UNIVERSITY OF LJUBLJANA

Faculty of Mechanical Engineering

Study of the rheological properties of multiplied HDPE recycled material

A Diploma's thesis of the fourth-cycle bachelor's study programme in
MECHANICAL ENGINEERING – a research and development programme.

Carlos Mir Díaz

Ljubljana, September 2021

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Advisor: Assist. prof. Lidija Slemenik Perše

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Candidate
Carlos MIR DÍAZ

VISOKOŠOLSKI STROKOVNI ŠTUDIJSKI PROGRAM I. STOPNJE STROJNIŠTVO: **VS I/958 E**
NASLOV TEME: Študij reoloških lastnosti večkrat recikliranega HDPE materiala

Ponovna uporaba polimernih materialov je pomembna za trajnostni razvoj, zato ima recikliranje pomembno vlogo pri zmanjševanju odpadnih materialov. Na žalost pa se lahko nekatere lastnosti recikliranih polimernih materialov med postopkom recikliranja spremenijo. Naloga bo osredotočena na polietilen visoke gostote (HDPE), ki je eden od najbolj pogosto recikliranih polimerov. Dolge, skoraj popolnoma nerazvejane polimerne verige so, v primerjaviz nekaterimi drugimi polimeri, odgovorne za visoko gostoto, visoko trdnost in visoko stabilnost materiala. HDPE se je prvotno uporabljal za cevi, odtoke in kanale. Dandanes je uporaba te plastike zelo razširjena tudi za izdelke, kot so vrči za mleko, posode za sok, vrečke za živila ali smeti, posode za motorna olja, steklenice za šampon in milo, posode za detergente in belila, ali igrače.
Cilj raziskave je proučiti spremembo lastnosti večkrat recikliranega HDPE. Mehansko recikliranje bo simulirano s postopkom ekstrudiranja, pri čemer bodo pripravljene mešanice čistega materiala z različnimi deleži večkrat recikliranega HDPE. Tako pripravljeni vzorci bodo omogočili študij vpliva dodajanja večkrat recikliranega HDPE osnovnemu, nerecikliranemu materialu na spreminjanje različnih lastnosti recikliranega HDPE, ki so močno povezane s postopki predelave in končno uporabo produktov.

Diplomsko delo je treba oddati v jezikovno in terminološko pravilnem angleškem jeziku. Rok za oddajo tega dela je šest mesecev od dneva prevzema.

1st CYCLE PROFESSIONAL STUDY PROGRAMME IN MECHANICAL ENGINEERING: **VS I/958 E**

TITLE: Study of the rheological properties of multiply recycled HDPE material

The reuse of polymeric materials is important for sustainable development, therefore the recycling plays an important role in reducing waste materials. Unfortunately, some of the properties of recycled polymer materials can change during the recycling process. The study will be focused on the high-density polyethylene (HDPE), which is the most recycled plastic. Its long virtually unbranched polymer chains are responsible for high density, high strength and high stability compared to some other polymers. HDPE was first used for pipes in storm sewers, drains and culverts, although nowadays the use of this plastic is very extended for products like milk jugs, juice containers, grocery or trash bags, motor oil containers, shampoo and soap bottles, detergent and bleach containers or toys.
The aim of the study is to investigate the properties of extensively recycled HDPE. The mechanical recycling will be simulated by an extrusion process. The mixtures of neat material with different ratios of extensively recycled HDPE will be used to determine how various properties of high-density polyethylene (HDPE), which are associated with the processing and final use of the product, change with repeated recycling and how the addition ofextensively recycled HDPE to neat material affects various properties.

The bachelor thesis must be written in standard English. It   must be submitted within a six-month period after it has been accepted.

Mentorica / Mentor

Assist. Prof. PhD. Lidija Slemenik Perše

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Acknowledgements

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Abstract (in English)

Study of the rheological properties of multiply recycled HDPE material

The aim of the study is to investigate the properties of extensively recycled HDPE. The mechanical recycling will be simulated by an extrusion process. The mixtures of neat material with different ratios of extensively recycled HDPE will be used to determine how various properties of high-density polyethylene (HDPE), which are associated with the processing and final use of the product, change with repeated recycling and how the addition of extensively recycled HDPE to neat material affects various properties.

Povzetek

Določanje vpliva večkrat recikliranega polietilena visoke gostote na lastnosti materiala

Ključne besede: recikliranje
                   polietilen visoke gostote

                   ponovna uporaba
                   predelava

Cilj raziskave je proučiti spremembo lastnosti večkrat recikliranega HDPE. Mehansko recikliranje bo simulirano s postopkom ekstrudiranja, pri čemer bodo pripravljene mešanice čistega materiala z različnimi deleži večkrat recikliranega HDPE. Tako pripravljeni vzorci bodo omogočili študij vpliva dodajanja večkrat recikliranega HDPE osnovnemu, nerecikliranemu materialu na spreminjanje različnih lastnosti recikliranega HDPE, ki so močno povezane s postopki predelave in končno uporabo produktov.

Table of contents

List of figures

List of tables

List of symbols used

Symbol	Unit	Meaning
A	m^2	Area
Cp	$J/kg \cdot K$	Heat capacity
D	m	Diameter
De	/	Deborah number
E	Pa	Young's modulus
F	N	Load
g	m/s^2	Gravity constant
h	m	Height
L	m	Length
m	kg	Mass
Mi	kg	Molecular weight of a chain
Mn	kg	Average molecular weight in number
Mv	kg	Viscous molecular weight
Mw	kg	Average molecular weight by weight
Mz	kg	Average molecular weights
Ni	/	Number of chains
q	W/m^2	Heat flow
t	s	Time
Tc	$°C$	Crystallization temperature
Tg	$°C$	Glass transition temperature
Tm	$°C$	Melting temperature
Wi	kg	Weight of molecular weight species
Δa	/	Change in saturation index to red
Δb	/	Change in saturation index to yellow
ΔE	/	Color change
ΔL	/	Change in luminance factor
ΔT	$°C$	Temperature variation
v	/	Poisson coefficient
τ	Pa	Shear stress
τ	s	Characteristic relaxation time
η	$Pa \cdot s$	Viscosity
β	°	Final angle of the pendulum
α	°	Starting angle of the pendulum
α_T	/	Shift factor
σ_o	Pa	Elastic limit
σ	Pa	Tension

List of acronyms used

Acronym	Meaning
AOX	Alternative oxidase
CO_2	Carbon dioxide
CH_2	Methylene
DNA	Absorbable organic halides
DSC	Differential scanning calorimetry
HCl	Hydrochloric acid
HDPE	High density polyethylene
H_2O	Water
LDPE	Low density polyethylene
MFI	Melt Flow Index
NH_3	Ammonia
NIR	Near-infrared radiation
P'	Macro-radical
PA	Polyamide
PC	Polycarbonate
PET	Polyethylene terephthalate
POO'	Peroxide radical
POOH	Hydroperoxide group
PP	Polypropilene
PS	Polystyrene
PVC	Polyvinyl chloride
UV	Ultraviolet

1. Introduction

1.1 Background

Today, plastic pollution can be considered the most serious environmental problem, especially for the seas, being the final destination of many plastic wastes thus endangering the health of aquatic ecosystems and the survival of the species that inhabit them. In the 50s the use of plastic barely reached 3 million tons a year, by the 90s almost 150 million tons were already reached, and today it can even reach 300 million tons of plastic used in a year.

Due to the increase in their use and their slow process of degradation, plastics can be considered the number one enemy of the seas and oceans, so it is essential to study their different properties when they are reprocessed, in order to extend their use to the maximum, and thus reduce the environmental problems associated with them.

1.2 Objectives

The aim of this study is to investigate the properties of extensively recycled HDPE, comparing its properties when it is used with different proportions of recycled materials, and using recycled materials that have been recycled 10, 50 or 100 times.

In chapter 2: *'Theoretical background'* general information of polymers is presented: the formation of polymer chains, their classification and their mechanical, thermal and rheological properties. It also presents the different types of material forming processes, the types of plastics that exist and how the use of additives can change their properties. Finally, this chapter focuses on polyethylene and more specifically on high-density polyethylene, defining its properties, uses and advantages and disadvantages, and explaining its recycling processes.

In chapter 3: *'Experiments from various literature studies'* is compared the effect of using HDPE recycled, analyzing its thermal, mechanical and thermal properties.

Finally, in the chapter 4 there is a conclusion of the work.

2. Theoretical background and overview of literature

2.1 Polymers

Polymers are natural or synthetic substances composed of a very large molecules, that are multiples of simpler chemical units called monomers. These monomers are combined due to a chemical reaction called polymerization to a very long chain molecule (polymer).

Both natural and synthetic polymers are nowadays very important due to their different properties and their high demand worldwide, as they are the components of the plastics that we commonly use daily. They are also crucial because they include the natural biopolymers as the DNA and the proteins.

Polymers have two basic types of molecular arrangement, amorphous and crystalline. In polymers with amorphous arrangement, the molecular chains have no order and are entangled. In some polymers crystal regions are formed, in which the molecules adopt a very ordered structure. The term used to name this type of polymers would be semi-crystalline, since the polymers do not fully crystallize, that is, the crystalline regions of a polymer are surrounded by amorphous regions.

The main characteristics of polymers are [1]:

- Resistance to corrosion and chemical products,
- Low electric and thermal conductivity,
- Low density,
- Absorption of vibrations and noises,
- Wide range of colors and transparencies,
- Ease to manufacture, allowing complex designs,
- Low cost,
- Low hardness and elastic modulus,
- High thermal expansion coefficient,

- Low range of service temperatures (<350 ˚C),
- Low dimensional stability.

2.1.1 Polymer chain formation

Polymeric materials are organic structures that are basically made up of carbon (C), hydrogen (H) and oxygen (O) atoms [1]. Polymers are made up of different atoms, which together form a basic unit called monomer, that repeats itself and forms a structure that is responsible for the behavior of the material on a physical, chemical, mechanical, or rheological level. The process by which a polymer chain is obtained from a basic unit or monomer is called polymerization.

2.1.1.1 Addition polymerization

In this polymerization process, the aim is to increase the molecular weight of the chains to obtain a solid. One of the first conditions that the monomer must present is the presence of at least one double bond. The monomer is introduced into a reactor and by the action of a catalyst, temperature and/or pressure, the double bond is broken, so that the monomer has two free bonds that allow the bond with other monomers, forming a chain of monomers. Addition polymerization has three stages [1]: initiation, propagation, and termination.

Initiation is the stage where the double or triple bond in the monomer is broken by using a catalyst or increasing the pressure and/or temperature. In this way, double or triple bonds in the monomers break, which leads to active ends that can be joint together to form polymer chains.

During the propagation stage, the monomers unite to form chains of greater length. At first, the growth of the chain is relatively fast, but as the polymerization progresses, the growth rate decreases. This is because the few remaining monomers have to bind to the ends of the chains.

The completion of the polymerization process can end in two ways: the first is when two unpaired electrons from two different chains that are growing meet resulting in their respective chains coupling, and the second occurs when two increasing chains are found, one of the unpaired electrons instead of simply coupling with the unpaired electron of the other chain, snatch a hydrogen atom, ending the growth and leaving the last chain with two unpaired electrons. Finally, a double bond is formed between those two unpaired electrons and that also closes this chain.

Figure 2.1 shows an addition polymerization process of the polyethylene.
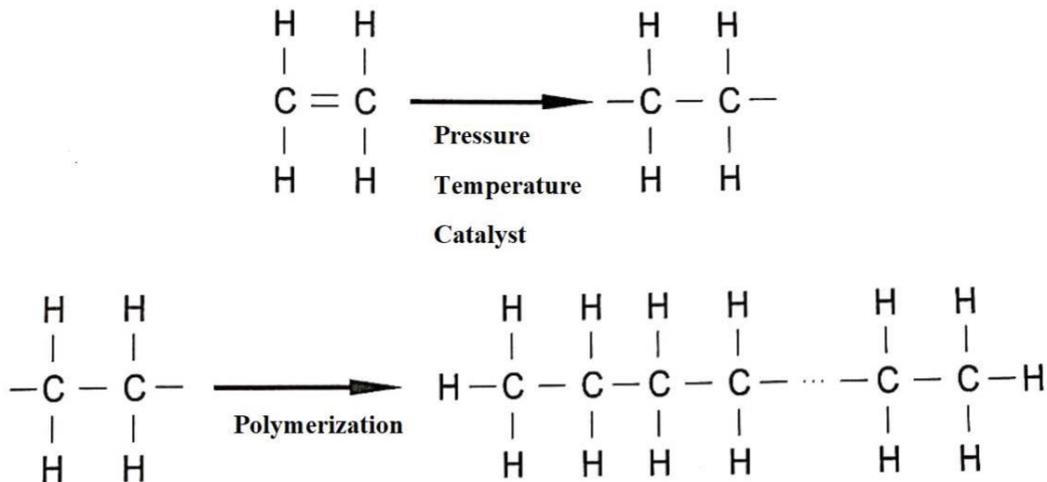
Figure 2.1: Formation of polyethylene chains by addition polymerization [1]

2.1.1.2   **Condensation polymerization**

In this process two monomers of different kind react, which gives off a simple molecule such as water (H_2O), ammonia (NH_3) or hydrochloric acid (HCl), which must be extracted to accelerate the reaction [1]. In this process the two reactants come together to form a third unit that repeats itself and forms the polymer chain. As with addition polymerization, pressure and temperature changes or a catalyst are responsible for the initiation of the reaction.

Polymerization occurs by the diffusion of monomers towards the ends of the chains. When diffusion makes it impossible to transport monomers to either end, the reaction is interrupted and polymerization ends. The polymeric materials that are formed by this type of polymerization are polycarbonate (PC) or polyamide (PA).

The process of condensation polymerization also takes place in nature, obtaining proteins, silk or cotton.

2.1.2 Classification

Polymers can be classified following several criteria [2]. According to their origin, we can find natural (they are obtained from the nature, like the DNA), semisynthetic (they are obtained though the transformation of natural polymers) and the synthetic (are formed by the industry from monomers).

Following their polymerization mechanism, we can find addition polymers (polymerization does not imply the release of any low molecular mass compound) and condensation polymers (polymerization reaction involves the formation of a molecule of low molecular mass at each step).

Due to their chemical composition, we can find organic polymers (formed by carbon atoms) and inorganic polymers (for example silicone, based on silicon atoms).

Following their applications, there are elastomers (they are materials with very low module of elasticity), adhesives (they are substances that combine high adhesion and high cohesion), fibres (they have high module of elasticity and low extensibility), plastics (polymers that in the face of sufficiently intense effort, deform irreversibly), coatings (substances that adhere to the surface of other materials to grant them some property).

Finally, depending on their behaviour at elevated temperature there are elastomers (plastics with elastic behaviour that can be easily deformed without breaking their bonds or modifying their structure), thermosets (all we get by heating them is that they decompose chemically, instead of flowing), and thermoplastics (go into the liquid state when heated and return to solid state again when cooled).

2.1.2.1 Elastomers

Elastomers present an elastic behavior; they are capable of recovering their original shape after being stretched to great extends. They can have high degrees of elongation due to their low intermolecular forces. With the application of force, the molecules straighten out in the direction they are being pulled.

Elastomers are at room temperature above their glass transition temperature, which means that they are in amorphous state and have a high deformation capacity (E = 3MPa at room temperature [3]). In addition, elastomeric materials have very high toughness values (they are capable to absorb very high energies under stress). Their most common use is in adhesive industry, as they have good adhesion and impermeability properties. Elastomeric materials are also used in nuclear industry, mostly for the sealing applications and electrical wire insulation.

2.1.2.2 Thermosets

They are infusible and insoluble polymers. After the polymerization process, thermosets go from a liquid to a solid and hard state, as is shown in the figure 2.2. Unlike thermoplastics, in thermosets when the temperature increases there is no transition to a soft and malleable material. If the temperature increases enough the material degrades, but does not become malleable. This is why these types of materials are not recyclable. The reason for this type of behavior is that the chains of these materials form a three-dimensional spatial network, intertwined with strong covalent bonds.
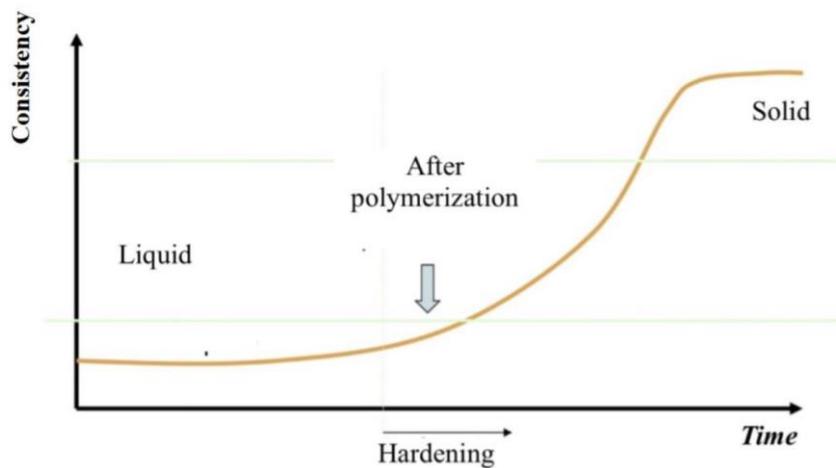
Figure 2.2: Thermosets behaviour [4]

Thermoset plastics have some advantageous properties compared to thermoplastics [4]. For example, better resistance to impact, solvents, gas permeation and extreme temperatures. Among the disadvantages are, generally, the difficulty of processing, the need for curing, the fragility of the material and the non-reinforcement when subjected to stress.

2.1.2.3   Thermoplastics

A thermoplastic is a plastic polymer material that can be melted and recast almost indefinitely. They represent the 70-80% total production of plastics [5]. The structure of thermoplastic polymers can be crystalline or amorphous.

Although there are types of thermoplastics that are expensive, strong and used in place of metal, most of them are used in common everyday products, because they are easy to mold and shape when they are hot and they have high melting point. Then, when they are cooled, they turn into hard and solid plastic.
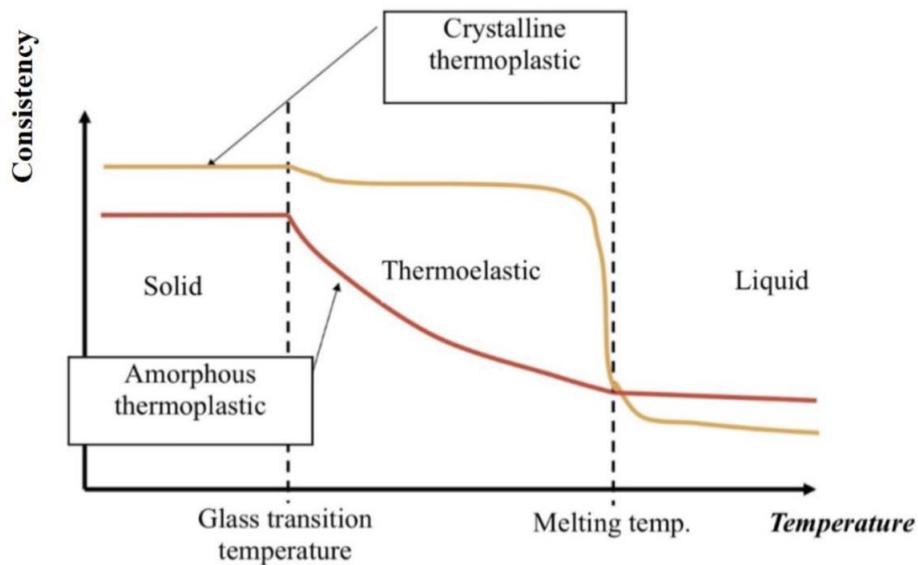
Figure 2.3: Thermoplastics behaviour [4]

The figure 2.3 describes the behavior of a crystalline thermoplastic polymer and an amorphous one. It is observed that below a temperature, called a glass transition temperature, both polymers behave as solid, hard and fragile materials, and above this temperature they are soft and ductile. The main difference between crystalline and amorphous thermoplastics is that the crystalline ones need a higher temperature to become soft and malleable. If the heating is prolonged and reach their melting temperature, the thermoplastics melt to a liquid.

Thermoplastics materials have large number of good properties. First, they are energy efficient in their manufacture and processing as they can be made in a very high volume with high precision and low cost. They can replace metals in some applications, with all the consequences that it has: weight saving, proper design and more tolerance to deflections. Another characteristic to keep in mind is that thermoplastics can be remolded and recycled without negatively affecting the material's physical properties.

The most common thermoplastic examples are [6]:
- Polycarbonate – PC
- Polyethylene – PE (HDPE and LDPE)
- Polyethylene terephthalate – PET
- Polyvinyl chloride – PVC
- Polypropylene – PP
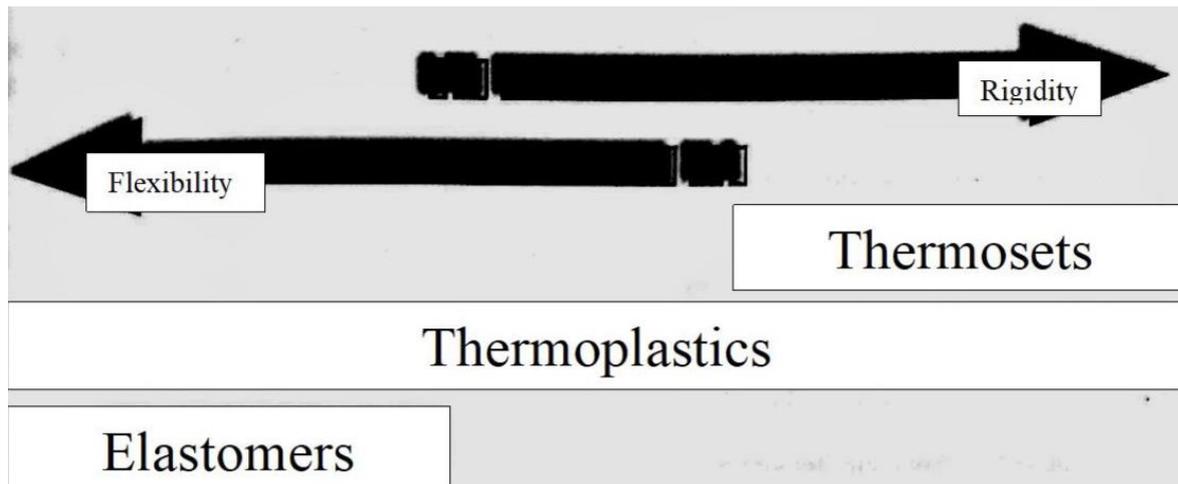
Figure 2.4: Selection of polymeric materials according to their behaviour, rigid or flexible [1]

Figure 2.4 shows a comparison between these three materials, with elastomers having greater flexibility and lower rigidity, and thermosets having the opposite behavior. Thermoplastic materials, being malleable, have a wide range in their rigid and flexible properties.

2.1.3 Thermal properties

Thermal properties describe the behavior of polymers in the face of heat action. Thermoplastics are the polymers that show a more important variation of their properties depending on the applied temperature. The determination of thermal properties is of crucial importance in the design of pieces that must follow a number of functional specifications.

The fundamental parameters for understanding the thermal behavior of polymers are the glass transition temperature and the melting temperature. The glass transition is the reversible change to an amorphous polymer or amorphous regions of a semi-crystalline polymer from (or to) a viscous or elastic condition to (or from) a rigid and relatively brittle condition. Melting temperature is the temperature at which a polymer changes from solid to liquid state at atmospheric pressure. At the melting point solid and liquid phase exist in equilibrium.

2.1.3.1 Softening temperature

It is necessary to determine the range of working temperatures of each class of thermoplastics and thus, know the limitations when a certain application is required with certain environmental conditions. From these conditions we find two types of properties [1]:

- Vicat's softening temperature.
- Thermal bending temperature.

Both temperatures are obtained by the combination of three parameters: application of loads, application of temperature and time. Once these parameters have been determined, the equipment must have a series of weights that allows the corresponding load to be applied, a

8

heating system that allows, in addition to applying temperature, the control of the speed at which this temperature is applied and a system that records the time that elapses and the deformation produced by the combined action of the load, temperature and time.

The equipment consists of a metal box that contains inside a series of electric heating elements that heat an oil bath. The box contains a hole that allows it to be emptied so that the oil is always kept in good condition. It also has two holes in the upper part: one for the introduction of a stirrer that allows the temperature of the oil to remain homogeneous and another for the introduction of a thermocouple to measure the temperature of the oil.

To obtain the Vicat softening temperature, the sample is supported on its entire surface, and the penetrator, with a contact surface of $1mm^2$, has to apply the load perpendicularly on the specimen and ensure that the point of contact is more than $3mm$ from the edges. On the other hand, for the determination of the thermal bending temperature, the assembly of the specimen and the load support is different: the sample is supported at its ends and the load is applied in the central part. Figure 2.5 shows the arrangement of each specimen to obtain both temperatures.
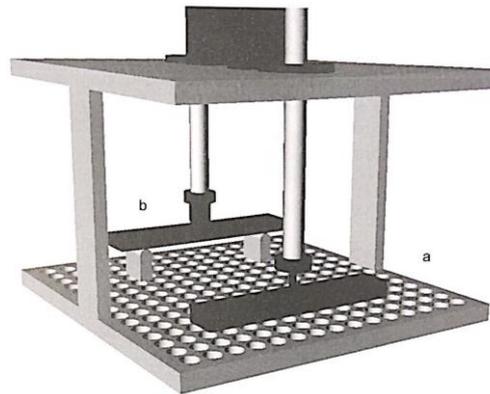
Figure 2.5: Placement of the samples and type of load support for obtaining (a) the Vicat softening temperature and (b) the thermal bending temperature [1]

The loads applied for each of the tests is different; in the case of the Vicat softening test, the loads can vary between 10 and 50 N, while for the bending test the applied load is measured by the following equation [1]:

$$F = \frac{2 \cdot \sigma \cdot h \cdot b^2}{3 \cdot L}$$

(2.1)

where the value of the tension, σ, can be taken from the following three values: 0.45, 1.8 or 8 *MPa*, h is the height of the specimen, b is the length of the base that is supported and L is the distance between supports.

The procedure for obtaining both softening temperatures is simple, since once the samples are assembled, the instrument is placed in an oil bath at room temperature. Then, indicating the heating rate ($50 - 120 °C·min^{-1}$), the equipment starts working, and when a deformation

of one millimeter is reached, the equipment emits an acoustic signal and the value of the temperature at which this deformation has occurred is recorded.

2.1.3.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is a technique used to study the behavior of a polymer when it is heated. It is used for the analysis of the thermal transitions of a polymer, such as the glass transition temperature and the melting temperature. The machinery used in this experiment is represented in the figure 2.6:
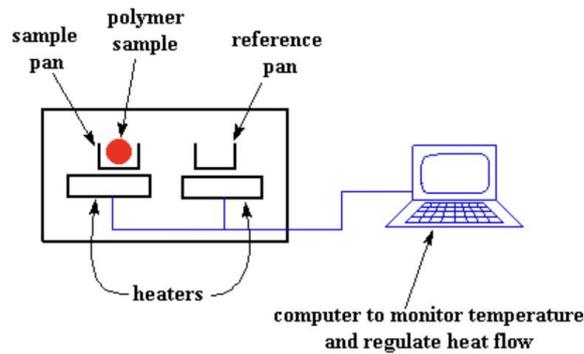
Figure 2.6: Device used to perform the DSC analysis [7]

There are two pans: one contains a polymer sample and the other is empty. Both pans are placed on heaters, which must heat them at a specific speed, usually at $10^o C \cdot min^{-1}$ [7]. The computer that is connected to both pans is used to ensure that the two pans are heated up at the same speed. This is because the pan containing the polymer sample will need more heat than the pan that remains empty, and the goal of this analysis is to get how much additional heat needs to be supplied. It is done by plotting a curve like the one represented on the figure 2.7, where the heat absorbed by the polymer is being plotted as a function of temperature.
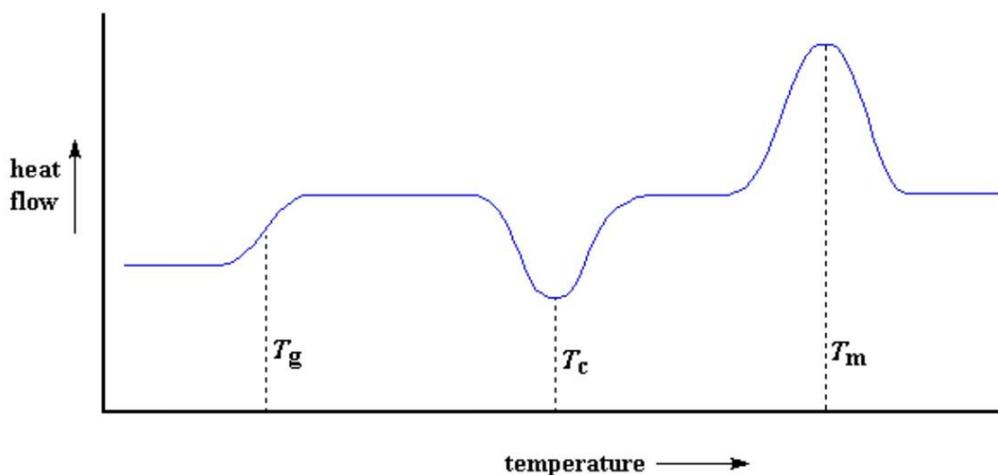
Figure 2.7: Heat flow versus temperature curve [7]

As both pans are heated, the computer will record the difference in heat production between the two heaters versus temperature, which means that the heat absorbed by the polymer is being plotted as a function of temperature.

If the values of the first part of the graph before reaching the glass transition temperature are taken as data, the heat supplied by the temperature increase (heat capacity, Cp) is obtained by dividing the heat flow by the heating rate as shown in the equation (2.2):

$$\frac{heat\ flow}{heating\ rate} = \frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T} = Cp \tag{2.2}$$

Where the heat flow is the heat that is supplied divided by a unit of time, the heating rate is the temperature increase divided by a unit of time and the heat capacity measures the amount of heat needed to produce a given temperature increase.

When the polymer is heated a little more it can be seen that the curve will take a sharp leap upwards, this happens because the polymer has reached the glass transition temperature, so it has increased its heat capacity.

If the sample continues to be heated slowly, it is possible that when exceeding the glass transition temperature, the chains will have enough mobility to crystallize at temperatures below the melting temperature. The crystallization process releases heat, so it is represented on the graph as a decreasing curve.

After this, the sample will reach its melting point, where the crystals of the polymer will begin to separate. At this point, the heater of the pan with the sample must supply a larger amount of heat in order to melt all crystals, which means that its temperature will continue increasing to be equal to the reference pan temperature. This translates into an elevation of the heat flow curve versus temperature.

Both depression (Tc) and increase (Tm) in the heat flow versus temperature curve will only be for polymers that are able to crystallize and melt, since for example there are 100% amorphous polymers that would not have such fluctuations in the curve because they are not able to crystallize, and therefore, to melt.

2.1.4 Mechanical properties

The mechanical properties of a material describe how it behaves to the application of loads on it. In the particular case of polymers knowing these properties is important because their mechanical behavior against stresses is very different from that of other metallic and ceramic materials [1]. For example, while metal parts are designed based on their response to short-term mechanical stresses, polymeric materials involve several factors that must be taken into account, such as the time of application of the loads, the service life of the product, the chemical environments to which the piece may be subjected or the working temperatures of the material.

2.1.4.1   Tensile tests

The tensile test consists of the application of a force on the section of a standard specimen with the aim of obtaining the following results [1]:

- Resistance
- Deformation
- Elastic modulus
- Poisson's coefficient

The most common device for performing this type of test is shown in the figure 2.8 and consists of two grips; one fixed and one mobile. A very important fact to consider is the speed of separation of the grips, as it can already mean a significant change in the results: at slow deformation rates the molecules can be oriented in the direction of the applied force, increasing their tenacity and elongation. Usually, the speed of separation of the grips is 50*mm/min* [1].
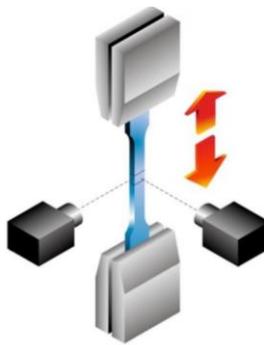
Figure 2.8: Tensile test with grips [8]

Knowing this force and the cross-sectional area of the sample, it is possible to determine the stress that the polymer is experiencing by following the formula (2.3), where *F* refers to the load that is being applied, and *A* is the cross-sectional area of the sample.

$$\frac{F}{A} = stress \tag{2.3}$$

In the field of polymers, we can talk about two different kinds of resistances: tensile strength, which is the maximum stress that the specimen supports during the test, and the creep stress, that if the stress remains constant causes an increase in deformation.

One way to know what happens to the sample while exerting the tensile strength is to measure the elongation. This parameter serves to know the change in the shape that the polymer will experience during this process. This type of study is important for elastomers, since it is important to know their elastic elongation, which is the percentage of elongation that can be achieved without the permanent deformation of the sample and it is measured using the formula (2.4), where both the initial *(L₀)* and final *(L)* length of the sample need to be measured.

$$\frac{L}{L_0} * 100 = elongation \ (\%)$$

(2.4)

To know how resistant a polymer is against elongation, its tensile modulus is measured. To carry out this process, the tension is slowly increased and the elongation experienced by the sample at each stress level is measured until it finally breaks. Then a stress-strain graph is represented as shown in the figure 2.9, where the modulus is the slope of the curve, therefore, the steeper the curve the more resistant to deformation the polymer will be.
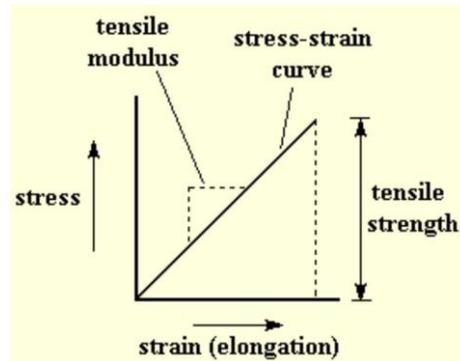
Figure 2.9: Stress-strain curve [9]

The stress-strain curve does not have to be a line like the one shown in the figure 2.9, since for example in the case of very flexible plastic it would adopt a more curved shape. In this type of case the initial slope of the curve is taken as the modulus.

By measuring the area under the stress-strain curve you get the hardness of the material, which is an amount of the energy that the sample can absorb before it breaks.

HDPE and all types of polyethylene in general are classified as flexible plastics. Looking at the yellow curve of the stress-strain graph in the figure 2.10, we see that this type of plastics do not support deformation as well as rigid ones, but they do not break, this is because their good deformation properties. The modulus is measured as the slope of the initial part of the curve, so it can be seen that polyethylene resists deformation for a while, but if enough stress is applied, it will eventually deform.
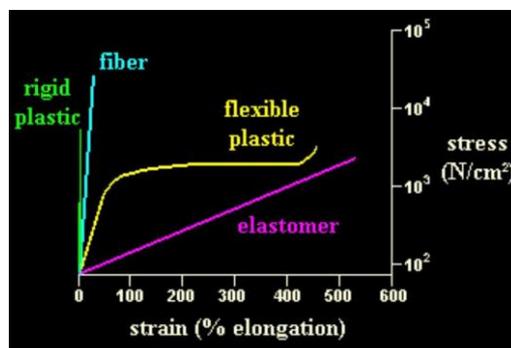
Figure 2.10: Stress-strain curve for differents types of plastics [9]

Another important parameter when performing the tensile test is the Poisson coefficient. As the sample is stretched, a contraction occurs in the directions perpendicular to the axial.
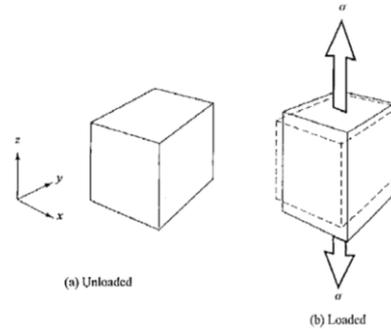
Figure 2.11: Applying an axial stress on the sample in the direction of the 'z' axis [10]

Taking the axes of the figure 2.11, when an axial load is applied to the sample, the axial elongation *(Ԑz)* will be positive, while the lateral contractions *(Ԑx, Ԑy)* will be negative. The Poisson coefficient is the ratio between such lateral contraction and axial deformation:

$$\nu = \frac{-\Box x}{\Box z} \tag{2.5}$$

Normally, Poisson coefficient varies between 0 and 0,5. If it is equal to 0,5 it means that the polymer is incompressible [11].

2.1.4.2   Bending tests

Another important mechanical property of polymers to be studied is the ability they have to withstand forces applied perpendicularly on their longitudinal axis. The objective of this test is to know the behavior of the material when bending is exerted.

The most used method for this type of test consists on the application of a load on a sample of rectangular section supported by its ends, without tension and with the load application on the half of its length. The modulus obtained in a bending test is calculated and has the same meaning as the modulus obtained in a tensile test [1].

2.1.4.3   Impact resistance

Impact resistance is understood as the resistance of a material to fracture by the shock of a load and is one of the most important mechanical properties of polymers.

The impact resistance depends on both the temperature of the polymer and the speed of the applied load. Thus, the lower the test temperature of the polymer and the higher the speed of application of the load, the lower the impact resistance.

There are two commonly known tests to measure the impact resistance of polymers: the pendulum-type test and the dart-type test [1].

The pendulum type test consists of hitting the sample of the plastic to be analyzed by means of a pendulum, as shown in the figure 2.12.
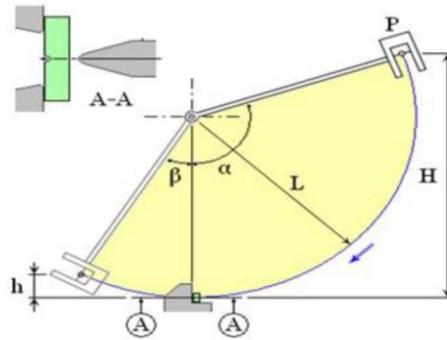
Figure 2.12: Charpy pendulum positions [12]

With this pendulum movement the sample is usually ruptured, and impact resistance can be calculated as the energy required to cause the break. The energy absorbed by the specimen is determined through the potential difference of the pendulum before and after impact, using the following formula [12]:

$$E = mgL[\cos(\beta) - \cos(\alpha)] \tag{2.6}$$

Where you have a mass m, which is coupled to the outside of the pendulum of length L, and is dropped from a height H, which will depend on the speed of application of the load. Alpha, α is the starting angle of the charge application and beta, β is the final angle at which the pendulum rises after complete specimen breakage. And g is the gravity constant.

On the other hand, the dart-type test (figure 2.13) consists of dropping a known mass on the polymer sample to know its impact resistance. It is used to know the energy that is required to damage a film by the impact of a dart in free fall under specific conditions.
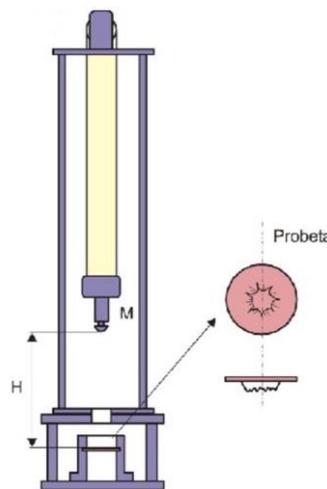
Figure 2.13: Darts-type impact test equipment and specimen shape [13]

To perform this test, the initial weight of the mass and its height are first estimated depending on the plastic sample to be analyzed. If the sample is broken, the mass of the dart should be reduced by reducing its falling height. A batch of 20 tests is usually performed, and if the number of broken samples is equal to 10, the test can be terminated. This can be achieved by statistically calculating a darting height considering the conditions under which there is a 50% probability of failure. If less than 10 samples are broken, the test must continue until this value is reached, and if the number of broken samples after 20 tests is greater than 10, more samples should continue to be tested until the number of unbroken samples is equal to 10 [1].

An advantage of this type of test compared to the pendulum type test is that in the dart-type real parts can be tested, such as covers of electronic devices, in addition, in this case the fracture surfaces of the sample can provide information on what type of breakage has occurred. In this type of equipment, the impact energy can be varied both by varying the mass of the darted and the desired height. The impact energy is calculated with the law of potential energy using the following formula:

$$E = mgh \tag{2.7}$$

Where m is the mass of the dart, g is the gravity constant and h is the free fall height of the dart.

2.1.5 Rheological properties

Rheology is the science that deals with the way matter is deformed when a force is applied to it; that is, it studies the relationship between the strength of a material and the deformation that occurs when it flows. In polymers, a rheological behavior is associated with different phenomena that are related to some degree to different molecular mechanisms.

Polymers show complex rheological behavior, which is important to know when using or producing these materials. This type of behavior refers to the viscosity of the molten sample, the flow behavior, the viscoelastic properties, the behavior as a function of temperature or the glass transition temperature. This quality control exercised on polymeric materials improves their processing behavior and allows the optimization of the final product, for example if plastics are manufactured for the automotive industry.

2.1.5.1   Viscosity

The viscosity of a fluid is a measure of its resistance to gradual deformations produced by shear or tensile stresses.

The group of polymers that has had the greatest expansion are thermoplastics because the increase in temperature causes a decrease in viscosity, so that they reach a certain fluidity, which allows them to be shaped in various forms.

Newton's viscosity law is used to show the behavior of a fluid. To better understand Newton's law on viscosity, figure 2.14 represents the behavior of a fluid that lies between two flat sheets and parallel to each other, of area A, and that are separated from each other a distance

y and if it is very small *dy*. If we assume that initially the system is at rest, but then the top sheet moves in the direction of the x-axis, with a velocity *v*, it has been determined for many fluids experimentally that the tangential force *F* applied to an area plate *A* is directly proportional to the velocity *v* and inversely proportional to the distance *y*.
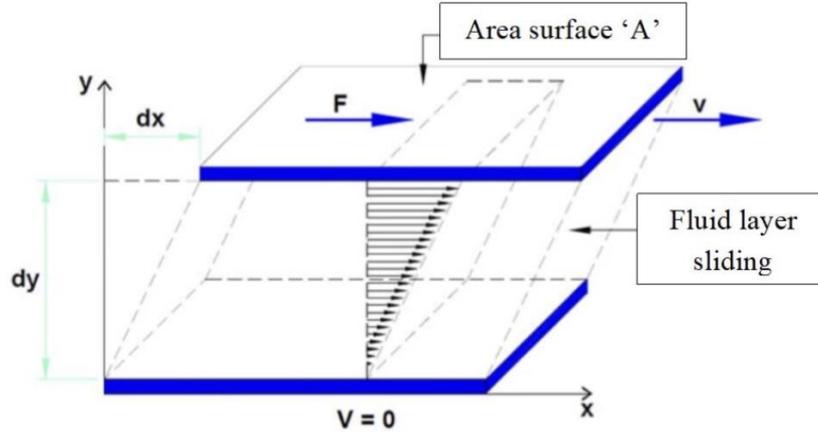
Figure 2.14: Behavior of a fluid between two parallel sheets [14]

The Newton's viscosity law can be expressed as:

$$\tau = \frac{F}{A} = \eta \cdot \gamma \tag{2.8}$$

where:

$$\gamma = \frac{\partial v}{\partial y} \tag{2.9}$$

From the formulas (2.8) and (2.9), γ is the differential of the shear rate with respect to the differential of the fluid thickness, τ is the shear stress on the fluid, v is the velocity of the fluid, *y* is the fluid thinkness, and η is the absolute viscosity of the fluid.

Many fluids, almost all of them of industrial interest, have deviations from Newton's law, and this type of fluids are known as non-Newtonian fluids. The big difference between Newtonian and non-Newtonian behavior is the length of the molecule of the fluid, so that those fluids that have small molecules have a Newtonian behavior as opposed to those with larger molecules.

The different behaviors of a non-Newtonian fluid can be classified as [14]:
- Shear thinning behavior. Viscosity decreases with shear force.
- Shear thickening behavior. Viscosity increases with increasing shear force.
- Plastic behavior. For low cutting speeds the material behaves like an elastic solid.

Plastic materials with non-Newtonian behavior, which indicates that the viscosity is not constant, do not present a linear relationship between stresses and velocities. This concept is important to understand the behavior of plastics during the forming process of these

materials. For example, the injection process is a process that involves a lot of shear and pressure on the material, substantially modifying its viscosity. As shown in the upper graph of the figure 2.15, with plastics, an increase in tension or shear stress will cause its viscosity to be drastically reduced.

The lower graph from the figure 2.15 shows how the behavior of the polymer can be divided into three zones depending on its viscosity and shear rate. Zone A is the constant viscosity zone at low shear rates, and in this zone the polymer has a Newtonian behavior. Zone B is the intermediate zone with intermediate shear velocities, where a drop in viscosity is observed as a function of the shear rate. The C zone is the end zone that occurs at high shear rates with constant viscosity, and again the behavior is Newtonian.
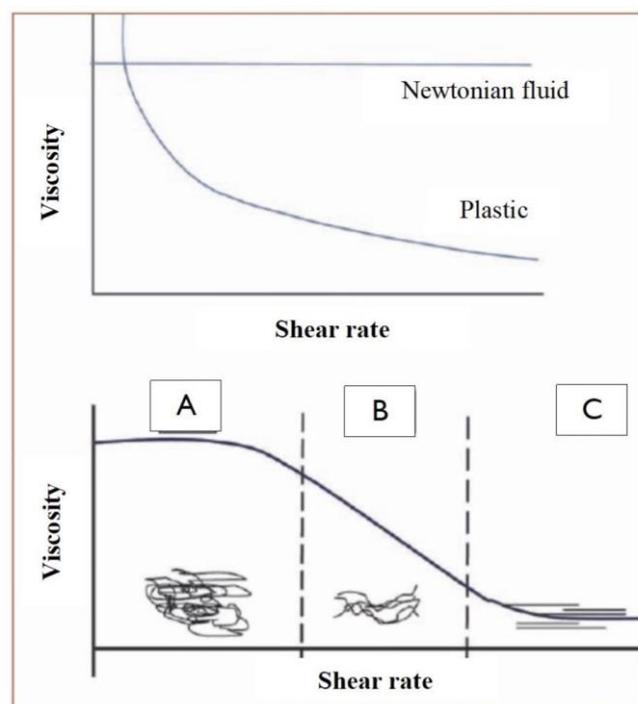
Figure 2.15: Graphic of the effect of shear on viscosity [15]

Given the relationship between viscosity and shear rate, it is important to define the following concepts to define a robust process [15]:

1) Select a range of speeds that enable stable viscosity behavior in wide range of speeds.

2) If a fluid is injected with a constant flow rate and pressure loss, the viscosity will be constant and, therefore, flow with the same characteristics will result in parts of identical dimensions and properties.

The temperature causes a considerable decrease in the viscosity of the polymers. An empirical model that fits this idea quite exactly is the Andrade equation [1], which relates the viscosity with the inverse of the temperature in absolute value in an exponential way:

$$\eta = A \cdot e^{b/T} \tag{2.10}$$

Where A and b are empirical values. They are constant values and specific to each polymer or material studied. And T is the temperature.

The value of b can be calculated from obtaining two viscosities at two different temperatures:

$$\eta_1 = A \cdot e^{b/T1} \tag{2.11}$$

$$\eta_2 = A \cdot e^{b/T2} \tag{2.12}$$

$$Ln\left(\frac{\eta_1}{\eta_2}\right) = b \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2.13}$$

The relationship from the formula (2.13) presents a good fit with reality as long as temperatures considered critical are not reached. Critical temperatures are low temperatures close to the glass transition temperature or high temperatures that cause the onset of material degradation.

For polymers which temperature is close to their glass transition temperature and for concentrated solutions, the Williams-Landel-Ferry equation [16] is usually used:

$$\log\left(\frac{\eta}{\eta_s}\right) = \log(\alpha_T) = \frac{-C_1 \cdot (T - T_s)}{C_2 + (T - T_s)} \tag{2.14}$$

Where η_s is the viscosity at a reference temperature, T_s. And α_T is the shift factor. Normally the glass transition temperature is taken as the reference temperature, being then $C_1 = 17.44$ and $C_2 = 51.6K$.

Melt flow index

The fluidity index is a basic rheological test that is performed on a polymer to know its fluidity. It is a simple test because few variables are needed (load and temperature), the equipment is not very complex and in addition, a difficult analysis of the results is not needed and it is a quick test, which can be carried out in about 20 minutes [1].

The measurement method consists of introducing a few polymer pellets and heating them to a normalized temperature depending on the plastic. As is shown in figure 2.16, pressure is applied through weights and the amount of molten material flowing through an output calibrated hole is measured in 10 minutes. This parameter is measured in *g/10min*.
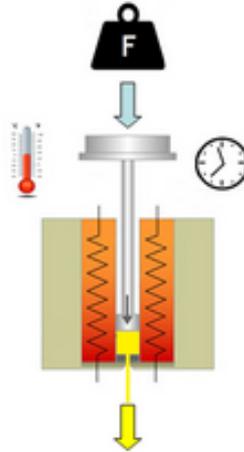
Figure 2.16: Normalized melt flow index test [17]

From this test, the Melt Flow Index (MFI) is obtained, which is the measure of the ability of a material to move in a softened state. Generally, a higher MFI indicates a lower viscosity. In the different classes of thermoplastics you can find a wide variety of viscosities, so when working with high viscosities (low fluidity) it must be used high values of load and temperature, while working with materials with high fluidity it is convenient to use low loads and temperatures.

2.1.5.2   Viscoelasticity

Viscoelasticity is a rheological behavior presented by certain materials that have both viscous and elastic properties. While applying stress on a viscous fluid , it will deform and not recover its initial shape. Fluids with viscoelastic behavior are those that recover part of their applied deformation.

In this case applying a stress even below the elastic limit of the polymeric material (σ_0) results in a time-dependent deformation. This deformation consists of an elastic component and a plastic component that occurs immediately ($\mathcal{E}e + \mathcal{E}p$). Then, the material delivers its viscous-type response through increasing deformation over time ($\mathcal{E}v$). Once the applied tension is eliminated ($t = tx$), an immediate elastic recovery occurs ($\mathcal{E}e$), and then there is a recovery of the viscous component. Finally, the deformation has a nonzero value so that the material is left with a residual permanent plastic deformation [18].

Figure 2.17 describes this process with the representation of two graphs: one of stress-time and another of deformation-time, with which it is possible to see how a viscoelastic polymer is deformed when stress is applied to it and then this stress is eliminated.
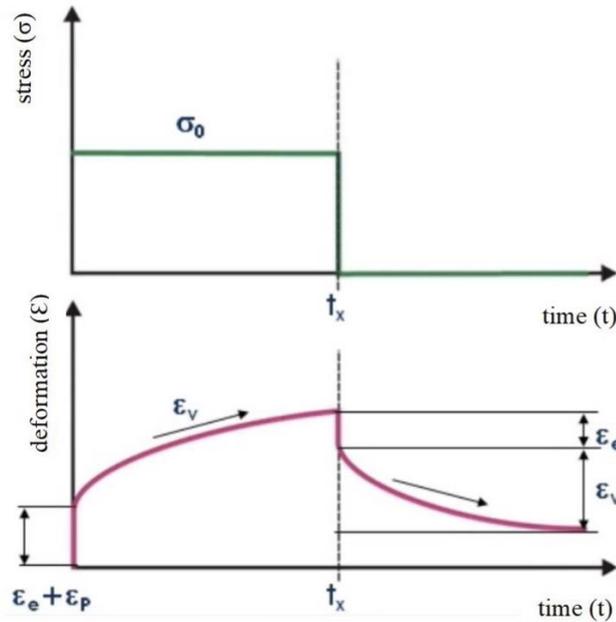
Figure 2.17: Curve of the viscoelastic behavior of polymers [18]

In a viscoelastic solid [18]:

- Deformation is usually time-dependent; even in the absence of forces, the deformation rate may be nonzero.

- The stresses resisted depend on both the deformation and the deformation rate. There are materials that have dependence on the deformation rate, so this characteristic can occur but not be viscoelastic.

- There is relaxation of stresses, that is, if the solid is subjected to a uniform deformation over time the stresses decrease while keeping the deformation constant.

- There is slow creep deformation, that is, subjected to a constant and uniform stress, the deformation increases slightly over time.

Linear or thermoplastic polymeric materials have a very characteristic structure in the form of a ball that conditions the type of behavior. The response of a polymeric material to a constant stress state has several components:

- Elastic component, which is linked to immediate non-permanent deformations
- Viscous component, which is linked to time-delayed deformations
- Plastic component, which is linked to permanent immediate deformations

A parameter used to characterize substances based on their elastic/viscous/viscoelastic behavior is the Deborah number [19], which is defined as:

$$De = \frac{\tau}{t} \tag{2.15}$$

21

Where t is the material time of the deformation process to which a given substance is subjected and τ is the characteristic relaxation time of that substance. Knowing this value, the behavior of all substances depending on its fluidity can be classified as:

- $De < 1$: viscous behavior
- $De > 1$: elastic behavior
- $De \approx 1$: viscoelastic behavior

2.1.5.3   Molar mass

Molar mass is the amount of mass that a substance contains in a mole, and its unit of measurement in the SI is the kilogram per mole (*kg/mol*), and is used to obtain the molecular weight of the polymers, which is the fundamental variable that controls its characteristics and properties.

The molar mass of the HDPE can be determined by measuring its viscosity at zero shear [20]. The zero shear viscosity of the sample is one of the most important properties of molten polymers, as it is proportional to the average molar mass. It is measured at very low shear rates and displays the viscosity of a material at rest. Frequency sweeps are used to obtain it, which are oscillation tests carried out at constant amplitude and variable frequencies. At low angular frequency values, it is possible to determine the value of the zero shear viscosity of the sample.

This test requires the use of a rheometer, which is a laboratory material used to measure the stress and viscosity with which a liquid flows, exposing it to a certain force.

Polymers consist of repetitive units (monomers) chemically bonded into long chains. All polymers contain chains of unequal length, so molecular weight is not a unique value, therefore the molecular weight of a polymer is described as an average molecular weight calculated from the molecular weights of all chains in the sample, and it has a distribution as the one shown in figure 2.18.
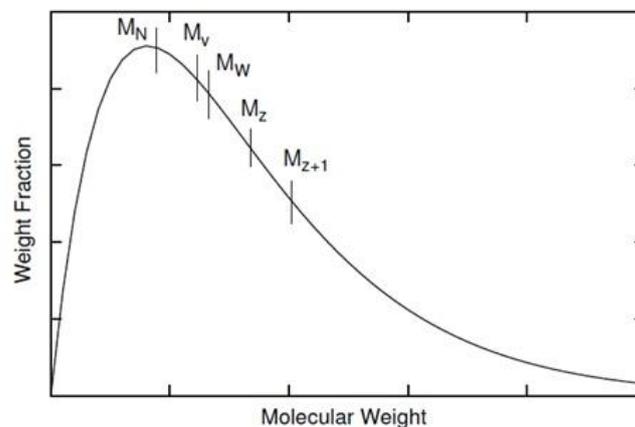
Figure 2.18: A schematic plot of a distribution of molecular weights along with the rankings of the various average molecular weights. [21]

- The average molecular weight in number, *Mn*, is the statistical average molecular weight of all polymer chains in the sample and is defined as:

$$M_n = \frac{\Sigma Ni \cdot Mi}{\Sigma Ni} \tag{2.16}$$

where *Mi* is the molecular weight of a chain and *Ni* is the number of chains of that molecular weight.

- The viscous molecular weight, *Mv*, is calculated from the viscosity of a polymer solution, and can be determined as:

$$M_v = \left(\frac{\Sigma Ni \cdot Mi^{a+1}}{\Sigma Ni \cdot Mi}\right)^{1/a} \tag{2.17}$$

where a is a parameter between 0.5 and 1 that is obtained by measurements of viscosity in the solution.

- The weight average molecular weight, *Mw*, takes into account the molecular weight of a chain to determine contributions to the average molecular weight, and is defined as:

$$M_w = \frac{\Sigma Wi \cdot Mi}{\Sigma Wi} \tag{2.18}$$

where *Mi* is the molecular weight of a chain and *Wi* is the weight of molecular weight species.

- In general, a series of average molecular weights, *Mz*, can be defined by the following equation:

$$M_z = \frac{\Sigma Ni \cdot Mi^{n+1}}{\Sigma Ni \cdot Mi^{n}} \tag{2.19}$$

2.1.6 Material forming processes

During the molding processes, the application of force and heating is combined to shape the material. Pression allows the obtainment of the precision geometry. The most common polymeric material forming processes are extrusion and injection molding, blowing and rotational molding.

2.1.6.1 Extrusion

The extrusion process has high productivity and is one of the most important processes to obtain plastic forms in production volume. Its operation is one of the simplest, because once the operating conditions have been established, production continues without problems as long as there is no major disturbance. Another advantage of this process is that, unlike other processes such as injection or blowing, extruder machines have low cost. However, parts with irregular or non-uniform shapes cannot be extruded, limiting this process to corrugated tubes, sheets, or pipes.

In the extrusion process [22], the preparation of the polymer material is the first step carried out, giving it a composition and suitable conditions to be introduced to the extruder machine through a feed hopper. Then it enters the spindle, which is a screw whose end is fixed to a motor that allows it to rotate at a certain angular speed. On the outer shell of the spindle there are located heaters, which provide heat to melt the material in a staggered way. The molten material before reaching the matrix that will give it the shape, goes through a mesh filter to remove impurities, and through a breaker plate to standardize the fluid.

The matrix is a fundamental part of the process since it generates the preform of the material. The design of this piece is very important since a poor flow output would cause the profile to be generated with defects and therefore, be useless. Its design must also take into account the expansion of the material, since due to the viscoelastic behavior, the extruded section is larger and with different shape than the output hole of the matrix.

The extruded profile comes out of the matrix hot (it can lose its shape), so it goes to a calibration and cooling equipment that ensures that said profile acquires the desired shape and lowers its temperature so that it can gain rigidity. Finally, it is removed in a solid state to the collection equipment that is the one that allows the material that is being processed to be extracted.

The figure 2.19 shows a drawing of an extruder machine pointing to the parts mentioned above.
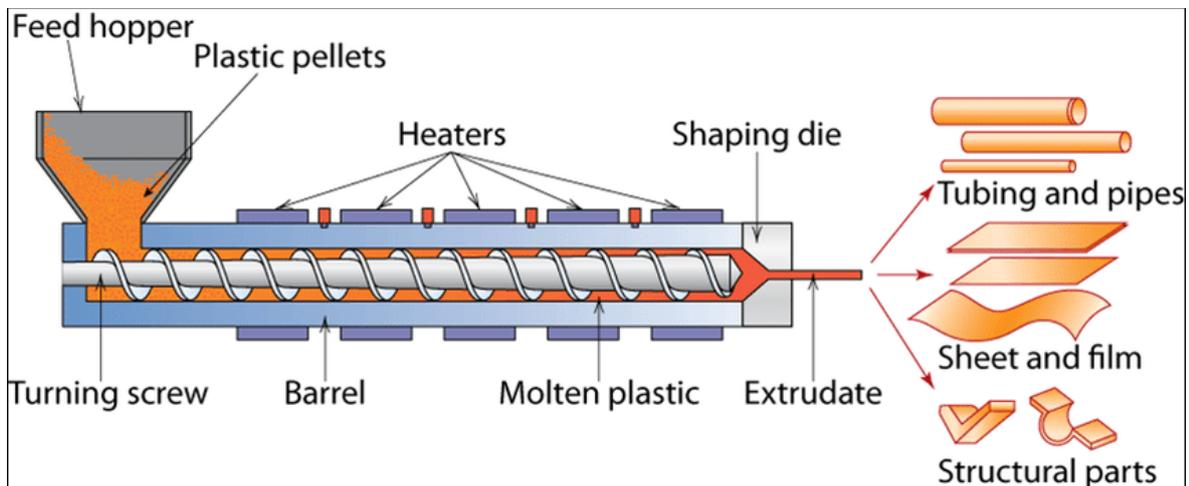
Figure 2.19: Extruder machine [23]

24

2.1.6.2   Injection

Injection is the most important thermoplastic transformation process. Its operation is very similar to that of the extrusion process: the basic difference is that when the material reaches the end of the shaft in the molten state, it is pushed forward to introduce it into a mold and make it take the desired shape.

Injection molding consists of heating the thermoplastic until it melts and injecting it under pressure into a metal mold where it cools and solidifies. The mold is cooled with water so that solidification occurs faster. Finally, when the piece has completely cooled down, ejectors are used to extract it from the mold. This process is for high production volumes [4] (10.000 – 1.000.000 pieces) due to the expensive cost of the machinery. The steps to follow during the injection process are [24]:

- Plasticization of material to inject
- Mold closure
- Injection of the material into the mold. Final overpressure.
- The screw begins to plasticize the material of the next injection.
- When the piece cools and solidifies, the mold opens and the piece is ejected.

The most important variable to take into account during this process is the working temperature. In the feeding zone, the temperature must not be very high, and the mold must be previously heated to avoid sudden changes in temperature and to be able to control the cooling speed of the pieces.

Both this process and the extrusion process are exclusive for thermoplastic materials, since the material needs to be melted and later solidified, in order to give it the desired geometric shape.

2.1.6.3   Blowing process

The blowing process is used to obtain seamless hollow parts in thermoplastic materials. This process consists on the blowing of air inside a material tube cast, placed in a mould, until it conforms to the cold mold walls [1]. Obtaining the molten thermoplastic tube can be by extrusion or by injection. Plastic bottles are obtained with this method.

2.1.6.4   Rotational molding method

During the rotational molding method, the polymer pellets are introduced into the cold mold, then heated in an oven while they are forced to rotate on 2 axes simultaneously. The pellets melt, covering the walls of the mold inside, with a thickness determined by the initial amount of pellets. This process is suitable for large, hollow and closed parts, but also for small pieces of thin walls. The thickness of the usual pieces is from 2,5 to 6*mm*, and the lot size is from 50 to 5 000 pieces [4].

2.1.7 Degradation

Polymer degradation is important in the production of materials, because the use of non-biodegradable polymers (they are traditional plastics derived from petroleum) generates serious environmental problems, since they take a long time to degrade. For example, HDPE can take more than 150 years to degrade [25].

However, biodegradable polymers are those that, at the end of their useful life, are transformed into simple substances or minor components such as water, carbon dioxide or biomass. The main disadvantages of this type of polymers is that the cost of their production is significantly higher and they have worse mechanical properties compared to traditional plastics.
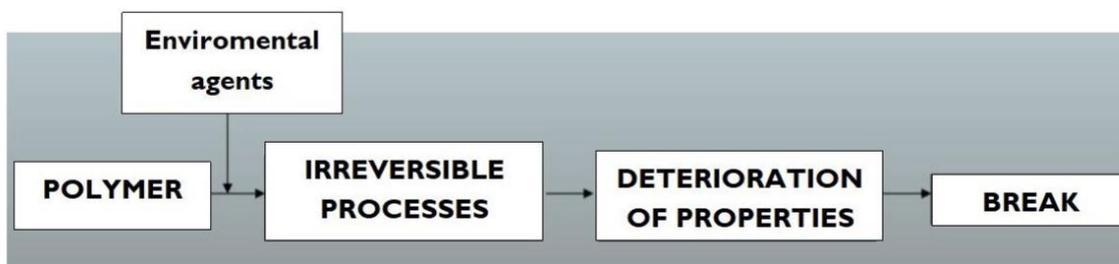
Figure 2.20: Explanatory scheme of polymer's life cycle [26]

Figure 2.20 shows schematically the life of biodegradable polymers: they are exposed to environmental agents, such as rain, sunlight or chemicals (acids, alkalines and some salts). This fact gives rise to a series of irreversible processes, such as oxidation, galvanic action or cracking, which leads to the deterioration of the properties of the polymer, leading to its breakage, and therefore the end of its useful life.

Four types of degradation can be distinguished [1]: thermal degradation, hydrolytic degradation, photodegradation and biodegradation.

- Thermal degradation is defined as the process by which the action of temperature causes a loss of material properties, both physical and chemical. With the increase in temperature, the polymers suffer the rupture of the covalent bonds of the chain or the lateral groups. In the processing and reprocessing of polymers, heat is directly involved, which is why it is important to study and understand this type of degradation. Normally this degradation occurs in conjunction with oxidative degradation if the material is in the presence of oxygen.

- Hydrolytic degradation occurs as a result of the contact of the material with an aqueous medium. The penetration of water into the matrix causes inflation, the breaking of intermolecular hydrogen bonds, the hydration of molecules, and finally the hydrolysis of unstable bonds, causing the decrease in molecular weight of the material that suffers this type od degradation.

- Photodegradation is the degradation of polymers due to solar radiation. Photodegradation begins with the production of the macro-radical (P') in the amorphous regions of the polymeric substrate. This radical reacts rapidly with

oxygen to give the peroxide radical (POO'), which extracts a hydrogen atom from the main polymer chain to produce a hydroperoxide group (POOH). This group is strongly bonded so that the highly reactive radicals are produced that allow the cycle of degradation of the chain in the polymer to continue, and the cycle ends when two radicals are combined.

Plastics contain imperfections that allow them to react with the energy delivered by ultraviolet rays, which can carry out degradation.

- Biodegradation refers to the transformation and deterioration that occurs in the polymer due to the action of enzymes and/or microorganisms such as bacteria, and this can be partial or total.

Partial degradation consists of the alteration in the chemical structure of the material accompanied by the loss of specific properties, while the total degradation of the material is completely degraded by the action of microorganisms with the production of CO_2 (under aerobic conditions) and methane (under anaerobic conditions), water, mineral salts and biomass.

2.1.8 Types of plastics

The main types of polymers are polyethylene terephthalate (PET), high-density polyethylene(HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS) [27].

The polyethylene terephthalate (PET) is the most commonly plastic used in our planet. It has the property of preventing oxygen from getting in and also helps to keep the carbon dioxide in carbonated drinks from getting out, which means that it is a good option for the packing of food and drinks. A disadvantage of this type of plastic is that it contains antimony trioxide, which is a difficulty in the recycling process of this plastic. It is used to produce soda and water bottles, medicine jars, food jars, comb, bean bags, rope, tote bags, carpet or fiberfill material in winter clothing.

The study of this thesis will be focused on the polyethylene, specifically on the high-density polyethylene (HDPE). It is the most commonly recycled plastic because its long virtually unbranched polymer chains make it denser, stronger and more stable compared to the polyethylene terephthalate. It was first used for pipes in storm sewers, drains and culverts, although nowadays the use of this plastic is very extended for products like milk jugs, juice containers, grocery or trash bags, motor oil containers, shampoo and soap bottles, detergent and bleach containers or toys.

Polyvinyl chloride (PVC) is one of the oldest synthetic materials in the industrial production. It was discovered by accident inside vinyl chloride flaks left exposed to sunlight. It is one of the least recycled plastic (only 1% of PVC plastic is recycled each year). PVC should be avoided at all costs because it is harmful to our health and to the environment as the use of it may leach a variety of toxic chemicals such as bisphenol A (BPA), phthalates, lead, dioxins, mercury and cadmium. It is used to produce some tote bags, plumbing pipes, grocery bags, tile, cling films, shoes, cutters, window frames, ducts or sewage pipes.

The low-density polyethylene (LDPE) is the type of plastic that has the simplest plastic polymer chemical structure, that is why it is very easy and cheap to process. It is considerate a separate material during the recycling process because it has less mass than the HDPE. Like other thermoplastics, LDPE can be easily recycled using the forming methods for thermoplastics, such as the extrusion and injection methods. It is used to produce cling wrap, grocery and frozen food bags or flexible container lids.

Polypropylene (PP) is considered a safer option for food and drink use and its strength quality is between LDPE and HDPE. It is used to produce tupperwares, yogurt containers, prescription bottles, take-out containers or disposable cups and plates. It has many utilities, but a small fraction of the products made out of this material are actually recycled.
Polystyrene (PS) was discovered accidentally while preparing medication. It is one of the most widely used plastics (several million tones of this plastic are used every year), because it is an inexpensive resin per unit weight. This material is nowadays very harmful to the environment, putting at risk marine animals. It is used in disposable coffee cups or plastic food boxes.

In order to make more effective the recycling of the plastic, a classification of them was created by The Society of the Plastics Industry in 1988 based on their properties and on how they are recycled. Each plastic mentioned above is assigned a number that is surrounded by the Möbius triangle (universal symbol of recycling), as shown in Figure 2.21. Number 7 refers to the remaining plastics, like polycarbonate, polylactide, acrylic, acrylonitrile butadiene, styrene, fiberglass or nylon.

Figure 2.21: Plastic recycling chart [28]

2.1.9 Additives

An easy way to modify polymers is the use of additives. Plastic additives are usually organic molecules that are added to polymers in small quantities during manufacturing, altering the physical or mechanical properties of plastic in order to improve them.

Additives can constitute around 50% of the total weight of the product in its final state of production. They have multiple uses, and depending on what their targets are they can be classified as shown below.

2.1.9.1   Processing

This type of additives facilitates the processing of the plastic material. Among the different additives that help in the processing of plastics we find stabilizers, that exert a retarding action on the degradation process of plastic, and lubricants, which serve to reduce the wear and tear of two bodies that rub against each other during the manufacturing process.

Table 2.1 shows the subdivision of the main stabilizing and lubricants additives [1].

Table 2.1: Types of additives that helps in the processing of plastics

STABILIZERS	Antioxidants: interrupt degradation reactions that occur in the material as a result of sudden and continuous temperature changes. This type of catalyst is important for certain polymers that tend to oxidize when exposed to the weather, causing the chain to break.
	Ultraviolet stabilizers: they are used to improve the durability of products exposed to ultraviolet radiation
	Thermal stabilizers: they are used for polymers that have a decomposition temperature lower than their processing temperature.
LUBRICANTS	External lubricants: their objective is to reduce and control the adhesion between the polymer and the metal parts of the transformation equipment. The use of this additive is essential for forming processes that take place at high temperatures.
	Internal lubricants: their function is to reduce friction between the polymer molecules themselves so that they improve the flow of the material. For their use it is only necessary that they are compatible with the polymer at high temperatures.

2.1.9.2   Flame retardant

Flame retardant additives are used to reduce the flammability of a material or to delay the spread of flames through or along its surface. This type of additive can act thanks to a physical effect or a chemical one.

By physical effect, the additives form a protective layer on the surface of the plastic not yet degraded by the heat of the flame, which decreases the thermal conductivity of the system

at the flame-plastic interface. This reduces the rate of degradation of the plastic mass and the formation of volatiles that feed the flame.

By chemical effect we find the flame retardants that, by the heat of the combustion, react chemically, decomposing thermally, and produce beneficial effect for the suppression of the flame.

2.1.9.3   Foamed structure

Foaming additives are organic or inorganic additives that produce a foamed structure. It is used in many types of polymers, such as polyvinyl chloride (PVC), polyethylene (PE) or polypropylene (PP) to improve its properties, such as its heat and noise insulating properties, its rigidity or its electrical properties. In addition, they improve their appearance, by eliminating plugs in injection molded parts.

2.1.9.4   Mechanical properties

Additives that improve the mechanical properties of plastics are known as impact modifiers. These work by absorbing the impact energy and dissipating it in a non-destructive way. They are typically elastomers and are added to many thermoplastic materials, such as polyvinyl chloride (PVC), polypropylene (PP) or polyethylene (PE), at levels of up to 20%.

2.1.9.5   Optical properties

Pigments and dyes are used to improve the optical properties of plastics. These are used with a very fine and small size to achieve the best dispersion in the polymer. Pigment mixtures are usually used to achieve different shades.

2.2   Polyethylene

Polyethylene (PE) is a light, versatile synthetic resin made from the polymerization of ethylene. It is one of the most used plastic in the world, being made for a large number of different products. It has the simplest structure of all commercial polymers.

Polyethylene (PE) is a thermoplastic polymer, which implies that it is possible to heat it until their melting point, cooled and reheated again without significant degradation. Another excellent property is that thermoplastics do not burn, which allows them to be used in common polymeric material forming processes, like injection or extrusion.

A molecule of polyethylene is a long chain of carbon atoms, with two hydrogen atoms attached to each carbon atoms. Ethylene molecules are composed by two methylene units (CH_2) that are linked together by a double bond between the carbon atoms. After polymerization, the double bond can be broken, and the resultant extra bond is used to link the carbon atom to another ethylene molecule, as shown in figure 2.22.
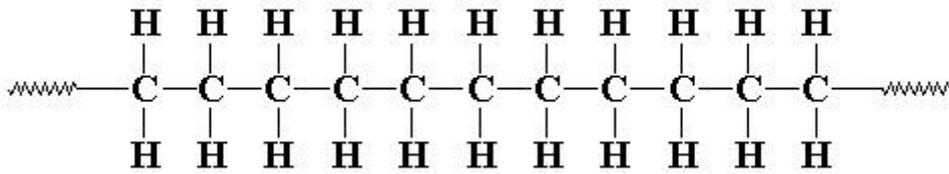
Figure 2.22: Chain of carbon atoms [29]

Depending on its density, polyethylene can be classified into high-density or low-density polyethylene. Low-density polyethylene (LDPE) has some carbons that instead of having hydrogens attached to them, have branches of polyethylene attached to them and the high-density polyethylene (HDPE) has no branching.

2.2.1 High-density polyethylene

High-density polyethylene (HDPE) is a thermoplastic polymer with different properties that made it ideal for a huge number of applications. HDPE materials are produced by either slurry polymerisation or gas phase polymerisation. Its formula is (-CH2-CH2-)n. What makes the difference in this type of polymer is the lack of branches, which gives it important properties, such as lightness, high tensile strength and high density. The lack of branching makes HDPE a linear polymer. The branching can be controlled and reduced by using specific catalysts during production.

The structure of the HDPE is essentially semi-crystalline, that is, given the size of the molecules it is common to find ordered areas scattered in amorphous zones. The relationship between amorphous and crystalline zones is known as the degree of crystallinity. The degree of crystallinity plays a fundamental role in the mechanical and thermal properties of HDPE, since these are favored the more crystalline the polymer is.

2.2.1.1   Properties

In the table 2.2 the main properties of the HDPE are presented [30]

Table 2.2: Properties of HDPE

PROPERTY	
Chemical structure	Low number of ramifications
Density	0,95 – 0,97 g/cm³
Flexibility	High crystallinity, which makes it though and rigid
Heat resistance	Able to withstand heat with temperatures more than 100 ˚C
Melting point	120 – 140 ˚C

Chemical resistance	Good resistance to solvents, alcohols, acids and alkalis; low resistance to most hydrocarbons
Strength	High tensile and specific strength
Transparency	Low, due to its high level of crystallinity (it is solid and colourless; almost opaque)
Maximum allowable stress at 20 ˚C	14 – 32 MPa
Tensile strenght	0.20– 0,40 N/mm²

2.2.1.2   Uses

Due to its molecular structure and properties this polymer is mostly use in applications where moisture resistance and cost-effectiveness are needed. When HDPE was created in the 1930s it was firstly used in high-frequency radar cables during World War II. Afterwards, when industrial revolution spread, HDPE was introduced to the market commercially.

Nowadays, this polymer is used in many different applications, that are exposed in the table 2.3 [31].

Table 2.3: Different uses of HDPE

Food industry	Plastic bottles, cups, milk jugs and other type of food containers	It is the optimal material for the production of food packaging for two main reasons: 1) it will not leach into the packaging 2) it is recyclable, which is crucial for these type of disposable products.
Domestic objects	Toys, protective devices, such as helmets or knee pads and for waterproofing in pools or pond	This polymer is UV resistant, which gives it fortress against ray's damaging and discoloring effects.
Chemical industry	Shampoo and soap containers, household cleaning products, motor oil, antifreeze and recycling bins.	Perfect for these applications due to its chemical resistant properties. The strength of these bottles can be increased by the processes of coloration and pigmentation.
Manufacturing industry	Prototypes and models of equipment and tools	Ideal because it can be cut, welded, bent, screwed and machined better than wood and other materials.
Pipe systems		HDPE has high level of impermeability and strong molecular bond, which make it suitable for high pressure pipelines.

2.2.1.3   Avantages and disadvantages

The main advantages and disadvantages of the HDPE matreial [31] are:

ADVANTAGES
1. Wide variety of uses
2. Affordable
3. High quality
4. High tensile strength
5. Able to resist low temperatures
6. Relatively strong and stiff
7. Waterproof property
8. Resistant to most chemicals
9. Good electrical insulation
10. Non-leaching
11. UV resistant
12. High durability

DISADVANTAGES
1. May crack under stress
2. Risk of mould shrinking
3. Not biodegradable
4. Not resistant to oxidizing acids and chlorinated hydrocarbons
5. High flammable

2.3   Recycling

Recycling is the basic process that consists of collecting and processing materials that would otherwise be thrown away as trash and turning them into new products. In this concept, can also be included the recovery of energy from waste materials. Recycling involves replacing raw materials, obtained from natural sources such as petroleum, natural gas or trees, with reused materials.

To better understand the importance of recycling, it is important to know what are the main polluting factors that we have to be aware of in order to preserve the environment and end global pollution. These polluting factors are mainly discharged in three areas:

- Air: the air pollution is caused by the incineration. The air is where all the odors and pollutants from factories accumulate.
- Water: this is where society pollutes most often, as this is where many of the industrial waste and polluting products are dumped.
- Ground: a lot of solid waste is deposited in large landfills, which means the pollution of the land and therefore endangers the natural environment and is a great economic expense to maintain.

The typical materials that are recycled include iron and steel scrap, aluminium cans, glass bottles, paper, wood, and plastics. The recyclability of these materials depends on their abilities to reacquire the properties they had on their original state.

Recycled materials are delivered to a household recycling center or picked up from different curbside bins depending on what type they are. Today we can find six different containers: gray is for waste in general, brown for organic, green for glass containers, yellow for plastics and metal containers, blue for paper and cardboard and red for hospital and infectious waste.

2.3.1 Types of recycling processes

There are four types of recycling processes [1]: mechanical, chemical, energetic and by residue.

The mechanical recycling process refers to all the recycling processes that are performed by handwork or by the action of machines. It is a process from which the plastic from consumption is recovered, subsequently allowing its use. During this process there is a change of shape of the plastics, but the macromolecules are not broken

The chemical recycling process is performed using techniques and procedures that involve the change of the chemical structure of the material, applying heat or catalysts. Its purpose is the decomposition of the polymer to obtain monomers. Its objective is to process the monomers obtained to obtain new plastics. This technique can be used as a complement to mechanical recycling

The energetic recycling process is used with material whose waste cannot be classified and recovered. Therefore, the purpose of this procedure is to obtain energy and some examples are waste incineration, pyrolysis and gasification.

The last type of recycling process is by residue. In this type what is sought is the degradation of all organic matter in the presence or absence of oxygen. If the organic matter is not separate, complementary mechanical processes must be used.

2.3.2 Recycling of HDPE materials

Nowadays, the high-density polyethylene material has a lot of different uses (30 tons/year of HDPE materials are used [32]), that is why the use of this material has a huge environmental impact. On the other hand, there are things to ensure the correct form to recycle this material, and therefore, protect our planet. That is also because these are one of the easiest polymers to be recycled and is processed in almost all recycling companies.

The benefits of recycling these materials are numerous. HDPE is non-biodegradable, and it takes long periods of time to decompose, so the first benefit would be to allow to reuse this material in order to protect the environment. Then, it is cheaper to produce a product from HDPE recycled material than to produce it from 'virgin' plastic. It is also a way to save energy, as the processing of post-consumer plastic is much more sustainable. It saves 100% crude oil and approximately 65% CO_2 equivalent therefore requiring approximately 88% less energy [33].

Steps of the recycling process of HDPE

1. The plastic items that arrive to the recycling company must be separated based on their thickness.
2. The plastic is sorted and cleaned to remove any unwanted debris.
3. Then, we have to ensure that only the HDPE is processed (by the homogenization of the plastics. To carry out this process the sink-float separation is usually used: due to the low density of the HDPE (0,955-0,961 g/cm^3) compared to the density of PET (1,370-1,455 g/cm^3) both materials float in different levels when they are submerged in a liquid. Then, to separate HPDE from other plastics near-infrared radiation (NIR) techniques can be used.
4. During this step, the HDPE is shredded and melted down in order to refine the polymer.
5. Finally, the plastic is cooled into pellets, as shown in figure 2.23. Some recycling companies use a baler in order to make easier the transport process.

Figure 2.23: Pellets of recycled HDPE [34]

3. Experiments from various literature studies

Although HDPE is one of the most consumed polymers worldwide due to its good properties, there are few studies on the variation of its chemical structure after being reprocessed in several cycles. To study these cases, it is necessary to know the degree of polymeric degradation suffered in HDPE after a certain number of reprocessing cycles, or how their properties change when using recycled HDPE in different proportions.

Polymer degradation is a change in the properties of a polymer, such as stress force, color or shape. It is due to the influence of one or more environmental factors such as heat, light or chemicals such as acids, alkaline and some salts. These property changes are usually undesirable, although they can be sought for the biodegradation process or for the reduction of the molecular weight of the polymer in order to be recycled.

3.1 Thermal properties

3.1.1 Determination of the thermal degradation of HDPE by color change analysis.

The objective of the study [35] was to determine the degree of thermal degradation of thermoplastic polymers based on their color change after being reprocessed by extrusion, injection or extrusion/injection.

For the extrusion process, a single-spindle extruder brand EXTRUDEX ED-N 45-30D was used, with a spindle diameter of 45mm and a length/diameter ratio of *L/D* of 30. The injection process was carried out with a Boy XS single-spindle injector, with a spindle diameter of 12mm, an L/D ratio of 19.6, a maximum injection speed of 24cm^3/s and a pressure of 3130bar. Finally, the extrusion/injection process was carried out: the polymer passed through the extruder and then through the injector, and the sample was taken at the end of the injection process.

The spindle rotation speed and temperature profile in the eight extruder heating zones varies as shown in Table 3.1.

Table 3.1: Operating conditions in the extrusion process

Cylinder temperature 1, ˚C	180
Cylinder temperature 2, ˚C	190
Cylinder temperature 3, ˚C	200
Cylinder temperature 4, ˚C	210
Flange temperature, ˚C	220
Homogenization temperature 1, ˚C	220
Homogenization temperature 2, ˚C	220
Homogenization temperature 3, ˚C	220
Feed temperature, ˚C	28
Screw speed, rpm	20 and 80

Each of the five polymer samples that underwent each of the three processes described above were subjected to drying, cooling with a reduction in size and a second drying.

To perform the color analysis after each reprocessing, the following three color stimuli were evaluated using a three-stimulus colorimeter, X-Rite Color Master 8200:
- Luminance factor (L): measures the brightness and darkness of the color.
- Red saturation index (a): measures the red-green character.
- Yellow saturation index (b): quantifies the yellow-blue character of the color.

From these parameters the colour change was determined by means of the following equation, named Hunter-Scotfield empirical equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \tag{3.1}$$

Where ΔL, Δa and Δb is the change in luminance factor, in saturation index to red and in saturation index to yellow, respectively, with respect to the color measured in the reference HDPE sample (virgin or raw polymer).

Analyzing the results of this experiment it was obtained that the luminance factor was progressively reduced as the number of processing cycles increased, which means that the sample when reprocessed reduces its luminosity and increases its opacity. While the saturation index Δb increased, meaning that the HDPE tends to take on a yellow hue. The variation of the saturation index to red is minimal, so there is no change towards shades of red.

Spindle rotational speed

As mentioned above, the extrusion process was carried out at two spindle rotation speeds. As shown in Figure 3.1, the polymer sample showed a greater color variation (and therefore greater degradation) when the spindle rotational speed was 20*rpm*, this is because the polymer spends more time inside the extruder machine than when the rotational speed is 80*rpm*.
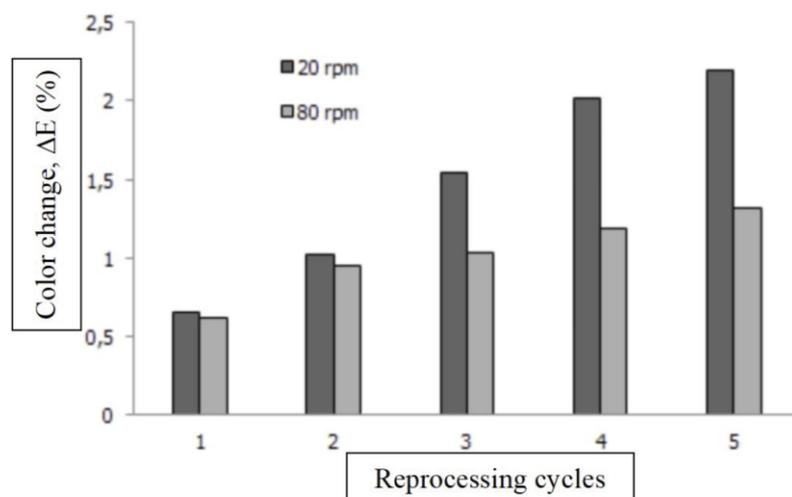

Figure 3.1: Comparison of the color change when subjecting the polymer sample to an extrusion process at two different spindle rotational speeds [35]

Effect of the type of processing

Analyzing the graph in Figure 3.2, it is observed that the color change of the polymer samples subjected only to the injection process is significantly greater (therefore, their thermal degradation is greater) than that suffered in the extrusion and extrusion/injection processes. This indicates that, if the HDPE undergoes an extrusion process and then an injection process, the degradation caused in the first process can reduce the degradation caused by the second process.
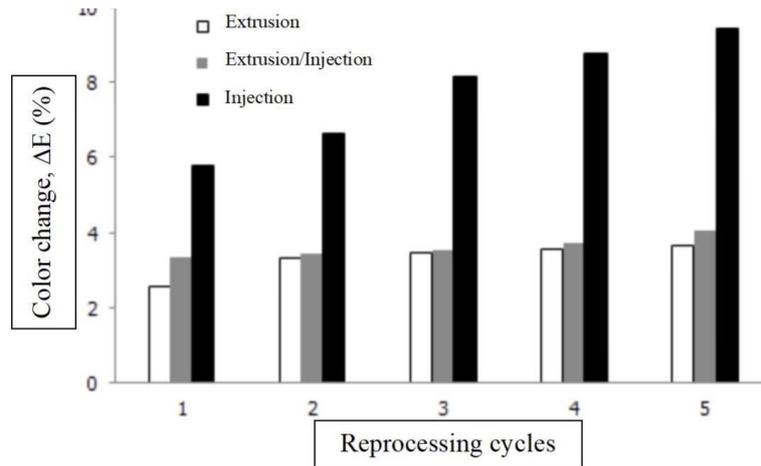
Figure 3.2: Comparison of color change when processing HDPE in three different ways [35]

3.1.2 Study of the melting point of HDPE samples with different amount of recycled material

In the following experiment, which was performed in the Laboratory for experimental mechanics, University of Ljubljana, three types of recycled HDPE were taken: one recycled 10 times, one 50 times and one 100 times. For each of these three cases, six different samples were taken: one with 10% recycled HDPE and the remaining 90% virgin, another with 30% recycled and 70% virgin, another with 50% recycled and the remaining 50% virgin, another with 70% recycled and the remaining 30% virgin, another with 90% recycled and the remaining 10% virgin and finally, a sample with 100% recycled HDPE.

It can be observed from the graph of the figure 3.3, that in samples containing recycled HDPE 10 times the melting temperature decreases slightly from the point of 10% of recycled material, to the point of 70%, where it reaches its minimum, which is approximately 135.5 °C. The melting temperature from this point to reach 100% recycled HDPE rises to a value of approximately 137.2 °C.
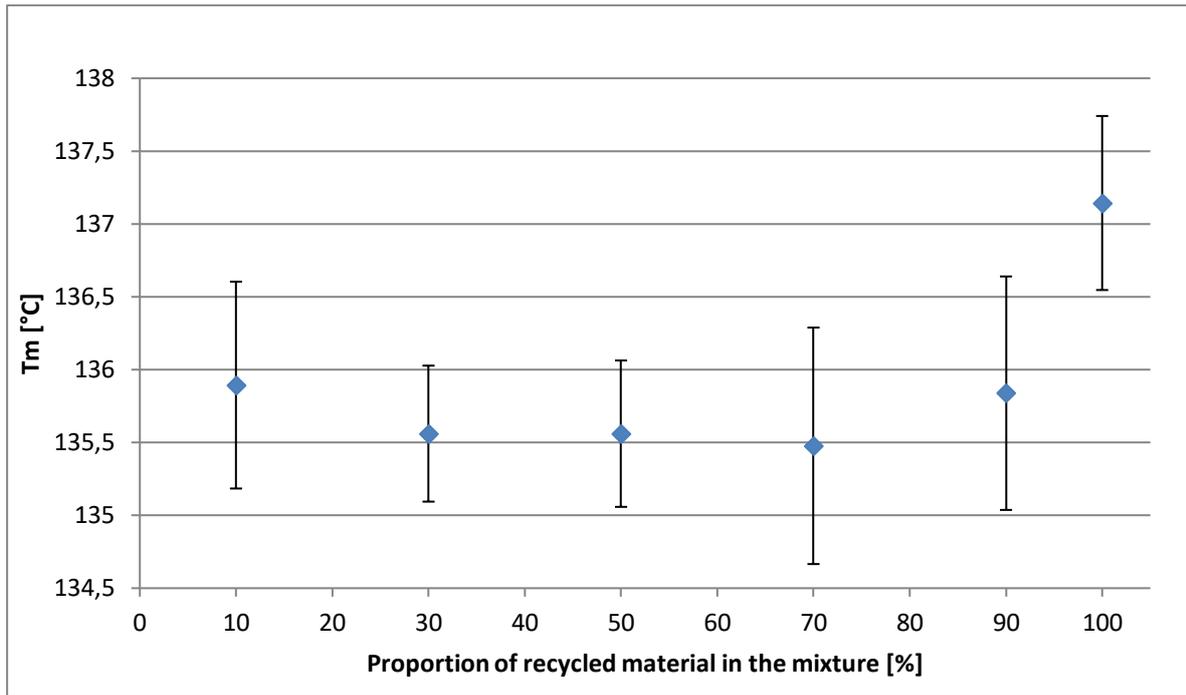
Figure 3.3: Melting temperature of samples with HDPE recycled 10 times

We see that the curves of materials that use HDPE recycled 50 and 100 times from the graphs of the figures 3.4 and 3.5, are much more similar: the melting temperature decreases more or less linearly as the percentage of recycled material in the mixture increases, reaching for the sample with HDPE 100% recycled a melting temperature of approximately 133 ˚C for the HDPE recycled 50 times and 131 ˚C for the one recycled 100 times.
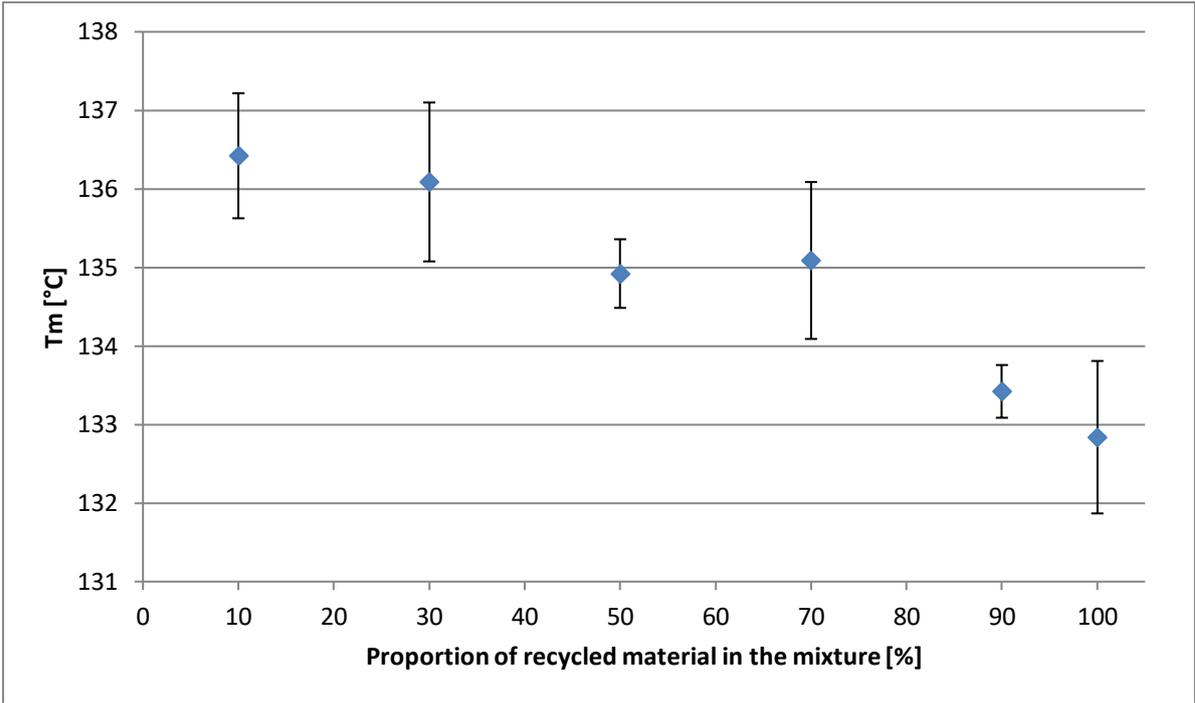
Figure 3.4: Melting temperature of samples with HDPE recycled 50 times
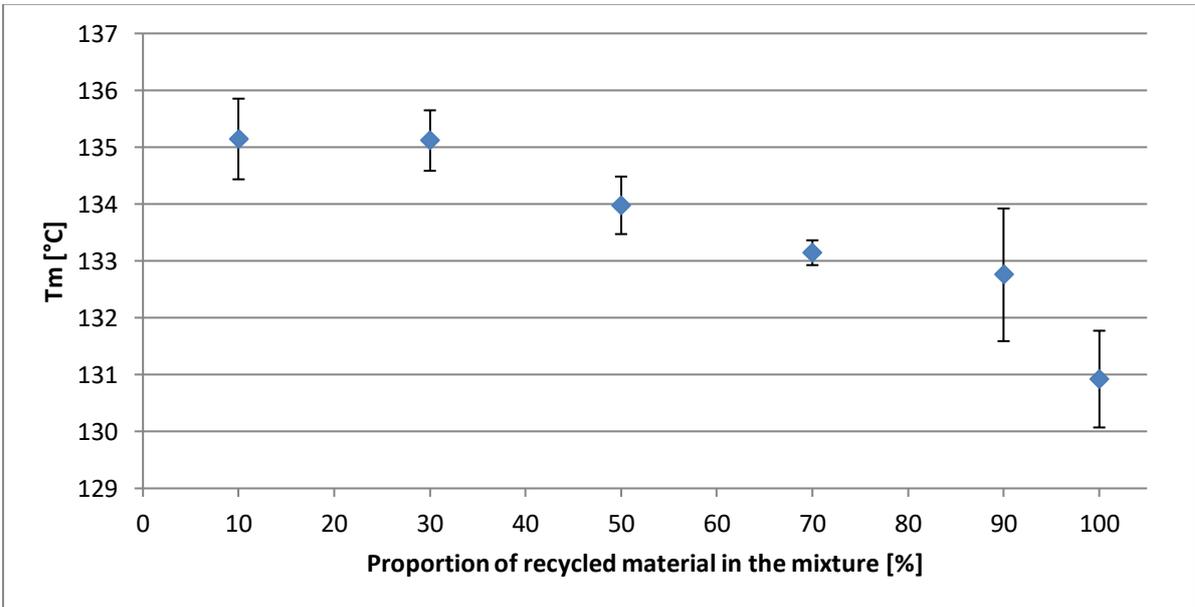
Figure 3.5: Melting temperature of samples with HDPE recycled 100 times

3.2 Mechanical and rheological properties

3.2.1 Study of the mechanical and rheological properties of HDPE with and without additives during five injection cycles

In the experiment, reported in [36], there were two bags of 10 kg each, one without additive (10kg of HDPE) and another with AOX additive (9,85kg of HDPE and 0,15kg of AOX). These were treated by the injection process. Since the HDPE has a melting point between 128 and 158 °C, it was injected at 190 °C. The process consisted of injecting these two types of materials five times, and for each time a quantity of material was taken out to perform the respective tests.

The additive used in this experiment was the antioxidant AOX. The function of this additive is to interrupt degradation reactions. This type of catalyst is important for certain polymers that tend to oxidize when exposed to the weather, causing the chain to break.

The number of specimens obtained from HDPE with and without additive is shown in the graph of the figure 3.6.
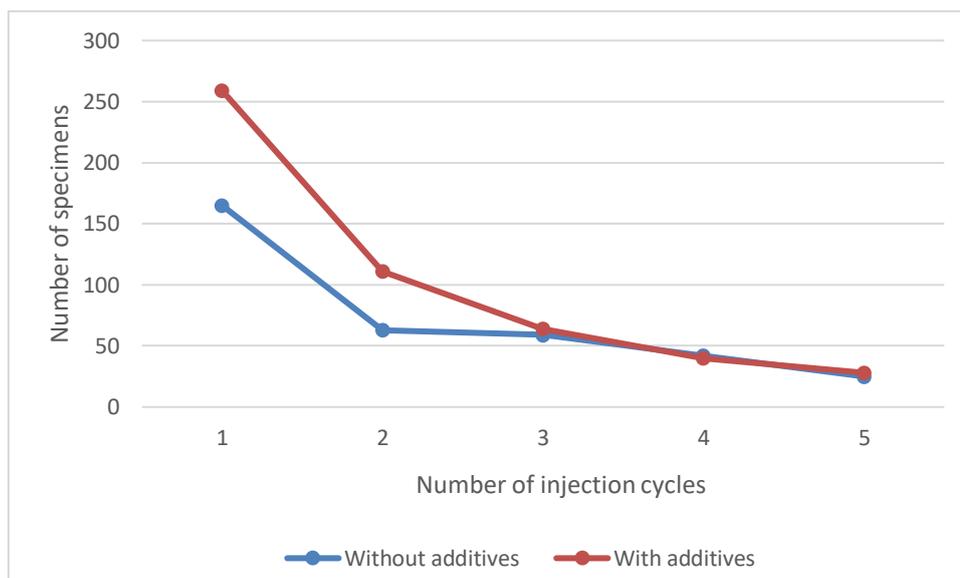

Figure 3.6: Number of specimens obtained in each injection cycle [36]

3.2.1.1 Melt flow index test

The fluidity index is closely related to molecular weight, and as this decreases the molecular weight increases, resulting in the following characteristics for HDPE:

- Lower permeability and solubility
- Better impact resistance

- Increased elastic tension stress
- Danger of rupture during extrusion
- Higher viscosity

The material fluidity index test was carried out using a Melt flow Tinius Olsen machine, and the MFI, density and viscosity of the samples were measured.

Melt Flow Index (MFI)

From the graph of the figure 3.7, it can be observed that the MFI increases with the number of injections, that is because like the entanglementsof the HDPE samples are lower, the resistance of the melt is also lower, and therefore, the melt flow index increases. It can be observed that in both cases the melt flow index increases significantly after the first injection cycle, but in the case of the HDPE sample with additve, it stabilizes after the second cycle.
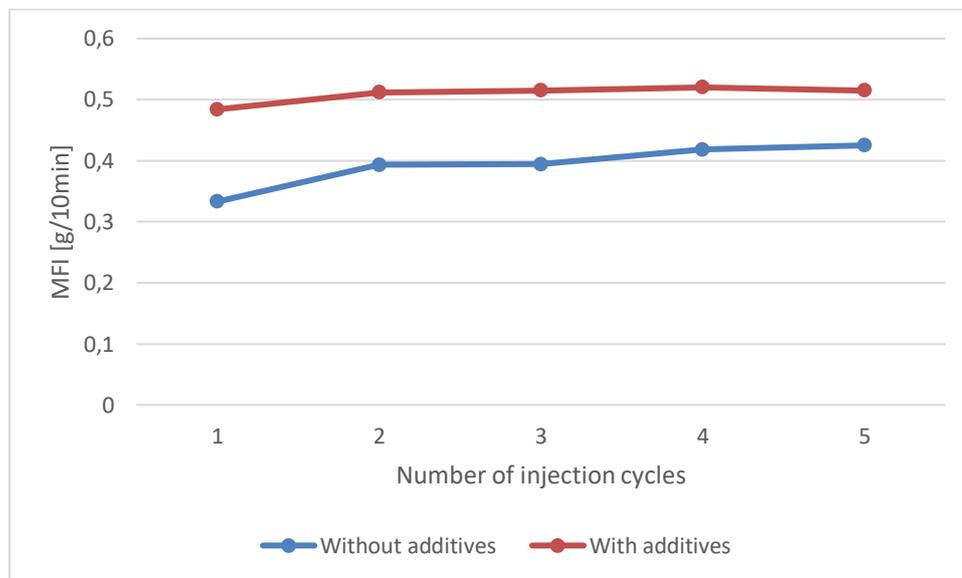

Figure 3.7: MFI of HDPE during five injection cycles with and without additives [36]

Viscosity

From the graph of the figure 3.8, it can be observed that viscosity is the opposite of the fluidity index; that is, when it increases, the viscosity decreases. For HDPE without additive, viscosity goes from approximately $25.000 Pa \cdot s$ to $19.000 Pa \cdot s$ as the number of injections increases. On the other hand, for HDPE with additive, after the second cycle, the viscosity value stabilizes at approximately $16.000 Pa \cdot s$.
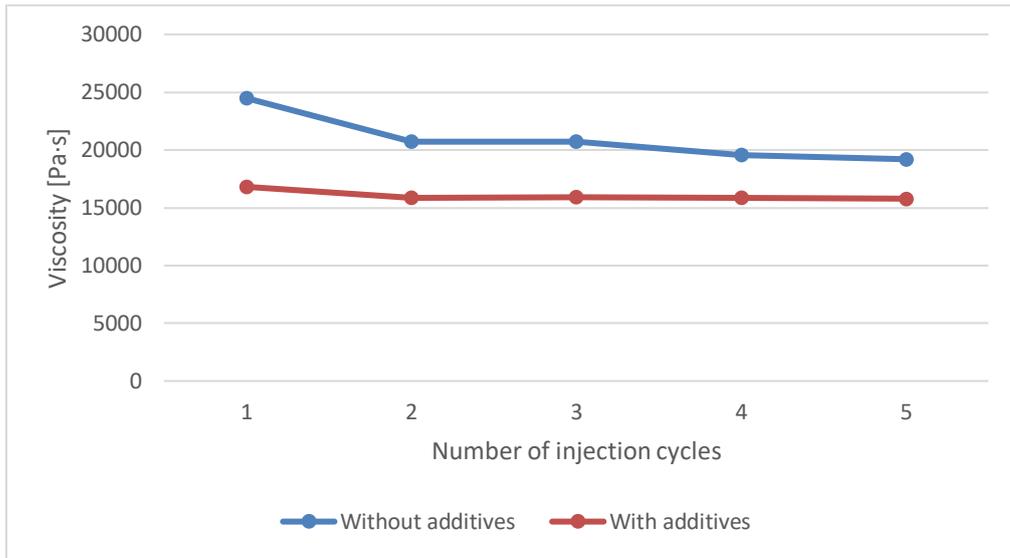
Figure 3.8: Viscosity of HDPE during five injection cycles with and without additives [36]

Density

As for the density it can be observed from the graph of the figure 3.9, that it varies discontinuously in both cases, since the used material is recycled HDPE, so that residues of other materials may also be present. However, this could have been avoided by using a mesh filter to avoid impurities.
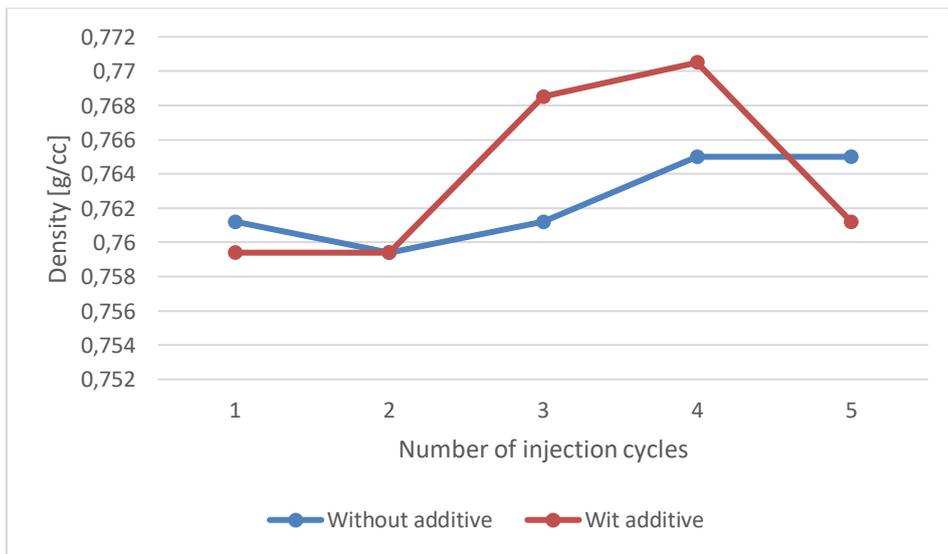

Figure 3.9: Density of HDPE during five injection cycles with and without additives [36]

3.2.1.2 Impact resistance test

Studying the impact of polymers is of crucial importance, as it is the most critical environment in which their toughness can be determined, and in addition, many polymers in service suffer impact situations such as falls or accidental blows. It is also a good test as a quality control of the polymer.

The impact test measures the ability of a sample or final part to withstand sudden loads. From an operational point of view, this type of test has the advantage of being fast, however, the impact resistance depends on the method used, then it is important to choose the correct method according to the use that the polymer will have.

In this experiment [36] the impact resistance of the HDPE samples was determined using a Tinius Olsen impact resistance equipment, which is the leading manufacturer and specialized supplier of equipment and software for material testing.

Specimens sized according to ASTM D256, such as the one shown in figure 3.10, were used as samples for this test.
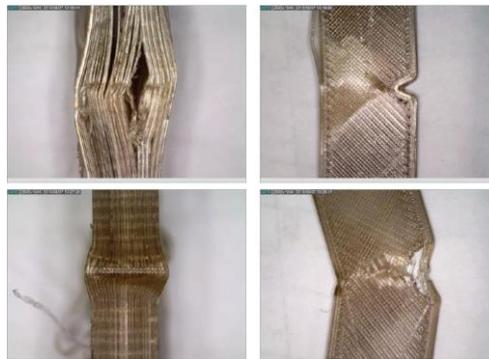

Figure 3.10: Specimen according to ASTM D256 [37]

Analyzing the graph shown in the figure 3.11, it can be seen that the HDPE without additives has greater resistance to impact than the HDPE with additives. On the other hand, HDPE without additives has an increasing impact resistance as the number of injection cycles increases, while HDPE with additives has almost constant impact resistance during the five injection cycles, which indicates that it can continue to be processed without having notorious variations in its mechanical properties.
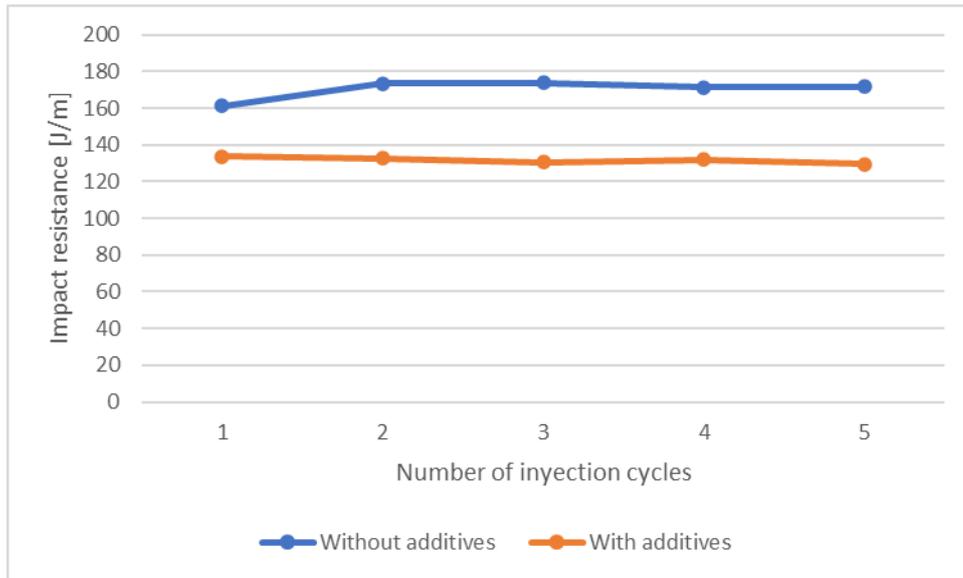
Figure 3.11: Impact resistance of HDPE during five injection cycles with and without additives [36]

Maximum load

In the graph from the figure 3.13 a very important mechanical propertie of the HDPE is shown: the maximum load. And it is done as in the previous essays; for two samples, one without additive and one with, and for five injection cycles.

The following considerations must be taken into account in order to perform this test:

- The specimen is according to ASTM D638, as shown in the figure 3.12
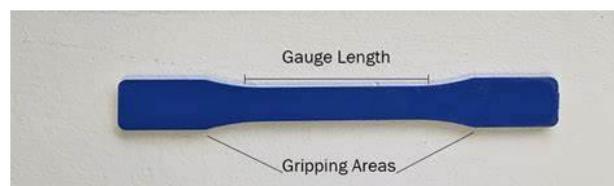

Figure 3.12: Specimen according to ASTM D638 [38]

- The length of the specimen should be approximately 200*mm*
- The speed of the moving grip is 208*mm/min*
- The thickness of the specimen must be between 5 and 25,4*mm*
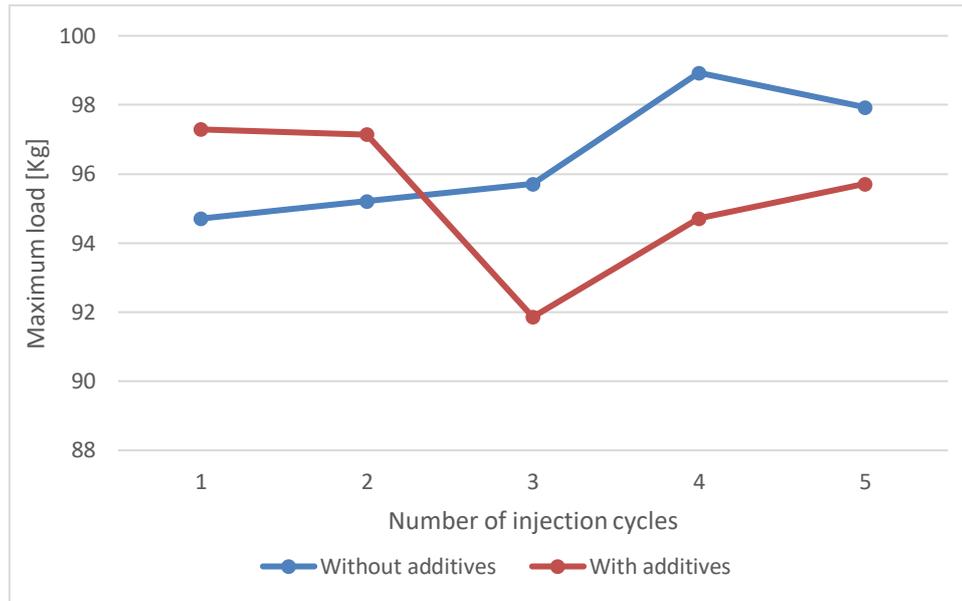
Figure 3.13: Maximum load of HDPE during five injection cycles with and without additives [36]

The graph of maximum loads shows that the maximum load of the specimen without additives remains more stable than the maximum loads with AOX, which varies at first decreasing during the first two injection cycles, but it stabilizes during the last three cycles.

Finally, it was observed that the color of the additive-free material degraded with each injection cycle, however, the color of the additive HDPE kept its color constant during the five injection cycles.

3.2.2 Study of the viscosity of HDPE samples with different concentration of recycled material

Next, we studied the rheological properties of different samples of HDPE, comparing them and studying their different behavior. For the realization of this experiment (which was performed in the Laboratory for experimental mechanics, University of Ljubljana) seven different samples were taken: basic HDPE without recycling, a sample with 10% of HDPE recycled and the remaining 90% un-recycled, another with 30% recycled and the remaining 70% un-recycled, another with 50% recycled and the remaining 50% un-recycled, another with 70% recycled and the remaining 30% un-recycled, another with 90% recycled and the remaining 10% un-recycled, and finally, a 100% recycled sample. This experiment was carried out in two parts: one using recycled material 50 times and another using recycled material 100 times.

In all these samples an initial shear stress of $10Pa$ was applied and, from that value, it went increaseing 100 more times, noting the viscosity in each case. Once this point is reached, this stress was released also for 100 different times until the initial shear stress of $10Pa$ is reached again, and also the viscosity data is recorded in each of these 100 tests.

In this way, we obtained the graphs Shear Stress – Viscosity shown in the figures 3.13 and 3.14, where the behavior of each one of the samples can be analyzed.
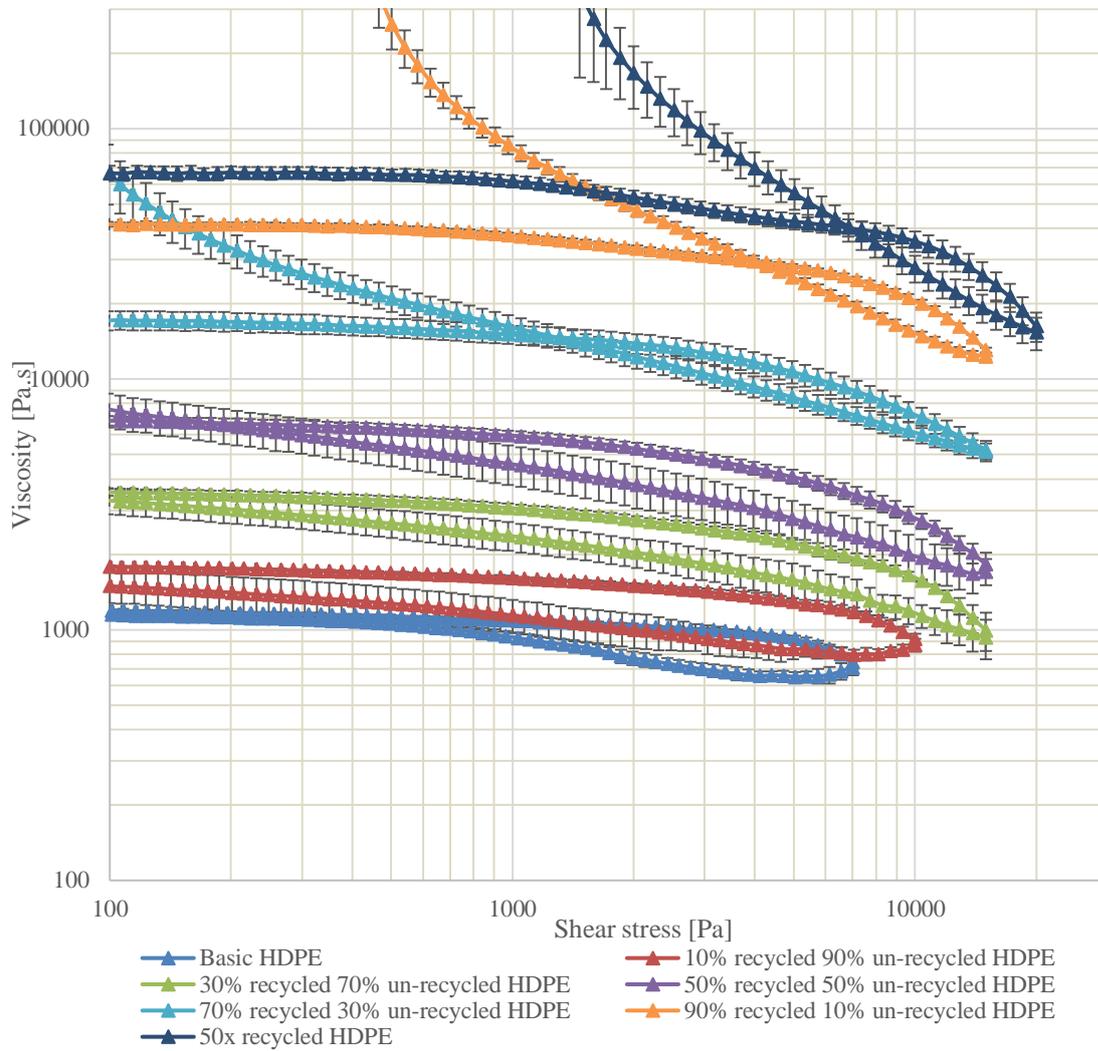

Figure 3.14: Shear stress – Viscosity graph using recycled HDPE 50 times
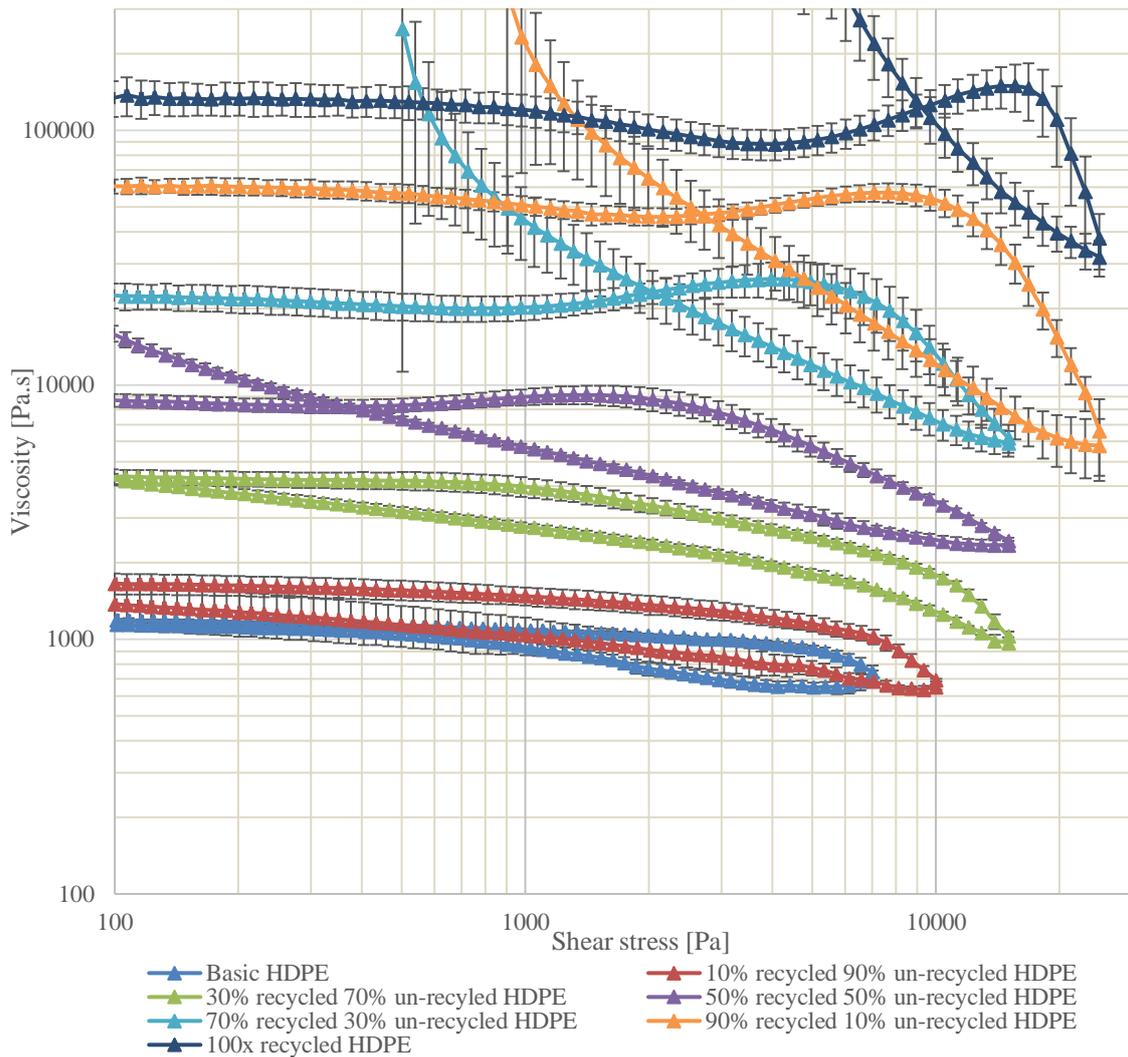
Figure 3.15: Shear stress – Viscosity graph using recycled HDPE 100 times

The relationship between these two graphs is the fact that the more percentage of recycled HDPE the sample has, the higher the viscosity of the polymer sample.

It can also be observed that, in the three samples with the highest amount of recycled material, the viscosity curve presents a steep drop as the shear stress is applied, and once the highest stress point is reached and then this is released, a much more stable curve can be observed.

The biggest difference between the two curves (between using recycled material 50 times or 100 times), can also be seen in materials with the highest amount of recycled HDPE. In those samples with recycled material 100 times it is observed that once the point of maximum shear stress has been reached, in the process of removing this stress gradually, the viscosity increases more pronouncedly than in those samples with recycled material 50 times.

4. Conclusion

Today, HDPE is one of the most widely used plastics worldwide, usually for single-use packaging. That is why the recycling of this plastic is essential to reduce the risks on the planet and, therefore, on public health, which generates the excessive use of this plastic.

As important as it is, there are not enough studies of how the properties of HDPE can vary when recycling this material. This work has been based on the study of the properties of HDPE when it is recycled.

The obtained conclusions from the studies are:

- The color change of a HDPE sample established by the Hunter-Scotfield equation, gives us an idea of the development of thermal degradation of HDPE when processed in multiple cycles and processes.

- The melting point of three HDPE samples with different amounts of recycled HDPE does not vary significantly if a mixture of 50% virgin HDPE and 50% recycled HDPE is used: using recycled HDPE 10, 50 and 100 times, the melting temperature varies in an approximate range of 135.5 to 134 $°C$. Therefore, it is possible to manufacturate HDPE objects with the half of material recycled 100 times and their thermal properties will not be greatly affected.

- From using HDPE with AOX additve processed over five injection cycles we obtain that, in terms of rheological properties, while the HDPE sample presents an increasing MFI, the HDPE sample with additive grows in the first three cycles, after the third to the fourth it stabilizes and in the fourth it slightly decreases, which indicates that it is possible to continue processing the HDPE sample with additive without affecting its rheological properties. In terms of mechanical properties, the HDPE sample with AOX additive processed over five injection cycles is stabilized after the third injection cycle, so that more cycles can continue without having high variations in these properties.

- From the last experiment, it is observed that the viscosity of the four samples with the lowest amount of recycled HDPE (a sample with basic HDPE un-recycled, a sample with 10% of recycled HDPE and the remaining 90% un-recycled, a sample with 30% of recycled HDPE and the remaining 70% un-recyceld, and a sample with 50% of recycled HDPE and the remaining 50% un-recycled) does not vary significantly with the use of 100 times recycled HDPE compared to the use of 50 times recycled HDPE. Therefore, using HDPE with 50% recycled material, its rheological properties will remain approximately constant using HDPE recycled 100 times and 50 times, indicating that this criterion is the best way to reduce the consumption of this plastic.

4.1 Ideas for the future work

Because the life of HDPE is often so short and its consumption today so high, in the future the behavior of HDPE samples could be studied with 50%, 30% and 10% recycled material 200 times. If the properties of this material were not too affected after this test, it would be a good way to reduce the consumption of this plastic.

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