hour Creep Tests – Test 2

4.2.1 Creep Tests

Figures 4.8to 4.12 contain the results for the 8 hour creep-tests. The sampling time was 5 seconds for the first 5 minutes and then it was changed to 5 minutes. Several general observations are to be noted:

- All six samples exhibit the same type of behavior, as expected.
- As stress level increases the curves become smoother and less noise in the data is observed.
- The instantaneous strain is usually about 50% of the strain after 8 hours.
- “Strain” refers to the engineering strain in all creep curves in this thesis. In other words it is assumed that the cross sectional area is constant throughout the test.

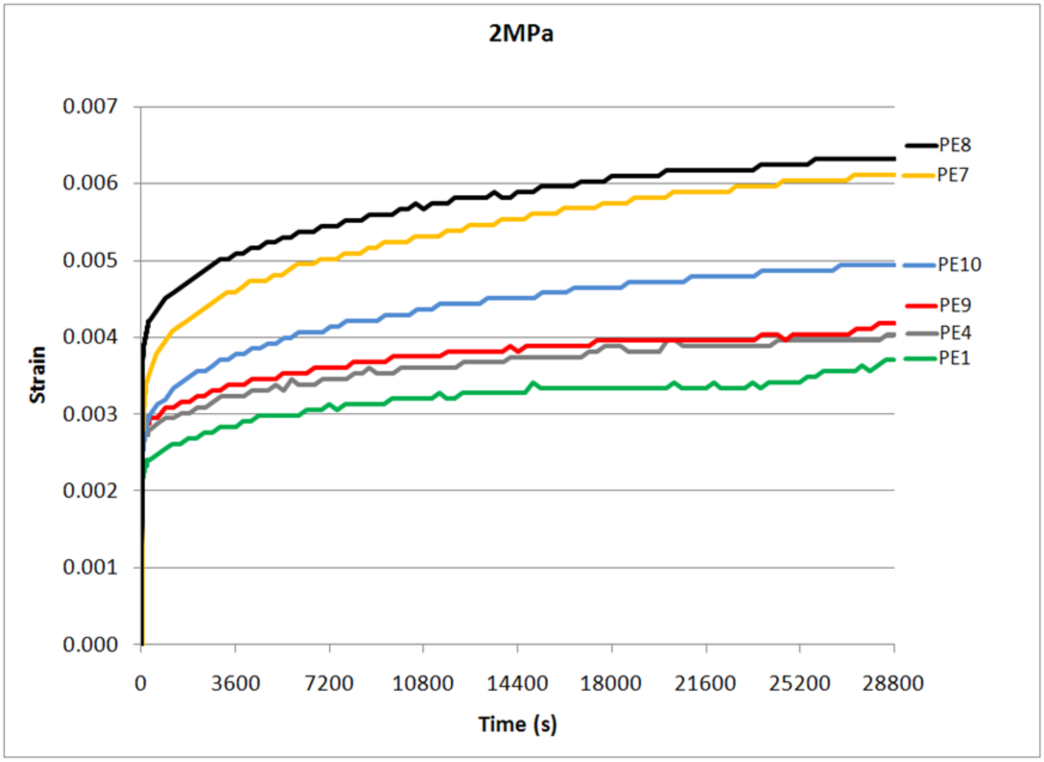


Figure 4.8 - 8-Hour Creep Tests at 2 MPa

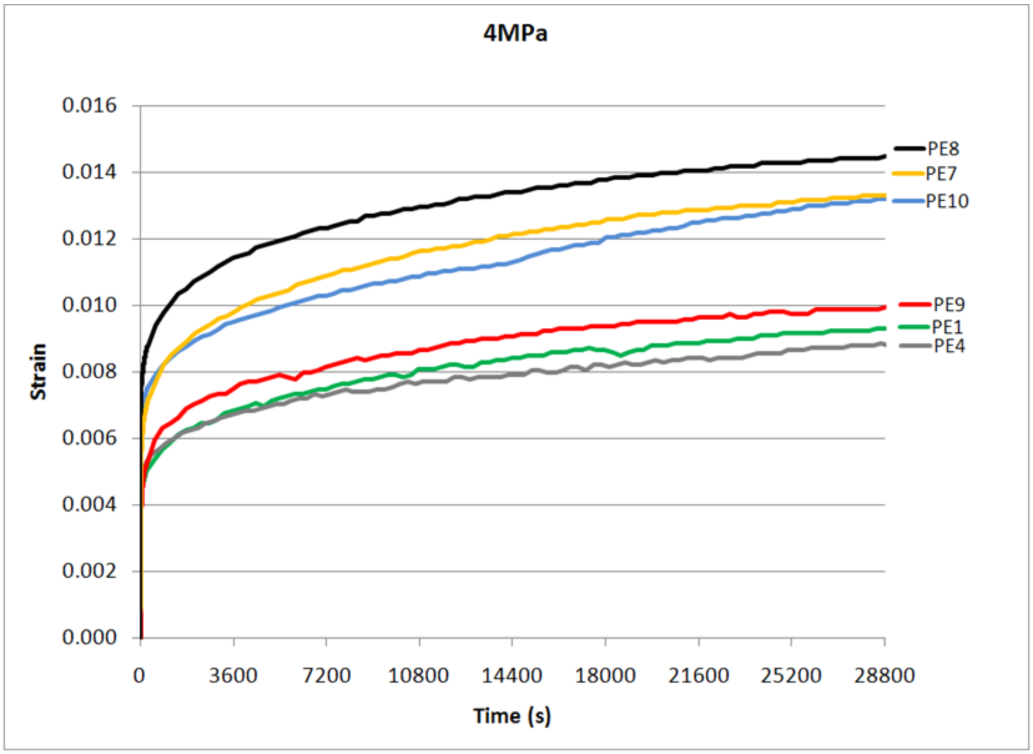


Figure 4.9 - 8-Hour Creep Tests at 4 MPa

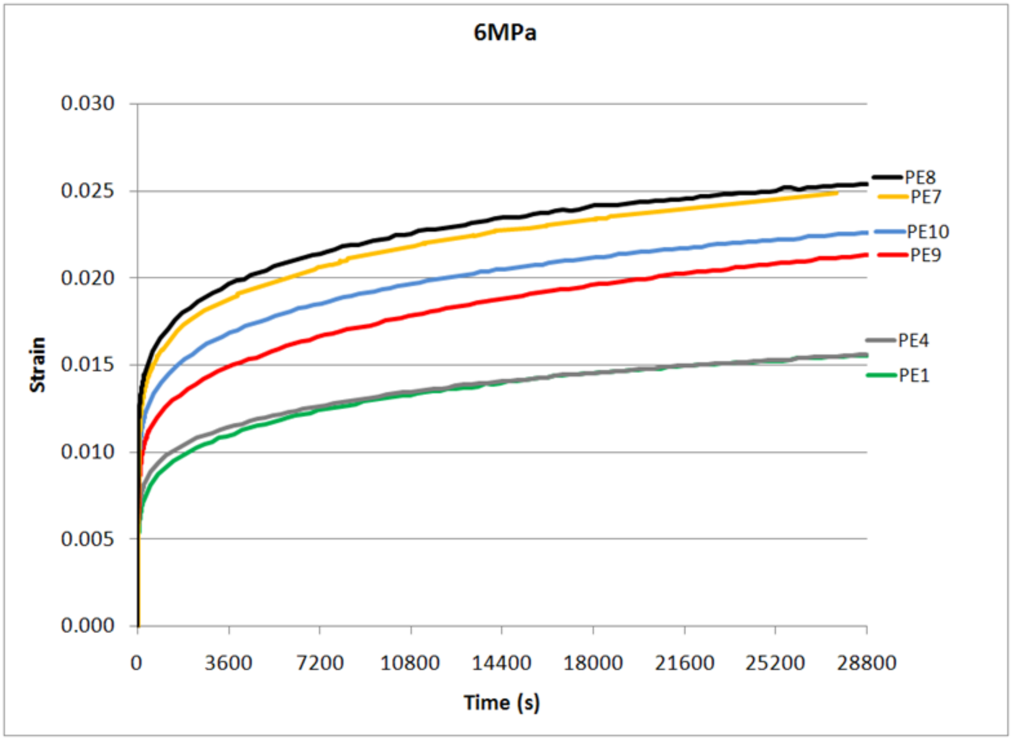


Figure 4.10- 8-Hour Creep Tests at 6 MPa

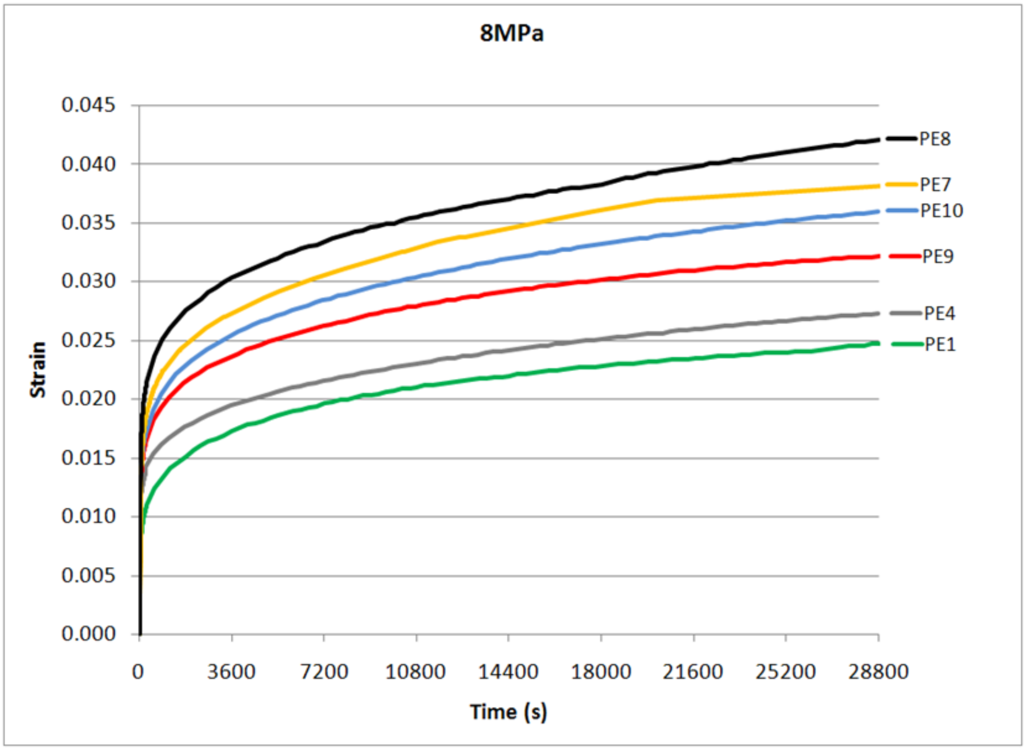


Figure 4.11 - 8-Hour Creep Tests at 8 MPa

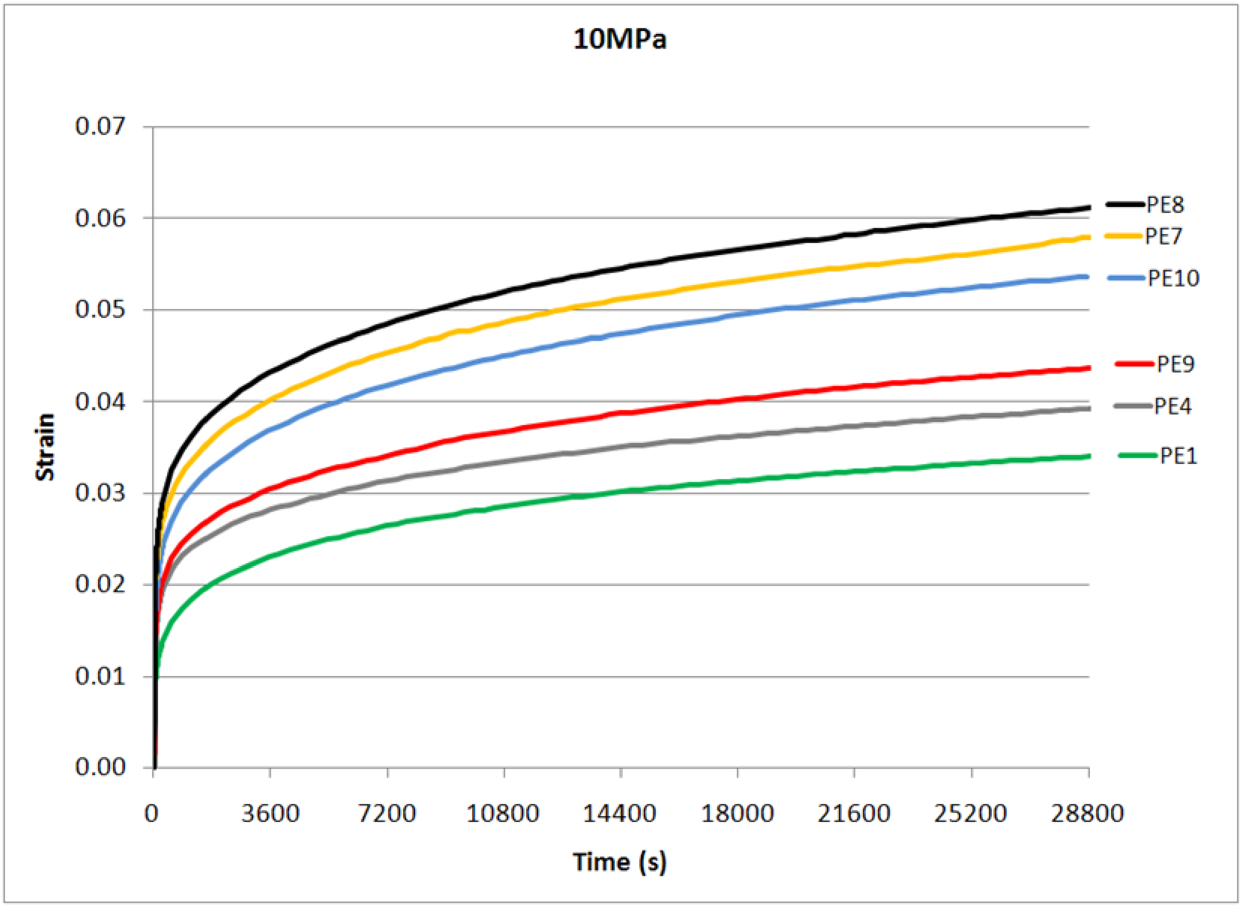


Figure 4.12 - 8-Hour Creep Tests at 10 MPa

It can be seen from the 8-hour creep tests that PE8 is the least stiff material at all stress levels. It has the lowest elastic response in all cases and highest strains. From the same group, group 2, PE7 and PE10 are stiffer than PE8, but still significantly softer that those in Group 1 that includes PE1 and PE4.

Table 3.2 summarized the values for ESCR for the six samples under study. It was seen that PE1 and PE4 had very little resistance to environmental stress cracking which is an indication of poor long-term performance. They can be grouped as ESCR-Type 1, having low ESCR. Resins PE7, PE8, PE9, and PE10 have much higher resistance to ESC and are grouped as ESCR-Type 2, having much higher ESCR. These observations suggest that good ESCR results in poor short-term properties and vice versa, however PE9 is an exception. PE9 and other resins must be analyzed on the micro scale from a chemical morphology perspective in order to attempt any conclusions. This analysis is done in Chapter 6. PE9 has excellent ESCR which makes it a good material from the long-term performance perspective, but also has lower strain values in the short-term creep tests than those in group 2 which makes it a better material from a short-term performance perspective.

4.2.2 Compliance Curves

Compliance function was defined in section 2.2.1. Assuming that cross sectional area remains constant it can be concluded that the stress is a constant and the compliance function can be derived by dividing the strain by the constant stress. Figures 4.13 to 4.18 contain the compliance curves for the corresponding 8 hour creep tests.

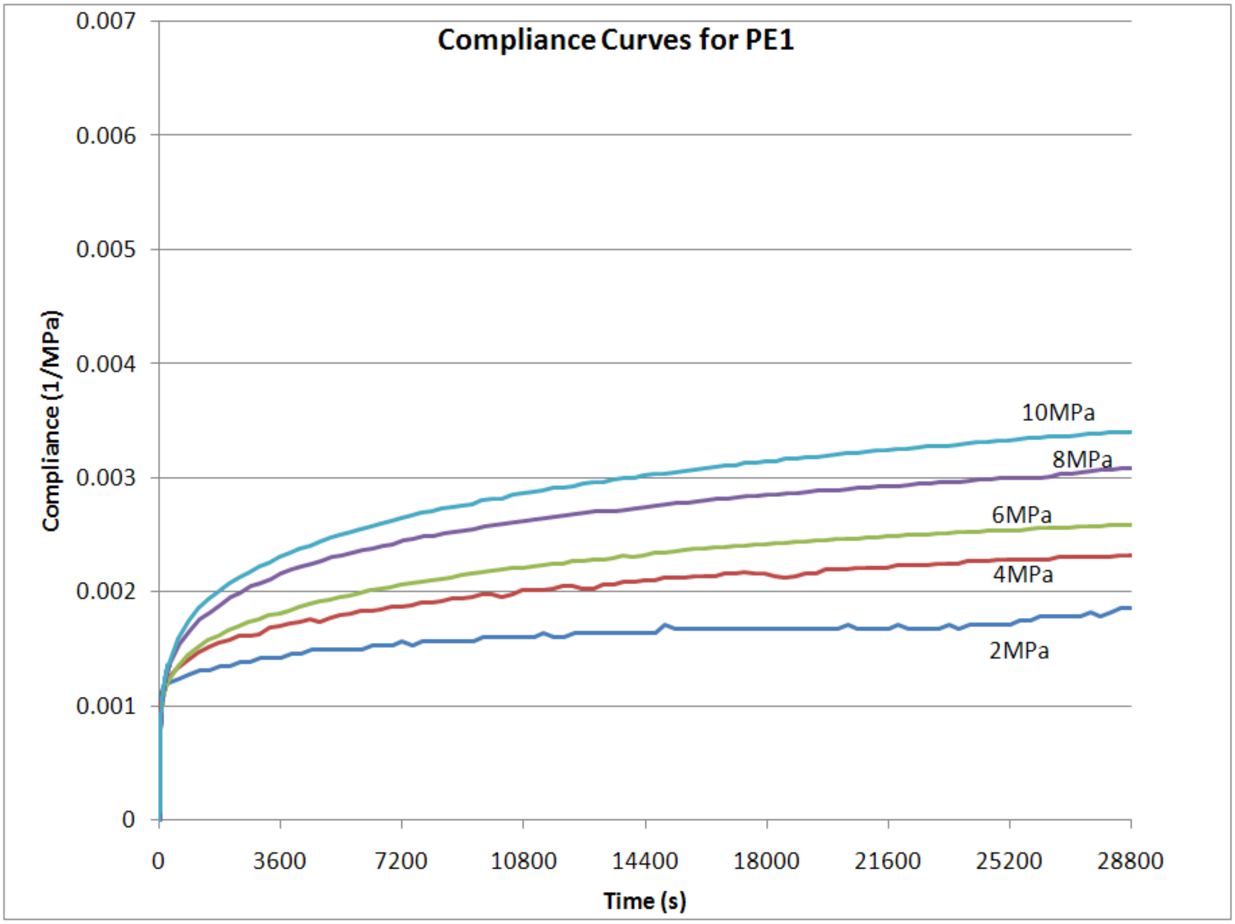


Figure 4.13 - Compliance Curves for PE1

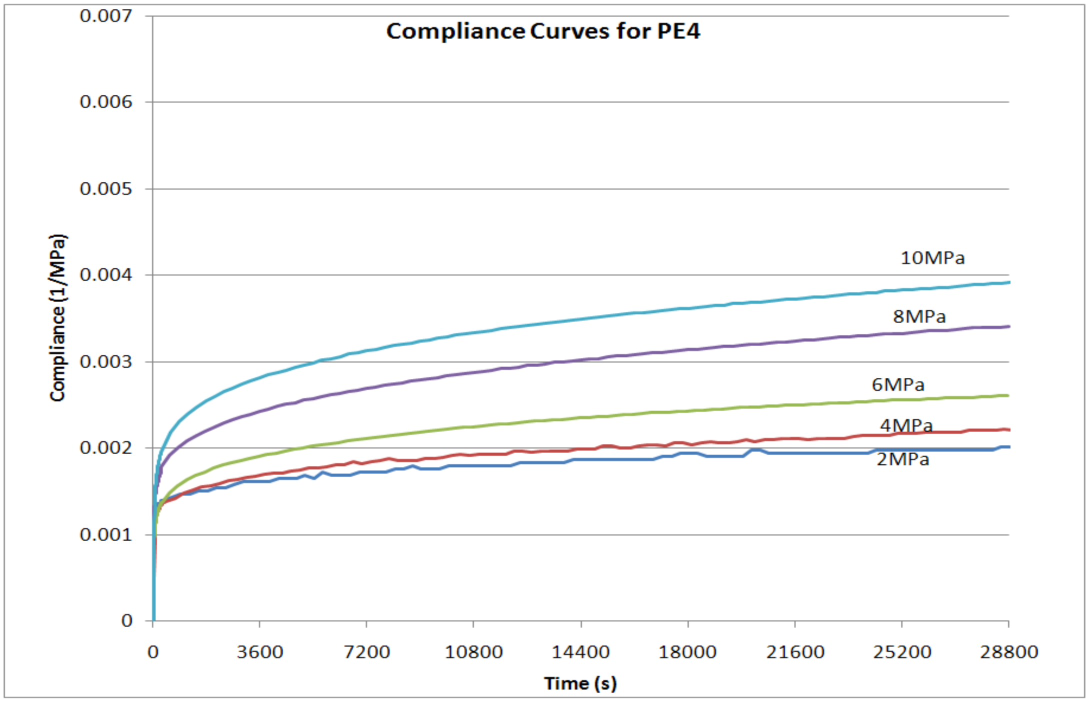


Figure 4.14 - Compliance Curves for PE4

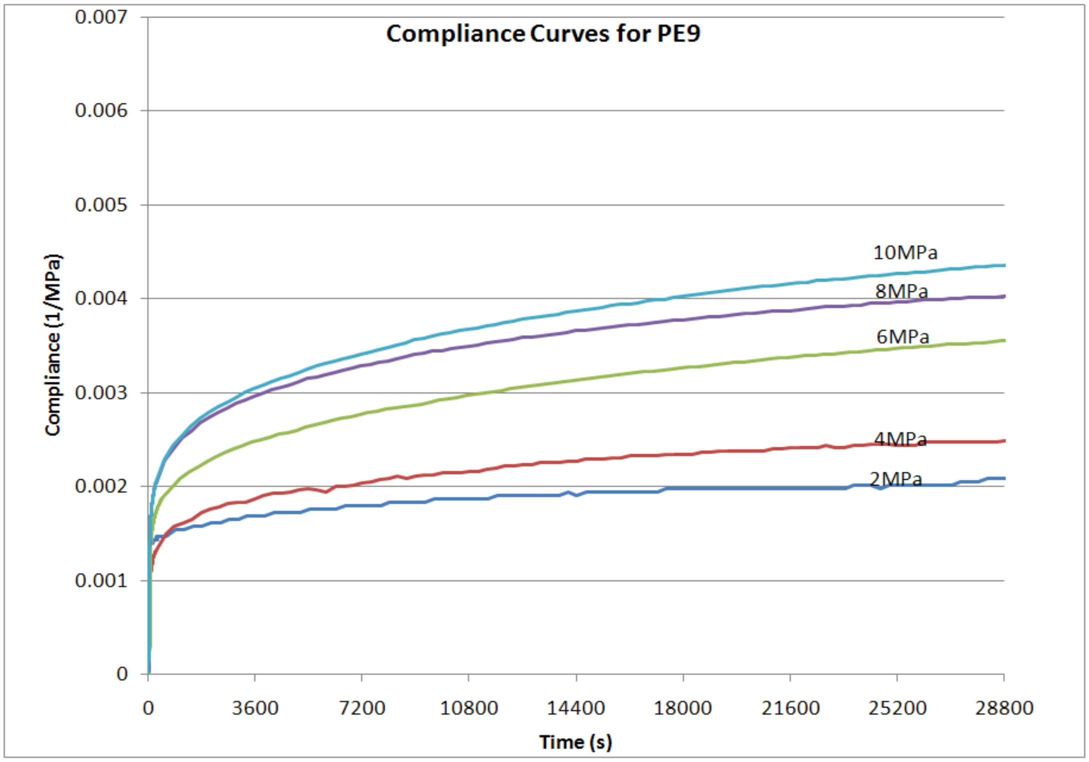


Figure 4.15 - Compliance Curves for PE9

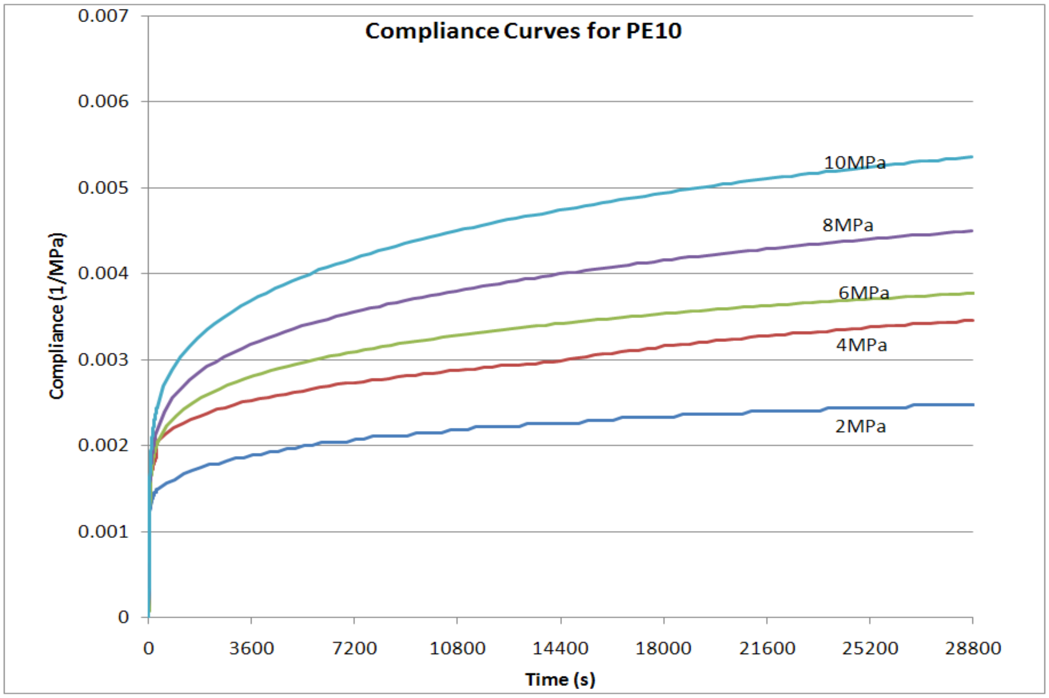


Figure 4.16 - Compliance Curves for PE10

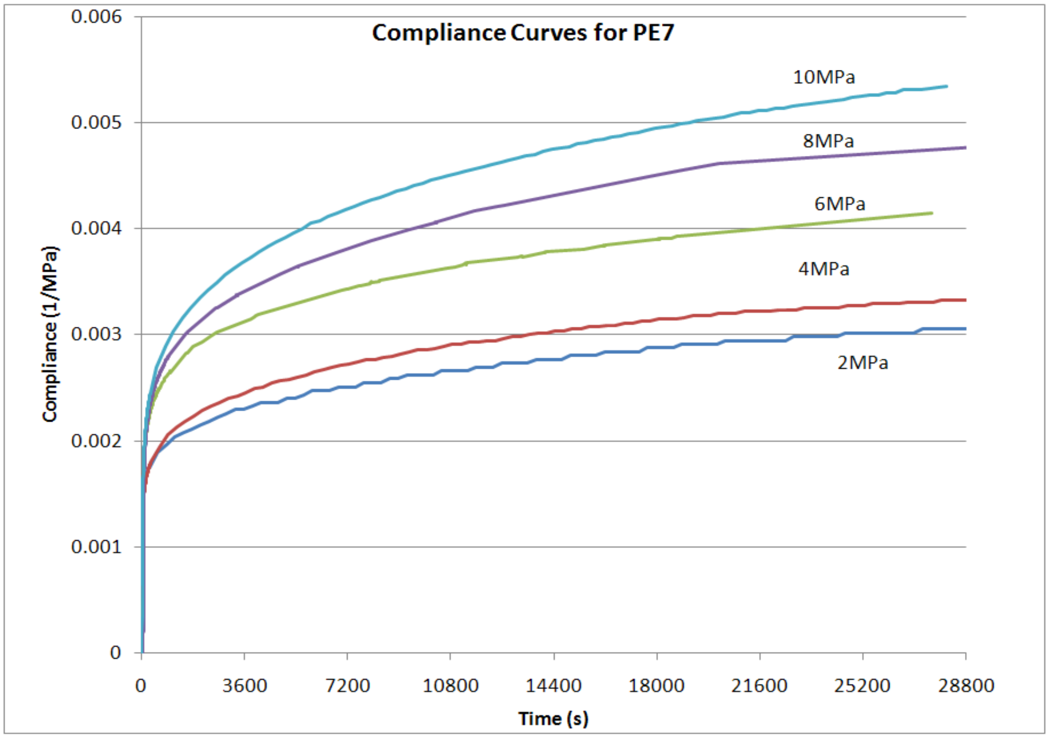


Figure 4.17 - Compliance Curves for PE7

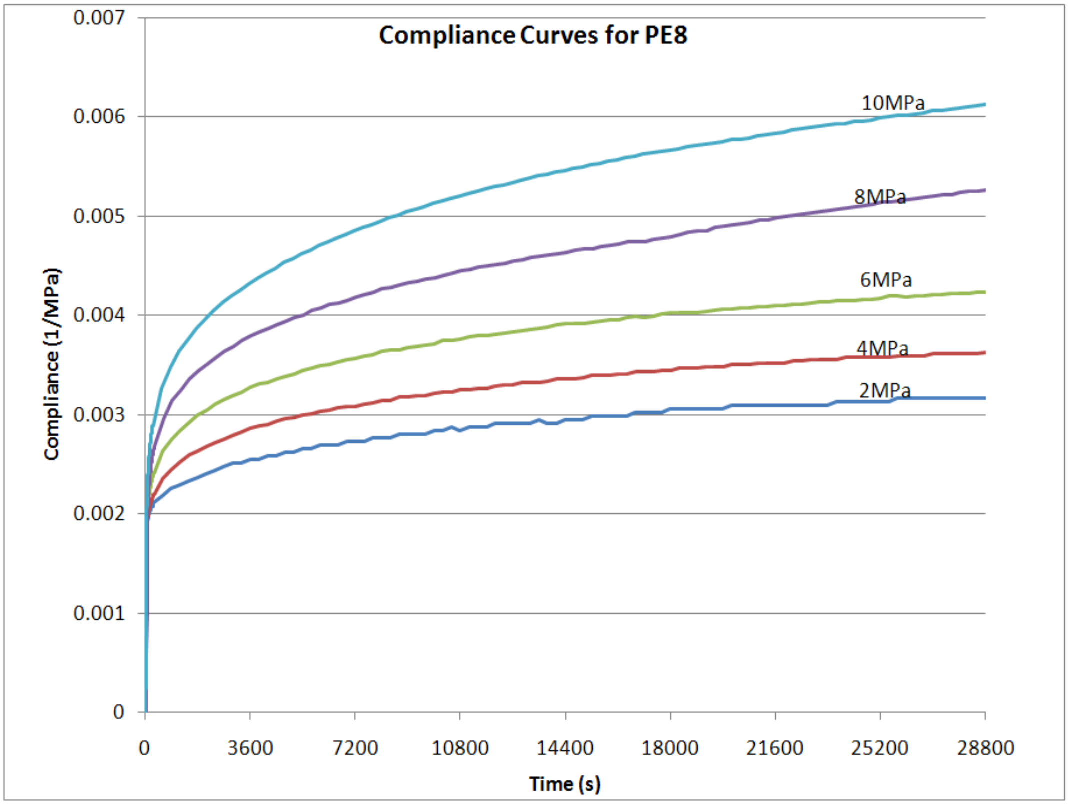


Figure 4.18 - Compliance Curves for PE8

Materials that are linearly visco-elastic have only one compliance curve at any given stress. From Figures 4.13 to 4.18 it can be concluded that polyethylene exhibits non-linear behavior as compliance curves increase in value as stress increases. It can also be concluded that the general shape of the creep function changes as the stress level changes. These findings are important for proper material modeling of polyethylene, discussed in Chapter 5.

4.2.3 Creep Curves at 20% Yield Stress

Often times creep curves are obtained for a percentage of yield stress, e.g. 20%. To compare the samples on this basis Figure 4.19 is provided. The values of yield stress considered for this test were obtained from the manufacturers, prior to performing the stress-strain tests, and they do not completely match the yield stress obtained from the testings done in this research, presented in Figure 4.7. The values used as yield stress for this test were: 27, 23.3, 22.5, 30.2, 29.9, and 29.9 MPa for PE1, PE4, PE7, PE8, PE9, and PE10, respectively.

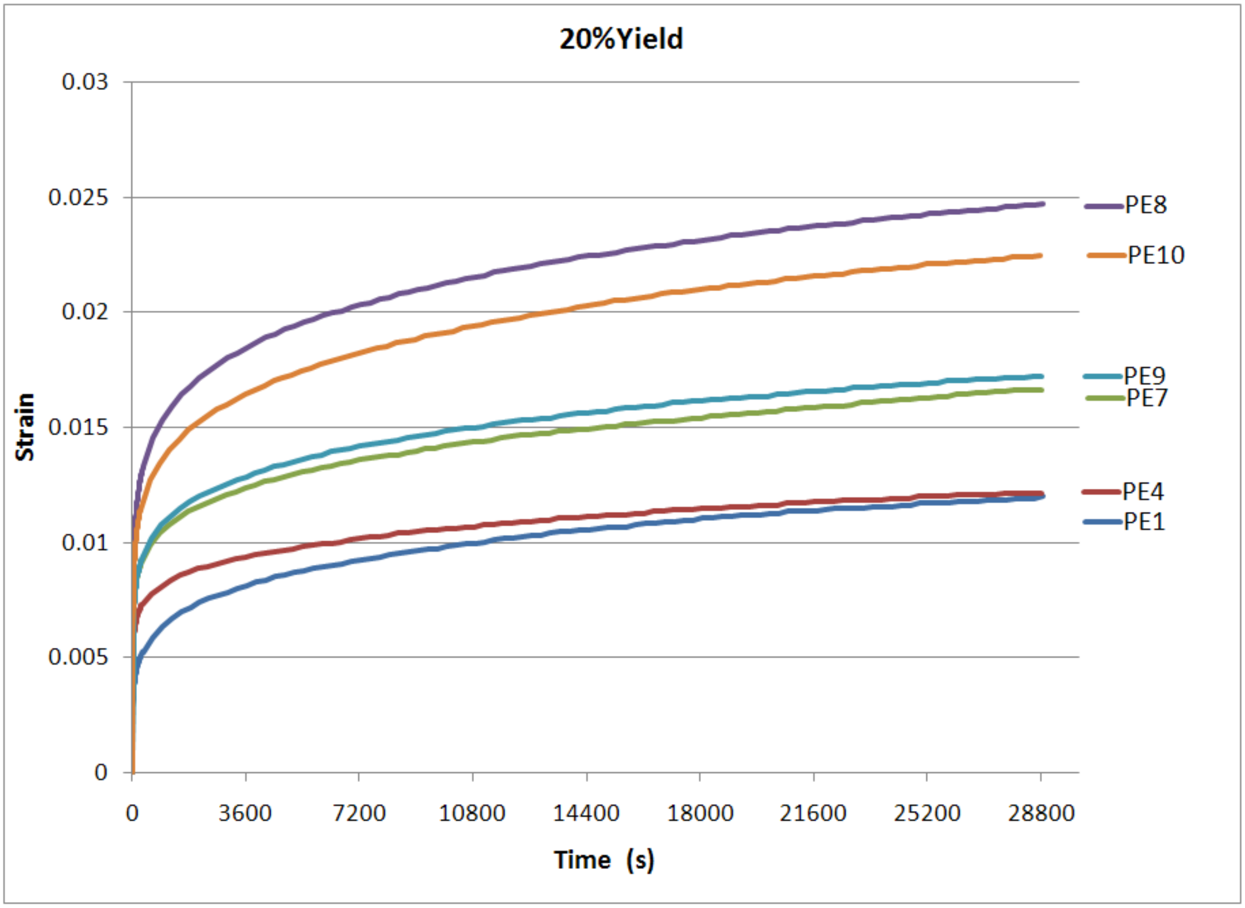


Figure 4.19 – Creep Curves at 20% Yield

From Figure 4.19 it can be seen that creep curves cannot be normalized for polyethylene based on a percentage yield of the material and separate tests need to be conducted to obtain the creep response.

4.3 Long Term Creep-Tests

From the 8-hour creep tests it was observed that the strains were still growing at significant rates after eight hours. To understand what happens beyond eight hours, a few longer term tests were conducted at 4MPa and 10MPa.

Based on the stress-strain tests and 8-hour creep tests, three resins were chosen for the long-term tests:

- PE1: Because it has the highest stiffness and low ESCR.
- PE8: Because it has the lowest stiffness and a high ESCR.

- PE9: Because it has much higher ESRC than those in Group 1 and higher stiffness than those in Group 2.

Figure 4.20 shows the long-term creep tests for PE1, PE9, and PE8 at 4MPa. The strain is visibly growing after 2 weeks for PE9 and after 1 week for PE1 and PE8.

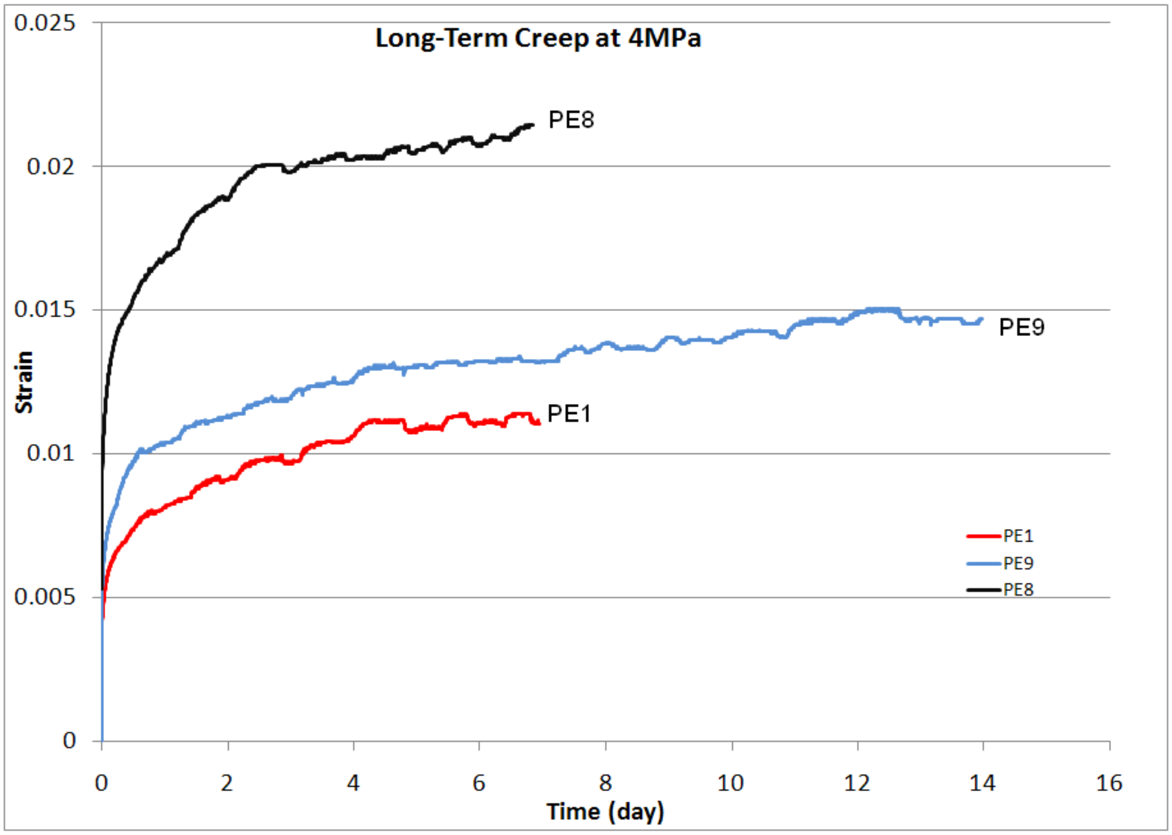


Figure 4.20 - Long-Term Tests at 4MPa

It can be observed that PE9, although slightly less stiff than PE1, performed very well in the long-term creep test at 4MPa. For all 3 resins, creep did not stop after one week or two as the case might be. This fact is also visible in the log-scale graph in Figure 4.21.

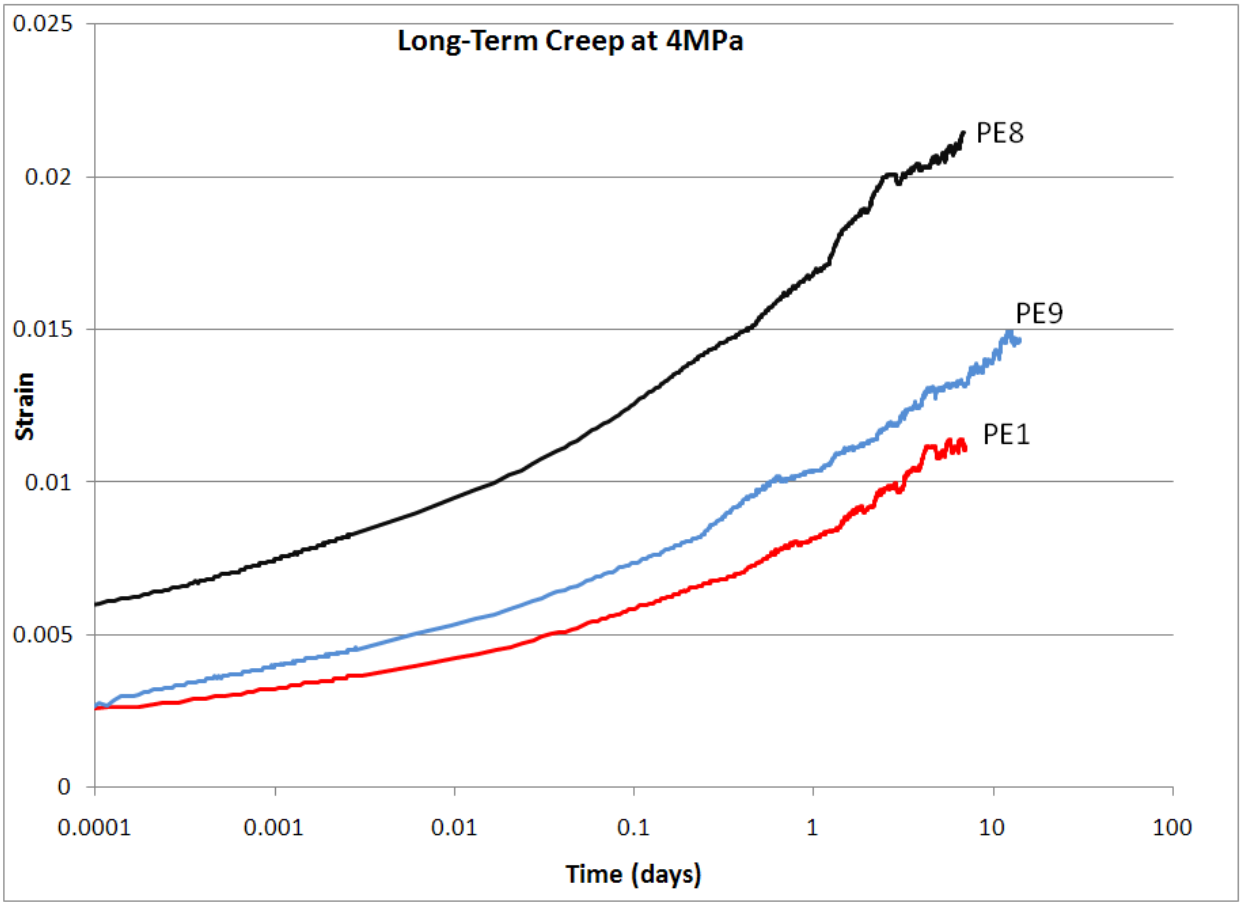


Figure 4. 21– Long-Term Tests at 4MPa Plotted on Log Scale

Figure 4.22 provides the results for long term tests at 10MPa. The results further reveal an excellent performance of PE9 which showed strains comparable to PE1 but was able to sustain the load for much longer than PE1. The test was stopped for PE1 after 2 and 3 days for the two trials because the material failed in a brittle and sudden way, without necking. This type of failure is similar to environmental stress cracking which is also sudden and brittle. PE8 was able to sustain the 10MPa stress but showed significantly higher strains than PE1 and PE9. It should also be noted that the ESCR is 5 hours for PE1, 200 hours for PE8, and 830 hours for PE9. It is also important to note that the material that has the smallest creep in the 8-hour tests, PE1, can fail after 2 or 3 days at a sustained stress of roughly equal to one third of its yield stress, obtained from the strain-controlled test, Test 1. The yield stress for PE1 in Test 1 was measured to be 27MPa.

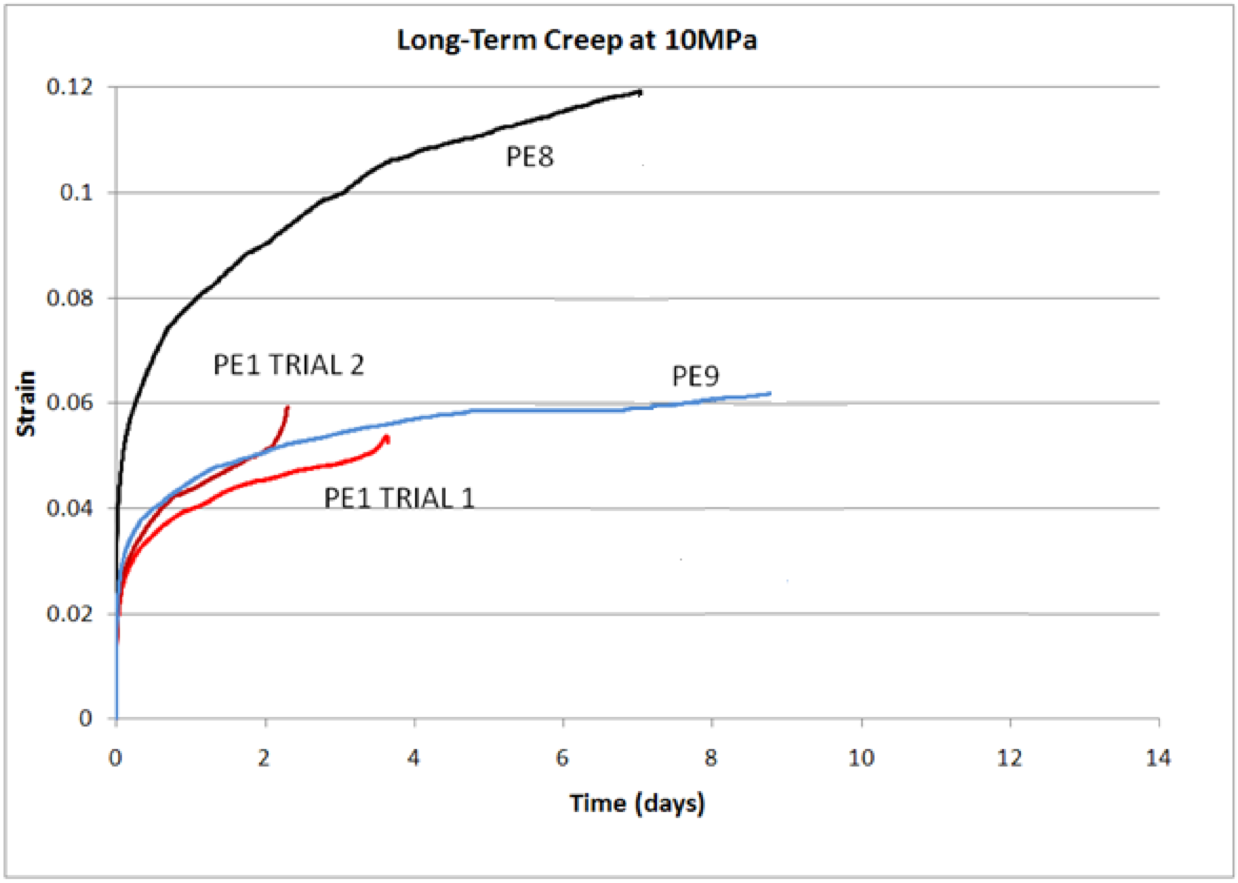


Figure 4.22 - Long Term Tests at 10MPa

Figure 4.22 shows that the strain after one week is almost equal to three times the strain right after the stress is applied. It also shows that the strain is still growing at a very considerable rate after one week. Therefore it is concluded that polyethylenes such as PE8 are not to be used at stress levels close to one third of their yield stress for engineering applications where excessive deformation is to be avoided. Figure 4.23 plots the data in Figure 4.22 on the log-scale.

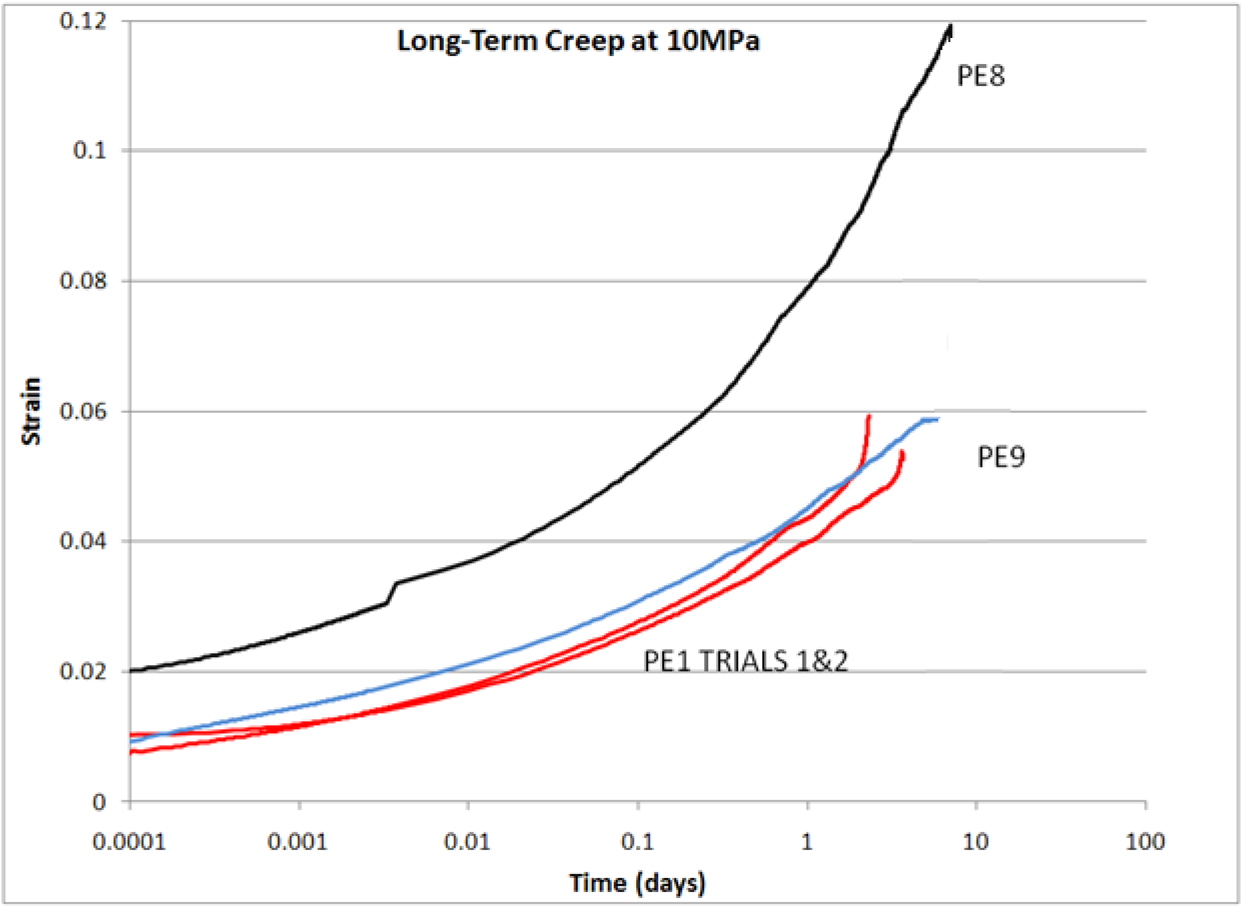


Figure 4.23 – Long-Term Tests at 10MPa Plotted on Log Scale

4.4 Repeatability of Creep Tests

It is important to investigate the possible sources of error present in tensile tests. Some of which were:

- Errors originated from length measurements
- Errors originated from small changes in ambient temperature
- Errors originated from the instrument readings

To assess the precision of the measured data, several tests were independently repeated. Creep tests were repeated at 2MPa for three resins as shown in Figure 4.24. The error between the repeats is within 10%. For most engineering applications such error is considered to be small.

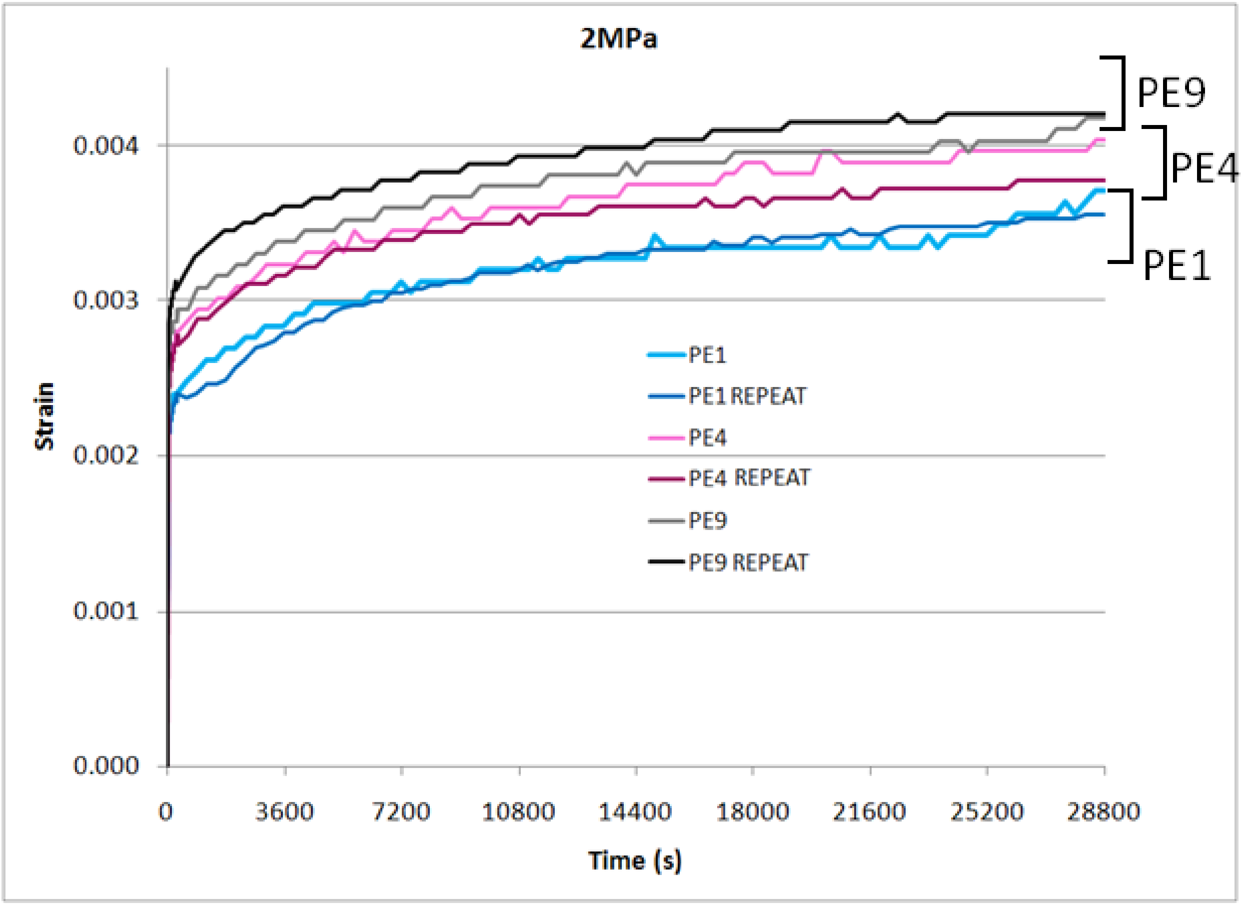


Figure 4.24 - Repeatability of Tests at 2MPa

Figure 4.25 shows the repeatability of creep tests at 4 MPa. The results are not as consistent as the ones at 2MPa, but they are still within 10% range. It can be seen that the elastic response is very close for each repeat. Discrepancies are however present in the creep strain measurements.

It can also be seen that the curves are smoother in Figure 4.25 than the ones in Figure 4.24. The reason for smoother curves is that the creep-strains are larger in creep curves at 4MPa than they are at 2MPa. Therefore the noise from the electronics that were used was less significant.

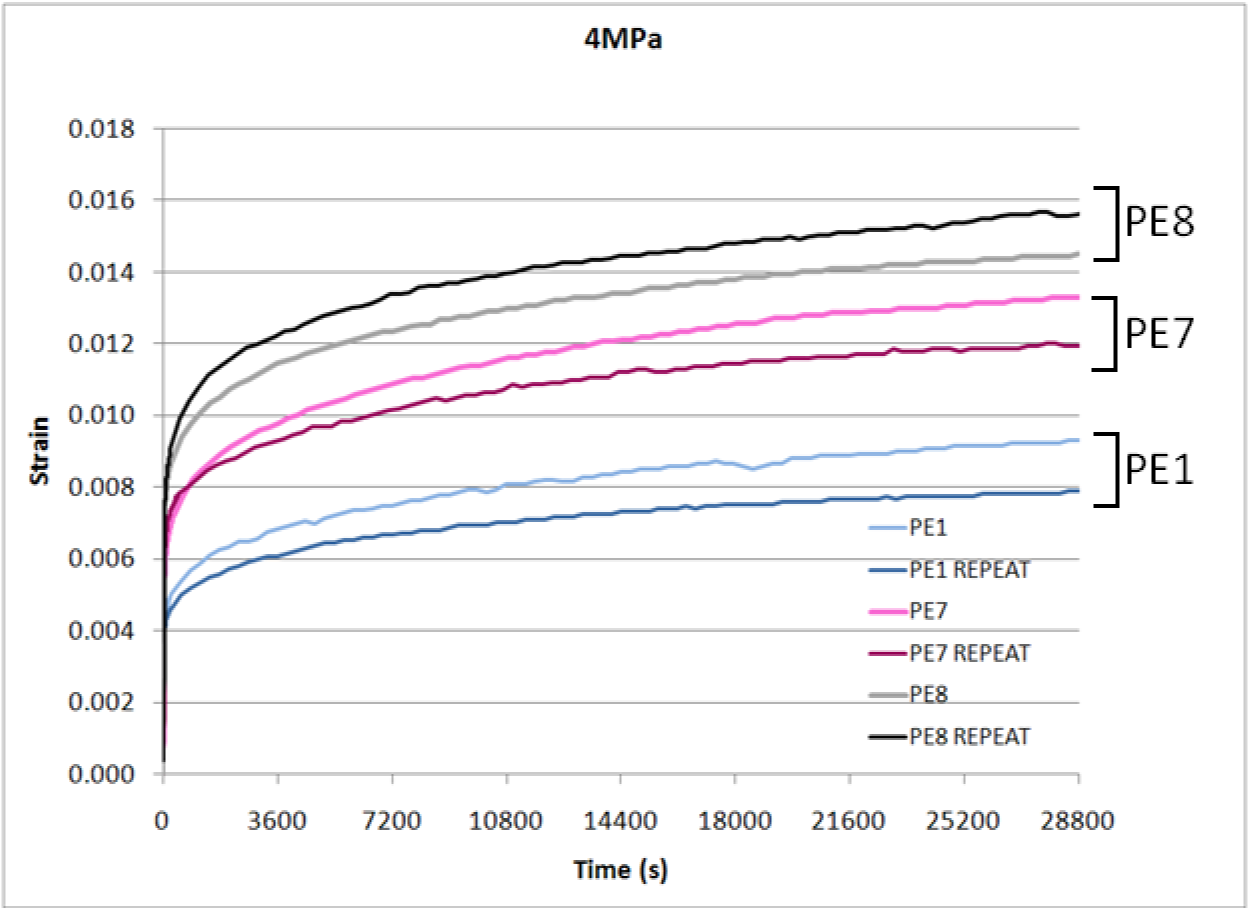


Figure 4.25 – Repeatability of Tests at 4MPa

Figure 4.26 shows the repeated tests at 6MPa. All three pairs of repeats have high repeatability. Figure 4.27 provides the repeated creep tests at 10MPa. The difference between the pairs ranges from 3% to 10% as it has been the case at other loads. It can be seen that as stress level increased the curves got smoother. However the repeatability of the obtained data did not change with the changed stress level, one way or another.

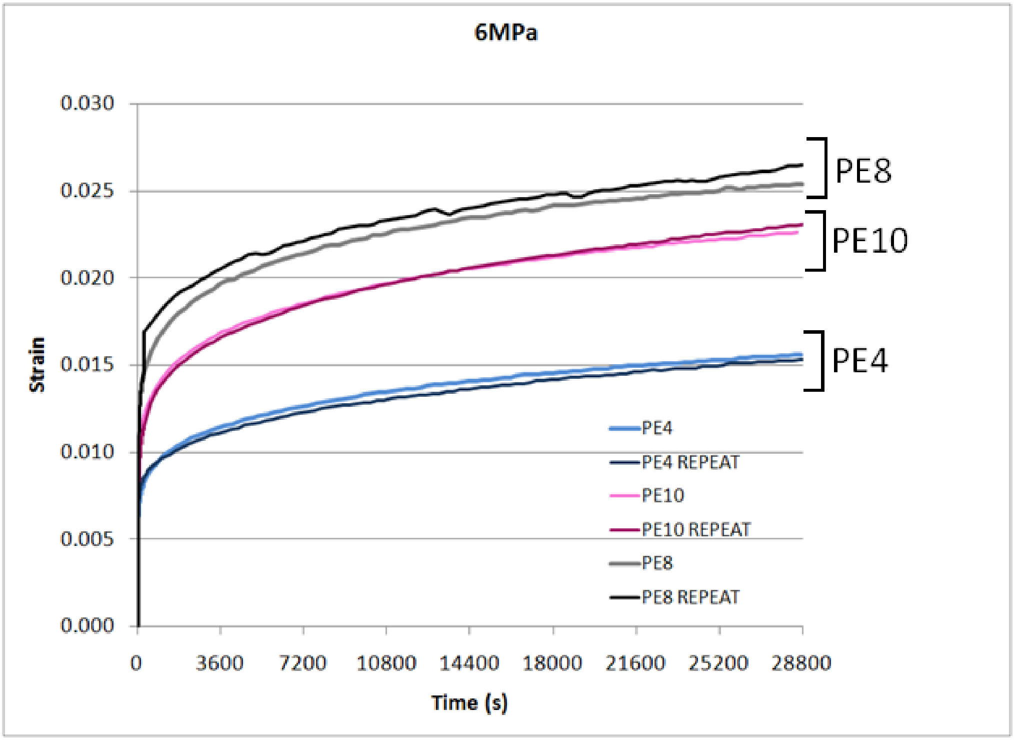


Figure 4.26 – Repeatability of Tests at 6MPa

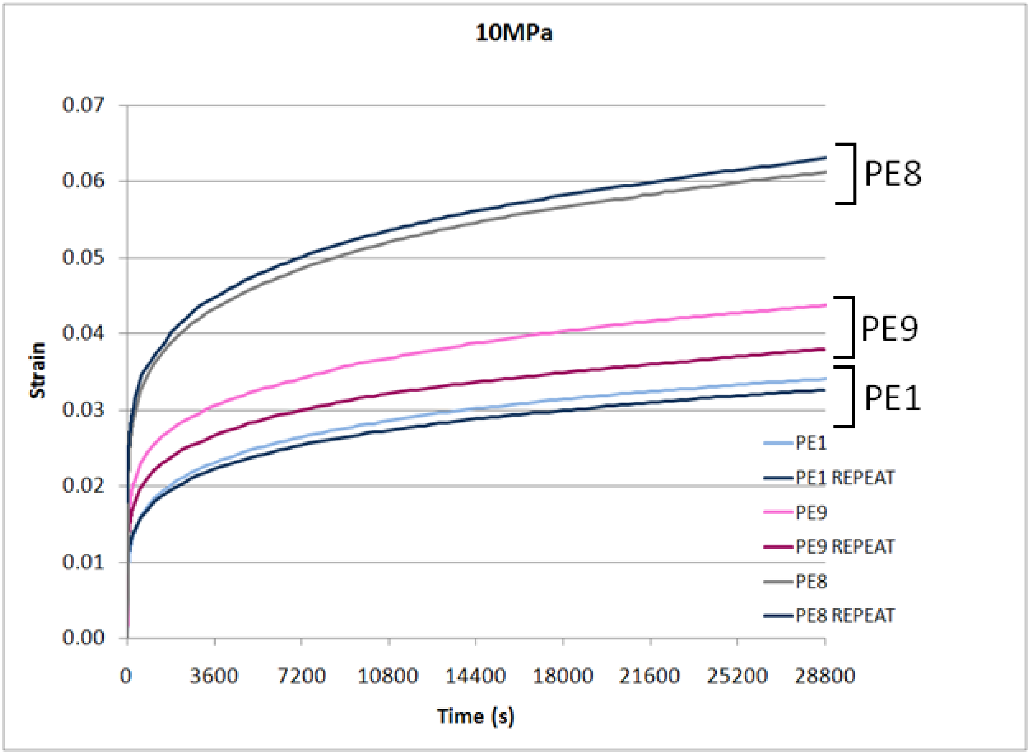


Figure 4.27 - Repeatability of Tests at 10MPa

5.0 Constitutive Modeling of Polyethylene

One of the main tasks of a structural or mechanical engineer is to determine the response of the structure to applied loading or imposed displacements. This requires, among other things, the proper mathematical modeling of the constitutive behavior of a material.

Response of a material to stress or strain is modeled using a constitutive model. Chapter 5 presents models that have been used to model the polyethylene's response. This thesis evaluates them based on the observed behavior of the materials. These models can be used as part of the input in structural analyses.

The issue of long-term strain prediction is also investigated. Most testing is done for short-time durations. Structural responses however, are often needed for longer periods of time.

5.1 Integral Form for Material Modeling

The integral form used for modeling of the material is in the following equation (Liu 2007):

$$\varepsilon(t) = \int_0^t \psi(t-\tau)\dot{\sigma}(\tau)d\tau \tag{5.1}$$

where Ψ is the creep function, ε is strain, σ is stress and, τ is relaxation time.

5.1.1 Linear Visco-elastic Modeling

The constitutive model in this section is comprised of multiple Kelvin elements in series with one spring, E_0, as shown in Figure 5.1. E_0 captures the elastic response of the material and the Kelvin elements model the delayed strain.

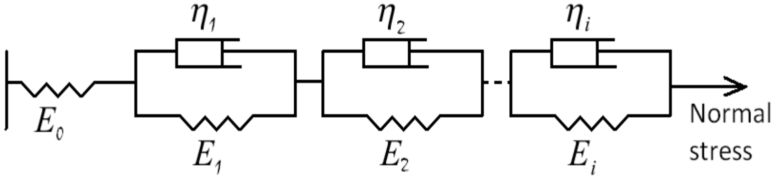


Figure 5.1 - Linear Visco-Elastic Model

The spring captures the instantaneous strain response of the material due to any imposed stress. For each Kelvin element a relaxation time, τ_i, is defined: $\tau_i = \eta_i / E_i$. Each τ_i corresponds to the material response at times smaller than τ_i. The total strain can be expressed as:

$$\varepsilon(t) = \int_0^t \left\{ \frac{1}{E_0} + \sum_{i=1}^{N} \frac{1}{E_i} \left\{ 1 - \exp\left(-\frac{t-\tau}{\tau_i} \right) \right\} \right\} \dot{\sigma}(\tau) d\tau \tag{5.2}$$

Furthermore the creep function can be expressed as:

$$\psi(t-\tau) = \frac{1}{E_0} + \sum_{1}^{\mathbf{N}} \frac{1}{E_i} \tag{5.3}$$

It can be seen that there are "N" expressions in the above function, equal to the number of Kelvin elements used. These expressions are algebraically added to the instantaneous response. Liu et al. (2008) showed how each relaxation time can be used to model a portion of the strain-response as shown in Figure 5.2.

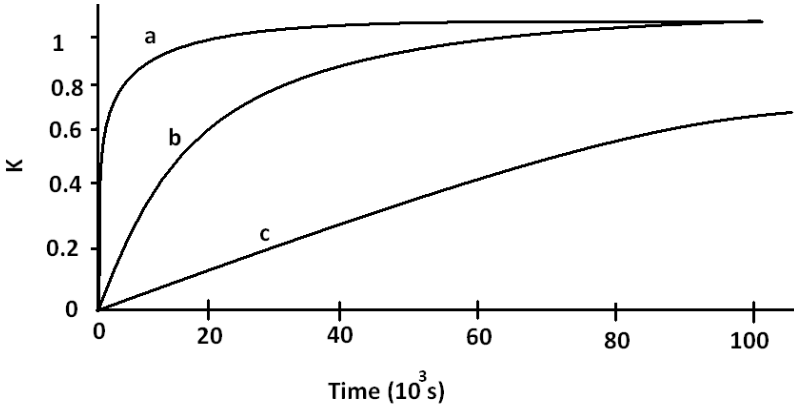


Figure 5.2 – Influence of Relaxation times – from Liu (2008)

In Figure 5.2, each K curve represents a creep function for each Kelvin element. K = 1- $e^{(-t/\tau)}$, τ_a = 500 seconds, τ_b = 10,000 seconds, and τ_c = 200,000 seconds.

The linear visco-elastic model assumes that E_i is independent of the stress level. In other words one compliance function is applicable to all stresses. The linearity of strain with respect to stress for the polyethylene samples was examined in section 4.2.2 and it was concluded that polyethylene exhibits non-linear behavior. Therefore it can be concluded that the linear visco-ealstic model can only be possibly useful in a small interval of 1 or 2 MPa, depending on the required accuracy.

In a linear visco-elastic model E_0 should also not depend on time or stress. Assuming a constant stress level, the assumption that the elastic response is independent of the history of loading was tested. Figure 5.3 shows the response of PE8 to 6MPa applied and taken off every hour. It is seen in Figure 5.3 that E_0 was consistently measured to be around 800 MPa. Hence it can be concluded that the value of E_0 is indeed independent of the loading history at 6MPa.

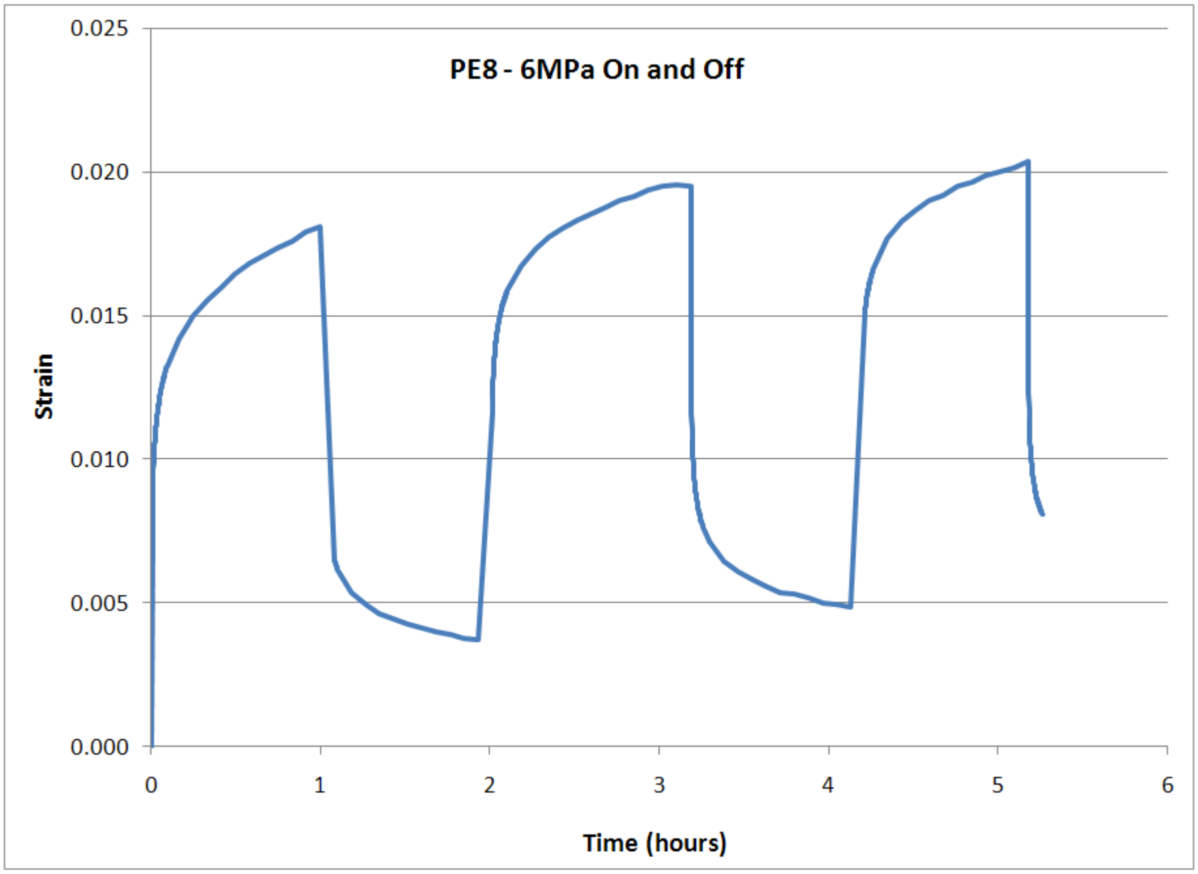


Figure 5.3 - 6MPa Applied to PE8 and Taken Away Periodically Every Hour

Similar experiment was conducted on PE1 at 6.22MPa. This time the load was applied and removed every 30 minutes and results are provided in Figure 5.4. The elastic response was around 890 MPa for all 10 times that it was measured. This experiment confirms that for high density polyethylene the elastic response can be considered independent of loading history.

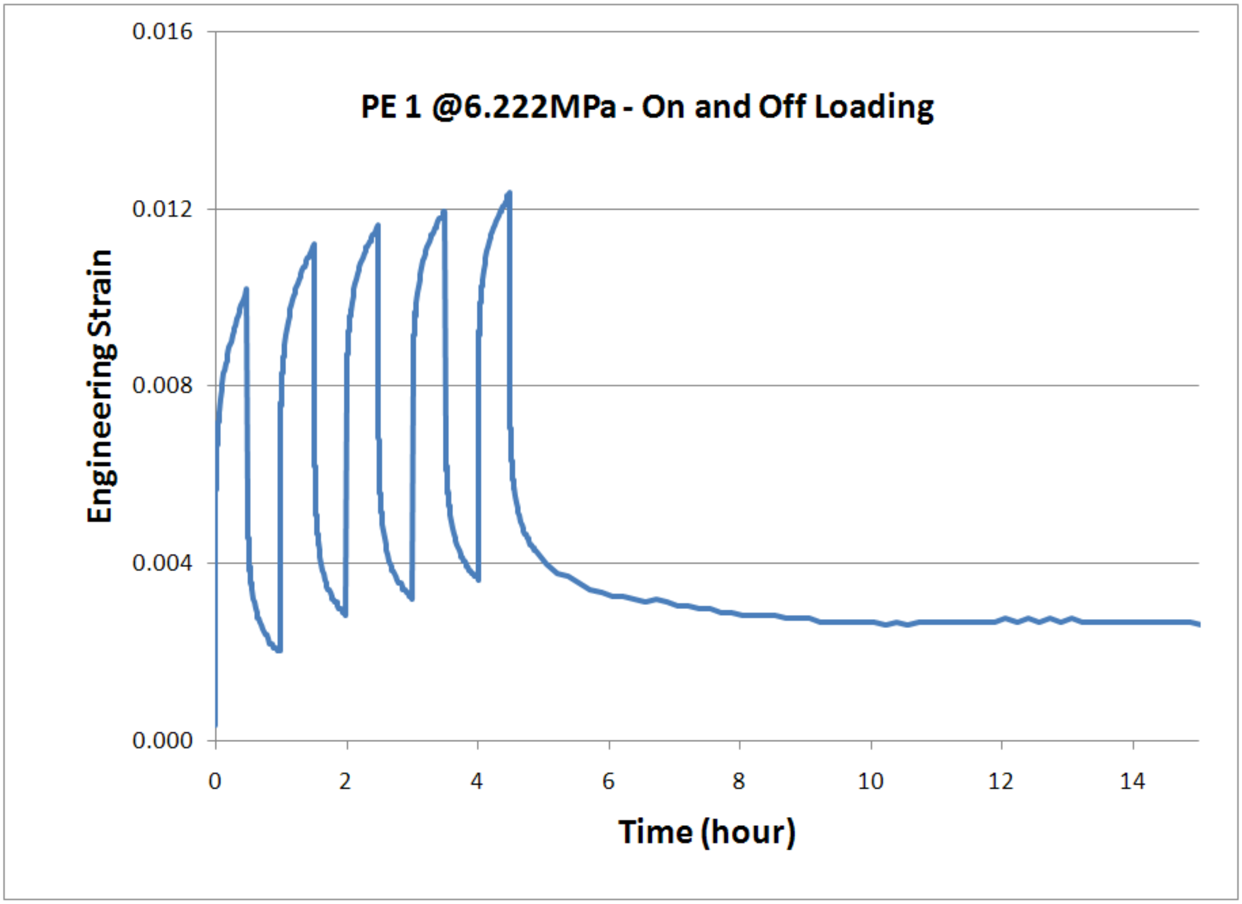


Figure 5.4 - 6.22MPa Applied to PE1 and Taken Away Periodically Every Half an Hour

It can be seen in figure 5.4 that after the load was taken off for the last time, the strain did not return to zero after 14 hours and some permanent deformation remained. Linear visco-elastic model does not account for any plastic or permanent deformation. To have a better judgment about the recoverability of strain after the load is taken off an experiment was conducted as shown in Figure 5.5. In this experiment PE7 was subjected to 10MPa for one full day and then the load was taken off allowing for the strain to recover. The strain was monitored for roughly 400 hours and it was seen that the strain caused by one day of constant stress equal to 10MPa was not fully recovered after 400 hours as the curve is still noticeably decreasing after 400 hours.

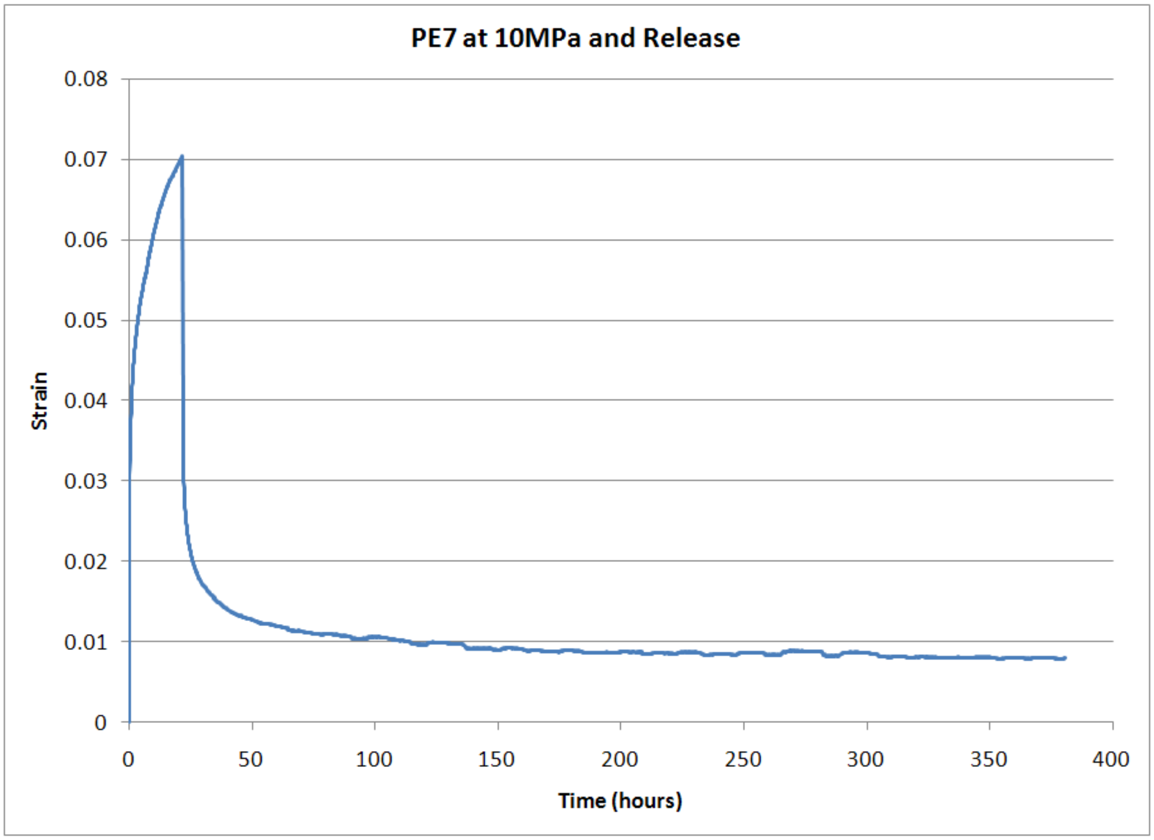


Figure 5.5 - PE7 at 10MPa and Release

Visco-elastic model has “N” number of Kelvin elements, each having a constant relaxation time. In the visco-elastic model observed data are curve fitted using these relaxation times and they are chosen such that they represent a full spectrum of the time during which creep occurs. The creep rate slows down with time as it can be seen in all of the creep curves that are shown in this thesis. Therefore, it is appropriate for the relaxation times to follow a geometric sequence as opposed to an arithmetic one.

Kelvin element has a finite strain for a given constant stress because the extension of the element can never exceed the extension of the spring present in the element due to the same constant stress. In other words, visco-elastic model has an underlying assumption that the strain will reach a constant value after long enough time from the when the load was applied. The highest chosen relaxation time will determine the theoretical time when the strain will reach the upper limit. None of the short term or long term creep tests present in this thesis show strain reaching an ultimate value at any of the stress levels.

Figure 5.6 shows the visco-elastic model fitted for 8 hour data. It includes the observed strains for PE1 subjected to 10MPa and the multi-Kelvin values. Relaxation times used were: 500, 10,000, and 200,000 seconds. The values of, E_0, E_1, E_2, and E_3 were found to be: 1137MPa, 297MPa, 301MPa, and 140MPa, respectively. The curve fitting was done using the least squares method which was carried out using the "Solver" program which is built in Microsoft Excel and uses a Generalized Reduced Gradient (GRG2) Algorithm.

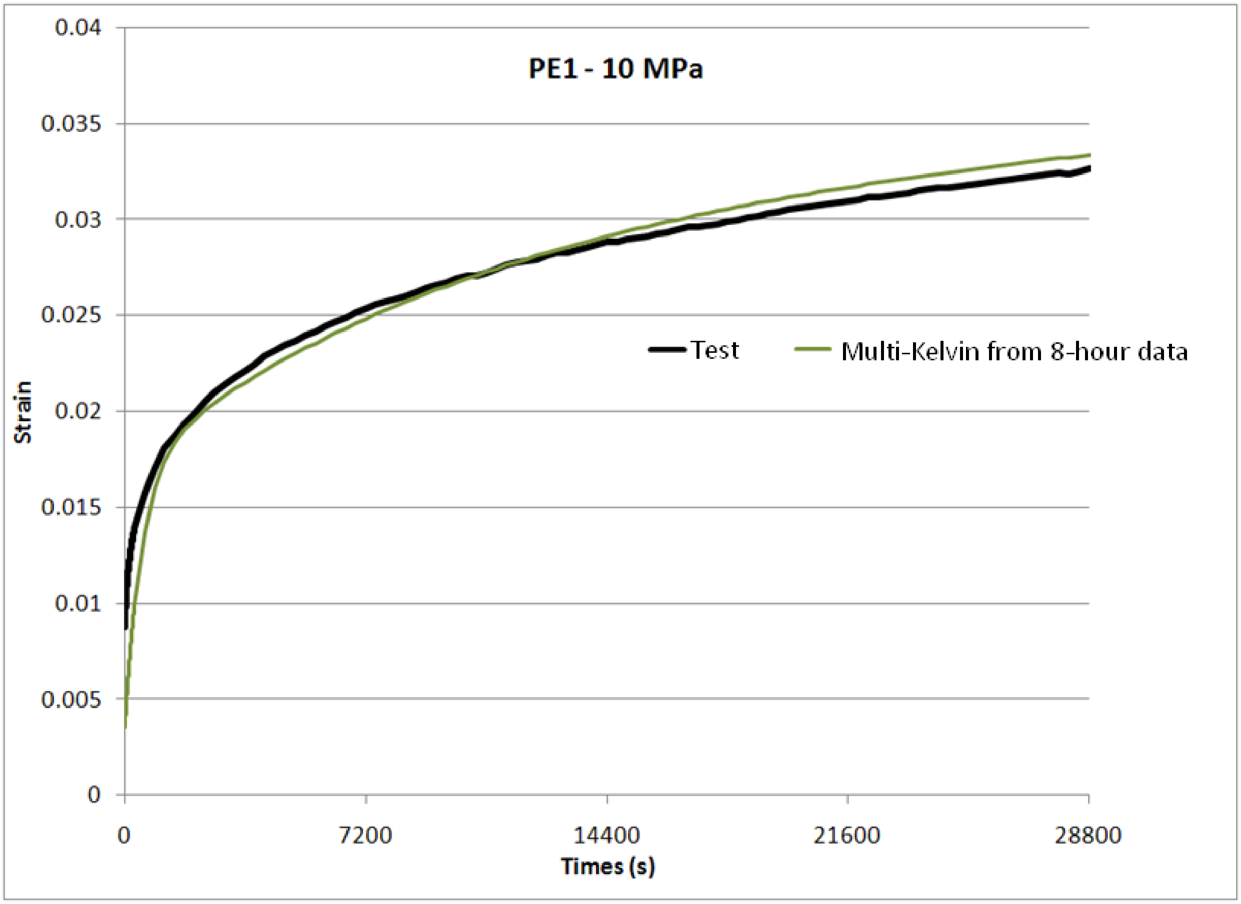


Figure 5.6 – Visco-Elastic Model Fitted Based on 8-Hour Data

The test was not stopped after 28800 second (8 hours), and was continued for more than three days before the samples broke in a sudden and brittle way. Hence the observed data could also be curve fitted for the entire strain history. Figure 5.7 shows the results. Relaxation times chosen were 500, 10,000, and 200,000 seconds and the values of E_0, E_1, E_2, and E_3, were found to be 1137MPa, 225MPa, 455MPa, and 152MPa, respectively.

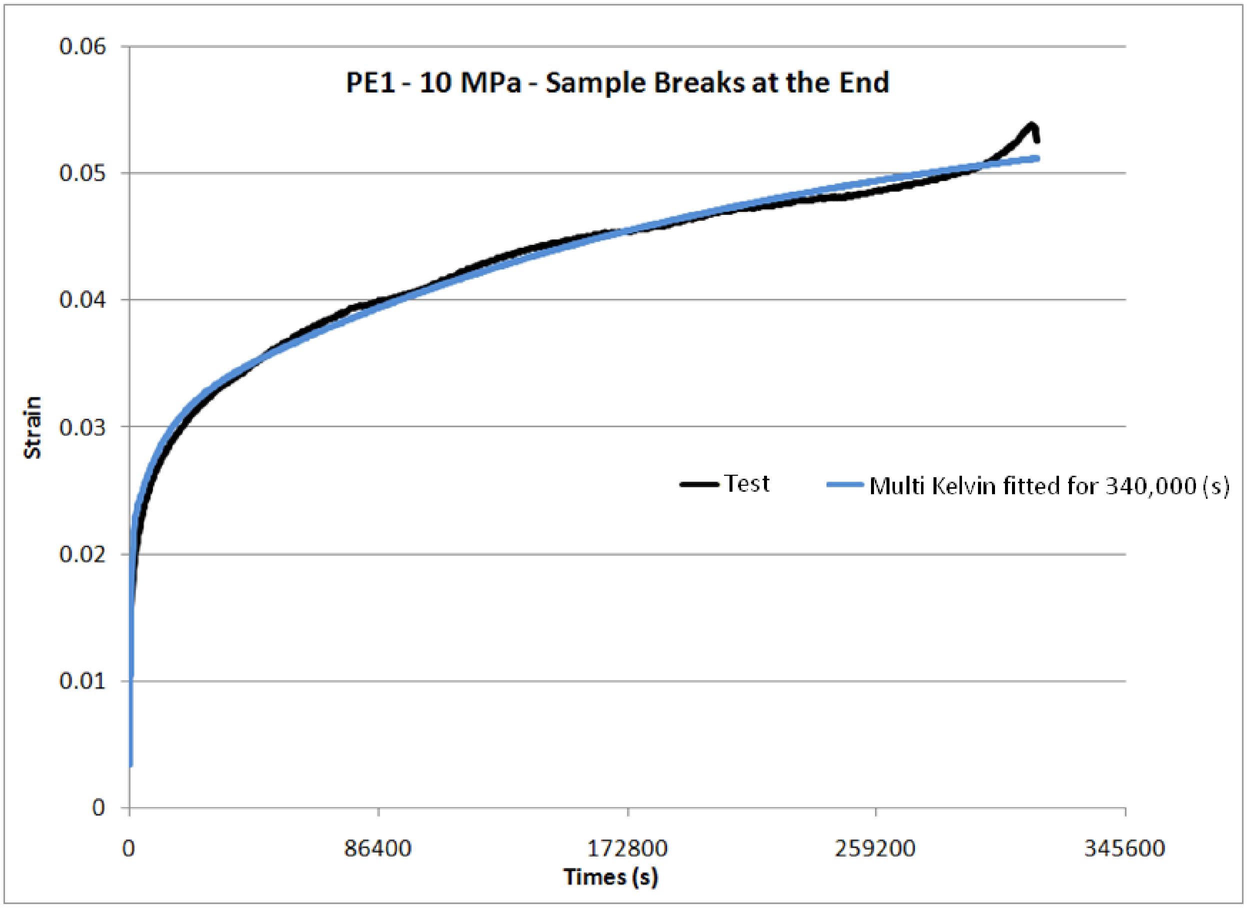


Figure 5.7 - Visco-elastic Model Curve Fitting Observed Strain for PE1 at 10MPa

Even though the same relaxation times were used to do the second curve fit as the first one, the numbers obtained as the model outputs are 10 to 30 percent different from what the model predicted using only eight hours of observation. They both however fit the curve with little error. The reasons for such difference in the output of the model are as follows:

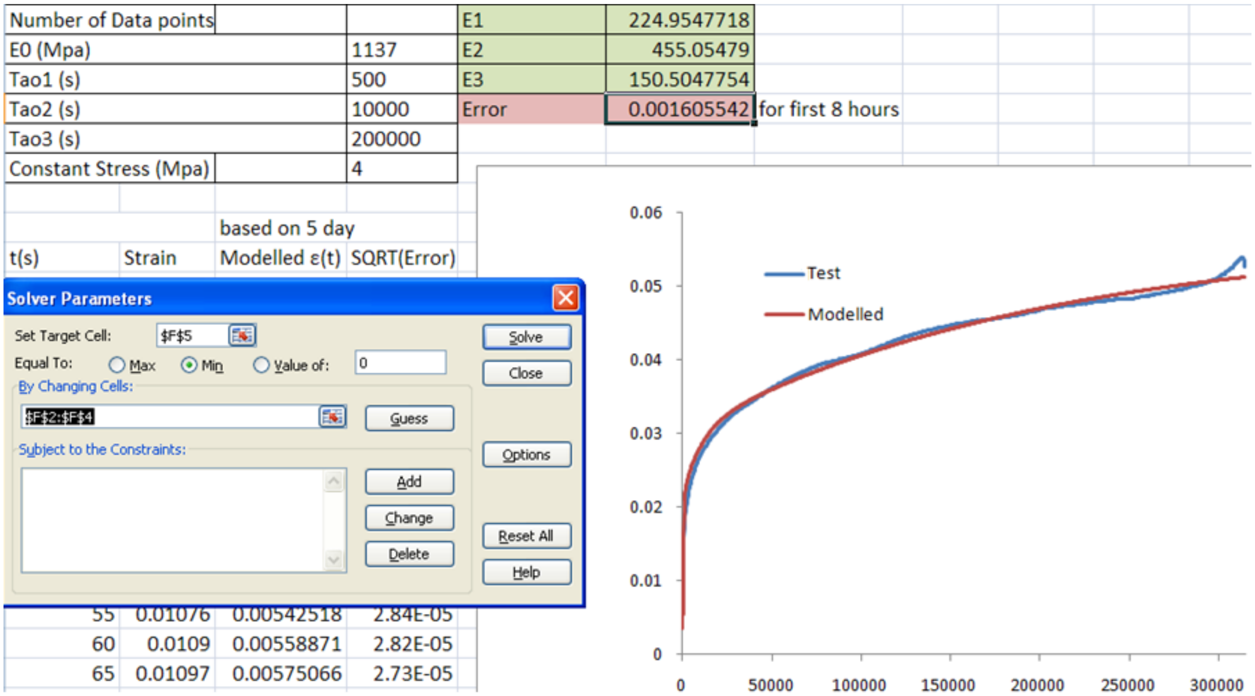
- Curve-fits are done by minimizing the cumulative squared error between the observed data and strain obtained from what the model finds based on current model parameters. Model parameters are varied in feasible region until the minimum value of cumulative squared of error is found.
- The test machine that samples strain does that every 5 seconds for the first 5 minutes and then every 5 minutes. Therefore between 5 minutes after the beginning of the test and the end of the test there is no preference between the two points in time when the error is to be minimized. This problem may be reduced if machine can sample time in a logarithmic way or

alternatively points in time following a geometric sequence can be used. The reason is that when creep curves are plotted on a logarithmic scale they look more linear than on the normal scale as it can be seen in Figure 4.21 and 4.23.

- Error in the curve fitting problem is a discrete function of model's output: E_0, E_1 …E_n. Therefore an error surface can be defined. This surface is a function of the observed lab results. Therefore it is expected to have multiple local minima. It can very well be the case that two very different sets of model outputs: E_0, E_1…E_n may lead to the same error.

Figure 5.8 shows how Excel was used for the curve-fit. To curve-fit the data the following procedure was followed:

- A family of visco-elastic curves was defined to curve fit the data having variable E_1, $E_{2,\text{ and}}$ E_3.
- The difference between the values measured for strain and the model's values for strain were calculated, squared, and then added as one quantity referred to as "error" in Figure 5.7
- The error was then minimized but changing the value of E_i using Excel's solver.



Number of Data points		E1	224.9547718	
E0 (Mpa)	1137	E2	455.05479	
Tao1 (s)	500	E3	150.5047754	
Tao2 (s)	10000	Error	0.001605542	for first 8 hours
Tao3 (s)	200000			
Constant Stress (Mpa)	4			

		based on 5 day	
t(s)	Strain	Modelled ε(t)	SQRT(Error)
55	0.01076	0.00542518	2.84E-05
60	0.0109	0.00558871	2.82E-05
65	0.01097	0.00575066	2.73E-05

Solver Parameters

Set Target Cell: $F$5

Equal To: ○ Max ● Min ○ Value of: 0

By Changing Cells: $F$2:$F$4

Subject to the Constraints:

Figure 5.8 – Screen Capture from Microsoft Excel's Solver Program

To see if an 8-hour test can predict the longer-term behavior of polyethylene, the values for strain that were obtained corresponding to Figure 5.6 were extended for three days. Figure 5.9 can be used to compare these values to the experimental data. A comparison between Figure 5.7 and Figure 5.9 shows the difference between modeling based on the three-day data and modeling based on 8-hours data that is extended to 3 days.

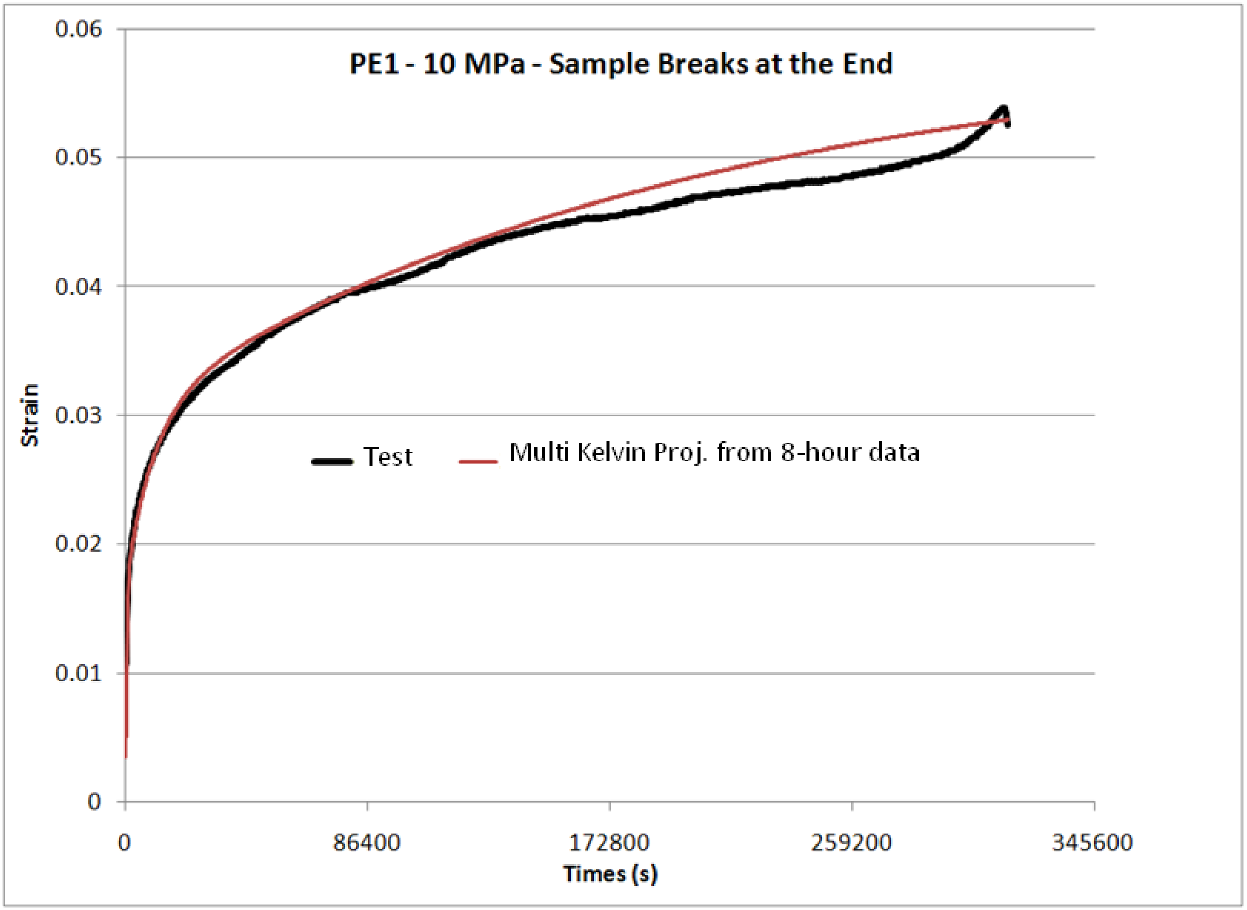


Figure 5.9 – Extended creep curve for 3 days based on 8 hour data

To demonstrate what happens if the two set of curves, fitting 8-hour data and 3-day data, were extended beyond 3 days, Figure 5.10 is provided. In this figure the fitted curves are extended to cover two weeks. It can be seen that both curves approximate a horizontal asymptote after 6 days. The reason for this behavior is that when the data were curve-fitted, the maximum relaxation value that was used was chosen to be 200,000 seconds or roughly 2.3 days. It is also important to mention that the relaxation time that is chosen cannot be much greater than the duration of the test. Hence extending the visco-elastic model in time will not provide any useful information about the long-term behavior of polyethylene.

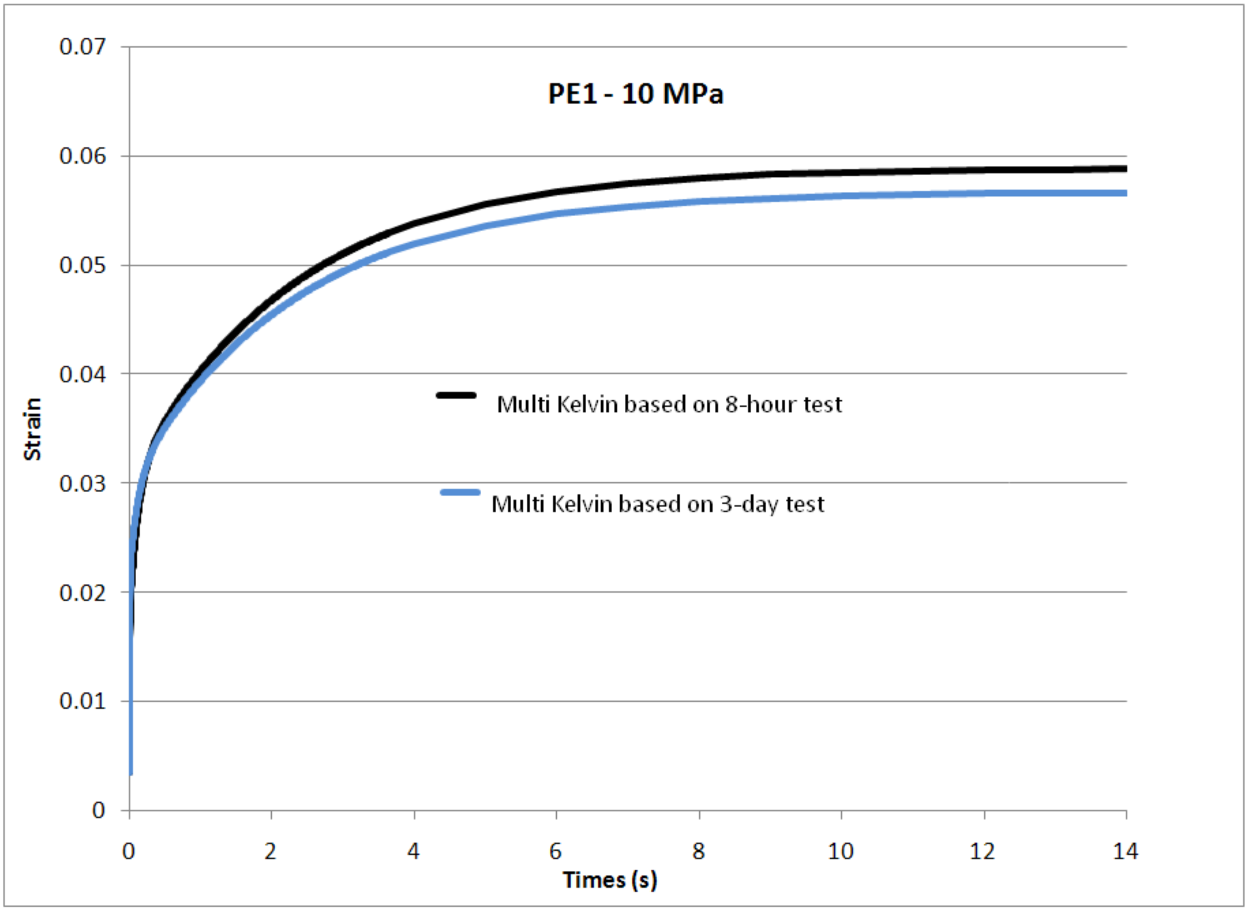


Figure 5.10 - Modeled curves based on 8-hour and 3-day creep data extended to two weeks

5.1.2 Visco-Elastic Modeling at different stress-levels – Non-Linear Modeling

Polyethylene exhibits non-linear behavior with varying stress. To account for this nonlinearity the E_i values in the non-linear model can be found as functions of stress. Liu et al. (2008) showed that a non-linear constitutive model can be constructed using the following formulation:

$$\varepsilon(\sigma,t)=\frac{1}{E_0(\sigma)}+\sum_{1}^{n}\frac{1}{E_i(\sigma)}\left[1-\exp\left(\frac{-t}{\tau_i(\sigma)}\right)\right]$$

The values of E_i at different stress levels can be calculated based on experimental creep compliances. Table 5.1 shows the 8-hour creep tests for different polyethylenes. In this Table the values for E_i are found at different given stress levels.

Stiffness of a material is expected to be reduced as load increases, and that is the case for most of the data presented in Table 5.1. However it can be seen that not all Es are reduced with an increase in load for a given polyethylene.

Table 5.1 – Non-Linear Model Parameters

All Values are in MPa									
PE1					PE10				
	E0	E1	E2	E3		E0	E1	E2	E3
2MPa	917	5743	5017	1352	2MPa	786	3162	2682	770
4MPa	933	3266	2837	687	4MPa	754	1624	2023	534
6MPa	1101	2484	1544	629	6MPa	724	1150	1237	612
8MPa	983	1614	1418	574	8MPa	706	1032	863	456
10MPa	1050	2009	1840	1009	10MPa	668	857	678	352
PE4					PE7				
	E0	E1	E2	E3		E0	E1	E2	E3
2MPa	965	3492	2895	1083	2MPa	764	1652	2074	621
4MPa	949	3300	2440	929	4MPa	744	1619	1420	631
6MPa	983	1991	1752	830	6MPa	666	964	1150	536
8MPa	902	1187	1523	536	8MPa	633	753	1082	441
10MPa	865	852	1514	458	10MPa	609	662	1042	365
PE9					PE8				
	E0	E1	E2	E3		E0	E1	E2	E3
2MPa	734	5081	4453	1684	2MPa	529	3149	2730	665
4MPa	1001	1795	1771	1266	4MPa	531	2087	1578	624
6MPa	809	1629	1376	434	6MPa	511	1204	1785	478
8MPa	706	1146	996	575	8MPa	524	980	852	388
10MPa	748	944	857	600	10MPa	546	687	642	345

It should also be noted that the data presented in Table 5.1 can be used to create a non-linear visco-elastic model. The values of the material parameters can be linearly interpolated to obtain the parameters at intermediate stress levels (Liu, et al. 2007).

5.2 Visco-Plastic Modeling

This section presents the power law model used by Liu (2007) et al. This model is referred to as a visco-plastic model because the modeled strain keeps growing, never reaching an asymptotic value. In the presented model the total strain due to a constant stress is modeled using Equation 5.4:

$$\varepsilon(t)=\int_0^t\left\{\frac{1}{E_0}+C_0(t-\tau)^{C_1}\right\}\dot{\sigma}(\tau)d\tau \tag{5.4}$$

In this model E_0, C_0 and C_1 are the model parameters. In linear visco-plastic model it is assumed that C_0 and C_1 are independent of the stress level. In non-linear visco-plastic model these values are assumed to be functions of the stress level and the model can be described as:

$$\varepsilon(t)=\int_0^t\left\{\frac{1}{E_0(\sigma)}+C_0(\sigma)t^{C_1(\sigma)}\right\}\dot{\sigma}(\tau)d\tau \tag{5.5}$$

Both viscoelastic and viscoplastic models were used to fit the experimental data, based on the three-day experimental data, and then extended to one week. The results are shown in figure 5.11. It can be seen that both models can fit the observed data with high precision during the test period, the first three days, but they start diverging as time grows. The power law model keeps growing and the viscoelastic model approaches an asymptote.

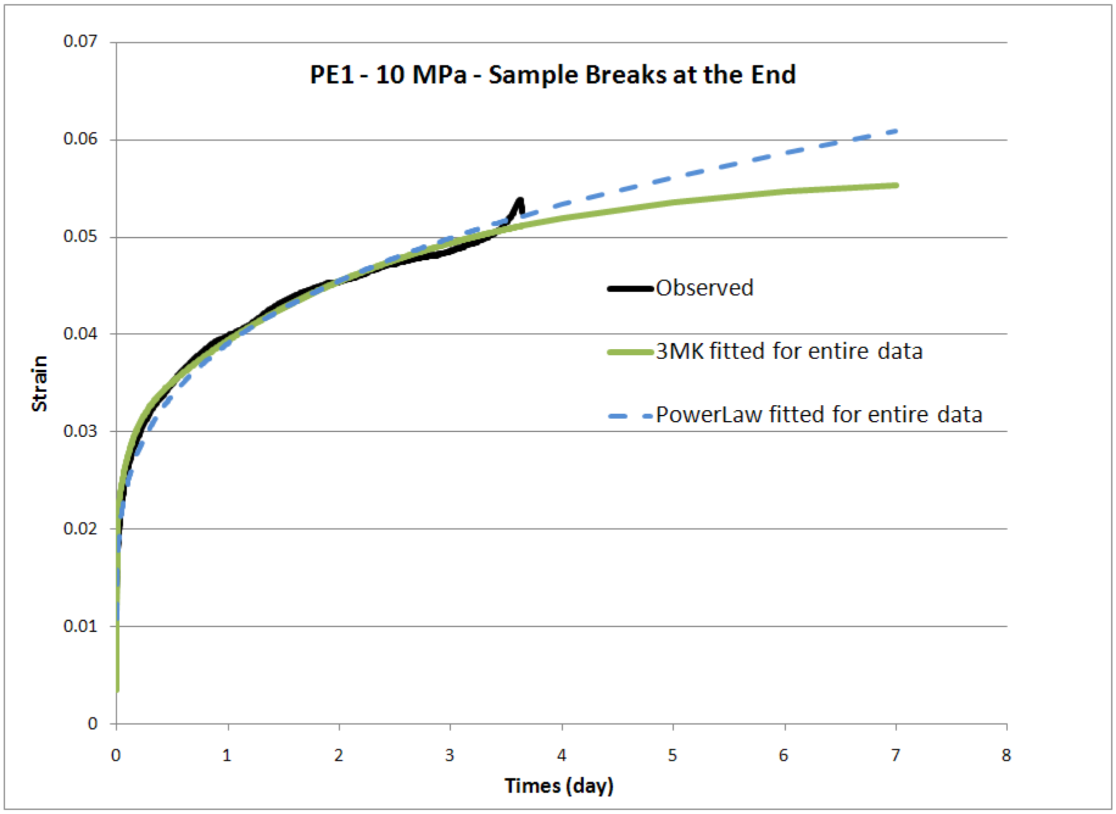


Figure 5.11 – Visco-Elastic and Visco-Plastic Models Fitting the Same Curve.

To have a better understanding of how the two models describe the strain at lower stress level, PE1 at 4MPa was considered. Figure 5.12 provides the observed behavior and the modeled strains using the visco-plastic model. It can be seen that the model can fit the curves at 4MPa very well during the test period. The two curves in Figure 5.12 would also diverge if they were to be extended as it was seen in Figure 5.11.

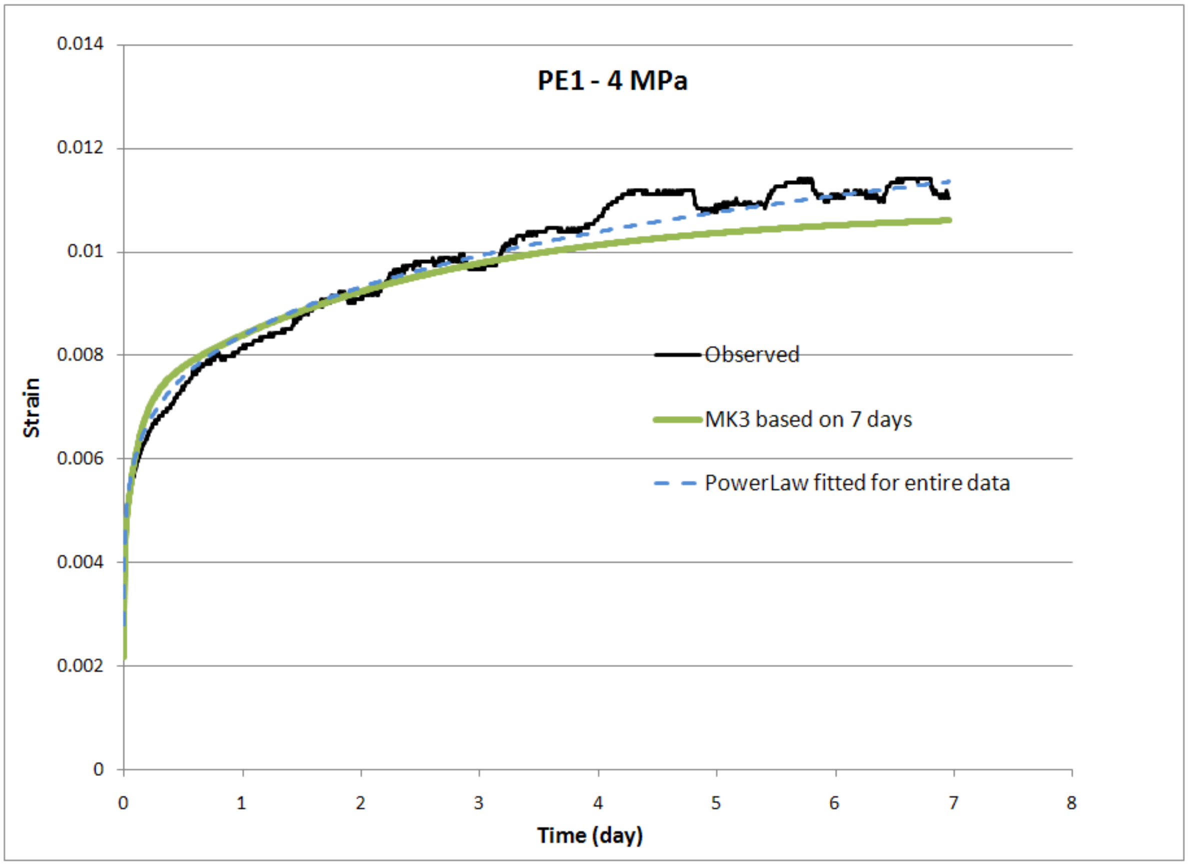
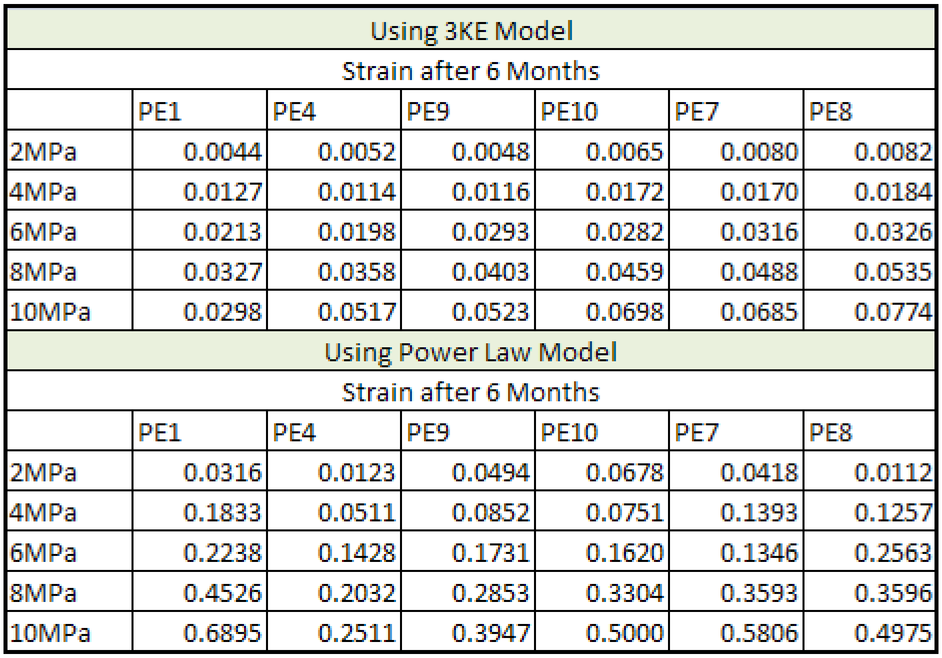


Figure 5.12 - PE1 at 4MPa Modeled Using Visco-plastic Model

Table 5.2 shows the theoretical long term results calculated using linear viscoelastic model and the power law model. It can be seen that the predictions based on the two models are very different. In some cases they vary by an order of magnitude. In all cases the power law model predicts a much higher value for strain. Further work is needed for long-term constitutive modeling of polyethylene. Since long-term material testing is not practical, short term testing must be extrapolated based on the knowledge of how polyethylene behaves under different stress levels.

Table 5.2 – Modeled Strains after Six Months

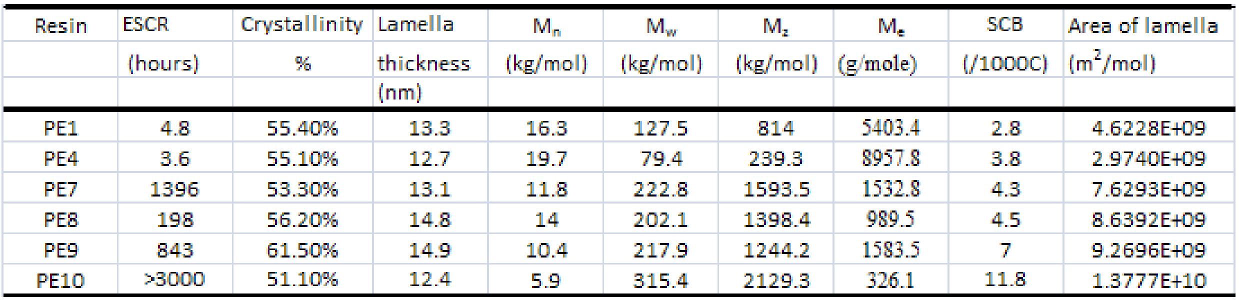


<table>
<tr><th colspan="7">Using 3KE Model</th></tr>
<tr><th colspan="7">Strain after 6 Months</th></tr>
<tr><th></th><th>PE1</th><th>PE4</th><th>PE9</th><th>PE10</th><th>PE7</th><th>PE8</th></tr>
<tr><td>2MPa</td><td>0.0044</td><td>0.0052</td><td>0.0048</td><td>0.0065</td><td>0.0080</td><td>0.0082</td></tr>
<tr><td>4MPa</td><td>0.0127</td><td>0.0114</td><td>0.0116</td><td>0.0172</td><td>0.0170</td><td>0.0184</td></tr>
<tr><td>6MPa</td><td>0.0213</td><td>0.0198</td><td>0.0293</td><td>0.0282</td><td>0.0316</td><td>0.0326</td></tr>
<tr><td>8MPa</td><td>0.0327</td><td>0.0358</td><td>0.0403</td><td>0.0459</td><td>0.0488</td><td>0.0535</td></tr>
<tr><td>10MPa</td><td>0.0298</td><td>0.0517</td><td>0.0523</td><td>0.0698</td><td>0.0685</td><td>0.0774</td></tr>
<tr><th colspan="7">Using Power Law Model</th></tr>
<tr><th colspan="7">Strain after 6 Months</th></tr>
<tr><th></th><th>PE1</th><th>PE4</th><th>PE9</th><th>PE10</th><th>PE7</th><th>PE8</th></tr>
<tr><td>2MPa</td><td>0.0316</td><td>0.0123</td><td>0.0494</td><td>0.0678</td><td>0.0418</td><td>0.0112</td></tr>
<tr><td>4MPa</td><td>0.1833</td><td>0.0511</td><td>0.0852</td><td>0.0751</td><td>0.1393</td><td>0.1257</td></tr>
<tr><td>6MPa</td><td>0.2238</td><td>0.1428</td><td>0.1731</td><td>0.1620</td><td>0.1346</td><td>0.2563</td></tr>
<tr><td>8MPa</td><td>0.4526</td><td>0.2032</td><td>0.2853</td><td>0.3304</td><td>0.3593</td><td>0.3596</td></tr>
<tr><td>10MPa</td><td>0.6895</td><td>0.2511</td><td>0.3947</td><td>0.5000</td><td>0.5806</td><td>0.4975</td></tr>
</table>

6.0 Influence of Molecular Properties on Mechanical Behavior

Each polyethylene has a unique set of molecular properties. For the six polyethylenes labeled in this research, molecular properties were obtained by Cheng (2008) and they are presented in Table 6.1. M_n, M_w, and M_z are defined in Equation 2.1, 2.2, and 2.3. SCB refers to short chain branching defined in section 6.3.

Table 6.1 – Molecular Properties of Polyethylenes



Resin	ESCR (hours)	Crystallinity %	Lamella thickness (nm)	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	M_e (g/mole)	SCB (/1000C)	Area of lamella (m^2/mol)
PE1	4.8	55.40%	13.3	16.3	127.5	814	5403.4	2.8	4.6228E+09
PE4	3.6	55.10%	12.7	19.7	79.4	239.3	8957.8	3.8	2.9740E+09
PE7	1396	53.30%	13.1	11.8	222.8	1593.5	1532.8	4.3	7.6293E+09
PE8	198	56.20%	14.8	14	202.1	1398.4	989.5	4.5	8.6392E+09
PE9	843	61.50%	14.9	10.4	217.9	1244.2	1583.5	7	9.2696E+09
PE10	>3000	51.10%	12.4	5.9	315.4	2129.3	326.1	11.8	1.3777E+10

Chapter 2 provided some background information about crystallinity, molecular weight distribution, branching, and environmental stress cracking. Chapter 6 studies these molecular properties in more depth and examines how they influence the 8-hour creep strain of polyethylene. It was shown in Chapter 4 that when different polyethylenes were ranked based on how much they creep in 8 hours, the order was kept the same at different stress levels. Therefore it was sufficient to study the 8-hour creep at only one stress level. 10 MPa was chosen as the stress level in Chapter 6.

It should be noted that the total creep strain after 8 hours of creep is considered here as a measure of stiffness of polyethylene. Smaller 8-hour creep strain means stiffer material.

To study the influence of a particular molecular property, for example, short chain branching, on short-term creep it is ideal to keep all other properties constant in a polyethylene sample and vary only SCB and then see how the creep function changes. However, from a practical point of view, it is impossible to do so, but it is still useful to study the relationship between each molecular property and creep for different polyethylenes while acknowledging that other properties are not held constant. Such study provides good insight into what molecular property is worth considering when designing polyethylene.

To study how these properties are related to creep in polyethylene, the molecular properties presented in Table 6.1 were plotted vs. total strain after 8 hours of creep due to a constant load of 10MPa.

6.1 Molecular Weight Distribution (MWD)

Figures 6.1 to 6.3 contain the molecular weight distributions for the six polyethylenes studied in this thesis. These distribution functions are obtained from Cheng (2008). It can be seen that PE1, 4, 7, and 8 have uni-modal distributions, having only one local maximum. PE9 and PE10 have a bi-modal distribution. The distribution function is much narrower for PE1 and PE4 than it is for PE7, PE8, PE9, and PE10. From 8 hour creep tests it was found that PE1 would deform the smallest amount when subjected to 10MPa. However PE1 did not withstand the load for more than 4 days and it broke repeatedly when subjected to 10MPa. This behavior could be linked to the fact that the material has a narrow MWD. Narrow MWD means higher short term stiffness but lower long-term strength.

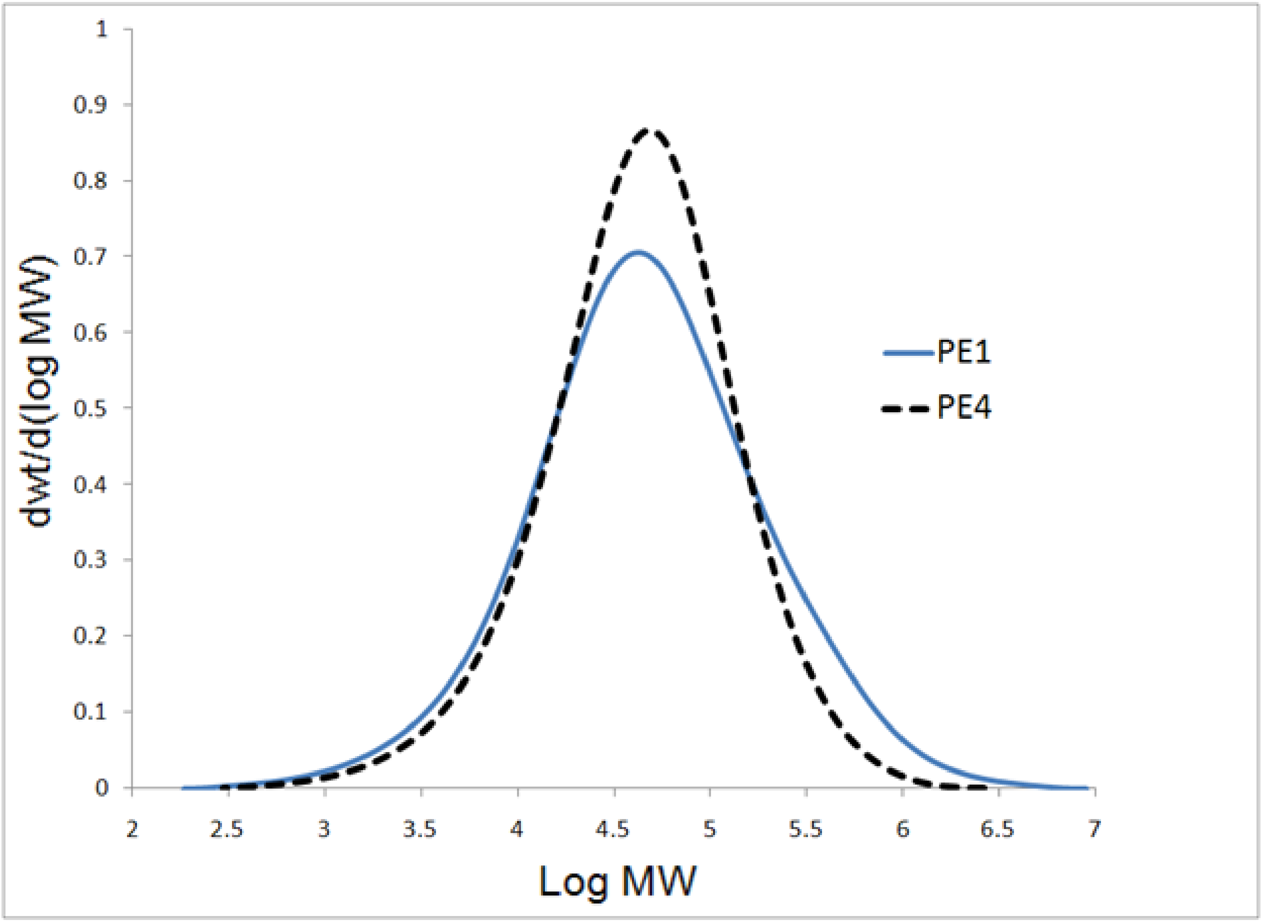


Figure 6.1 - MWD for PE1 and PE4

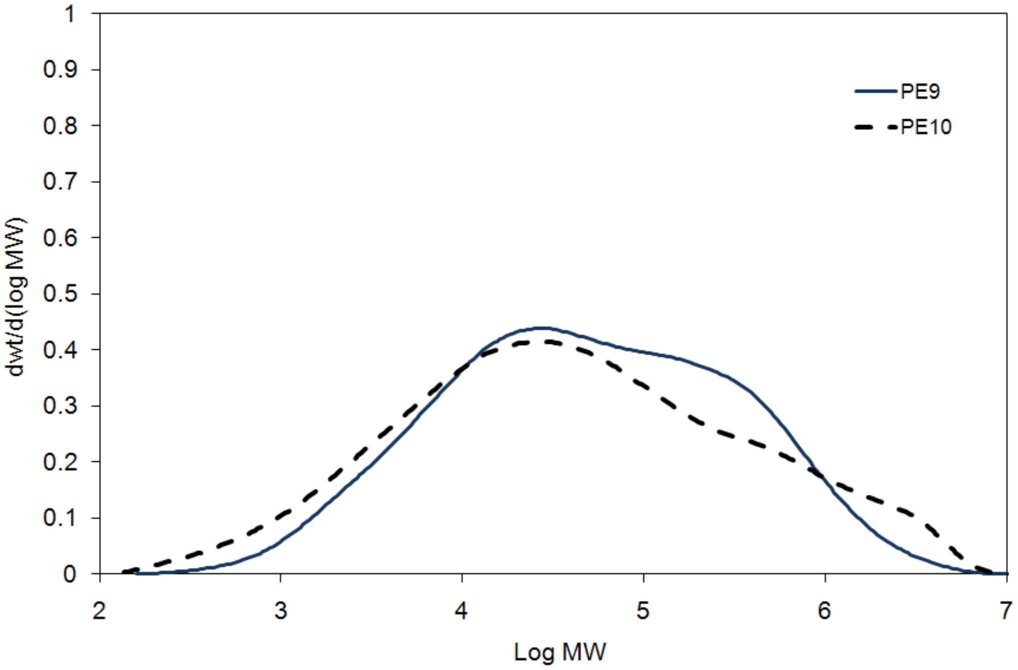


Figure 6.2 - MWD for PE9 and PE10

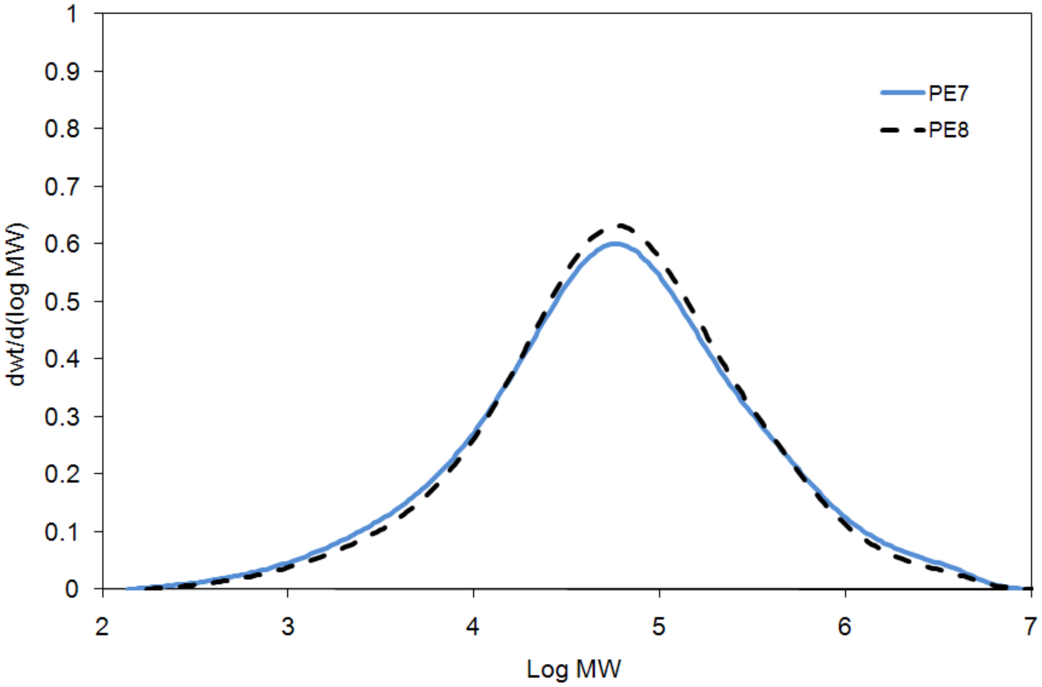
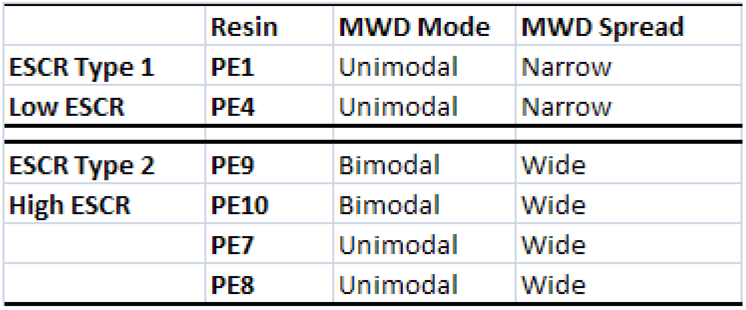


Figure 6.3 - MWD for PE7 and PE8

In the 8-hour creep tests and the stress-strain tests it was seen that PE1 and PE4 had the highest stiffness and lowest creep-stains among the 6 polyethylenes. From the molecular weight distribution functions provided in Figures 6.1, 6.2, and 6.3, it is seen that these two samples have relatively narrow distributions. These results are in agreement with the information provided by The Plastic Pipe Institute (2006), which states that as molecular weight distribution broadens stiffness “decreases slightly”.

Table 6.1 contains the values for ESCR. It can be seen that PE1 and PE4 have much lower resistance to environmental stress cracking than the other four resins. Therefore it makes sense to group PE1 and PE4 in one group, Type 1, and group the other 4 having large ESRC in one group, Type 2. This grouping is based on ESCR. Another distinguishing property of polyethylene is MWD. It was seen in this section that there is great variability in MWD among the resins. The distribution can be uni-modal, or bimodal. It can also be relatively narrow or wide. To summarize these properties for the resins under study Table 6.2 is provided.

Table 6.2 – Grouping Resins based on MWD and ESCR



	Resin	**MWD Mode**	**MWD Spread**
ESCR Type 1	**PE1**	Unimodal	Narrow
Low ESCR	**PE4**	Unimodal	Narrow
ESCR Type 2	**PE9**	Bimodal	Wide
High ESCR	**PE10**	Bimodal	Wide
	PE7	Unimodal	Wide
	PE8	Unimodal	Wide

Mn, Mw, and Mz were defined in Chapter 2. Figures 6.4, 6.5, and 6.6 plot these values versus the 8-hour creep strains at 10MPa. If the ESCR Type 1 and 2 were analyzed separately, one could say that the higher M_n means more creep-strain, higher M_w means less creep-strain and higher M_z means less creep strain. The conclusions do not however apply to PE9 which does not follow the trend of either group.

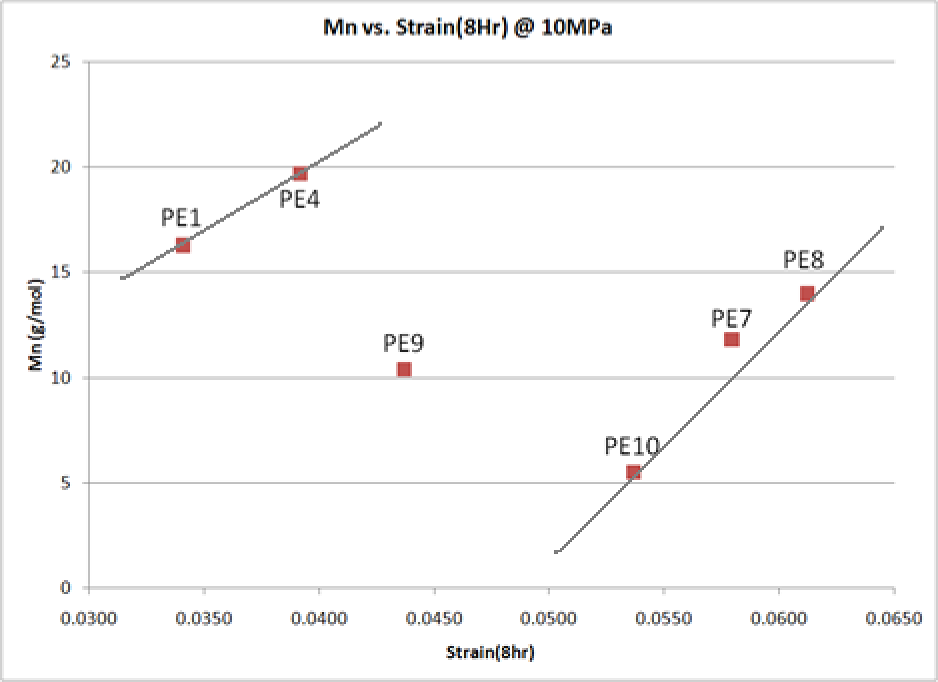


Figure 6.4 - M_n vs. Strain (8hours) at 10MPa

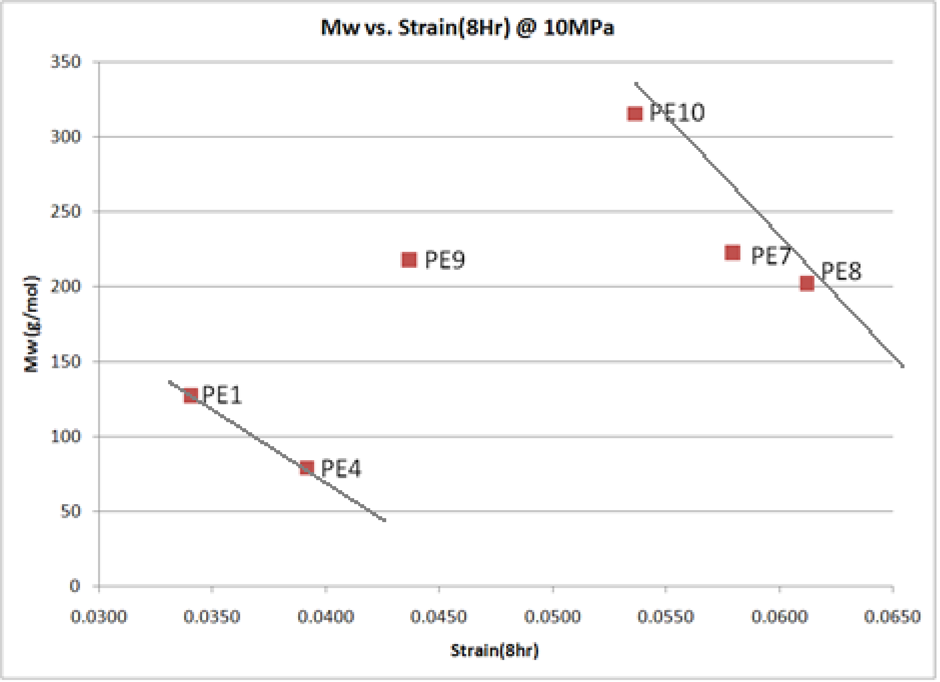


Figure 6.5 - M_W vs. Strain (8hours) at 10MPa

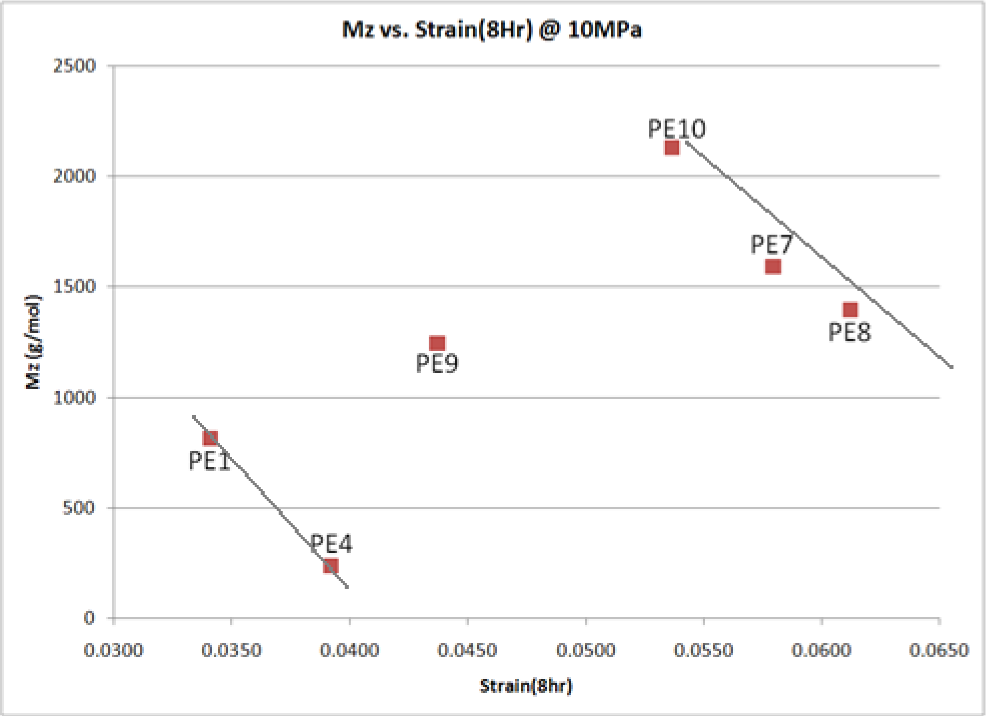


Figure 6.6 - M_Z vs. Strain (8hours) at 10MPa

6.2 Influence of Environmental Stress Cracking Resistance (ESCR) on Short-Term Creep

ESCR values in this thesis were measured by Cheng (2008) using a Notch Constant Load Test (NCLT). In her NCLT tests the following procedure was adopted: polyethylene plates were made using compression molding at 190°C±5°. Each plate had a thickness of 1.8±0.1mm. After making the plates, dogbones were cut out using a sharp-edged die. The dimensions of the dogbones produced are shown in Figure 6.7.

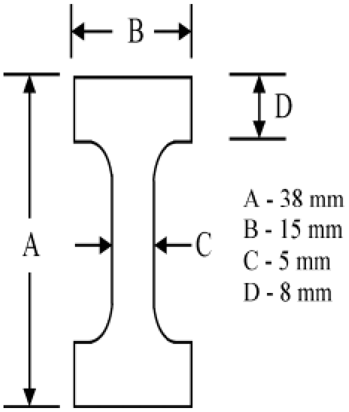


Figure 6.7 – Dimensions of the dogbones used for NCLT

These dogbones were then notched in the middle by 40% of their thickness and subjected to a constant stress equal to 15% of their yield stress. ASTM D5397 recommends notching the dogbones to only 20%. This change in procedure was done in order to speed up the failure as some samples would not fail when they were notched by 20%.

After notching the dogbones, they were placed in a small solution bath that contained 90% water and 10% igepal, (nonylphenyl ether glycol, C19H19-C6H4-O-(CH2CH2O)8-CH2CH2OH), by volume, (ASTM D5397), while being subjected to 15% of their yield stress. The temperature of the solution was kept constant at 50°C. The time before the samples ruptured was measured for each dogbone and the value was assigned as the ESCR for the resin.

In the NCLT test, igepal's function is to simulate an aggressive environment that accelerates failure and the notch is made to initiate cracking of the sample. The failure mechanism is as follows:

- While polyethylene is subjected to tensile stress the chains slowly reorganize themselves, deforming the original shape of the dogbone. This mechanism is also known as the unraveling on the polymeric chains.
- As the load is sustained the crack gradually grows until the sample breaks

Figure 6.8 shows a schematic of the test setup.

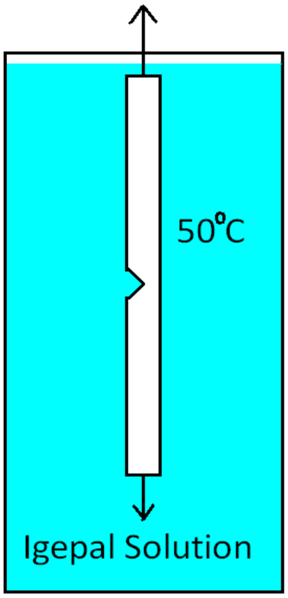


Figure 6.8 – ESCR Test Setup

Figure 6.9 shows the relationship that is observed between ESCR and the total creep strain at 10MPa after 8 hours. ESCR is plotted on a log scale due to high variability of the number. It can clearly be seen that polyethylenes that have relatively high ESCR, PE7, 8, and 9, have significantly higher strains, or lower stiffness, whereas PE1 and PE4 with very low ESCR have low strains. PE9 is an exception in Figure 6.9. It has an ESCR almost 1000 hours but at the same time does not creep much more that PE4 which has an ESCR equal to 4 hours. This desirable behavior of PE9 could possibly be attributed to its bimodal MWD as shown in Figure 6.2.

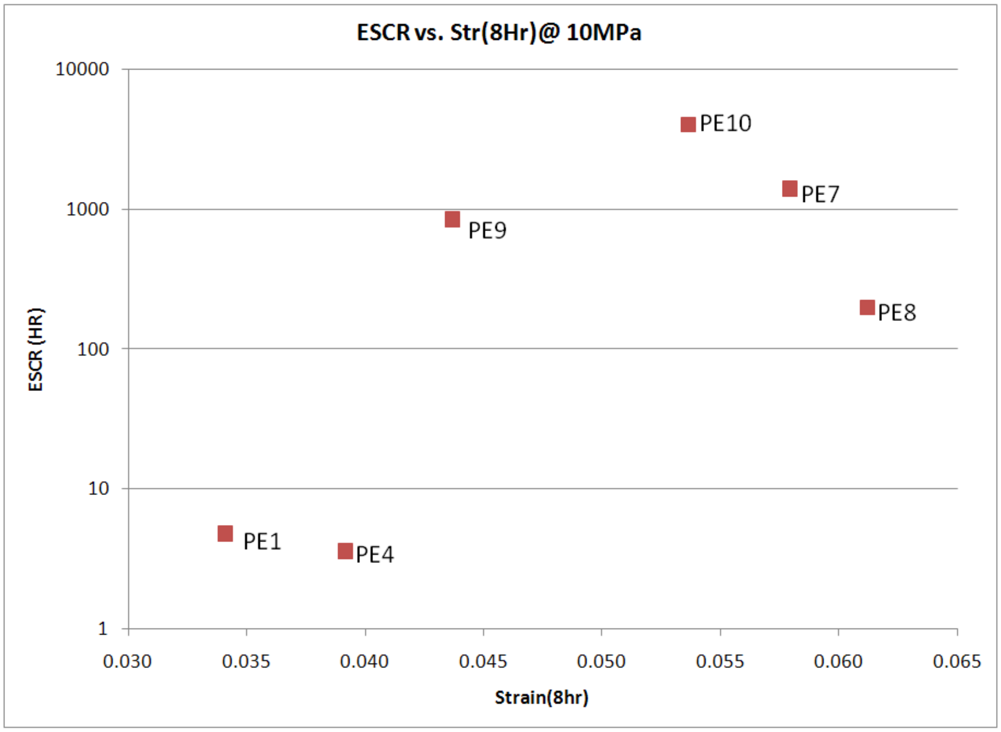


Figure 6.9 - ESCR vs. Strain (8hours) at 10MPa

6.3 Influence of Short-Chain Branching (SCB) on Short-term Creep

Branching was discussed in Chapter 2. According to Cheng (2008), high SCB can lead to high inter-lamellar links that cause high ESCR. To study how SCB influences creep-strains Figure 6.10 is provided. It plots SCB per 1000 carbon atoms vs. the observed creep strain after 8 hours at 10MPa. The points on Figure 6.10 are scattered indicating that SCB is probably not a direct factor in short term creep of polyethylene. There is however a general trend suggesting that strains increase as SCB increases. This observation can be explained as follows: when there are many branches present in polyethylene, fewer crystals can be formed and also the amorphous phase is more entangled. In such conditions strains can grow at a higher rate because of the unraveling that can occur by rearranging the polymeric chains. These entanglements however can play a positive role in avoiding ESC failure and the experimental data support that theory.

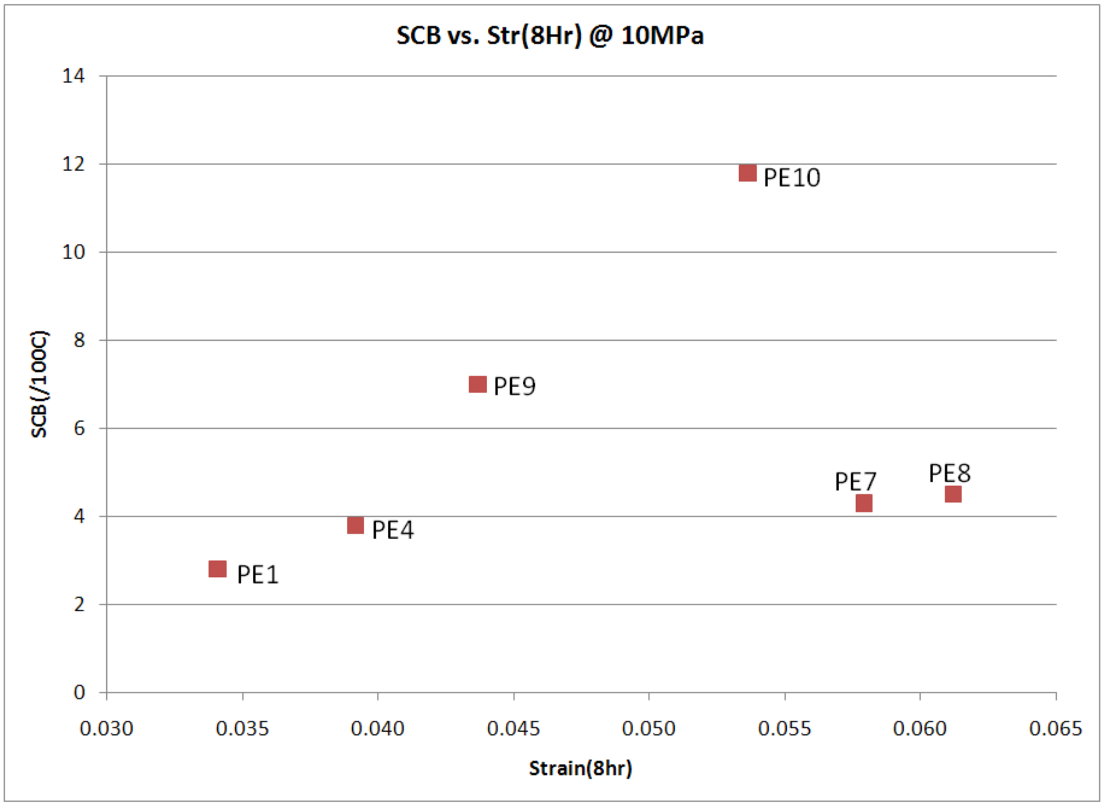


Figure 6.10 - SCB vs. Strain (8hours) at 10MPa

6.4 Influence of Molecular Entanglement Mass, M_e, and Short-Term Creep

M_e is a measure of entanglements in polyethylene. A higher value for M_e indicates that there is, on average, more mass present between entanglements and hence there are fewer entanglements. Figure 6.10 plots M_e vs. strains after 8 hours at 10MPa. It can be seen that PE1 and PE4, having shorter chains than PE7, PE8, PE9, and PE10, have much higher M_e which is probably a contributing factor to their relatively small strains.

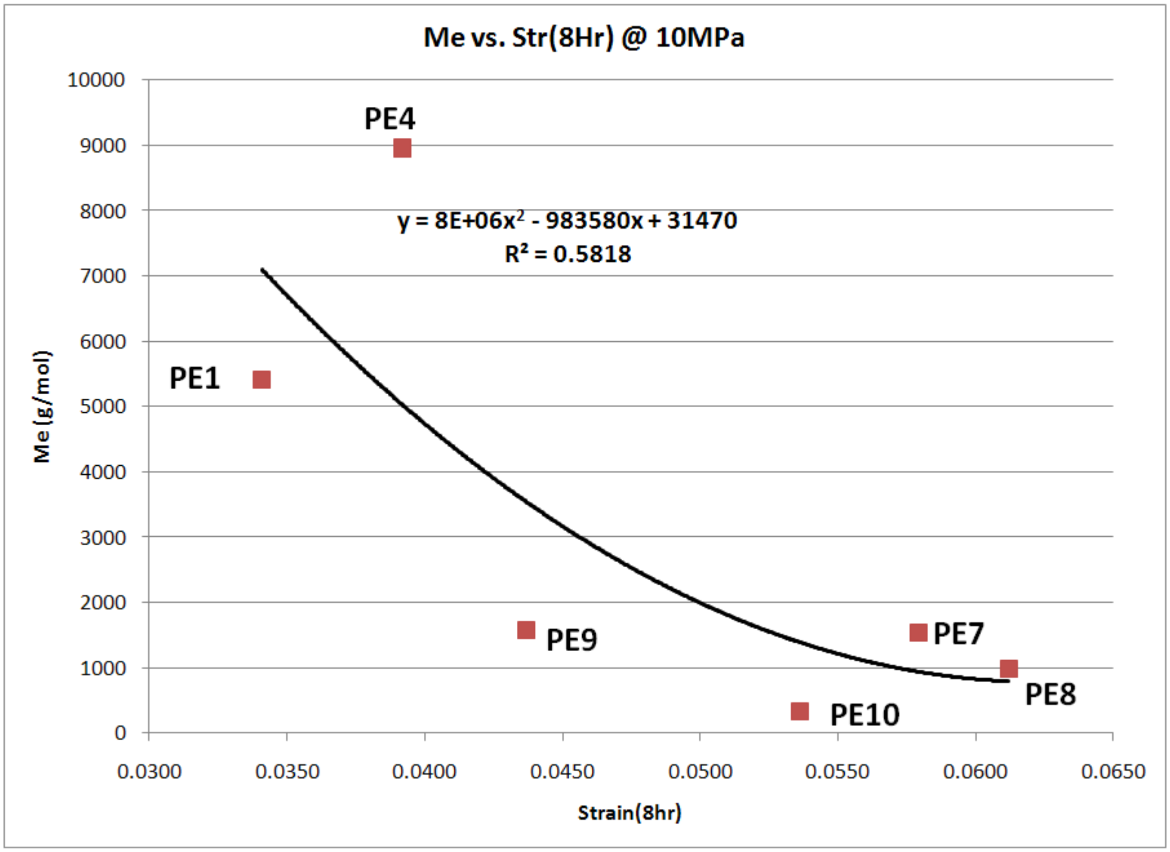


Figure 6.11 - M_e vs. Strain (8hours) at 10MPa

6.5 Influence of Lamellar Area on Short-Term Creep

Polyethylene is a two-phase material. The crystalline phase is in the form of lamellar micro-plates. It was seen in Table 6.1 that crystallinity in the six samples varies from 51% to 61%. The lamellar thickness however can vary by up to almost an order of magnitude among the six resins, which also results in a varying lamellar area among resins.

Figure 6.12 plots lamellar area vs. strain. It can be seen that there is a direct correlation between lamellar area and strains. Given that the polyethylenes under study have more or less the same crystallinity, it can be concluded that the ones with lower lamellar area, which implies more lamellar micro-plates, have lower creep-strains. Therefore it can be stated that more pieces of crystalline phase play a role in reducing the short term creep of polyethylene.

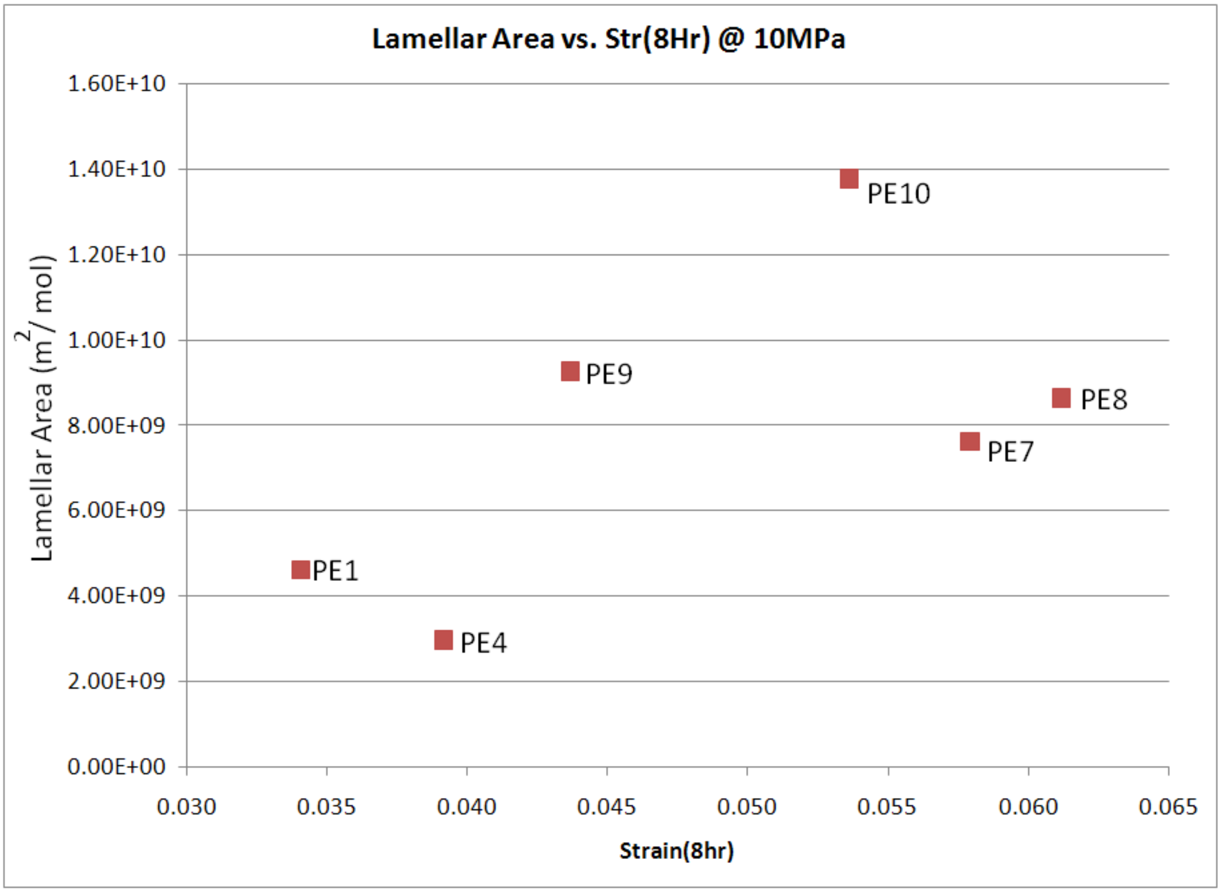


Figure 6.12 – Lamellar Area vs. Strain (8hours) at 10MPa

7.0 Conclusions

Different kinds of polyethylene, having different molecular properties, were compared against each other. Two kinds of conclusions are presented: ones that provide information about the general mechanical behavior of polyethylene as a material and ones that relate molecular properties to short and long term mechanical properties.

The conclusions that are drawn purely from the mechanical tests performed, namely strain controlled, short-term creep, and long term creep tests are as follows:

1. Polyethylenes exhibit non-linear behavior with respect to stress. This conclusion is drawn from the observation that creep compliance curves differ at different stress levels.
2. The maximum stress that the samples of high density polyethylene under study could withstand in strain controlled tests at 7 mm/min varied between 20MPa and 27MPa.
3. This maximum stress occurred at around 10% strain.
4. Visco-elastic and visco-plastic models can be curve-fitted to experimental creep data with high precision but when used to predict strains that would occur far beyond the experimental time period, they produce very different results.
5. When polyethylene was subjected to 4MPa and 10MPa stress, the strain was still visibly growing after 2 weeks, meaning it continued to creep.
6. Plastic deformation was observed in the creep tests at 4MPa and 10PMa.
7. The strain-controlled test and the 8 hour creep tests are fairly repeatable with an error that is usually less than 10%.
8. The creep function at a given stress level for different kinds of high density polyethylene, having different molecular properties, can vary by a factor of two.
9. There is a danger in evaluating polyethylene based on its short-term creep performance because from observations it was seen that the sample with lowest short-term creep and highest stiffness suddenly broke in a brittle way when the load was sustained for a few days.
10. There is a direct relationship observed between maximum stress a polyethylene sample could withstand and how much it creeps due to constant stress such that ones with higher maximum

stress consistently creep less. This fact is partly due to the relationship between yield stress and modulus of elasticity.

The conclusions that relate molecular properties of polyethylene to its short-term and long-term mechanical behavior are as follows:

1. Creep properties of polyethylene are influenced by the presence of long chains since it was observed that creep strains were more dependent on M_z or M_w than M_n. It was seen that as M_n increased, creep strains decreased, but as M_w and M_z increased the creep strains increased.
2. The presence of long chains and/or a wide molecular weight distribution can make the material softer and creep more but could potentially increase the resistance to environmental stress cracking and other forms of brittle failure.
3. The samples with larger M_e were observed to creep less, meaning more entanglements in a polyethylene makes it creep more. At the same time, larger M_e, or fewer entanglements, results in lower ESCR.
4. Having a bimodal MWD, like the one for PE9, can improve short-term creep behavior and prevent brittle failure due to sustained load, improve ESCR and long-term strength.
5. Generally it was observed that good long-term performance, as measured by ESCR, results in a reduced short-term stiffness. The exception was PE9. It showed very good ESCR, equal to 843 hours, at the same time it had relatively high stiffness in short-term tests. More research is needed to draw definite conclusions.

8.0 Recommendations for Future Work

The following recommendations are to be considered for future work:

- Repeat notch constant load test on polyethylene resins examined by Cheng (2008) to study the repeatability on the values obtained for ESCR.
- Perform notch constant load test on new polyethylene resins to see if the ESCR can be predicted based on molecular structure of the materials.
- Group new materials based on having similar ESCR and MWD and study how molecular properties influence creep behavior in each group by performing short-term and long-term creep tests.
- Develop a model for polyethylene structures that can be used in finite element analysis in order to assess the long-term performance of the structures.

References

1. Alvarado-Contreras, J. A. (2007), Micromechanical Modeling of Polyethylene, PhD Thesis, Department of Civil Engineering, University of Waterloo, Waterloo, Ontario, Canada.
2. Book of ASTM Standards (2007), Section Eight, Vol. 08.01
3. Cheng, J., (2008), PhD Thesis: Mechanical and Chemical Properties of High Density Polyethylene: Effects of Microstructure on Creep Characteristics, Department of Chemical Engineering, University of Waterloo, Waterloo, On, Canada.
4. Clegg, D.W., Collyer, A.A, (1993), Polymeric Materials, The Institute of Materials
5. Daniels, C.A., (1989), Polymers: Structure and Properties, Technomic Publishing Co., Inc.
6. Drozdov, A.D., and Kalamkarov, A. L., (1996), A Constitutive Model for Nonlinear Visco-elastic Behavior of Polymers, Polymer Engineering and Science, July 1996, Vol. 36, No. 14.
7. Ferry, J.D., (1970), Viscoelastic Properties of Polymers, Second Edition, John Wiley and Sons Inc.
8. Hearle, J.W.S, (1982), Polymers and their Properties: Fundamentals of Structure and Mechanics, vol 1, Ellis Horwood Ltd.
9. Krishnaswamy, P., Tuttle, M. E., & Emery, A. F. (1992), Finite element modeling of the time-dependent behavior of nonlinear ductile polymers, Polymer Engineering and Science, vol. 32, no. 16, pp. 1086-1096.
10. Liu, H., (2007), Material Modeling of for Structural analysis of Polyethylene, Department of Civil Engineering, University of Waterloo, Waterloo, On Canada.
11. Liu, H., Polak, M.A., Penlidis, A. (2008), A practical Approach to Modeling Time-Dependent Nonlinear Creep Behavior for Structural Applications, Wiley InterScience, Society of Plastic Engineers.
12. Lockett, F. J., (1972), Nonlinear Visco-elastic Solids, Academic Press, 1972.
13. Mills, N.J., (2005), Plastics: Macrostructure and Engineering Applications, Butterworth-Heinmann.
14. Schapery, R.A., (1969), On the Characterization of Nonlinear Viscoelastic Materials, Polymer Engineering and Science, 9(42), 295-310.
15. The Plastic Pipe Institute, Inc. (2006), Engineering Properties of Polyethylene.
16. Zhang C., and Moore, I.D., (1997), Nonlinear Mechanical Response of High Density Polyethylene. Part I: Experimental Investigation and Model Evaluation, Polymer Engineering and Science, Feb 1997, Vol. 37, No. 2.