



VILNIUS GEDIMINAS TECHNICAL UNIVERSITY
FACULTY OF MECHANICS
DEPARTMENT OF MECHANICAL ENGINEERING

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**RECYCLED POLYETHYLENE-TEREPHTHALATE FOR
BICYCLE FRAME INJECTION MOULDING**

Master Degree Thesis

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The Academic Reference to MSc Thesis of Elena Juan Riol:

This thesis stays an example of highly professional R&D project which successfully covers all the essential part of a reasonable contemporary high profile industrial R&D. The thesis effectively discloses both the economic valuation and the technical availability.

Academic Supervisor

Dr G Šmelin

RESUM

Aquest projecte tracta de realitzar un estudi de la posada en marxa d'una nova línia de producció per a quadres de bicicletes fetes de plàstic reciclat. Aquest tema va ser escollit per l'interès en projectes que tinguin un compromís amb el medi ambient combinat amb la afició personal pel ciclisme. Els propòsits són col·laborar en solucionar el problema de la enorme quantitat de rebuig de plàstic difícil de processar i promulgar l'ús de la bicicleta com a medi de transport.

El projecte es divideix en dues parts: *Literature Review* (Revisió Literària), on es fa un estudi general del material, manera de processament i antecedents; i *Calculations* (Càlculs) on es duen a terme les operacions numèriques necessàries per acotar determinats paràmetres del projecte, com la geometria de la peça.

Primerament, es fa un estudi en profunditat dels polímers en general i les seves propietats, tot intentant entendre intramolecularment el perquè dels canvis en les seves propietats, de què depenen i com varien. A més, s'explica també el procés d'injecció de polímers. Tot això per tal de poder escollir el polímer adequat pels objectius abans especificats. Com a resultat d'aquesta primera part s'obté que el polímer adient per aquest tipus de producció és el politereftalat d'etilè, tant per les seves propietats mecàniques de rigidesa com per la seva facilitat de reciclatge i consum mundial.

La segona part es divideix en dos tipus de càlculs: els que fan referència a la viabilitat econòmica i, per altre banda, el disseny de la peça. Per la primera part, s'han tingut en compte els costos de producció més directes sobre la producció, que són els de la maquinària, el material, lloguer del local, consum elèctric i mà d'obra. Amb aquestes despeses i realitzant dos torns diaris, es calcula un benefici de 13,54€ per cada bicicleta produïda durant el torn de dia i de 13,86€ durant el torn de nit. Per tant, es conclou que el projecte es econòmicament viable ja que l'estudi previ preveu una bona demanda del sector.

Finalment, pel que fa al disseny de la peça s'ha utilitzat el criteri del màxim moment flector per definir la secció mínima que suportaria les carregues del pes d'una persona, aplicades al manillar i al seient amb un coeficient de seguretat. Es va decidir que la secció seria ovalada per tal d'incrementar el moment d'inèrcia. Finalment, es va obtenir mitjançant una simulació una tensió màxima de 7,38 MPa. Per tant aplicant el criteri de fallida demostra que la peça no trencaria i que podria dur a terme correctament la funció per la que ha estat dissenyada.

List of Content

List of Figures	III
List of Tables.....	V
Introduction	1
Literature Review	3
1. Polymers and their properties	3
1.1 Intermolecular secondary forces and their effects on physical properties	3
1.2 Crystallinity and Their Effects on Mechanical Properties	7
1.3 Geometry and Flexibility of a Polymeric Chain	7
1.4 Crystalline Melting Point T_m and Glass Transition Temperature T_g	9
1.5 Models Explaining the Dynamic Polymeric Behavior	13
1.6 Relaxation in Polymers.....	14
1.7 Rheology of Polymers: Viscoelastic Behaviour	15
1.8 Reinforcing Fillers.....	19
1.8.1 Rules of Mixtures for Composites	21
2. Injection Moulding of Polymers	22
2.1 Process Characteristics.....	22
2.1.1 Thermoplastics	23
2.1.2 Thermosets.....	24
2.1.3 Differences	25
2.2 Machinery	26
2.2.1 Injection Unit.....	26
2.2.2 Closing Unit	27
2.2.3 Mould	27
2.3 Factors Involved in the Process.....	29
2.3.1 Moulding Cycle.....	30
2.3.2 Crystallinity and Contraction of the Part.....	31
2.4 Applications.....	32
3. Plastic Recycling	33
3.1 Recyclable Plastics.....	33
3.2 Recycling Process	34
3.2.1 Primary Recycling	34
3.2.2 Secondary Recycling.....	35

3.2.3 Tertiary Recycling	35
3.2.4 Quaternary Recycling	36
3.3 Recycling Steps	36
3.3.1 Mechanical Recycling	36
3.3.2 Chemical Recycling	37
3.4 Major Existing Processes	37
4. Material Selection	39
5. Polyethylene-terephthalate (PET)	40
5.1 Properties	41
6. Economical Study	44
6.1 The Bicycle Market	44
6.2 Current Situation of Recycled Pet	47
Calculations	50
7. Economics Value	50
8. Geometry and Sizing	54
8.1 Structure Model and First Solution	54
8.1.1 Solutions	57
8.2 Optimization Process	58
8.3 Final Part	60
8.4 Improvements	62
8.5 Mould Design	64
Conclusions	68
APPENDIX I: Latest Data Released by the Ministry of Promoting Spain on Daily Mobility	69
REFERENCES	73

List of Figures

Figure 1: John Wesley Hyatt	1
Figure 2: PET Wasting and Recycling Evolution	2
Figure 3: Dipole-Dipole Interaction	3
Figure 4: Hydrogen Bonding in Water	4
Figure 5: Interaction between Molecules of Methane, Chloromethane and Methanol	6
Figure 6: Silicon to Oxygen Bond	8
Figure 7: Nitrogen to Carbon Bond in Aramids	8
Figure 8: Carbon to Oxygen Bond in Polyurethane	9
Figure 9: Relaxation Modulus Behaviour versus Temperature	11
Figure 10: Stress-Strain Curve for a Hypothetical Material	13
Figure 11: Schematic Diagram of log of Relaxation Modulus versus Temperature (left) and Relaxation Modulus versus log of Time (right) for a Hypothetical Amorphous Polymer	15
Figure 12: Schematic Diagram of log of the Frequency Dependence of log of the Modules G' , G'' and their Ratio $\tan(\delta)$	17
Figure 13: Schematic Diagram of the Temperature Dependence of log of the Modules G' , G'' and $\tan \delta$ for an Amorphous Polymer	18
Figure 14: Temperature Dependence Schematic Diagram of log of the Storage Modulus (top) and $\tan \delta$ (bottom) of High Density Polyethylene (HPDE) and Low Density Polyethylene (LPDE)	18
Figure 15: A Cylindrical Reinforcing Fibre in a Polymer Matrix: (a) in the Undeformed State;	20
Figure 16: Surface Area-to-volume Ratio A/V of a Cylindrical Particle Plotted versus Aspect Ratio $\alpha=l/d$	20
Figure 17: Injection Moulding Process	24
Figure 18: Injection Moulding Machine	25
Figure 19: Differences between Thermoplastic and Thermoset Injection Machines	25
Figure 20: Picture of a Mould Cavity	28
Figure 21: Plastic's Classification Code by the American Society of Plastic Industry	33
Figure 22: Polyethylene-terephthalate (PET)	40
Figure 23: Graphic of Alternatives of Transport in Spain	44
Figure 24: Bicycle Users in Barcelona	45
Figure 25: Tendency of Bicycle's Prices	46
Figure 26: Supply's Tendency	47

Figure 27: Uses of Recycled Pet in Europe in 2005	49
Figure 28: Measures of the Bicycle Frame Structure	54
Figure 29: Geometry of the First Model with 8 cm Diameter	55
Figure 30: Details of the Subjections of the Frame	55
Figure 31: Frame Model with the Forces and the Fixations	56
Figure 32: Model Mesh	56
Figure 33: Distribution of Von Misses Stress with its values	57
Figure 34: Nodal Displacement with its Values	57
Figure 35: Representation of the Model with the Restrictions in ftool	58
Figure 36: Bending Moment Diagram	58
Figure 37: Circle and Tubular Section	59
Figure 38: Final Design	61
Figure 39: Distribution of Von Misses Stress of the Final Design with its values	61
Figure 40: Nodal Displacement of the Final Design with Its Values	62
Figure 41: Dimensions of the Final Section of the Bars (mm)	62
Figure 42: Final Frame Geometry	63
Figure 43: Distribution of Von Misses Stress with the Oval Section	63
Figure 44: Nodal Displacement with the Oval Section	64
Figure 45: Symmetric Parts of the Mould	65
Figure 46: Back Part of the Mould	65
Figure 47: Assembled Mould	66
Figure 48: log Viscosity – log Shear Stress Depending on Temperature	66

List of Tables

Table 1: Comparison of the Crystalline Melting Temperatures, T_m , of Common Polymers	10
Table 2: Comparison of the Glass Transition Temperature, T_g , of a few Common Polymers	12
Table 3: Contraction Values of Different Polymers	32
Table 4: Physical Properties of PET	43
Table 5: Comparison of Prices, Turnover and Manufactured Bicycles in the Last Three Years	46
Table 6: Demand Distribution of Pet Purposes	48
Table 7: Summary of Costs and Benefits of the Manufacturing Process	52
Table 8: Summary of Costs and Benefits of the Manufacturing Process in the Night Shift	53
Table 9: Reactions Values	59

Introduction

Celluloid was invented in 1851 by Alexander Parkes, but it was not until 1868 when John Wesley Hyatt, who can be seen in Figure 1, an enterprising young gentleman, improved it in order it could be processed into finished. This material was supposed to substitute ivory, which was becoming expensive and difficult to obtain. Hyatt used it to manufacture billiard balls but, unfortunately, some billiard balls exploded on impact during a demonstration (due to the chemical instability and high flammability of celluloid). Hence, in 1872 Hyatt and his brother Isaiah patented the first injection moulding machine in which they could mould celluloid plastic. Over the next 40 to 50 years, others began to investigate this new process and by 1920 the injection moulding industry had set its foundation and it has been building ever since. During the 1940s, the plastic injection moulding industry exploded as the World War II created a demand for inexpensive, mass-produced products. New materials were invented for the process on a regular basis and technical advances resulted in more and more successful applications [1].



Figure 1: John Wesley Hyatt

Almost at the same time, between 1939 and 1941, polyethylene-terephthalate (PET) was patented by the British scientists John Rex Whinfield and James Tennant Dickson. Just the same as the injection moulding machine, the war forced these two men to find out a substitute to the cotton from Egypt. From 1946 PET was used industrially as a fibre and its textile use is still has continued until the present. In 1976 it was used as food packaging for the first time and nowadays is the most used polymer to this aim [2].

A couple of main causes were the reasons to start work in the recycling and reuse of PET. First, an environmental pressure to improve waste management and the second - PET products has a slow rate of natural decomposition. Procedures need to be operated in order to make it

degrade biologically which tend to be complicated and expensive [3]. Moreover, as the price of virgin PET remain stable, new and cheaper technologies for recycling PET give and added value to the PET recycling industry, which have not stopped increasing since 1994, as Figure 2 shows.

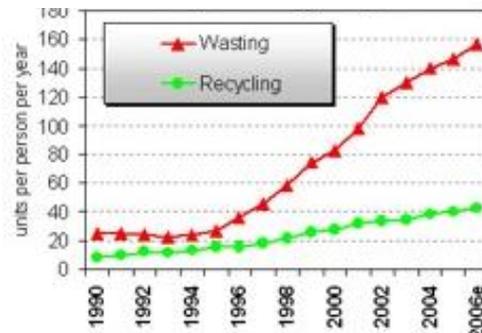


Figure 2: PET Wasting and Recycling Evolution

The entire world should understand the fragility of our environment and the importance of its protection. Recycling and reducing plastic waste is one of the many ways that requires in order to take care of our planet. Moreover, as in many countries of Europe, Spain is suffering an economical recession. For that reason, it seems as a suitable moment to look for different ways to save money. A use of a bicycle as transport is a good manner to avoid unnecessary expenses and, what is more, it protects the environment too. This project was born from combining these two ideas in order to preserve and protect the environment and help people in their personal economy [4]. A bicycle made with recycled PET have a lot of advantages in front of the current ones. It is lighter and cheaper than aluminium or steel one, and as it will be demonstrate in this project, it could be as resistant as the normal ones if an adequate study is done.

Hence, this project starts with an introduction in polymers to try to understand which their properties are and how are they influenced by different factors. The aim of this study is to find out if it is possible to use these properties as advantages to manufacture a recycled bicycle frame. The objective is to get a part that would make the same function as an aluminium or steel frame but lighter, cheaper and ecological. The results of this project would be considered successful if at the end of it, it is possible to prove that a bicycle frame with these characteristics could be resistant to all the forces to which a bike is submit and the project is economically viable.

Literature Review

1. Polymers and their properties

A polymer is a large chain composed of many repeated subunits (monomers) with a broad range of properties which are the reason of their multiple uses in industry. These properties depend on the monomer residues that compound the polymer and its affects to the physical, mechanical and chemical properties in different ways.

1.1 Intermolecular secondary forces and their effects on physical properties

Intermolecular forces are forces of attraction or repulsion which act between neighboring particles (atoms, molecules or ions). Although intermolecular forces have lower value than intramolecular forces, major properties of polymers depends on them. There are three different types: dipole-dipole, ion-dipole and van der Waals forces.

Dipole-dipole forces are electrostatic interactions between permanent dipoles in molecules that tend to align the molecule to increase attraction. The positive end of a polar molecule will attract the negative end of the other molecule and influence its position. This interaction can be seen in hydrogen chloride (HCl) as Figure 3 shows and in chloroform (CHCl₃).



Figure 3: Dipole-Dipole Interaction

Ion-dipole and ion-induced dipole forces are similar to dipole-dipole and induced-dipole interactions but involve ions, instead of only polar and non-polar molecules. Ion-dipole and ion-induced dipole forces are stronger than dipole-dipole interactions because the charge of any ion is much greater than the charge of a dipole moment. Ion-dipole bonding is stronger than hydrogen bonding.

An ion-dipole force consists of an ion and a polar molecule interacting. They align in a manner that the positive and negative groups are next to one another, allowing for maximum attraction.

An ion-induced dipole force consists of an ion and a non-polar molecule interacting. Like a dipole-induced dipole force, the charge of the ion causes distortion of the electron cloud on the non-polar molecule

A hydrogen bond is the attraction between the lone pair of an electronegative atom and a hydrogen atom that is bonded to either nitrogen, oxygen, or fluorine. The hydrogen bond is often described as a strong electrostatic dipole-dipole interaction. However, it also has some features of covalent bonding: it is directional, stronger than van der Waals interaction, produces interatomic distances shorter than the sum of van der Waals radius, and usually involves a limited number of interaction partners, which can be interpreted as a kind of valence. Figure 4 represents an hydrogen bonding in a molecule of water.

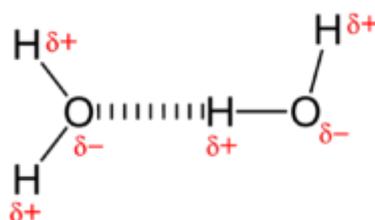


Figure 4: Hydrogen Bonding in Water

Van der Waals forces include attractions and repulsions between atoms, molecules, and surfaces, as well as other intermolecular forces. They differ from covalent and ionic bonding in that they are caused by correlations in the fluctuating polarizations of nearby particles (a consequence of quantum dynamics). Intermolecular forces have four major contributions:

- A repulsive component resulting from the Pauli Exclusion Principle that prevents the collapse of molecules.
- Attractive or repulsive electrostatic interactions between permanent charges (in the case of molecular ions), dipoles (in the case of molecules without inversion centre), quadrupoles (all molecules with symmetry lower than cubic), and in general between permanent multipoles. The electrostatic interaction is sometimes called the Keesom interaction or Keesom force after Willem Hendrik Keesom.

- Induction (also known as polarization), which is the attractive interaction between a permanent multipole on one molecule with an induced multipole on another. This interaction is sometimes called Debye force after Peter J.W. Debye.
- Dispersion (usually named after Fritz London), which is the attractive interaction between any pair of molecules, including non-polar atoms, arising from the interactions of instantaneous multipoles.

Different texts refer to different things using the term "van der Waals force". Some texts mean by the van der Waals' force the totality of forces (including repulsion); others mean all the attractive forces (and then sometimes distinguish van der Waals-Keesom, van der Waals-Debye, and van der Waals-London).

All intermolecular/van der Waals' forces are anisotropic (except those between two noble gas atoms), which means that they depend on the relative orientation of the molecules. The induction and dispersion interactions are always attractive, irrespective of orientation, but the electrostatic interaction changes sign upon rotation of the molecules. That is, the electrostatic force can be attractive or repulsive, depending on the mutual orientation of the molecules. When molecules are in thermal motion, as they are in the gas and liquid phase, the electrostatic force is averaged out to a large extent, because the molecules thermally rotate and thus probe both repulsive and attractive parts of the electrostatic force. Sometimes this effect is expressed by the statement that "random thermal motion around room temperature can usually overcome or disrupt them" (which refers to the electrostatic component of the van der Waals force). Clearly, the thermal averaging effect is much less pronounced for the attractive induction and dispersion forces.

Particularly, interaction between polymeric chains is influenced by the ability of the chains to build a strong hydrogen bond between the neighbouring polymolecules, relatively weak van der Waals forces or, in some special cases, caused by free volume and also molecular configuration [5]. One of the properties of the polymers that can show the influence of this interaction between molecules is the boiling point.

In order to notice that influence is enough to know the different melting points of methane, chloromethane and methanol, three similar molecules with relatively similar weight and size represented in Figure 5. But these three molecules have very different boiling temperatures, being the methanol's one the higher one, even though the chlorine creates bigger dipole with carbon than oxygen does. It is due to the hydrogen bond that appears between two molecules of methanol, thanks to the fact that oxygen atom is smaller than chlorine one and that

effectively prevents chlorine from forming such a strong bond with hydrogen, as the comparatively small atoms of oxygen or nitrogen are able to [6]. The electrostatic force of point charges has a reciprocal relationship to the square of the rising distance between the charges:

$$F = \frac{q_1 \cdot q_2}{4\pi\epsilon\epsilon_0(r_{dq})^2} \quad (1)$$

Where F is the force of the bond, q_1 and q_2 are the electrical charges of both atoms, ϵ is a dielectric constant, ϵ_0 is a constant called the permittivity of free space and r_{dq} is the distance between the electrical charges. Distance between two molecules of methanol is lower than the distance between two of chloromethane (due to the hydrogen bond mentioned before). Hence, melting temperature of methanol is 64.7°C and chloromethane's is -24.2°C .

Moreover, chloromethane boils at a higher temperature than methane, which is attracted to its neighbouring molecules of methane by a weak van der Waals force. On the other hand, chlorine atom is much more electronegative than carbon, hence it creates an electrostatic dipole that attracts its neighbouring molecules of chloromethane, harder than the molecules of methane does and making its boiling temperature higher.

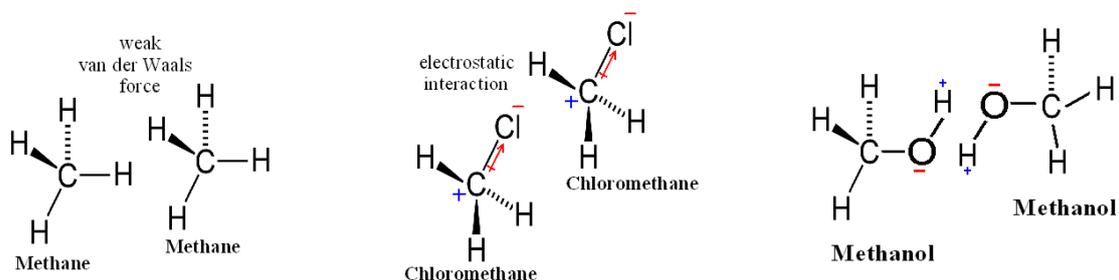


Figure 5: Interaction between Molecules of Methane, Chloromethane and Methanol

In conclusion, intermolecular secondary forces affect the physical properties of short molecules. The more polar the molecules, the stronger the connecting force. Polymers containing high numbers of polar groups in the chain normally exhibit much higher T_g and T_m at room temperature in comparison to those which are connected through weak van der Waals forces [7]. However, a molecule with bigger molecular weight can have a higher boiling temperature even if it has more polarity than other. It happens for example when bromomethane and chloromethane are compared. Bromomethane's interaction with neighbouring molecules is even smaller in comparison to that between molecules of

chloromethane, but still it has a boiling temperature above to the chloromethane's because of its higher molecular weight [6,8].

1.2 Crystallinity and Their Effects on Mechanical Properties

In the previous section, it has been shown interaction between molecules can have an influence not only in physical properties, but mechanical properties as well. For example, the stress relaxation of polymers containing hydrogen bonds is strongly influenced by it. A hydrogen bond is generally keeping both molecules strung together during thermal oscillations [9]. But apart from intermolecular forces, other factors are also involved in influencing the possible mechanical properties of a polymer.

A good example to introduce crystallinity effects on a polymer is the case of polyethylene (PE). PE is a thermoplastic that tends to perfectly crystallized when it is cool from molten with the necessary time and forms HDPE (high density polyethylene), which is the toughest thermoplastic known. In contrast, if PE is copolymerized with other vinyls (LDPE: low density polyethylene) it loses some crystallinity and density, and so does tensile strength. The polymer becomes soft and flexible then [7]. Even more so, if ethylene is copolymerized randomly with 25 % of propylene in one resultant isotactic polymolecule, such molecules are effectively prevented from forming a crystalline structure and the polymer is elastic enough to be an elastomer.

1.3 Geometry and Flexibility of a Polymeric Chain

One is able to conclude that the more crystalline a polymer, the closer can it be to their neighbours and stronger will be the forces that keep them attached. It makes more difficult to break links between molecules and it leads to a higher mechanical properties. Hence, it is easier to a straighter chain to be closer to its neighbours and to decrease the free polymeric volume between chains, fact that would help to increase mechanical strength by having stronger secondary intermolecular forces. Thus, by predicting the influence of geometry on the mechanical properties of a polymer, it is not strange to discover that in polymer industry a small amount of an immiscible monomer is added to a polymeric mass in order to decrease its

density and preventing chains from reaching maximum proximity to each other. In such a case, the monomer would act like a lubricant [7].

The essential difference in the polymer behaviour (i.e., rigidity) lies in the flexibility of the valence bonds (i.e., how easy it is to change the molecular shape by molecular thermal oscillations (IR phonons) - the conformational change of a molecule) [9, 10]. The more flexible molecules are PDMS (polydimethylsiloxane), followed by polyethers and polyolefins which also are quite flexible. On the other hand, polyphenyls, polystyrenes, aramides tend to be always rigid at room temperature.

PDMS's property of flexibility is given by the silicon in its bond with the oxygen (represented in Figure 6) which, at the same time, gives quite a flexible valance bond with carbon.

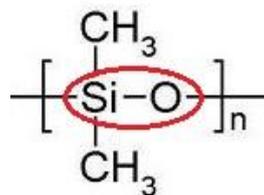


Figure 6: Silicon to Oxygen Bond

The main bond in the principal chain of polyolefins is from carbon to carbon, i.e., -C-C-. The energetical barrier of conformational change has a low value but is still being higher than the silicon or carbon to oxygen bond, so that is the reason why PDMS is more flexible than polyolefins. Moreover, the rearrangement's energy of a double carbon to carbon bond is about twenty times higher than a single's bond, so normally the chain stays rigid.

The nitrogen to carbon bond is very rigid with an energetical barrier similar to the double carbon to carbon bond. Because of this bond, aramids just give stiff polymers. The nitrogen to carbon bond in an aramid is shown in Figure 7.

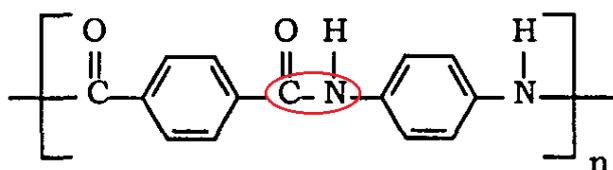


Figure 7: Nitrogen to Carbon Bond in Aramids

Otherwise, polyurethane for example can give a variety of flexible rubbers due to the carbon to oxygen bond shown in Figure 8 that it has in the main chain which gives to the polymer flexibility.

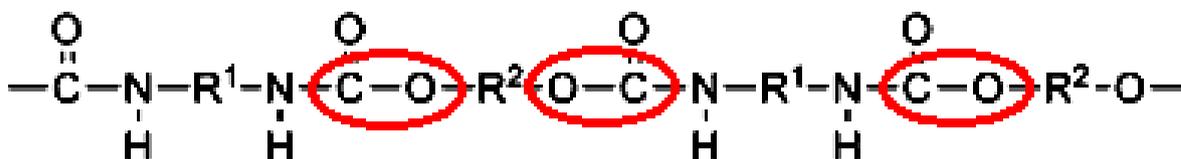


Figure 8: Carbon to Oxygen Bond in Polyurethane

1.4 Crystalline Melting Point T_m and Glass Transition Temperature T_g

These two properties effecting temperatures of a polymer have a relevant importance, especially in injection moulding, a process where the plastic is reaching many different temperatures during the process.

The melting point (T_m) is defined by the temperature at which all the crystals in a polymer disappeared and are completely melted. Above this temperature, the polymer will not have any crystalline structure and will be a viscous liquid [7]. On the other hand, glass transition temperature (T_g) affects the amorphous areas of the structure. Below this temperature and due to a free volume of molecular reconformations, polymolecule is fixed in place by secondary forces from neighbouring molecules in such way that only very short parts of the molecule are free enough for vibrational movements [9].

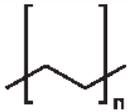
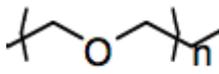
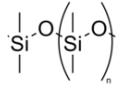
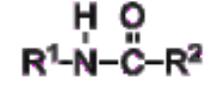
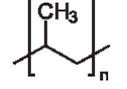
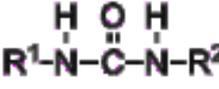
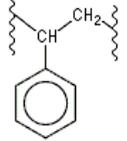
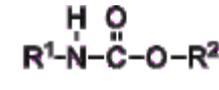
The crystalline melting temperature T_m may be described by the Gibbs free energy from equation 2:

$$T_m = \Delta H / \Delta S \quad (2)$$

In this case, the change in enthalpy ΔH represents the difference in cohesive energies between chains in the crystalline and liquid states, while the change in entropy ΔS represents the difference in the degree of order between polymer molecules in the two states [9,11].

Hence, melting point of polymers changes depending on different factors. Below it is shown a summary table with the melting temperatures values of different polymers with different characteristics to ease this exposition.

Table 1: Comparison of the Crystalline Melting Temperatures, T_m , of Common Polymers

		T_m (°C)			T_m (°C)
Polyethylene		135	polyethylene oxide		66
Polydimethylsiloxane		Unknown	Nylon 6,6		265
Polypropylene		165	ureas		370
Polystyrene		240	urethanes		200

As it was mentioned above, the melting temperature is influenced by the enthalpy energy, which is increase with the polar groups because cohesive energy grows. The nitrogen in Nylon, ureas and urethanes allows the molecule to form strong hydrogen bonds; hence its melting temperatures are higher than polyethylene's [7]. As it was shown, the crystallinity is also important for the interaction between chains, and that is the reason why those molecules which have defects or tends to have less degree of crystallinity would have lower values of T_m .

Otherwise, entropy depends not only on molecular weight and chain geometry, but also on structural factors like chain stiffness. Chains that are flexible in the molten state would be capable of assuming a relatively larger number of conformations that stiffen and therefore result in a large ΔS [7]. Hence, if ΔS increase, T_m is lower, and that explains why polyethylene oxide has lower melting point than PE. The oxygen bond gives to the molecule a flexibility that PE does not have. This phenomenon explains why urethane has lower T_m than Nylon too, although they two have the nitrogen to carbon bond, the oxygen confers more flexibility to the urethane.

ΔS decreases due to the mobility reduction that bulkiness groups provoke. Hence, the melting temperatures in polymers with large substitutes, such as polystyrene tend to have higher melting points [5]. But there are some cases with the bulkiness groups that may have the opposite consequence. This is the case, for example of some PDMS where bulky substitutions of phenyl groups in a main siloxane chain create more free volume and it makes the ΔS to get higher [12].

In contrast to crystallization, which is purely a thermodynamic process, glass transition is a kinetic process and is due to a free volume of molecular reconformations. As it was pointed in this work, bellow T_g amorphous parts of the polymer stay in the same place and just a very few parts are allowed to move [9].

For an ideally amorphous polymer a relaxation modulus dependence of temperature is shown in Figure 9:

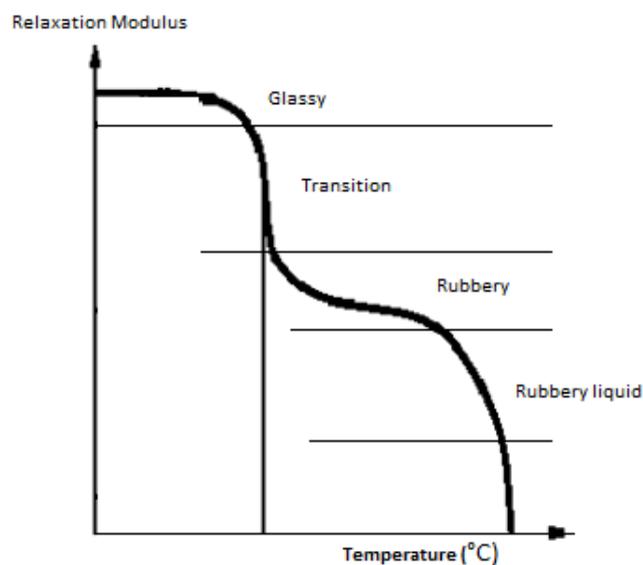


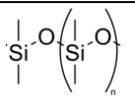
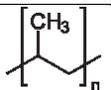
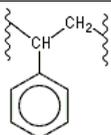
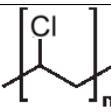
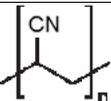
Figure 9: Relaxation Modulus Behaviour versus Temperature

Four different zones are shown. The first one is the glassy zone, where the modulus has its high value. This zone is associated with molecular mobility impaired due to insufficient thermal energy to activate the atomic movements. The second zone found - is the transition zone. In this area is possible certain molecular movement so it is possible too to get a higher deformation with the same effort than in the previous zone, and this causes a drop in the relaxation modulus. The next zone, the rubbery one, it is only present in branched polymers or

in the ones with a high molecular mass. Polymers with low molecular mass go directly to the rubbery liquid zone, where the molecular movement is large enough to make impossible to avoid the flow of the material.

In order to explain the behaviour of T_g depending on different aspects, a summary in Table 2 is provided:

Table 2: Comparison of the Glass Transition Temperature, T_g , of a few Common Polymers

		T_g (°C)
Polyethylene		-120
Polydimethylsiloxane (PDMS)		-123
Polypropylene		-10
Polystyrene		100
Poly(vinyl chloride)		87
Polyacrylonitrile		103

The more flexible the polymer, the more difficult will be to prevent the molecular movement, and hence the lower the temperature should be. Such an effect is particularly vital for PDMS, which has the very flexible bonds in its polymeric back-bone chain [5, 13].

Bulky substitutions reduce the T_g too. That kind of groups create more free volume what makes more difficult to fix the atoms, and the glass transition temperature becomes lower. But some opposite effects could be quite strong, because a bulky substitution may decrease the mobility of a polymeric chain, and also such a polymeric chain would inevitably require more empty space in order to be able to slide between its neighbours [13]. Hence polystyrene (PS), where a bulky benzene ring is attached to the polymeric chain, has a much higher T_g in comparison with polyethylene [7].

For the same reason that in the part of the melting point, polarity in molecules influences the glass transition point. Strong polar forces create tough connexions between the chains that reduce the possible movement. Hydrogen bonds are especially difficult to break, as it was explained in section 1.1 in the case of methanol molecules. It explains the difference in T_g between polystyrene, poly(vinyl-chloride) and polyacrylonitrile that gets higher as the intermolecular forces increase.

1.5 Models Explaining the Dynamic Polymeric Behavior

Elastic properties of some materials, such as some ceramics or perfect crystalline structures and metals can be specified by knowing their Young's modulus (E) and Poisson's ratio (ν) because their behaviour under stress can be considered linear until failure and their stress-strain curve without plastic deformation can be assumed as shown in Figure 10:

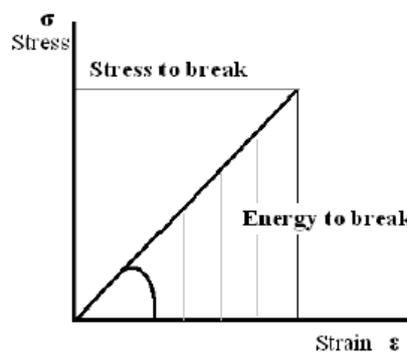


Figure 10: Stress-Strain Curve for a Hypothetical Material

Otherwise, polymeric behaviour cannot be represented with this graphic because polymers do not have a linear response to the stress. It is extremely difficult to predict their elastic reaction in order to be able to process them mechanically in a more efficient manner and that is the reason why some models have tried to explain and predict their behaviour and give a solution to the manufacturing industry, which constantly is looking for an increase of the speed of the technological processing. Even though, this task is still incomplete, but there are some existing semiempirical models that shows some useful approximations [14].

Exists a model developed by Ferry, Rouse and Beuche, which can only explain the behaviour of an oligomeric material, underestimating the effect of the entanglements, although their effect on the polymer's response is important [15]. The polymeric relaxation model suggests that a

molecular chain works as a set of beads linked by springs that vibrate in many different ways, depending on the stiffness and the force constant of the spring. There are various types of vibrations of a molecular chain which are normal modes of IR oscillation of a molecular chain and each is characterized by a certain frequency at given temperature. At the same time, there is a specific relaxation time for each one of these different modes of vibration and also, this model attributes to the vibration mode with the higher relaxation time the flow behaviour of the polymer melt [10].

Furthermore, for Rouse-like constrain release (CR) relaxation, this theory predicts that the viscosity η should be directly proportional to the molecular weight, which is only true to the entanglement limit:

$$\eta = K \cdot (DP)_w^{1.0} \quad (3)$$

here K is constant and $(DP)_w$ is the degree of polymerization, beyond which the viscosity becomes proportional to the molecular weight to the power 3.4, as shown in equation 4:

$$\eta = K \cdot (DP)_w^{3.4} \quad (4)$$

In order to take into account the effect of the entanglement, de Gennes suggested the “reptation” relaxation model, which assumes that the entanglements act as obstacles that the chains cannot avoid and that constrain the large-scale movements, but that they can slither through them with motions similar to a snake movement, hence the name reptation.

De Gennes found that the diffusion coefficient D_k of a chain in the melt should depend inversely on the square of the molecular weight M_n , hence, the melt viscosity η directly on the third power [15].

1.6 Relaxation in Polymers

To start with this paragraph is useful to refresh two concepts. First, that temperature is strictly linked to movement of molecules. As the temperature increases, particles start to vibrate more and more as higher is the temperature. The second one is that there are energy barriers inhibiting bond rotation that allows the molecules to remain in a determinate conformation in low temperatures but, if the temperature is increased enough, these barriers can be overcome and achieved new conformations.

There are various types of complex coupled motions or relaxation processes and these are usually referred to as “modes”. Each of these modes will have a different characteristic relaxation time or range of times, as it was explained in the section 1.5.

Relaxation of a polymer is a strong function of temperature. If the temperature gets closer to the T_g , movement in the chain becomes more difficult so relaxation time is longer. In the glassy state, conformational changes involving coupled bond rotations are severely inhibited, although they can occur over very long time periods, and local conformational transitions and side chain motions can occur. In the region of the glass transition there is now sufficient thermal energy that various cooperative motions involving longer chain sequences occur.

There are similar results if the temperature remains constant and relaxation time changes. At short periods of time, the maximum value of relaxation modulus is obtained, characteristic of the glassy state. Moreover, as time goes on, the stress required to maintain the given strain starts to decrease sharply until it reaches the rubbery plateau. Figure 11 shows the relation between the Relaxation Modulus and temperature and time.

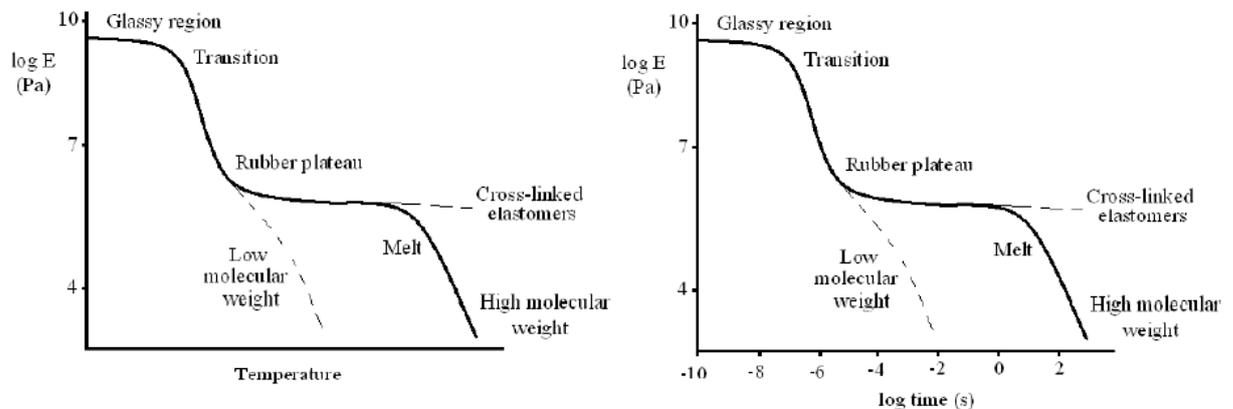


Figure 11: Schematic Diagram of log of Relaxation Modulus versus Temperature (left) and Relaxation Modulus versus log of Time (right) for a Hypothetical Amorphous Polymer

1.7 Rheology of Polymers: Viscoelastic Behaviour

One of the most useful methods for determining viscoelastic behaviour is the measurement of dynamic mechanical properties. In this type of experiment an oscillatory stress is applied to the sample. If the sample happens to be perfectly elastic and if the applied stress varies sinusoidally, then the strain γ would be completely in-phase with the applied stress and would vary as:

$$\gamma = \gamma_0 \cdot \sin(\omega \cdot t) \quad (5)$$

where ω is the angular frequency of the applied stress, t is the time and γ_0 is the original strain. If one is to consider experiments involving shear stresses and strains and small amplitudes of vibration then it possible to write Hooke's law as:

$$\tau(t) = G \cdot \gamma_0 \cdot \sin(\omega \cdot t) \quad (6)$$

where the symbol $\tau(t)$ indicates that the applied shear stress varies with time.

For a Newtonian viscous liquid with viscosity η , the resulting strain γ will be exactly 90° out-of-phase with the stress, because:

$$\tau(t) = \eta \cdot \dot{\gamma}(t) = \eta \cdot \frac{d(\gamma_0 \cdot \sin(\omega \cdot t))}{dt} \quad (7)$$

For a viscoelastic material the response expected to be characterized by a phase angle somewhere between 0° and 90° should be related to the dissipation of energy (viscous type response) relative to its storage (elastic type response). If a sinusoidal stress is applied to a viscoelastic material such as a polymer it should be expected for the resulting measured strain to lag behind by some degree, which is possible to define in terms of phase angle δ , so it is possible to express the stress in terms of an in-phase component and an out-of-phase component with respect to the strain. The relationship between stress and strain can now be defined in terms of these in-phase and out-of-phase components by:

$$\tau(t) = \gamma_0 [G'(\omega) \cdot \sin(\omega \cdot t) + G''(\omega) \cdot \cos(\omega \cdot t)] \quad (8)$$

Where:

$$G'(\omega) = \frac{\tau_0}{\gamma_0 \cdot \cos \delta} \quad (9)$$

and:

$$G''(\omega) = \frac{\tau_0}{\gamma_0 \cdot \sin \delta} \quad (10)$$

The in-phase component, $G'(\omega)$ is called the storage modulus, while the out-of-phase component, $G''(\omega)$ is called the loss modulus:

$$\tan \delta = \frac{G''(\omega)}{G'(\omega)} \quad (11)$$

A schematic representation of the dependence of $G''(\omega)$, $G'(\omega)$ and $\tan \delta$ upon the frequency of oscillation ω is shown in Figure 12 for an amorphous polymer. This is an idealized representation and real data can often appear more complex. Nevertheless, the key features correspond to those observed for all amorphous polymers. At a constant temperature, firstly, at low frequencies the storage modulus $G'(\omega)$ is characteristic of that found in rubbers. As the frequency increases this modulus increases several orders of magnitude and levels out at a value of the modulus characteristic of the glassy state. At room temperature both a glassy polymer and a rubber would give this type of curve, and these curves would be shifted along the frequency axis to one another.

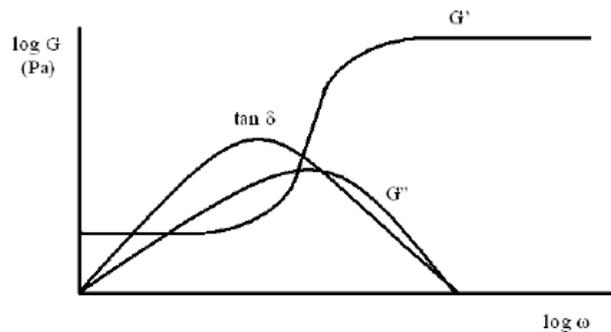


Figure 12: Schematic Diagram of log of the Frequency Dependence of log of the Modulus G' , G'' and their Ratio $\tan(\delta)$

It can also be seen that the loss modulus $G''(\omega)$ starts at low values and also increases with frequency, while $\tan \delta$ goes through a maximum and displays a peak in the range where $G'(\omega)$ is changing its value from one characteristic of rubber to one characteristic of the glassy state. [15,16]

Clearly $\tan \delta$ is showing a maximum at a position that is characteristic of a T_g . If a sample was subjected to an oscillatory stress at a specific frequency and the temperatures were allowed to vary, then a typical result would be shown as in Figure 13 [17].

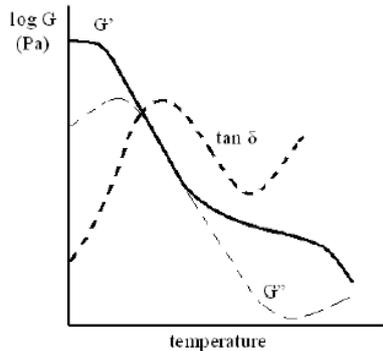


Figure 13: Schematic Diagram of the Temperature Dependence of log of the Modules G' , G'' and $\tan \delta$ for an Amorphous Polymer

So far relaxation in a purely amorphous polymer has been discussed and one would expect similar relaxation processes to occur in the amorphous domains of semi-crystalline polymers, but here motion is suppressed and constrained by crystallites. The viscoelastic behaviour of semicrystalline polymers is far more complex, because of the superposition of behaviour of the crystalline and amorphous domains. In some polymers, where the degree of crystallinity is not too high, transitions characteristic of amorphous state can be observed superimposed upon those due to the crystalline domains. This superposition is not necessarily linear, however, and coupling of responses can occur, particularly as the degree of crystallinity of a sample is increased and the amorphous regions become constrained by the crystalline domains. Because of these factors the behaviour of semicrystalline polymers is much less uniform than those that are purely amorphous, displaying individual idiosyncrasies that often have to be described separately. There is one generalization that it is possible to make, however, and that concerns the large change in the modulus that is observed at the crystalline melting point T_m .

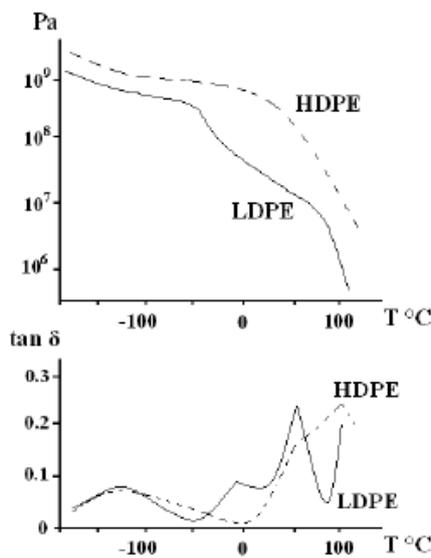


Figure 14: Temperature Dependence Schematic Diagram of log of the Storage Modulus (top) and $\tan \delta$ (bottom) of High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE)

Figure 14 displays schematically the type of storage modulus and $\tan \delta$ versus temperature behaviour for high and low density polyethylene polymers, which are highly crystalline polymers [9]. There are small regions of amorphous material that are constrained by hard crystalline domains, so at low temperatures both samples display a high modulus. Melting of smaller and less perfect crystals can occur at temperatures below the melting of the bulk of the crystalline domains, so the modulus decreases somewhat as the temperature is raised, but the largest change in modulus occurs at what is define as T_m . At this temperature the polymer becomes entirely amorphous and subsequently displays a rubbery plateau.

1.8 Reinforcing Fillers

Traditionally, most fillers were considered as additives, which, because of their unfavourable geometrical features, surface area, or surface chemical composition, could only moderately increase the modulus of the polymer, whereas the tear strength remained unchanged or even decreased. Their major contribution was in lowering the cost of materials by replacing the most expensive polymer; other possible economic advantages were faster moulding cycles as a result of increased thermal conductivity and fewer rejected parts due to warpage. Depending on the type of filler, other polymer properties could be affected; for example, melt viscosity could be significantly increased through the incorporation of fibrous materials. On the other hand, mould shrinkage and thermal expansion would be reduced, a common effect of most inorganic fillers [18].

The term reinforcing filler is used to describe discontinuous additives, the form, shape, and/or surface chemistry of which have been suitably modified with the objective of improving the mechanical properties of the polymer, particularly tensile strength. Inorganic reinforcing fillers are stiffer than the matrix and deform less, causing an overall reduction in the matrix strain, especially in the vicinity of the particle as a result of the particle–matrix interface. As shown in Figure 15, the fibre pinches the polymer in its vicinity, reducing strain and increasing stiffness.

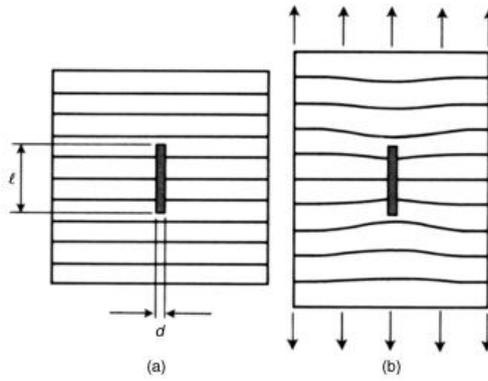


Figure 15: A Cylindrical Reinforcing Fibre in a Polymer Matrix: (a) in the Undeformed State; (b) Under a Tensile Load

Reinforcing fillers are characterized by relatively high aspect ratio α , defined as the ratio of length over diameter for a fibre or the ratio of diameter over thickness for platelets and flakes. For spheres, which have minimal reinforcing capacity, the aspect ratio is unity. A useful parameter for characterizing the effectiveness of a filler is the ratio of its surface area A to its volume V , which needs to be as high as possible for effective reinforcement. Figure 16 shows that maximizing A/V and particle–matrix interaction through the interface requires $\alpha \gg 1$ for fibres and $1/\alpha \ll 1$ for platelets [18].

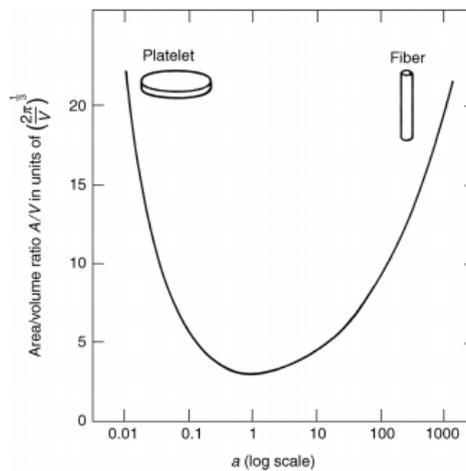


Figure 16: Surface Area-to-volume Ratio A/V of a Cylindrical Particle Plotted versus Aspect Ratio $\alpha=l/d$

1.8.1 Rules of Mixtures for Composites

Rule of mixtures equations (often modified according to the type, shape, and orientation of the reinforcement/filler) are commonly used to describe certain properties of the composites.

1) Concentrations are usually expressed by volume, as volume fractions of filler (V_f) and matrix (V_m), obtained from the volumes v_f and v_m of the individual components:

$$V_f = \frac{v_f}{v_f + v_m} \quad (12)$$

$$V_m = \frac{v_m}{v_f + v_m} \quad (13)$$

$$V_f + V_m = 1 \quad (14)$$

2) Volume fractions are also used to predict a theoretical density of the composite ρ , based on the respective densities of the components and assuming a total absence of voids:

$$\rho = V_f \cdot \rho_f + (1 - V_f) \cdot \rho_m \quad (15)$$

3) The total cost per unit weight of the composite C can also be calculated from the volume fractions and the costs of the individual components and the cost of compounding per unit weight of the composite C_i :

$$C = \frac{V_f \cdot \rho_f}{\rho \cdot C_f} + \frac{(1 - V_f) \cdot \rho_m}{\rho \cdot C_m} + C_i \quad (16)$$

2. Injection Moulding of Polymers

In spite of the relatively expensive tooling cost, injection moulding remains the most popular manufacturing process for plastic materials in mass production, thanks to its low operational cost, high throughput, and the flexibility to make parts with complex shapes. It can be used for producing parts from both thermoplastic and thermoset polymers. The process usually begins with taking the polymers in the form of pellets or granules and heating them to the molten state. The melt is then injected into a chamber formed by a split-die mould. The melt remains in the mould, and it is either chilled down to solidify (thermoplastics) or heated up to cure (thermosets). The mould is then opened and the part is ejected.

2.1 Process Characteristics

It is most commonly used to process both thermoplastic and thermosetting polymers, being the first one considerably more prolific in terms of annual material volumes processed. Thermoplastics are prevalent due to characteristics which make them highly suitable for injection moulding, such as the ease with which they may be recycled, their versatility allowing them to be used in a wide variety of applications. Thermoplastics also have an element of safety over thermosets; if a thermosetting polymer is not ejected from the injection barrel in a timely manner, chemical crosslinking may occur causing the screw and check valves to seize and potentially damaging the injection moulding machine [20].

With injection moulding, granular plastic is fed by gravity from a hopper into a heated barrel. As the granules are slowly moved forward by a screw-type plunger, the plastic is forced into a heated chamber, where it is melted. As the plunger advances, the melted plastic is forced through a nozzle that rests against the mould, allowing it to enter the mould cavity through a gate and runner system. The mould remains cold so the plastic solidifies almost as soon as the mould is filled. Polymers conserve their shape when they are cool under their T_g and hence, under their melt temperature to semicrystallines. Amorphous polymers have their movements between chains (disentanglement of chains) prevented under T_g . It is for that reason that they maintain their shape under this temperature. Semicrystalline polymers have also the characteristic to form crystals. These crystals provide stability to the molecule which is also

thermodynamically stable in those areas. Molecule's entropy decreases drastically due to the order of the molecules in crystals.

The sequence of events during the injection mould of a plastic part is called the injection moulding cycle. The cycle begins when the mould closes, followed by the injection of the polymer into the mould cavity. Once the cavity is filled, a holding pressure is maintained to compensate for the material shrinkage. In the next step, the screw turns, feeding the next shot to the front screw. This causes the screw to retract as the next shot is prepared. Once the part is sufficiently cool, the mould opens and the part is ejected [19].

Polymers commonly used for injection moulding include polystyrene, acrylonitrile butadiene styrene (ABS), polyamide (PA), polypropylene (PP), polyethylene (PE), polyvinylchloride (PVC) and other short fibres reinforced plastics.

2.1.1 Thermoplastics

When thermoplastics are moulded, typically pelletized raw material is fed through a hopper into a heated barrel with a reciprocating screw. Thermal energy increases due to the entrance of the material to the barrel and this causes the weakening of the van der Waals forces, which combine with the polymeric tendency to the rheological dynamic viscosity reduction effect, thus it significantly reduces the material's viscosity which enables the polymer to flow easily. The screw pushes the raw material forward, mixes and homogenizes the thermal and viscous distributions of the polymer, and reduces the required heating time by mechanically shearing the material and adding a significant amount of frictional heating to the polymer. The material feeds forward through a check valve and collects at the front of the screw into a volume known as a shot. Shot is the volume of material which is used to fill the mould cavity, compensate for shrinkage, and provide a cushion to transfer pressure from the screw to the mould cavity [19]. Often injection times are well under 1 second. Once the screw reaches the transfer position the packing pressure is applied which completes mould filling and compensates for thermal shrinkage, which is quite high for thermoplastics relative to many other materials. The packing pressure is applied until the gate (cavity entrance) solidifies. Once the gate solidifies, no more material can enter the cavity; accordingly, the screw reciprocates and acquires material for the next cycle while the material within the mould cools so that it can be ejected. This cooling duration is dramatically reduced by the use of cooling lines circulating water. Once the required temperature has been achieved, the mould opens and the

pieces are driven forward to demould the article. Then, the mould closes and the process is repeated. This process is represented in Figure 17.

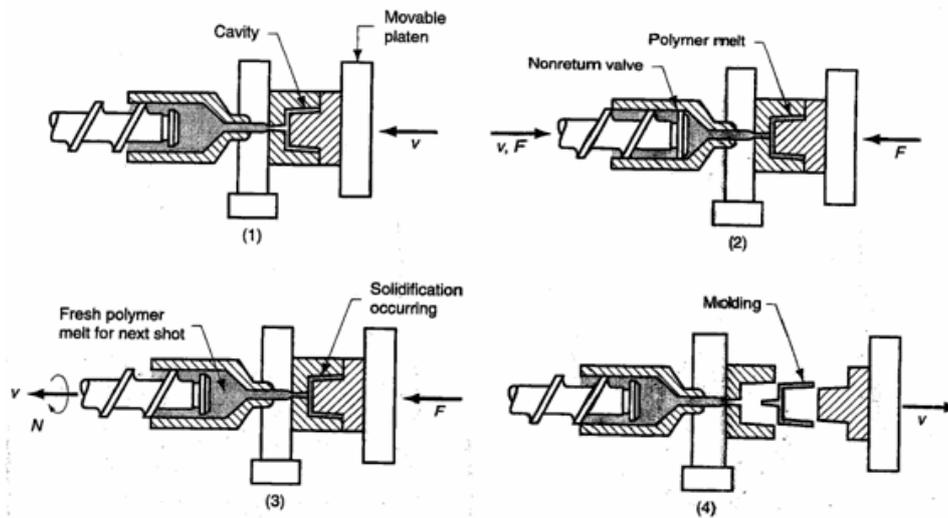


Figure 17: Injection Moulding Process

2.1.2 Thermosets

For thermosets, typically two different chemical components are injected into the barrel. These components immediately begin irreversible chemical reaction which eventually crosslinks the material into a single connected network of molecules. As the chemical reaction occurs the two fluid components permanently transform into a viscoelastic solid. Solidification in the injection barrel and screw can be problematic and have economical impact. Therefore, minimizing the thermoset curing inside the barrel is important. This typically means that the residence time and temperature of the chemical components is minimized in the injection unit. The residence time can be reduced by minimizing the barrel's volume capacity and by maximizing the cycle times. These factors have led to the use of a thermally isolated mould, which increases the rate of chemical reactions and results in shorter time required to achieve a solidified thermoset component. After the part has solidified valves close, isolating the injection system and chemical precursors, and the mould opens ejecting the moulded parts. Then, the mould closes and the process repeats. All the parts of the injection machine named in this part are represented below in Figure 18.

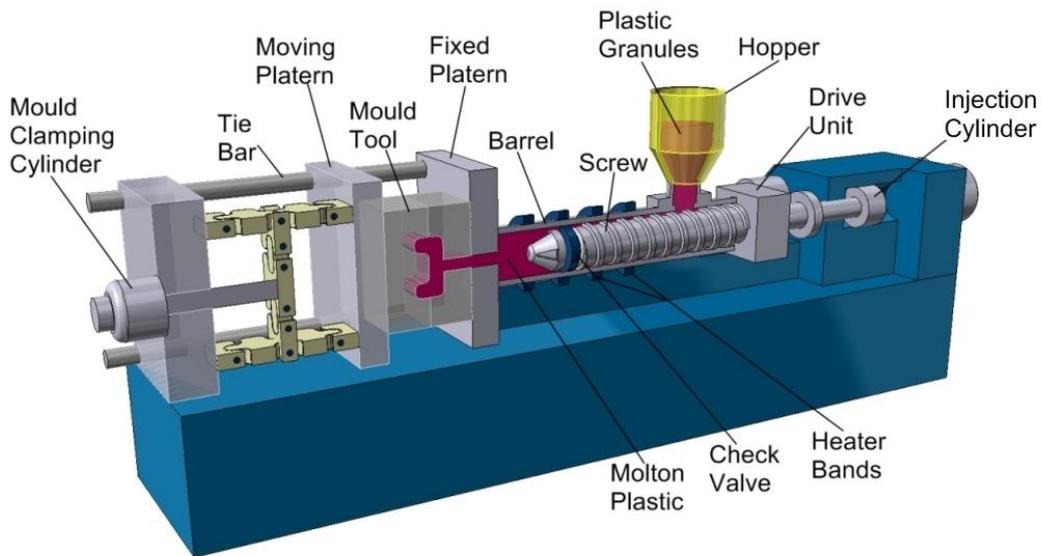


Figure 18: Injection Moulding Machine

2.1.3 Differences

Figure 19 shows the main differences between thermoplastic injection moulding and thermoset injection moulding:

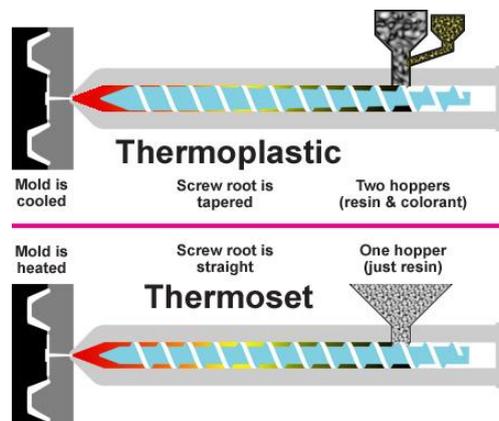


Figure 19: Differences between Thermoplastic and Thermoset Injection Machines

As the picture shows, there are two main differences: the screw and the number of hoppers. Screw root of thermoplastic is tapered, meanwhile the thermoset's one is straight. In thermoplastic injection moulding, the moulded parts retain their shape after they cool below their melting point, therefore it is vital in the process to get the resin up to its melt point as

quickly as possible and then to get the resin down below its melt point once it is in the mould (which is why the mould is cooled). Having the screw root tapered, the resin is compressed as it is squeezed into the continually shrinking space between the barrel wall and the root of the screw and it increases the resin's temperature. Moreover, the tapered screw helps the resin and colorant to be mixed. On the other hand, in thermoset injection moulding, the moulded parts retain their shape after they are heated above their cure point — the point at which crosslinking occurs. Therefore, the primary objective of the thermoset injection moulding process is to get the resin up to its melt point (so it can be injected into the mould), but not to get it up to its cure point until after it is in the mould (which is why the mould is heated). Since the resin can be brought up to melt temperature more accurately by controlling the barrel heat, no additional compression heating is needed, and thus the screw root is straight. Also, since colour additives are rarely used in thermoset moulding, the mixing action of a tapered screw is not needed.

2.2 Machinery

2.2.1 Injection Unit

Main function of injection unit is to melt, mix and inject the polymer. In order to achieve it, different screws are used depending on the polymer that has to be casted. One is able to define this part of the machine, three thermodynamic conditions should be taken in account:

1. Processing temperature of the polymer
2. Heat capacity (C_p) of the polymer [kJ/g °C]
3. If the polymer is crystalline, latent heat of fusion

Melting process involves an increase in the heat of the polymer, as a result of the temperature's increase and of the friction between the barrel and the screw. Friction and shear forces are determinant for an efficient melt, due to the fact that polymers are not good heat conductors. As the polymer's temperature increase, viscosity decreases, and the same happens when speed is increased. Hence, both of these parameters have to be well adjusted. There are some standard metals to every polymer in order to avoid corrosion or degradation [21].

The injection unit was originally an extrusion machine with a single spindle, having the barrel heaters and sensors to maintain a constant temperature programmed. The depth between the axis and channel decreases gradually (or drastic in special applications) from the feeding area to the area of dosage. Thus, the pressure in the barrel gradually increases. The mechanical stress, shear and compression system adds heat to the system and melt the polymer more efficiently than if there was only the heat[19].

The main difference between this process and the extrusion one is the existence of an extra part called camera booking, where the melt polymer is accumulated to be injected. This camera acts like a piston; the whole unit behaves like a plunger that pushes the material. Both in injection and extrusion pressure-volume-temperature (PvT) relations have to be taken in account.

2.2.2 Closing Unit

The closing unit is a hydraulic or mechanic press with a quite high closing force that counteracts the force made by the melt polymer when it is injected into the mould. Some located forces can produce pressures of hundreds of MPa.

This parameter is very important in the process because if the closing force is insufficient, the material could escape and induce to the opening of the mould. It is common to use the projected area of a piece to determine the required clamping force, excluding any gaps or holes in the piece.

$$F = P_a \cdot A_p \quad (17)$$

Where F is the force in Newtons, P_a , the average pressure, and A_p the projected area.

2.2.3 Mould

A mould consists of two primary components, the injection mould (A plate) and the ejector mould (B plate). Plastic resin enters the mould through a sprue or gate in the injection mould; the sprue bushing is to seal tightly against the nozzle of the injection barrel of the moulding machine and to allow molten plastic to flow from the barrel into the mould or cavity. The

sprue bushing directs the molten plastic to the cavity images through channels that are machined into the faces of the A and B plates, called runners. The molten plastic flows through the runner and enters one or more specialized gates and into the cavity.

It is important for the mould to have air vents that are ground into the parting line of the mould because if trapped air is not allowed to escape it is compressed by the pressure and can cause different defects. A parting line in mould making is the place where two or more parts of the mould meet. Parting lines occur due to tiny inherent spaces between two of the die. The material filling into these gaps is generally called moulding flash or simply flashing.

A mould is usually designed so that the moulded part remains on the ejector (B) side of the mould when it opens, and draws the runner and the sprue out of the (A) side. The piece then falls freely when ejected from the (B) side. Tunnel gates, also known as submarine or mould gates, are located below the parting line or mould surface. The moulded part is cut (by the mould) from the runner system on ejection from the mould. Ejector pins, also known as knockout pins, are circular pins placed in either half of the mould (usually the ejector half), which push the finished moulded product, or runner system out of a mould. Figure 20 shows the shape of a mould cavity.

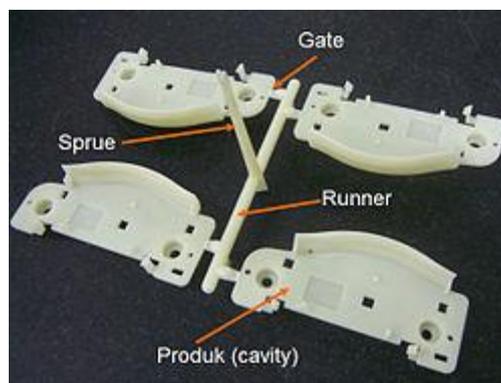


Figure 20: Picture of a Mould Cavity

The standard method of cooling is passing a coolant (usually water) through some holes drilled through the mould plates and connected by hoses to form a continuous pathway. The coolant absorbs heat from the mould, which has absorbed heat from the hot plastic, and keeps the mould at a suitable temperature to solidify the plastic at the most efficient rate.

It is possible to make variations of the same part by dividing cavities into pieces, called inserts, and sub-assemblies, also called insert, blocks or chase blocks and these substituting interchangeable inserts.

Some moulds allow previously moulded parts to be reinserted to allow a new plastic layer to form around the first part. This is called overmoulding. Two-shot or multi-shot moulds are designed to “overmould” in a unique moulding cycle and must be processed on specialized injection moulding machines with two or more injection units. This process is actually an injection moulding process in two steps. In the first step, the base colour material is moulded into a basic shape, which contains spaces for the second shot. Then the second material, a different colour, is injected into those spaces.

A mould can produce more than one copy of the same part in one shot. A tool with one impression will often be called a single impression mould. A mould with two or more cavities of the same parts will likely be referred to as multiple impression mould. Some moulds with extremely high production can have over 128 cavities, as those for bottle caps. In some cases, multiple cavity tooling can mould different parts in the same tool.

Tool steel or beryllium-copper are often used. Mild steel, aluminium, nickel or epoxy are suitable only for prototype or very short production runs. Modern hard aluminium (7075 and 2024 alloys) with proper mould design can easily make moulds capable of 100,000 or more part life with proper mould maintenance.

2.3 Factors Involved in the Process

The most important variables that can affect the process are temperature, pressure, time and distance [21].

- Injection Temperature: the temperature suitable for the material when it enters in the injection machine, and it increases since the first moment it gets in the topper until it reaches the mould. This temperature depends on the material and it cannot be higher than its decomposition temperature, but it has to be enough high to ease the material to flow.

- Mould Temperature: It is the mould's surface temperature. It has to be enough cold to cool the material and get solidify. It is important because the cooling rate can change depending on this temperature and the part can suffer some defects.
- Filling Pressure: the pressure applied at the beginning of the filling and that is a consequence of the screw movement. Thanks to that pressure, the material flows forward and fills the mould. In ideal conditions, it has to be as higher as possible to fill fast the mould, but it would affect the others factors involved in the process. (i.e., polymeric rheology, etc).
- Holding Pressure: It is the term to define the pressure applied at the end of the material injection, when the mould is almost full. It is done when some zones of the part have started to solidify and to shrink and it helps to fill the whole mould and to get a uniformed density part.
- Back Pressure: When the holding step is finished, this pressure is applied in the screw to make it return to its initial position. When the mould is completely filled, the excess material pushes the screw back, but there has to be a pressure in order not to let the screw free movement.
- Initial Injection Time: It depends on how much material has to be injected, its viscosity, mould characteristics, etc. It is the time that the screw spends to arrive to the mould and rarely exceeds 2 or 3 seconds.
- Holding Time: After the initial time injection, the screw stays in the limit position to maintain the correct pressure in the mould and this time is extended until the material in the cavity's entrance start to solidify. This is the holding time.
- Cooling Time: Is one of the most important variables involved in the process and it shows how many time the part spend to solidify and it is rigid enough to be extracted. Areas close to the wall get cold faster than the others, so in the cooling time, at least 95% of the part has to be solidified. Then, the bigger is the part, the higher is the cooling time.

2.3.1 Moulding Cycle

There are six main steps in the moulding cycle, even though some authors can differentiate up to nine [21].

1. Mould closed and empty. The injection unit is filled of melt polymer.
2. Polymer is injected by opening the valve and with the extrusion screw that acts like a piston, material flows to the mould.
3. Pressure remains constant to ensure that the appropriate sized of the part is achieved, because when it cools, the part tend to shrink.
4. Pressure is removed. The valve is closed and the screw turns and moves back.
5. The part is cool down in the mould, the press removes the pressure and the mould is opened. The part is expulsed.
6. The closing unit is closed again and the cycle starts again.

2.3.2 Crystallinity and Contraction of the Part

Contraction occurred during cooling is due to the variation in the density value, which is different for every kind of polymer. It can be isotropic or anisotropic. Hence, different parts would suffer different contraction depending on the raw material. However, for an isotropic contraction the contraction can be quantified by the following equations:

$$C_v = \frac{V_m - V_{mp}}{V_m} = 1 - \frac{V_{mp}}{V_m} \quad (18)$$

$$C_L = \frac{L_m - L_{mp}}{L_m} = 1 - \frac{L_{mp}}{L_m} \quad (19)$$

$$C_v \approx 3 \cdot C_L \quad (20)$$

Where L_m is the length of the mould; L_{mp} is the length of the moulded part; C_v is the volumetric contraction; C_L is the linear contraction; V_m is the volume of the mould and V_{mp} is the volume of the moulded part.

Semicrystallines polymers modify their size depending on the temperature at which they are able to crystallize. Polymeric chains that can crystallize occupy less space (which implies major density) than the amorphous polymers. Hereby, crystallinity is directly related with the final density of the part. Mould temperature and cooling time have to be the appropriate to obtain quality parts.

In the following table can be seen different values of contraction of different common injection polymers. Nevertheless, to design a mould is convenient to request to the supplier the specific parameters of the polymer that is going to be used.

Table 3: Contraction Values of Different Polymers

Polymer	Contraction (%)
Acrylonitrile butadiene styrene (ABS)	0.4-0.8
Polyacetal	0.1-2.3
Polymethylmethacrylate (PMMA)	0.2-0.7
Cellulose acetate	0.5
Nylon 6,6	1.4-1.6
Polycarbonate	0.6
LDPE	4-4.5
Polypropylene	1.3-1.6
Polystyrene	0.4-0.7
PVC	0.6-1.2
Plasticized PVC	1.0-4.5

2.4 Applications

Injection moulding is used in production of multiple goods such as wire spools, packaging, bottle caps, automotive dashboards, pocket combs, some musical instruments (and parts of them), one-piece chairs and small tables, storage containers, mechanical parts (including gears), and most other plastic products available today. Injection moulding is the most common modern method of part manufacturing; it is ideal for producing high volumes of the same object.

3. Plastic Recycling

3.1 Recyclable Plastics

Despite the fact that several different kinds of plastics exist, not all of them can be recycled and some of those which can be recycled cannot be accepted by a recycling plant. In order to know what plastics can be treated in a particular zone is necessary to get in contact with the recycling plants in that area.

It is essential to separate the different types of plastics correctly, because even a tiny quantity of the wrong plastic could destroy the melt mass already done. Because of this, plastic classification is a critic step in the recycling process.

To facilitate identification and classification of recyclable plastics, the American Society of Plastic Industry developed a standard code. This code identifies the type of plastic used to produce that object. The code is showed in the bottom of the plastic container and consists of three arrows rotating clockwise. There is a number inside the triangle to identify what kind of plastic the object was manufactured of and below it there is a combination of letters and numbers corresponding to the identifying number inside the triangle as the ones showed in Figure 21 [22].

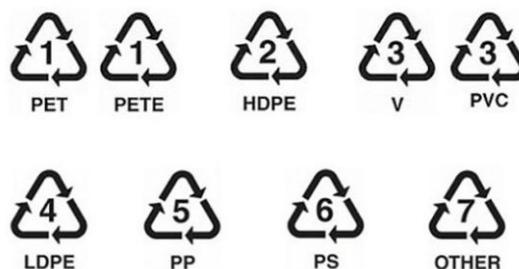


Figure 21: Plastic's Classification Code by the American Society of Plastic Industry

There are seven types of plastics that can be identified with the code explained before [22, 23]:

- PET (polyethylene-terephthalate) is the most current plastic of food and beverage packaging. It spends about 150 years to decompose. Once it has been recycled, PET

can be used in furniture, carpets, textiles, auto pieces and occasionally into new food packaging.

- HDPE (high density polyethylene). It is versatile and rugged. It is used to package household cleaning products, shampoos and detergent, as well as milk, juice, yogurt containers. It takes more than 150 years to decompose but if it is recycled can be used in pipes, detergent bottles, furniture, etc.
- PVC (polyvinyl-chloride) is very rugged. It can be seen in water bottles or shampoos. It can spend 1000 years to decompose. When is recycled can be used in road gutters, cable liner, among other materials.
- PS (polystyrene) is used in disposable plates and cups, egg cups, meat trays, fruit, yogurt containers etc. It has a low melt temperature and it can last 1000 years to decompose.
- LDPE (low density polyethylene). A strong, flexible and transparent plastic, which can be found in some bottles or plastic bags for single use. It takes 150 years to decompose, and once is recycled can be found in containers, bins, envelopes, pipes or tiles.
- PP (polypropylene). Its high melt temperature allows it to package hot liquids and food. It is often used in medical packaging, straws, ketchup bottles, caps, shampoos, etc. May take to decompose between 100 and 1000 years. If recycled can be used to produce light signals, battery cables, brooms, brushes, bicycle racks and others.

3.2 Recycling Process

Recycling process has become very important during the last years and some techniques have been developed to improve it. Some of these processes started to be developed in the 70's, when some countries started to burn their plastic waste. Since then, there have been a lot of advances and as a result of that nowadays exist four types of plastic recycling: primary, secondary, tertiary and quaternary recycling.

3.2.1 Primary Recycling

It involves the conversion of the plastic waste items with identical physical and chemical properties to the original material. The plastics that can be treated with this process are PET, HDPE, LDPE, PP, PS or PVC. It is carried out in four steps [24]:

1. Separation: separation methods can be classified into macro, micro and molecular level. The macro-separation is done on the complete product using optical recognition of colour or shape. The micro-separation can be done by a physical property specific size, weight, density, etc.

2. Granulate: Using an industrial process, the plastic is ground and becomes like granules of cereal flakes.

3. Cleaning: The plastic granules are usually contaminated with food, paper, stones, dust, glue, etc. and that is why it must be cleaned first.

4. Pelletizing: granulate plastic should be melted and passed through a thin tube to take the form of spaghetti cooled in a water bath. When it is cold enough is cut into small pieces called pellets.

3.2.2 Secondary Recycling

In this type of recycling plastics become plastic articles with properties that are inferior to those of the original polymer. Examples of such plastics recovered by this form are thermosets or contaminated plastic. This process eliminates the need to separate and clean the plastics, instead of this, plastics are mixed (including aluminum caps, paper, powder, etc.), ground and melted together in an extruder. Then, the plastic mass pass through a plastics tube with a large opening into a water bath and are then cut to various lengths depending on the customer specifications [24].

3.2.3 Tertiary Recycling

This recycling process degrades the polymer into basic chemicals and fuels. It is different from the first two because it also involves a chemical change, apart from the physical change. Nowadays the tertiary recycling has two main methods: pyrolysis and gasification. In the first

one, the first raw materials of plastics are recovered, so that it can rebuild pure polymers with improved properties and less pollution. And in the second one, gas is obtained by heating of the plastics which can be used to produce electricity, methanol or ammonia [24].

3.2.4 Quaternary Recycling

It consists of heating the plastic in order to use the thermal energy released from this process to carry out other processes. It means that plastic is used as fuel for energy recycling [24].

3.3 Recycling Steps

1. Collection: the recycling process starts at home or in industry, when the plastic waste is separate from the rest of the rubbish to be collected and brought to the recycling plant.
2. Recycling plant: here are received mixed plastic waste compacted into bales that are stored outdoors. There are limitations to long-term storage under these conditions, because ultraviolet radiation can affect the structure of the material, which is why it is advisable not exposed material having more than three months.
3. Classification: after receiving the plastic classification is made by type and colour. While this can be done manually, it has been developed automatic classification technologies that are used in developed countries. This process would be easier if there would be a differentiated delivery of this material.

3.3.1 Mechanical Recycling

Mechanical recycling is a physical process whereby the post-consumer plastic or manufacturing (scrap) is recovered, allowing further use. Plastics recycled mechanically come from two major sources [24]:

- Plastic waste from manufacturing processes. It means waste that rest in the machine or nearby, in the petrochemical and in processing industry. This kind of waste is called scrap. Scrap is easier to recycle because it has not been mixed with other types of plastic, so it is clean and homogeneous in composition. Some processes of

transformation (such as thermoforming) generated 30-50% of scrap, which is usually recycled.

- Plastic waste mass from Municipal Solid Waste (MSW). These are divided into three classes:
 1. Simple type Plastic waste: those of different classes have been classified and separated.
 2. Mixed waste: the different types of plastics are mixed together.
 3. Combined mixed plastic waste with other waste paper, cardboard, metals.

3.3.2 Chemical Recycling

Consists in different processes by which the polymer molecules are cracked (broken) giving rise again to the basic raw material which can be used to manufacture new plastics.

Chemical recycling began to be developed by the petrochemical industry in order to achieve the goals proposed for the optimization of resources and recovery of waste. Some chemical recycling methods have the advantage of not having to separate plastic resin types, so they can take mixed plastic waste reducing the cost of collecting and sorting, giving rise to final products of exceptional quality [24].

3.4 Major Existing Processes

- Pyrolysis: the cracking of the molecules by heating in a vacuum. This process generates solid or liquid hydrocarbons, which can then be processed in refineries.
- Hydrogenation: in this case the plastics are treated with hydrogen and heat. The polymer chains are broken and converted into synthetic oil that can be used in refineries and chemical plants.
- Gasification: the plastics are heated in absence of air or oxygen. The following synthesis gases are obtained: carbon monoxide and hydrogen, which can be used for the production of methanol or ammonia or as agents for the production of steel in furnaces vent.

- Chemolysis: This process applies to polyester, polyacetal and polyamide. It requires high amounts of resins separated by type. It involves applying solvolytic processes as hydrolysis or alcoholysis glycolysis for recycling and transform back into their basic monomers for repolymerization in new plastics.
- Methanolysis: is an advanced recycling process which involves the application of methanol in the PET, which is broken down into its basic molecules. Various polyethylene producers are trying to develop this process for use in carbonated beverage bottles, it has been shown that the monomers resulting from chemical recycling are pure enough to be reused in the manufacture of new PET bottles.

4. Material Selection

By a careful consideration of the all given restrictions, i.e., which the polymer will be submitted when would be injected, the best candidate for this production seems as polyethylene-terephthalate (PET).

First, PET has unique characteristics that make it adequate for the injection moulding. It has satisfactory mechanics properties, dimensional and thermal stability. Moreover, acceptable results in stiffness are achieved, and it also resistant to abrasion.

But there are many other polymers that have similar properties when are injected. One of the main reasons that make the PET a better candidate than other polymer is its price. It has suffered fewer fluctuations than other polymers such as PVC, PP, LPDE or GPPS in the last years. Furthermore, it is easily recyclable. The world's capacity of PET production is about 15 millions of tones every year and is continuously increasing, fact that makes very efficient to recycle this polymer, in order to reduce the quantity of waste. Moreover, thanks to the recycling, energy and natural resources are saved, apart from the economic saving rises the environmental protection.

5. Polyethylene-terephthalate (PET)

Polyethylene-terephthalate is a thermoplastic derivative from petroleum. It can be reused and modified several times with mechanic or thermal force, which means that it is a plastic which is 100% recyclable. PET can be injected, extruded, laminated and blown. It is one of the most used materials in the industry.

PET consists of polymerized units of the monomer ethylene terephthalate, with repeating $C_{10}H_8O_4$ units disposed as in Figure 22. Depending on its processing and thermal history, polyethylene-terephthalate may exist both as an amorphous (transparent) and as a semicrystalline (opaque) polymer. The semicrystalline material might appear transparent (particle size < 500 nm) or opaque and white (particle size up to a few microns) depending on its crystal structure and particle size. Its monomer (bis- β -hydroxyterephthalate) can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct, or by transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a byproduct. Polymerization is through a polycondensation reaction of the monomers (done immediately after esterification/transesterification) with water as the byproduct.

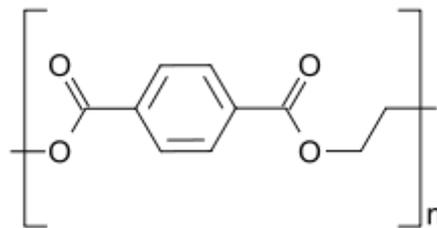


Figure 22: Polyethylene-terephthalate (PET)

The first industrial application of PET was textile during the Second World War, as a substitutive of natural fibbers. It is used to manufacture synthetic fibbers, mainly polyester (which is how textile PET is called) to substitute cotton and linen. However, the main application of the PET is produce containers. It is due to its resistance against chemicals, transparency, lightness and low manufacturing cost.

5.1 Properties

Because of the presence of aromatic rings in its chain PET has a molecular flexibility that is made clear in its glass transition temperature, which is between 70 and 80°C. It makes its capacity to crystallize to be controlled by the cooling conditions. Hence, density of PET can vary from 1,33-1,34 g/cm³ (if it is amorphous) to 1,45-1,51 g/cm³ (if it is semicrystalline) [26].

Solubility parameter of PET, which provides an approximate value of the degree of interaction between different materials, is about 21,8 MPa^{1/2}. It means that it is soluble in ketones, chlorinated and alcohols with 4 or 8 carbons. However, semicrystalline structures are only proton donor solvents are able of interacting with the ester groups effectively [25].

Its electrical insulating properties at room temperature are good at high frequencies, although it is a polar polymer. This is because below T_g it has restrictions in the dipoles orientation.

Another factor to have in account while PET is processed is its capacity to absorb humidity from its surroundings (hygroscopy) and the fact that in melt state it is sensible to hydrolytic degradation. Thus, before the resin can be processed in a moulding machine, it must be dried. Drying is achieved through the use of a desiccant or dryers before the PET is fed into the processing equipment. Inside the dryer, hot dry air is pumped into the bottom of the hopper containing the resin so that it flows up through the pellets, removing moisture on its way. The hot wet air leaves the top of the hopper and is first run through an after-cooler, because it is easier to remove moisture from cold air than hot air. The resulting cool wet air is then passed through a desiccant bed. Finally, the cool dry air leaving the desiccant bed is re-heated in a process heater and sent back through the same processes in a closed loop. Typically, residual moisture levels in the resin must be less than 50 parts per million (parts of water per million parts of resin, by weight) before processing. Dryer residence time should not be shorter than about four hours. This is because drying the material in less than 4 hours would require a temperature above 160 °C, at which level hydrolysis would begin inside the pellets before they could be dried out [25].

At the beginning of being moulded by injection one of the factors that limited its use was the low viscosity, which is highly sensitive to the temperature. Hence, processing temperatures are closer to T_m (between 270-290°C) [26].

The first moulded products of PET were parts where crystallization was promoted by adding nucleating agents. This ends on a high stiffness, grating surface resistance and opacity, and being able to be used between its T_g and T_m without dimensional problems. Nevertheless, interest in these products was limited until the utility of the glass fibre reinforcement was discovered [25]. Then, semicrystalline PET was used to produce electrical products.

But the real interest on the PET appears when the utility of bi-orientated products in combination with the copolymerization with isophthalic acid or 1,4-cyclohexane dimethanol was discovered. The bi-orientation process modifies the molecular structure of the polymer. The amorphous structure becomes laminar structure, in which molecules maintain their entanglement while they are aligned. Actually, the process consists in stretching the molecular chains in two directions (at 90 ° to each other), the axial and radial while the material is extruded. This molecular orientation confers special properties to the material, including higher impact resistance, high resistance to pressure hydrostatic and low cost of installation [25].

Moreover, PET is a light polymer and resistant to sterilization. Besides, it has excellent qualities to the conservation of products. PET is a polyester and that means that it does not contain additives and it is chemically inherent. Packages made with PET are inoffensive in touch with products for human consumption [26].

To sum up, the main properties of PET would be:

- Crystallinity and/or transparency
- Wear resistance
- Chemical resistance
- Advanced thermal properties
- Recyclable
- Appropriate to be used with food
- High stiffness and hardness
- Good frictional properties and abrasion resistance
- Good electrical insulating

The table below shows a sample of its physical properties:

Table 4: Physical Properties of PET

Property	Value
Elasticity Modulus	2800-3100 MPa
Tensile strength	55 MPa (N/mm ²)
T _g	75°C
T _m	260°C
Thermal conductivity	0,24 W/m·K
Coefficient of linear expansion	7·10 ⁻⁵ /K
Specific heat	1 kJ/kg·K

6. Economical Study

6.1 The Bicycle Market

Bicycles were more sold than automobiles on the first trimester on 2013 in the Eurozone. This information was given by de European Association of Automobiles. The economic recession and the increasing feeling of the population that the environment should be protected have ended in this unusual fact [27].

From 2000 to 2013 the number of sold bicycles have increased from 18,9 to 20 millions, which means a growth of 5.5% in thirteen years, and it is predicted that it will continue in the following years[28].

Otherwise, this growth has not been in the same way in all the European countries. In Germany, bicycle use increased more than 50% from 2002 to 2011. In Italy, 1.75 millions of bicycles were sold, which means 2000 units more than cars. This evolution is being observed for many years in Europe, and that is the reason why European capitals (including Spanish capitals) have every year more and more cyclists [27].

The situation in Spain is difficult to define, because although the government and the population in general are everyday more concerned about the importance and benefits of the bicycle, there are no specific statistics about the use of the bicycle. For example, in the mobility plans of the government, the bicycle is not studied independently. Instead of this, bicycle is included in groups like 'pedestrians and cyclists' [29]. Moreover, the latest data released by the ministry of promoting Spain on daily mobility are the following (Appendix I) and they are summarized in Figure 23:

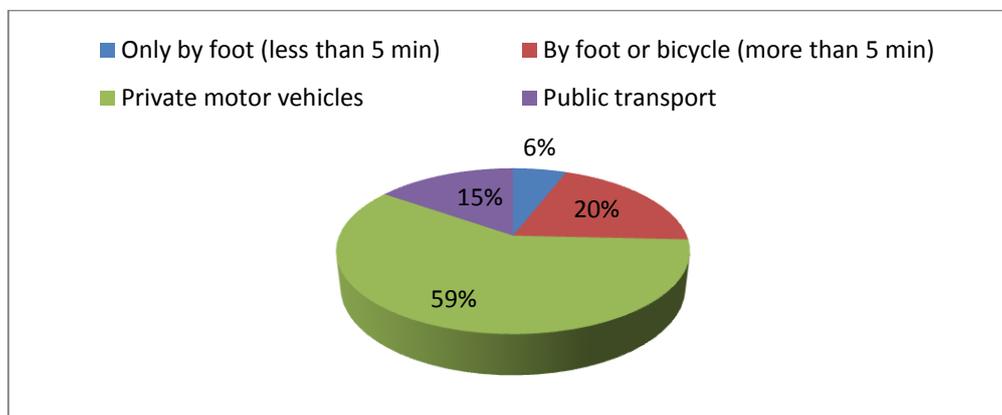


Figure 23: Graphic of Alternatives of Transport in Spain

These percentages do not change significantly depending on the population of the city, but there are some cities in Spain that are more informed or the government supports, more this way of transport than in other ones. That is the case of cities like Barcelona, Sevilla or Madrid, which have an increasingly tendency of the use of the bicycle year after year. For example, in Barcelona, the number of bicycle users grew from 47.561 in 2006 to 86.406 in 2007 when a new project named 'Bicing' that allowed people to take public bicycles in the street with a low periodic cost was set up in the city. A part of this, the demand of bicycles had already started to grow before 'Bicing', and it has continued growing during these years. Actually, since 2004 the bicycle users in Barcelona have increased their number in 237%. The evolution of bicycle users in Barcelona from 2004 until 2010 is shown in Figure 24 [30].

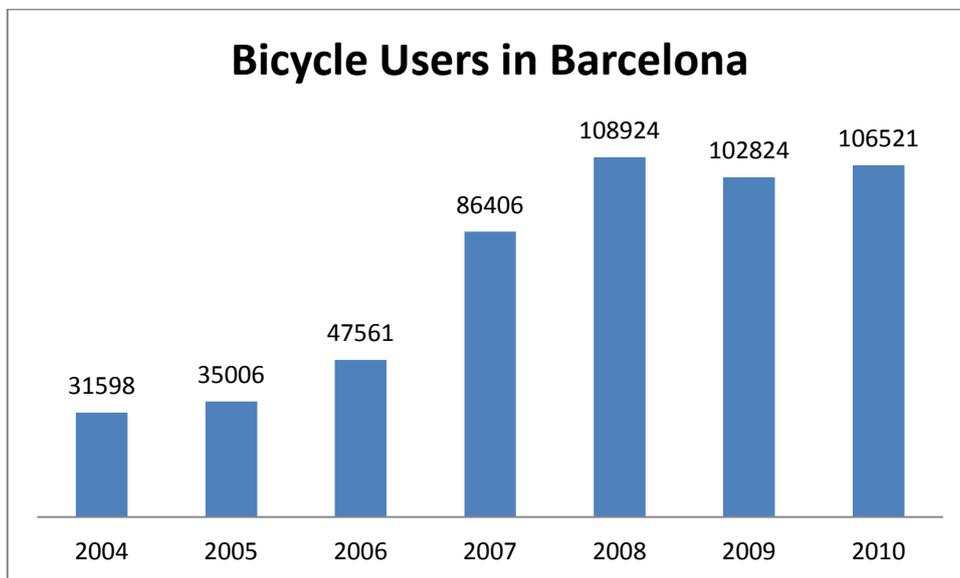


Figure 24: Bicycle Users in Barcelona

The Ministry of Industry published the Statistics of bicycles manufacture in the first semester of this year. The numbers confirms the tendency: there are fewer bicycles manufactured but turnover increases, which means that the medium price paid for a bicycle is increasing.

In the first semester of 2013, 172.967 bicycles were manufactured in Spain, 3,52% less than in the six firsts months of 2012. However, turnover achieve 31.723.000 Euros, which means 3,31% more than the same period of time but in 2012. This tendency has already appeared in 2012 in comparison with 2011. In 2012 370.299 bicycles were manufactured in Spain with an economical value of 65.901.000. This data means an 8,23% less of manufactured bicycles than

in 2011 but an 18,84% more of Euros in value. The table below shows the summary of the tendency with the medium price of the bicycles from 2011 until nowadays [27, 26].

Table 5: Comparison of Prices, Turnover and Manufactured Bicycles in the Last Three Years

	Manufactured Bicycles	Turnover(€)	Medium Price (€)
2011	403.507	55.453.551	137
2012	370.299	65.901.000	178
2013	172.967	31.723.000	183

If the bicycle market remains in such a way, the medium prize predicted for the 2014 is 212€, as it is shown in the tendency graphic below, Figure25.

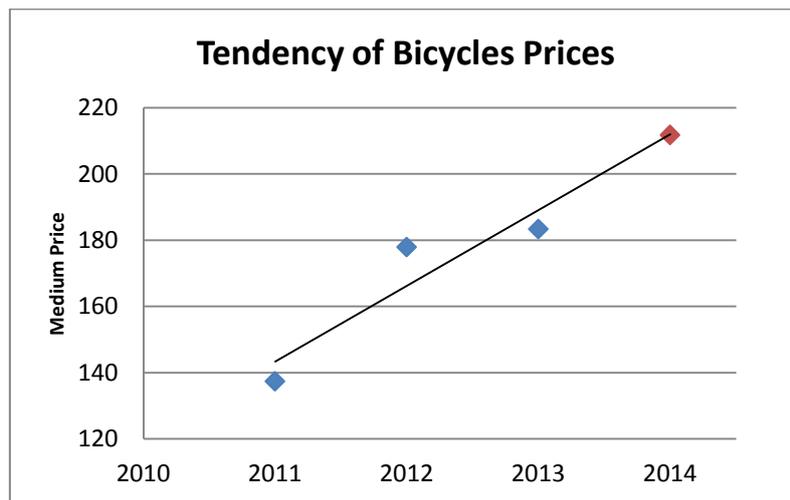


Figure 25: Tendency of Bicycle's Prices

With this data, one is able to conclude basing this information on the supply and demand low that the prizes are increasing because of a growth of the demand of bicycles in Spain. Moreover, this material provides information about the supply, which has the tendency to decrease year after year. If the supply continues with same tendency that the last year, around 316141 are predicted to be manufactured, as the shows the Figure 26 below [27, 28].

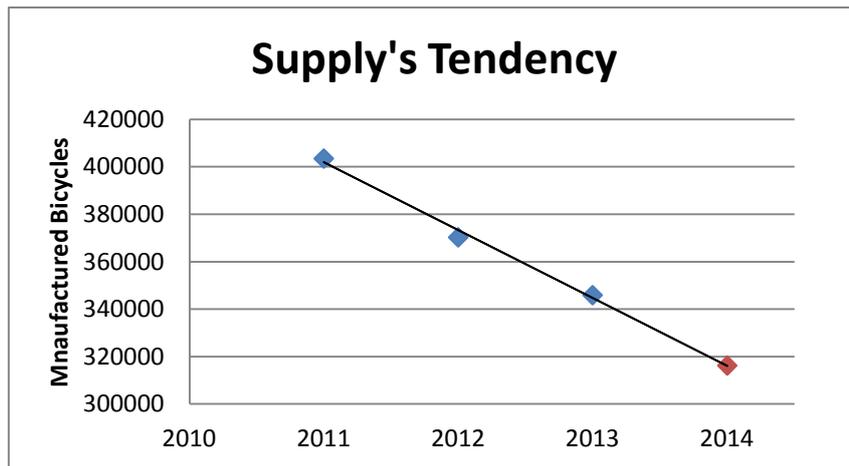


Figure 26: Supply's Tendency

To sum up, the information collected the last years shows that the medium prices of bicycles in Spain are increasing, as well as demand does. On the other hand, supply is decreasing. This data shows that it could be the suitable moment for a market of recycled bicycles, which would be cheaper than the current ones in a society with an increasing interest in such a way of transport.

6.2 Current Situation of Recycled Pet

Pet recycling is nowadays a growing market due to the environmental awareness of the population around the world. But there are still some barriers that should be overcome. The most important obstacle is the perception that recycled plastics have worst characteristics than the original, and is one of the prejudices that is being fought by the industry.

Japan is the most advanced country in this aspect. Its recycling rate of PET bottles recycled (total volume of recollection/ volume of sold bottles) is about 80%. This rate in Europe is around 50% according to the European Association of Recycling of PET Containers (Petcore) and in United States is about 28% according to Petra. In South America Brazil is the leader followed by Argentina with a rate of 55,6% and 34% each one, according to sources of the Brazilian Association of PET Industry (Abipet).

In Spain, the distribution of the PET demand in 2005 according to the Spanish Plastics Centre (CEP, *Centro Español de Plásticos*) is shown in table 6.

Table 6: Demand Distribution of Pet Purposes

<i>Purpose</i>	<i>Demand (tones)</i>
Films	20.300
Photographic Base	10.000
Isolation applications	5.200
Packaging, laminates	4.100
Printing, drawing	1.000
Paints and adhesives	11.200
Bottles	460.900
Carbonated drinks	235.800
Water	180.500
Oil	44.600
Others (cosmetics, pharmaceuticals, detergents and similar)	23.300
TOTAL	515.700
Abroad Business	
Importation	31.544
Exportation	35.874
DEMAND	511.370

622.300 tones of recycled PET granule were obtained in 2006 from the 943.900 tones of collected PET in Europe (129.400 tones were exported and 192.200 tones were lost during the process). It is predicted a 10% of growing of the collection and recycling in the near future [31].

In 2005 in Spain 56.749 tones of PET were recycled from the packaging industry. The main uses of the recycled PET in Europe nowadays are represented in Figure 27 [32]:

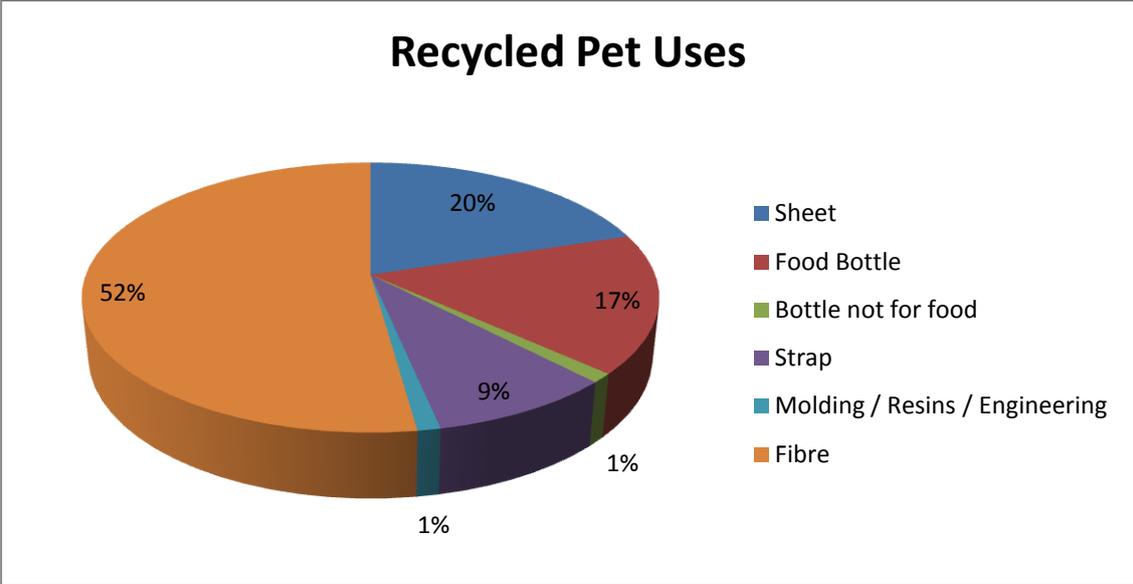


Figure 27: Uses of Recycled Pet in Europe in 2005

Calculations

7. Economics Value

In order to calculate the expected benefits that a factory of recycled bicycle would have some aspects have to be taken in account. A bicycle frame is about 5000 cm^3 , which is the volume of plastic that will be injected per bicycle. The injection capacity of the injection machine used to manufacture this frames is $500 \text{ cm}^3/\text{s}$ [33]. This speed allows the machine to inject the recycled PET once in 10 seconds. Hence, the cycle time will be 430 seconds with the three minutes needed to the solidification and three more to demoulding. Moreover, a year has about 252 working days with one shift of 8 hours per day; the total amount of bicycle frame that could be manufactured would be 16.878 per year that should be sold for $\geq 50\text{€}$ each one.

A machine with the characteristics described above costs 15.000€ and it lasts about 10 years on average [33]. Hence, the cost that it would suppose this price in every bicycle frame can be calculated:

$$\frac{15000\text{€}}{10 \text{ year}} \cdot \frac{1\text{year}}{16.878\text{bicycles}} = 0.09\text{€/bicycle} \quad (21)$$

The importance of avoiding possible mistakes before they appear is becoming more important every day. The time and the money lost if something unexpected happens may be significant. Due to these reasons maintenance time of the machine should be also taken into account. To reduce expenses, the operator of the machine should be trained to make on his/her-own this basic maintenance and be ready to solve any mishap that may occur, because he or she is the person who should know the machine working parameters in its best. Hence, this kind of machinery needs two hours weekly of routine maintenance and a more exhaustive maintenance of 16 hours once in trimester [33]. It makes 168 hours every year, in which any bicycle would be produced by the machine while it remains stopped. An hour of the stopping of the machine during the labour shift has been valued in 419 € because considering that 8,37 bike frames are produced in one hour and that one frame would be sold for 50€, 419 € is the money that the industry could gain but do not do it because of the maintenance time. It will mean 70.325 €/year, hence:

$$70325 \frac{\text{€}}{\text{year}} \cdot \frac{1 \text{ year}}{16878 \text{ bicycles}} = 4,17 \text{ €/bicycle} \quad (22)$$

Moreover, the third machinery cost that should be taken in account is the mould cost. It has to be designed and bought by a cost of 5000 €. It has a shorter life than the machine and lasts 5 years because it is exposed to high temperatures. Hence the cost per bicycle due to the mould is:

$$\frac{5000\text{€}}{5 \text{ year}} \cdot \frac{1\text{year}}{16878 \text{ bicycles}} = 0.06\text{€/bicycle} \quad (23)$$

Finally, the last machinery cost is due to the lifting machinery cost. The dimensions of the mould for this kind of parts are heavies and it is necessary a machinery that support at least 800 Kg to ease the demoulding process. Renting a lifting machine with this properties cost 50 €/week, and hence:

$$50 \frac{\text{€}}{\text{week}} \cdot \frac{1\text{week}}{5 \text{ days}} \cdot \frac{1 \text{ day}}{8 \text{ hours}} \cdot \frac{1 \text{ hour}}{8,4 \text{ bicycles}} = 0.15 \text{ €/bicycle} \quad (24)$$

Apart from the machinery cost, the process would not be possible without the raw material, the recycled PET, which every tone is valued in about 500€ nowadays [34]. Density of PET is reduced when it is recycled, but with some methods of compaction it can achieve values of 1200 kg/m³.

$$500 \frac{\text{€}}{\text{tone}} \cdot \frac{1200 \text{ kg}}{1\text{m}^3} \cdot \frac{0.005 \text{ m}^3}{1 \text{ bicycle}} = 3 \text{ €/bicycle} \quad (25)$$

Besides, the cost of an injector machine operator for a company is of 15€/h-operator.

$$2 \text{ operators} \cdot 15 \frac{\text{€}}{\text{hour}} \cdot \frac{1 \text{ hour}}{8,4 \text{ bicycles}} = 3,58 \text{ €/bicycle} \quad (26)$$

Moreover industrial building is necessary. It is appropriate a location in a city next to Barcelona of 580 m², which is enough for the machine and a space to store the production. It is valued in 2200€/month [35]. Hence, it impacts on every bike with a price of:

$$26400 \frac{\text{€}}{\text{year}} \cdot \frac{1 \text{ year}}{16878 \text{ bicycles}} = 1,56 \text{ €/bicycle} \quad (27)$$

To finish, electricity consume is an important spending in industry sector. The price per consumed kWh in Spain is 0.1495€ from 8:00 to 16:00 and an injection machine like the one used to this production spends 8kW.

$$0.1495 \frac{\text{€}}{\text{kWh}} \cdot 8\text{kW} \cdot \frac{1 \text{ h}}{8.4 \text{ bicycles}} = 0.14 \frac{\text{€}}{\text{bicycle}} \quad (28)$$

To sum up all the costs involved in the manufacturing process and the benefit achieved for each bicycle are shown in the table 7:

Table 7: Summary of Costs and Benefits of the Manufacturing Process

Manufacturing Costs	17,08 €/bicycle
Material	3 €/bicycle
Labour Cost	3,58 €/bicycle
Machinery	4,32 €/bicycle
Machine's Amortization	0,09 €/bicycle
Maintenance	4,17 €/bicycle
Mould	0,06 €/bicycle
Lifting Machine	0,15 €/bicycle
Renting	1,56 €/bicycle
Electricity	0,14 €/bicycle
Bicycle Frame Price	50 €/bicycle
BENEFIT	32,99 €/bicycle

In consideration of the provided information and with the expected production level calculated, the benefits of the owner of the company would be 46.306 €/month, supposing that all the bicycle frames would be sold. Moreover, the industrial building that has been rent could be big enough with a good organization to have two of such machines, fact that would double the final benefits in a future if the demand continues increasing.

Moreover, the current employment status in Spain is not in its best. Unemployment is high and working conditions are worse than some years ago. However nowadays, labour cost in Spain increase 35% from 22:00 pm to 6:00 am. It would be possible to double the production, from 29.030 bicycles every year to 58.060 half of them produced during the evening/night and the other half during the day shift. The price of manufacture a bicycle during the evening/night shift should be the same excepting the labour cost and also the electricity consume, which is reduced 56% due to it is consumed during the night period.

$$(15 \cdot 2 \cdot 1.35) \frac{\text{€}}{\text{hour}} \cdot \frac{1 \text{ hour}}{8,4 \text{ bicycles}} = 4.84 \text{ €/bicycle} \quad (29)$$

$$(0.1495 \cdot 0.44) \frac{\text{€}}{\text{kWh}} \cdot 8 \text{ kW} \cdot \frac{1 \text{ h}}{14.4 \text{ bicycles}} = 0.06 \text{ €/bicycle} \quad (30)$$

Hence, benefits of the bicycles manufactured during the night are detailed in table 8:

Table 8: Summary of Costs and Benefits of the Manufacturing Process in the Night Shift

Manufacturing Costs	18,25 €/bicycle
Material	3 €/bicycle
Labour Cost	4,84 €/bicycle
Machinery	4,32 €/bicycle
Machine's Amortization	0,09 €/bicycle
Maintenance	4,17 €/bicycle
Mould	0,06 €/bicycle
Lifting Machine	0,15 €/bicycle
Renting	1,56 €/bicycle
Electricity	0,06 €/bicycle
Bicycle Frame Price	50 €/bicycle
BENEFIT	31,75 €/bicycle

It would achieved a benefit of 44.655 €/month due the night shift, which added to the 46.306 €/month achieved during the day, would mean a final benefit of 90961 €/month. It has been possible to almost double the benefit with an extra shift during the night.

8. Geometry and Sizing

In this part of the project the part of study is going to be design and studied with the help of two different software's, which are SolidWorks and ftool.

8.1 Structure Model and First Solution

The part which is going to be produced is a bicycle frame. That is the main component onto which wheels and other components are fitted. The modern and most common frame design for an upright bicycle is based on the safety bicycle, and consists of two triangles, a main triangle and a paired rear triangle. This is known as the diamond frame.

The frame that is going to be produced is thought to be useful for the major part of the population having standard measures to be comfortable and resistant enough at the same time. Hence, the structure of the frame can be modelled as the Figure 28.

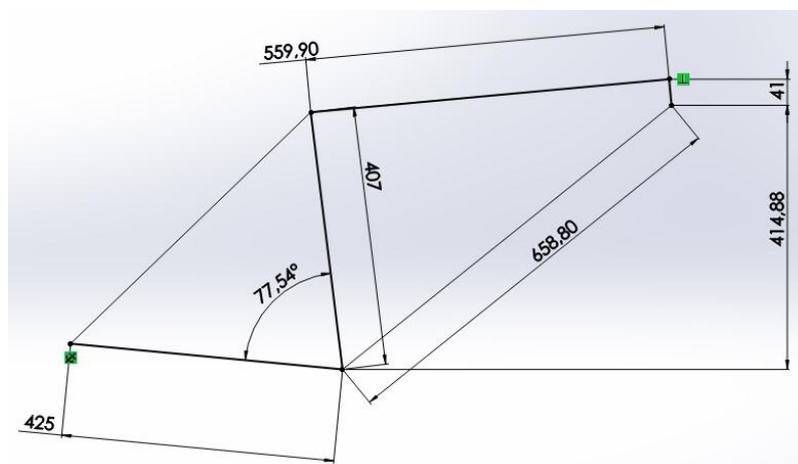


Figure 28: Measures of the Bicycle Frame Structure

These measures are going to be constants during the frame's design. Hence, the variable that should be optimized and that would ensure that the frame is resistant enough will be the bars diameter. It has to be big enough to support the weight of the person and, at the same time it has to be as thin as possible in order to reduce the weight of the frame as much as possible.

To start with the design, the charges to which the part is subjected and the different restrains have been simulated thanks to the software SolidWorks with a first diameter of 8 cm. The geometry of the model is shown in Figure 29.



Figure 29: Geometry of the First Model with 8 cm Diameter

To simulate the restrictions of movement of the piece three surfaces of the frame have been fixed, having prohibit the horizontal and vertical movement and the rotation. These three surfaces are the two holes that would contain the axis of the rear wheel and the hole for the driving wheel, as shows the Figure 30.

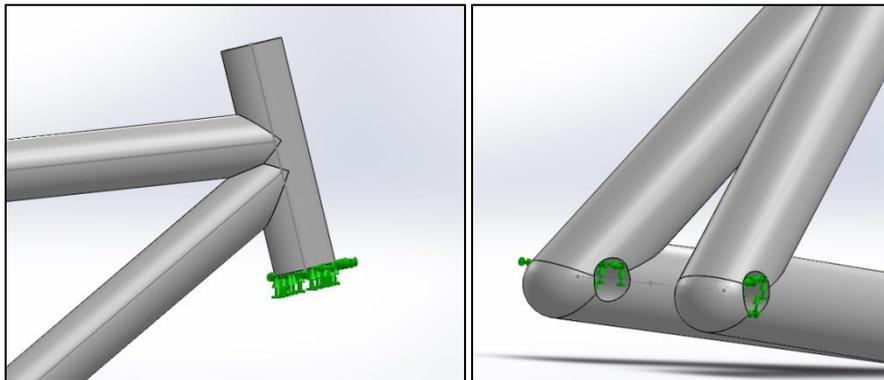


Figure 30: Details of the Subjections of the Frame

It is known that the medium weight of the Spanish population is about 75 kg. However, the forces simulate a weigh of about 200 kg (2000 N) to include a security factor that simulates external forces that an inaccurate driving can produce. Hence, 1700 N are applied on the surface where the bicycle seat will be and the others 300 are considered to be applied on the handlebar. Both forces are perpendicular to the ground. All restrictions of the model are shown in Figure 31.

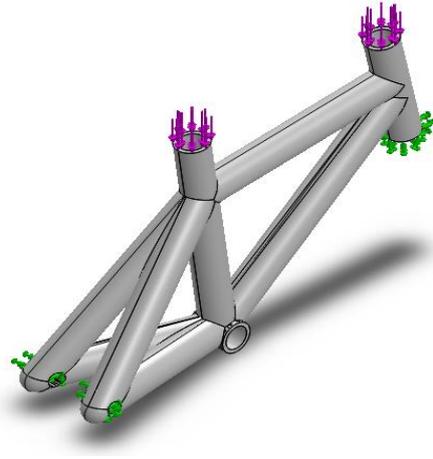


Figure 31: Frame Model with the Forces and the Fixations

The SolidWorks simulator uses the finite element method to solve and analyse the part. Hence, this methodology needs a mesh to be solved. The one used in this model is represented in Figure 32 and contains 11735 finite elements with 19868 nodes.

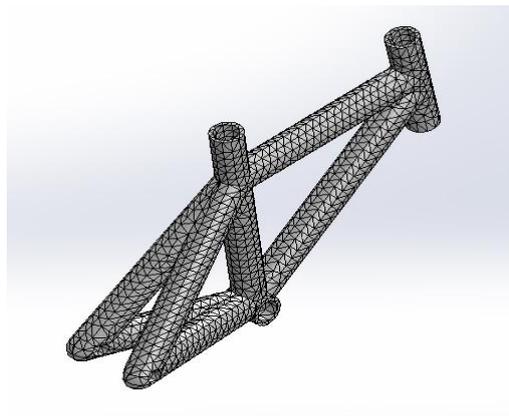


Figure 32: Model Mesh

To finish with the restrictions the last thing that has to be specified is the material. As the SolidWorks simulator does not have the recycled PET in its database, a new material with its characteristics has been created. It means a new plastic with an Elastic Modulus of 1630 MPa instead of the 2960 MPa of the original PET and a rupture stress of 24 MPa, instead of the 47 MPa of the PET [36].

8.1.1 Solutions

Once the model is solved two aspects of the simulation are important for this study. The first one is the stress of the components and the other one is the displacement.

The solution of the first part of the study, the internal stress is the one shown in Figure 33.

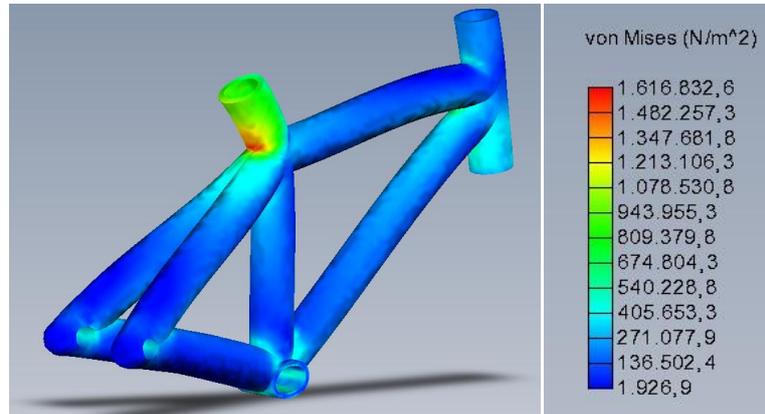


Figure 33: Distribution of Von Misses Stress with its values

As the Figure 33 shows, the biggest stress is located in the bottom of the tube that will support the seat. This result was predictable because is the bar which support the higher force and moreover, the section where the force is applied is not solid, but hollow due to the hole for the seat. Its value is 1,62 MPa, far away from the rupture limit which, as it was said before is 24 MPa. That result demonstrates that the diameter can be reduced because the part is far away from the rupture limit. Moreover, the displacement solution is represented in Figure 34 and shows similar conclusions, being the maximum displacement located in the same tube and has a value of 0.17 mm.

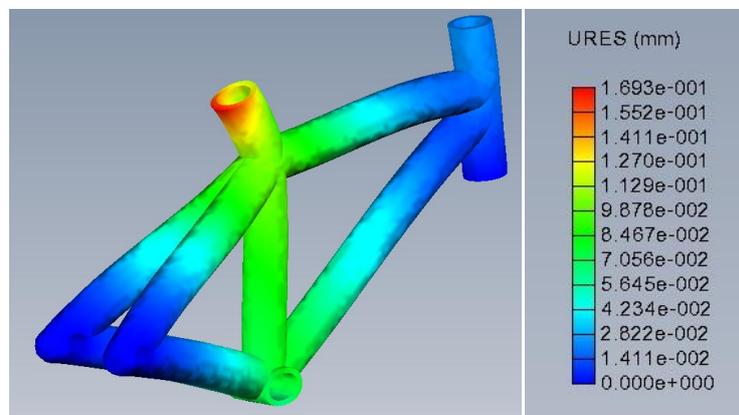


Figure 34: Nodal Displacement with its Values

8.2 Optimization Process

The structure of the frame is going to be studied in order to determine the minimum section of every bar that can hold the specified weight. With this aim, the software ftool is used to simplify some of the calculations. Hence, the structure has been simulated on it with the same specifications explained in section 2.1 as Figure 35 shows.

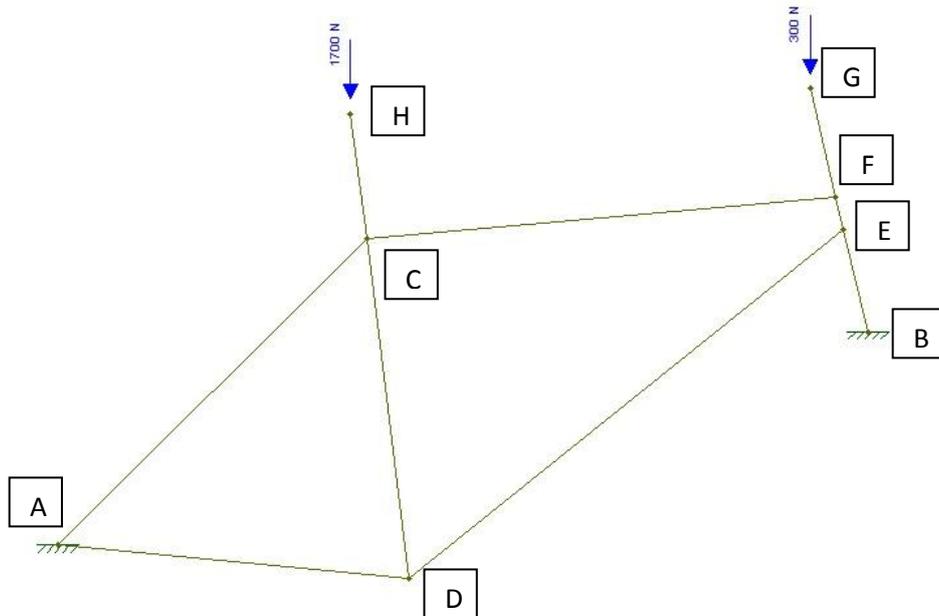


Figure 35: Representation of the Model with the Restrictions in ftool

The different nodes have been named with letters from A to H to simplify the following explanations. The criterion to define the minimum section is the maximum bending moment. ftool gives the torque diagram in which is possible to see the behaviour in every bar in Figure 36.

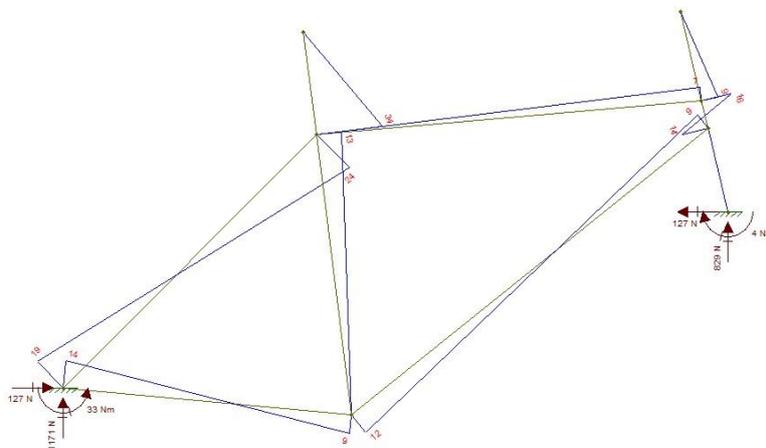


Figure 36: Bending Moment Diagram

The torque diagram shows that the maximum stress is in the node named C and its value is 34 N·m. It was predictable because is the zone of the frame that suffer more stress in the simulation. Some reactions appear in the points which have restrictions of movement. Table 9 summarizes these values.

Table 9: Reactions Values

Reactions in A	
Horizontal	127 N
Vertical	1171 N
Torque	33 Nm
Reactions in B	
Horizontal	127 N
Vertical	829 N
Torque	4 Nm

With these values it is possible to calculate now the theoretical section of the bars.

The criterion is that the bending stress σ (formula 31) in the point of every bar where the torque is maximum has to be below the rupture modulus of the material, the recycled PET in this case.

$$\sigma = \frac{M}{I} \cdot y_{max} \quad (31)$$

Where M is the torque, I is the moment of inertia, and y_{max} is the major distance to the neutral plane. In this structure there are tubular and circle sections represented in Figure 37, hence:

$$I_{circle} = \frac{\pi \cdot R^4}{4} \quad (32) \quad I_{tube} = \frac{\pi \cdot (R^4 - r^4)}{4} \quad (33)$$

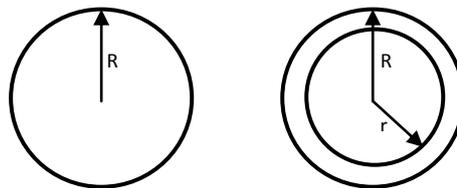


Figure 37: Circle and Tubular Section

$$y_{max} = R \quad (34)$$

The equations 35 and 36 can be deduced combining equations 31, 32 and 34.

$$\sigma = \frac{M}{\frac{\pi \cdot R^3}{4}} \quad (35)$$

$$R_{circle} = \sqrt[3]{\frac{M}{\frac{\sigma \cdot \pi}{4}}} \quad (36)$$

The equation 37 can be deduced combining equations 31, 33 and 34.

$$\sigma = \frac{M}{\frac{\pi \cdot (R^4 - r^4)}{4}} \quad (37)$$

There are two unknown values in equations 35 and 37 (R and r). Hence it can be solved as an equation system with two equations and two unknowns.

$$24 \cdot 10^6 = \frac{13}{\frac{\pi \cdot R^3}{4}} \quad (38)$$

$$24 \cdot 10^6 = \frac{34}{\frac{\pi \cdot (R^4 - r^4)}{4}} \quad (39)$$

This equation system does not have a solution. That means that the diameter which will minimize the circle section is not enough for the bars with the tubular section. For this reason, a different procedure is needed. To start, it is calculated the minimum radius for the circle section, with equation 36, which results 0.88 cm. Starting with this value the equations are going to be solved by iteration. Hence, the final values for each radius that theoretically support the forces are the following ones:

$R = 2 \text{ cm} \longrightarrow D = 4 \text{ cm}$ $r = 1.8 \text{ cm} \longrightarrow d = 3.6 \text{ cm}$
--

With these values now it is possible to create and simulate the optimized frame.

8.3 Final Part

Finished the calculation part, the optimized frame that is going to be produced weight 6,2 kg. It means that the weight of the first design has been reduced 18 Kg with the procedure of optimization and this final design can be seen in Figure 38.

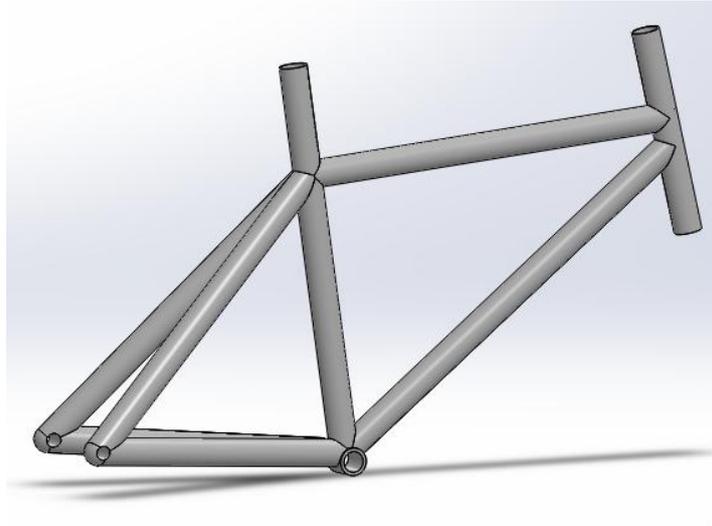


Figure 38: Final Design

Once the part is constructed, it is necessary to do a final simulation in order to prove that the calculations were correct and the frame would support the conditions explained in section 2.1. The first solution obtained is the Von Misses Stress in Figure 39.

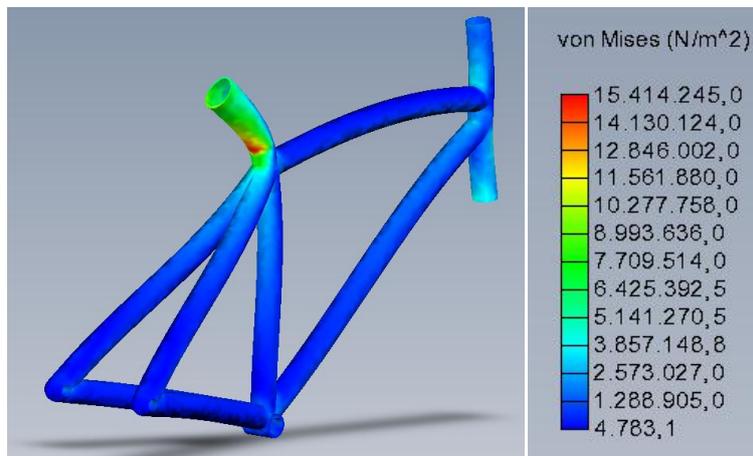


Figure 39: Distribution of Von Misses Stress of the Final Design with its values

The maximum stress is again in the bar that sustains the seat and its value is 15 MPa. This value is closer to the rupture limit which is 24 MPa, but it is low enough to assure that the frame would support the forces with a security factor.

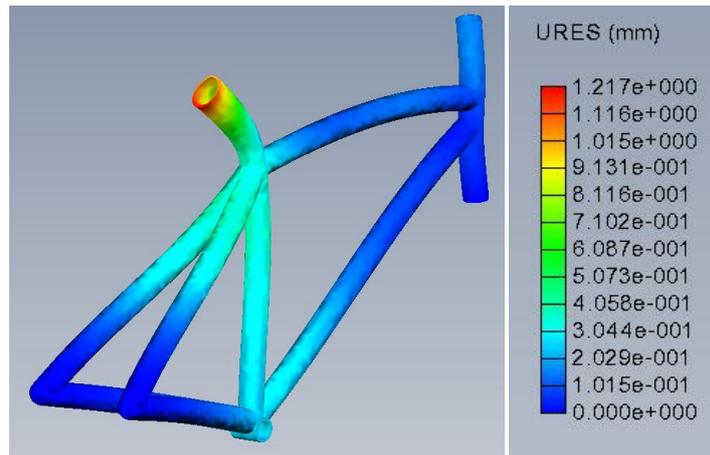


Figure 40: Nodal Displacement of the Final Design with Its Values

Concerning the displacement showed in Figure 40, this time the zone coloured in red will move about 1 mm. This is an acceptable displacement, having in account that the forces to which is submit the piece are extreme and they double the current values to have a security coefficient.

8.4 Improvements

The frame design explained in 8.5 would work properly as it was demonstrated. But there is a last improvement that would help the part to suffer less stress in the critical zones. As it was explained in the optimization process, the inertial moment of the bars section is a critical value to determine the stress in these sections. Due to this, it was decided to design the model with an oval section instead of the circle one. This change would decrease the stress by increasing the inertial moment and having a similar mass. For this reason, the final design has the section dimensions as Figure 41 shows.

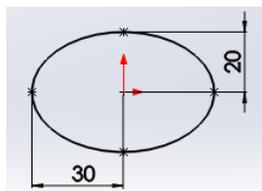


Figure 41: Dimensions of the Final Section of the Bars (mm)

Finally, the produced frame would have a shape as the shown in Figure 42.

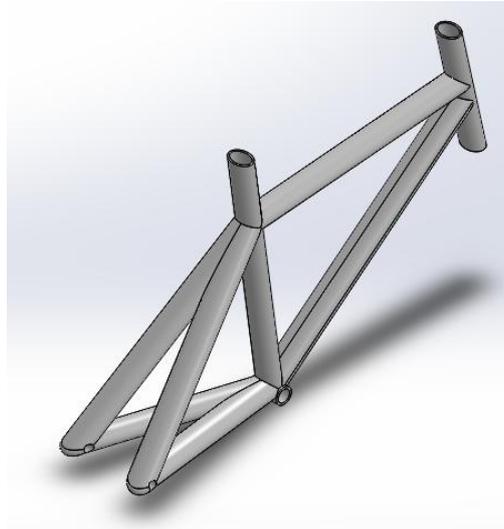


Figure 42: Final Frame Geometry

Again, it is necessary to simulate the forces to prove that the new geometry would support them. It is shown in Figures 43 and 44.

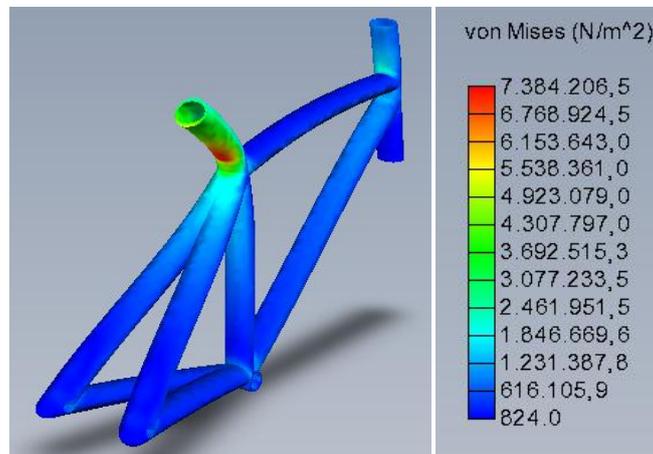


Figure 43: Distribution of Von Misses Stress with the Oval Section

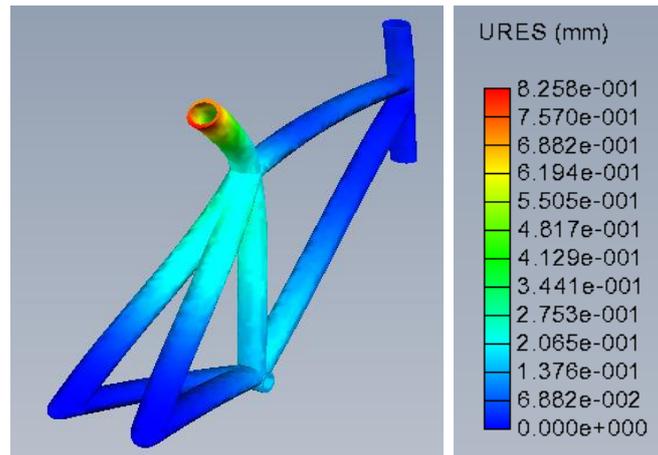


Figure 44: Nodal Displacement with the Oval Section

As it can be seen in Figure 43 the maximum stress with the new section is placed in the same zone that the final design in section 8.3, but it has been reduced until 7.4 MPa thanks to the inertial moment of the oval section. In regards to the displacement, the maximum displacement is 0.82 mm. Otherwise, the frame weight now 9,5 Kg, instead of the 6 Kg of the final design. It means that it is now a bit heavier than before, but the stress reduction is more significantly in comparison. Hence, this will be the geometry manufactured.

8.5 Mould Design

Once the part has been totally designed the next step is make the mould with the geometry of the final frame. In this case, the mould had to be divided in three different parts in order to achieve a correct demoulding. It is impossible due the geometry in different planes of this piece to have a simple mould with two parts. Hence, there are two equal parts of the mould that involve de structure as shows Figure 45.

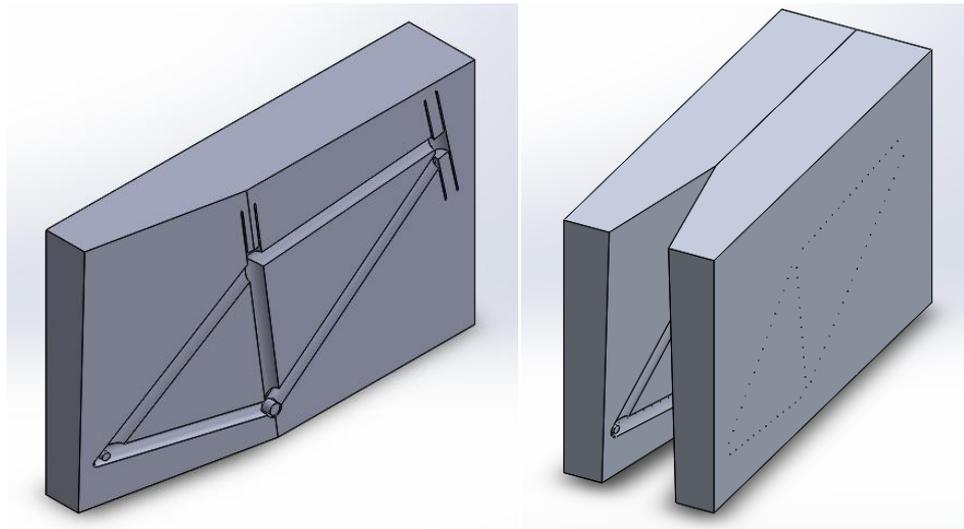


Figure 45: Symmetric Parts of the Mould

The part that would complete such a mould is the one which cut the solid cube that involve the frame with the planes that contain the paired rear triangles. Hence, the piece obtained due to this intersection is shown in Figure 46.

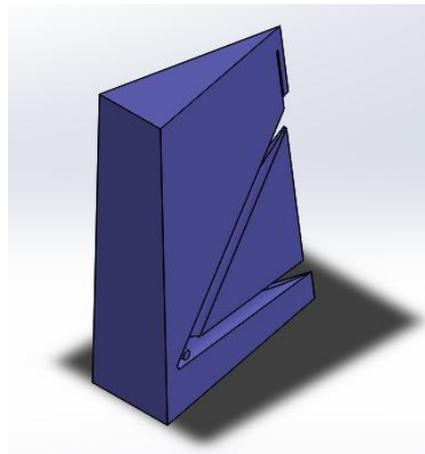


Figure 46: Back Part of the Mould

Thus, if the three parts are assembled as in Figure 37, the mould adopts a cubic shape that can fit in the machine and easy demoulding process. In addition, the mould has to have some lockers in order to maintain it in the correct position during all the injection cycle.

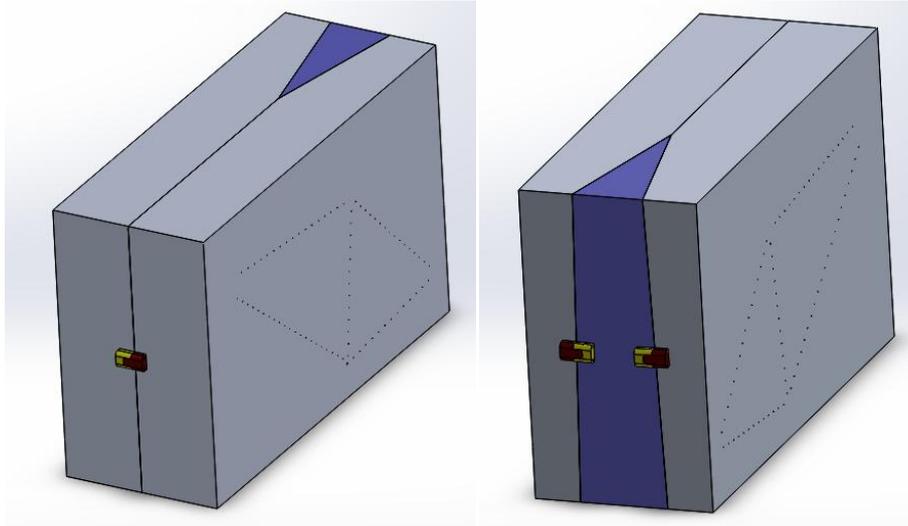


Figure 47: Assembled Mould

The material chosen to manufacture the mould is 2024 Aluminium alloy, because is proper to mould design and can easily make moulds capable of 100.000 or more part life with proper maintenance. Aluminium's density is 2800 kg/m^3 , and the final dimensions of the mould (see Appendix II) are $1100 \times 400 \times 700 \text{ mm}^3$, which means a volume of 0.308 m^3 . Hence, the total weight of the three parts together is 850,14 kg.

Moreover, there has to be a gate where the raw material can enter by. Gate, in plastic injection moulding plays an important role which has always been overlooked. The gate in a mould is designed to reheat the molten polymer at perhaps the most crucial cycle time, mainly filling. This is the place at the molten paths where other possibilities such as heating elements, screw actions, and others are non-existent [37]. Shear rate and temperature affect the viscosity of the material; hence they are two important factors in injection moulding. It can be seen in Figure 48 how shear stress is related with viscosity and moreover, this relation changes at different temperatures.

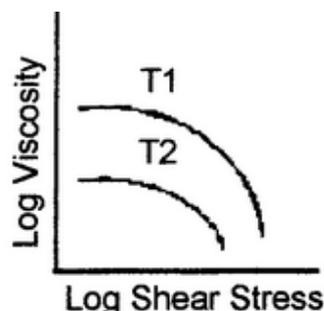


Figure 48: log Viscosity – log Shear Stress Depending on Temperature

It could be assumed that by raising the shear rate sufficient heat can be added to the melt to allow processing with no additional external heat input. Hence, the higher the shear rate, the better the injection process. However, every material has a critical shear rate determined by the suppliers adequate to injection (in the case of PET this critical value is $50.000s^{-1}$). Above this rate, the polymer melts fracture and the molecular weight is reduced. This reduction will debase the material properties. In some cases where the shear rate has been exceeded the effect may be very local and only in the area where the problem occurred. Hence, the speed should be matched with the gate size. The critical dimensions for the gate are the gate width and the gate thickness or diameter. The smaller the thickness, the lower is the safety threshold for gate shear rate [38].

$$S.R. = \frac{32 \cdot Q}{\pi \cdot D^3} \quad (40)$$

Where S.R. means Shear Rate (s^{-1}); Q is volume flow rate (cm^3/s) and D the diameter of the gate (cm). Hence, the adequate diameter in this case is calculated in equation 41.

$$D = \sqrt[3]{\frac{32 \cdot 500}{\pi \cdot 50 \cdot 10^3}} = 0.46 \text{ cm} \quad (41)$$

Drawings of the final mould design with its gate and the lockers can be seen in Appendix II .

Conclusions

The original objectives of this project were to discover a ready commercially available polymer with the adequate properties in order to manufacture the frame of a bicycle, at the same time caring as much as possible about the environment. Besides, if this polymer exists, it is necessary to review the injection moulding possibilities that to design the part and, also, find out if a production of such frames is economically viable.

After the initial discussion on the essential properties of the chosen polymer and its possible properties' variations which depend on a number of different factors (i.e., polymer rheology, etc.), the conclusion has been made that a recycled polyethylene-terephthalate (PET) considered as the exact polymeric candidate that fits with the specifications imposed, which are described at the thesis beginning. Moreover, PET is a polymer that easy to mould by injection moulding and it has the adequate properties of stiffness and strength to perform the function of the bicycle frame.

The discussed in the thesis recycled PET remains its main mechanical properties quite similar to a virgin PET. This reinforces the initial choice of the recycled PET as the main project material, as it also should provide a step forward towards some reduction of plastic waste growing up in our planet, which becomes even more worrisome on a daily bases. Thus, such an industrial R&D project specifically targeting use of a recycled plastic looks as a reasonable initiative to tackle the rising problem. This material also means an advantage for the industry as it stays lighter, cheaper and easier to process than aluminium or steel.

The provided economical studies show that the bicycle market has been a growing trend in recent years. Hence, it seems a suitable moment to start a business in the sector. Furthermore, if the predictions have done well, this project for Barcelona looks currently extremely viable.

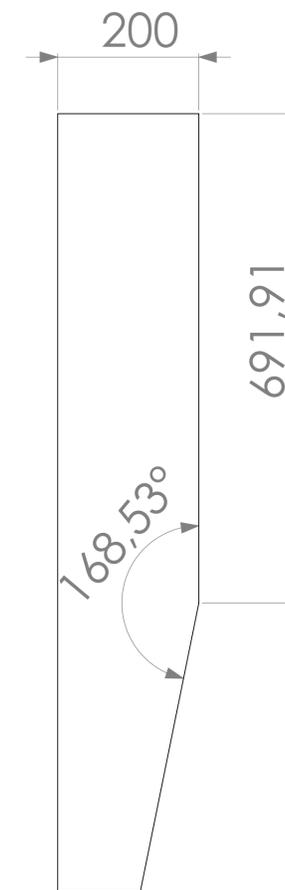
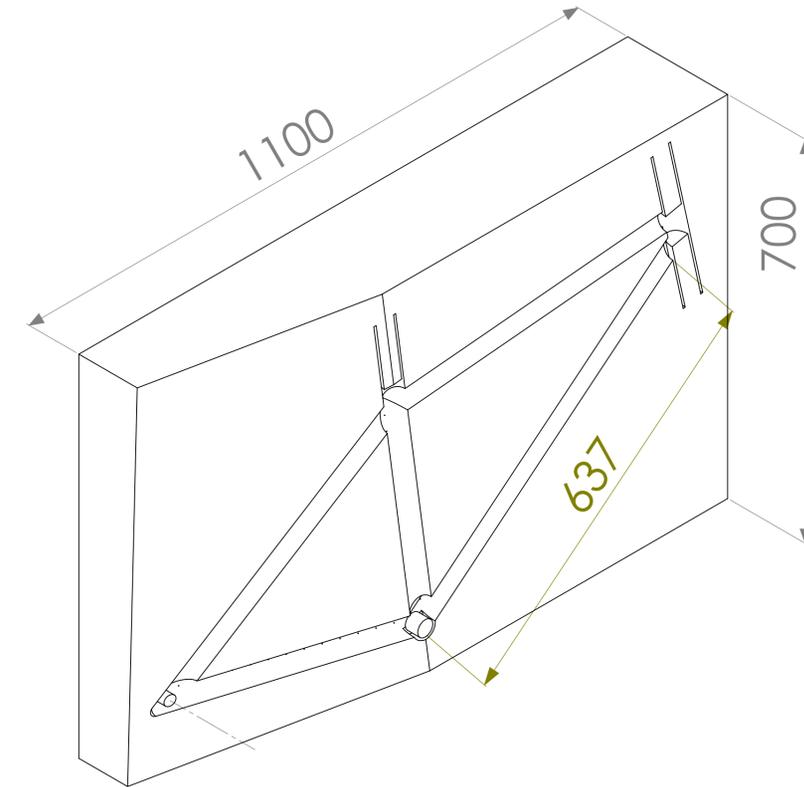
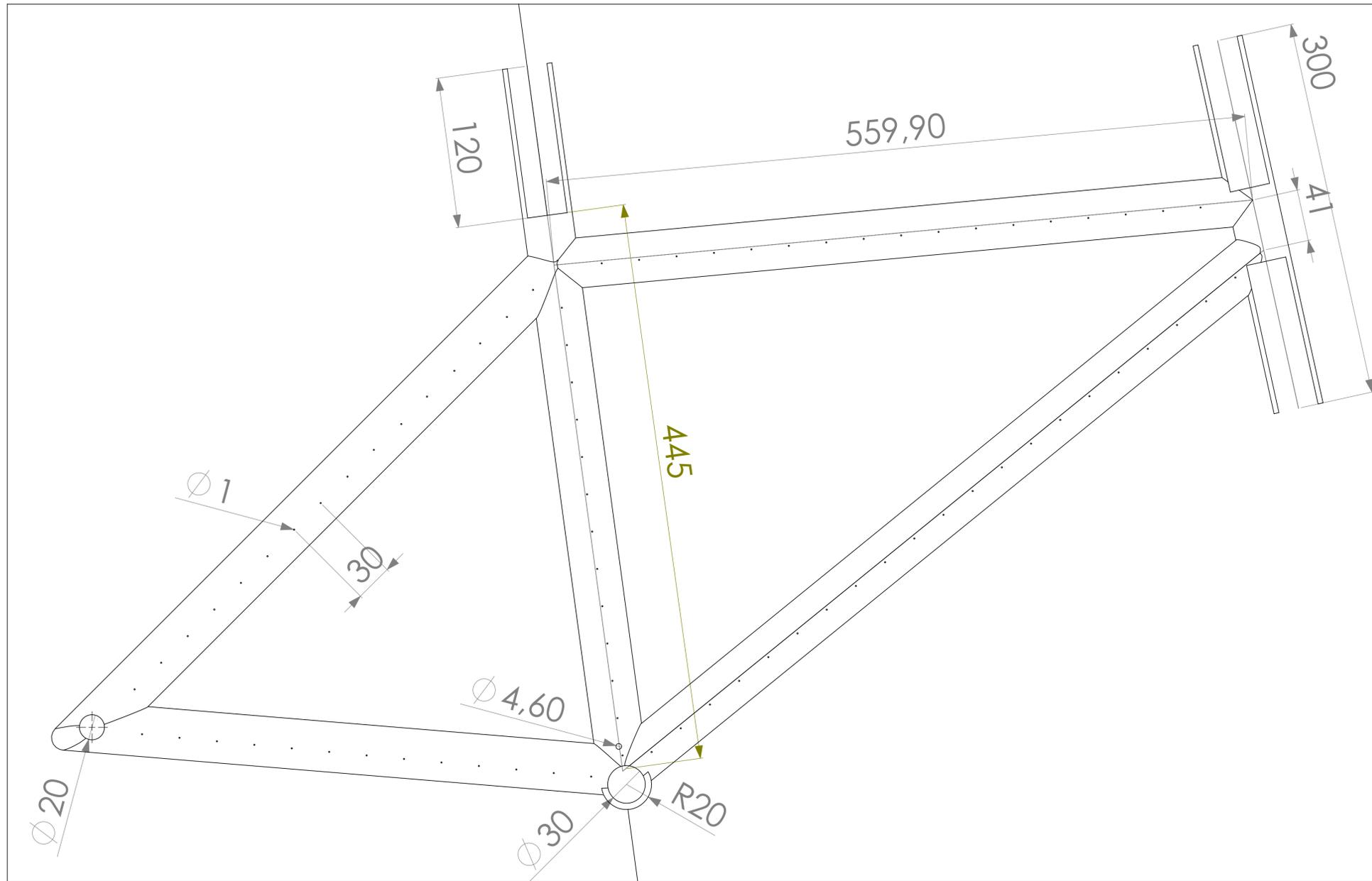
In regards to the frame design the obtained in the thesis results state that with a maximum diameter of 4 cm the bars are able to support up to 2.000 N forces distributed between the seat and the handlebar. The initial mechanical design may also be further improved by use of oval frame cross-section rather than the circle one. The maximum possible operational stress and strain imposed on the frame will be reduced. On the other hand, the frame will suffer from some tolerable mass increase.

Once the dimensions of the frame had been fixed the suitable aluminium mould was designed, where the polymer feeding gates must be ≥ 0.46 cm of diameter to achieve a correct injection, apart from the air releasing holes which must be approximately of 1 mm in diameter.

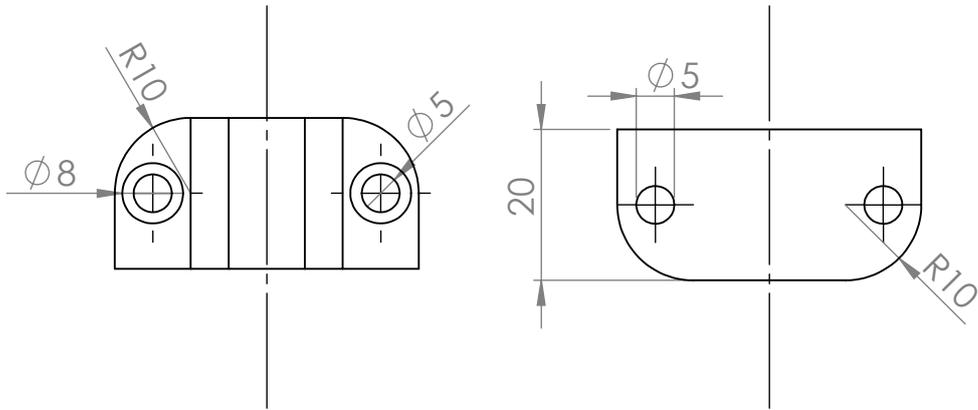
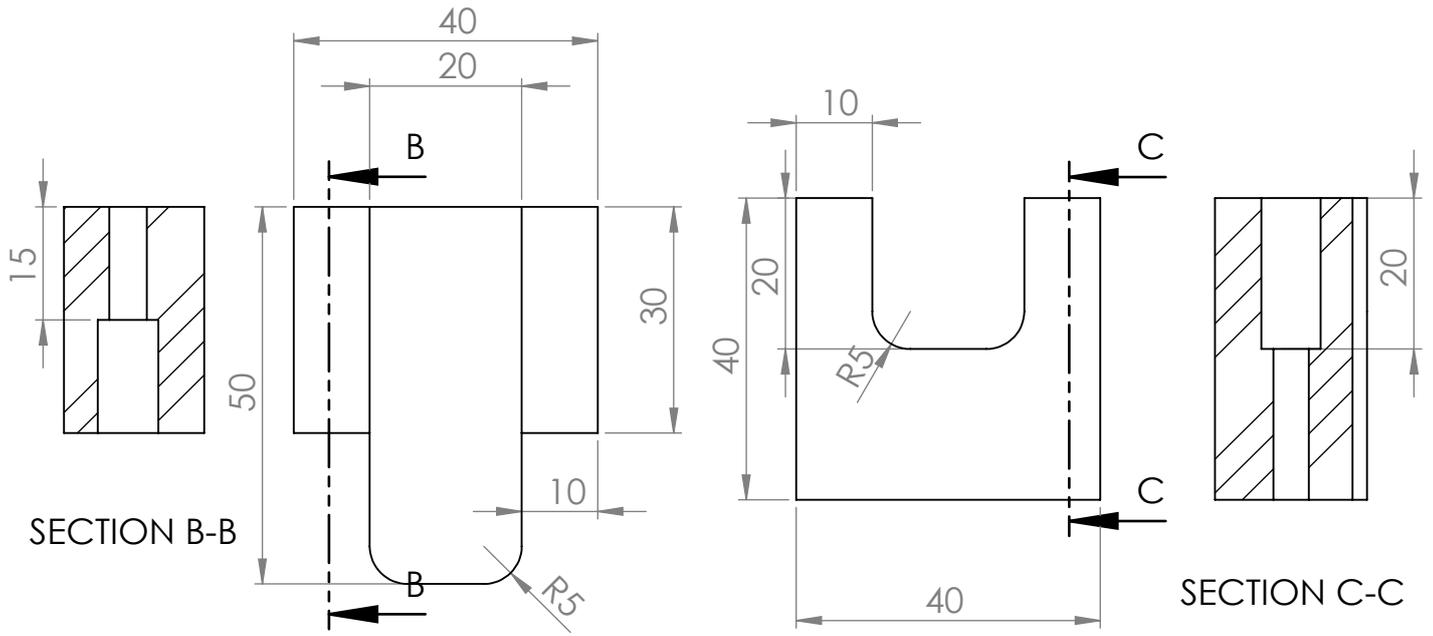
APPENDIX I: Latest Data Released by the Ministry of Promoting Spain on Daily Mobility

19. Centros habituales de trabajo. Desplazamiento más habitual. Modos empleados (ida o vuelta) por provincia

Total centros	MODOS EMPLEADOS				
	Sólo a pie menos de 5 min.	Más 5 min. a pie o bicicleta	Modos privados a motor	Modos públicos	
Total	17.820,6	1.125,5	3.803,2	11.294,2	2.922,1
Alava	133,9	7,9	34,3	81,2	12,6
Albacete	134,9	10,7	37,0	88,7	1,9
Alicante/Alacant	657,8	54,1	164,6	437,1	28,2
Almería	254,8	20,0	41,4	188,0	10,3
Ávila	58,4	9,4	11,0	36,8	2,9
Badajoz	225,6	20,0	44,6	155,5	8,4
Balears (Illes)	445,8	23,5	90,3	300,3	48,6
Barcelona	2.414,5	165,8	696,9	1.273,8	679,3
Burgos	150,8	9,8	39,1	92,8	12,1
Cáceres	139,5	10,8	34,2	92,4	4,4
Cádiz	414,1	30,6	76,5	291,9	28,6
Castellón/Castello	249,6	22,8	54,5	171,8	8,7
Ciudad Real	174,8	14,0	34,8	123,0	5,6
Córdoba	268,0	19,3	61,6	182,8	11,9
Coruña (A)	393,9	28,2	62,5	288,3	29,7
Cuenca	74,8	6,6	19,5	48,0	1,2
Girona	298,0	21,8	79,2	218,6	12,1
Granada	297,8	17,3	59,7	206,1	20,0
Guadalajara	96,0	5,4	14,3	73,5	11,2
Guipúzcoa	293,4	18,8	62,7	184,1	38,4
Huelva	177,0	8,6	44,4	121,6	6,9
Huesca	94,0	9,3	25,5	62,4	1,4
Jaén	205,4	17,4	36,2	150,3	5,4
León	174,2	12,2	40,2	116,2	8,0
Lleida	180,2	6,9	51,7	117,5	9,1
Rioja (La)	126,8	7,7	33,2	82,3	8,4
Lugo	105,4	7,4	23,7	80,4	4,4
Madrid	2.698,3	74,2	551,8	1.385,4	1.066,0
Málaga	533,2	27,3	100,2	368,8	57,0
Murcia	520,5	56,6	83,8	374,2	22,8
Navarra	254,1	16,1	46,2	177,4	23,4
Ourense	111,7	13,9	23,4	71,7	4,4
Asturias	363,7	20,0	87,3	223,1	46,3
Palencia	56,2	6,1	18,4	32,1	2,4
Palmas (Las)	432,3	14,6	63,0	314,7	62,5
Pontevedra	334,6	19,6	49,0	254,6	20,5
Salamanca	126,9	11,0	38,3	72,5	9,3
Santa Cruz de Tenerife	347,2	13,4	48,8	252,8	50,1
Cantabria	228,6	14,1	36,6	166,2	24,7
Segovia	64,2	8,0	10,7	43,1	4,1
Sevilla	668,7	33,9	90,8	496,6	70,5
Soria	38,1	4,6	14,6	20,1	0,4
Tarragona	306,8	33,8	57,1	205,2	18,0
Teruel	51,4	9,8	8,3	32,4	1,8
Toledo	236,6	18,3	35,9	170,7	19,7
Valencia/València	1.018,2	71,5	181,7	667,9	134,8
Valladolid	204,3	14,5	33,8	133,0	24,7
Vizcaya	477,9	25,2	123,6	253,3	146,2
Zamora	63,7	6,7	16,7	40,0	1,7
Zaragoza	395,2	23,3	97,6	239,3	89,7
Ceuta	24,8	1,1	8,2	14,1	1,8
Melilla	24,5	1,2	3,6	19,7	0,2



DIMENSIONS IN MILLIMETERS				DO NOT CHANGE THE SCALE		REVIEW
NAME:	SIGNATURE	DATE:		TITLE		
ELENA, JIAN		03.03.14		Bicycle Frame Mould		
				DRAWING NUMBER	1	A1
			MATERIAL: ALUMINIUM	SCALE: 1:10		PAGE 1/3
			WEIGHT: 382,56 Kg			



DIMENSIONS IN MILLIMETERS		FINISHED		DO NOT CHANGE THE SCALE		REVIEW	
NAME:		SIGNATURE		DATE:		TITLE:	
ELENA JUAN				03.03.14		Mould Locker	
				MATERIAL: ALUMINIUM		DRAWING NUMBER	
						3	
				WEIGHT: 0,38 Kg		A4	
				SCALE:1:1		PAGE 3/3	

REFERENCES

1. Bryce, D. M. (1996). *Plastics Injection Moulding. Manufacturing Process Fundamentals*. SME Dearborn.
2. Mary Bellis; (2006). <http://inventors.about.com/>. Accessed on February 2014.
3. Edge M, Hayes M, Mohammadian M, Allen NS, Jewitt TS, Brems K, Jones K;(1991). Aspects of poly (ethylene terephthalate) degradation for archival life and environmental degradation. *Polym Degrad Stab*
4. Taringa News; (2012) "Cuadro de Bicicletas de botellas de coca cola recicladas" available in www.taringa.net
5. Alfred Rubin; (1998) "The Elements of Polymer Science and Engineering" Academic Press, University of Waterloo
6. Andrew Streitwieser, Clayton H. Heathcock and Edward M. Kosower; (1998) "Introduction to Organic Chemistry" Prentice Hall, New Jersey
7. Robert O. Ebewele; (2000) "Polymer Science and Technology" CRC Press LLC, USA
8. Fluka- Sigma Aldrich on-line catalogue (includes Charles J. Pouchert; (1975) "The Aldrich Library of IR Spectra")
9. Paul C. Painter and Michael M. Coleman; (1997) "Fundamentals of Polymer Science" A Technomic Publishing Company
10. Prof. J. Storasta; (2002) Course of Lectures for Postgraduate Students in a Light Absorption in Polymolecular Materials, Physics Faculty, Vilnius University
11. Edward M. Kosower; (1968) "Physical Organic Chemistry" John Wiley & Sons, Inc.
12. G. G. Freeman; (1962) "Silicones an Introduction to Their Chemistry and Applications" published for the Plastic Institute, London
13. Stephen J. Clarson and J. Anthony Semlyen; (1993) "Siloxane Polymers" PTR prentice Hall, Englewood Cliffs, New Jersey
14. Haifa El-Sadi, Nabil Esmail and Ibrahim Hassan; (2007) "Numerical Modelling of Non-Newtonian Flow in Viscous Micropump" *Journal of the Society of Rheology* Vol. 36, No 1, pp 51-58
15. M. Doi and S. F. Edwards; (1986) "The Theory of Polymer Dynamics", Clarendon Press, Oxford
16. J. D. Ferry; (1980) "Viscoelastic Properties of Polymers" Third edition, Wiley, New York
17. L. E. Nielsen; (1962) "Mechanical Properties of Polymer" Reinhold, New York
18. Verlang GmbH & Co. KGaA; (2010) "Functional Fillers for Plastics: Second, updated and enlarged edition" Marino Xanthos, Weinheim

19. Douglas M. Bryce; (1996) "Plastics Injection Molding. Manufacturing Process Fundamentals" SME, Dearborn
20. Herbert Rees; (1994) "Understanding Injection Molding Technology" Hanser Publishers, New York, 1994
21. Ramón Anguita Delgado; (1975) "Moldeo por Inyección" Ed. Blume
22. Interficto SEO LinkBuilding; (2010) "Tipos de plásticos que pueden ser reciclados", articulo.org
23. TransformaHogar; "Como identificar los seis tipos de plásticos más habituales en envases y para que se pueden reutilizar", available in www.transformahogar.com
24. Scrap y Rezagos srl (2013), "Reciclado de Plástico", available in www.rezagos.com
25. Quimic Department (2005) "Propiedades y Características del PET" Universidad de Valladolid
26. Industrias JQ; (2013) "Polietileno Tereftalato: Propiedades" available in www.jq.com.ar
27. Marga Castillo; (2013) "En España ya se venden más bicicletas que coches", published in Expansion Diary
28. CMD Sports; (2013); "El precio medio de las bicicletas sigue escalando" available in www.cmdsport.com
29. Consorcio Investigador ProBici in association with Government of Spain; (2007) "ProBici: Guía de la Movilidad Ciclista"
30. "Informe d'activitats de la Mobilitat a Barcelona" Prevention, Security and Mobility Section of the Government of Barcelona
31. Kunststoffe internacional 10/2007. Carl Hanser Verlag, Munich, Germany. World Market.
32. PCI, PETCORE ; (2007) "Post Consumer PET Recycling in Europe 2006 and Prospects to 2011" Report October
33. Budget of Industrias Romi S.A. ; (2013) available in www.romi.com
34. Budget for Recycled PET of QuimiNet; (2013) available in www.quiminet.com
35. www.buscador.habitaclia.es
36. Mariano; (2011)"Proceso de Reciclado del PET" available in www.tecnologiadelosplasticos.blogspot.com
37. Dr. M. Tabrizi; "The Importance of Gate and Gate Size in Injection Mold" Center for Plastics Processing Technology Focus on Energy
38. J. Barry Smith; (1999) "Injection Moulding - Gates and Runners" The JBS consultancy

