Master Thesis

Comparative study of properties of HDPE-100, pipe recycled HDPE and their blends

Tomislav Horvat
Amanda Salazar del Campo

Department of Materials and Production
Aalborg University
Denmark
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Materials Science and Engineering
Fibigerstraede 16
DK-9220 Aalborg O, Danmark
http://www.m-tech.aau.dk

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Students:

Tomislav Horvat
Amanda Salazar del Campo

Supervisors:

Jesper de Claville Christiansen
Aleksey D. Drozdov

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Abstract

Polymer waste is an issue that has proven to be one of the greatest challenges of our times. Finding new ways of reintroducing waste polymer materials in manufacturing processes has therefore become increasingly important. Presented study is trying to provide a small magnitude contribution to the big problem. In this case, High Density Polyethylene that is used for piping systems is characterized, and so is the recycled High Density Polyethylene (rHDPE). The goal is to analyze and assess weather or not is it possible to reintroduce the rHDPE in the manufacturing process as a part of a blend with vHDPE without compromising the final properties of the end material.

Differential scanning calorimetry (DSC) tests was done to analyze the differences in crystallinity of vHDPE and rHDPE. Following that, it was of interest to measure the stability of rHDPE and vHDPE, particularly due to the concern of possible degradation in rHDPE. This was done by the Oxidation Induction Time (OIT) test, where information about the time of starting degradation of both vHDPE and rHDPE, at certain temperatures were obtained. Furthermore, rheometry (oscillatory and time) tests, using plate-and-plate geometry, was to identify differences in molecular weight and molecular weight distribution, and the flow of rHDPE and vHDPE. Also, Indications on the occurring degradation mechanisms in materials have been traced.

Tensile tests were done to see the differences in mechanical properties. Moreover long term tests: creep, relaxation and cyclical tests provided information about vHDPE and rHDPE materials behavior under long term loading conditions.After the characterization of both materials independently, blends were made in following ratios: 30% - 70 %, 50% - 50 %, 70% - 30 %, and assessed in the tensile test. The results are presented in property-composition graphs.

DSC results showed minimum difference between vHDPE and rHDPE crystallinity (50.61 %, and 51.37 % respectively). On the other hand, OIT tests proved that rHDPE is less stable than vHDPE, as it required less time for the start of the degradation.

Furthermore, rheology tests displayed that rHDPE starts degrading sooner then vHDPE at 240 °C. It was also proven by means of rheology that rHDPE exhibits lower viscosity, lower molecular weight, and higher molecular weight distribution. Although, the differences in all those parameter between vHDPE and rHDPE are minor.

Tensile test results showed lower yield strength and higher strain at yield for rHDPE compared to vHDPE at different testing cross-head speeds. However, the differences between the tested properties lie within the range of 7%-14% of variation, and rHDPE does not perform considerably worse then the vHDPE.

Creep tests at 10MPa, and relaxations tests at 6% strain provided results were no differences between rHDPE and vHDPE were seen. However, in creep test at 15MPa, rHDPE exhibited less deformation in 20 minutes than vHDPE, suggested to be due to the presence of cross-links.

Indication of cross-links presence in rHDPE was also found in cyclical loading test, where rHDPE fractured at lower number of cycles then vHDPE ($\approx$ 10 for rHDPE, compared to $\approx$ 300 for vHDPE), at maximum applied stresses close to the yield stress.

For all the blends done in all compositions, these performed lower then vHDPE and higher than rHDPE, with no significant differences in between them.

All being said, it is concluded that rHDPE and vHDPE behave alike in low stress and strain conditions, however in long term application, at higher possible loading conditions caution needs to be raised and materials further tested.

Preface

This project is concluded by students of 4th semester in Materials Technology at Aalborg University in the June of 2019 as the master thesis.

We are grateful for the opportunity to work with professors Jesper de Claville Christiansen and Aleksey D. Drozdov. Thank you for your time, dedication, and inspiring us to tackle important challenges.

We send our gratitude to the personal in the workshop of the Department of Materials and Production, especially to Thomas Sørensen for always offering his support and knowledge.

We are grateful for our colleagues, who shared with us this delightful and challenging experience. Together we got through!

Finally to the whole Department of Materials and Production at Aalborg University. Thank you for your commitment to make from us professionals prepared for "Breaking New Ground".

Personally, I am grateful for my family that was the unconditional supportive network I always had to accomplish this goal. My friends, Fernanda, Paula and Christian, thank you for always making life easier.
Amanda

My personal gratitude goes to my parents, my brother, and Ana. Thank you for your sacrifices and everlasting support, even at hardest of times. I am truly standing on shoulders of giants.
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Introduction 1

1.1 Project Background

According to R. Geyer et al. [1], polyethylene (PE) was the largest tonnage produced plastics material in 2015. Also, Zion Research Report [2] presented polyethylene as the most sought out plastic in the world. The projected global demand, it is estimated to grow even further (4%, to reach a value of approx. USD 215 billion by 2024). This is attributed to PE's low production cost as well as its properties such as, excellent electrical insulation, very good chemical resistance, good processability, and toughness [3].

Motivated by this tendency, an increasing number of new directives and policies towards sustainability enhances the demands of including polymer waste into the manufacturing processes of new products. This has driven companies to find solutions in order to fulfill those requirements [4]. As a consequence, a need of innovative solutions for the produced waste is of high interest. To accomplish the demands, an understanding of the life cycle of the material as well as its post-used properties is required.

One solution for the produced waste is mechanical recycling, as this has been one of the most attractive processes due to the cost and environmental impact. The mechanical recycling consist on the reintegration of the recovered material into the manufacturing process after it is grinded and supplied with additives or other polymers to ease further processing. [5].

The main complication of recovered plastic waste is the possibility of degradation through the life cycle of the material that is used. Degradation is understood as the loss of the desirable properties of the material due to different happening mechanisms within. Degradation is dependant on the environmental conditions in which the material was employed as well as the initial polymer structure and manufacturing back history [6, 7].

With the purpose of restoring the properties of the recovered polymer, mixture with additives is normally used to help the polymer improve its properties. Nevertheless, this is sometimes not enough to achieve the desired final product performance, so blending the recycled material with other polymers results as a better solution. Not only polymer blends are used to reduce the produced scrap, but they offer a new set of benefits for the industry as lower manufacturing cost, processability improvement,etc [8].

Therefore, parting from a virgin polymer resin designed for a certain purpose, different paths of degradation happen, depending on the use of the polymer. As the polymer is recycled, the most optimal path to recover its properties need to be designed. The complex nature of the system requires clear boundary conditions in which the designed solutions are optimal.

With that in mind, this project is an attempt to understand the degradation mechanisms happening in recovered PE. Moreover, this knowledge will be utilized to compound it with virgin PE and compare the modification of the polymer properties. So the questions arisen are: in what extent the properties of the virgin HDPE vary when compared to the recycled HDPE

(High density polyethylene)? If the properties of the recycled material have deteriorated, can polymer blending improve the properties of the material? Which are the optimal blending ratios of virgin and recycled HDPE?

1.2 Project Description

The Directive 2008/98/EC [9] that defines the legislation of waste management in the European Union (EU) defines recycling as " any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes".

Three important concepts have to be considered: "waste", "reprocessed" and "purpose". As mentioned before, the recovered material (waste), has a back history in which the polymer chains were probably modified. As a consequence, the desired performance of the polymer (purpose) is affected, this being the main reason of the impracticability of polymer reintroduction into the manufacturing process. Therefore, the material is upgraded (reprocessed) by, in this case, polymer blends.

PE being one of the most common polymers used in numerous applications, it is important to understand the properties of the virgin HDPE (vHDPE). In order to accomplish what is stated by the legislation regarding the use of recycled materials, the main questions to be answered are: how the polymer structure is modified from its initial (vHDPE) to the final state (recycled HDPE - rHDPE)? And, what are the resultant properties of the polymers due to these modifications?

Therefore, the proposed hypothesis are:

1. The constrain of a recycled material is the experienced degradation, as a result it will not perform the same as the virgin material. Then, it cannot be used as the main primary resource at manufacturing process.
2. If degradation modifies the polymer chain structure, the occurring mechanisms can be related to final properties such as viscosity and mechanical performance.
3. Recycled material can be upgraded by adding virgin material. By compounding, the blend should have properties similar to the virgin material.

1.2.1 Problem Statement

According to what is is presented in CH.1, the main matter for the present study is to characterize and compare the main thermo-mechanical properties of vHDPE and rHDPE. Due to the previous use of rHDPE, it might be degraded so an attempt to identify the degradation mechanism is done. Further, the optimal blends are designed and tested.

In order to resolute this, thermal testing such as differential scanning calorimetry (DSC) and rheometry are done to evaluate the molecular dynamics of the polymer. Furthermore, short term and long term mechanical testings are performed. If rHDPE results considerably differ from vHDPE, the polymer properties are recovered by polymer blends and further tested.

Literature Review 2

2.1 Polyethylene

PE is a synthetic polymer that embodies the most basic structure (a repetition of CH_2 units), and has its origins that dates back to 1933 in the work of Eric Fawcett and Reginal Gibson of Imperial Chemical Industries [10, 11].

It is produced by polymerization of ethylene ($CH_2 = CH_2$) through the action of initiators and catalysts. Ethylene is the simplest alkene (olefin), and alkenes are in organic chemistry known as unsaturated chemical molecules containing at least one carbon double bond [12].

The polymerization equation of ethylene can be seen in Eq.2.1 [10], and the graphical representation in Fig.2.1.

$$nCH_2 = CH_2 \xrightarrow{\text{catalyst}} CH_2CH_2n \tag{2.1}$$

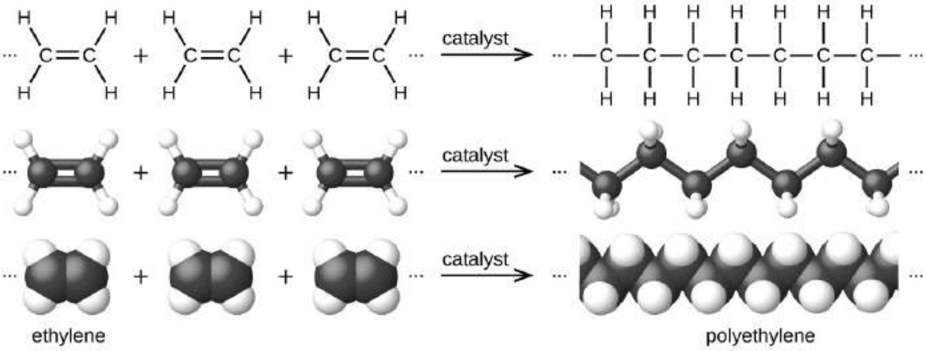


Figure 2.1: Formation of Polyethylene chain by reaction of multiple ethylene molecules in the presence of a catalyst [13]

What needs to be noted is that there are multiple possible PE polymerization processes. Conditions for polymerization have wide variations, different catalysts and chain transfer agents that lead to different end groups. These are primarily alkyl groups, therefore PE is often regarded as a mixture of high molecular weight alkanes [10].

Main polymerization processes that are used for preparation of different types of polyethylene from ethylene are [11]:

1. High-pressure processes
2. Ziegler-Natta process
3. The Phillips process

4. The Standard Oil (Indiana) Process
5. Metallocene Process

Generally polymer materials are divided in two major categories (thermosets & thermoplastics) depending on their thermal properties. PE falls in the thermoplastic material category. There is a range of melting points of PE, depending on molecular weight, crystallinity (or amorphous content) and chain branching. In the molten state PE is a viscous fluid and it behaves like a "non-Newtonian fluid" (its flow is not directly proportional to the pressure) [10]. In regards to mechanical properties of PE, they also vary based on the molecular weigh and degree of branching, but also on testing rate, temperature of test, preparation method, and shape and dimensions of specimens [11].That being said, the importance of chain mobility and the relation to, in this case, mechanical properties, is crucial.

Currently there are multiple hundreds of PE grades, and they exhibit different properties that mostly arise from variables like [11]:

- Degree of short chain branching
- Degree of long chain branching
- Avg. molecular weight
- Molecular weight distribution
- Presence of comonomer residues
- Presence of impurities or polimerization residues

2.1.1 High Density Polyethylene (HDPE)

Polymers are usually classified by acronyms defined by The American Society for Testing and Materials (ASTM) in ASTM D 883-19a [14] publication "Standard Terminology Relating to Plastics", these mainly describe the molecular structure of the polymer [10], such as:

- High Density Polyethylene (HDPE): $>$ 0,941 g/cm^3
- Linear Low Density Polyethylene (LLDPE): 0,919 - 0,925 g/cm^3
- Low Density Polyethylene (LDPE): 0,910 - 0,925 g/cm^3

These three major PE types (HDPE, LDPE, LLDPE), most often used in the industry have the chain structure as presented in the Fig.2.2 [10]. That being said, there are wide range of polyethylenes, so the classification has further been subdivided to offer more convenient measures (like describing molecular weight or employed comonomer), but generally this is the characterization mostly used.

Each polymerization processes previously listed, results in different types of PE, for example the High-pressure process results in the manufacturing LDPE and on the other hand the Ziegler-Natta process and the Phillips process are used to produce HDPE. Because of the conditions at which each polymer is processed, polymer results in the various molecular structures, for example HDPE has a much lower degree of branching (0,5 - 3 vs. 15-30 side chains per 500 monomer units) therefore it has a different structure than the one obtained by free radical polimerization. This can be seen in Fig. 2.2 [12]. Therefore, HDPE is referred to as a linear polyethylene and LDPE on the other hand as branched polyethylene [12].

As previously mentioned, HDPE can be produced by polymerization of ethylene by using either Ziegler-Natta or Phillips organometallic catalyst that control the formation of the chain [10, 16].

1. **Ziegler - Natta process (ZN)**: - often referred to as co-ordination polimerization, because the mechanism involves a catalyst-monomer co-ordination complex that controls

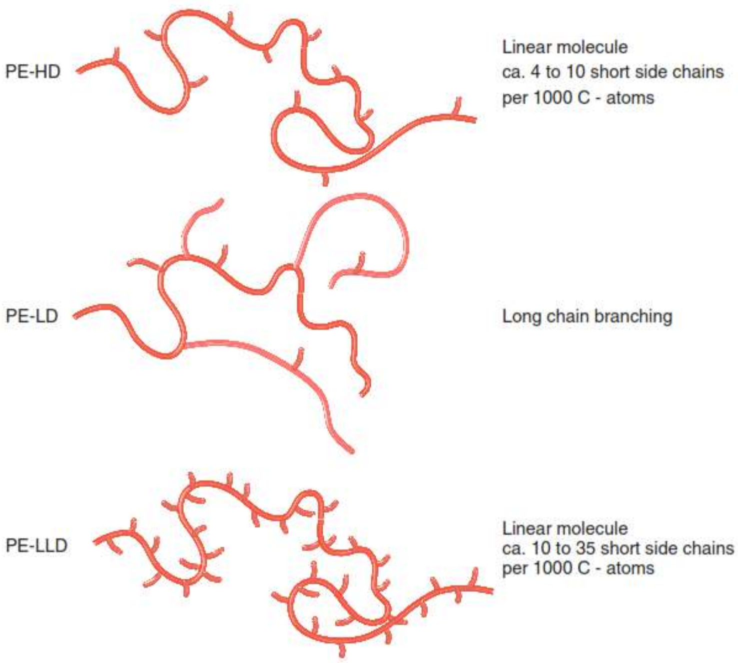


Figure 2.2: Schematic representation of three major PE types, where bold middle line is representing the "backbone" and the shorter side-lines the chain branches. [15]

the way monomer approaches the chain. A typical ZN catalyst system usually contains two parts: a transition metal (Group IV - VIII) compound and an alkyl of Group I-III metals (co-catalyst). Examples of ZN catalyst systems would be $TiCl_4 + Et_3Al$ and $TiCl_3 + AlEt_2Cl$. ZN process is a tool to polymerize α-olefins with high linearity and stereoselectivity [11]. Polymers obtained by Ziegler-Natta process have an intermediate density (around $0,945 g/cm^3$), and when comparing with what can be obtained with other processes it would be between high-pressure polyethylenes and those produced by Phillips and Standard Oil processes. In regards to molecular weights, a wide range can be obtained by varying catalysts Al-Ti ratio, by varying the reaction temperature, and by introducing hydrogen as a chain transfer agent [11].

2. **The Phillips process (Phillips supported chromium catalyst)**: - ethylene that is dissolved in a liquid hydrocarbon (like cyclohexane) is being polymerized by a metal oxide catalyst (at 130-160 °C and 1,4-3,5 MPa). The catalyst consists of a chromium oxide supported on a silica gel. By this process, polymers with a melt flow index (MFI) in the range from 0,1 to 600+ can be obtained, although commercial products are in the range of 0,2-5. From all commercial poylethylenes they have the highest density (approx. $0,96 g/cm^3$) [11]. Molecular weight of the polymer depends highly on the temperature. In a typical process MFI can be increased by 40 times, and molecular weight decreased correspondingly, when raising the polimerization temp. from 140 to 170 [11]. In regards to pressure, above 2.8 MPa, the reaction pressure has little influence on molecular weight or polymer yield, but at lower pressures there is a decrease in yield and in molecular weight [11].

One of the main differences on the resultant HDPE produced by these methods, is the amount of terminal vinyl unsaturations. Due to this, different degradation mechanisms could be favored as previously analyzed [17, 18]. By means of stability, a double carbon bond is easier to break and react with the environment compared to the C-C single bond. If there is a high concentration of vinyl groups, then these will promptly react to form branched chains compared to the other case where mainly experiences chain scission [12, 19, 20].

Low branching degree is the reason for HDPE's high crystallinity (70-90%) and high crystallization velocity, while on the other hand, LDPE that has a high degree of branching (40-60 % crystallinity) [12]. As a result, this influences the increase in density for HDPE and the crystalline melting temperature (130-138°C vs 105-115°C) [12].

The high degrees of crystallinity, also result in good mechanical properties. HDPE has the highest stiffness and lowest permeability out of all types of PE [19]. This particular combination of properties is beneficial for liquid containers, detergent bottles, and chemical storage tanks, where HDPE finds its application. Furthermore, resistance to corrosion, stiffness, and good tensile strength make HDPE suitable for manufacturing pipes, short-term load bearing film applications, or other household and commercial low load capacity applications, like food storage containers, pallets, and toys [19]. When the application requires more aggressive conditions, cross-linking can be used to further improve chemical resistance, and mechanical properties [19].

Additives - Carbon Black (CB)

To maintain the physical properties of polymers, enhance their performance and behaviour at different exploitation environment conditions, a wide range of additives is used, carbon black being one of them [21].

Plastics additive is defined by European Union food contact regulation as: "a substance which is intentionally added to plastics to achieve a physical or chemical effect during processing of the plastic or in the final material" [21].

Carbon Black (CB) are a family of, mostly amorphous, or paracrystalline carbon particles formed in aggregates of variety of shapes and sizes [21, 22]. Most commonly it is being used as an reinforcing filler, color pigment, for electrical conductivity, and to prevent thermal and photodegradation [21, 23, 24].

The efficiency of CB in regards of improving some of those parameters depends on the type of CB, the size of the particles, concentration and the dispersion [24]. It has been reported that the optimum particle size of CB, to improve photodegradation resistance of polyethylene is around 20nm, and in the concentration range of 2-8% [24]. However, it is a challenging task to achieve good dispersion of CB with that particle size and concentration. On the other hand, if the dispersion of CB in HDPE is well done and there are good inter facial interactions between CB and HDPE, then increasing the % of CB in HDPE matrix will have a positive impact on tensile properties of the material [24].

2.1.2 Polymer physics

2.1.2.1 Molecular Weight

The molecular weight of any polymer is a sum of all the individual atom weights that form a molecule, and it indicates the avg. length of the bulk resin's polymer chains [25]. It needs to be noted that not all polymers of specific grade have the same molecular weight. There is rather a distribution of molecular weights, as it is shown in the Fig.2.3 for a typical thermoplastic polymer [15, 25]. There are two main ways of characterizing polymers molecular weight, first one being number-average molecular weight, M_n [25].

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \tag{2.2}$$

i - the number of polymer molecules
N_i - the number of molecules that have the molecular weight M_i

The other calculation is the weight-average molecular weight [25]:

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{2.3}$$

The ratio M_w/M_n is called molar mass dispersity index, and if all polymer chains are the same, then $M_w = M_n$, and the molar mass dispersity index or polydispersity (PI) $= 1$. The molecular weight distribution will be wider as the index is higher [15, 25, 26], Fig.2.3.

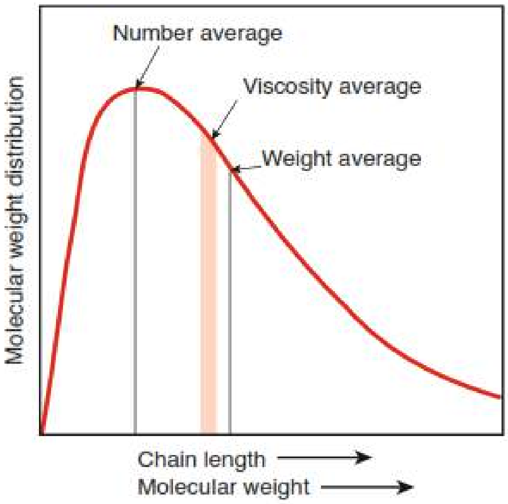


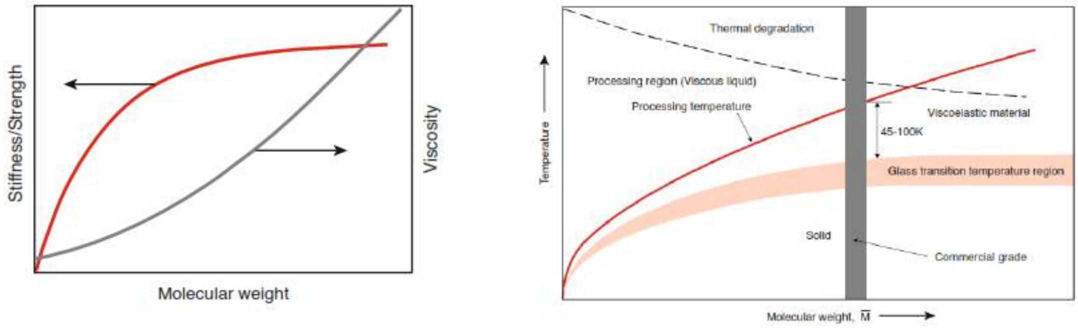
Figure 2.3: Distribution of Molecular weight for a typical thermoplastic [15]

Molecular weight is a strongly influential factor on the properties of polymers, which can also be seen from the graph presented in Fig.2.4 [15]. The increase of the variation of the viscosity and the flow temperature in respect of the the molecular weight is represented in Fig.2.4a. On the other hand, the temperature for the polymer to be degraded increases as the molecular weight increases, Fig.2.4b. Molecular weight is then determinant for the polymer performance, therefore important to be identified. The polydispersity of the material can be modified in order to achieve desired properties and ensure the flow properties that will enable processing in the manufacturing [15].

2.1.2.2 Polymer Crystallization and Morphology

Most polyolefins, including polyethylene, are semicrystalline [19]. Their semicrystalline structure consists of two or more solid phases, one of which has molecular chain segments that are packed into 3D regular arrays (crystalline), and in the other chains are disordered (amorphous, non-crystalline) [19].

In the interface between crystallite surfaces and disordered regions is a third phase, often called the interface, or partially ordered region, which consists of chain segments that have



(a) Molecular Weight vs Stiffness and Viscosity (b) Molecular Weight vs Temperature

Figure 2.4: Representation of the relation between Mw, temperature and properties of a typical thermoplastic polymer [15]

different degrees of order as they traverse it [19]. The schematic of the three-phase morphology in PE is shown in the Fig. 2.5.

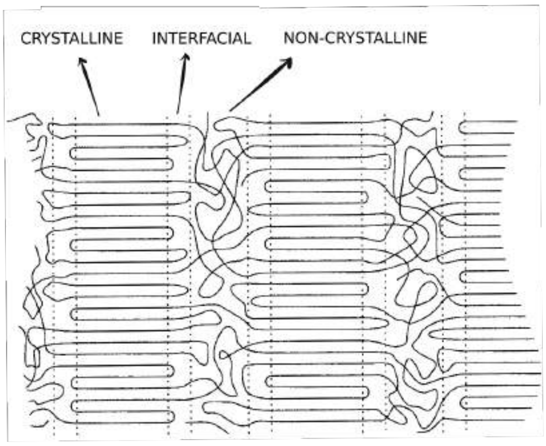


Figure 2.5: Schematic representation of three-phase morphology of polyethylene (PE) [26]

The process when material from the amorphous state is transformed into the crystalline state from solution or melt is called crystallization [27].

When polymer chains crystallize, they fold on themselves and form a structural element called lamellae, which consists of crystalline core of folded chains and two amorphous regions next to the core [26]. The largest morphological unit of linear low branched types of polyethylene resins that crystallize from melt are spherulites [26]. Spherulites structure is multiple fibrils (rays) radiating in all directions from one center and that are made of stacked lamellae [26]. The graphical representation of that can be seen in Fig 2.6.

Crystallization of polyethylene occurs when prevailing conditions make the crystalline state more stable than the disordered state [19]. Thermodynamics is the driving force behind crystallization. The system is trying to achieve the lowest possible free energy state, but this is hindered by different factors like polymer chain entanglements, viscosity or non-crystallizable entities like cross-links [19]. Difference in structure of crystalline regions depending on the level of branching in different polyethylene types, as can be seen in Fig.2.7.

The quantitative characterization of semicrystalline nature of different polyethylene samples is done by the 'degree of crystallinity' [19]. The value can be obtained experimentally by multiple methods including X-ray spectroscopy, infrared spectroscopy (IR), differential

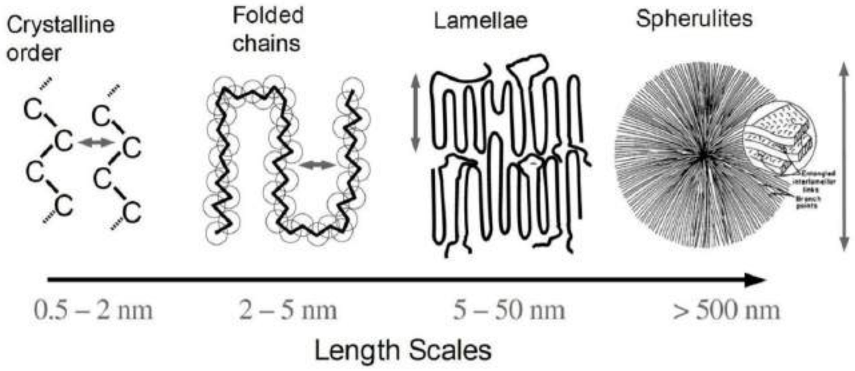


Figure 2.6: Polymer Crystal in the scale of length [27]

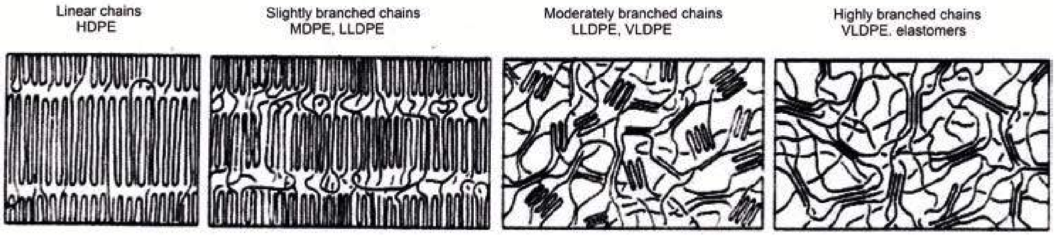


Figure 2.7: Morphological features in different polyethylene types [26]

scanning calorimetry (DSC), ultrasonic method, etc. [19,26]. For LDPE resins the 'degree of crystallinity' can be from 5 - 10%, while on the other hand for some HDPE grades it can be $>$ 70% [26]. Polyethylenes degree of crystallinity will determine its physical and mechanical properties [19].

2.1.3 Relation of structure to polymer physics

Polyethylene physical properties is a combination of the balance between the molecular weight distribution in the melted state and the crystallinity in the solid state. As it was described previously, there is an inherent relation between polymer physics and the thermal and mechanical properties of PE, as these are influenced by the combination of its crystalline and amorphous phase and the links between them. [19,26]

When the material is recovered and reprocessed (recycled), this undergoes modifications at its molecular level due to the stress and temperatures it is subjected. The resistance to these changes relays on the stability of the molecular structure. If while being recycled the material degrades, there will be an alteration on its performance as the morphology is expected to be affected. By way of illustration, the hard crystalline solid behaviour HDPE shows when virgin can change to a flexible crystalline solid by chain scission occurring during reprocessing or to a rigid crystalline solid by cross-linking, further insight is given after.

In this case, the processability of the material as well as the mechanical properties change. Properties such as melting point and therefore viscosity, or regularity of the structure and therefore young modulus or compliance change, as illustrated in Fig.2.4. On the premise that the recycled material or its blends need to perform close to the thresholds values of the virgin material, different properties need to be characterized and compared.

2.1.3.1 Polymer Flow

In the molten form, many deformation forces that PE can be subjected to will influence its resulting solid-state properties, considering the limits imposed by molecular characteristics [19]. PE resins are known to be non-Newtonian liquids, their viscosity varies depending on the speed of the flow, the faster the melt of PE flows the less viscous it becomes [26]. Or in other words, the viscosity of molted PE decreases, as the shear rate increases. This is also known as shear thinning [19].

As mentioned, PE can be deformed in molten state, but when the force that is deforming is removed, the PE tends to come back to its original dimensions. The amount of elastic recovery and viscosity of PE are a function of molecular entanglements, and those entanglements are dependent on molecular weight distribution and branching [19]. Reducing the concentration of entanglements will result in lowering PE's viscosity.

The model that describes such a behavior, the behavior of viscoelastic liquids is the Maxwell model, according to which a deforming force acts on a spring and dash-pot that are aligned in a series as can be seen in the Fig.2.8. Tensile force applied to such a system will result in the elongation of the spring and the displacement of piston based on the resistance provided by dash-pot. Once the force is released, the spring moves back but the dash-pot retains the permanent set, see Fig. 2.8. Thus, spring resembles the elastic constant of polymer chains sections between entanglements, and the dash-pot corresponds to the entanglements that control the rate at which polymer molecules can slide past each other [19].

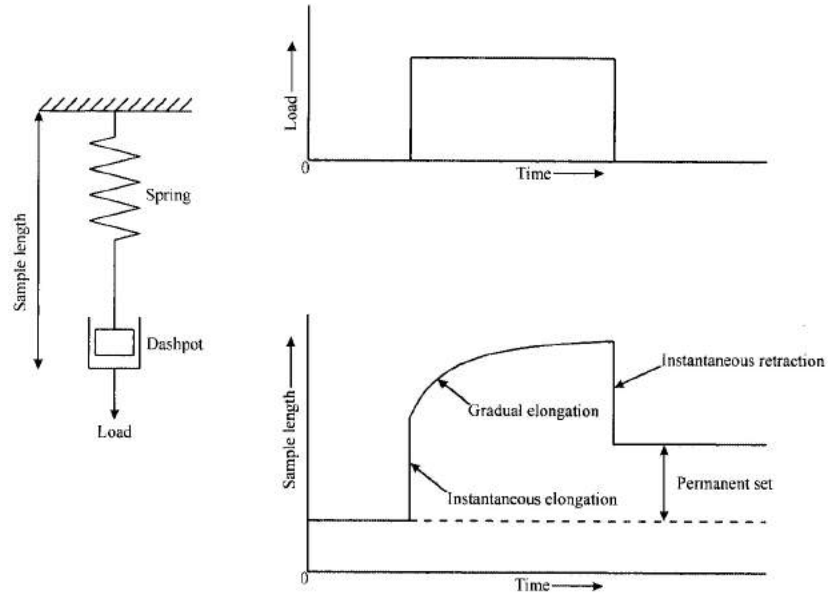


Figure 2.8: The Maxwell model that is describing behavior of viscoelastic liquid [19]

When doing the characterization of inherent polymer properties by performing rheological tests, it is very important that measurements are done in linear viscoelastic range. The deformation needs to be kept small, so that the molecules have enough time to relax through the Brownian motion, and so that the structure of polymer remains unchanged, and that there is no disruption of entangled and coiled state of molecules [28].This relaxation of the molecules is described by the relaxation modulus - G [28].

One of the experiments used to characterize linear viscoelastic properties of polymers is the Small Amplitude Oscillatory Shear (SAOS). In SAOS, the polymer is loaded dynamically at small predefined strain amplitude under changing frequency. In oscillatory shear, the deformation is sinusoidal with viscoelasticity being signified as a lag in phase between the stress and strain, which is described by the phase angle δ, and can be seen in the Fig. 2.9 [28].

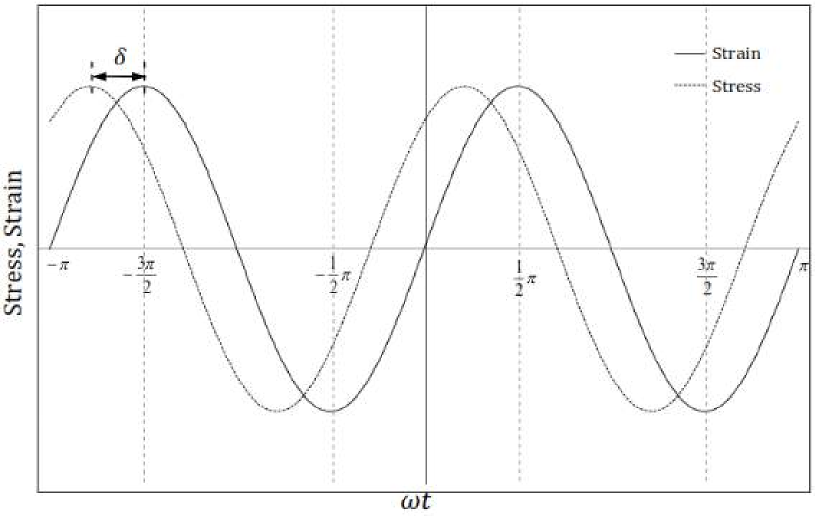


Figure 2.9: Sinusoidal output of stress and strain in a viscoelastic material [28]

The data obtained in such tests, that allows for characterization of the polymer includes the viscoelastic moduli: storage modulus G' that is representing the elastic part (energy being stored in the polymer), and loss modulus G'' representing the viscous part (energy dissipated in deformation) [28].

$$G' = \frac{\tau_0'}{\gamma_0} \tag{2.4}$$

$$G'' = \frac{\tau_0''}{\gamma_0} \tag{2.5}$$

The τ_0', and τ_0'' stand for in phase, and out of phase stress, respectively. While, γ_0 is the strain amplitude.

There is also the complex viscosity, which is the relation between the moduli and the frequency and is expressed by the following equation [28]:

$$\eta* = \sqrt{\eta'^2 + \eta''^2} = \sqrt{\frac{G'}{\omega}^2 + \frac{G''}{\omega}^2} = \frac{G^*}{\omega} \tag{2.6}$$

The resulting curves obtained from a typical SAOS test are shown in Fig.2.10. At lower frequencies, as it can be seen, the loss modulus (G”) is higher, so the polymer is having an liquid-like behavior, while at high frequencies the storage modulus is higher and so the solid-like behavior is apparent. Looking at the crossing point, where G’ and G” are equal, it is possible to get an indication of the avg. molecular weight (M_w), and molecular weight distribution (MWD), as can be seen from the Fig.2.10. In the current study, this cross-point is used to analyze the possible molecular changes in rHDPE compared to vHDPE.

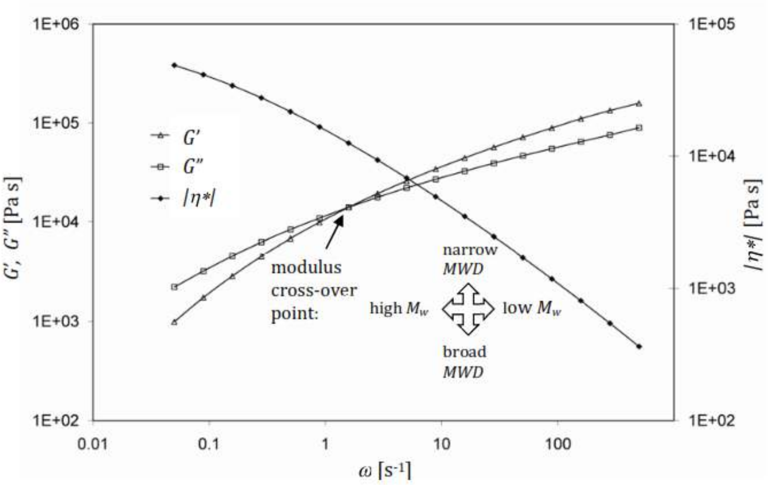


Figure 2.10: SAOS test result curves, with emphasises the crossing point of G' and G" as it gives the information about the polymers molecular weight and the molecular weight distribution [28]

2.1.3.2 Cross-linking and Chain Scission

The molecular degradation of PE may follow a range of ways, including chain scission, cross-linking, inclusion of external chemical functional groups, and it is caused by either thermal, mechanical, photo-oxidative, or radiological processes [19]. Following that, the molecular degradation affects mechanical, physical, and rheological properties of long chain polymers [19, 29]. Both chain scission and cross-linking, are causing changes in polymer's molecular weight, which affects rheological and mechanical properties of the solid polymer. Chain scission is decreasing the average molecular weight of the polymer, while on the other hand cross-linking is increasing it [19]. The balance of both competing mechanisms (chain scission and cross-linking) depends on the chemical environment, temperature, used stabilizers and their effectiveness [19].

Cross-linking is a process where adjacent polymer chains form covalent bonds, either directly carbon-carbon, or indirectly via bridging group. The chemical cross-linking can be classified into reactions that take place between carbon backbone atoms of polymer's chains, and those that involve reactions of side groups connected to the backbone [19]. In PE cross-links can vary from isolated bonds that are linking pairs of adjacent chains, to multiple links between adjacent chains that are forming a whole single interconnected network [19]. When each polymer chain is connected to 2 or more neighboring chains, the entire sample forms a single molecule where each atom is connected to other by a series of covalent bonds.

The average length of the molecular segments between the cross-links, will determine the physical properties of a cross-liked network [19]. Resulting effect of the cross-links in a polymer is dependent on their density, chemical structure, molecular mobility, morphology, and also their distributions [29]. It has to be noted that even low cross-link density can have profound effect on properties of the polymer [19, 29].

Cross-linking is incorporated in PE when its dimensional stability at high temperatures, or impact resistance need to be improved. It is also used to reduce the propensity to stress crack [19]. At room temperatures cross-links positively influence PE's tensile properties, but even more importantly cross-links hinder molecular slippage in noncrystalline regions. Therefore, creep and stress-cracking can be significantly reduced by cross-linking, because of the reduced segmental movements in noncrystalline regions between crystallites [19], further described in CH.2.1.3.3. As the degree of crystallinity and crystallite thickness decrease, consequently, the elastic modulus, yield stress, elongation at break, and peak melting temperature all decrease as well [19].

2.1.3.3 Mechanical behaviour

Polymers inter-molecular attraction, molecular weight and the type and amount of crystalline structure all influence the mechanical properties. Under an applied strength, polymers tend to rearrange its chains in order to have the lowest structural energy level. The rearrange can be described in a macro-scale with terms such as elastic modulus or creep. [19, 30]

That being said, as presented in polymer flow (CH.2.1.3.1), the material can be described as a spring and dash-pot system. Therefore, the solid state of the polymer can either behave elastically or viscous. The polymer's response is determined by its molecular characteristics. As a consequence, the response of the polymer depends on the conditions at which the material is tested and the previous history of the material.

The elastic behaviour of the material is described as the inability of the polymer to dissipate energy during and after loading, at least before the yielding stress [31], mainly due to the high stability on the ordered polymer network [19, 26]. This is commonly studied by the stress-strain relation in which the uni-axial constitutive law is represented by,

$$\epsilon = \frac{\sigma}{E} \tag{2.7}$$

Where E is the tensile or young modulus, and it represents the spring constant, Fig.2.8. Therefore, E characterizes the stiffness of the material.

On the other hand, the viscous behaviour of the material emulate a fluid. This means that the material cannot stand normal stresses but is affected instead by shear stress and pure hydrostatic loading [31]. The constitutive law that characterizes this behaviour is,

$$\epsilon = \frac{\sigma t}{\eta} \tag{2.8}$$

The combination of this models in different configurations describe the visco-elastic behaviour of polymers. This material visco-elastic behaviour, where either the elastic or the viscous part is dominating, is controlled either by morphological features or molecular characteristics, depending on the strain [19, 20, 26] as seen in Fig.2.11.

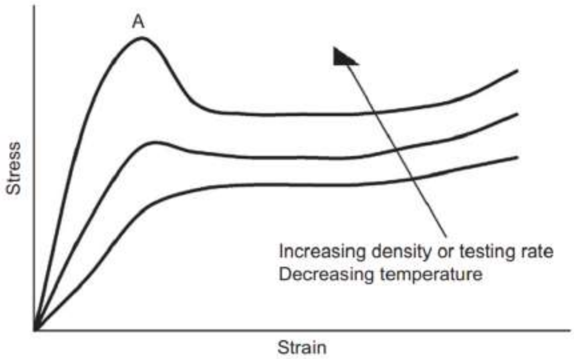


Figure 2.11: Consequence of different factors on stress-strain curve of PE [11]

For example, it is seen in Fig.2.11 that as crystallinity/density (morphology of the polymer) increases, the tensile strength at yield becomes notable as a sharper resultant curve. Furthermore, the crystallinity also influences the tensile modulus, E. On the other hand, molecular weight distributions (MWD) govern the ultimate tensile strength (CH.2.1.2), showed by the dependence of the curves on temperature and test rate. This means that chain mobility becomes an important determinant factor of the shape of the stress/strain curves.

Tensile properties

A common measurement to characterize the deformation of the polymer is by applying an uniaxial force and record the elongation of the sample. The resultant measured deformation in reference to the applied force characterizes the tensile properties of the material. The stress can be plotted against percentage of deformation, however it is important to notice that commonly the reported values are "engineering" values, as it is still hard to record the instant deformation [19, 31]. That being said, in this study, the presented values are "engineering" values, which means the force per the initial cross section of the specimen.

The mechanical changes are expressed by stress/strain curves, normally obtained by the uniaxial application of stress on the sample. Under this analysis, PE is reported as a resin with ductile properties and low fracture toughness [11, 19, 20, 26, 30]. Therefore, the normal deformation of PE under an applied force is the yielding, strain hardening, necking and fracture. From this curve it can be obtained values such as the Young modulus, E, yield stress, σ_y and the breaking strain, ϵ_{br} [19, 26]. The response of these variables depends on the morphology of the material, suchlike the resultant magnitude of the material strength governed by crystallinity. Therefore, a general curve cannot be obtained for all polyethylenes, confirming the complexity of the system. This is seen on Fig.2.12, where different behaviours depending on the nature of the polymers are observed. As mentioned before, PE generally behaves as a ductile (though) material. However, this behaviour varies depending on molecular modifications of the polymer and testing conditions.

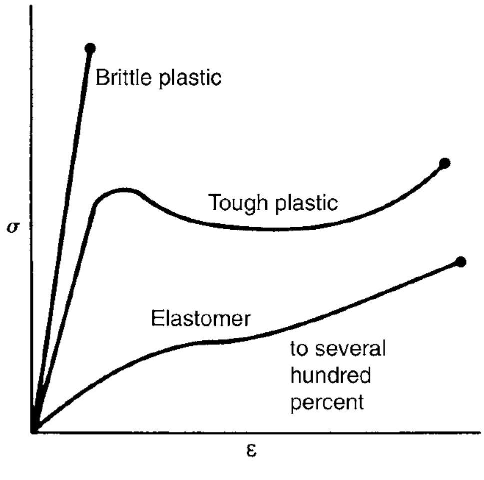


Figure 2.12: Stress/strain behaviour of different types of polymers

Independently on the stress/strain behaviour, the curve is mainly described by the following variables [19, 20, 26]:

- yield stress, σ_y (MPa)
- yield strain, ϵ_y (%)
- fracture tensile stress, σ_{br} (MPa)

- elongation at break, ϵ_{br}.(%)
  Remember that all stresses measurements are done on the initial cross-sectional area.

The elastic region is defined by the linear behavior of the curve until σ_y. In this region the elastic modulus,Young modulus or initial modulus is calculated. This value represents the rigidity of the material, higher values are characteristic of stiffer materials. Then, if crystallinity is the morphological characteristic that defines the strength of the material, it is expected that the elastic modulus varies linearly with the crystallinity.

The yield stress, σ_y is a critical value in the curve as it determines the onset force that the sample can withstand before its dimensions are irreversibly changed. For example, it is reported that typical yield stress for HDPE is, $\sigma_y \approx 29$ to 33 MPa. On the other hand, the value for LLDPE is $\sigma_y \approx 9$ to 15 MPa [19, 26]. The main reason for the difference in values is the polymer chain structure, in which due to the packed configuration of the chains, the HDPE comes to be stronger than LLDPE [15, 19, 26]. Consequently, the tensile modulus (E) and yield (σ_y) are determinant when comparing vHDPE and rHDPE, as these polymers are expected to perform for the same requirements.

Long-Term Mechanical properties

A special case of the time dependant mechanical performance is creep. This phenomena occurs when constant load (σ_0) is applied on the material and this experiences continuous deformation. When enough time is provided, the time-dependant permanent deformation of the material occurs [31]. Further times can lead to a catastrophic creep fracture, therefore creep is dependant of certain conditions of time and temperature.

Under prolonged loading, the material experiences progressive increases in strain. This is described in three phases, primary (I), secondary (II) and tertiary (III) creep, as shown in Fig.2.13. The first one is characterized by the rapid decrease of the strain rate, the second one is the steady increase strain phase and the third one is the region in which strain increases up to fracture.

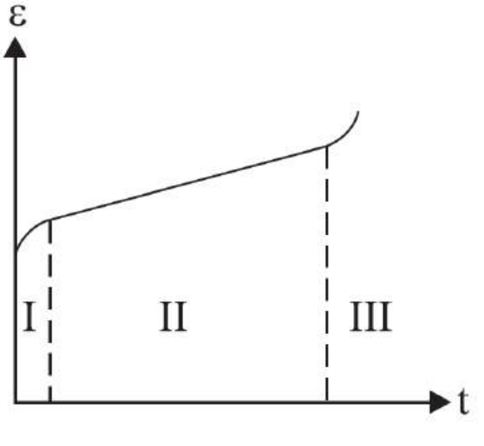


Figure 2.13: Creep curve [31]

Creep is a phenomenon that is affected by the release of applied stresses when molecular rearrangement occur. If there is a much larger freedom in molecular motion, the faster the relaxation of the stress will happen and the material keeps its integrity at long times. Therefore, chain mobility when evaluating mechanical properties of the material is crucial. As degradation changes the molecular structure of the polymers, degradation mechanisms can significantly affect mechanical properties.

This study analyzes the difference of properties between a virgin and a recovered material, the degradation that the latest experiences is important to consider. Whatever mechanism that hinders or enables chain mobility, have a beneficial or disadvantageous effect on the polymer performance. For example the possible chain modifications that hinder chain movement are entanglements, branching and cross-linking. This is seen in HDPE resins that have lower draw ration at break that LDPE due to the amount of branching [19]. Moreover, cross-linking helps on dimensional stability at high temperatures and reduces creep and stress cracking, but affects viscosity.

To visualize the previous arguments of chain mobility mechanisms, an alternative scheme of Fig.2.5 is seen in Fig.2.14, in which the different elements of molecular networks at the inter-facial zone are presented. This zone has a crucial role on polymer strength and therefore chain mobility, as this is the region at which stress transmission happens through elements of the molecular networks such as entanglements [32].

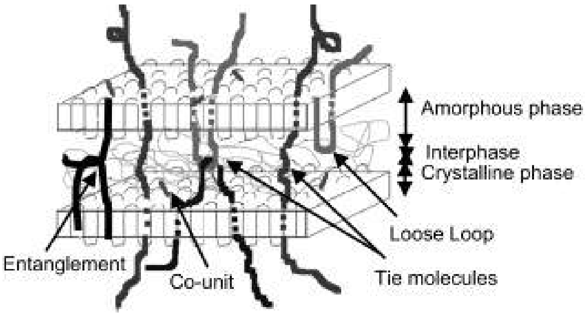


Figure 2.14: Scheme of the crystal lamella and amorphous regions, tied by chains compatible with both structures [32]

Humbert et.al. [32] has proposed various arguments that relates crystallinity with polymer yielding and elastic modulus. For polymer yielding, his argument is similar to the previously presented. He supports the fact that before yielding, the deformation of the polymers is dependant on the amorphous phase. Furthermore, the yielding value is considered to be dependant on crystalline thickness and what he calls "stress transmitters (ST)". His main idea is that the mechanical coupling between the phases is determined by the amount of ST and the slip of crystallites due to the amount of applied stress transferred. So if the polymer has conditions in which the ST are favoured, the material could become brittle and vice-versa.

Moreover, CH.2.1.2 described the enhancement of chain movement due to changes in temperature. Therefore, when measuring long term mechanical properties it is important to define the work temperature range of the material as this influences the relaxation rate of the chains.

Finally, in order to certify the reliability of the polymer to withstand loading, cycling test is a tool that can provide this information. Cyclic loading consists on inducing progressive deformation on the material in order to characterize the possible discontinuities inside it. For instance, cross-links emerge as initiators of cracks as they are flaws already present in the material due to the manufacturing process or previous history.

As the material is loaded and unloaded, the residual strength of the material decreases due to the propagation of the damage within the material, depending on the applied stress range. That being said, a cyclic loading test can provide valuable information about the state of the material and long time resistance [33–35].

2.1.4 Orientation of Polyethylene

Orientation of PE is referring to the alignment of polymer's molecular segments. Oriented solid-state polymers can be obtained by either solidification from an oriented melt, solid-state deformation below the melting temperature, or some combination of those two [19]. The main difference being in reduced capacity for relaxation of molecules in solid-state orientation. In the solid state is not possible for molecules to reach equilibrium state as they are in oriented melts. Instead, molecular segments that get oriented in noncrystalline regions remain oriented [19].

Different morphologies of oriented polymers can be obtained, and all depending on the starting orientation of the melt, the time duration the melt has to relax between orientation and solidification, and the temperature rate at which solid-state deformation happened [19]. Nevertheless, generally, at high degrees of polymer orientation two types of morphologies can be found: fibrillar - result of cold drawing, or stacked lamallae - result from crystallization of highly oriented melts, both of which can be found illustrated in the Fig.2.15 [19].

Molecular characteristics have a big influence on resins response to the orientation conditions. Linear polyethelene, like HDPE, can be oriented more effectively than branched polyethylenes. For HDPE with broad molecular weight distribution, chains with higher molecular weigh, therefore larger number of entanglements and generally longer times of relaxation, will consequently get more aligned than shorter chains [19].

The attained alignment will have strong impact on the properties of the final polymer product, as higher orientation level magnifies the anisotropic response to external influences [19]. At very high levels of orientation, the anisotropy degree of HDPE is higher than in any other organic polymer, except carbon fibers [19]. Most prominent effect of this orientation is visible in mechanical properties, especially in increase of the tensile modulus. What can also be outlined is the positive effect of increased molecular alignment on the degree of crystallinity of PE, avg. crystallite thickness and melting temperature [19]

As far as elastic modulus goes, very high values have been obtained for PE when tested parallel with the chain axis, with some of the values being in the range of 230-264 GPa [19, 36], and even above 500 GPa [37, 38]. The reason for this is that much more force is required for molecular stretching that is needed to extend the all-trans configuration of PE [19]. Absence of branches, high molecular weight, reduced entanglement density, and elevated temperatures all favour high molecular orientation of PE [19, 39].

Tensile strength is increased linearly with the degree of molecular orientation. For achieving the highest values of tensile strength, it needs to be noted that high tensile strength of PE is favored by high molecular weight, narrow molecular weight distribution, reduced entanglement density, and high draw ratio [19, 40, 41]. To put in the context, tensile strengths for some UHMWPE were obtained even as high as 9.9 GPa [19].

What is to be noted is the fact that for PE, the elongation at break is inversely proportional to the orientation. Therefore highly oriented PE specimens have elongations at break lower than 10% at room temp [19].

Effect of Orientation in Injection Moulding

The molecular orientation discussed in this chapter can occur in the injection moulding process, the reason being alignment and stretching of the molecules that happens in the direction of the polymer flow during injection [39]. This effect is most-prominent close to the mould wall, where molecules get frozen in their stretched phase. The obtained molecular

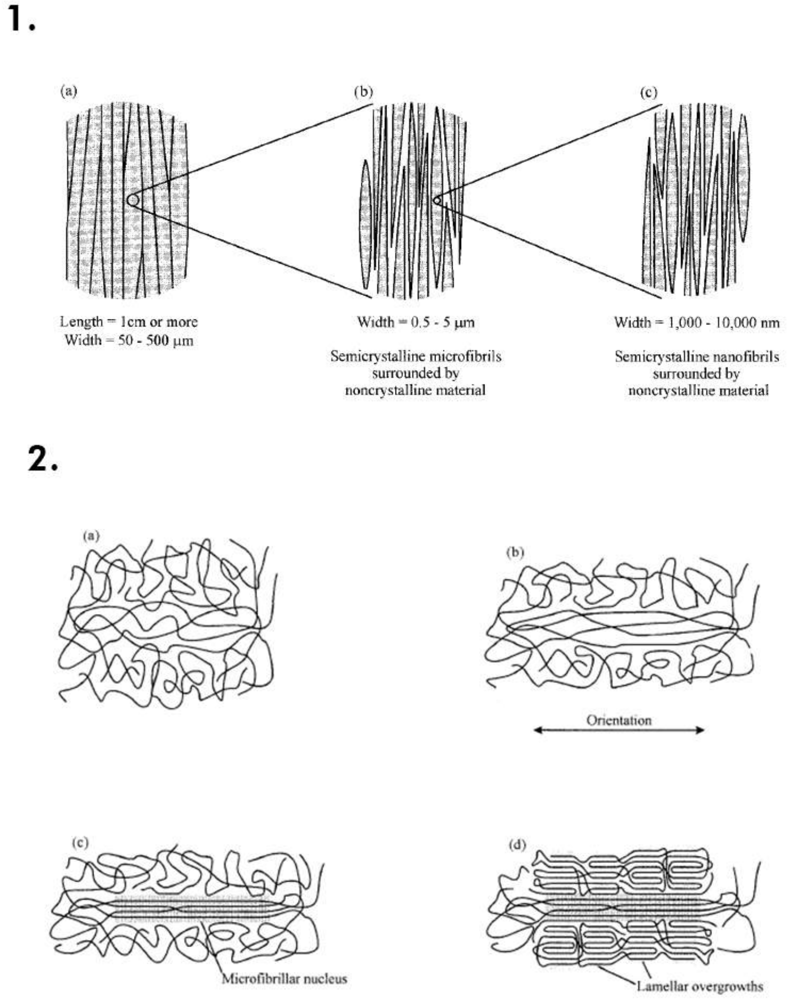


Figure 2.15: 1) Structures comprising fibrillar morphology; 2) Generation of a cylindrite from random melt (a), to oriented melt (b), microfibrillar nucleus (c) and lamellar overgrowth (d) [19].

orientation in the injection moulding is affecting the properties, both in the flow, and transverse of the flow direction of the samples. It is ultimately leading to following changes in polymer flow direction [39] :

- Higher Tensile strength
- Increased shrinkage, better crack resistance
- Improved environmental stress crack resistance
- Lower elongation at break

An important factor contributing to the molecular orientation is size of the molecules. Longer PE molecules, higher molecular weight, tend to orient more under moulding conditions [39]. Temperature of injection also plays an important role. At lower injection temperatures of PE, orientation will become more prominent because the polymer solidifies faster and the molecules tend to set-in an oriented state, because of lack of time for relaxation [39].

2.1.5 Degradation mechanisms

The modification of the polymer structure caused by reactions that induce the loss of its desired properties is referred as degradation [6, 7, 42]. Polymer structure and conditions at which the polymer is subjected, such as temperature and atmosphere, determine the degradation type. These factors determine the rate of degradation and degradation mechanisms that can occur. Depending on the path of degradation that the polymer will follow, its properties will be changed. Many types of degradation had been proposed [7] but the nature of this project reduces to thermal and mechanical degradation, described as follows:

1. Thermal degradation occurs when high temperature is applied to the polymer causing oxidation, chain scission or/and cross-linking.
2. Mechanical degradation occurs when force is applied to the polymer, enabling the possibility of chain scission.

As a consequence, either chemical and physical properties are modified. The determinant factors that decide which of the properties are the most affected are the polymer structures and additive packages.

For example, degradation either reduces the size of the chains or create a rigid polymer chain structure caused by cross-linking [11](CH.2.1.3.2). As a consequence, the mechanical properties of the polymer are affected. The decomposition of the chains within the polymer is governed by reactions. Property changes are controlled by the rate at which these reactions happen. In such a case, it is crucial to clarify the final use of the material. Depending on the grade of decomposition the material can fail. The conditions in which the material is designed to perform, determine if the failure caused by degradation makes the material available for use or dis-functional.

PE degradation is dominated by random bond scission mechanisms [42–46]. As the strength of the C-C bonds in PE is the same, except for those at the end of the chain or where branching occurs, the backbone polymer randomly breaks and the polymer molecules are converted into large macro-radicals. Decomposition mainly happens in the molten state of the polymer, as it is the condition in which enough energy is provided for polymer chain motion to be accelerated and supply enough energy for the bonds in the backbone of the chain to brake.

The proposed kinetics for the occurring degradation mechanism under absence on any external reactant is illustrated on App.A.1. Down below the summarized mechanism [19,43,45,47,48]:

1. Initiation: The bonds in the polymer chain backbone break and create two radicals per scission (k_1).
2. Propagation: Each radical experience either hydrogen transfer within the same polymer chain (k_2), β-scission reaction that forms more radicals (k_3) or hydrogen removal form other chains. (k_4)
3. Termination: Recombination of the radicals, enabling the cross-linking. (k_6)

The competition between mechanisms in the propagation stage [44,45,49] determines the rates at which the system will decompose. Depending on the temperature and heating rate [48], some reactions will be favoured. It is suggested [43, 48] that at high temperatures chain scission due to formation of short radicals by inter-molecular hydrogen absorption is favoured, increasing the production of short chain radicals that later react to form volatiles.

The rates of reaction that regulate the amount of chain scission or the recombination of the radicals during the degradation process affects the molecular weight. It is suggested [44] that during polymer degradation the molecular average weight is increased as well as the

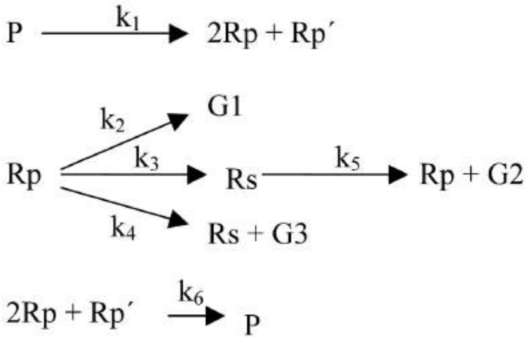


Figure 2.16: HDPE schematic decomposition [48]. Polymeric chain (P), Primary free radical (Rp), Secondary free radical(Rs), Products: Ethene(G1), alkenes(G2), alkanes(G3)

polydispersity of the polymer. This polymeric characteristics are intrinsically related to the mechanical properties.

2.1.5.1 Thermo-Oxidative degradation

While manufacturing or reprocessing, it is not common for the process to be carried out at an inert atmosphere, therefore it is crucial to understand the possible changes of the polymer while it is transformed under air atmosphere.

The proposed kinetics for the occurring degradation mechanism at the presence of oxygen is detailed showed in App.A.2. Down below the summarized mechanism:

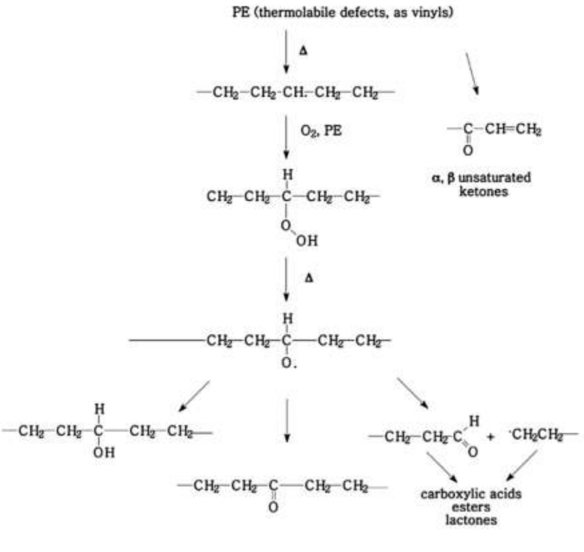


Figure 2.17: HDPE schematic thermo-oxidative decomposition [50]

Similar to the previous mechanism, the degradation process has an initiation, propagation and termination stage. Also, same as the thermal degradation, cross-linking, molecular enlargement and chain scission within the polymer happens, leading to the change of molecular weight by either increasing or decreasing its value [51–53].

Detailed studies [50–52, 54] of the possible mechanism happening within the polymer chains when the sample is subjected to stress in an oxygen atmosphere had been proposed. Same as the thermal degradation, the process starts form the scission of the polymer chain due to temperature or stress and generates free radicals. These free radicals react with oxygen or same as the thermal degradation, abstract hydrogen atoms in order to form long chain branching or, now in the presence of oxygen, the formation of different oxidation products such as ketones, calboxylic acids, and aldehydes [50, 52, 54]. Also, the previous catalyst has been proposed to be a factor to determine the preferred degradation path of the polymer, as the saturation state affects which reaction can happen easier [50, 51, 55].

The complexity of the mechanism characterization to simplify and predict the behaviour when the material is subjected to optimal degradation conditions, relays on the amount of variables to control, fx. oxygen content, heat input, shear stress or catalyst residues, as the determination of the dominant reaction depends on this. Later, the study of reprocessed HDPE is discussed to provide better background of further discussion of the behaviour of the present system to be analyzed.

In the context of recycling, the trace of thermo-mechanical and thermo-oxidative degradation from its origins to its final consequences, is advantageous information that can be used while designing the composition of the a new material made from recycled raw material. The characterization of degradation allow to decide the most suitable additives to control degradation or the conditions at which the polymer will not degrade, fx.recycling cycles number the material can resist. Additionally, by developing the methods to trace degradation, information about the most suitable experimental methods to characterize it are obtained [42, 44, 56]. Therefore, the process of recovery can be optimized such as the best blending process when the material is recovered by compounding it with a virgin polymer can be easily selected.

That being said, the complexity of polymer recovery relays on the diversity of variables suchlike polymer structure or polymer additives, and the diversity of conditions like temperature and atmosphere. The heart of the matter is: *in what extent the polymer degradation affect the properties of studied rHDPE in comparison with vHDPE?.*

2.1.6 Polymer Blends

One of the possible scenarios of using recycled polymer materials in industrial application has been to form blends with virgin polymers, that would then potentially exhibit similar properties as the virgin material. However, the biggest challenge has always been selection of the right amount of the right recycled polymer, to eliminate significant variations of the blend from virgin polymer, and not to compromise the final material properties [57, 58].

Although recycled polymer and virgin polymer are based on the same material, their blend could perform significantly below the linear composition law. Potential degradation mechanism in recycled polymer could result in formation of new functional groups (CH.2.1.5 that will affect the miscibility and properties of the final blend [57]. The reason for this lies in different molecular weights and structure between the virgin and recycled components, and changes in crystalline morphology.

It has been observed, particularly for PE, that even if blends were made of materials with the same chemical composition, but had some differences in molecular weight, and chain structure, caused drastic compromise in PE blend properties even at low contents of recycled PE [57]. This is known as inverse rule of mixtures.

Recovered PE to be used in blends, often contains oxygenated groups that are product of photo-oxidation, crosslinks, additives and stabilisers, CH.2.1.5. This can significantly influence difference in properties between virgin and recycled polymer and give rise to an incompatible blend [19, 57]. Therefore, detailed and thorough characterization of both components prior to blending is crucial. Often, the final properties of the blends are shown in a property-composition graph, which describe the property of interest with reference of content of added polymer.

A representation of the resultant polymer performance based on added recycled polymer for PE is seen in Fig. 2.18, obtained from research by F.P. La Mantia et.al. [57]. From the graph, a drastic drop in tensile strength is seen at a small amount of rHDPE (20%) added content. However, further addition of rHDPE does not substantially modifies the property. On the other hand, by means of elongation at break, continuously adding rHDPE consistently decreases the value.

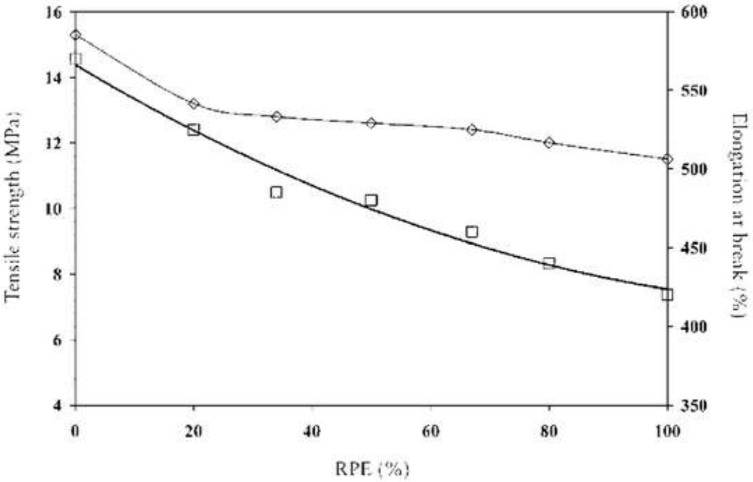


Figure 2.18: Tensile strength and elongation at break for rHDPE and vPE blends as a function of rPE content. (line with sqares=elongation at break [57])

All things considered, it can be concluded that final blend properties will depend on the amount of degraded polymer in the blend and the extend of degradation. Differences in morphology, molecular weight, crystallinity, presence of crosslinks, contamination, can lead to incompatibility and poor performance of the blend. However, blends done with polymers that have undergone few cycles of reprocessing, and don't show incompatibility effects between rPE and vPE can achieve desirable properties, close to the virgin material [57].

2.2 State-of-the-art literature

For the performance of a polymer to be considered functional, it must have an optimal [59]:

1. Rigidity
2. Toughness
3. Resistance to long term deformation
4. Recovery from deformation on release of stress
5. Resistance to thermal degradation adversely affecting properties

Numerous studies regarding polymer reprocessing to generate alternative materials that can be used as raw materials for manufacturing processes have been done. The principal focus in all the studies is to accomplish as much as possible of the enumerated characteristics, for a successful polymer design.

As has been stated, due to the contribution of different and many variables such as temperature, applied stress, atmosphere, processing time, these studies have gotten a variety of results that cannot be generalized. However, these studies are the starting point for the further discussion to be made for the polymer of interest. Therefore, a summary of HDPE reprocessing, by itself or as a blend, as well as the rheology and mechanical performance research is presented.

2.2.1 High density polyethylene reprocessing

Changes at the polymer structure (CH.2.1) of polyethylene by chain scission, branching and cross-linking of molecules as well as the introduction of oxygen into the polymer molecules, changes the regularity of the structure, hereby the material performance. Therefore, compared to the virgin material, the recovered polymers had decreased their functioning. The summary of the possible reactions of PE when reprocessed are shown in Fig.2.19

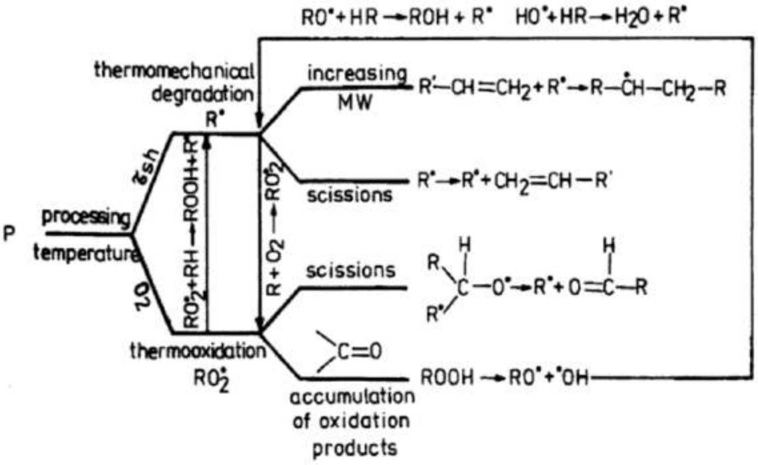


Figure 2.19: PE sumarized degradation mechanisms, thermo-mechanical and thermo-oxidative [55]

The detailed degradation mechanisms (CH. 2.1.5) and the conditions at which this happens had been evaluated in the study of reprocessing HDPE. As stated before, at high temperatures, cross-linking is favored due to the optimal amount of energy available in the system. This behaviour is seen by Mendes et. al. [60] which studied the degradation of different kind of PE while subjected to many injection cycles. The results stated that no matter if it is LDPE or HDPE, at high temperatures cross-linking is preferred to happen within the polymeric matrix. The study reported that at the initial steps there is a competition of chain-scission and cross-linking, but in the end, cross-linking dominates after many cycles. In addition, Mendes et. al. [60] reported that high molecular polymers are the ones more affected by degradation. Considering these results, the study proposed that primary recycling of HDPE is optimal on a controlled set of conditions that depend on each material.

Later, Oblak et. al. [61] reported the progression of the degradation mechanisms. For this study, HDPE is subjected to 100 extrusion cycles. Same as Mendes, this study revealed the progression of the degradation of the polymer while being constantly reprocessed. The first mechanism to happen is the chain branching and after 30 cycles chain-scission occurs; still at the 100^{th} cycle, the polymer is dominated by chain scission but now a quarter of the polymer is cross-linked, mechanism that happens after the 60^{th} cycle. Oblak measured crystallinity, viscosity and creep, with conclusion being that the material still preserves 80%

of its mechanical properties after the 100 cycles. In addition, the processability of the material started to require higher inputs of energy, such that after the 30^{th} cycle the material became much more viscous due the the reduction of chain mobility caused by the chain branching.

Not only the manufacturing conditions influence the final degradation mechanisms, but also the production methods of HDPE. CH.2.1 described the different types of industrial production of HDPE, such as Ziegler-Natta and Phillips. Where the main difference in the final product is the amount of vynil saturation in the polymer matrix. While degrading, this sites are prompt to react compared to others. With this in mind, Moos et. al. [51] analyzed a Ziegler-Natta and Phillips HDPE. Their conclusion is that in the Ziegler-Natta HDPE, chain scission predominates and on the Phillips HDPE, cross-linking is the dominant mechanism.

Pinheiro et.al. [17] delves into the matter by relating extruding conditions to the resultant saturation amount on the polymer matrix based on the production way of HDPE. The study traces the mechanism of degradation while HDPE is submitted to different residence times, temperatures and vinyl saturation. To degrade the material, HDPE is extruded 5 times in a different configurations of twin extruders, at two different temperature profiles, 200°C and 240°C. The study propose that degradation is due to the length of the chains and the amount of vinyl saturation. By means of length, chain scission of long chains is promoted by the applied shear and temperature; short chains produces chain branching. The Phillips based HDPE is described to be prompt to chain branching as the vinyl saturation is higher,and Ziegler-Natta leads to chain scission.

The authors aim to find overall threshold values for the conditions in which the polymer can be reprocesses and will continue to perform as desired. The success is not reached due to the complexity of the variable control while processing. Because of this, other researches tried to narrow the analysis and studied how HDPE recovery is affected based on singular variables.

Erbetta et.al. [62] traced HDPE degradation by means of temperature. The study again points out the importance of heat input and presence of oxygen. The research studied the HDPE thermal and rheological behaviour by subjecting the polymer at 3 different temperatures. No changes on the polymer is detected by oxidation induction time (OIT), until the temperature is increased up to 230°C. The same behaviour is seen in the rheometry test, however another variable is introduced. When the sample is tested by oscillatory rheometry, depending on time of the test, either cross-linking or chain scission occur. Using the final results, the study proposed to process the polymer at a temperature less than 230°C, as over this temperature degradation impacts significantly the performance of the material.

In addition, Cruz et. al. [63] studied the degradation mechanisms of HDPE in order to find the best method to re-stabilize the polymer. Cruz states the degradation of the polymer by cross-linking with the presence of oxygen and shear is in moderate amounts. In order to overcome this, the study suggest the addition of antioxidants.

Further, while these studies were done [17, 53, 60, 61, 63], it was recognized the sensibility of rheology to evaluate the molecular changes within the polymer matrix as well as the functionality of FTIR to trace the possible degradation state. Additionally, as the mechanical performance of the material is important, other studies had characterized the degradation by the effect of it on the mechanical properties.

The dependence of the mechanical properties on crystallization (CH.2.1) has been described. Fayolle et.al. [64], described this effect as a critical molar mass value at which the polymer mobility changes from being tough to be brittle, while degraded. The study emphasized the importance of entanglements, as these provide ductility to the polymer matrix. In the investigation the polymer is thermally aged at 80°C and 90°C, and then is characterized by DSC and rheology. As Fayolle limited the study to polymers in which cross-linking was negligible, the main focus on the effect of chain scission as the dominant degradation mechanism proved the brittleness of the system because of its predominance. This reduces the critical molecular weight for entanglements and as a consequence, reduced the range for plastic deformation.

Alzerreca et.al. [65] compared the performance of virgin and different grades of recovered HDPE. The study evaluated the mechanical properties and the influence of the purity of the material. The argument is based on the fact that recovered materials contain contamination that hinders the optimal MWD and crystallinity. Also, the contaminants represent micro-voids that decrease the mechanical properties. Same as Fayolle, this study found that the chain size is reduced in the recycled material, affecting both short and long-term mechanical properties.

Different researches agree on the high dependency of the polymer on its initial state and the processing conditions. Nevertheless, in all cases HDPE experiences the degradation mechanisms presented in Fig.2.19. With that on mind, different methods to recover the mechanical properties of the material are suggested. On one hand the addition of additives that re-stabilize the material, but this has been reported to normally be an expensive process [66]. On the other hand, lately, polymer melt-compounding has become of interest due to the facility of blending different polymers [57, 58, 67].

The main obstacle of polymer blending is the compatibility between the species and the resultant final properties of the blend, such as thermal and mechanical, CH.2.1.6. Due to the easiness to find used HDPE,PP and LDPE together in waste sources, the blends between these polymers are of high interest [8, 57, 58] due to the low cost compared to the other methods. However, because of the incompatibilities between them it has been hard to obtain successful results [8, 66].

Moreover, in behalf of new legal demands [9], industry is interested in recycling their own material. With that in mind, the blend of vHDPE and rHDPE has being analyzed form recovered sources such as HDPE recovered from bottles, pipes and random sources. The studies recover the polymer either by blending it with rHDPE, adding fillers [65] and stabilizers [67] but not many information about blending of vHDPE/rHDPE is found. Nevertheless, the made studies propose that further testing needs to be done in order to propose a better prediction of the performance of polymer blends.

That being said, the current study follows the same line of investigation to characterize on this specific polymer system that is studied, the dominant processability and mechanical behaviours. Therefore, based on the review of previous works, the proposed hypotheses can once again be recalled (CH.1.2):

1. Depending on the nature of the polymer, reprocessing conditions and number of reprocessing cycles, recycled materials experience degradation following the proposed paths in CH.2.1.5.
2. The experienced degradation affects thermo-mechanical properties of the polymer.
3. The change in properties due to degradation can be improved by blending vHDPE with rHDPE.

With this in mind, the experiment designed is done and the obtained results are presented, discussed and compared in the following chapters.

Materials And Methods 3

3.1 Materials

Polymers provided, vHDPE and rHDPE, are studied. For vHPDE, the recommended processing temperatures by supplier are 190°C - 230°C. In addition, the supplier reported the content of carbon black being 2.25%. This material is optimal for extrusion, injection and compression molding.(Fig.3.1a)

On the other hand, rHDPE follows Aage Vestergaard Larsen standards, where the material comes from recycled pipes, then it contains different HDPE varieties. Nevertheless, the producer indicate that it also contains $< 1\%$ of carbon black and a process temperature in the range of 190°C - 250°C. (Fig.3.1b)

(a) vHDPE (b) rHDPE

Figure 3.1: Used material

The material is processes by different methods. The detailed description of the manufacturing methods are specified in App.B. The summarized list for the different manufacturing methods is as follows:

(1) Material "As received".
(2) Material Injected Molded at AAU,Method1 (AAU M1)
(3) Material Injected Molded at AAU,Method2 (AAU M2)
(4) Material Injected Molded at Supplier (Supplier)

3.2 Methods

The material "as received" and its blends are tested and analyzed as described below. This characterization provides the needed information to screen the properties of vHDPE and rHDPE, and support the analysis of the performance of the material considering that one of them has already been utilised.

3.2.1 Differential Scanning Calorimetry (DSC)

Previously, it is described the influence of the polymer morphology on the thermal response of the polymer. In order to know the crystallinity as well as the stability of the material, thermal characterization is done at the TA Instruments,Q2000 DSC. The samples are taken from the material "as received" and all materials are tested in aluminum pans.

To determine the amount of crystallinity of the polymer and its thermal properties, the test is done in a heat-cool-heat program at nitrogen atmosphere. From the obtained thermogram, the peak melting temperature (T_m) and peak crystallization temperature (T_c) is obtained, as well as the corresponding energies to produce this changes.

The samples weighted varied 5± 1 mg. The method for the heat/cool/heat program is: from a temperature of 30°C up to 250°C and back to 30°C. The program design outline is based on the recommended processing temperature that lays within the range of 190°C to 230°C (Sec.3.1).

The level of order in the polymer matrix is closely related to the heat of fusion ($\mathit{\Delta} H_f$). This is the energy needed to enable the disorder in the polymer matrix. If rHDPE has discontinuities in its arrangement, such as chain branching or cross-linking, it is expected to observe a difference in its $\mathit{\Delta} H_f$ value (CH.2.1.2). As a consequence, the degree of crystallinity between the polymers should be different.

The degree of crystallinity (X_c,%) is defined by the ratio of the heat of fusion of the polymer sample, $\mathit{\Delta} H_f$, and the melting heat of a pure polymer crystal, $\mathit{\Delta} H_c$, Eq.3.1

$$X_c = \frac{\mathit{\Delta} H_f}{\mathit{\Delta} H_c} \cdot 100\% \tag{3.1}$$

To obtain $\mathit{\Delta} H_f$ the area between the endothermic peak and the baseline is calculated; $\mathit{\Delta} H_c$ is reported in literature.

Moreover, the stability of the material is measured by the OIT test (Oxidation Induction Time) [68].The samples weight varied 5± 1 mg, and these are heated at a rate of 20°C/min up to a temperature range of 200-250°C in an inert atmosphere. When the temperature is reached, the change of gas to air at a flow rate of 50±1 mL/min is done. After the changeover point, isothermic conditions are maintained until steepest point of the exotherm is displayed, which indicates the time at which degradation of the polymer happens. From the obtained curve, the material resistance to oxidative decomposition is determined.

3.2.2 Oscillatory Rheology

The main purpose for the rheometry test is to characterize the molecular weight distribution (MWD) of vHDPE and rHDPE and identify its differences. As two competing degradation mechanisms can occur during processing, chain-scission and cross-linking, molecular weight and in consequence structural behaviour of the polymer is changed [69].

To characterize the progression of the polymers molecular changes, the viscosity is measured in an oscillatory test. The oscillatory and time tests are done in a RHEOPLUS/32 V3 rheomether, using a plate-and-plate geometry.Three repetitions of each test are done.

To characterize the temperature at which the polymer will have molecular changes that affect its viscosity, time sweep test is done. The conditions of the test are 200°C and 240°C at 1rad/s. To characterize the molecular changes, frequency sweep is done at 250°C at 5% strain. The isothermal frequency sweep test is performed from 600 to 0.06 rad/s.

3.2.3 Mechanical Tests

Both materials, vHDPE and rHDPE, are made into dog-bones. The conditions for sample manufacturing are presented in detailed in App.B and the samples dimensions are reported in Tab.3.1. The tests are performed at Instron 5568 testing machine with a 50kN load cell and an Instron 2630-107 resistivity extensometer, to trace the deformation of the sample.

mm	**AAU M1**	**AAU M2**	**Supplier**
Lenght	40	100	100
Width	3.7	9.7	6.5
Thickness	1.85	3.5	5.5

Table 3.1: Tested dog-bones dimensions

All tests are performed at an isothermal temperature of 20°C. Only engineering values are reported.

Tensile

Following ASTMED638 [70], the stress/strain curves are determined for vHDPE and rHDPE at different cross-head speeds, 1 mm/min, 20 mm/min and 100 mm/min, all at 20°C for both AAU M1 and AAU M2 specimens for 20min.

The mechanical properties such as, tensile strength at yield, elongation at yield and tensile modulus are obtained [70]. Due to the behaviour of the curves, the secant modulus, $E_{1\%}$, is calculated by obtaining the slope of the experimental data on the strain range 0.01-1%.

Long term tests

The applied force to measure creep has to be lower than the tensile strength at yield, σ_y. After conducting the tensile test, the applied force is decided to be constant at a value of 50 MPa for AAU M1 samples, and 10 and 15 MPa for AAU M2 samples, all at 20°C.

Moreover, considering the tensile test, the applied deformation to measure relaxation is 1% for AAU M1 samples and 6% for AAU M2 samples. The test is carried at 20 °C for 20 min to measure the distribution of the stress through the sample.

Finally, for specimens made by AAU M2 cyclic tests were carried out at crosshead speed of 100 mm/min, for 29 MPa - 1 MPa, 28.5 MPa - 1 MPa, and 28 MPa - 1 MPa.

Results And Discussion 4

The literature review proposed the following mechanisms showed in Fig.4.1 to be occurring when polymer recycling happens. Considering that the final use of the material relies on the mechanical performance, it is suggested to keep in mind that elements of the polymer structure presented in Fig.4.1 can either improve or deteriorate the mechanical properties.

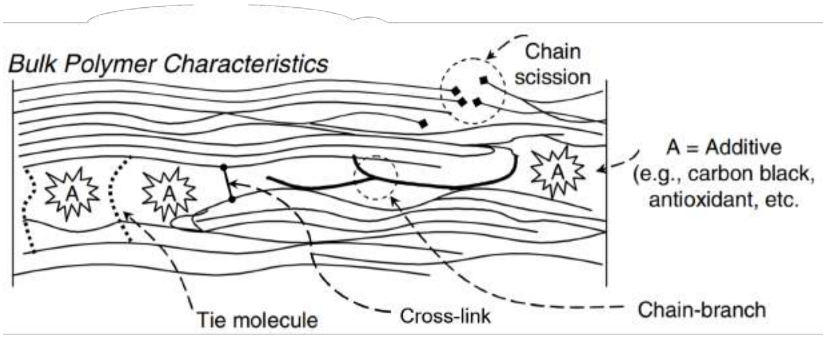


Figure 4.1: Representation of Bulk Polymer Degradation Mechanism

That being said, the thermo-mechanical characterization identifies if these mechanisms are happening as the polymer is recovered and recycled and if so, which of these mechanism dominate the degradation of the studied polymers.

4.1 DSC

The difference of the materials in its degree of crystallinity is an indication of possible occurring changes due to material recycling. As the system is trying to achieve the lowest possible free energy state (ordered), any factor that does not allow this to happen will be identified by the difference in the DSC thermograms between vHDPE and rHDPE. Because the purpose of the current test is to trace possible morphological changes between vHDPE and rHDPE, the second heating cycle in DSC is analyzed as that cycle is characterizing the material after "previous history" is erased.

Comparing the thermograms for vHDPE and rHDPE, Fig.4.2, it is seen that the thermogram of rHDPE overlaps vHDPE. This is an indication that morphologically the polymer structure does not deviate after recycling. However, rHDPE thermogram is slightly sharper than vHDPE, suggested to be due to the slightly higher uniformity in the rHDPE crystal's size.

Eq.3.1, that calculates the degree of crystallynity (%X), is founded on the thermodynamics of the system, where ΔH_f is the threshold value to overcome in order to create a phase change. The crystallinity average results for three runs[1] are as shown in Tab.4.1.

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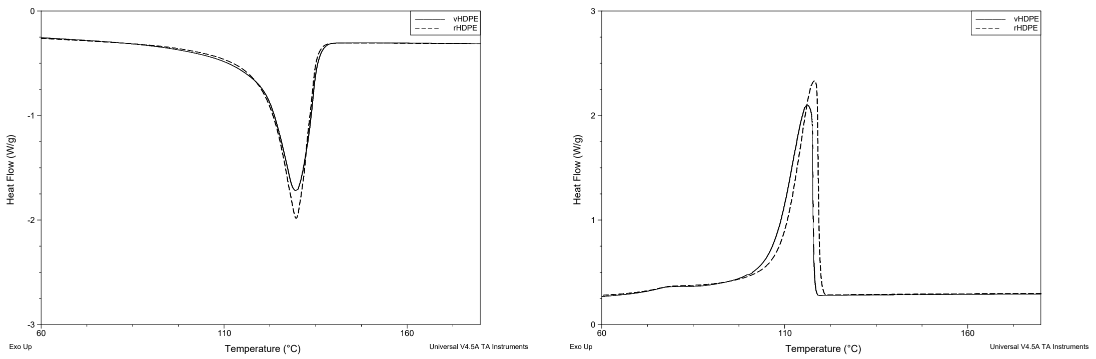
[1] The detailed results are presented in App.C



(a) Endothermic (b) Exothermic

Figure 4.2: vHDPE and rHDPE Thermograms

	Onset °C	Maximum °C	Stop °C	Crystallinity %
vHDPE	119.10	129.47	150	50.61
rHDPE	120.10	129.63	150	51.37

Table 4.1: vHDPE vs rHDPE Average Thermal values

As the value of ΔH_f is close between rHDPE and vHDPE, the resultant degree of crystallinity, as can be seen in Tab.4.1, vary by less than 1%. For this reason it is suggested that the materials, vHDPE and rHDPE "as received", behave thermally alike.

Previous studies [60, 61, 65, 71] indicated that the material has to go through many cycles of shear and heat before it shows significant degradation. By means of the thermal characterization, this theory is supported as no significant change can be observed in the previous presented results, suggesting that rHDPE has gone through less recovery cycles than needed to create a morphological change.

After performing the mechanical tests on samples made from different manufacturing processes, a significant difference in the tensile strength, stiffness and elongation at yield values is noticed. Therefore, it is decided to perform DSC testing on the material at different manufacturing conditions. Tab.4.2 show the results of the second heating cycle. The difference between the process (2) and (3) is the machine used. On the other hand, No.(4) is manufactured at the supplier's process, where there is a better control of parameters and a thicker sample is produced (Tab.3.1).

	Onset °C	Max. °C	X %
(1)	119.10	129.47	50.61
(2)	119.68	128.61	50.96
(3)	119.33	130.41	51.23
(4)	119.45	131.80	50.78

(a) Endothermic

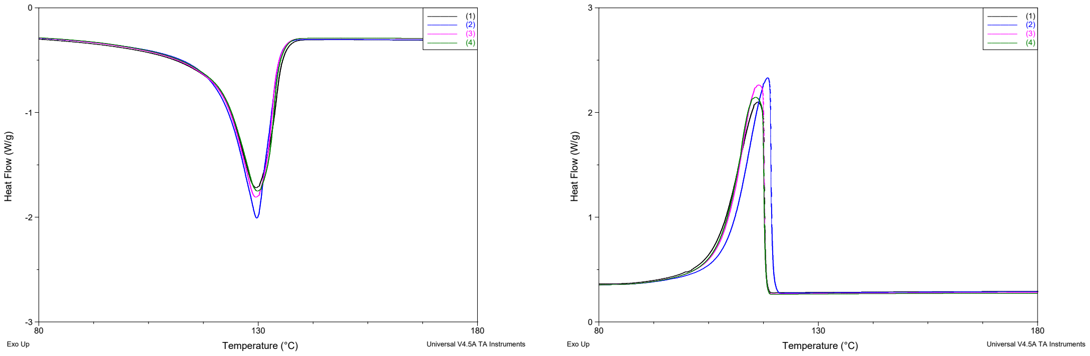
	Onset °C	Max. °C	X %
(1)	117.83	116.08	46.01
(2)	119.42	118.38	47.27
(3)	117.76	116.36	46.86
(4)	117.85	115.67	46.55

(b) Exothermic

Table 4.2: Thermogram values for vHDPE: (1) As received, (2)AAU M1, (3)AAU M2, (4)Supplier

The degree of crystallinity, Tab.4.2 of all the samples is independent from the manufacturing processes and remains almost the same.

When comparing the thermograms of the different manufacturing processes, the curves overlapped each other. Yet, for AAU M1 (2) a slightly sharper curve can be observed, Fig.4.3. Again, this is suggested to be due to the uniformity on the type of the crystallites, consequence of the cooling method. Nevertheless, the results lead to conclusion that the observed difference is negligible, and that both rHDPE and vHDPE behave alike.



(a) Endothermic

(b) Exothermic

Figure 4.3: vHDPE thermograms at different processing methods: (1) As received, (2)AAU M1, (3)AAU M2, (4)Supplier

It needs to be noted that the supplier stabilizes the rHDPE by the incorporation of additives. With the purpose of evaluating the impact of the stabilization between both polymers, by means of primary antioxidants, the OIT test is performed.

The test is firstly performed following the corresponding standard on vHDPE, ASTMED 3895 [68], using the temperature of 200°C. However, no significant degradation is observed in a time frame of 30 minutes. Because of this, the isotherm value is raised to screen the conditions at which vHDPE lost thermal stability. This method resulted in the set of data presented in Tab.4.3, in which at the 230°C isothermal, the oxidative reactions start to take place. Later, the same temperatures are used to test the properties of rHDPE. Tab.4.3 displays that the higher isothermal temperature, the shorter the induction time, for both materials.

Temp.	**OIT (min)**		
°C	*vHDPE*	*rHDPE*	*Diff.*
250	4.96	3.24	35%
240	12.78	10.38	19%
230	27.88	23.97	14%

Table 4.3: OIT test for vHPDE and rHDPE at different temperatures

Tab.4.3 shows the resultant time needed for the material to degrade. vHDPE samples are more stable at subjected testing conditions because it takes longer time for degradation to start happening than for rHDPE samples. Even though there is a time difference in the OIT, the values can be considered minor. Fig.4.4 shows the heat flow in function of time. The increase in the heat flow represents the exothermic contribution of the degradation mechanisms of PE(CH.2.1.5). Fig.4.4 illustrates the decrease in time to degradation as the temperature increases.

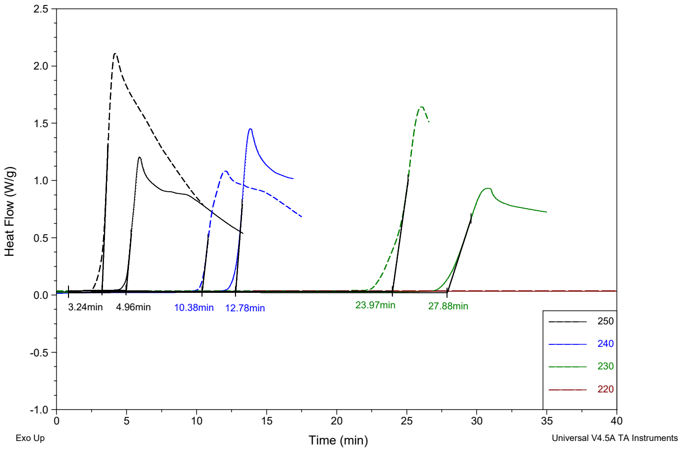


Figure 4.4: OIT curves for HDPE at different values of T(°C), vHDPE-solid line; rHDPE-dashed line

The obtained information can be extrapolated to predict the stability of the material at room temperature by means of the Arrhenius equation, Eq.4.1 [72, 73]. This equation can be used in order to calculate the needed activation energy (E_a) for the reactions to take place.

$$\kappa = Ae^{\frac{-E_a}{RT}} \tag{4.1}$$

Plotting the inverse of the temperature, expressed in Kelvins, against the logarithm of the time needed for oxidation to happen, the activation energy is obtained by the premise of the possibility for Eq.4.1 to be arranged as the equation of a straight line, where $\frac{E_a}{R}$ is the slope, Fig.4.5

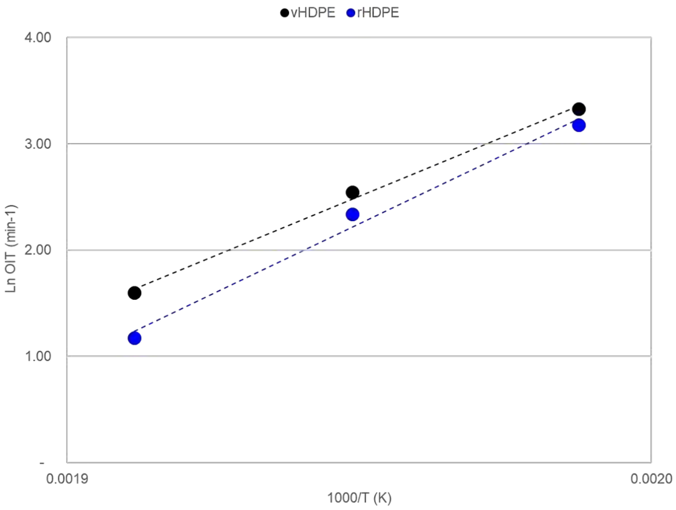


Figure 4.5: Arrhenius plot for HDPE. *vHDPE-filled marker; rHDPE-empty marker*

The resultant E_a is reported in Tab.4.4 and is in accordance with previous presented values [72]. The high value of rHDPE, compared to vHDPE, further validate the higher sensitivity of the material to temperature changes. Using the calculated values of E_a, the degradation time prediction at room temperature results in 5.8 billion years for vHDPE and 8.4 billion

	vHDPE	*rHDPE*
Ea(kJ/mol)	188.77	218.72

Table 4.4: Calculated activation energy by means of OIT test at different temperatures (230°C - 250°C)

years for rHDPE. Based on that data, the comparison of the materials at low temperatures result in times with magnitudes that are considered not to be of relevance at low temperature.

Nevertheless, the OIT is a characterization technique that is recommended to considered for further analysis, if further stabilization of the material or additives want to be designed. The analysis of the oxidative mechanisms is out of the scope of this study, nevertheless, the literature for its study is provided [46, 49, 51, 74].

4.2 Rheology

In rheological tests, vHDPE and rHDPE polymer flow (2.1.3.1) was analyzed in order to get information about differences in viscosity, molecular weight, and molecular weight distribution, which consequently can help identify and describe degradation mechanisms, if those are present.

The first test was the time sweep test, which records the change in modulus at a constant frequency in function of time at constant temperature. The obtained results characterize the melt degradation. The second test was a frequency sweep tests, which registers the complex viscosity (η^*) in dependence of applied frequency (ω). By means of this test, it is possible to describe the molecular structure of the polymer.

Considering a time frame of 30 min, different temperatures were tested in order to identify the conditions at which degradation starts to happen in vHDPE. The mean curves for 200°C and 240°C at 1Hz are shown in Fig.4.6. At 200°C no change is seen, however at 240°C a change in the slope of the G' curve starts to happen at approximate 600s.

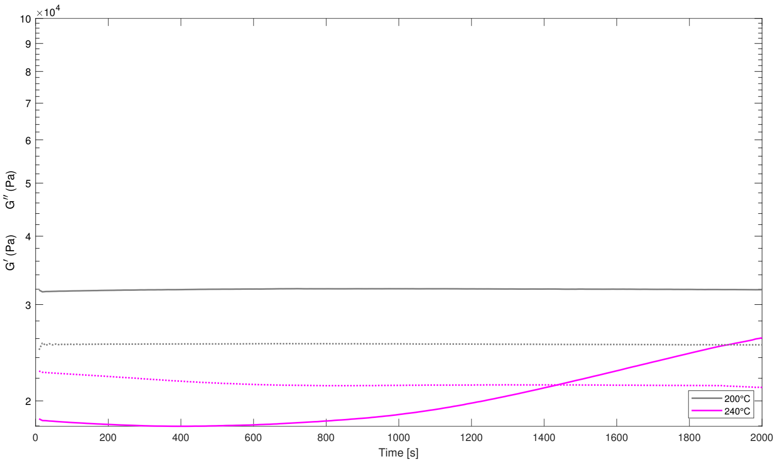


Figure 4.6: Time sweep test for vHDPE at 200 °C and 240 °C, where the effect of temperature on the storage and loss modulus at 1Hz is visible. Dashed line G", and full line is G'

Further, time sweep was performed at 240°C and 1Hz in vHDPE and rHDPE. Even-though a difference is seen in the graph, the material behaves similar juts with the slight difference

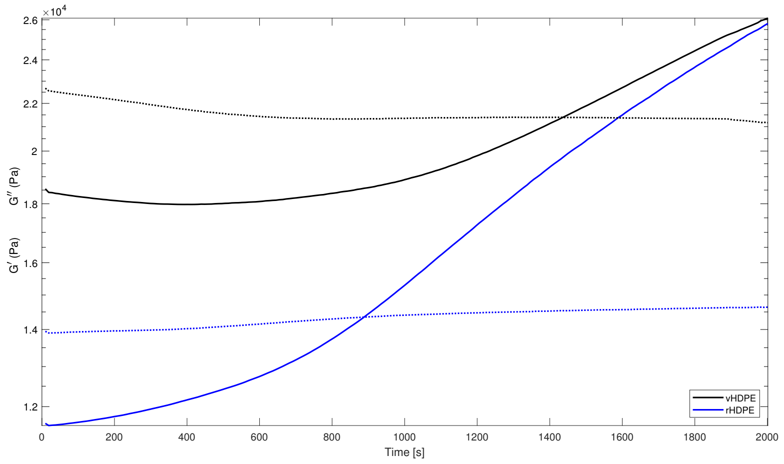


Figure 4.7: vHDPE vs rHDPE time sweep at 240°C and 1Hz. Dashed line G”, and full line is G’

of lower viscosity on rHDPE. Also, both materials arrive to the same state at longer times, Fig.4.7.

In addition to time sweep test, frequency sweep was also performed. Stated in CH.2.1.3.1, where at lower frequencies G” (loss modulus), representing the viscous behavior of polymers, is higher than the G’ (storage modulus), representing elastic behavior of polymers. This would indicate that the polymer is at lower frequencies behaving like a liquid. On the other hand, at higher frequencies we are seeing the opposite, G’> G” which is an indication of viscous, solid-like behavior of the polymer, due to less time the materials have for relaxation. The same behaviour is seen in Fig.4.8, for both rHDPE and vHDPE which corresponds to the presented theory.

Looking at the crossing point of G’ curve and G” curve in Fig.4.8 for rHDPE and comparing that crossing point with the one from vHDPE, a small shift in the crossing point for rHDPE can be seen to the right and downwards, what would essentially indicate lower molecular weight (M_w) and broader M_w distribution [28] for rHDPE compared to vHDPE, as described in Fig.2.10.

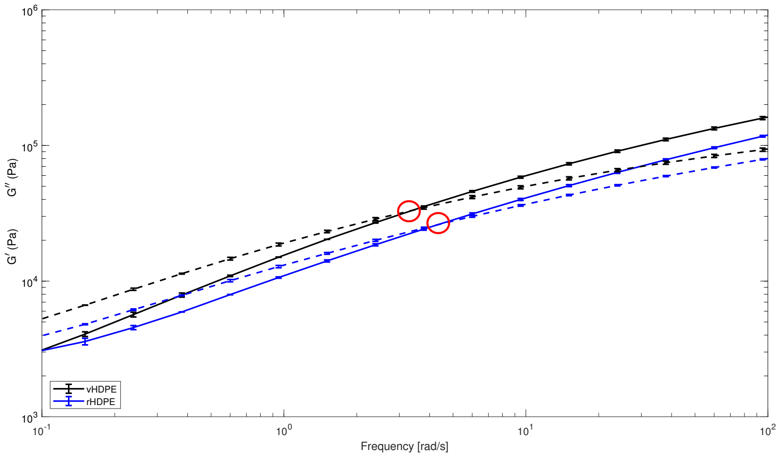


Figure 4.8: vHDPE vs rHDPE Cross Over point at 250°C. Dashed line G”, and full line is G’

Furthermore, complex viscosity as a function of frequency is presented in Fig.4.9. It can be seen that viscosity is increasing with an decrease in frequency for both rHDPE and vHDPE. This is an indication of shear thinning phenomena explained in the CH.2.1.3.1. However, comparing the values of viscosity throughout the experiment it can be seen that rHDPE has lower complex viscosity than vHDPE, although they are in general close and even finish at the same value at lower frequencies, same as the time-sweep test, Fig.4.7.

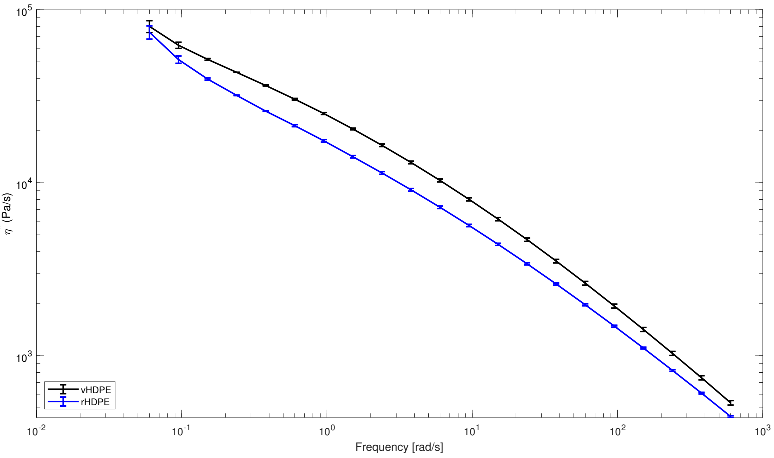


Figure 4.9: Complex Viscosity vHDPE, and rHDPE vs frequency at 250°C, with standard deviation obtained from 3 tests

Considering the previous results in which rHDPE showed lower $\eta*$ and a shift in the crossing point of the G' curve and G" curve, it is suggested that chain-scission is taking place. For this reason, at this stage of the recycling of rHDPE, initial steps of degradation are happening (CH.2.1.5). Taking this into account as well as previous studies made on HDPE [53, 61], it is important to keep track of the threshold value of recycling cycles in which the polymer will show significant degradation for this material.

Based on the rheological tests, at low frequencies, the last points show what is considered cross-link degradation due to the sudden increase in complex-viscosity. This result is in accordance with the OIT test at which at temperatures higher than 220°C, oxidation occurs in a time range of approx. 25 min. Throughout the test, rHDPE and vHDPE behave similarly, and very little differences in values for complex viscosity, loss and storage modulus can be observed. Therefore, it is proposed the both polymers will perform likewise.

4.3 Mechanical Test

The thermal characterization and the rheology study of the samples, showed a negligible difference between the materials. Therefore, a similar behaviour could be expected from the mechanical testing. As described in CH.2.1.3.3, values such as, tensile modulus (E) and yield stress (σ_y), as well as, creep and relaxation behaviour, provide crucial information to describe the possible morphological changes between vHDPE and rHDPE.

As mentioned in CH.3, specimens were firstly produced by AAU M1, but the results were highly influenced by the specific production method. Therefore, AAU M2 was utilized to produce another batch of specimens. The methods are presented in detail in App.B.

In order to characterize the mechanical performance of vHDPE and rHDPE and identify the factors affecting it, mechanical test results for specimens produced by both methods are given, analyzed and compared in following chapters.

4.3.1 Tensile

The stress-stain curve normally exhibits linear behavior up to the yield value of the test. However, the obtained curves showed a slight curvature in this region. Although this phenomena was not eliminated completely, it was minimized by applying initial testing pre-stress. For the analysis of the tensile modulus, the secant modulus is used.

AAU M1

The resultant curves for vHDPE and rHDPE at an applied cross-head speed of 20mm/min are shown in Fig.4.10, and the values are given in Tab.4.5. From this, figure the value of σ_Y for vHDPE is 82.10 MPa and for rHDPE 64.82 MPa. For both vHDPE and rHDPE, the values are significantly higher, approximately 4 times and 3 times respectively, than the reported data [19, 26] and the data given by supplier (23MPa).

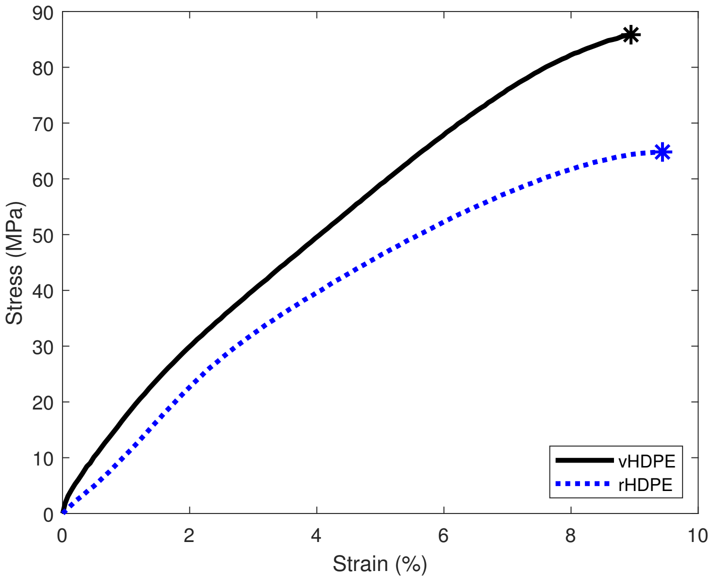


Figure 4.10: vHDPE vs rHDPE, AAU M1 tensile sample behaviour at 20 mm/min crosshead speed at 20°C

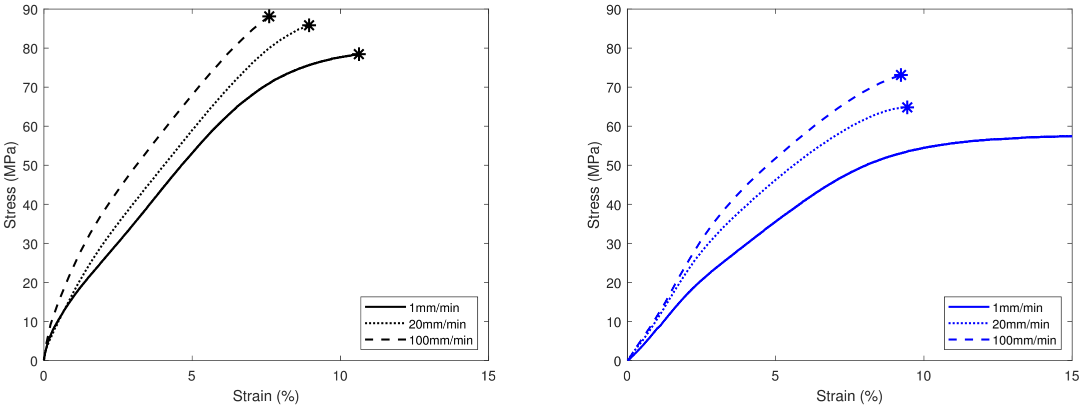
This behaviour is suggested to be due to chain orientation happening during the manufacturing process of the tested samples as explained in CH.2.1.4.

Furthermore, the vHDPE and rHDPE samples manufactured by AAU M1 are tested at different cross-head speeds. The resultant curves are shown in Fig.4.11. The stiffness and maximum strength of the material is directly proportional to the applied strain rate [75]. On that premise, by subjecting the material to different strain rates, its viscoelastic properties can be characterized. Overall, the values for vHDPE are higher than the values for rHDPE, as can be seen in Fig. 4.11 and Tab. 4.5.

Tab.4.5 shows the values for secant modulus at 1%. For both materials, vHDPE and rHDPE, the σ_y of the material decreases as the cross-head speed increases. However, due to the high influence of orientation caused by the production method of the samples and the test itself, the results are not conclusive for the purpose of the study.

		vHDPE		**rHDPE**	
		avg.	st.d.	avg.	
1mm/min	σ_Y (MPa)	77.4		57.5	
	ϵ_Y (%)	9.7		15.2	
	Sec.Mod (MPa)	1592.2		832.2	
20mm/min	σ_Y (MPa)	82.1	3.2	64.8	
	ϵ_Y (%)	9.0	0.5	9.4	
	Sec.Mod (MPa)	1081.1	569.1	1060.6	
100mm/min	σ_Y (MPa)	88.1		73.1	
	ϵ_Y (%)	7.6		9.2	
	Sec Mod (MPa)	2350		1164.3	

Table 4.5: Tensile Test data for test specimens manufactured by AAU M1 at 20°C



(a) vHDPE (b) rHDPE

Figure 4.11: Sample tensile behaviour at different cross-head speed (100 mm/min, 20mm/min, 1mm/min) at 20°C

AAU M2

In the obtained values for the samples made by AAU M2, it can be seen that yield strength and tensile modulus of rHDPE are lower than vHDPE, as presented in Tab.4.6. vHDPE shows an σ_y value of 27.92 MPa compared to 25.05 MPa obtained for rHDPE. And this is to be expected based on the theory provided in earlier chapters, and it correlates well to other results [17, 60, 65] and the rheology test.

Moreover, the elastic region between vHDPE and rHDPE, defined in this study by secant modulus at 1%, is very similar, 8.82 ±0.56 and 9.23 ±0.44 respectively. This can be supported with the DSC results, where no difference in crystallinity was seen [11, 19, 20].

		vHDPE		**rHDPE**	
		avg.	st.d.	avg.	st.d.
1mm/min	σ_Y (MPa)	25.133	0.498	23.252	0.532
	ϵ_Y (%)	11.318	0.743	15.333	3.669
	Sec.Mod (MPa)	563.6	2.472	409.6	0.200
20mm/min	σ_Y (MPa)	27.921	0.417	25.057	0.035
	ϵ_Y (%)	9.561	0.795	10.447	1.208
	Sec.Mod (MPa)	880.3	0.517	914.5	0.684
100mm/min	σ_Y (MPa)	34.185	0.438	29.670	0.418
	ϵ_Y (%)	8.312	1.044	11.221	1.588
	Sec Mod (MPa)	990.6	4.994	464.5	0.296

Table 4.6: Tensile Test data for test specimens manufactured by AAU M2 at 20°C

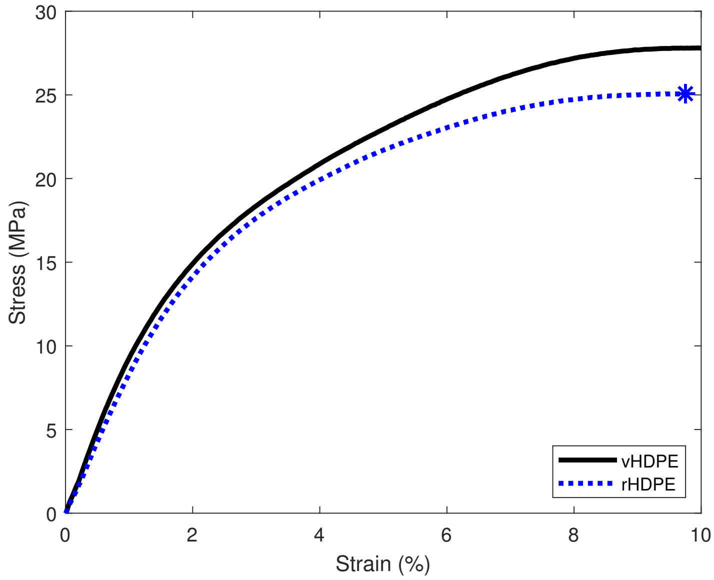
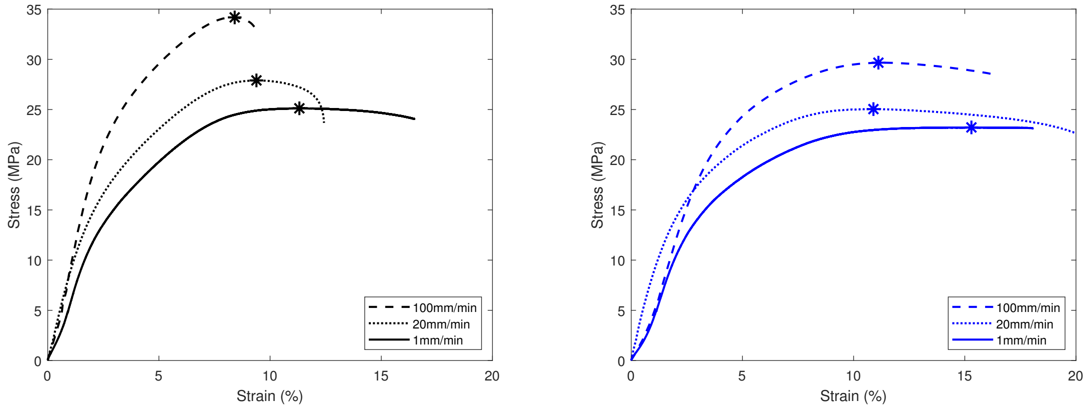


Figure 4.12: vHDPE vs rHDPE, AAU M2 tensile sample behaviour at 20 mm/min crosshead speed at 20°C



(a) vHDPE

(b) rHDPE

Figure 4.13: Sample tensile behaviour at different cross-head speed (100 mm/min, 20mm/min, 1mm/min) at 20°C

The result of the evaluation of the viscoelasticity of the samples manufactured by AAU M2 is seen in Fig.4.13. For both materials, vHDPE and rHDPE, the stiffness of the material decreases as the strain rate increases, Tab.4.6. Due to viscoelasticity, the polymer tends to behave like a fluid at lower rates of deformation as there is more time for the evolution of chain disentanglement and chain orientation to happen [75].

Considering the previous rheology results, that suggested chain-scission as the dominant degradation mechanism for rHDPE in the tested conditions, follow up this theory as lower strength and improved chain mobility of material is a result of chain-scission [15,19,26,64,65].

Even-though there are differences between the values of secant modulus and yield strength for rHDPE compared to vHDPE, for the purpose of this study, these are minor.

Manufacturing Method Comparison

Comparing AAU M1 with AAU M2, specimens manufactured by AAU M1 showed higher tensile strength exceeding the values given by the supplier 4 times as seen in Fig.4.14, and supported by theory in CH.2.1.3.3. Also, from Fig.4.14, higher brittleness of AAU M1 specimens can be observed. This is possible due to higher degree of orientation which can be attributed to the manufacturing process. The detailed values are presented in the Tab.4.7.

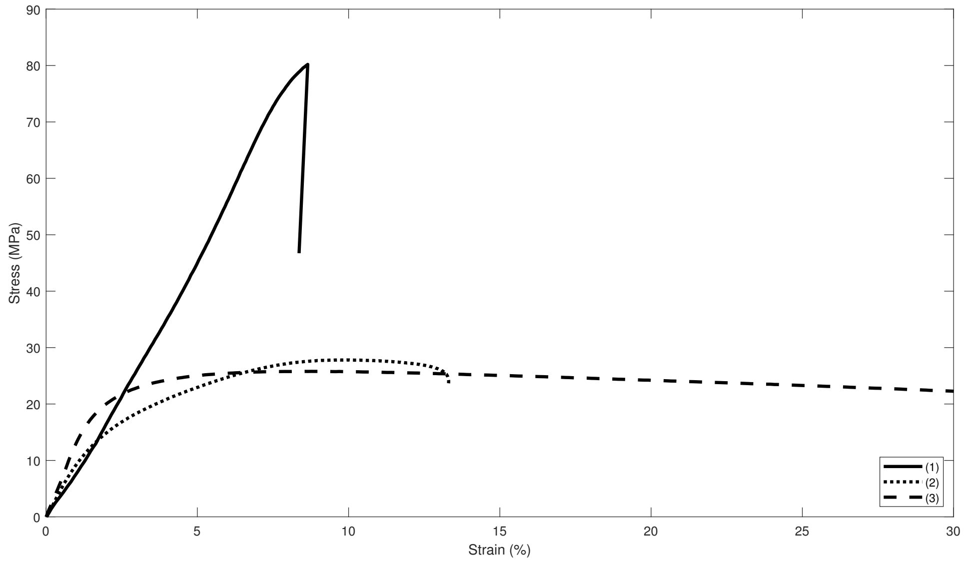


Figure 4.14: vHDPE Tensile test at 20mm/min and 20°C of samples manufactured by different conditions:(2) AAU M1, (3) AAU M4, (4)Supplier

	AAU M1	**AAU M2**	**Supplier**
σ_y (MPa)	82.104	27.921	25.784
ϵ_y(%)	9.047	9.561	8.276
Sec. Mod (MPa)	1081.1	880.3	1313

Table 4.7: vHDPE tensile values at 20°C of samples manufactured by different processing methods, App.B

Based on the obtained results, the visible effect of chain orientation influencing mechanical properties of the material is seen. The same resin is processed by two methods and much lower values that correlate with supplier data sheet were obtained with AAU M2. Due to inconsistency in the values obtained in the testing caused by the manufacturing method AAU M1, and deviation from purpose of the study, AAU M2 was further considered.

4.3.2 Long term properties

The main purpose of the analyzed material requires it to perform for long periods (>10 yrs). Therefore, in the following sections, results obtained by creep, relaxation tests and cyclic test on specimens produced by both AAU M1 and AAU M2, will be presented, discussed and analyzed.

AAU M1

Considering the values obtained for the tensile strength at yield, an arbitrary value of 50MPa is chosen as the applied strength to perform the creep test for 20 minutes. The creep curves for the vHDPE and rHDPE samples prepared by AAU M1 are presented in Fig.4.15, in which strain is plotted against time.

For rHDPE it can be seen that the material underwent all three stages of creep and finally it fractured at 800 s and 19% strain. On the other hand, vHDPE stayed in second stage of creeping, and within the time frame of 20 minutes it did not fracture. The difference is therefore high, as rHDPE exhibits higher deformation. Moreover, the relaxation done at 1% strain for 20 min is shown in Fig.4.16. During the test, rHDPE requires less stress than vHDPE to keep the applied deformation at 1%.

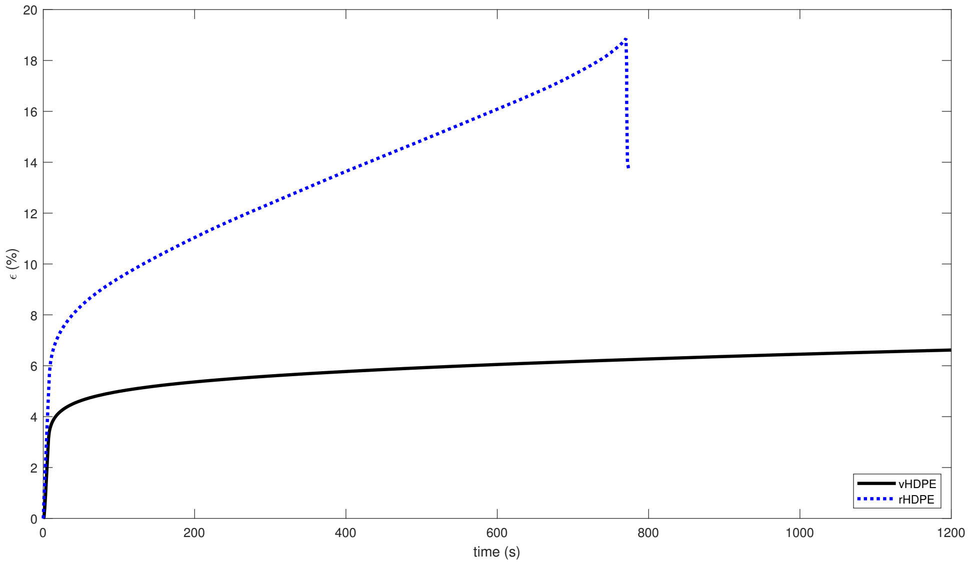


Figure 4.15: HDPE Creep Test at and applied stress of 50MPa, AAU M1

By means of these tests, the performance of vHDPE is better at long term applications. However, it needs to be taken in account that chain orientation caused by manufacturing process of the specimens affected the results and their consistency, so the results are not conclusive for the purpose of the study.

AAU M2

Creep and relaxation tests were done also on specimens produced by AAU M2, and resultant graphs are presented in Fig.4.17a and Fig.4.18 respectively. Creep tests were performed at

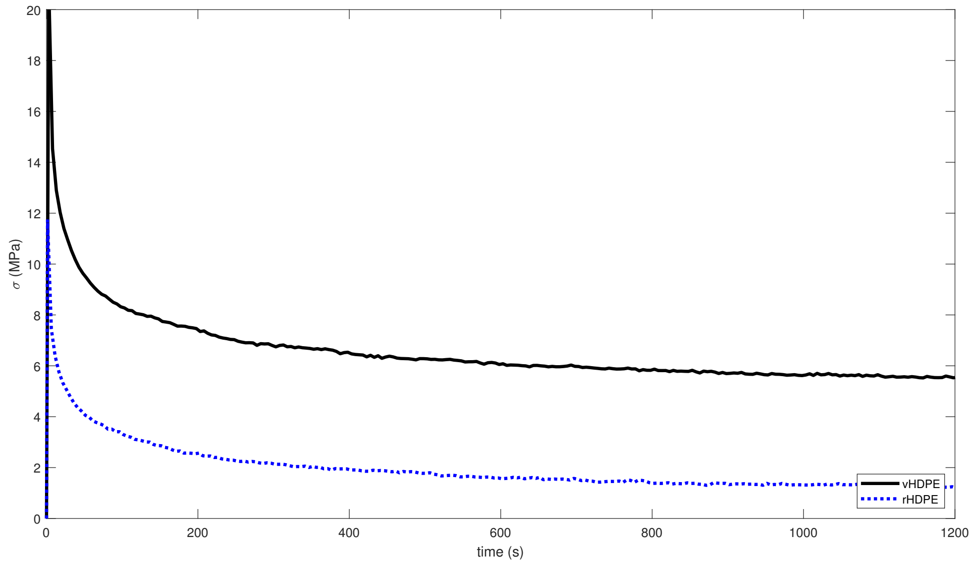


Figure 4.16: vHDPE Relaxation Test at 1% deformation

both 10MPa and 15MPa for 20 minutes at 20°C, and in that time neither rHDPE nor vHDPE reached third creep stage - steep increase in strain and specimen fracture.

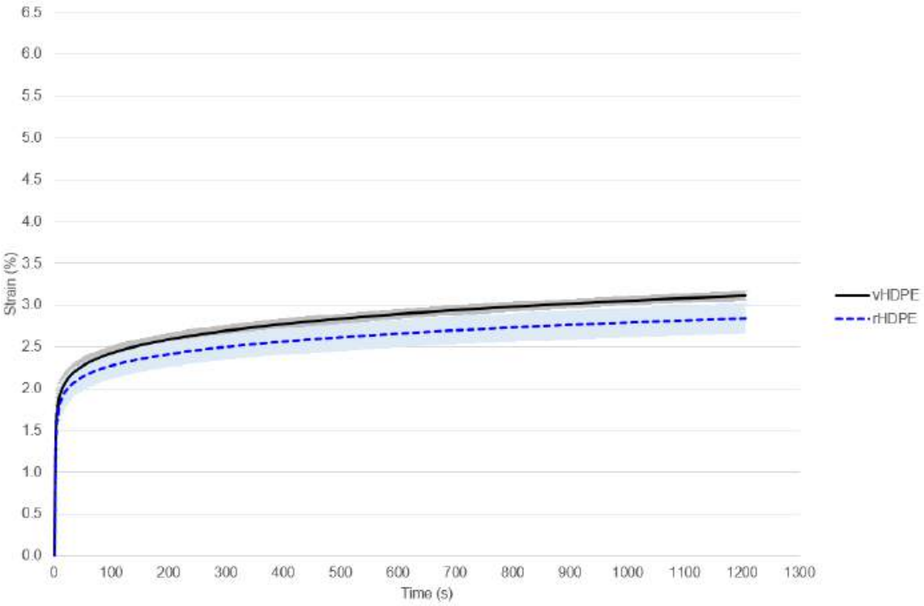
What can be read out of creep tests, Fig.4.17, is that vHDPE deforms more than rHDPE during the testing time, or in other words, creep is reduced for rHDPE. This does not correlate with previous results, but the potential reason for this could be the presence of cross-links, as discussed in CH.2.1.3.2. Moreover, rheology test at low frequencies supports this phenomena.

The relaxation graph for rHDPE and vHDPE is given in Fig 4.18. The specimens were subjected to 6% strain at 20°C and kept at this value for 20 minutes. Load required to maintain this strain was measured and stress decay was observed. rHDPE needs more stress to maintain the 6% strain than vHDPE, which is supporting results obtained at tensile test that showed rHDPE being stiffer then vHDPE.

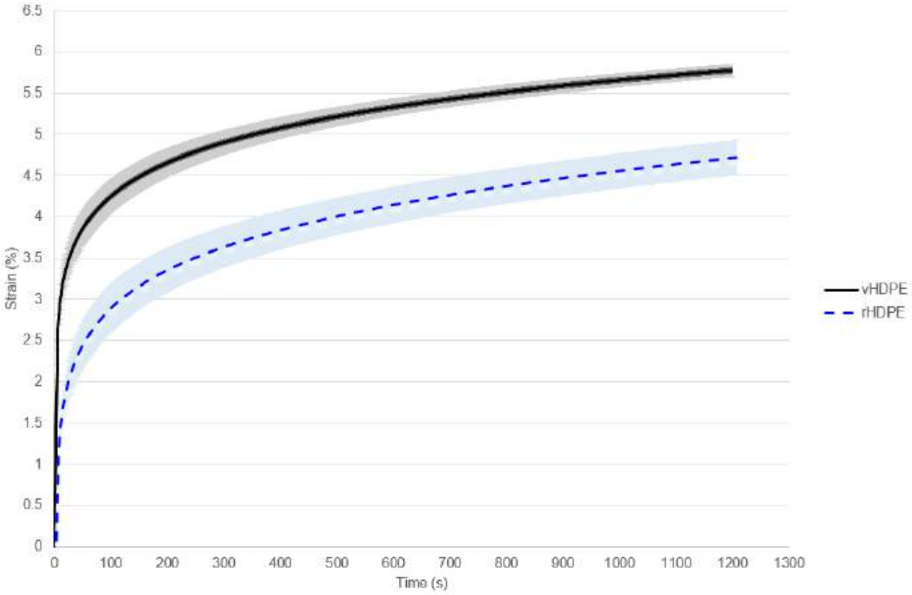
Nevertheless, all things considered, the differences between creep at 10MPa and relaxation curves for rHDPE and vHDPE, although present, are minor and can be neglected. To prove this, normalization to initial creep strain was done for creep curves at 10MPa, and normalization to maximum stress was done for the relaxation curves. The graphs are presented in Fig. 4.19. It can be seen that for both creep at 10MPa and relaxation, the curves for vHDPE and rHDPE fall on each other and are showing the same behavior.

Due to these similarities, creep test at applied stress of 15 MPa at 20°C is done, Fig.4.17b. At these conditions, the difference between vHDPE and rHDPE is more prominent because the applied stress causes non-uniform deformation and therefore a higher deviation on the resultant values. Moreover, vHDPE takes in more deformation than rHDPE during the given time of 20 minutes, this difference is argued to be due to the hindering of chain mobility caused by cross-linking in rHDPE.

The primary creep response is governed by the tensile modulus. Considering that the values of tensile modulus and σ_y are similar for both materials, the fact that the graphs fall on each other is consistent with previous tests at the elastic region of the samples. However, when entering the plastic region, deformation becomes governed by the amorphous phase and other polymer matrix elements such as cross-links.



(a) Load:10 MPa



(b) Load:15 MPa

Figure 4.17: Creep test for rHDPE and vHDPE at 15MPa and 20 °C, with standard deviation for 3 tests shown in gray zone

Creep and relaxation are prompt to be sensitive to cross-links [19]. Even-though in other tests, such as DSC and rheology the effect of cross-links is not visible as such, long term testing is an effective method to identify predominant degradation mechanisms and their effects.

Finally, cyclic tests have been performed for AAU M2 specimens at 20°C, cross-head speed of 100 mm/min, and for following cyclical stress inputs: 29MPa-1MPa, 28.5MPa-1MPa, 28MPa-1MPa.

The cyclic curves representing number of cycles required for a specimen to break at a particular maximum applied stress are shown in Fig.4.20. All maximum applied stress values (29 MPa, 28.5 MPa, and 28 MPa) are very close to the yield stress of both rHDPE and vHDPE

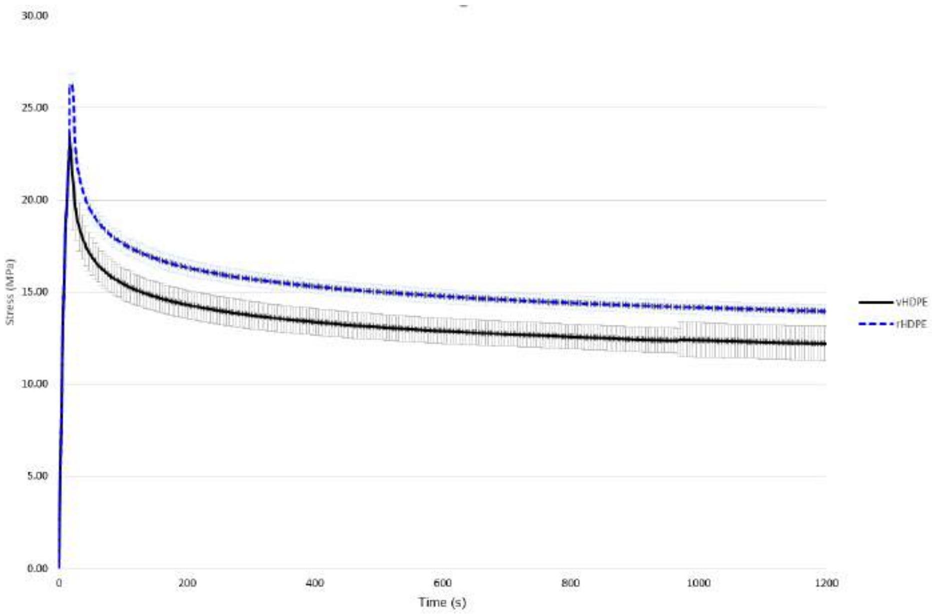


Figure 4.18: Relaxation Test done at 6% strain at 20°C for rHDPE and vHDPE, with standard deviation for 3 tests shown in gray zone

specimens. To get more complete curves 15 different maximum stress conditions should be carried out, also going to lower values of maximum stress. [33–35] Nevertheless, even presented values at only 3 different maximum stress conditions provide conclusive results.

Looking at the graph in Fig.4.20, it can be seen that rHDPE specimens broke at approximately 10 cycles and vHDPE specimens at approximately 300 to 400 cycles for all three loading conditions. Consistently with previous mechanical test, the difference in performance between both materials is significant at high applied stress (above the elastic region), were rHDPE does not perform as good as vHDPE. Moreover, presence of cross-links that was argued in creep test results can also be supported here, since it was previously shown that cross-linking compromises resistance to cyclic stress cracking [33–35].

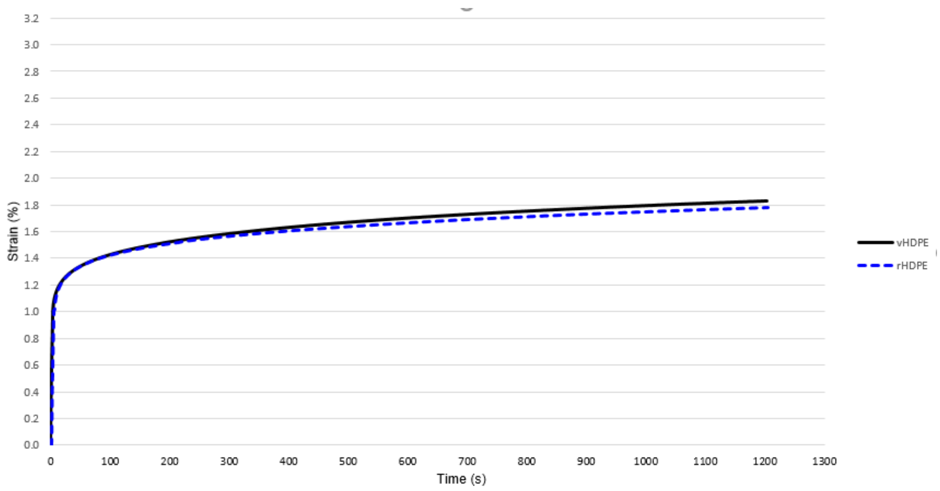
4.3.3 Polymer Blends

The purpose of the study was to analyze the possibility of reintroducing rHDPE into the manufacturing process, without compromising final properties of the material, especially mechanical properties.

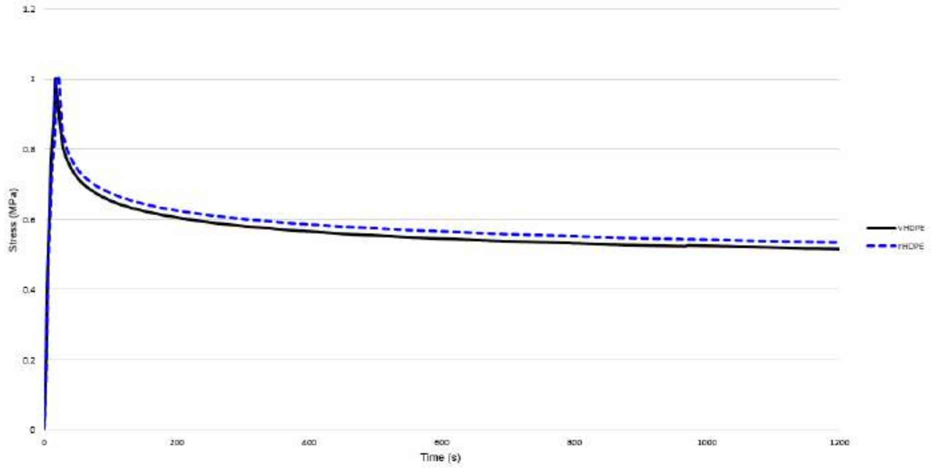
With this in mind, blends with vHDPE and rHDPE were done in following ratios:

- 100 % vHDPE
- 70 % vHDPE : 30 % rHDPE
- 50 % vHDPE : 50 % rHDPE
- 30 % vHDPE : 70 % rHDPE
- 100 % rHDPE

The stress/strain curves for the blends at 20mm/min cross-head speed are presented in Fig.4.21. As an initial observation, the obtained curves for the blends fall in between the behaviour of the pure rHDPE and vHDPE. For further analysis, the behaviour of tensile modulus, yield strength, and strain at yield, in relation to the amount of rHDPE is presented in Fig.4.22.



(a) Creep



(b) Relaxation

Figure 4.19: Creep normalized to initial strain in figure a), and Relaxation normalized to maximum stress in figure b)

What can be seen from graph in Fig.4.22a, where σ_Y is plotted as a function of % rHDPE in the blend, is a behavior of additive rule of mixture. As the amount of rHDPE increases, σ_Y deteriorates, while reaching the lowest value for pure rHDPE.

On the other hand, Fig.4.22b where ϵ_Y is plotted with respect to % rHDPE in the blend, a slight increase in elongation is visible with increase of the rHDPE content. Fig.4.22c, shows no significant difference in elastic modulus change, no matter the composition of rHDPE in the blend.

The property-composition graphs therefore indicate that rHDPE content in the blend, even in the amounts as high as 70%, is not significantly compromising the secant modulus and yield strength of the material.

Summary

Summarizing, even though significant difference is not observed neither in DSC resultant crystallinity nor in the rheology characterization, mechanical testing showed high sensitivity to characterize changes in the material. Similar behaviour was previously seen [65], where in thermal testing the values were similar and high variations became noticeable in the mechanical testing. The values in Tab.4.5 are in accordance with [65], as the rHDPE decreased

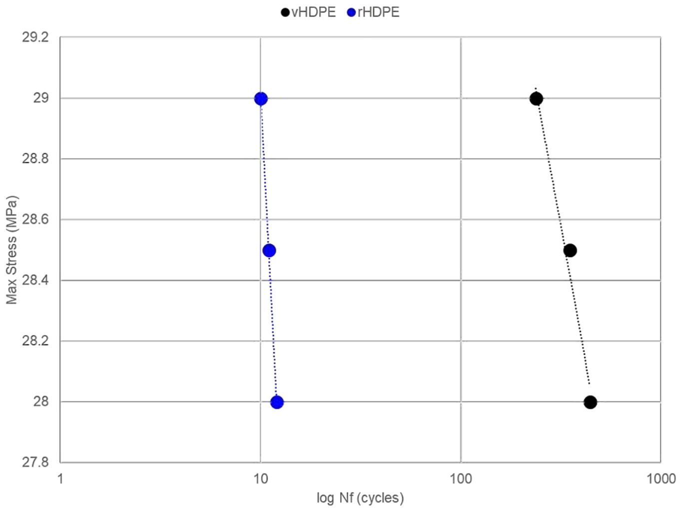


Figure 4.20: rHDPE and vHDPE performance under cyclic test at 100 mm/min and 20°C

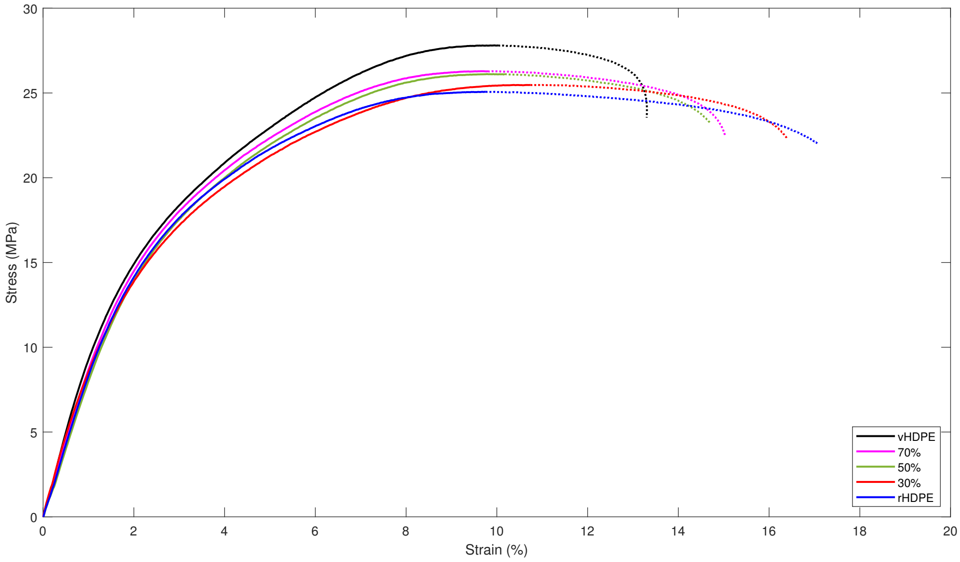
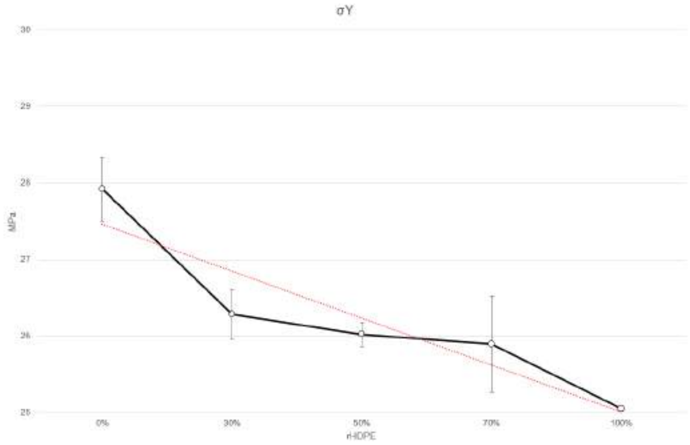
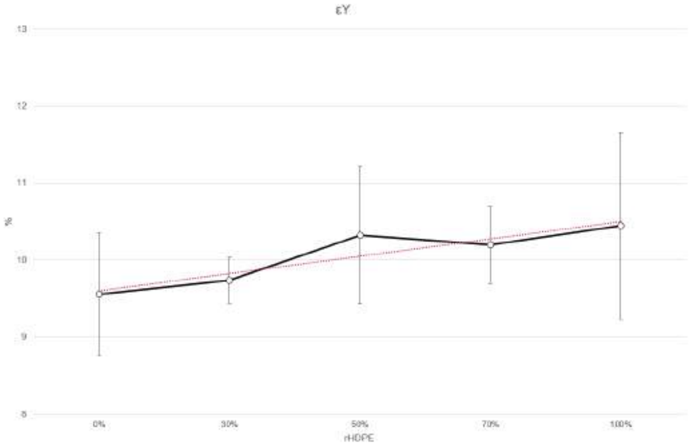


Figure 4.21: Tensile Test Blends representative values, Samples AAU M2

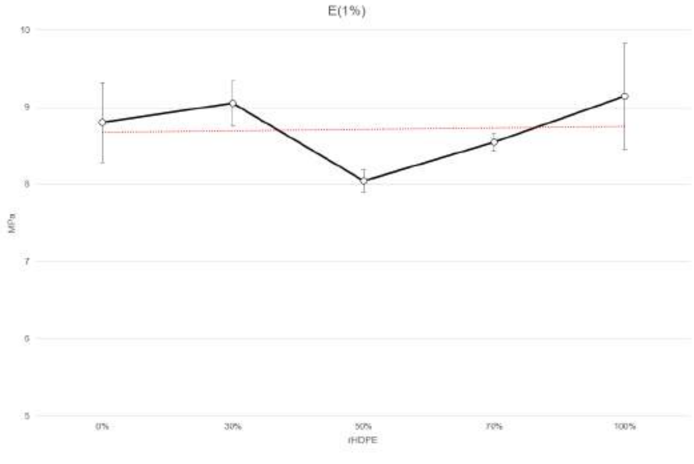
the tensile strength but increased plasticity. Moreover, creep and relaxation have proven to be sensible methods to identifying presence and the effect of cross-links.



(a) σ_Y



(b) ϵ_Y



(c) Elastic Modulus

Figure 4.22: Mechanical properties in function of composition of rHDPE, at 20mm/min and 20°C

Conclusion 5

In this study, given specific vHDPE and rHDPE materials, described in detail in CH.3, were characterized. Their performance was analyzed in thermal testing as well as in both short and long term mechanical tests. Finally, blends of given vHDPE and rHDPE materials were made in various ratios, and their performance in mechanical testings was analyzed, to see weather or not rHDPE can be upgraded by a certain amount of vHDPE and be reintroduced to the manufacturing process as such.

Thermal characterization of vHDPE and rHDPE analyzed in this study lead to the following conclusions:

- DSC tests have shown that both vHDPE and rHDPE do not differ in their structure. They behave alike, as their thermograms overlapped each other, and their measured degree of cristallinity was very close (50.61%, and 51.37% respectively).
- OIT tests gave the information that vHDPE material was more stable since at the given conditions (230°C, 240°C, 250°C) it took longer time for degradation to start. Following this test, E_a (activation energy) was calculated, and the values (188.77 kJ/mol for vHDPE, 218.72 kJ/mol for rHDPE) validated the higher sensitivity of rHDPE to temperature.
- Following the OIT test, time sweep rheology tests showed that rHDPE started degrading sooner than vHDPE at 240°C.
- Moreover, frequency sweep displayed that rHDPE has lower complex viscosity, lower molecular weight and higher molecular weight distribution than vHDPE.However, it needs to be emphasised that although there are minor differences, the materials in general exhibit very similar behavior.

Mechanical testing of rHDPE and vHDPE brought the following remarks:

- Tensile test results display lower yield strength, and higher strain at yield for rHDPE compared to vHDPE at all tested cross-head speeds (1mm/min, 20mm/min, 100mm/min). However, the differences again are low (7% -14%), and can be considered minor. Moreover, the sensitivity of the material to cross-head speeds is seen as the Sec.Mod varied depending on the applied speed. Being higher for vHDPE than rHDPE at 1mm/min and 100mm/min, and lower at 20mm/min.
- Creep tests done at 10MPa, show no difference between rHDPE and vHDPE. However, at 15MPa, vHDPE creeps more than rHDPE. This was argued by the presence of crosslinks in rHDPE, for what an indication was seen in the last points of the frequency sweep rheological test and long times in the time sweep rheological test.

- Relaxation tests done at 6% strain, show no difference between rHDPE and vHDPE .
- Cyclic tests findings were that rHDPE fractured at lower number of cycles than vHDPE (≈ 10, compared to ≈ 300) at maximum applied stresses close to the yield stress of both materials (29MPa, 28.5MPa, 28MPa at 100mm/min). The reason for this, again can be found in the presence of crosslinks in rHDPE.

All that being said, rHDPE and vHDPE in general behave alike. By means of processability, the rHDPE can be reintroduced in the manufacturing process using the same conditions as for vHDPE. Furthermore, in low applied strain and stresses not much difference can be observed. However, long term tests have shown that subjecting rHDPE to higher loads (above elastic region) could be concerning. Therefore further testing is recommended.

Finally, blends of rHDPE and vHDPE materials have been made in the ratios: 30:70% ,50:50% , 70:30%, and tensile tested. The resultant blend properties remained in within the values of the pure substances. Based on the results and property-composition graphs, it can be concluded that blends in all ratios, have not compromised the properties of the material. Due to the general similarities between rHDPE and vHDPE materials in the tests done in this study, blending them together should give a material that will behave similar to pure vHDPE. However, further testing need to be done to confirm these findings.

Future Work 6

Following up the results and findings presented in the report, were the initial characterization and performance of the specific vHDPE and rHDPE materials and their blends used in this particular study, additional tests are recommended to verify and provide robust analysis for material design to support those findings.

First of all, as the polymerization method, various additives and stabilizers affect the final properties of the material, it is proposed to leverage spectroscopy analysis (Raman, Fourier-Transform Infrared Spectroscopy) to obtain better initial information of vHDPE and rHDPE polymers.

For studied rHDPE, the competition between cross-links and chain-scission is evident as no dominant degradation mechanism is conclusive in all the tests. In case the polymer is subjected to further recycling cycles, it is recommended to characterize the degradation paths happening in the studied polymers.

Considering this, the evaluation of degradation is of crucial importance due to its deterministic effect on the materials properties. This is recommended to be further characterized by TGA (Thermogravimetric analysis), spectroscopy and GPC (Gel Permeation Chromatography). By obtaining this information, better design of further material stabilization can be done.

The material exhibited a sensitivity to the manufacturing process, as high orientation was seen for AAU M1, which highly influenced the final properties. Therefore, special attention to the processing method and conditions needs to be considered. This is argued to be due to the chain orientation happening while processing the resin.

Moreover, long term mechanical testing are sensitive to the recognition of cross-links, showing that their influence on final properties could be significant even at low densities. Further analysis is recommended, such as spectroscopy, as it provides valuable information about presence of the cross links as well as the swelling study.

Finally, the mechanical properties of both materials, and blends, since the need for long lasting application, is recommended to be analyzed in longer times, and in more aggressive conditions (both higher and lower temperatures, and also during immersion in water and other media). Cyclical loading test should be further performed to gain minimum of 15 points at 15 different maximum stresses in the loading cycles.

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Radical Chain Degradation Mechanisms

A

A.1 Inert atmosphere

The schematic representation of the described mechanism is illustrated in Fig.A.1.As the strength of the C-C bonds in polyethylene is the same within the polymer, except for those at the end of the chain or where branching occurs, the backbone polymer randomly breaks and initiates the mechanism [43, 48].

1. **Initiation**: The bond in a random position of the chain (P) breaks and form two primary free radicals (R_p)
2. **Propagation**: Depending on the temperature, free radicals transfer within or between molecules. The result is low amount of long radical chains.
    - At low temperature intra-molecular hydrogen transfer (3) lead to the formation of a secondary radical, as this is more stable than R_p.
    - Subsequent decomposition of secondary radicals (4, 4') by β-scission occurs and forms primary radicals in each step, leading to propagation.The scission form alkenes (4) or a polymer chain terminated with a double bond (4').
    - At higher temperature the inter-molecular hydrogen transfer (5) leads the formation of alkenes and the formation of relative short radical chains.
3. **Termination**: Proposed to be by recombination of primary free radicals.

A.2 Oxidative atmosphere

The proposed mechanism for a themo-oxidative reaction is illustrated on Fig.A.2. The mechanisms begins with the formation of radicals generated by temperature input (1). Oxygen then takes part of the propagation by forming peroxy radicals (2) and abstracting hydrogen from other chains (3-7) . Depending on the content of available oxygen and the catalyst used to produce the polymer,this experience simultaneous radical reactions leading to cross-linking, chain enlargement or chain scission.

If the content of oxygen is not enough, the degradation will terminate by the recombination of alkyl radicals (10) the same as the thermal-degradation, Fig.A.1 (6),leading to cross-linking. On the other hand, the peroxy radicals can join between each other or with and alkyl radical (8,9) and, if the concentration of double bonds, such as vinyl groups, is high,the radical can add to these molecules. All this previous reactions are possible paths to increase the size of the chains and cross-linking. Finally, chain scission is due to the oxidation reactions which yield to disproportionation of the chains (6) [51, 52, 54, 76]

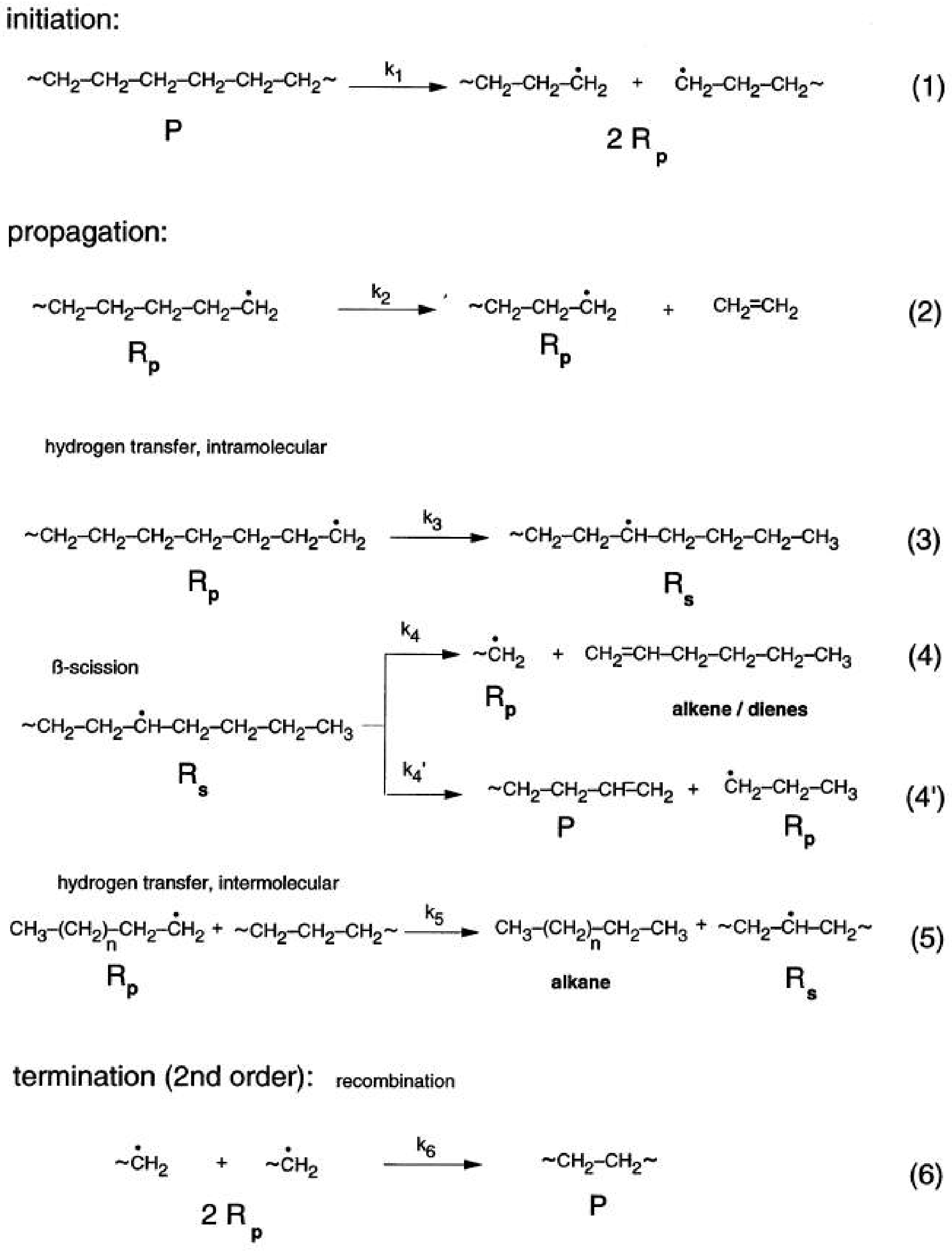
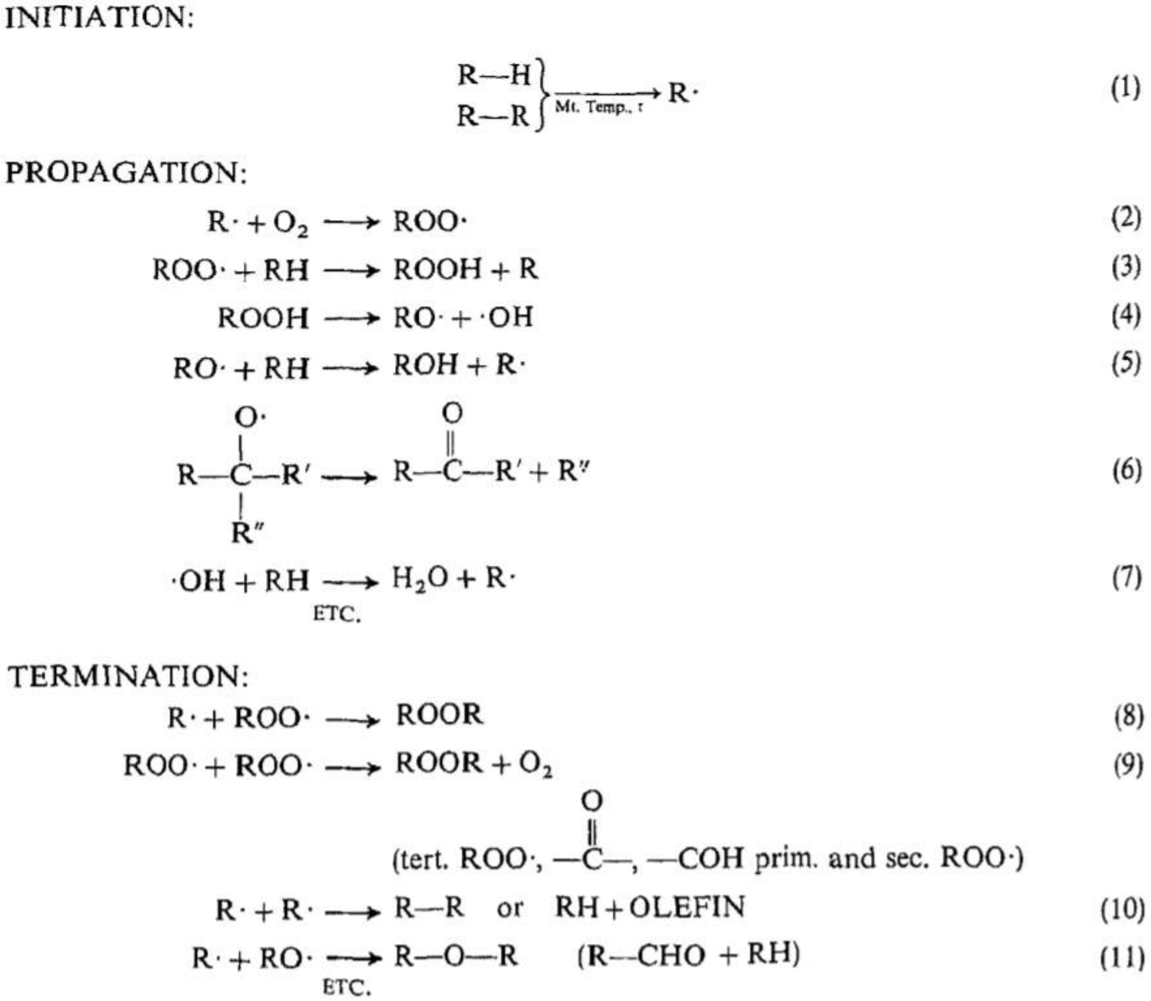


Figure A.1: Reaction mechanism for polyethylene degradation in an inert atmosphere [43]



INITIATION:

$$\left.\begin{matrix} R{-}H \\ R{-}R \end{matrix}\right\} \xrightarrow[\text{Mt, Temp., } \tau]{} R\cdot \qquad (1)$$

PROPAGATION:

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (2)$$

$$ROO\cdot + RH \longrightarrow ROOH + R \qquad (3)$$

$$ROOH \longrightarrow RO\cdot + \cdot OH \qquad (4)$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot \qquad (5)$$

$$R{-}\underset{\displaystyle R''}{\overset{\displaystyle O\cdot}{C}}{-}R' \longrightarrow R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R' + R'' \qquad (6)$$

$$\cdot OH + RH \xrightarrow[\text{ETC.}]{} H_2O + R\cdot \qquad (7)$$

TERMINATION:

$$R\cdot + ROO\cdot \longrightarrow ROOR \qquad (8)$$

$$ROO\cdot + ROO\cdot \longrightarrow ROOR + O_2 \qquad (9)$$

$$(\text{tert. } ROO\cdot,\ {-}\overset{\displaystyle O}{\overset{\|}{C}}{-},\ {-}COH \text{ prim. and sec. } ROO\cdot)$$

$$R\cdot + R\cdot \longrightarrow R{-}R \quad \text{or} \quad RH + \text{OLEFIN} \qquad (10)$$

$$R\cdot + RO\cdot \xrightarrow[\text{ETC.}]{} R{-}O{-}R \qquad (R{-}CHO + RH) \qquad (11)$$

Figure A.2: Reaction mechanism for polyethylene degradation in an oxidative atmosphere [51]

Sample Manufacturing B

Granulated material is reprocessed through injection molding. The material is used "as received" state and injection molded into dogbone shaped samples according to ASTM D3641 - 15 [77] standards with different injection-molding machines.

Method 1

Machine: Babyplast 6/12 Standard

- Shot size: 8,0 cc
- Cooling time: 10 sec
- First injection pressure: 150 bar
- First injection pressure time: 4 sec
- First injection temperature : 200 ° C
- Second injection pressure: 130 bar
- Second injection pressure time: 20 sec
- Second injection temperature : 200 ° C
- Decompression: 0,0 mm
- Injection speed: 100 %
- Second injection speed: 100 %
- Intrusion time: 0,0 sec

Ten specimens of both rHDPE and vHDPE were manufactured, and weight after each injection to reassure the mould was filled properly after each injection and that the specimens don't vary in weight. What can also be seen from the table below.

	vHDPE	**rHDPE**
g	$5,89 \pm 0,011$	$5,91 \pm 0,049$

Method 2

Machine: Ferromatic Milacron K110

1. Plasticising
   - Temperature: 230°C (through all the sections, except feeding, 50°C)
   - Back Pressure: 30 bar
   - Screw speed: 60 rpm
   - Cooling Time: 40 s
2. Injection Process
   - No.Injection Stages: 3
   - Injection Pressure: 130 bar
   - Injection Speed: 70 mm/s
   - Mould Temperature: 80°C

	vHDPE	rHDPE
g	21.10 ± 0.14	21.25 ± 0.09

(a) 30 (b) 40 (c) 41

(d) 44 (e) 49 (f) 50

(g) 51 (h) 52 (i) 80

Figure B.1: Injection Conditions

Average Sample Weight: Injected samples, 11

Machine Program:

Average Sample Weight - final dogbone samples for Mechanical Tests: Injected samples, 11

	100 % vHDPE	**70 % vHDPE** **30 % rHDPE**	**50 % vHDPE** **50 % rHDPE**	**30 % vHDPE** **70 % rHDPE**	**100 % rHDPE**
g	$6,47 \pm 0,008$	$6,48 \pm 0,005$	$6,47 \pm 0,006$	$6,465 \pm 0,005$	$6,48 \pm 0,006$

Average Sample Weight - final dogbone samples for Mechanical Tests: Second Batch

100 % vHDPE		**70 % vHDPE** **30 % rHDPE**	**50 % vHDPE** **50 % rHDPE**	**30 % vHDPE** **70 % rHDPE**	**100 % rHDPE**
g	$6,26 \pm 0,12$	$6,30 \pm 0,01$	$6,28 \pm 0,01$	$6,28 \pm 0,01$	$6,31 \pm 0,01

Detailed Results C

C.1 DSC

Overall Values The second thermal cycle for each tested sample is further analyzed. The average value of the onset temperature, melting temperature and the area under the curve is calculated.

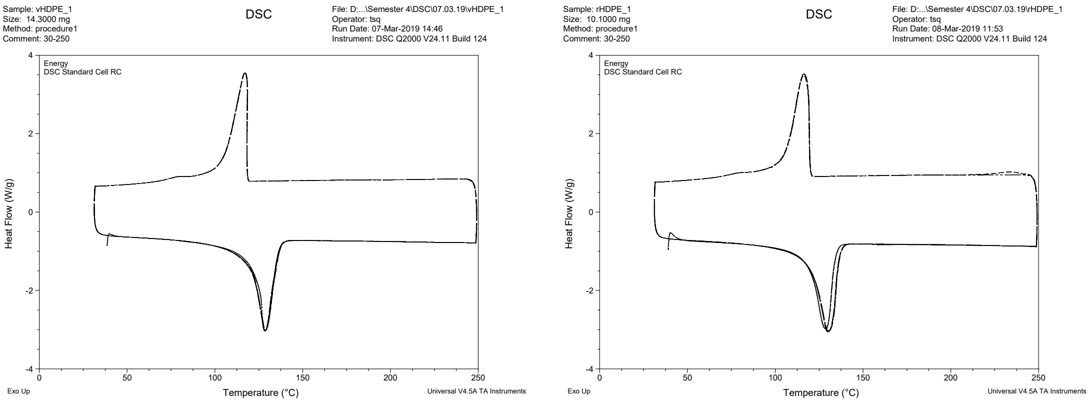
Further he degree of crystallinity (X$_c$, %) is defined by the ratio of the melting heat of the polymer sample $\varDelta H_{sc}$, and the melting heat of a pure polymer crystal, $\varDelta H_c$,

$$X_c = \frac{\varDelta H_{sc}}{\varDelta H_c} \cdot 100\% \tag{C.1}$$

To obtain $\varDelta H_{sc}$ the area between the endothermic peak and the baseline is calculated; $\varDelta H_c$ is reported in literature.

	Start	Onset	Maximum	Stop	Area	Crystallinity
	°C	°C	°C	°C	J/g	%
vHDPE	35	119.06	129.175	150	253.25	86.43
	140	118.11	116.525	35	219.55	74.93
rHDPE	35	119.265	129.76	150	255.9	87.34
	140	119.545	116.69	35	232.25	79.27

Table C.1: vHDPE vs rHDPE Average Thermal values



(a) vHDPE (b) rHDPE

Figure C.1: DSC Representative thermal curves

Oxidation Induction Time (OIT)

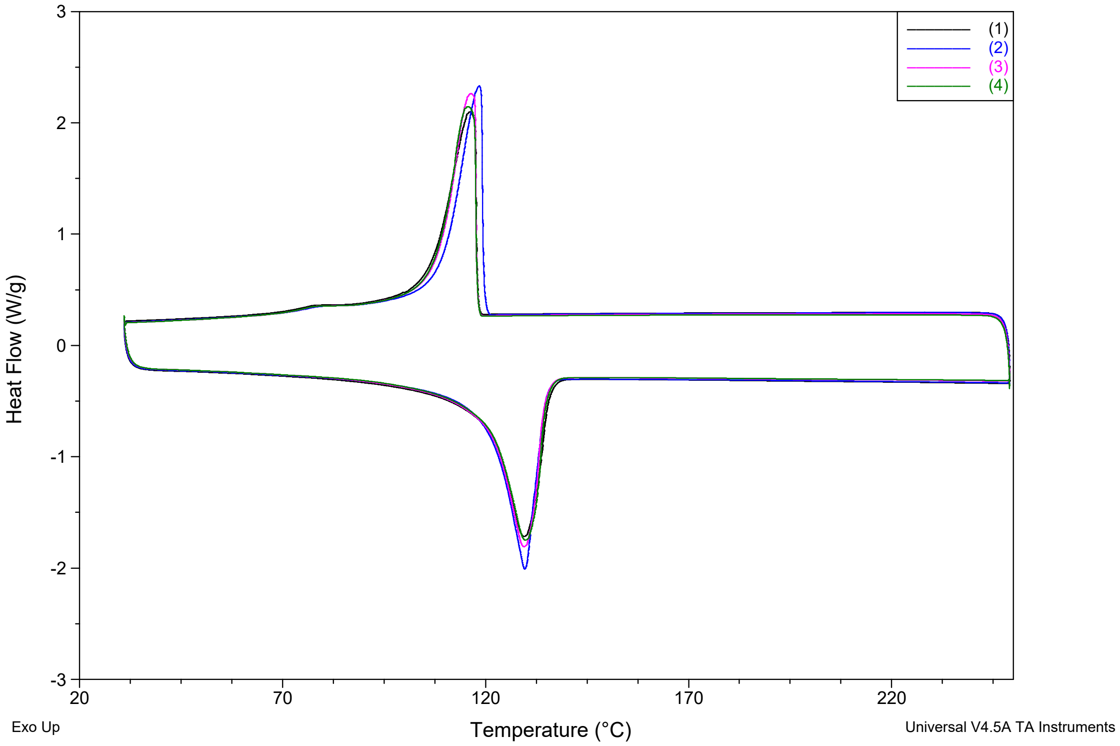


Figure C.2: vHDPE thermograms at different processing methods: (1) As received, (2)AAU M1, (3)AAU M2, (4)Supplier

Temp.	**OIT (min)**	
°C	*vHDPE*	*rHDPE*
250	4.46	2.69
240	12.31	9.88
230	27.39	23.64

Table C.2: OIT test for vHPDE and rHDPE at different temperatures

C.2 Rheometry

Sample conditioning:

1. **Instrument:** RHEOPLUS/32 V3.41D100712 21000520-33025
2. **Geometry:** 25 mm diameter and 1mm gap
3. **Frequency range:** 600 - 0.06 rad/s
4. **Strain:** 5 %
5. **Atmosphere:** Air
6. **Average sample weight:** 0.5 grams
7. **Repetition per test:** 3

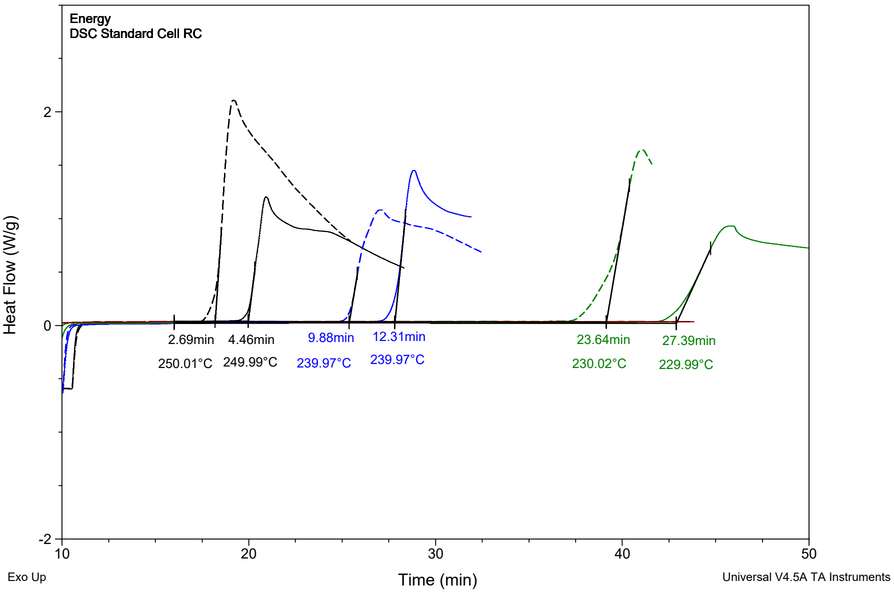
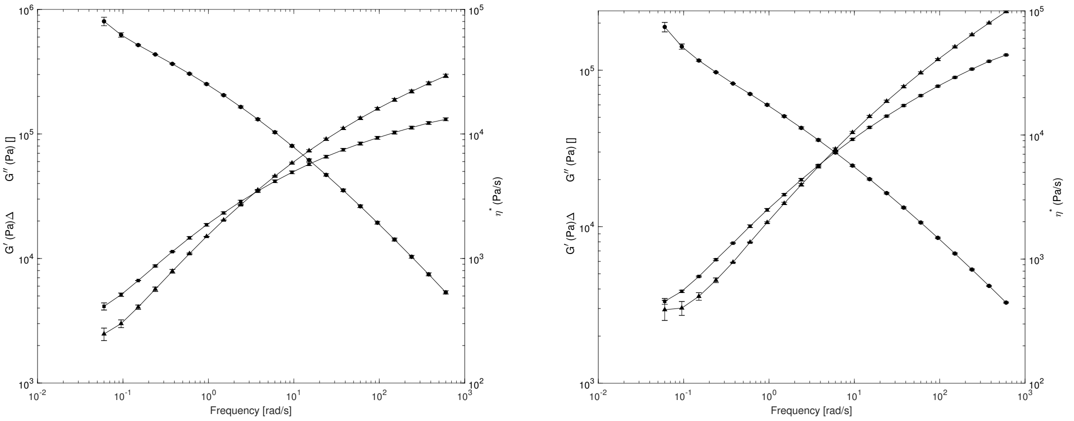


Figure C.3: OIT test for vHPDE and rHDPE at different temperatures



(a) vHDPE

(b) rHDPE

Figure C.4: Evolution of storage, loss moduli and complex viscosity with frequency at 250°C under air atmosphere

C.3 Mechanical Testing

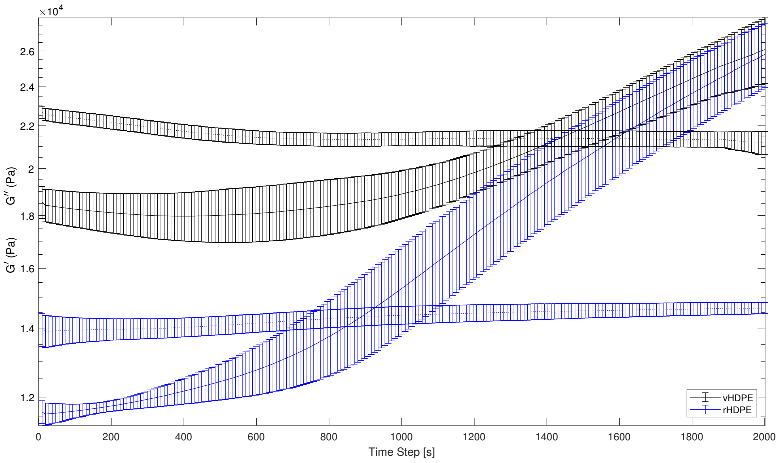


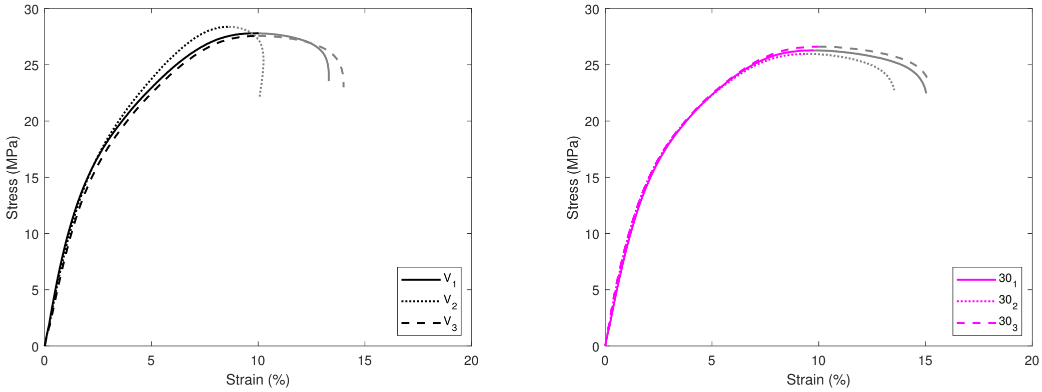
Figure C.5: vHDPE vs rHDPE time sweep at 240°C

		vHDPE		**rHDPE**	
		avg.	st.d.	avg.	
1mm/min	σ_Y (MPa)	77.378		57.518	
	ϵ_Y (%)	9.715		15.160	
	Sec.Mod (MPa)	1592.2		832.2	
20mm/min	σ_Y (MPa)	82.104	3.242	64.822	
	ϵ_Y (%)	9.047	0.459	9.438	
	Sec.Mod (MPa)	1081.1	569.1	1060.6	
100mm/min	σ_Y (MPa)	88.129		73.1123	
	ϵ_Y (%)	7.600		9.2274	
	Sec Mod (MPa)	2350		1164.29	

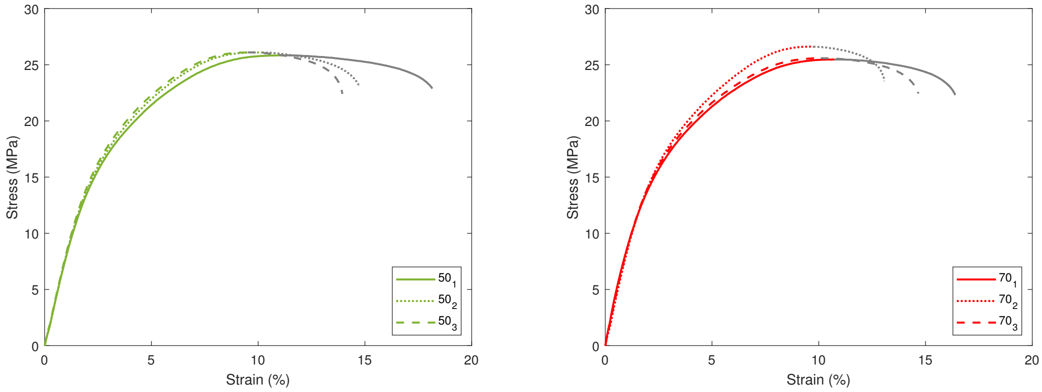
Table C.3: Tensile Test data for test specimens manufactured by AAU M1

		0 % rHDPE		**30% rHDPE**		**50% rHDPE**		**70% rHDPE**		**100% rHDPE**	
		avg.	st.d.	avg.	st.d.	avg.	st.d.	avg.	st.d.	avg.	st.d.
1 mm/min	σ_y (MPa)	25.13	0.49			25.50	0.44			23.25	0.53
	ϵ_Y (%)	11.32	0.74			12.87	1.04			15.33	3.67
	Sec Mod (MPa)	564	2.47			405	0.99			409	0.20
20 mm/min	σ_y (MPa)	27.92	0.42	26.28	0.32	26.02	0.15	25.89	0.63	25.06	0.03
	ϵ_Y (%)	9.56	0.79	9.74	0.29	10.32	0.89	10.19	0.50	10.45	1.21
	Sec Mod (MPa)	880	0.52	905	0.29	805	0.14	855	0.11	915	0.68
100 mm/min	σ_y (MPa)	34.18	0.44			33.46	0.68			29.67	0.42
	ϵ_Y (%)	8.312	1.044			10.440	0.411			11.221	1.588
	Sec Mod (MPa)	990.6	4.994			549.8	0.056			464.5	0.296

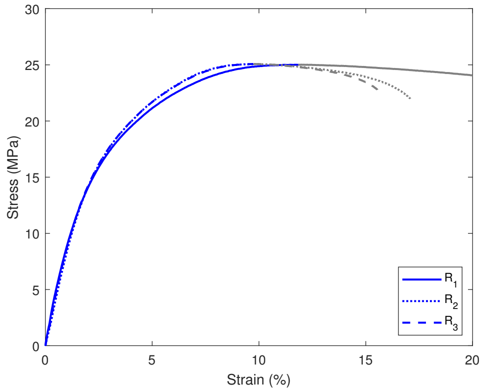
Table C.4: Tensile test data obtained for AAU M2 Specimens



(a) vHDPE (b) vHDPE 70%



(c) vHDPE 50% (d) vHDPE 30%



(e) rHDPE

Figure C.6: Blends Tensile Test Repeatability, Samples AAU M2, color difference indicates before and after σ_Y