escola superior de tecnologia e gestão
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CircularSeas

Master in Product Design Engineering

Ana Costa

Leiria, September of 2020

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Master's Projet report held under the guidance of Doctor ESTG Supervisor Fábio Simões, Professor of the Higher School of Technology and Management of the Polytechnic Institute of Leiria and co-orientation of Doctor ESTG Co-Supervisor Artur Mateus, Professor at the Higher School of Technology and Management of the Polytechnic Institute of Leiria.

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Abstract

In recent years the problem of pollution has been increasingly debated, and one of the main issues discussed is related to the degradation of the oceans as a consequence of human activities. Polymeric materials are one of the main elements identified both on the coast and in the ocean itself, which causes several consequent adversities, both for human life and for the natural world. In order to analyze the possibility of reusing or reprocessing material usually considered waste, it is important to determine the type of properties that have been altered and what effect it would have on its use as a new raw material. Due to the limited amount of literature available on this subject, a large amount of polymeric material was collected from Peniche and Vieira beaches, Leiria, Portugal. As most identifiable objects were octopus traps and fishing nets, and knowing that this type of product is usually made of high-density polyethylene and polyamide, respectively, these were the materials chosen for analysis. The high density polyethylene was analysed both before and after processing, while on the case of the polyamide, only the processed material was analysed. Tensile, Dynamic Mechanical Analysis and hardness tests were performed after the necessary preparation. Comparing the values obtained in each case with the respective measurement of the virgin material, it was possible to observe that some properties, such as Young's modulus, tension and tensile strength decreased considerably. Hardness was also affected, although it was less notorious. Seawater absorption tests were also carried out on virgin high density polyethylene in order to determine the amount of time the waste was under the influence of environmental degradation by comparing its density values over time with the density of waste material. However it was not possible to draw concrete conclusions since, in the case of density, it can easily vary depending on the type of conditions to which the material was subjected, which are unknown; on the other hand, the Dynamic Mechanical Analysis tests, used in the determination of the glass transition temperature, were inconclusive regarding high-density polyethylene since the value of this characteristic in the virgin material is lower than zero and, as the initial temperature used in the tests was the ambient temperature, it was not possible to determine the desired result, while this characteristic on the nylon waste decreased due to the material's deterioration. After this project was carried out it was concluded that it is very important to correctly characterize this type of materials, not only at the mechanical level, but regarding other engineering fields, for example, at chemical level. Although some advantageous characteristics of virgin materials are lost, waste is still usable in different forms for new purposes, and can be treated as a new source of raw material.

Keywords: Marine litter, ocean pollution, mechanical properties, high density polyethylene, polyamide

Resumo

Nos últimos anos o problema da poluição tem sido cada vez mais debatido, sendo uma das principais questões relacionada com a degradação dos oceanos como consequência das atividades humanas. Os materiais poliméricos são um dos principais elementos identificados tanto na costa como no oceano, facto que acarreta diversas consequências, tanto para a vivência humana como para o mundo natural. Com o objetivo de analisar a possibilidade de reprocessar material desperdíçado, é importante determinar o tipo de propriedades que foram afetadas e o efeito que teria na sua utilização como nova matéria prima. Devido à limitada literatura disponível sobre esta matéria, uma grande quantidade de material foi recolhido das praias de Leiria, Portugal. A maioria dos objetos identificáveis eram armadilhas de polvos e redes de pesca, sabendo que a este tipo de produto é normalmente feito de polietileno de alta densidade e poliamida, respetivamente, estes foram os materiais escolhidos para analise. Após a limpeza das armadilhas, foram efetuados testes mecânicos a uma parte do material e o restante foi triturado e processado. Neste caso, testes à tração, à dureza e Dynamic Mechanical Analysis foram efetuados tanto ao material recolhido como ao injetado, no caso das redes de pesca apenas o material processado foi analisado. Comparando os valores obtidos em cada caso com a respetiva medida do material virgem, foi possível observar que propriedades como o modulo de Young e a resistência à tração diminuíram consideravelmente. A dureza também foi afetada, apesar de ser menos notório. Foram também efetuados testes de absorção de água do mar ao polietileno com o objetivo de determinar a quantidade de tempo que o desperdício esteve abandonado através da comparação dos seus valores da densidade ao longo do tempo com a densidade do material recolhido. No entanto, não foi possível retirar conclusões concretas uma vez que os valores podem facilmente variar dependendo do tipo de condições a que foi sujeito. Já os testes de Dynamic Mechanical Analysis no polietileno, foram inconclusivos uma vez que o valor desta característica no material virgem é menor do que zero e como a temperatura inicial usada nos testes foi a temperatura ambiente, não foi possível determinar o resultado pretendido, enquanto que no caso da poliamida esta caracteristica térmica diminuiu de valor devido à degradação que sofreu. Após efetuado este projeto verificou-se que é importante proceder á correta caracterização deste tipo de materiais, não só a nível mecânico, mas também outro tipo de áreas de engenharia. Apesar de serem perdidas algumas características vantajosas dos materiais virgens, o desperdício não deixa de ser utilizável de diferentes formas e para novos fins, podendo ser tratado como uma nova fonte de matéria prima.

Palavras-chave: Lixo marinho, poluição marinha, propriedades mecânicas, polietileno de alta densidade, poliamida

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ε_{tB}	Nominal strain at tensile strength
ε_{tM}	Nominal strain at break
ε_{Y}	Yield strain
ρ	Material density
$\rho_{water@T^{\circ}C}$	Water density at certain temperature
σ_{B}	Stress at break
σ_{M}	Tensile strength
σ_{x1}	Stress at x_1% strain
σ_{Y}	Yiels strength
A_0	Cross-section area
A_1	Increment applied on the first wall of the square
A_2	Increment applied on the second wall of the square
A_3	Increment applied on the third wall of the square
A_4	Increment applied on the fourth wall of the square
b	Specimen width
E	Young’s modulus
h	Specimen thickness
m_{out}	Material’s mass outside water
$m_{submerged}$	Material’s mass submerged
Tc	Crystallization Temperature
Tg	Glass Transition Temperature
Tm	Melting Temperature
x_1	Angle applied on the first wall of the square
x_2	Angle applied on the second wall of the square
x_3	Angle applied on the third wall of the square
x_4	Angle applied on the fourth wall of the square

Acronym List

3D	Three-Dimensional
ABS	Acrylonitrile Butadiene Styrene
CHN	Carbon, Hydrogen and Nitrogen rate
DMA	Dynamic Mechanical Analysis
DSC	DifferentialScanning Calorimetry
ESTG	Escola Superior de Tecnologia e Gestão
FDM	Fused Deposition Modeling
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
MFI	Melt Flow Index
PA	Polyamide
PE	Polyethylene
PET	Polyethylene Terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
SEM	Scaning Eletron Microscope

Contents

1 Introduction

On the last decades the production and application of plastic has developed to the point of becoming one of the most common and widely used materials in diverse applications. It is estimated that the global production of plastic materials increased "dramatically from 1,5 million tonnes in the 1950s to approximately 322 million tonnes in 2015". Although there are several options for a controlled debris' disposal created by the intense utilization of this kind of elements, a large quantity ends up on landfills or lost, and must of the times this waste reaches the ocean. These plastic components represent 97% of all the litter in the ocean, being now not only a environmental issue, but also a public health problem [1].

This is why it is important to develop new ways of creating an alternative future for these materials and implement them as far as possible. This project will analyse the possibility of using ocean polymeric waste as material to produce pellets or even filament for rapid manufacturing processes.

On an initial stage a large quantity of litter was collected and treated in order to evaluate the mechanical and thermal properties through several studies made, including Dynamic Mechanical Analysis, tensile, hardness and sea water absorption tests. The main goal is to identify the mechanical properties of the waste material and compare them will both the virgin equivalent material and the final processed material obtained. After this test phase it will be possible to analyse the possibility to process it by injection molding or filament extrusion after the proper material preparation.

2 Initial Concepts

Today the waste management is a regularly discussed issue. Although several legislations were revised to increase control, studies developed to research new solutions and summits organized all around the world with active interventions on the problems identified, yet according to numerous scientists and experts there is not much done to actually reverse the predicted hazards.

2.1 Oceans and Beaches Litter Current Situation

Marine litter “Marine litter is defined as any persistent, manufactured or processed solid material discarded, disposed or abandoned in the marine and coastal environment” [2]. Either these elements were left on the environment intentionally or not, their presence is very harmful. Most of the materials found are plastics, paper, metal, wood and textiles. Although the beginning of industrial utilization and production of polymeric materials was relatively recent (beginning of the 20th century), plastics have gained the title of one of the most used materials around the world and in a widely range of applications. Due to its place in actual society, its presence on the environment as a residue is a dominant problem [3].

Polymeric materials in marine litter Polymeric materials represent the vast majority of marine litter found, it is estimated that between 60 and 80% of the total debris found are made of this type of material [2]. Figure 2.1 represents a summary of the information obtained during a study along the Portuguese and Moroccan coasts. The goal was to identify the main types of litter found on the Atlantic southern Europe and Northern African coasts, since this area is still very unknown on this matter. These results represent a situation recurrent on other akin literature [1].

Types of plastic litter There are two different types of plastic litter that can be classified depending on its dimensions, micro (dimensions smaller than 5 millimeters) and macro plastics (dimentions greater than 5 millimeters). Usually, the macro plastics tend to brittle and crumble into fragments increasingly smaller, reaching eventually the micro scale. However, the time that it takes for the polymeric material to degrade in marine conditions is yet unknown. Six major groups of polymeric material constitutes about 90% of the total production

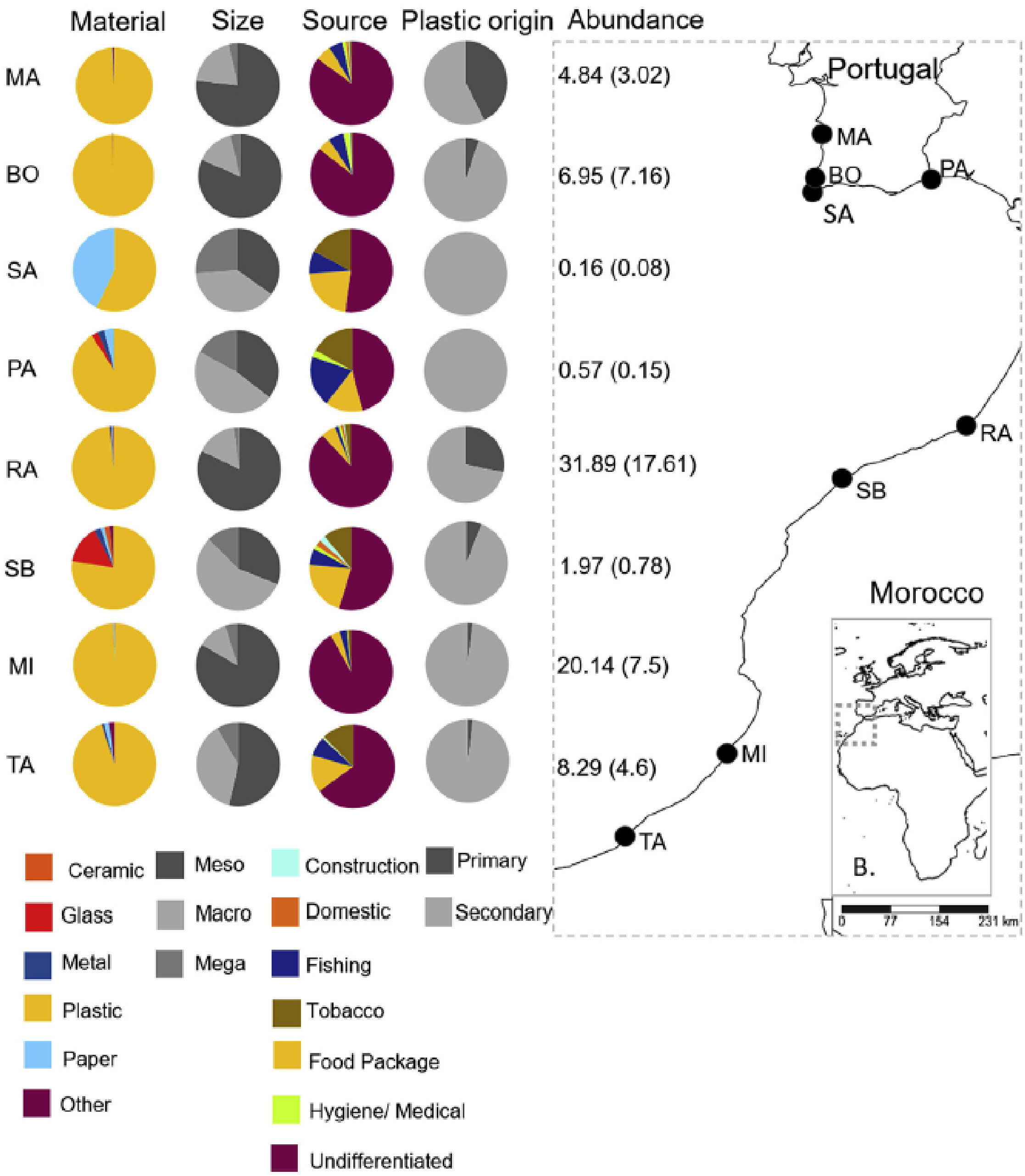


Figure 2.1: Material diversity along the southern Portuguese and Atlantic Moroccan shores (Meso- sample dimensions between 0.5 mm and 2 cm; Macro- samples from 2 cm to 10 cm; and Mega- samples larger than 10 cm) [1].

of plastic in the world and consequently, are also the most commonly found on the natural environment, they are High Density Polyethylene (HDPE), Low Density Polyethylene (LDPE), Polyvinyl Chloride (PVC), Polystyrene (PS), Polypropylene (PP) and Polyethylene Terephthalate (PET). One of the reasons these materials are so widely used is due to their corrosion resistance, making them classified as hard to degrade. This means that some of them might take centuries to disappear from the environment. Table 2.1 gives a summary of several examples of polymers properties from materials collected around the world, including western Portuguese coast, relating some of its characteristics such as the type as size of the plastic material.

Table 2.1: Properties of plastic debris found in beaches worldwide [3].

Location	**Occurance**	**Plastic Type**	**Plastic Sizes**
Edinburgh coast, UK	Average density of 0.8 items m^{-2}	-	-
Mumbai, India	Average abundance of 7.49 g and 68.83 items m^{-2}	Microplastics and macroplastic	<5 mm to 100 mm
Tasmania, Australia	Average abundance of 113 items or 1.69 kg of debris per beach.	-	-
Nakdong River Estuary, South Korea	Average abundances of 8205 particles m^{-2} in May and 27,606 particles m^{-2} in September	Microplastics and macroplastic	1 mm to >25 mm
San Diego, California	2453 individual plastic debris	Microplastics and macroplastic	<5 mm to 50 mm
UK	Maximum 8 particles kg^{-1}	-	-
Hong Kong	Average abundance of 5595 items m^{-2} and maximum 258,408 items m^{-2}	Microplastics	0.315 to >5 mm
Western coast of Portugal	Average density of 185.1 items m^{-2}	Microplastics (72%), macroplastic (18%)	50 μm to 20 cm
Hawaii	Average weight of debris per sample was 23.38 g plastic	Microplastics and macroplastic	1–2.8 mm (43%), 2.8–4.75 mm (48%), >4.75 mm (9%)
Belgian coast	Average 92.8 particles kg^{-1} dry sediment	Microplastics	38 μm to 1mm
Norderney	Mean 1.76 kg^{-1} dry sediment	Microplastics and macroplastic	<1 mm to >2 cm
East Frisian Islands, Germany	Maximum 621 particles per 10 g	-	-
Singapore	Maximum 3 particles kg^{-1}	-	-
North Atlantic Coast	Average density of 0.15–12.5 items m^{-2}	-	-
Northeast Brazilian Coast	Average density of 82.1 items m^{-2}	-	-
Malta Island	>1000 particles m^{-2}	Microplastics	1.9 to 5.6 mm

The origin of the discarded material The origins of the discarded material are the several activities taking place on land, which are transported with water streams, wastewater treatment works, wind or even during more extreme natural conditions. This represents about 80% of all the litter found worldwide. The remaining 20% are due to work developed on the ocean, such as fishing and tourism.

Problems entailed by plastic materials These elements in nature entail a great variety of problems, specially since their presence is increasing rapidly. These complications include chemical contamination; decreased aesthetic quality of the environment; and ingestion, possible injuries and moving limitations to several organisms, for instance seabirds, turtles, crustaceans and fish. Consequences of the ingestion of this materials by animals include blockage of the intestinal tract, inhibition of gastric enzyme secretion, reduced feeding stimuli, decreased steroid hormone levels, delays in ovulation and failure to reproduce, which will influence the species' capacity to multiply and ensure its success. Due to the predatory activity of other animals this reality intensifies and covers a even wider range of affected organisms.

Degradation of polymeric materials The degradation rate of the polymeric materials under the environmental conditions is influenced by a wide variety of causes. For example, the molecular weight highly affects the amount of time a piece takes to be decomposed by microorganisms, since the particles need to me small enough for it to happen. Other important aspects to take into consideration are the material's biodegradability and photodegradation resistance which directly influence the degradation rate, being this last property more critical when the material reaches the shore. Figure 2.2 summarizes the usual lifecycle of litter material [3].

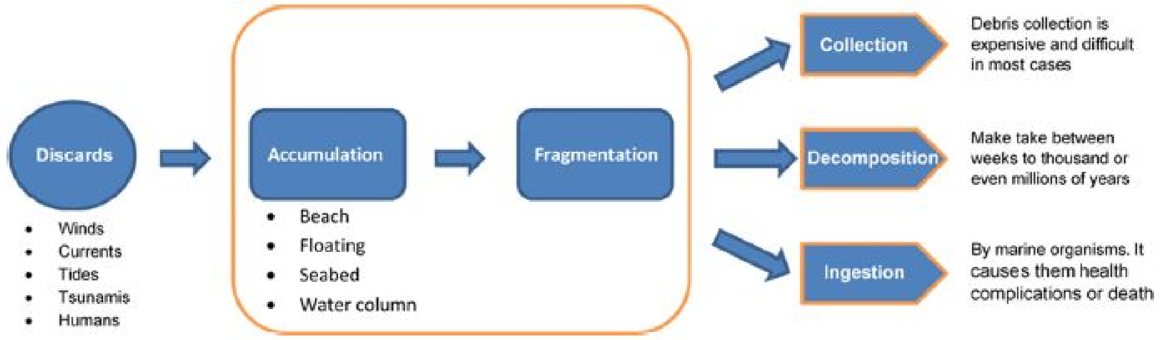


Figure 2.2: Typical lifecycle of marine debris [2].

2.2 Common Waste Materials

It is important to take into consideration the common types of polymers found. As previously said, HDPE, LDPE, PVC, PS, PP and PET are the most produced plastics in the world, which means that they are probably the ones most commonly found as ocean litter.

Based on the same case study referred to before, at the southern Portuguese and Atlantic Moroccan coasts the materials collected in greater quantities are PET, Polyethylene (PE), PP and PS as it can be observed on figure 2.3. This is information relative to microplastics.

In case of Portugal In the specific case of Portugal, one other survey was developed along the coast line of the country, selecting five specific beaches for data collection. In order to

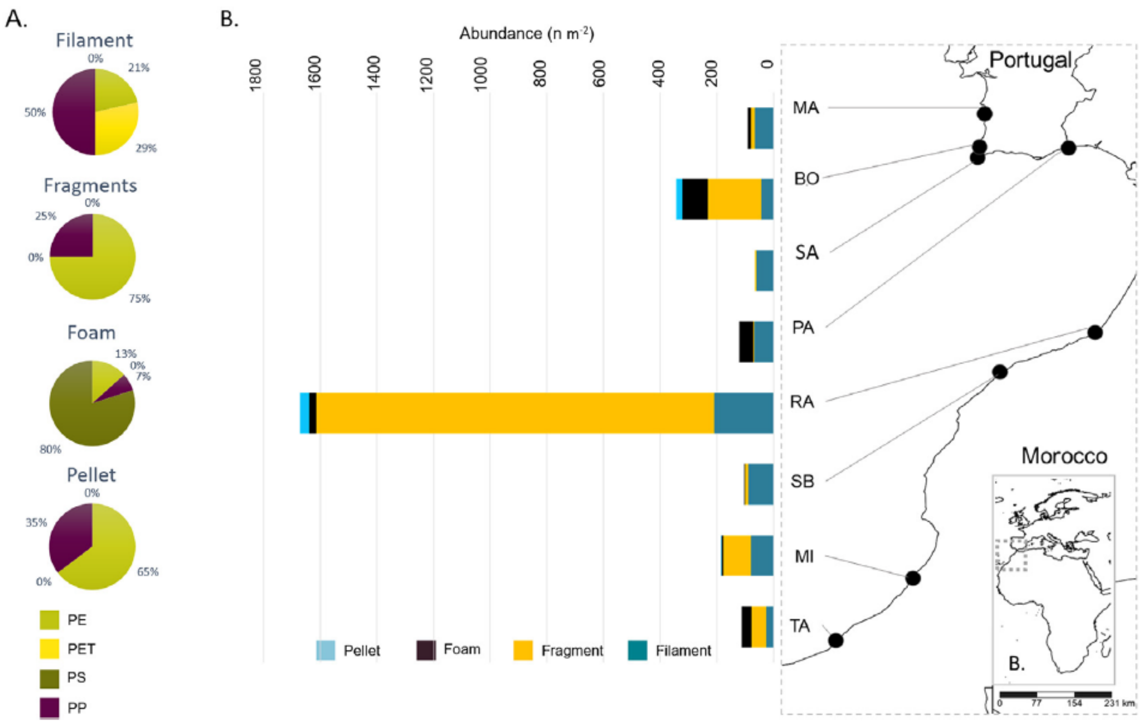


Figure 2.3: Types of material collected during the study ate the different locations [1].

obtain the greater amount of material, the beaches were chosen based on their accessibility and the dominant orientation of the wind. Agudela, Cova de Alfarroba, Fonte da Telha and Bordeira, mapped on figure 2.4, were the ones picked. Several samples of sand were gathered and the polymeric material separated from the remaining materials. The plastic was then measured, counted, weighted and classified according to the following criteria from table 2.2.

Table 2.2: Dimensional criteria for the sample classification [4].

	Lower Limit [mm]	Upper Limit [mm]
Class 1	-	≤ 1
Class 2	$1 >$	≤ 2
Class 3	$2 >$	≤ 3
Class 4	$3 >$	≤ 4
Class 5	$4 >$	≤ 5
Class 6	$5 >$	≤ 6
Class 7	$6 >$	≤ 7
Class 8	$7 >$	≤ 8
Class 9	$8 >$	≤ 9
Class 10	$9 >$	≤ 10
Class 11	$10 >$	-

About 2,3 kilograms of plastic were recovered, ranging from 50 micrometer to 20 centimeters with an average density of 185,1 items per square meter. As it can be analysed on figure 2.5, 72% of the material has dimensions smaller than 5 millimeters, which means

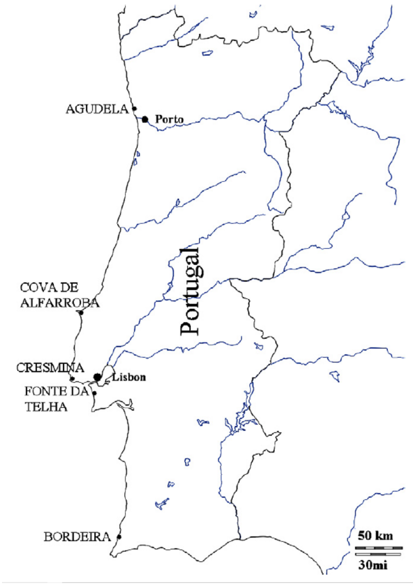


Figure 2.4: Beaches' locations for the data collection [4].

that a great majority are microplastics, while 10% is larger than 10 millimeters. It was also made a relation between the particle's dimensions, represented on figure 2.6. As it would be expected, the larger pieces represent about 90% of the total weight.

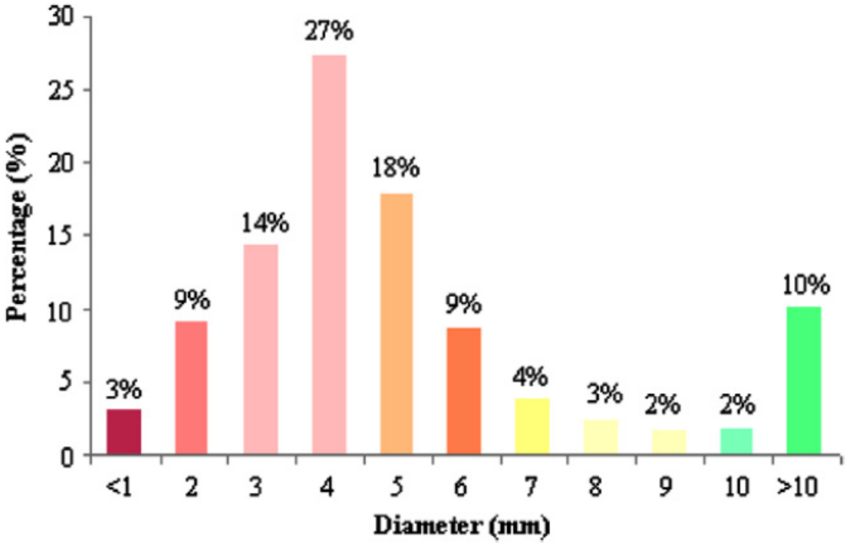


Figure 2.5: Quantity of material per class in percentage [4].

An identification of the type of polymers presented on the samples was made using an Infra-red Spectroscopy with Fourier Transformation. With this test, it was possible to identify a majority of PE, Polyester and PS among the material samples [4]. Using this information, it is now possible to conclude that the most common materials are PE (specifically HDPE and LDPE), PP, PET and PS.

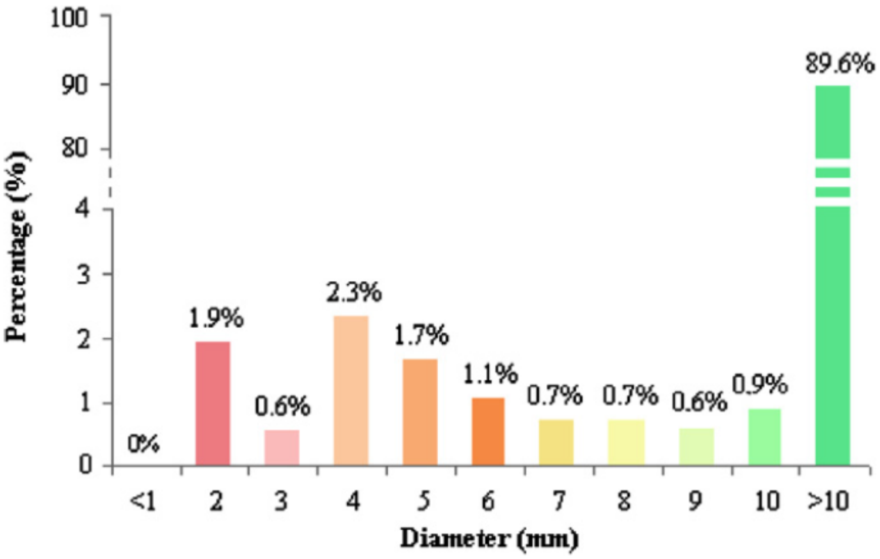


Figure 2.6: Weight of material per class in percentage [4].

Polyamides (PA) are another important material considered for this project development, because is one of the most essential materials used in fishing. It is used to produce fishing nets and lines which usually end up in the ocean due to its continuous degradation, getting stuck or lost, or even being discarded during or after its usage.

2.2.1 High Density Polyethylene (HDPE)

This is one of the two most used PE in the world. It is a versatile material widely used on packaging of several different products, such as food, due to its chemical inertia, moisture barrier properties and low cost.

HDPE is a recyclable material and has diverse applications when used as a new potential material, since it is possible to produce long-life products. Usually, PE is a material with high calorific value, this means that it makes the incineration process highly efficient. It is flexible, possible to produce translucent products, is easily processed by the most common methods and has a good toughness at low temperatures.

The main applications for this material are chemical drums, jerrycans, carboys, toys, picnic ware, household and kitchenware, cable insulation, carrier bags, food wrapping material, among others [5].

2.2.2 Low Density Polyethylene (LDPE)

Another highly used PE material is the LDPE. Similarly to the HDPE, it is possible to produce translucent parts and is processed by most means. It is a semi-rigid material, has low water absorption rate and good chemical resistance.

Due to its high toughness, low cost and waterproof properties it is possible to produce several components used in various areas of application such as squeeze bottles, toys, carrier bags, high frequency insulation, chemical tank linings, heavy duty sacks, general packaging and gas and water pipes [6].

2.2.3 Polypropylene (PP)

This is a material with properties very similar to the PE. The main characteristics which differentiate them are: PP has better temperature resistance, lower density, higher softening point and higher rigidity and hardness. However, it has lower ultraviolet radiation resistance, higher mould shrinkage and thermal expansion. It is also possible to process this material by essentially all the process usually used on thermoplastics.

It is usually used as fiber for textiles; as component for toys and medical parts; and for packaging, such as bowls, crates, bottle caps, cases and buckets [7].

2.2.4 Polystyrene (PS)

It is possible to create several different types of materials with PS depending on the intended application. Not only it is low cost but it is also an easily processed material which represents about seven percent of the total thermoplastic market. It is used for food packaging, disposable consumer plastic goods, parts for optical, electronic/electrical and medical applications. The main materials produced based on PS are General Purpose Polystyrene, High Impact Polystyrene, Expandable Polystyrene and Acrylonitrile Butadiene Styrene.

It has low crystallinity which creates excellent optical clarity. The material is a very good electrical insulator and has good chemical resistance. However, its upper temperature limit for continual use is rather low, is relatively brittle and has poor oxygen and UV resistances [8].

2.2.5 Polyethylene Terephthalate (PET)

This is one of the polymers used in applications where performance is an important factor. Most of the times there has to be a balance between cost and performance, but in the case of performance polymer applications, the material selection tends to give priority to performance. Some areas where PET is widely used are transportation, automotive, electronic, appliances, industry, buildings, textile bobbins, meter housings and small niche applications.

The material properties are the characteristics which enable the usage of the material in the identified applications. On the case of PET, it has excellent electrical and wear properties, chemical resistance, dimensional stability. It is also characterized by its low creep at high temperatures, good heat resistance, high stress crack resistance and extremely low water absorption rate [9].

2.2.6 Polyamide (PA)

"Nylons" is a common name used to refer to amide based polymers usually applied in textiles, fishing lines and carpets. Several metals are often replaced by this material due to its properties, for example in bearings, since it is a self-lubricating material, and in electrical systems, thanks to its electrical insulation, corrosion resistance and toughness. These materials have good thermal and chemical resistances and are very tough.

A characteristic important to take into consideration is the impact that moisture has on its properties. It is a material with high tendency to absorb the surrounding moisture. This not only affects its dimensional stability, but also its impact resistance, and its flexibility tends to increase, while strength and stiffness tend to decrease [10].

2.3 Waste Management Technologies

Usually the waste collection in coast and marine areas is responsibility for the port of each region. This process might be related to the floating litter or the materials which end up on the seabed. Some countries are using specific mechanisms to fulfill these obligations. For example, Korea uses a containment system used to draw the floating litter before it reaches the open ocean. It is constituted by a long chain of floating material made specifically to resist collisions with the waste material to collect. Under water there is a net fixed to the buoys used to prevent the material dispersion in the ocean due to water currents. On a regular basis, this system is gathered and the litter is dispatched to its proper destination. As for the collection of sinking waste, the technology used depends on various aspects, such as the depth on which the operation will be made and the type of seabed (could be a more rocky or sandy floor).

Usually they are processes done by divers, using bottom trawl nets or even submersibles. Following its collection, the material is distributed to several treatment facilities.

Some of the available technologies already used to treat degraded plastic are incineration, by decomposing materials at extremely high temperatures, reducing its volume and enabling the acquisition of energy and/or chemicals; production of Refuse-Derived Fuel, produced with several types of waste; and recycling, used to incorporate worn and virgin materials into new ones. In order to do these types of management, it is necessary to pre-treat them, a procedure which depends on the main technology used to treat the wastes, but it usually involves sorting, cutting, separating lead, grinding and cleaning of salt sand sludge. The pre-treatment process is very important to ensure mechanical stability and reduce the amount of contaminants in the material, such as sodium, improving the material's overall quality and processability.

The initial approach taken during this project is similar to the pre-treatment performed on the particular case of plastic recycling. It involves separation of embedded organisms, cleaning of salts and sludge, grinding and drying [2].

2.4 State of the Art

In order to better identify the most important material properties to study, two case studies will be firstly analysed. The bibliography available on this matter is very limited, mostly because it is more usual to treat plastic residues from a general source, not only from marine litter. This is the main reason why it is specially important to analyse further this issue.

2.4.1 Case Study 1

This first case study focuses on the mass, size and composition of plastic debris collected from the western north Atlantic ocean in several expeditions made between 1991 and 2007. A sample of 748 components was analysed, starting with their visual identification, rough separation from contaminants, drying and storage in a room with no light. The pieces were then measured, weighted and their shape was associated to one of several categories. Density and Carbon, Hydrogen and Nitrogen rate (CHN) present in the samples were the properties chosen as identifier of the polymer. The information obtained is represented on figures 2.7, 2.8 and table 2.3. On figure 2.8 the horizontal lines between the diagrams identify the usual densities of major consumer plastics, in this case PP, LDPE, HDPE, PS, PVC and PET, and the dashed vertical line is the mean density measured for the western North Atlantic surface seawater.

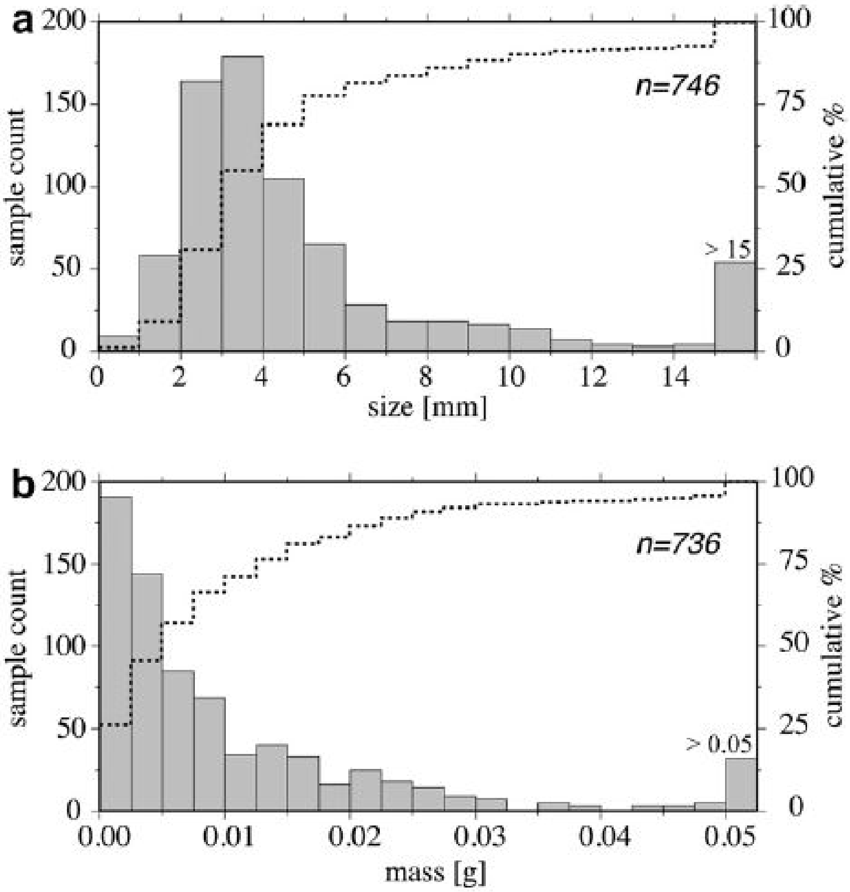


Figure 2.7: Plastic sample (a) size and (b) mass histograms [11].

Table 2.3: Composition of several polymeric samples (CHN content rate) [11].

Sample	Density [g/ml]	C [%]	H [%]	N [%]
1	0,859	84,82	13,51	0,47
2	0,889	85,09	14,53	0,42
3	0,892	83,36	13,39	0,63
4	0,896	84,87	13,86	0,05
5	0,906	84,52	13,96	0,40
6	0,921	83,41	13,74	0,54
7	0,923	85,79	13,77	0,41
8	0,940	82,85	13,53	0,82
9	0,942	84,63	13,69	0,59
10	0,957	84,36	13,61	0,03
11	0,960	85,33	14,15	0,52
12	0,960	84,34	13,96	0,45
13	0,960	84,16	13,74	1,07
14	0,980	83,56	13,83	0,62
15	0,980	79,13	13,10	0,79
16	0,980	82,55	13,75	0,41
17	0,996	83,48	13,81	0,61
18	0,998	81,62	13,46	0,45
19	1,042	83,27	13,81	0,60

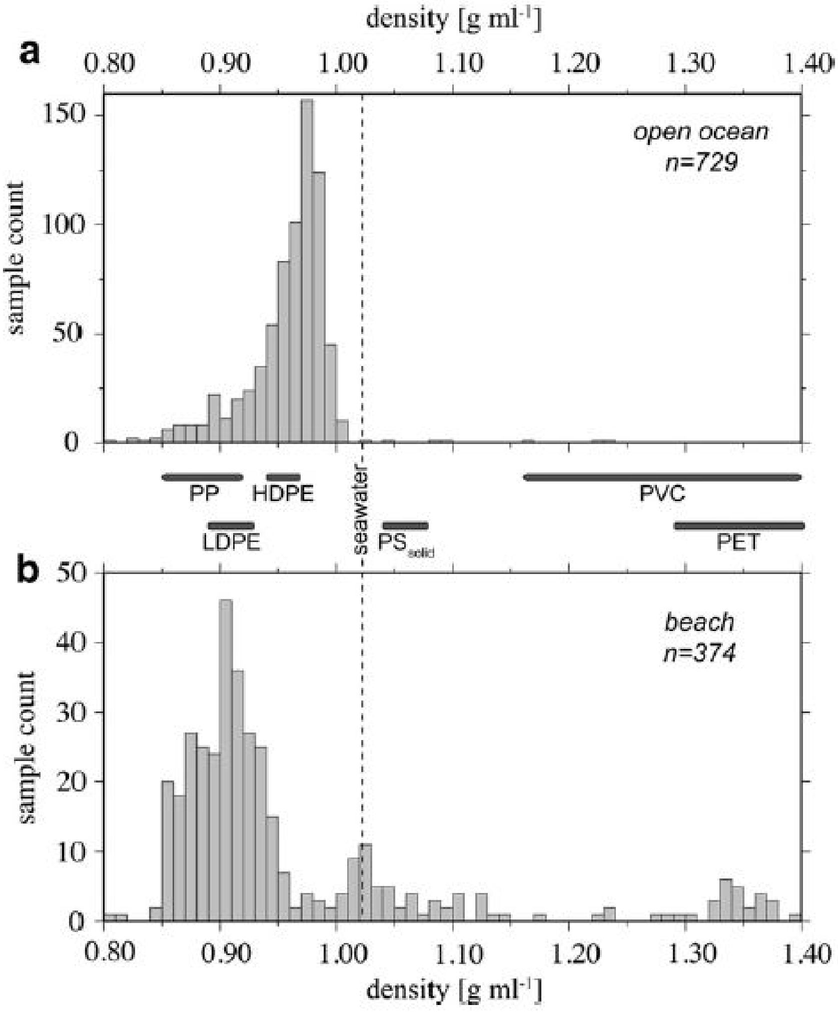


Figure 2.8: Plastic density histograms of (a) open ocean and (b) beach samples [11].

From the analysis of this graphs it was observed that the values obtained for the CHN was reduced comparing to the virgin material. It was concluded the main types of materials acquired were high- and low-density polypropylene and polypropylene. The density has probably increased due to possible biomass accumulation and the environment itself, such as weathering, photochemical breakdown and prolonged mechanical abrasion [11].

2.4.2 Case Study 2

This case study is a part of the international project Circular Oceans, with the goal of reducing the amount of waste on the oceans by investigating new solutions to reuse used fishing nets. The nets, made in HDPE, were collected from a dump-site in Greenland and tensile tests were made in order to evaluate the material capacity to be integrated as reinforcement in construction materials, such as concrete. After collected, the nets were cleaned with fresh water, examined by Scaning Eletron Microscope (SEM) and were then made the tensile tests. The obtained values for the mechanical properties are shown on table 2.4 and the image taken by SEM is represented on figure 2.9, in both images the equivalent data of new fibers is also given in order to easily compare the characteristics. The Young's Modulus obtained for the waste fibers was 1036 MPa while new fibers usually have values of 1002 MPa.

Table 2.4: Mechanical properties of new and waste fibers, where the values in parentheses are standard deviation [12].

Waste fiber - Unconditioned

Length l_0 [mm]	**Peak strength F_{max}[N]**	**Tensile strength σ_t [MPa]**	**Peak elongation Δ L [mm]**	**Peak strain ε_t [%]**	**Δ L/F_t [mm/N]**	**l_0/A [m^{-1}]**
20	26,2 (5,0)	370,8 (70,1)	6,7 (1,2)	33,3 (5,9)	0,26	0,14
25	25,1 (1,8)	355,0 (25,6)	6,7 (0,8)	26,7 (3,3)	0,27	0,18
30	22,1 (4,8)	311,9 (67,8)	8,1 (1,4)	27,1 (4,7)	0,37	0,21
Mean	**24,5**	**345,9**	**7,2**	**29,0**		

New fiber - Unconditioned

Length l_0 [mm]	**Peak strength F_{max} [N]**	**Tensile strength σ_t [MPa]**	**Peak elongation Δ L [mm]**	**Peak strain ε_t [%]**	**Δ L/F_t [mm/N]**	**l_0/A [m^{-1}]**
20	29,4 (1,9)	415,4 (26,5)	6,1 (0,6)	30,6 (2,8)	0,21	0,14
25	31,2 (3,0)	441,7 (41,8)	6,8 (1,2)	27,2 (4,8)	0,22	0,18
30	28,5 (3,4)	403,7 (47,8)	8,5 (1,9)	28,5 (6,3)	0,30	0,21
Mean	**29,7**	**420,7**	**7,2**	**28,8**		

This study has shown that although the fibers were damaged, it's surface was still very smooth, which would hinder the bounding between fibers and concrete matrix. The tensile strength was significantly reduced, in 20%, comparing to new fibers, however the elongation strain and Young's Modulus were similar to the original material [12].

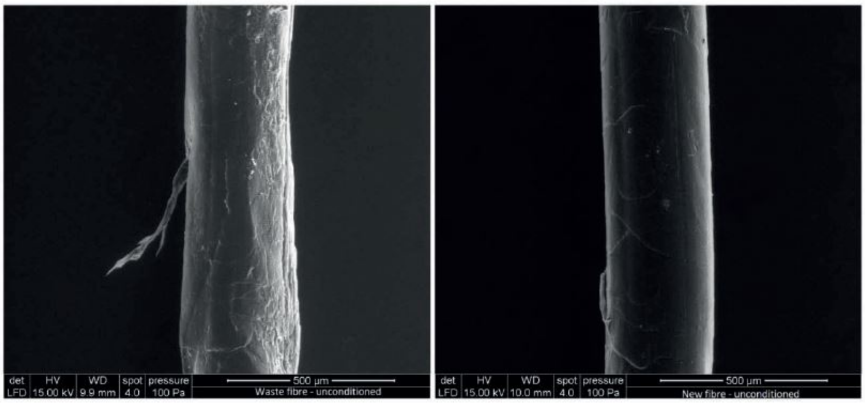


Figure 2.9: SEM images (300x) of waste fibre (left) and new fibre (right) of polyethylene [12].

2.5 Chapter Outcomes

After a proper analysis of the information gathered it is now possible to conclude that it is very important to define new solutions and applications for the great amount of polymeric residues present on the beaches and oceans. In order to make this possible it is important to obtain as much data as possible about these materials. The last two case studies approach variables such as the mass, size and composition of plastic debris recovered throughout a long time and some of the HDPE mechanical properties and surface quality with the specific purpose of analysing the possibility to be used as reinforcement material in concrete.

Although these papers are on the right track it is still not enough to fully understand the potential of these kind of materials. For this reason this paper will examine some of the mechanical and thermal characteristics of two of the most commonly found waste polymeric materials on beaches and in the oceans, HDPE and PA, comparing the waste material with the corresponding virgin material and the material obtained after processing.

3 Litter Characterisation

On an initial stage of the project, waste material was recovered from the beaches so that a careful analysis of its properties may be done allowing its comparison with the original raw material and the material obtained after its processing, a schematic plan of action for each material is represented on figure 3.1 regarding the HDPE and figure 3.2 for PA. Thus, on this chapter the waste collection and the tests processes and results will be approached.

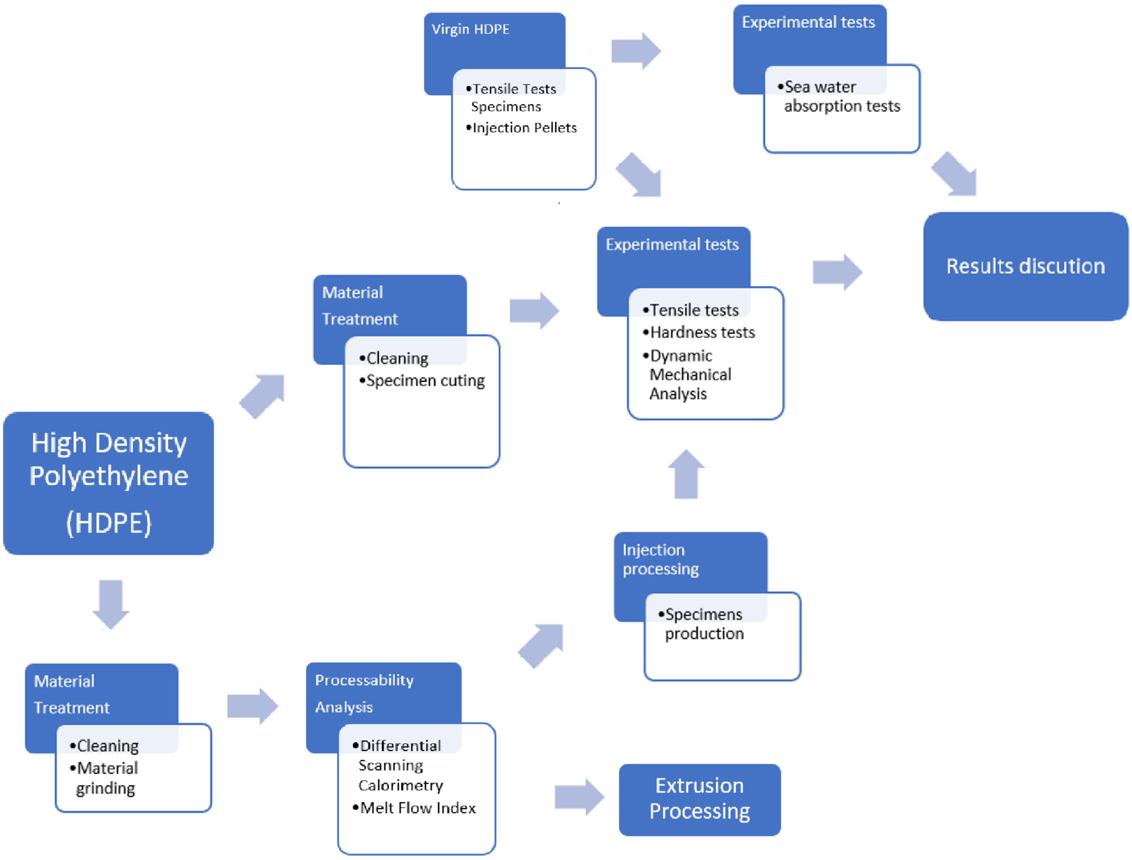


Figure 3.1: Scheme of the intended plan of action for the project regarding the HDPE.

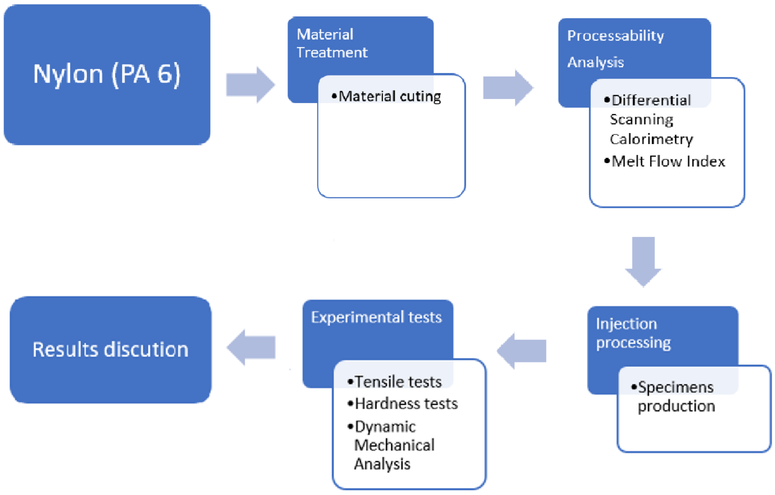


Figure 3.2: Scheme of the intended plan of action for the project regarding the PA.

3.1 Waste Collection

In order to begin the evaluation of the plastic characteristics, it is necessary to obtain material to test. For this reason and having in consideration the crisis regarding the litter that reaches the ocean and, ultimately, the beaches, a large quantity of waste was recovered from a beach close by, in this case Vieira beach in Leiria, Portugal.

Most of the materials collected were plastic but a vast majority could not be identified without the proper chemical tests. Usually these materials were wrapped on several fishing nets which made the process of recovering nylon waste more difficult, for this reason the fishing net used further was turned in by a local fisherman. This made it easier to identify the material's composition, PA 6, since it was possible to access its datasheet properly [13]. Although it was not possible to obtain a conclusive analysis regarding the variety of material found, one element spotted in great quantities was Alcatruzes, a type of trap for octopuses, usually made with HDPE or, more traditionally, clay. It is common for these traps to be stuck on rocks when they are used, but it is also possible that their users throw them away to the sea or beaches when they are broken or out of use.

3.2 Experimental Procedure

The experimental procedure used to determine some of the litter properties before processing was only applied to the HDPE waste material. This is due to the geometric conditions of the materials, it was possible to obtain proper specimens from the octopus traps but, regarding the Polyamide, this was only possible to acquire these elements by processing the material.

Thus, this chapter will address, specifically, the characterization of the HDPE marine litter and compare them with the corresponding virgin raw material. The HDPE and PA processed materials will be discussed further. Tensile tests, water absorption test, Dynamic Mechanical Analysis (DMA) and hardness tests were the studies chosen for this initial part.

3.2.1 Tensile Tests

Eighteen tensile tests were made, from which only nine were considered acceptable, since only on these cases the specimen broke down between the extensometer's length. The specimens used were from three different traps, which could be identified and distinguished by color, as it can be seen on figure 3.3. This allows to arrange the specimens in three groups and obtain results for the different cases. The gray specimens are from the first group, red specimens were identified as the second group and the black ones belong to the third group. A fourth group was also studied, this time with specimens of already injected virgin HDPE, in order to have practical information to compare the obtained values.

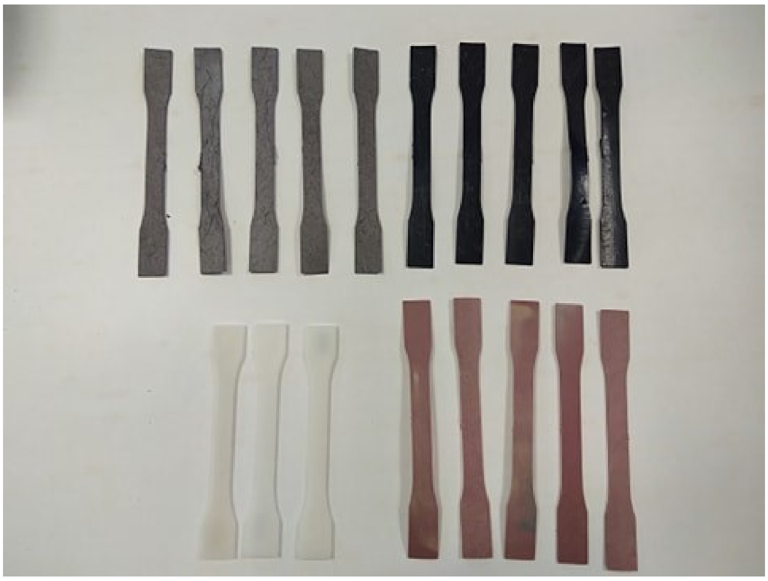


Figure 3.3: Specimens used on the tensile tests. Top left are the grey specimens (first group), top right are the black specimens (third group), bottom right is the red specimens (second group) and bottom left is the virgin HDPE.

Later on, additional tensile tests will be executed with the injected waste material, where further conclusions will be taken. The tests were made until at least three attempts of each group were acceptable. A total of eighteen attempts were made and fourteen of them were approved.

The specimens were cut using a pneumatic press, DTS FAAR, in order to acquire a standard shape, proper for the tensile test. Based on the standard ISO 527:1993 and resorting on the Zwick Z100 available, the results listed on table 3.1 were obtained for the accepted exemplars, as well as the following charts 3.4, 3.6, 3.7 and 3.5.

Table 3.1: Obtained values with the tensile tests for the collected material.

	σ_{x1}	σ_Y	ε_Y	σ_M	ε_{tM}	σ_B	ε_{tB}
	MPa	**MPa**	**%**	**MPa**	**%**	**MPa**	**%**
Virgin$_1$	26,85	27,04	8,87				
Virgin$_2$	22,44	22,46	7,35				
Virgin$_3$	22,98	23,13	6,4				
Virgin$_4$	27,76	27,78	7,57				
Virgin$_5$	22,53	22,65	8,89				
Average	24,51	24,61	7,82				
Standard Deviation	2,31	2,31	0,95				
Collected$_{sup1}$	13,51	13,47	6,34				
Collected$_{sup2}$	13,30	13,23	6,23				
Collected$_{sup3}$	15,82	15,73	6,66				
Average	14,21	14,14	6,41				
Standard Deviation	1,14	1,13	0,18				
Collected$_{red1}$	17,03	17,74	6,94	17,86	8,41	10,22	20,02
Collected$_{red3}$	19,09	19,84	7,47	20,05	9,09	7,54	25,01
Collected$_{red5}$	17,47	18,11	6,86	18,47	8,43	7,83	15,55
Average	17,86	18,56	7,09	18,79	8,64	8,53	20,20
Standard Deviation	0,89	0,91	0,27	0,92	0,32	1,20	3,87
Collected$_{black4}$	16,15	15,87	6,634				
Collected$_{black5}$	17,18	17,07	6,58				
Collected$_{black8}$	16,99	16,93	6,77				
Average	16,77	16,62	6,66				
Standard Deviation	0,45	0,54	0,08				

As we can observe on table 3.1, the overall values of stress and yield strain of the waste material are lower than the virgin material. It was also verified during the tests that the litter tended to deform a lot less than usual before breaking comparing to usual polymeric materials. This might be caused by potential cracks on the material caused by the deterioration.

Comparing the graphs obtained it is possible to observe that the waste material has much more serrations on the stress values than the virgin material. This might be an other sign of potential cracks on the material. Doing an average of the results of each waste material group and comparing with the virgin material it is observed that the first group is the one with greater discrepancy, followed by the third group. The second group is the one whose values are the most similar to the virgin material.

Further on, more tensile test will be done, specifically with the processed material. There, additional and more developed comparisons will be made considering all the results obtained.

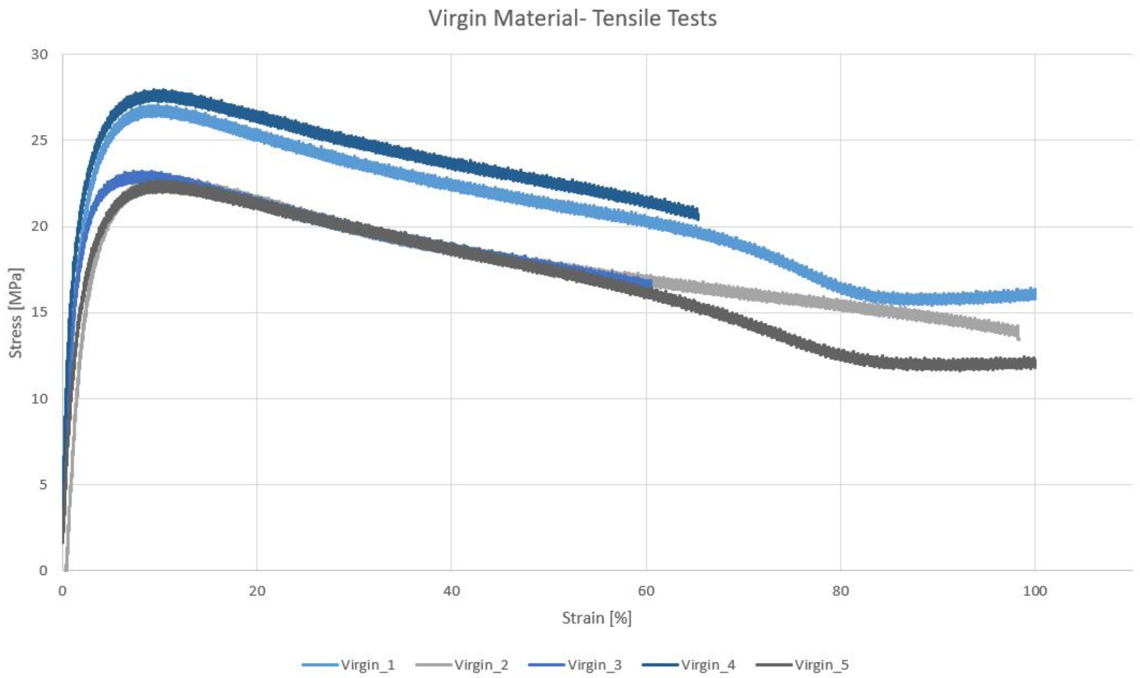


Figure 3.4: Tensile tests for the five different specimens of virgin HDPE material.

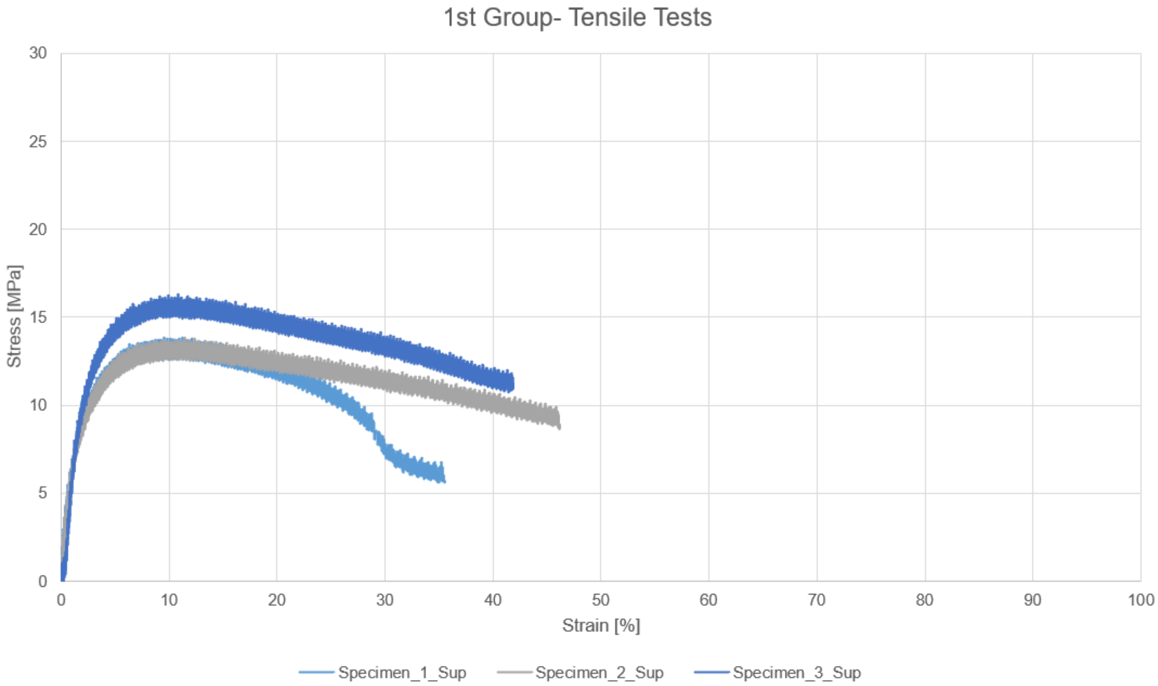


Figure 3.5: Tensile tests for the three different specimens of waste material from the first group.

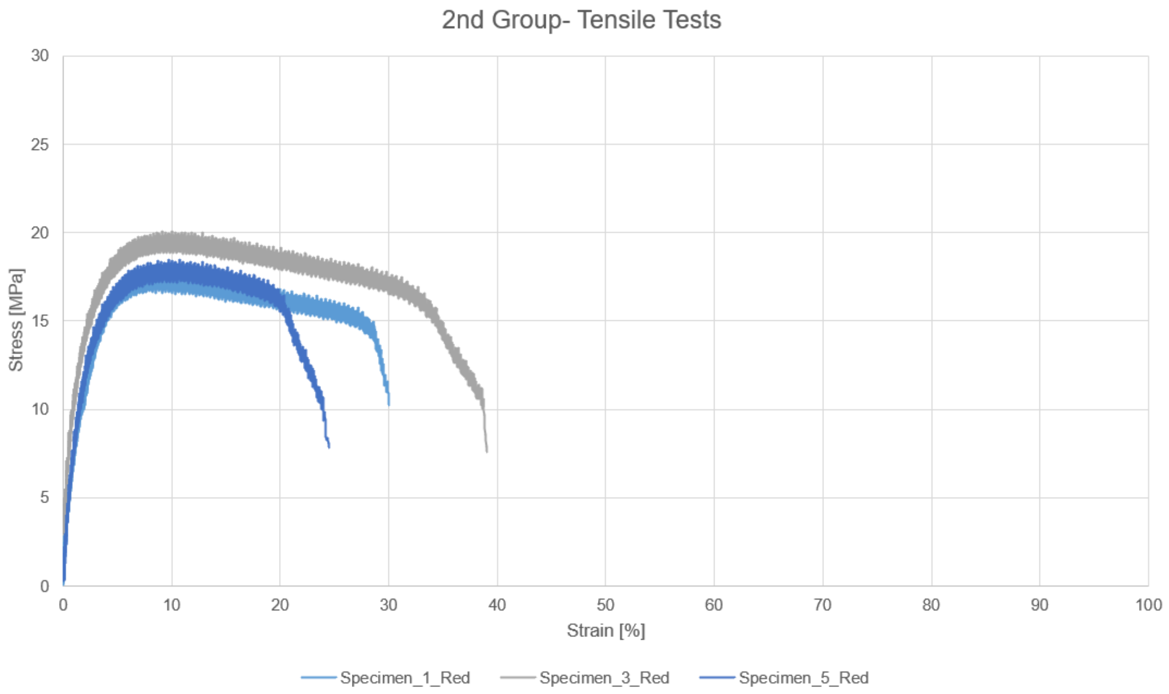


Figure 3.6: Tensile tests for the three different specimens of waste material from the second group.

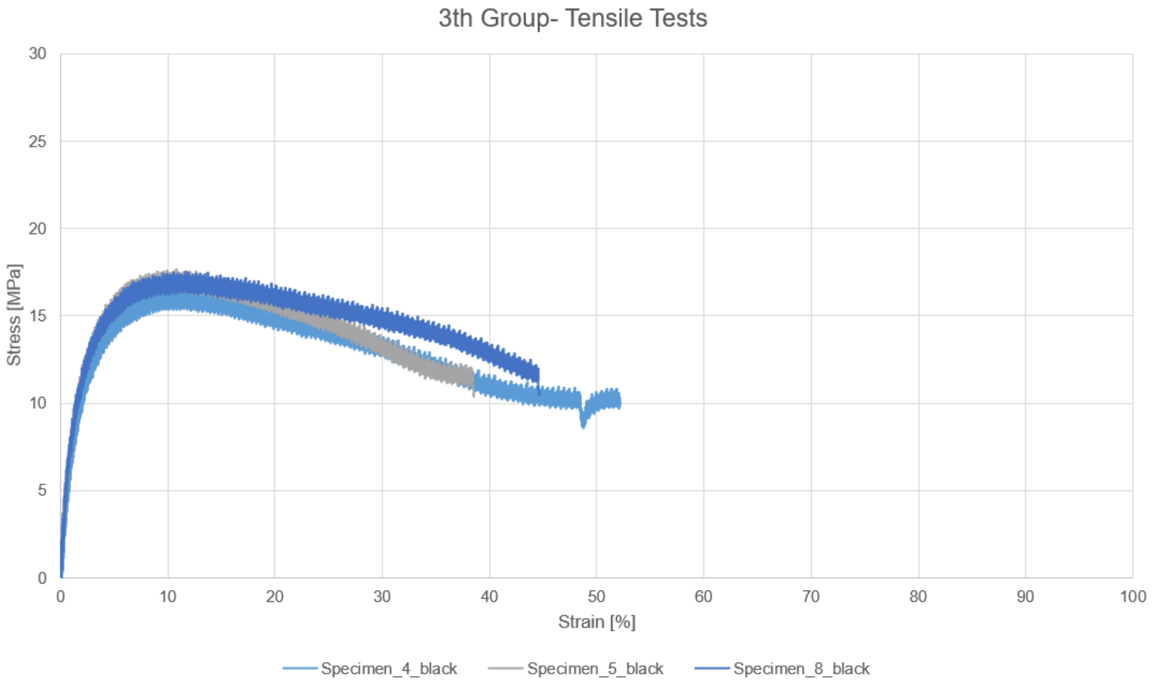


Figure 3.7: Tensile tests for the three different specimens of waste material from the third group.

3.2.2 Dynamic Mechanical Analysis (DMA)

The second part of the tests made was the DMA. The main purpose was to determine if the thermal properties of the material are still similar to the virgin material, specifically the glass transition temperature. This information will also be important for the parameterization of the processing temperature.

The equipment used was a Tritec 2000 DMA, available on the Technology and Management School of the Polytechnic Institute of Leiria. The method chosen was three point bending and the procedure was based on the indications found on the equipment manual. Three different tests were made where the specimens were cut with the standard dimensions of 50 x 10 x 1,5 mm.

Usually the type of chart expected to be obtained on these types of tests is represented on figure 3.8. The sudden decrease of the Young's modulus is the indicator of the region where the material's glass transition temperature averages. In order to obtain the desired values, this is the type of curve necessary to be obtained.

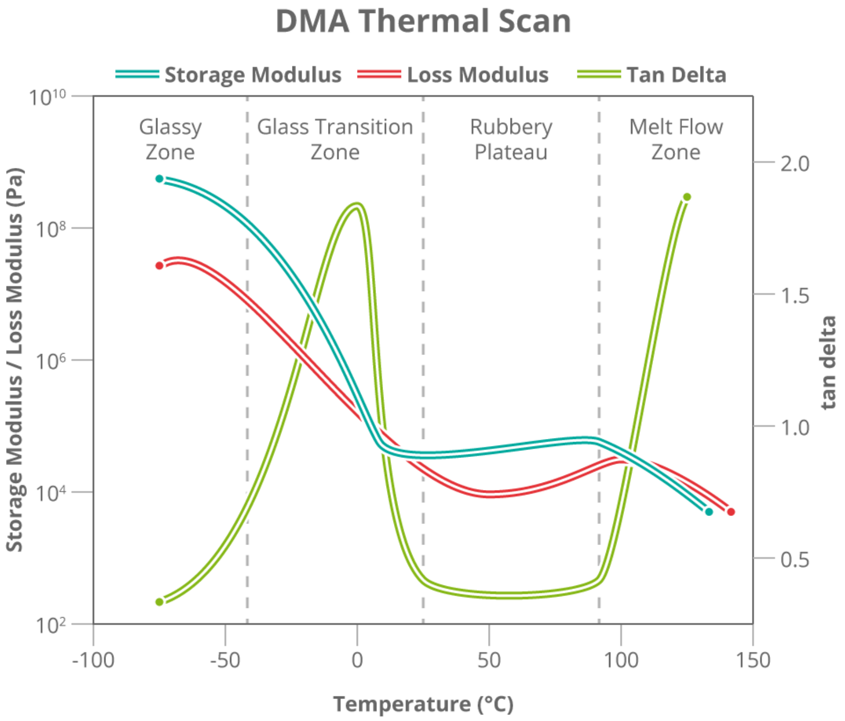


Figure 3.8: Chart type expected to be obtained [14, 15].

The important factors which influence the test results are summarized on table 3.2 and the charts obtained can be analysed on figure 3.9 and appendixes A and B, for the first, second and third specimens, respectively.

Table 3.2: Parameters used during the DMA test.

Frequency [Hz]	1
Single frequency / Single strain	
Specimen's Geometry [mm]	
Length	20
Width	10
Thickness	1,5
Type of Load	Static and Dynamic
End Temperature [°C]	120

The sudden decrease of Young's Modulus necessary to be obtained in order to determine the glass transition temperature is not present on the charts. Taking in consideration that the material is a polymer, which usually has low glass transition temperatures, and that the tests were made with an initial temperature around 20 °C (room temperature), this means that the glass transition temperature of this material is lower than 20 °C.

Theoretically, virgin HDPE has a glass transition temperature of around -100 °C [16]. With this information, it is not possible to take a concrete conclusion, since this thermal property could be different from the original without reaching the 20°C.

3.2.3 Hardness Tests

The third test made was regarding the waste material hardness in order to compare the obtained values with the processed and the virgin materials.

The procedure was based on the ISO 868 standard. Four specimens were used made with pieces of material on top of each other in order to reach a thickness higher than 3 millimeters. This method was applied on both the traps and the virgin material. Although this alternative method might create some measurement errors, it is the only way to obtain the desired results. The waste and the virgin materials used were the same as the ones used for the tensile tests.

The equipment used was a Bareiss shore D hardness tester. It is composed by a a small needle which penetrates the material, a hardness dial with the desired information and a mass of 5 kilograms which allows to obtain the hardness of the material when it is released on the needle.

Four calculations were made in four different places along the length of each specimen and each one of the measurements was divided in two phases. A first value is obtained on the moment when the weight is released and a second one is withdrawn fifteen seconds

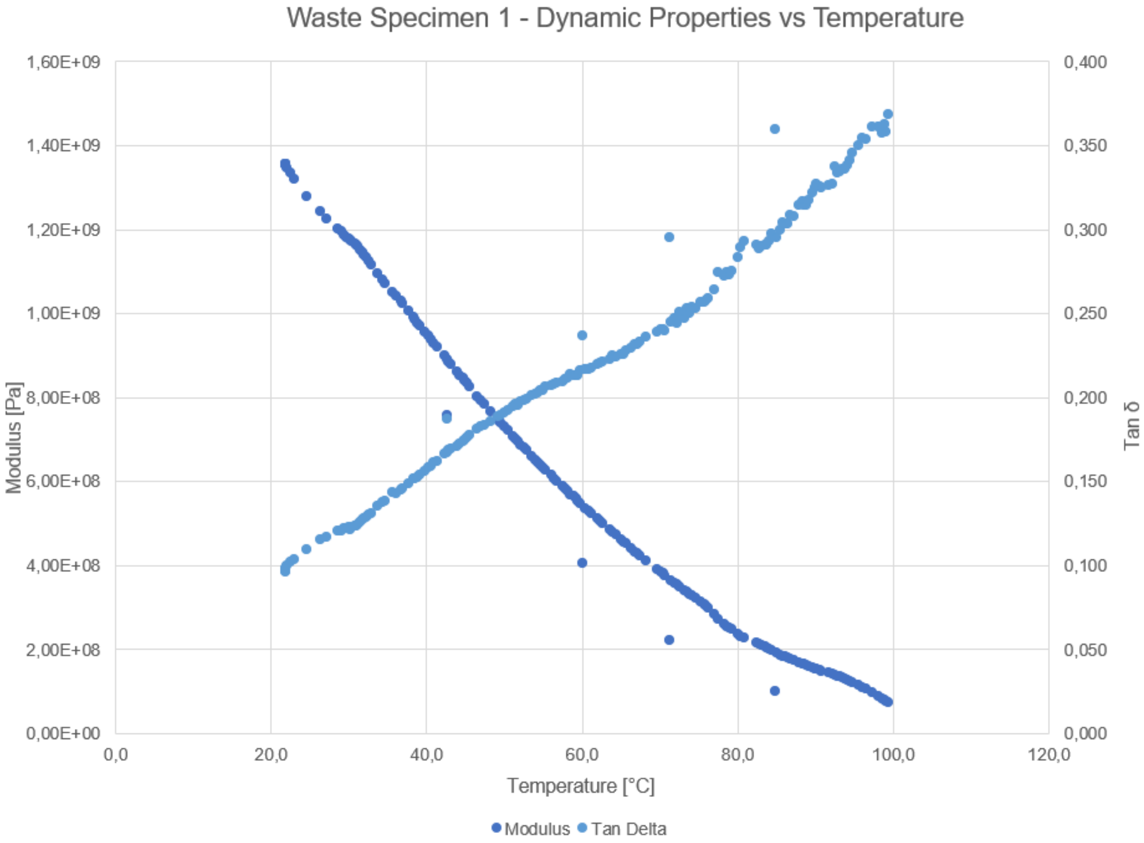


Figure 3.9: DMA results for the first specimen.

after that occasion. The obtained values are summarized on table 3.3 with the averages of the results obtained which listed on appendix C regarding the waste material, and the virgin material on appendix D.

Table 3.3: Average values for each specimen or group of waste and virgin material, as well as the theoretical hardness interval of HDPE.

	Waste	**Virgin**	**Theoretical**
Specimen 1 /Group 1	50,44	61,75	50-76
Specimen 2 /Group 2	57,69	62,00	
Specimen 3 /Group 3	56,69	69,38	
Specimen 4	-	68,88	

With this information it is possible to calculate an average value for the material hardness. Regarding the waste material, the first group as an average of 50,44, the second group 57,69 and, finally, the third group obtained an average hardness of 56,69 Shore D. Theoretically, virgin HDPE has hardness between 50 and 76 Shore D and according to table 3.3, the test results for the virgin HDPE sits between 61 and 70 shore D. This makes it possible to conclude that the hardness changed from its original value, although it is still between the theoretical values. Further conclusions will be taken when the same test will be made for the injected material.

3.2.4 Sea Water Absorption Tests

This part of the project had the goal of determine a rough approximation for the amount of time some of the recovered HDPE material was abandoned and take the possible conclusions regarding the cause of its deterioration.

The plan was to test the absorption rate of virgin HDPE and determine its density variation through time and compare the results with equivalent waste material. Using this information, it will theoretically be possible to determine how long the material was on the sea. In order to properly execute this procedure, this part of the project was based in two ASTM standards, ASTM D 570-77 related to water absorption of polymers, and ASTM 792-00 about the density determination.

Fifteen small samples of virgin HDPE, were submerged, for fifty days, in water collected from the sea, figure 3.10. Although the conditions in which the waste material was subjected cannot be exactly simulated in this circumstances, it should be enough to calculate the approximation intended.

Figure 3.10: Samples of virgin HDPE used for the absorption tests.

Initially the data was measured every day for 3 weeks and from then on, every week, process based on ASTM D 570-77. As explained on the ASTM 792-00 the means for density calculation require the measurement of the specimen's mass and its impulsion by weighing the material both outside water, m_{out}, and submerged in distilled water, $m_{submerged}$, using a sinker, illustrated on figure 3.11.

Figure 3.11: Equipment used to determine the mass and impulsion of each sample.

With this information and the water temperature during the measurements, which will allow to determine the water's density on the conditions when the measurements took place ($\rho_{water@T^{o}C}$), it is now possible to obtain the density of each piece of material applying the equation 3.1.

$$\rho = \frac{m_{out}}{m_{out} - m_{submerged}} \times \rho_{water@T^{o}C} \tag{3.1}$$

On appendix E is represented the line chart of the average density, mass out and under water of the material for each measurement. Some specific days it was not possible to check the corresponding values, since the equipment is not available on Sundays and measurements started in December which means that the building was closed a few days as a result of Christmas and New Year's celebrations.

As it can be analysed, the material has an initial absorption rate quite high which eventually stabilizes, in this case it would be around day fifteen. It can also be seen that days two and five do not have the expected density values and clearly stand out on the chart as possible measurement errors.

During this process the density of several pieces of waste material was also calculated using the same criteria. The specimens used are from the same traps used for the tensile tests. The obtained values are presented on table 3.4.

Table 3.4: Waste material density values for each specimen of each group of material.

	Specimen 1	Specimen 2	Specimen 3	Specimen 4	Standard Deviation	Average
1st Group	0,9369	0,9275	0,9401	0,9291	0,0053	0,9334
2nd Group	0,9401	0,9401	0,9464	0,9626	0,0092	0,9473
3rd Group	0,9505	0,9449	0,9540	0,9515	0,0033	0,9502

As we previously observed on the tensile tests results, the group with greater variations on their values in comparison to the virgin material is the first one, followed by the third and finally the second group. However, the density calculations reveal that the third group has greater density than the others. This reveals that the third group is not only the second most deteriorated, but also was probably the one that remained more time at sea or in contact with water.

Comparing the densities of the waste material and the ones obtained with the absorption tests, it is inconclusive the amount of time each trap was abandoned. Only after fifteen days the absorption rate of the virgin material was already stabilized and the density did not vary much from then on. As it can be analysed on the chart on appendix E, there is not much difference between a material submerged for fifteen days or fifty.

With this information is possible to presume that, although it is not possible to estimate the amount of time the material was on the ocean, the first and second groups of waste material either did not absorb a great quantity of water or if they did, remained on shore long enough for the humidity to be evaporated by the sun. While the third group still had a lot of moisture, making it possible to assume that this trap was in the ocean and didn't has much time on the beach for the humidity to be eliminated.

It is also important to consider the deterioration caused by other means than its contact with water, such as the wind, the sand and rubble, contact with bio-organisms and even the effect of the solar radiation.

4 Plastic Litter Processing

After testing the waste material, it is important to evaluate the possibility of processing it and how its final properties were affected. On an initial phase, both materials, HDPE and PA, were prepared to be injected and create new specimens to make similar tests as before with these new materials. After the injection process, the remaining grinded HDPE was used to produce parts by extrusion with a robot, as it will be explained further on. Using this method, it will be possible to evaluate the processability of this material by 3D printing.

4.1 Melt Flow Index (MFI)

The Melt Flow Index (MFI) is a test usually used to evaluate the processability of polymeric materials. The measurement is obtained by extruding heated material through a capillary tube using a piston actuated with a standard weight. The material's temperature and the weight used are defined according to the standard used [17]. This is an interesting test to make, with its results we will be able to understand directly how much the degradation of these materials affect their processability.

During this procedure the ASTM D1238-01 was the guide line applied and a RayRan Melt Flow System was the equipment used. A sample of five to eight grams of HDPE was weighted for the test and, after a few minutes heating and homogenizing the material, it was extruded for one minute and the filament obtained during this time was weighted. The mass of this filament is then multiplied by a specified factor, on this case, ten. The conditions used during the test were a chamber temperature of 190 ^{o}C and a mass of 2,16 kg. The same procedure was repeated for the nylon. The tests with virgin PA 66 where made with a sample between five and eight grams, the chamber's temperature was 275 ^{o}C and the mass used was 0,325 kg, the tests lasted one minute and the factor used was ten. While the waste PA 6 had different conditions used, the initial sample was between four and eight grams, the extrusion was made during fifty seconds, the temperature was 235 degrees Celsius, the weight was 2,16 kilograms and the factor is twenty. The conditions of the nylon samples differ between the waste and the virgin material, because the virgin material could not be extruded with a 235 degrees Celsius temperature, the material would not be hot enough to flow through the die. Each test result obtained and MFI calculated are shown on table 4.1.

All the values obtained from the tests are between the theoretical interval, but as it can

Table 4.1: MFI results obtained for each test and material and respective average and theoretical values [14, 15, 18]

	Mass [g]							MFIg/10min>g/10min	Theoretical MFI [g/10min]
	Specimen 1	Specimen 2	Specimen 3	Specimen 4	Specimen 5	Average	Standard Deviation		
Waste HDPE	0,0234	0,0184	0,0187	0,0203	0,0190	0,0200	0,0018	0,20	0,0250 - 1610
Virgin HDPE	0,3351	0,3340	0,3373	0,3325	0,3432	0,3364	0,0037	3,36	
Waste PA 6	0,7447	0,7618	0,8331	0,7810	0,8148	0,7871	0,0327	15,74	1 - 198
Virgin PA 66	0,2496	0,2415	0,1785	0,2101	0,1722	0,2104	0,0316	2,10	2 - 148

observed, this MFI range is very wide. The virgin material used is a KS 10100 UE HDPE, according to its datasheet the expected value for the melt index is 4 g/10 min in the same conditions as the test was made [19]. Comparing this value with the waste HDPE MFI, the difference is significant, although it is still within the theoretical values. This means that the material is clearly degraded and it affected its processability.

A similar situation occurs with the nylon's case, only in this case it is not possible to compare the virgin PA 66 with the waste PA 6, since the obtained values are lower for the virgin material, which might be due to the fact that these are different materials. The waste material's MFI is within the theoretical interval, nonetheless it is expected that the original value was higher than the one obtained. In conclusion, both materials' MFI were clearly affected, yet their processability does not seem to be hampered.

4.2 Differential Scanning Calorimetry (DSC)

In order to have a general idea of the parameters in which each equipment will operate, it is necessary to determine a few thermal properties of each material before initiating its processing, such as melting (Tm), crystallization (Tc) and glass transition temperatures (Tg). A Differential Scanning Calorimetry (DSC) was made to obtain these values. The typical curve obtained during these tests is represented on figure 4.1 and there are two different temperature ramps, a first one of heating and another of cooling.

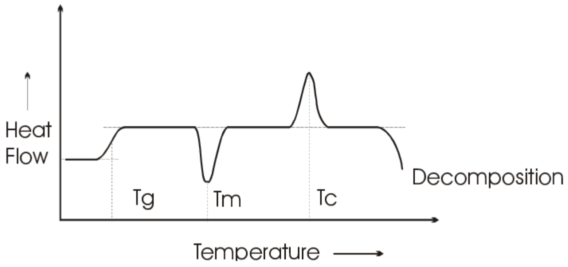


Figure 4.1: Typical DCS curve obtained for polymeric materials.

There are three obvious distortions, a rapid variation of heat flow is associated to the glass transition temperature and two different peaks, one referring to the melting temperature and the other to the crystallization temperature, this last characteristic is the only property observed during the cooling phase.

The tests were made for both waste materials and a Setaram DSC 131 was used. Following the equipment's instruction manual a mass of 0,0373 grams of HDPE and 0,0146 grams of nylon were placed inside the heating chamber and the following charts were obtained, figure 4.2 for the HDPE and figure 4.3 for the nylon. The approximate results for the thermal characteristics of each material and their corresponding theoretical values are listed on table 4.2.

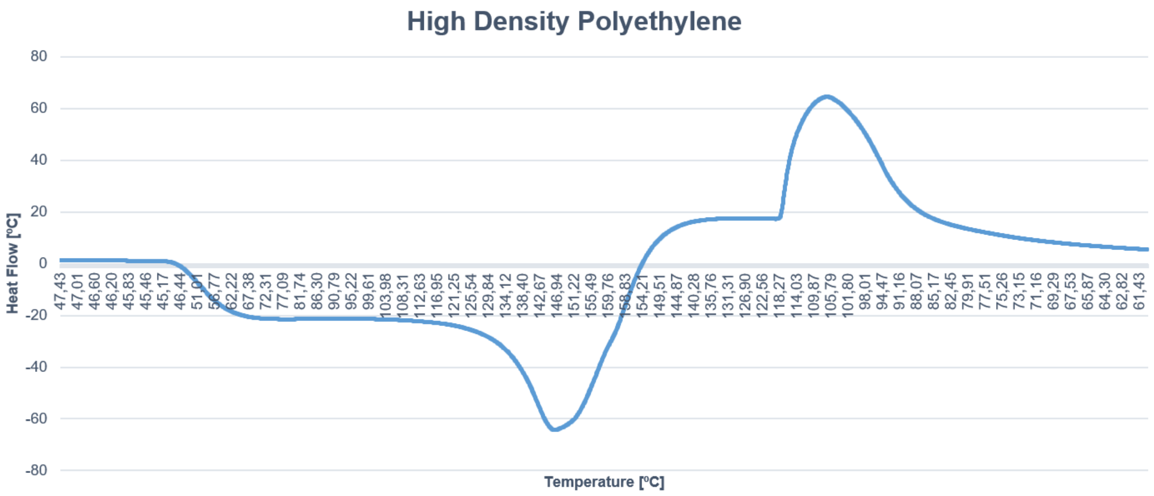


Figure 4.2: DCS chart of waste HDPE.

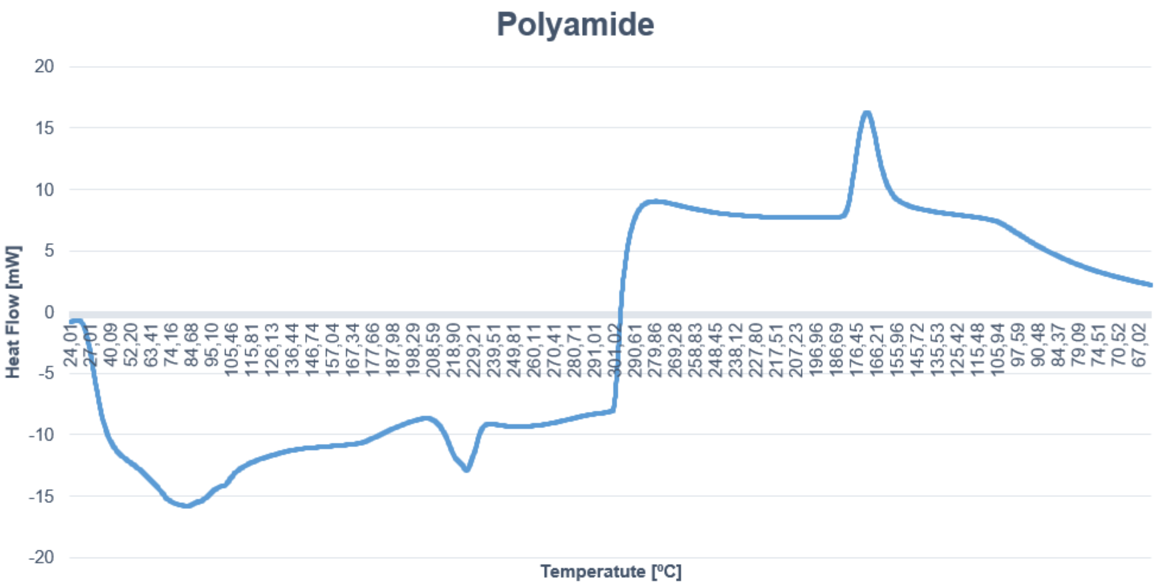


Figure 4.3: DCS chart of waste PA.

Table 4.2: Approximate obtained and theoretical values for the glass transition, melting and crystallization temperatures [16, 14, 18, 20]

		Heat Flow (mW)	**Temperature (°C)**	**Theoretical temperature (°C)**
HDPE	**Glass transition**	N/A	N/A	-110
	Melting	-64,36	146,43	118-137
	Crystallization	64,52	106,80	108-120
		Heat Flow (mW)	**Temperature (°C)**	**Theoretical temperature (°C)**
PA 6	**Glass transition**		30-80	60-142
	Melting	-12,91	225,81	141-315
	Crystallization	16,27	170,95	177

From what we can observe from the data acquired, it is possible to conclude that the thermal characteristics of the HDPE change to the point where they are no longer within the theoretical range, unlike the nylon. Both melting and crystallization temperatures have changed, the first one is higher than the theoretical values, while the second is lower. This difference, however, is not great, which means that the capability of processing should not be precluded.

PA properties are very similar to the virgin material, but this does not mean that they did not change from the original value, since there are a lot of different types of nylon and the net datasheet provided did not have that information. Having that into consideration, it is expected that the properties have changed slightly.

4.3 High Density Polyethylene (HDPE)

This material was possible to be processed through both injection molding and extrusion. As it will be further explained the initial plan was to produce filament for Fused Deposition Modeling (FDM), but it was not possible to obtain a calibrated filament, thus the alternative used was a small extruder moved by a robot arm, allowing the possibility to build parts directly from pellets or crushed materials.

4.3.1 Waste High Density Polyethylene Preparation

In order to inject the litter, it was necessary to prepare the material first. As previously said on the initial concepts the recycling pre-treatment process usually involves separation of embedded organisms, salts and sludge cleaning, grinding and drying. For this reason, the traps were initially cleared of sand and the majority of the loose sediments with water; they were then cut in pieces to facilitate the cleaning process; in order to eliminate the remaining debris and organic matter, the fragments were sanded; and finally the material was grinded into pieces small enough to be processed.

4.3.2 Waste High Density Polyethylene Injection

Before the injection process it self, the material was dried at 50 degrees Celsius for about one hour and a half. The injector used was a EuroInj's Inautom D80 and there were two phases of the process where parameters used differentiate. The first one was used to produce tensile specimens, the criteria used is specified on table 4.3. The second part produced bending specimens, its parameters are stated on table 4.4.

Table 4.3: Parameters used during the first part of the injection process to obtain the tensile specimens.

Temperatures			
Nozzle	Zone 2	Zone 3	Zone 4
210	185	170	160
Injection			
	Pressure [bar]	Velocity [%]	Position [mm]
	110	55	15
Load /Decompression / Cooling			
	Pressure [bar]	Velocity [%]	Position [mm]
Load	60	50	47
Decompression	35	50	2
	Pressure [bar]	Velocity [%]	Time [s]
Cooling	50	55	0

Table 4.4: Parameters used during the second part of the injection process to obtain the bending specimens.

Temperatures			
Nozzle	Zone 2	Zone 3	Zone 4
210	185	170	160
Injection			
	Pressure [bar]	Velocity [%]	Position [mm]
	115	60	4
Load /Decompression / Cooling			
	Pressure [bar]	Velocity [%]	Position [mm]
Load	70	50	50
Decompression	35	50	2
	Pressure [bar]	Velocity [%]	Time [s]
Cooling	50	55	0

The tensile specimens were produced to make new tensile tests and the bending specimens were made with the DMA and hardness tests in mind.

The parameters used differentiate due to complications found when injecting the waste material. The specimens, even with several adjustments done during the several tries, had some visible defects related to its homogeneity as it can be seen on figure 4.4.

Figure 4.4: Homogeneity obtained on the specimens due to the material's injection difficulties.

The parameters used were based on the theoretical recommendation according to MatWeb on figure 4.5 [18]. Although the used values are within the range, the homogeneity and the specimens quality was not the best possible. Due to the limited material available for injection, it was not possible to improve the specimens' condition. This situation would possibly be avoided if further thermal tests were developed or if more tries would be done during the injection process, adjusting the parameters.

Table 4.5: Recommended parameters for injection of virgin HDPE.

Processing Temperature [ºC]	82,2-274
Nozzle Temperature [ºC]	160-275
Melt Temperature [ºC]	130-280
Mold Temperature [ºC]	5-65,6
Drying Temperature [ºC]	37,8-70
Injection Pressure [MPa]	2,76-103

Tensile Tests

Using the same method as previously explained with the specimens cut directly from the waste material, the tensile tests were made and image 4.5 represents the obtained chart for each one of the acceptable results and table 4.6 has the values obtained for the stress, yield strain and tensile strength.

Table 4.6: Obtained values with the tensile tests for the injected material.

	σ_{x1} **MPa**	σ_Y **MPa**	ε_Y **%**
Specimen$_5$	18,49	18,59	11,65
Specimen$_7$	21,02	21,19	12,59
Specimen$_{11}$	20,51	20,63	12,03
Average	20,01	20,14	12,09
Standard Deviation	1,09	1,12	0,39

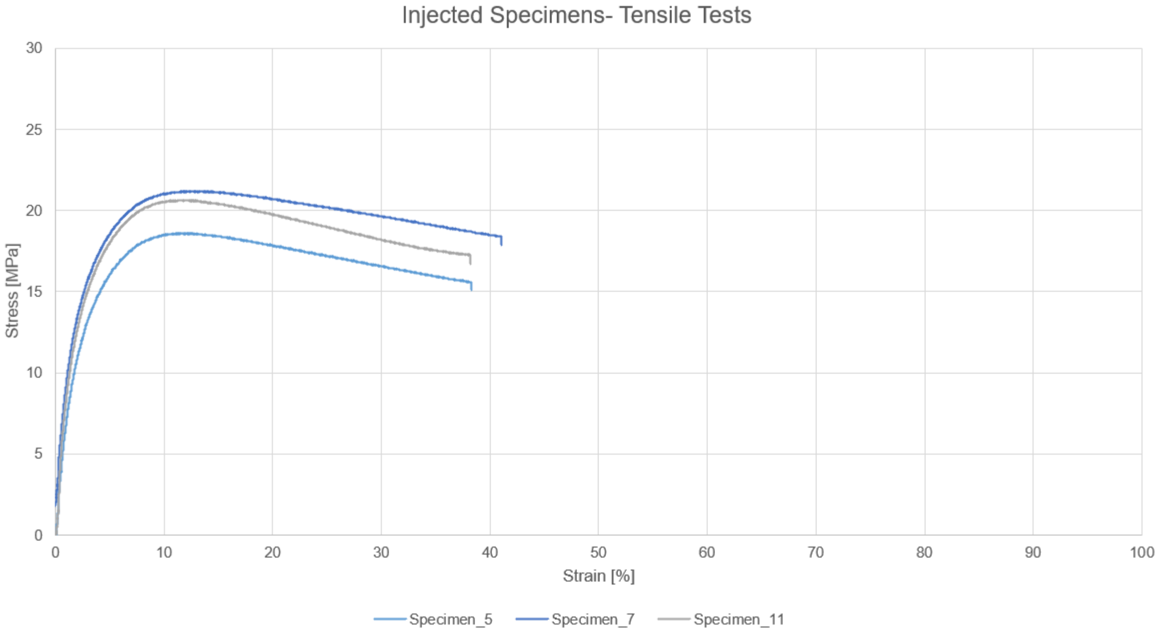


Figure 4.5: Tensile tests for the three specimens of injected waste material.

As it can be analysed from the chart, the line obtained distinguishes itself from the ones obtained on the specimens directly cut from the waste materials. This time the line is much more straight then previously observed. This means that the material has greater quality and less cracks, making it more stable during the process. Also, the specimen did not reached a point of near breaking, if the test continued longer, the specimen would probably have had a similar behaviour as a virgin material.

In order to have a better understanding of how the results of each type of material differentiate from each other, table 4.7 summarizes the information obtained during the different tensile tests with a average of all the specimens for the different material, virgin, injected and each group of waste material.

Table 4.7: Average of the values obtained for the different materials studied.

	σ_{x1}	σ_Y	ε_Y	b	h	A_0
	MPa	**MPa**	**%**	**mm**	**mm**	**mm^2**
Virgin	24,51	24,61	7,82	9,7	3,9	37,83
1st Group	14,21	14,14	6,41	13	1,5	19,5
2nd Group	17,86	18,56	7,09	13	1,5	19,5
3rd Group	16,77	16,62	6,66	13	1,5	19,5
Injected	20,01	20,14	12,09	10	4,7	47

As it can be observed the injected material, for all the parameters, the results are higher than the waste material. This means that it is more similar to the virgin HDPE than the waste.

Dynamic Mechanical Analysis (DMA)

In order to develop this second phase of thermal tests, it was necessary to cut the specimens injected with geometry usually used for bending tests. The final geometry of each of the used specimens are summarized on table 4.8 as well as the reference length used during the test programming and the measurement limits necessary to take into account. A conventional milling machine, Otto Holke's Holke F10V, was used to obtain the designed geometry. The parameters used during the tests are the same as the ones applied for the waste material case.

Table 4.8: Specimens' geometry obtained after the cutting process.

	Reference Length [mm]	**Length [mm]**	**Width [mm]**	**Thickness [mm]**
Specimen 1	20	47,7	9,5	3,7
Specimen 2		46,6	8,7	4
Specimen 3		48.5	9.4	3.4
Geometry Intended		40-50	<10	1-4

With the tests completed, the following charts were obtained, figure 4.6 for the first specimen, the second specimen on appendix F and the third on appendix G.

Similarly to the previous DMA tests, the conclusions taken from this charts is that the glass transition temperature is lower than 20°C, but it is inconclusive its actual value or if it is identical to the virgin material.

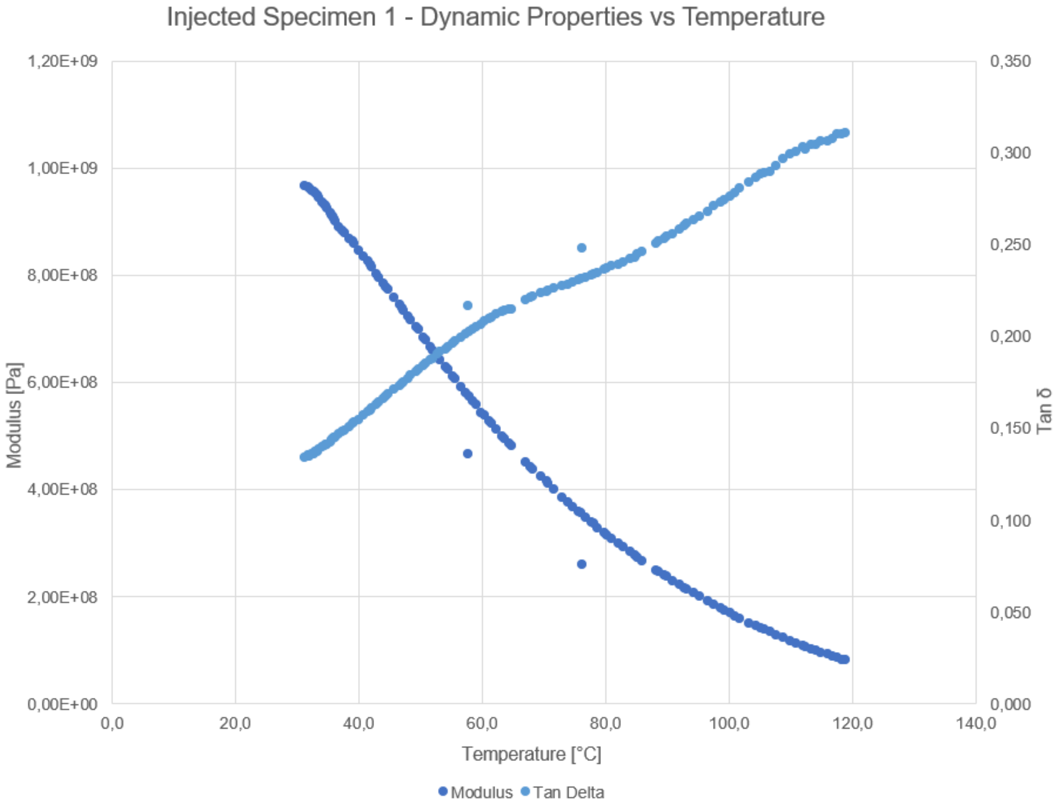


Figure 4.6: DMA results for the first specimen.

Hardness Tests

The method used for this test is the same that was used for the waste material. The bending specimens were used for this tests and once again they did not had enough thickness, to resolve this situation, two specimens were stacked together and used the same way as for the waste material. The obtained values are organised on appendix H and summarized on table 4.9.

Table 4.9: Average values for each specimen or group of waste and injected material, as well as the theoretical hardness interval of virgin HDPE.

	Waste	**Injected**	**Virgin**	**Theoretical**
Specimen 1 /Group 1	50,44	51,63	61,75	50-76
Specimen 2 /Group 2	57,69	55,75	62,00	
Specimen 3 /Group 3	56,69	55,19	69,38	
Specimen 4	-	50,19	68,88	

The conclusions to take from this results are similar to the waste case. The averages obtained are 51,63 Shore D for the fist specimen, the second averages 55,75 Shore D, while the third has a average of 55,19 Shore D, and 50,19 Shore D is the average for the fourth specimen. All the values are between the theoretical interval of the virgin material. On the chart on figure 4.7 it is easily observed the similarity between the hardness of the waste and injected material.

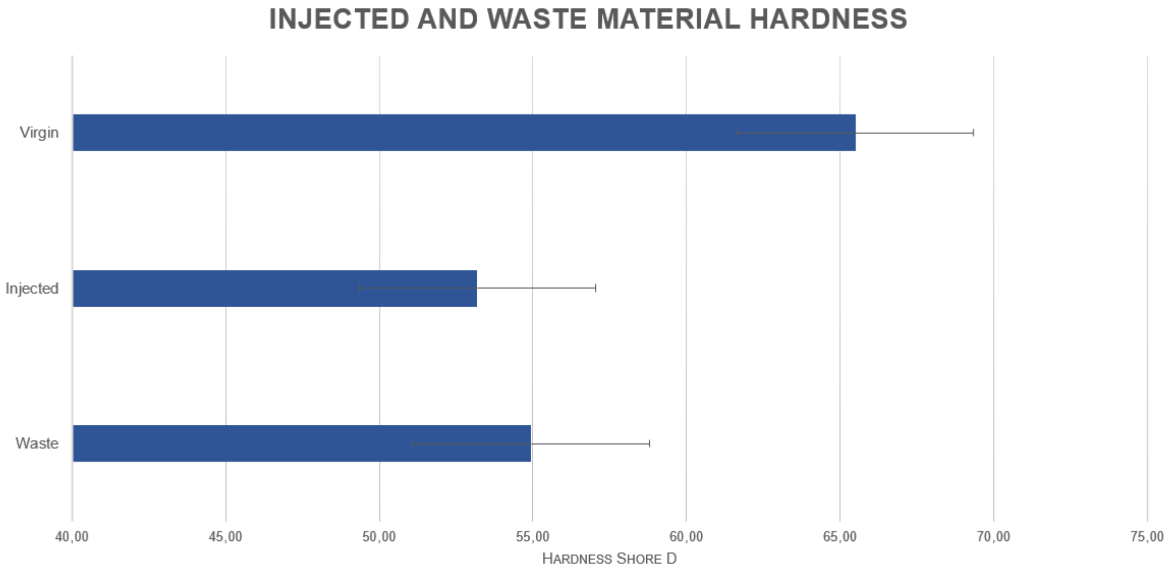


Figure 4.7: Injected, virgin and waste material hardness in shore D.

The results for the waste and injected materials are not far apart, all of the averages are between fifty and fifty eight Shore D. Although observing the calculated average values for the cases of waste and injected materials are between the anticipated interval, they are on the lower half the the gap and with clear lower results when comparing to the virgin material. This means that it is possible that the material's hardness might have been reduced from its original value due to the degradation it was subjected to. The difference is specially noticeable on the first group of waste material and the fourth specimen of injected material, since they are the closest values to the lower limit.

4.3.3 Waste High Density Polyethylene Rapid Manufacturing

Another important way of understanding the processability of this material is to test it in FDM. Initially, the crushed material was extruded in order to obtain filament using a K-tron extruder. Although it was possible to produce the intended thread, it was not possible to use it on a FDM equipment, this was because the extruder used did not have a calibrator, this means that the transversal geometry not only was not circular, but also was not constant along the filament length.

For this reason, it was necessary to use an alternative process. A robot from Roboplan with an extruder attached was used instead. This type of equipment uses pellets of material to directly build parts.

An initial test geometry was build in order to analyse the proper processing parameters and the building limitations that might be observed. The chosen model is a square in which the side's dimensions increase with each layer that is placed, figure 4.8. Each side of the final part will have a different angle, thus it is possible to evaluate some of the building limitations.

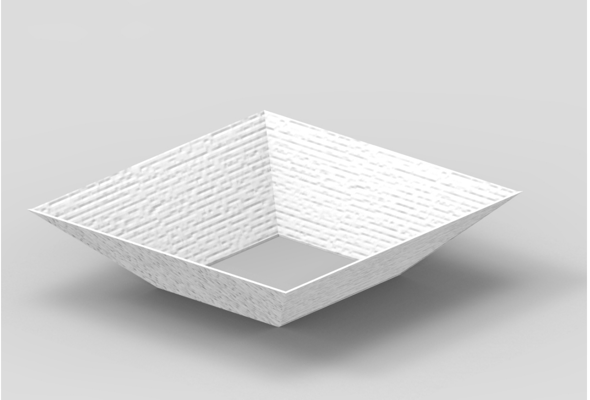


Figure 4.8: Three dimensional model of the final part intended to build.

The equipment used is programmed using a system of three dimensional coordinates. The initial program used had already been used for other projects and several parts were constructed using it. The working principle is to build an initial square with one layer of material on the platform and when building the next one, the robot would increase the distance between each side of the square and its center differently, as shown on figure 4.9. The first side of the square to build would have a difference of 1 millimeter between layers on x axis, the second side would have 1,5 millimeters on y axis, the third 2 millimeters on x axis and the fourth 2,5 millimeters on y axis. The height increase between each layer (movement in z axis) was initially of 2 millimeters and decreased later to 1,2 millimeters.

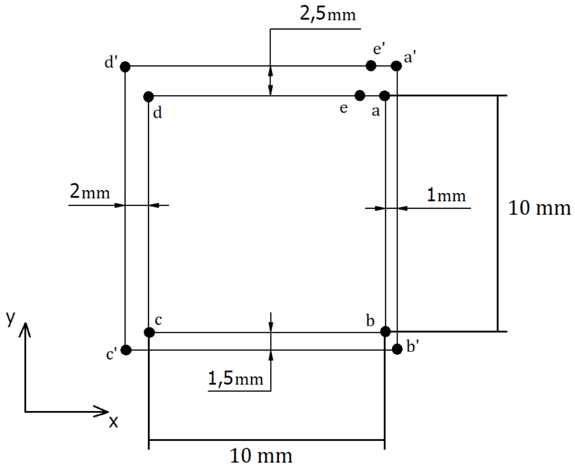


Figure 4.9: Draft of the building process between layers, where the inner square is the previous layer build (points a, b, c, d and e) and the outer square is the new one (points a', b', c', d' and e').

The building program has to be constituted by five different points for each layer, four of them represent the edges of each section (points a,b,c and d on figure 4.9), where the robot changes direction, and the fifth corresponds to the movement in z axis (point e). The same building process repeats every layer until the part is completed.

During an initial phase, the virgin HDPE used for the MFI test was used for this extrusions with the purpose of not only to compare the building capabilities of both waste and virgin materials, but also to find the general parameters to be used when processing the waste material. These parameters were adapted in order to attain the best possible geometry and were based on the information available on MatWeb [21]. Figure 4.10 represents some of these models build and the respective parameters used are listed on table 4.10.

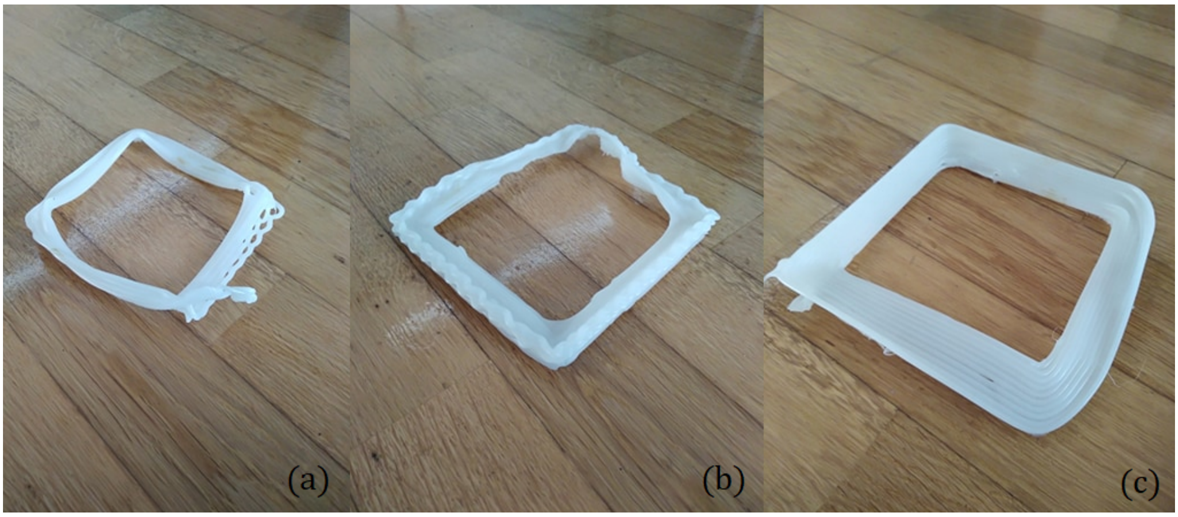


Figure 4.10: Parts and respective parameters obtained during the first building phase with virgin HDPE where (a) is Part 1, (b) is Part 2 and (c) is Part 3 on table 4.10.

Table 4.10: Parameters used during the first phase of material extrusion.

Processing Conditions - Phase 1

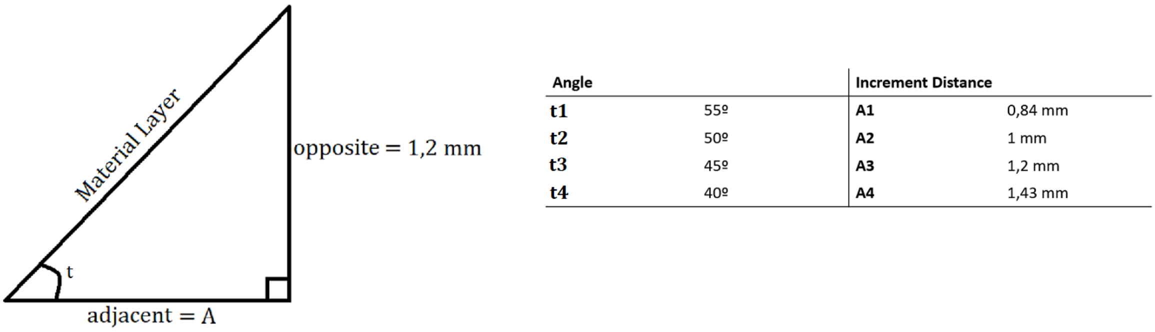
	Part 1	Part 2	Part 3
Bed Temperature [ºC]	90	120	120
Extruder Temperature [ºC]	230	180	180
Material Output [rpm]	35	35	15
Z axis offset [mm]	2	2	1,2
Cooling	Fast	Fast	Fast

As it can be analysed from the images, specially from the figure 4.10c , two of the sides could not be build properly, this is due the fact that the difference in distance between the layers (in x and y axis) is greater than the filament diameter, 2 millimeters. This causes the robot to be extruding material on top of the platform without even connecting with the previous layer build. This resulted on the modification of the initial program.

When changing the program it was decided that, instead of choosing a specific distance between layers while the angles between the part wall and the platform were a dependent measure, the other way around would be applied.

The angles would have to be chosen carefully, since the distance between layers could not reach 2 millimeters. Using the tangent of each angle chosen (t on figure 4.11) with equation 4.1, the distance between layers on axis x and y (A) is obtained.

$$\tan t = \frac{opposite}{adjacent} \tag{4.1}$$



Angle		Increment Distance	
t1	55º	**A1**	0,84 mm
t2	50º	**A2**	1 mm
t3	45º	**A3**	1,2 mm
t4	40º	**A4**	1,43 mm

Figure 4.11: Draft of the transversal section of the side of the square and final measures obtained for the angle x and increment A.

With the new values for x and y axis increment on each square side, it is possible to update the program and build new parts. Using virgin HDPE, with the new program and the parameters tested on the first phase, on this second building process all the walls of the parts were build successfully, as represented on figure 4.12. The parameters used during this part of the project are listed on table 4.11.

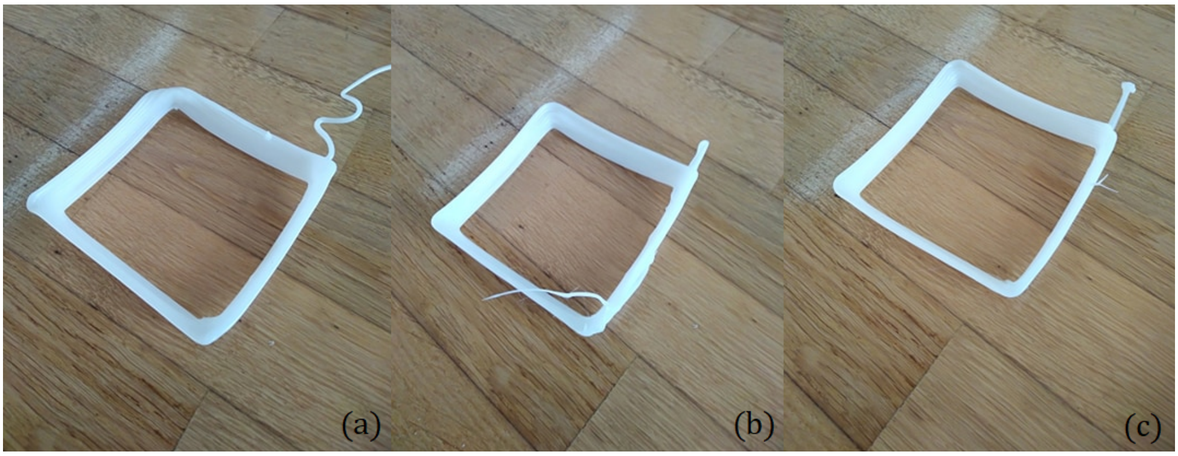


Figure 4.12: Parts and respective parameters obtained during the second building phase with virgin HDPE.

Table 4.11: Parameters used during the second phase of material extrusion.

Processing Conditions - Phase 2			
	Part 1	**Part 2**	**Part 3**
Bed Temperature [ºC]	110	110	110
Extruder Temperature [ºC]	180	180	180
Material Output [rpm]	15	15	15
Cooling	Fast	Slow	Slow

During the third phase, waste HDPE was used as building material. This time the grinded material's shape was not spherical or cylindrical as usually pellets are, which made the robot's feeding process harder than before. This difficulty not only is due to the specific system used on the robot, but would also be easily overpass by extruding pellets with a more rounded shape.

Although the parameters used were the same as the second phase (table 4.12), it was not possible to successfully build more than one part. The biggest struggle found was the inability to attach the first layer of material to the platform, even adjusting both the platform and extruder temperatures. This would make the part warp even before finishing the first layer. Only one model was build, with five layers, represented on figure 4.13.

Figure 4.13: Parts and respective parameters obtained during the third building phase with waste HDPE.

Table 4.12: Parameters used during the third phase of material extrusion.

Processing Conditions - Phase 3	
Bed Temperature [ºC]	110
Extruder Temperature [ºC]	180
Material Output [rpm]	15
Z axis offset [mm]	1,2
Cooling	Slow

4.4 Polyamide (PA)

As it was possible to observe previously, one of the elements more commonly found in beaches are fishing nets. Which makes this another great material to study as a possible new raw material for several applications. as it will be proven in this section.

As it will be further on explained, it was not possible to obtain specimens of virgin material to compare their properties with the waste material, for this reason tests done dor PA 66 specimens and theoretical PA 6 values for each property will be used as comparison.

4.4.1 Waste Polyamide Preparation

The initial net was obtained in Peniche beach, made available by a local fisherman. This made it possible to obtain the datasheet of the material, since the fisherman knew where he obtained the net. It was concluded that the net was made of PA 6.

The net was too big to be grinned without being cut in smaller pieces, for this reason the material was prepared for that purpose. However, the pieces of net wrapped themselves around the crusher shaft, which prevented the use of this process. As an alternative, the material was melted with a torch and later inside a oven (figure 4.14), with the purpose of turning the net into a solid and more dense object to be crushed, but it was concluded that these processes would alter the materials properties, which would directly affect the tests planed to be made. It was then decided to cut the net with scissors to a size small enough for the injection process.

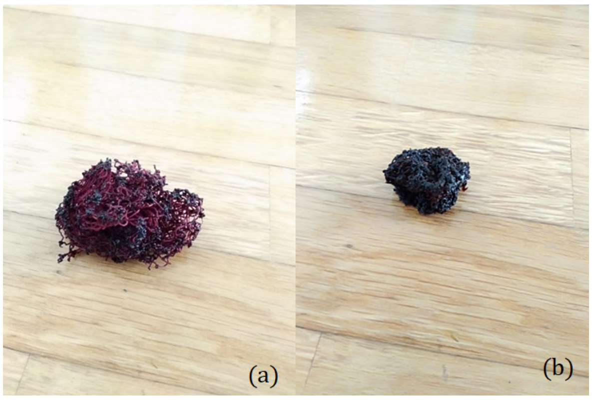


Figure 4.14: Material obtained by melting the net with a torch (a) and inside an oven (b).

4.4.2 Waste Polyamide Injection

The material cut was directly injected. Although, such as the case of the HDPE, it would be possible to extrude the material to make pellets for a easier feeding process. The parameters used during this procedure were based on the values recommended by the MatWeb, these parameters are listed on table 4.13 [14]. The equipment used was a Boy 22A and table 4.14 represents the parameters used to inject the waste nylon material.

Table 4.13: Parameters recommended by MatWeb for the nylon's processing [14].

Processing Temperature [°C]	80.0 - 335
Nozzle Temperature [°C]	210 - 290
Melt Temperature [°C]	200 - 330
Mold Temperature [°C]	21.1 - 120
Injection Pressure [Mpa]	3.45 - 172

Table 4.14: Parameters used during the nylon's injection process

	Zone 5	**Zone 4**	**Zone 3**	**Zone 2**	**Zone 1**
Temperature [°C]	240	235	235	230	230
Pressure [bar]	1800		2500		
Material Output [cm3]	361,17				

As it was expected, the feeding process was difficult, as the net tended to warp around itself, which made its entry on the extruder screw hard. The final specimens obtained had great quality, with good homogeneity and with no burrs.

Tensile Tests

The tensile tests were made using a Instron 4505 available on the Centre for Rapid and Sustainable Product Development (CDRSP). Using the same procedure as the HDPE, these tensile tests were done for the specimens obtained from the injection process and a similar equivalent virgin material. In this particular case, there was not virgin PA 6 material available to inject neither there were specimens already made of this specific material. The only options available were to use PA 66 (a similar material with slight changes on its properties) or a composite of PA 6 with 30% of glass fiber. Between these two materials the most similar to the intended material is PA 66. For this reason the processed waste material properties will be compared with the corresponding theoretical PA 6 values and the results obtained from tests made to the PA 66 specimens.

The results obtained from the test and the theoretical values of each material are listed on table 4.15. The obtained charts are represented on figures 4.15 and 4.16, for the waste polyamide 6 and the virgin polyamide 66 respectively.

Table 4.15: Obtained values from the tensile tests for the virgin PA 66 and waste PA 6 materials [14, 22].

		E	σ_Y	ε_Y	σ_M	ε_{tM}	σ_B	ε_{tB}
		MPa	**MPa**	**%**	**MPa**	**%**	**MPa**	**%**
Virgin PA 66	**Specimen 1**	6279,51	60,86	1,3667	108,98	4,1083	107,54	4,9683
	Specimen 3	6807,15	51,37	1,1083	108,00	4,0183	107,41	4,4350
	Specimen 5	6135,74	57,60	1,3300	114,74	4,2800	114,23	4,3317
	Specimen 6	6377,62	52,28	1,1867	106,52	4,1350	106,41	3,9850
	Specimen 8	5839,66	56,60	1,3667	105,06	4,1083	103,93	4,8833
Average		6287,93	55,74	1,2717	108,66	4,1300	107,91	4,5207
Standard Deviation		316,80	3,51	0,1052	3,32	0,0848	3,42	0,3638
Theoretical PA 66		600-25000	30-98	1,50-210	7,52-260			1-300
Waste PA 6	**Specimen 1**	1697,37	19,65	1,5917	45,03	16,9333	40,74	34,2667
	Specimen 3	2405,50	37,33	1,7517	53,01	5,1633	50,94	10,2300
	Specimen 5	2217,73	36,72	2,1900	52,19	7,1933	51,86	8,7717
	Specimen 7	2237,95	26,41	1,6183	52,17	13,8367	47,56	23,6333
	Specimen 8	2051,30	27,86	1,5583	43,45	14,1500	41,40	21,7500
Average		2121,97	29,59	1,7420	49,17	11,4553	46,50	19,7303
Standard Deviation		240,12	6,67	0,2334	4,07	4,4876	4,66	9,3911
Theoretical PA 6		210-16600	3,45-100	1,50-140	20-225			0,4-500

From the values calculated, it is concluded that the virgin material has much more consistency, the curves obtained on the charts are very similar to each other. All the values are between the theoretical interval, although they are on the lower range, it is not a critical difference. This facts might not only be related to the degradation of the waste material, but also to the injection process. Nylon is a material with high absorption rate, which means that it is important to take that into consideration when processing and testing this material. If the material was tested or injected with different parameters or conditions, it would likely affect the overall properties of the material.

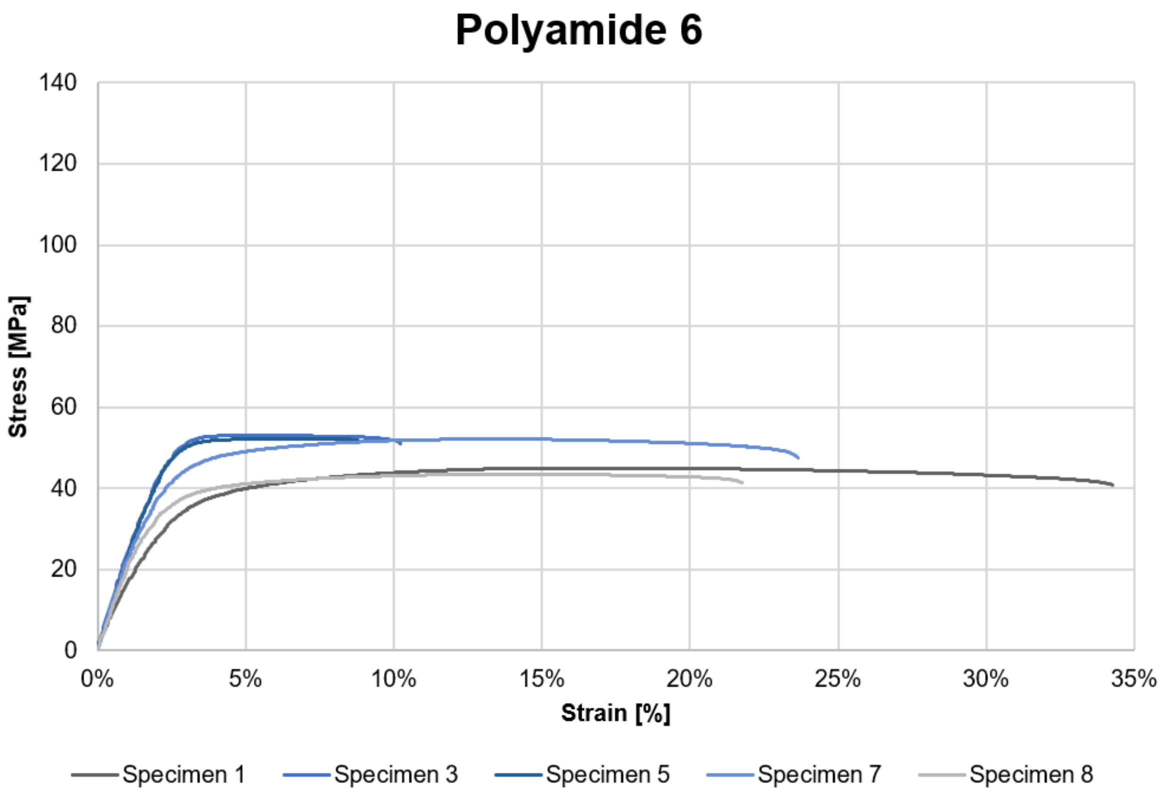


Figure 4.15: Charts obtained for each specimen of virgin polyamide 6 with acceptable results in tensile tests.

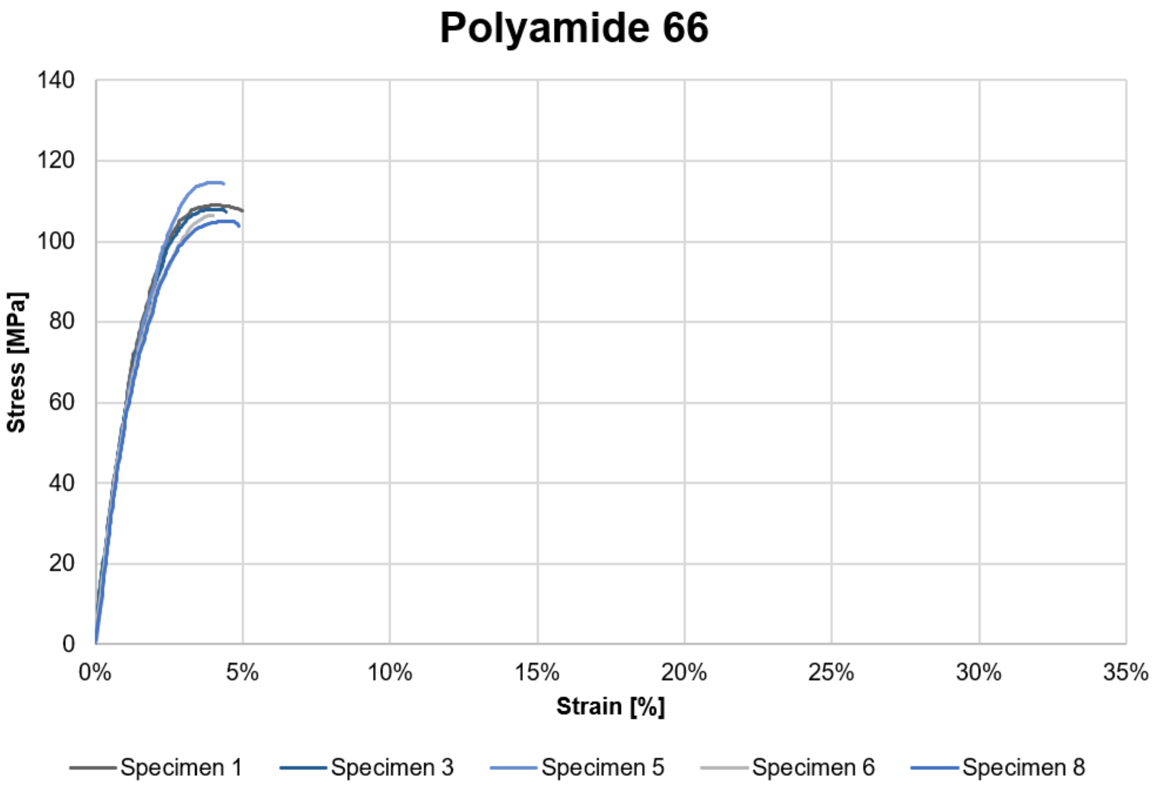


Figure 4.16: Charts obtained for each specimen of waste polyamide 66 with acceptable results in tensile tests.

Dynamic Mechanical Analysis

The procedure used during the polyamids DMA tests is based on the same plan of action used with the HDPE, only this time the maximum temperature reached by the equipment was 180 °C. Theoretically, the glass transition temperatures of PA 6 is between 60 and 142 °C and PA 66 55 °C [16, 14]. Once again, it was necessary to cut some of the parts obained from injection to a proper geometry for the test, table 4.16 lists the intended and obtained dimensional values for each specimen of each material.

Table 4.16: Specimens' geometry obtained after the cutting process of the nylon's specimens.

		Reference Length [mm]	Length [mm]	With [mm]	Thickness [mm]
PA 6	**Specimen 1**	20	50	10	3,4
	Specimen 2		50	9,7	3,7
	Specimen 3		50	9,7	3,1
PA 66	**Specimen 1**	20	50	9,7	3,7
	Specimen 2		50	9,4	3,7
	Specimen 3		50	9,7	3,8
Geometry Intended		20	40-50	<10	1-4

Three tests were made for each material where, unlike HDPE, it was expected that the obtained charts would have the characteristic sudden decrease of Young Modulus between 60 and 142 °C. The charts constructed from the acquired data are on figure 4.17, appendixes I and J regarding the waste PA 6 and figure 4.18, appendixes K, and L for the PA 66.

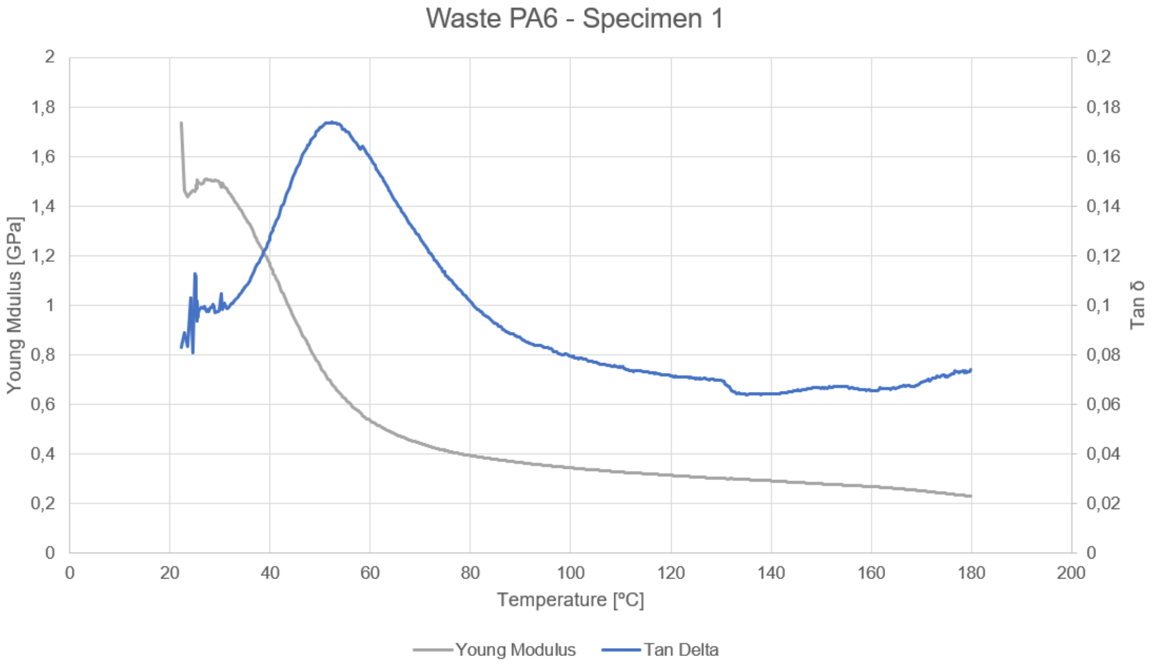


Figure 4.17: Chart obtained for the first specimen of injected PA6 material.

As expected, it is possible to observe a completely different chart than the one regarding HDPE. However, the sudden decrease of Young's Modulus, indicating the general area where the glass transition temperature is, occurs earlier than the theoretical 60 °C. The first chart indicates that this thermal characteristic is between 30 and 50 °C, the second around 35 and 60 degrees and the third between 30 and 60 °C.

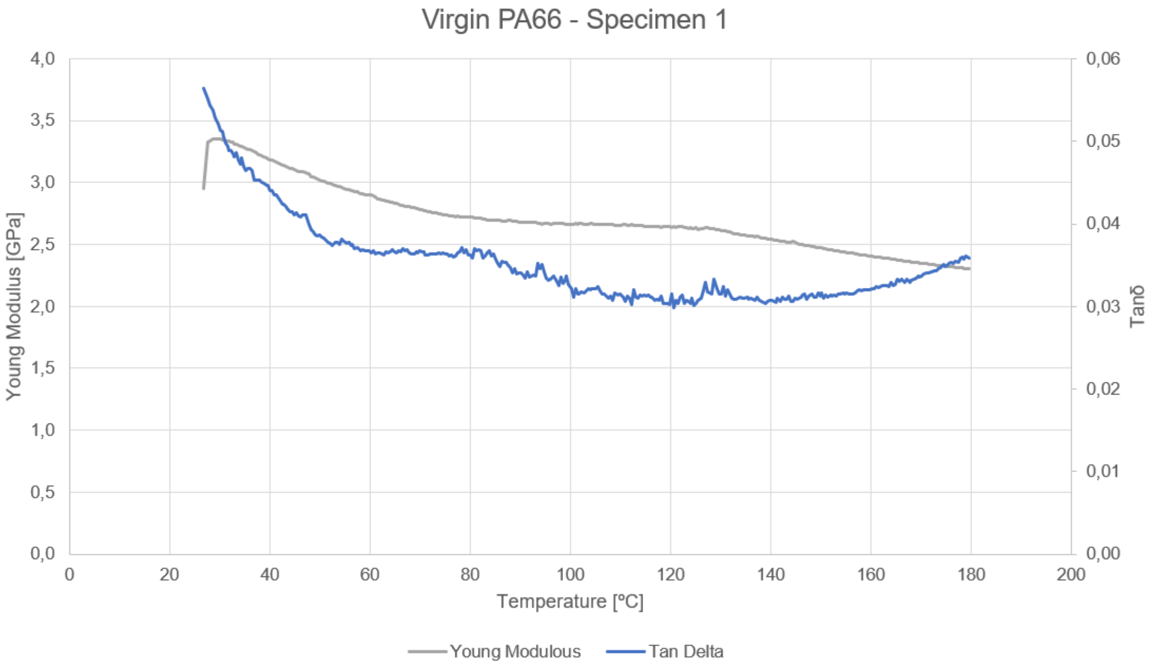


Figure 4.18: Chart obtained for the first specimen of injected PA66 material.

This PA 66 charts are a lot harder to analyse than the waste PA 6 material. The decrease of Young's Modulus is much more smother than expected, making it harder to pinpoint the glass transition temperature. Only the second specimen's chart indicates that this temperature could be around 65 °C, a much higher temperature than expected.

Since it was not possible to obtain a specific value or interval regarding the virgin PA 66 material, it is only possible to compare the waste PA 6 results to the theoretical values. Although it is hard to know exactly the value for this property based on the obtained charts, it is possible to observe that there was a decrease in glass transition temperature. This change might be due to the degradation on the material. It was also not possible to obtain a specific value for the glass transition temperature using the DSC test, it was only possible to estimate a possible interval (30 to 80 °C), but the DMA results are within the estimated range. Regarding the initial Young's Modulus measured, it is lower than the values obtained from the tensile tests, but the difference is not significant, making them reliable.

Hardness Test

The procedure used for this test was the one previously explained for the HDPE, using the ISO 868 standard. Once again the specimens had not enough thickness to be used directly, instead two specimens were placed on top of each other to make up the minimum thickness. The obtained values for the waste material and the PA 66 specimens are listed on appendixes M and N, respectively, and summarized on table 4.17.

Table 4.17: Average values for each specimen of waste and virgin material, as well as the theoretical Shore D hardness interval of each corresponding materials [14, 15]

	Waste PA 6	**Virgin PA 66**
Specimen 1	79,08	82,00
Specimen 2	78,19	75,75
Specimen 3	77,56	78,00
Specimen 4	76,50	78,25
Theoretical	57-87	78-88

As it can be observed the values obtained for the processed waste material are not very different from the PA 66 specimens. This comparison is easily analysed on the chart 4.19.

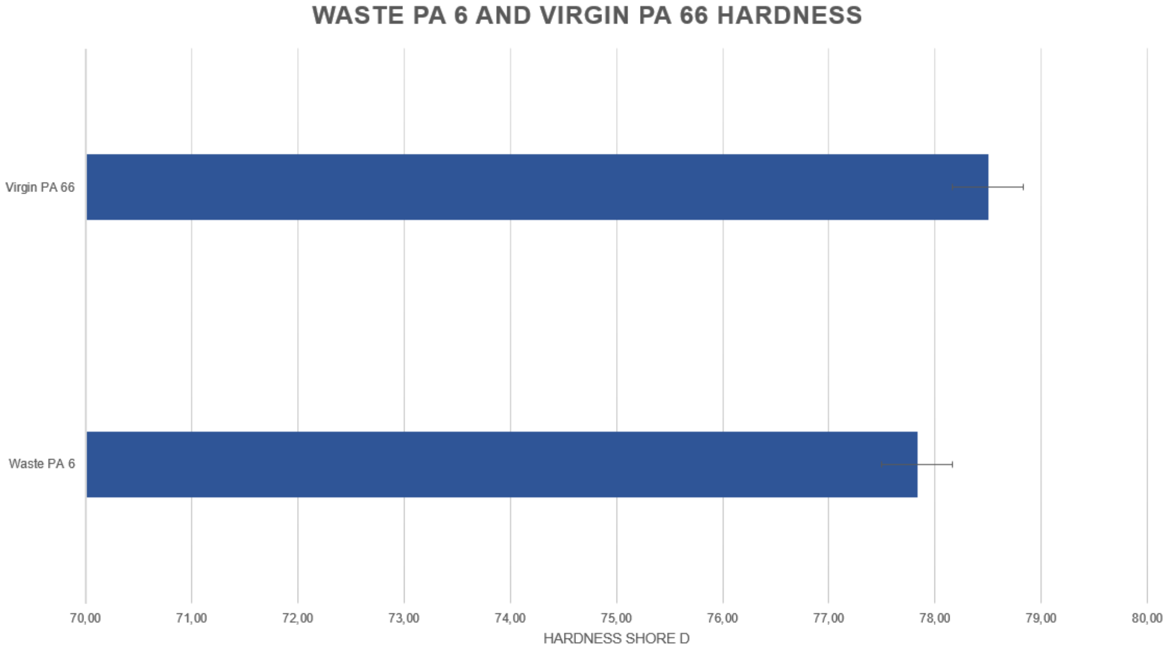


Figure 4.19: Waste PA 6 and virgin PA 66 hardness in shore D.

All the values obtained from the tests are between the theoretical intervals, which suggests that the material's degradation did not affect its hardness. But it is important to take into consideration that there are several different types of nylon 6 with different properties. Since the comparison was not made with the exact corresponding virgin material, it is only possible to conclude that the material's hardness was not affected significantly.

5 Conclusions

It is now possible to conclude that the deterioration of the materials clearly affected their properties, nevertheless they are still usable as new raw materials. The difference between the obtained results and the expected values from the MFI and the DSC test is not significant enough to preclude the processing of both the nylon 6 and the high density polyethylene, and the obtained results from the injected material were very similar to the virgin material and the theoretical projection. This means that it is not necessary to mix virgin materials with waste to obtain good results. Thus, instead of producing new polymers, the waste should be used instead, allowing a constant and gradual cleaning of oceans, beaches and overall earth.

This possibility could also be applied to other materials, therefor it is important to further investigate other polymers and properties and evaluate how this new raw materials could be used and in which applications. If it is not possible to use them in the usual areas we need to think of other ones, for example if the properties of one specific type of material are too much affected, instead of using them in the usual applications it is possible to apply them in simple storage for homes and companies, or other types of objects that do not require specific mechanical properties.

To make this possible it is necessary to improve the collection process of specific materials, specially in coastal areas and harbors. Tourism companies, fishermen and other fields working in the coast should be encouraged to take the used materials to the proper place, since these are the biggest sources of oceanic pollution.

Even if the processability of some materials might be affected, for instance the extrusion of high density polyethylene, it does not mean that the material is not processable with this method. Instead, the processing conditions should be adapted. Some of this deteriorated polymeric materials need to be classified as new materials and their properties and processing conditions standardized, rather then trying to get the same characteristics as the original material from them.

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Appendices

Appendix A

The chart obtained at the end of the second DMA test done to the waste High Density Polyethylene is represented on this appendix.

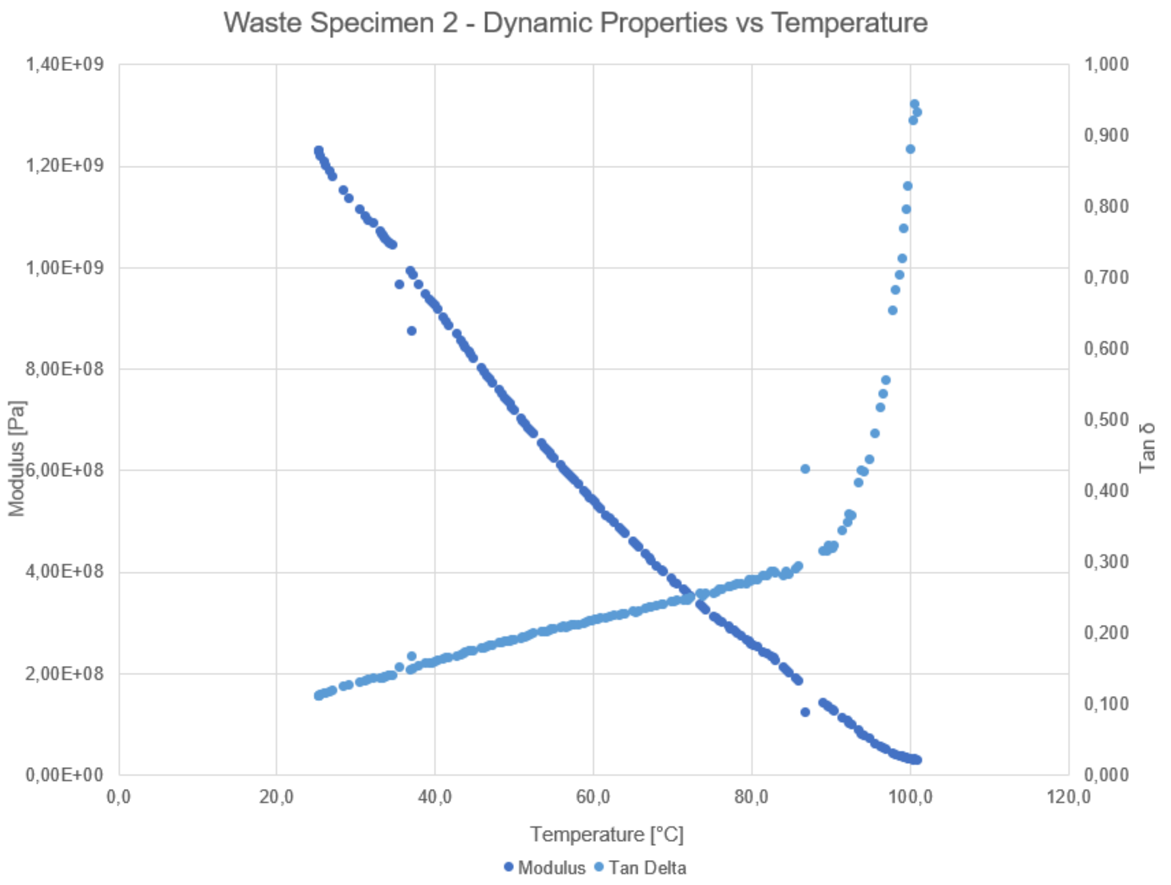


Figure 5.1: DMA results for the second specimen.

Appendix B

This appendix represents the obtained chart regarding the third DMA test done on the waste High Density Polyethylene specimens.

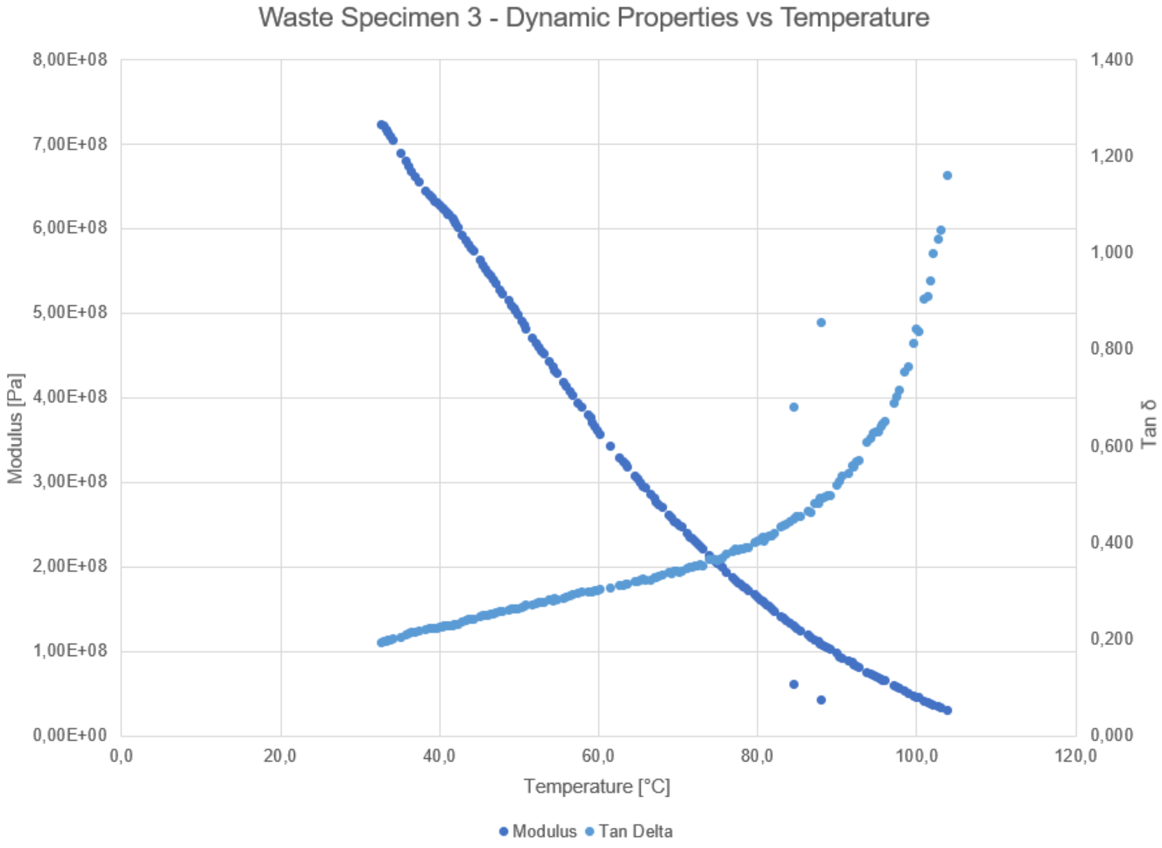


Figure 5.2: DMA results for the third specimen.

Appendix C

On the following table are listed the obtained values for the hardness in shore D (zero and fifteen second after releasing the weight) of the virgin High Density Polyethylene.

Table 5.1: Obtained values for the Shore D hardness of the virgin HDPE.

	Specimen 1				**Average**	**Standard Deviation**
0s	65	64	65	64	64,50	0,50
15s	59	58,5	60	58,5	59,00	0,61
Final Average	62	61,25	62,50	61,25	**61,75**	0,53
Standard Deviation	3	2,75	2,5	2,75	2,75	
	Specimen 2				**Average**	**Standard Deviation**
0s	66	65	64	66	65,25	0,83
15s	59,5	58,5	58,5	58,5	58,75	0,43
Final Average	62,75	61,75	61	62,25	**62,00**	0,56
Standard Deviation	3,25	3,25	2,75	3,75	3,25	
	Specimen 3				**Average**	**Standard Deviation**
0s	64	65	66	66	79,00	0,83
15s	60	59	60	60	59,75	0,43
Final Average	62,0	62,0	63,0	63,00	**69,38**	0,50
Standard Deviation	2	3	3	3	9,63	
	Specimen 4				**Average**	**Standard Deviation**
0s	66	63	65	64	79,00	1,12
15s	59	58,5	59	58,5	58,75	0,25
Final Average	62,5	60,8	62,0	61,25	**68,88**	0,67
Standard Deviation	3,5	2,25	3	2,75	10,13	

Appendix D

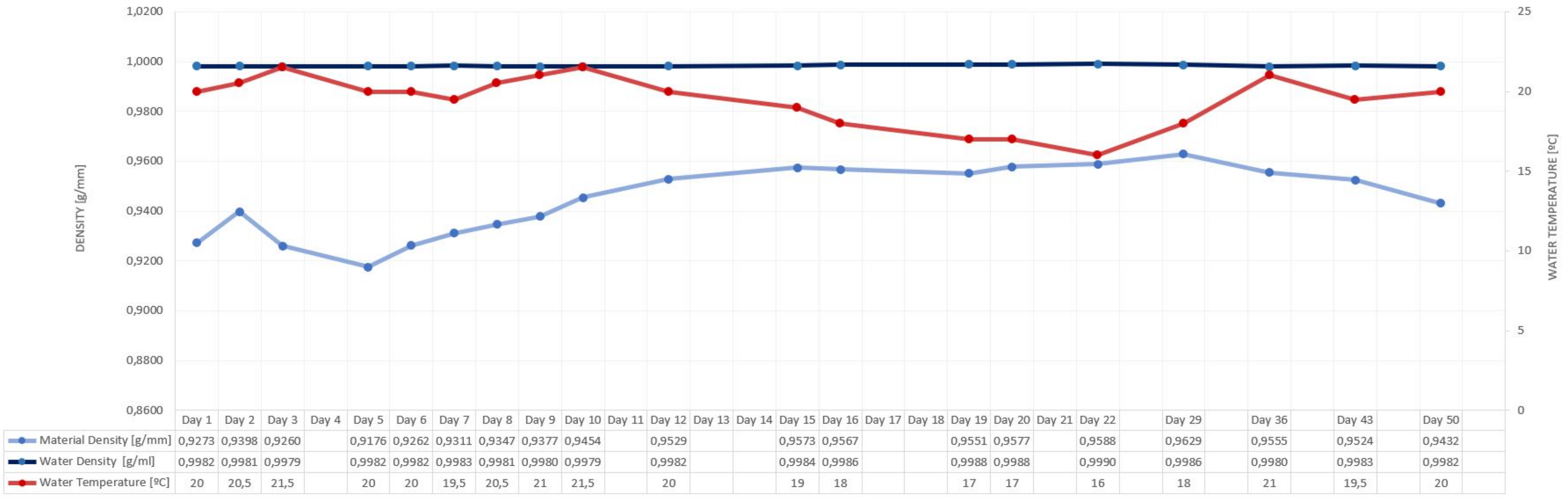
This appendix lists the obtained values of hardness in shore D zero and fifteen seconds after releasing the weight on the waste High Density Polyethylene specimens.

Table 5.2: Obtained values for the Shore D hardness of the waste HDPE.

	Group 1				**Average**	**Standard Deviation**
0s	50	51	56	54	52,75	2,38
15s	44	47,5	50,5	50,5	48,13	2,68
Final Average	47	49,25	53,25	52,25	**50,44**	2,47
Standard Deviation	3	1,75	2,75	1,75	2,31	
	Group 2				**Average**	**Standard Deviation**
0s	60	63	62	61	61,50	1,12
15s	52,5	54,5	54	54,5	53,88	0,82
Final Average	56,25	58,75	58	57,75	**57,69**	0,91
Standard Deviation	3,75	4,25	4	3,25	3,81	
	Group 3				**Average**	**Standard Deviation**
0s	60	61	60	62	60,75	0,83
15s	53	52	53	52,5	52,63	0,41
Final Average	56,5	56,5	56,5	57,25	**56,69**	0,32
Standard Deviation	3,5	4,5	3,5	4,75	4,06	

Appendix E

This appendix represents the gradual increase in density of the virgin HDPE specimens during the sea water absorption test, as well as the corresponding mass out and under water for each measurement.



	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10	Day 11	Day 12	Day 13	Day 14	Day 15	Day 16	Day 17	Day 18	Day 19	Day 20	Day 21	Day 22		Day 29		Day 36		Day 43		Day 50	
Material Density [g/mm]	0,9273	0,9398	0,9260		0,9176	0,9262	0,9311	0,9347	0,9377	0,9454		0,9529			0,9573	0,9567			0,9551	0,9577		0,9588		0,9629		0,9555		0,9524		0,9432	
Water Density [g/ml]	0,9982	0,9981	0,9979		0,9982	0,9982	0,9983	0,9981	0,9980	0,9979		0,9982			0,9984	0,9986			0,9988	0,9988		0,9990		0,9986		0,9980		0,9983		0,9982	
Water Temperature [ºC]	20	20,5	21,5		20	20	19,5	20,5	21	21,5		20			19	18			17	17		16		18		21		19,5		20	

Figure 5.3: Evolution of the material’s density though time, depending on water temperature.

Appendix F

This appendix represents the obtained chart from the second DMA test with the injected waste High Density Polyethylene.

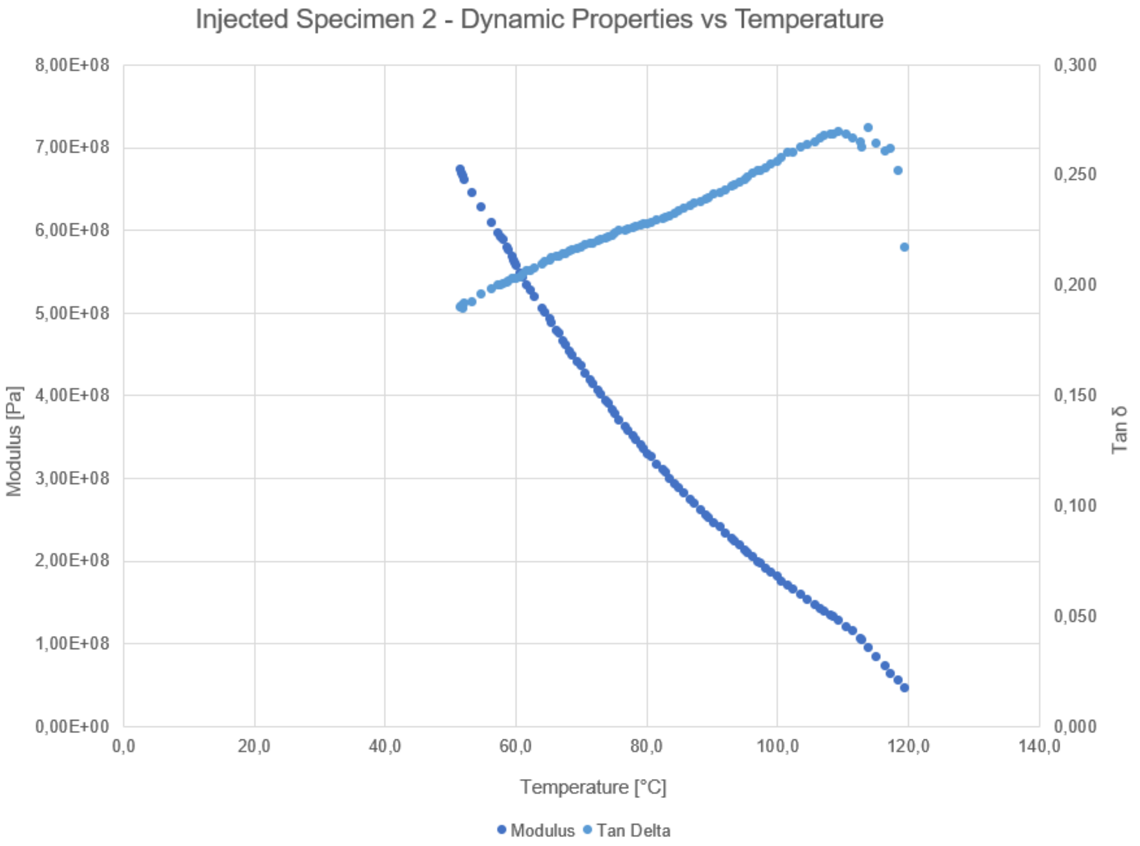


Figure 5.4: DMA results for the second specimen.

Appendix G

The chart obtained from the third DMA test with the injected waste High Density Polyethylene specimens is presented on the following figure.

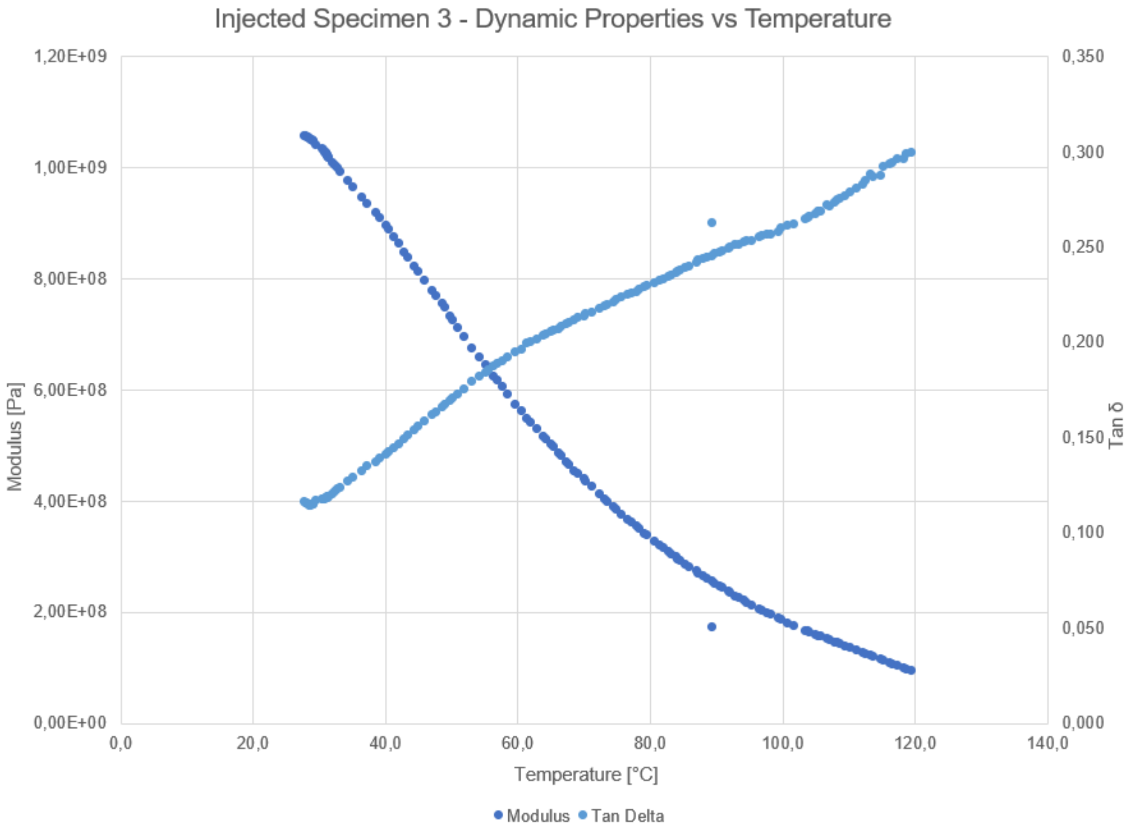


Figure 5.5: DMA results for the third specimen.

Appendix H

This appendix lists the specified results of the hardness tests on the injected waste High Density Polyethylene.

Table 5.3: Obtained values for the Shore D hardness of the injected material.

	Specimen 1				**Average**	**Standard Deviation**
0s	60	55	50	53	54,5	3,64
15s	53	50	46,5	45,5	48,75	2,97
Final Average	56,5	52,5	48,25	49,25	**51,63**	3,22
Standard Deviation	3,5	2,5	1,75	3,75	2,88	
	Specimen 2				**Average**	**Standard Deviation**
0s	55	55	62	62	58,5	3,50
15s	50,5	49	55,5	57	53	3,34
Final Average	52,75	52	58,75	59,5	**55,75**	3,4
Standard Deviation	2,25	3	3,25	2,5	2,75	
	Specimen 3				**Average**	**Standard Deviation**
0s	60	57	61	55	58,25	2,38
15s	55,5	50	55	48	52,13	3,21
Final Average	57,75	53,5	58	51,5	**55,19**	2,78
Standard Deviation	2,25	3,5	3	3,5	3,06	
	Specimen 4				**Average**	**Standard Deviation**
0s	50	50	55	56	52,75	2,77
15s	50	46	49,5	50	47,63	2,16
Final Average	47,5	48	52,25	53	**50,19**	2,46
Standard Deviation	2,5	2	2,75	3	2,56	

Appendix I

The following figure represents the DMA test results of the second specimens of injected waste Polyamide 6.

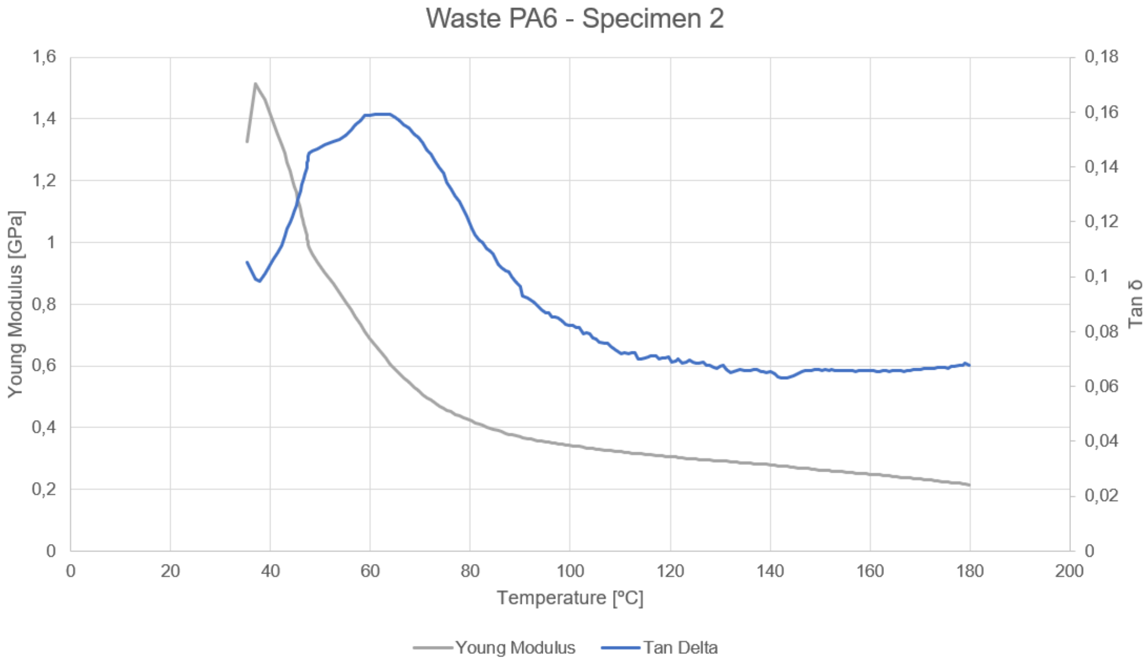


Figure 5.6: Chart obtained for the second specimen of injected PA6 material.

Appendix J

This appendix represents the chart obtained from the DMA test using the third injected waste Polyamide 6 specimen.

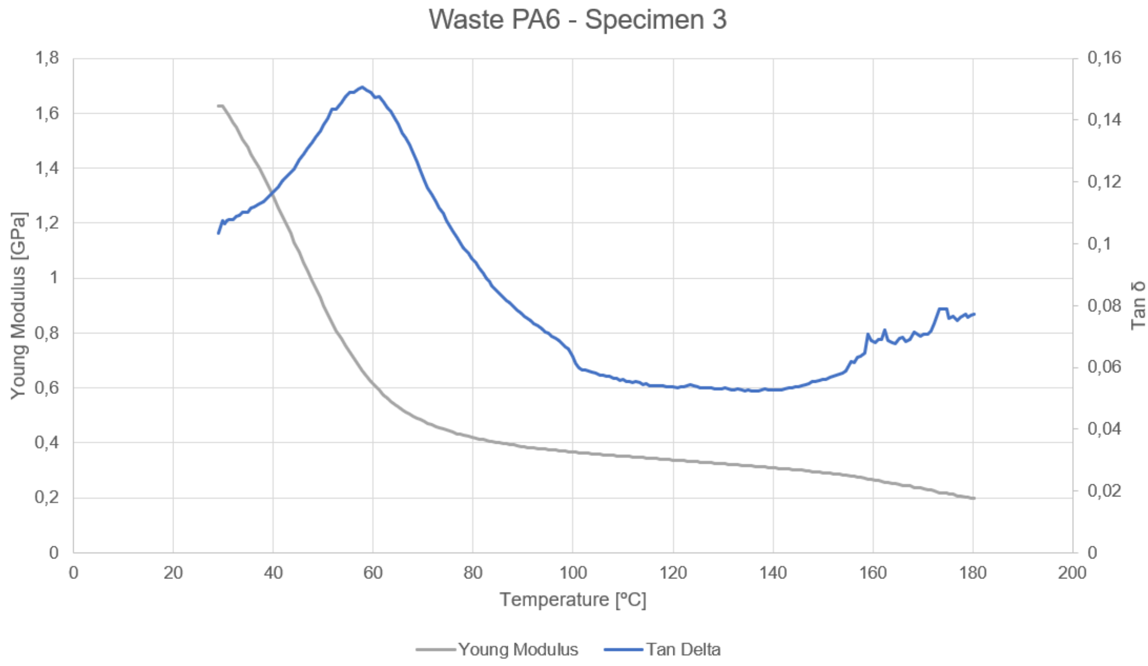


Figure 5.7: Chart obtained for the third specimen of injected PA6 material.

Appendix K

The chart obtained from the second DMA test using the virgin Polyamide 66 is represented on the following figure.

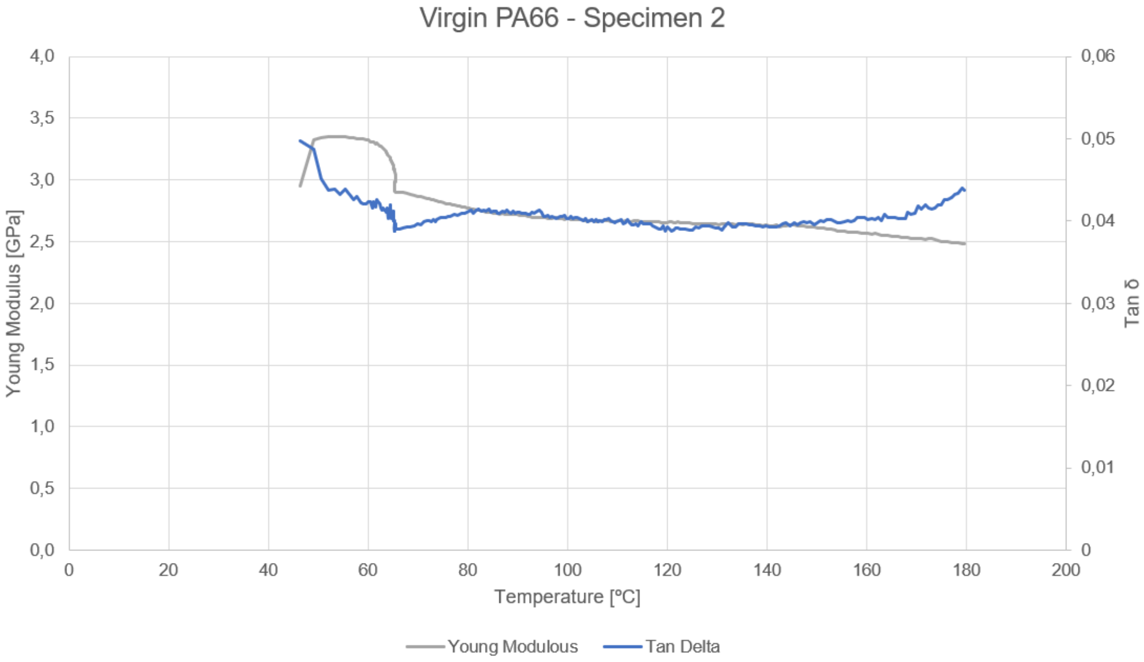


Figure 5.8: Chart obtained for the second specimen of injected PA66 material.

Appendix L

This appendix represents the third DMA test done with the virgin Polyamide 66.

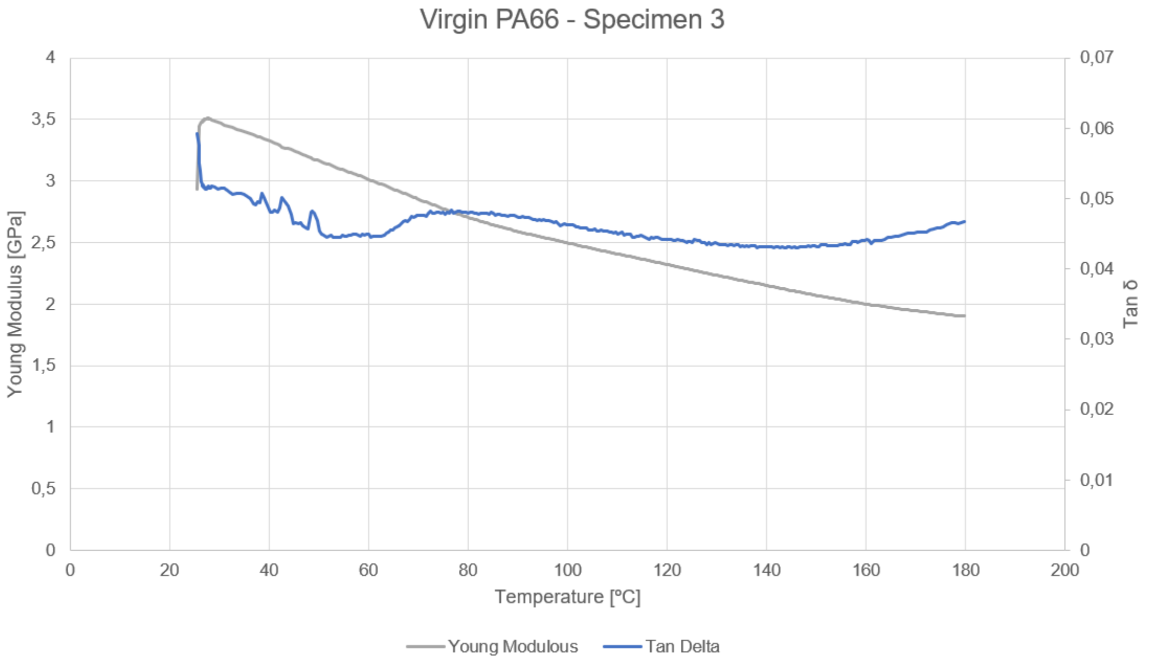


Figure 5.9: Chart obtained for the third specimen of injected PA66 material.

Appendix M

The hardness test results regarding the injected waste PA6 material are specified on the following table.

Table 5.4: Obtained values for the Shore D hardness of the injected waste PA6 material.

	Specimen 1				**Average**	**Standard Deviation**
0s	81	82	82	80	81,25	0,83
15s	77	77	77	76,6	76,90	0,17
Final Average	79	79,5	79,5	78,3	**79,08**	0,49
Standard Deviation	2	2,5	2,5	1,7	2,18	
	Specimen 2				**Average**	**Standard Deviation**
0s	80	79	79	81	79,75	0,83
15s	76,5	77	75	78	76,625	1,08
Final Average	78,25	78	77	79,5	**78,19**	0,89
Standard Deviation	1,75	1	2	1,5	1,56	
	Specimen 3				**Average**	**Standard Deviation**
0s	80	81	79	79	79,75	0,83
15s	76	76	74,5	75	75,38	0,65
Final Average	78	78,5	76,75	77	**77,56**	0,72
Standard Deviation	2	2,5	2,25	2	2,19	
	Specimen 4				**Average**	**Standard Deviation**
0s	79	78	78	77	78	0,71
15s	74	73	73,5	73,5	75,00	0,35
Final Average	76,5	75,5	75,75	75,25	**76,5**	0,47
Standard Deviation	2,5	2,5	2,25	1,75	1,5	

Appendix N

This appendix represents the specific results obtained from the hardness tests done on the virgin Polyamide 66.

Table 5.5: Obtained values for the Shore D hardness of the PA66 material.

	Specimen 1				**Average**	**Standard Deviation**
0s	85	84	85	84	84,50	0,50
15s	80	79,5	79,5	79	79,50	0,35
Final Average	83	81,75	82,25	81,50	**82,00**	0,4
Standard Deviation	2,5	2,25	2,75	2,5	2,5	
	Specimen 2				**Average**	**Standard Deviation**
0s	80	82	80	80	80,50	0,87
15s	72,5	71	71	69,5	71,00	1,06
Final Average	76,25	76,50	76	74,75	**75,75**	0,68
Standard Deviation	3,75	5,5	4,5	5,25	4,75	
	Specimen 3				**Average**	**Standard Deviation**
0s	85	83	83	81	79,00	1,41
15s	78	78	78	74	77,00	1,73
Final Average	81,5	80,5	80,5	77,50	**78,00**	1,5
Standard Deviation	3,5	2,5	2,5	3,5	1	
	Specimen 4				**Average**	**Standard Deviation**
0s	83	82	80	81	79,00	1,12
15s	79	78	77	76	77,50	1,12
Final Average	81	80	78,5	78,5	**78,25**	1,06
Standard Deviation	2	2	1,5	2,5	0,75	