

Faculdade de Engenharia da Universidade do Porto



Master in Mechanical Engineering

**Comparison between PLA filaments from  
different suppliers: an analysis of the effects of  
process parameters and polymeric degradation  
mechanisms on the quality of FFF parts**

João Pedro Valente Ramalho

**Supervisor:** Prof. Dr. Fernando Jorge Lino Alves

**Co-Supervisor:** Dr. Leonardo Santana

Porto, 2022

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*“We keep moving forward, opening new doors, and doing new things, because  
we’re curious and curiosity keeps leading us down new paths.”*

Walt Disney

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## **Resumo:**

Os movimentos de código aberto na Fabricação por Filamentos Fundidos (FFF) são um fator importante na popularização e democratização desta tecnologia para utilizadores entusiastas, tornando a Impressão 3D numa ferramenta para uso doméstico. Para além disso, estas iniciativas têm motivado a criação de novas empresas focadas no desenvolvimento de novas máquinas de impressão 3D. No que diz respeito aos materiais disponíveis, o conceito “*open material*” destas impressoras 3D promoveu o crescimento de um mercado de filamentos com muitas opções de bases poliméricas e tipos de aditivos, entre os quais os pigmentos se destacam. Contudo, o efeito dos pigmentos no processo de parametrização e na qualidade final das peças é muito negligenciado pelos fabricantes de filamentos e pode tornar-se num problema para os utilizadores na impressão por FFF. Estudos recentes mostram que para o mesmo fornecedor, a variação na cor dos filamentos de Ácido Polilático (PLA) é um factor significativo, com influência nas propriedades mecânicas, especialmente quando o pigmento é o vermelho. Nesse sentido, surgiu uma oportunidade de desenvolver um estudo em que o factor cor é fixo (vermelho) e a influência de três fornecedores de filamento de PLA na qualidade de peças impressas por FFF é avaliada. Experimentalmente, este estudo foi dividido em três partes. A primeira, onde os filamentos são caracterizados por medição de densidade, Espectroscopia no Infravermelho por Transformada de Fourier (FTIR) e Análise Dinâmico Mecânica (DMA). A segunda parte consistiu num estudo isoparamétrico com o objectivo de avaliar os efeitos de mecanismos de degradação (em terra, humidade e solução salina) nas propriedades mecânicas e na massa de peças impressas. Finalmente, um estudo para avaliar a qualidade das peças impressas (mecânica e massa), nos três filamentos analisados, em função da variação de parâmetros estratégicos da tecnologia FFF. Deste modo, foi aplicado um planeamento experimental de Taguchi baseado em quatro fatores (espessura de camada, temperatura de extrusão, velocidade de impressão e multiplicador de extrusão), cada um com três níveis. Depois, os melhores níveis de cada fator, por cada resposta, foram selecionados para criar uma configuração de impressão global, ou modelo de verificação, para cada fornecedor. Os estudos de degradação provaram que a maioria das amostras se degradou pelo menos a algum nível no entanto, a condição de exposição à solução salina mostrou ser o mecanismo com maior influência nas propriedades mecânicas, reduzindo os valores das respostas. Parametricamente, os fornecedores responderam de maneira diferente às configurações de impressão, sendo os parâmetros espessura de camada e multiplicador de extrusão os mais significativos em todos os materiais. Em todos os casos, as respostas obtidas pelos denominados “modelos de verificação” foram sempre melhores que as respostas obtidas em peças impressas com configurações fixas da literatura. Isto demonstrou a necessidade do utilizador em adaptar o sistema de parâmetros de acordo com o fabricante escolhido. Apesar de se usar a mesma base polimérica, PLA, diferentes fornecedores de filamento usam diferentes conjuntos de aditivos que podem modificar, por exemplo, a reologia e as temperaturas de transição dos materiais, afetando assim a sistemática de parametrização e a qualidade de impressão. Estudos também destacam a importância da criação de mecanismos de regulamentação de qualidade na produção e comercialização de filamentos termoplásticos pigmentados para impressão 3D FFF.

**Palavras-Chave:** FFF, PLA, Fornecedores de filamentos, Mecanismos de Degradação, Parâmetros de impressão.

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## **Abstract**

The development of open-source movements in Fused Filament Fabrication (FFF) has been important for the popularization of this technology for entry level users, but also for motivating the emergence of numerous companies focused on manufacturing machines and printing materials. Regarding materials, many options are available on the market, with the most varied polymer bases and types of additives, among which pigments stand out. However, most of the time, the effect of the pigment in the parameterization process and in the final quality of parts is neglected by the filament suppliers, and that often becomes a problem for users while printing. Recent studies show that for the same supplier, color variation in Poly (lactic acid) (PLA) filaments is a significant factor for changes in mechanical properties, especially when the pigment is red. In this sense, there was an opportunity to develop a study where the color factor is fixed (red) and the influence of three different PLA filaments suppliers on the quality of FFF printed parts was evaluated. Experimentally, this work was divided in three main stages. First, the filaments were characterized by density measurement, Fourier Transform Infrared Spectroscopy (FTIR), and Dynamic Mechanical Analysis (DMA). Second, an isoparametric study that aimed to evaluate the effects of degradation mechanisms on the mechanical properties and mass of printed parts in three different situations: (i) landfill, (ii) humidity, and (iii) salt solution. Finally, a parametric study where the influence of three suppliers is evaluated in the parametric configuration planning and, consequently, in the integrity of the parts obtained. To achieve this, a Taguchi experiment was carried out to evaluate the flexural mechanical properties and mass of the printed parts, considering the variation of four factors (layer thickness, extrusion temperature, print speed and extrusion multiplier), at three levels. Afterwards, the best levels of phase two parameters, for each supplier, were used in the third stage to create a special printing setup for each material. The printed parts were evaluated by the same responses as in the previous step. Finally, the results of phase three were compared to those obtained from a fixed parameter setting from the literature used to print parts made from materials that have been selected for this study. As for the conclusions, despite the degradation study has proved that most samples had somehow degraded at some level, the saline solution has proved to have greater influence on the mechanical responses. Parametrically, the red PLA filaments responded differently to the printing parameters, requiring, in some specific cases, an improved extruder to produce the parts. Compared with the responses obtained by parts printed with a fixed setting from the literature, the “verification models” printing configurations have enhanced all responses which demonstrates the need for the user to adapt the system according to the chosen supplier, especially for controlling the extrusion flow rate. In summary, despite using the same polymer base, PLA, different suppliers most probably use their own sets of additives either to modify the color or stabilize the material, which in turn influences the rheology and thermal behavior of its filaments, leading to printing settings, mechanical properties, and mass variations of parts. These studies also highlight the importance of considering the determination of quality regulatory mechanisms in the production and commercialization of pigmented thermoplastic filaments for FFF 3D printing.

**Keywords:** FFF, PLA, Filament Supplier, Printing Parameters, Degradation Mechanism.

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## Scientific Disclosures

- Future paper: Effects of degradation mechanisms on FFF 3D printed PLA parts made from different filament suppliers. Journal: Rapid Prototyping Journal;
- Effects of printing parameters on the quality of FFF printed parts with red PLA filaments from different suppliers. **1<sup>st</sup> International Conference on Engineering Manufacture.** Presentation date: 05/05/2022;



Lucas Filipe Martins da Silva  
Professor of Mechanical Engineering  
Tel: +351 22 5081706  
[lucas@fe.up.pt](mailto:lucas@fe.up.pt)  
[www.ajpu.pt](http://www.ajpu.pt)

26 November 2021

Mr JP Ramalho  
Faculdade de Engenharia da Universidade do Porto,  
Porto, Portugal

Dear Mr JP Ramalho,

It is my pleasure to inform you that your abstract entitled 'Effects of printing parameters on the quality of FFF printed parts with red PLA filaments from different suppliers' by JP Ramalho, L Santana, HT Idogava and JL Alves has been accepted for ORAL presentation for the 1st International Conference on Engineering Manufacture (EM2022) which will be held at in Porto (FEUP), Portugal, 5-6 May 2022.

I am looking forward to welcoming in Sintra,

A handwritten signature in black ink that reads 'Lucas Silva'.

Prof. Lucas Filipe Martins da Silva  
Chairman of EM2022

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## **Acknowledgments**

Esta dissertação é o culminar de um longo e árduo caminho durante o qual estiveram presentes pessoas às quais devo um muito sincero obrigado.

Em primeiro lugar, deixar um agradecimento muito especial ao Professor Jorge Lino pela oportunidade que me deu pela atribuição deste tema de dissertação muito ligada a uma área que muito me fascina, a impressão 3D, e por todo o acompanhamento, disponibilidade e fornecimento de recursos essenciais à realização deste projeto.

Deixar também um grande agradecimento ao Dr. Leonardo Santana cuja orientação, visão, disponibilidade, paciência e partilha de experiências foram indispensáveis para atingir os ambiciosos objectivos desta dissertação.

Ao Eng. Henrique Takashi Idogava pelo seu acompanhamento, amizade e partilha de conhecimento durante toda a componente experimental desta dissertação.

Ao Dr. Marco Marques do Laboratório de Produtos e de Serviços da FEUP por toda a ajuda e disponibilidade para que nunca faltasse nada à realização deste projecto.

Agradeço a todos e meus colegas do LPDS que estiveram sempre presentes e acompanharam de perto todo o meu desenvolvimento ao longo deste projecto. Em especial, à Ana Pais e ao Bruno Areias por toda a amizade e momentos de descontração.

À Dra. Beatriz Graça do Instituto de Ciência e Inovação em Engenharia Mecânica e Engenharia Industrial (INEGI) pelo acompanhamento nos ensaios de FTIR. Agradecer também à Dna. Emília Soares do Departamento de Engenharia Mecânica pela sua disponibilidade e por ceder o equipamento necessário à realização dos ensaios de medição de densidades.

Ao Prof. Guilherme Mariz de Oliveira Barra da Universidade Federal de Sta. Catarina por ceder a balança de medição de densidades e o equipamento para análise de DMA.

Finalmente, um agradecimento muito sentido e especial aos meus pais por serem os maiores alicerces da minha vida. Obrigado por todo o vosso carinho, paciência, educação e apoio incondicional que me permitiram superar inúmeras dificuldades e terminar esta etapa da minha vida com sucesso. À minha irmã, por todos os momentos de brincadeira e de aprendizagem. Ao meu avô Valente pela transmissão desde muito jovem de valores como a disciplina, o trabalho e o rigor. A toda a restante família um muito obrigado por todos os bons momentos e por fazerem de mim a pessoa que sou.

Por último, um grande agradecimento a todos os meus amigos que me acompanharam ao longo de todos estes anos e por se preocuparem comigo. Deixar também uma palavra de apreço ao grupo dos “Aparadores” pelas experiências e por todos os bons momentos que passamos e vamos continuar a passar juntos!

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## **Acronym List**

ABS – Acrylonitrile Butadiene Styrene

AM – Additive Manufacturing

ANOVA – Analysis of Variance

ASTM – American Society for Testing and Material

CAD – Computer Aided Design

CV – Coefficient of Variance

DMA – Dynamic Mechanical Analysis

FDM – Fused Deposition Modelling

FM – Flexural Modulus

FTIR – Fourier Transformed Infrared Spectroscopy

LOM – Laminated Object Manufacturing

LPDS – Laboratório de Desenvolvimento de Produtos e Serviços

MFS – Maximum Flexural Strength

PA – Polyamide

PC – Polycarbonate

PEEK – Poly (ether-ether ketone)

PET – Poly (ethylene terephthalate)

PETG – Poly (ethylene terephthalate glycol)

PLA – Poly (lactic acid)

SLA – Stereolithography

SLS – Selective laser sintering

STL – Standard Triangle Language

UV – Ultraviolet

VM – Verification Model

3D – Three Dimensional

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## **List of Symbols**

$\alpha$  – Significance level of the statistical analysis (ANOVA)

$\rho$  – Density

$E_m$  – Extrusion multiplier

$E_t$  – Extrusion temperature

$L_t$  – Layer Thickness

$P_s$  – Print speed

$T_G$  – Glass transition temperature

$T_M$  – Melting temperature

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# 1. Introduction

## 1.1 Contextualization

Additive Manufacturing (AM), popularly known as 3D printing, is a technological revolution towards the industry 4.0 and is set to change the manufacturing sector in countless fields. An iconic example is the recent outbreak of the novel coronavirus (Covid-19) which has led AM to meet explosive demands for medical equipment to ease the health disaster worldwide.

Unlike the conventional manufacturing processes, that build components by removing material, AM does not rely on many tooling processes and instead builds objects layer by layer to achieve the final product's shape. Among the available 3D printing technologies, Fused Filament Fabrication (FFF) is the most used one. It's basically composed by a wide range of printing devices that employs thermoplastics filaments as raw material which are extruded through a heated nozzle onto a building platform.

There're multiple types of filaments out there on the market. Most of them are made from composites and are known for their good overall mechanical properties, low cost, and some of them are biodegradable which includes the Polylactic Acid (PLA). This thermoplastic is the most used in FFF and has a wide range of uses thanks to its unique mechanical and thermal properties. However, the quality of the printed parts differs from the type of filament used since each manufacturer uses different additives/fillers in the polymeric matrix to amplify the material features. Among the used additives are the coloured pigments which according to many studies, have proved to influence the mechanical properties of FFF printed parts.

In this context, the inconsistency of results leaves a gap for further investigation on commercially available PLA manufacturers. On one hand, few studies have devoted to evaluating the impact of adverse environments on FFF printed parts made of polylactide acid (PLA). On the other hand, despite the availability of numerous studies regarding parametric appraisal on the final part's mechanical properties, there's still a lot of room for improvement specially when multiple material's suppliers are at stake.

## 1.2 Objectives

### 1.2.1 Main Objective

The main goal of this work is to evaluate the effects of different PLA filament suppliers on the final quality of parts obtained by FFF through the analysis of mechanical properties and mass of parts exposed to degradation mechanics and different parametric configurations.

### 1.2.2 Specific Objectives

This master's dissertation has the following topics as specific objectives:

- Selection and characterization of multiple filament suppliers;
- Evaluate the mechanical and mass behaviour of polymers exposed to degradation mechanisms;
- Perform a series of multiple mechanical trials;
- Calibrate the printing parameters for different filament suppliers through the analysis of the mechanical and mass properties of printed parts;
- Validate the best parametric settings by comparing their results with the available setups in the literature;

## 2. State of the Art

The main goal of this chapter is to provide the most relevant aspects of the universe of Additive Manufacturing, especially the Fused Filament Fabrication. It will also be addressed the most relevant materials as well as their most important proprieties.

### 2.1 Polymeric Materials

A polymer is a material that people have been using for thousands of years but its chemical manipulation dates to the 19<sup>th</sup> century [1]. At the time they were simply considered as colloidal aggregates of small molecules. However, the rapid development of technology in the last decades allowed the invention of highly effective catalytic polymerization processes [2]. Consequently, petroleum derived polymers have been explored and trivialized ever since especially because of their low production cost. Nowadays, billions of tons of multiple types of polymers are produced every year which represents an increase of 160 times in 60 years and there's evidence that the demand will grow further as shown in Table 1 [1].

Table 1 – World Consumption Forecast [1] (adapted).

| Market Sector         | 2006 (Thousand MT) | 2016 (Thousand MT) | 2006 – 2016<br>Compound Annual<br>Growth Rate (%) |
|-----------------------|--------------------|--------------------|---------------------------------------------------|
| Food                  | 42.025             | 71.774             | 5.5                                               |
| Textiles              | 32.176             | 51.630             | 4.8                                               |
| Furniture             | 13.687             | 22.993             | 5.3                                               |
| Printing              | 780                | 1.220              | 4.6                                               |
| Plastic Products      | 43.500             | 78.361             | 6.1                                               |
| Fabricated metals     | 1.519              | 2.259              | 4.0                                               |
| Machinery             | 2.397              | 3.658              | 4.3                                               |
| Electrical/electronic | 13.810             | 25.499             | 6.3                                               |
| Other transportation  | 9.330              | 16.181             | 5.7                                               |
| Vehicles and parts    | 10.746             | 15.625             | 3.8                                               |
| Other equipment       | 3.852              | 6.334              | 5.1                                               |
| Other manufacturing   | 21.238             | 33.569             | 4.7                                               |
| Construction          | 45.886             | 72.919             | 4.7                                               |
| <b>Total</b>          | <b>240.947</b>     | <b>402.022</b>     | <b>5.3</b>                                        |

However, these polymers have had a huge environmental impact since they took hundreds of years to decompose into harmless substances. Despite all efforts to educate people about the environmental impact cause by the exploration of these plastics, they continue to represent a huge proportion of domestic waste. Some countries have even imposed regulations to reduce the use of nondegradable polymers [1].

Nowadays, because humanity is so dependant of polymeric materials, their use is not entirely avoidable. As a result, a lot of research on biodegradable polymers has been carried on for years on multiple universities/companies around the world. Its main goal is to create alternative polymers which not only are environmentally friendly but also suits a set of mechanical, thermal, chemical, etc properties depending on the final product requirements [3].

Polymers are natural, and synthetic at some point and are created by a process called polymerization. The natural component of these polymers is found in animal and plant organisms such as lipids, proteins, natural rubber among others. For the current project the focus will be mainly on thermoplastics, more precisely the PLA. This is a type of biopolymer whose molecular structure can either assume a semicrystalline or amorphous form which will be further studied in this work [1]. In Figure 1 there's a schematic about the evolution of polymers.

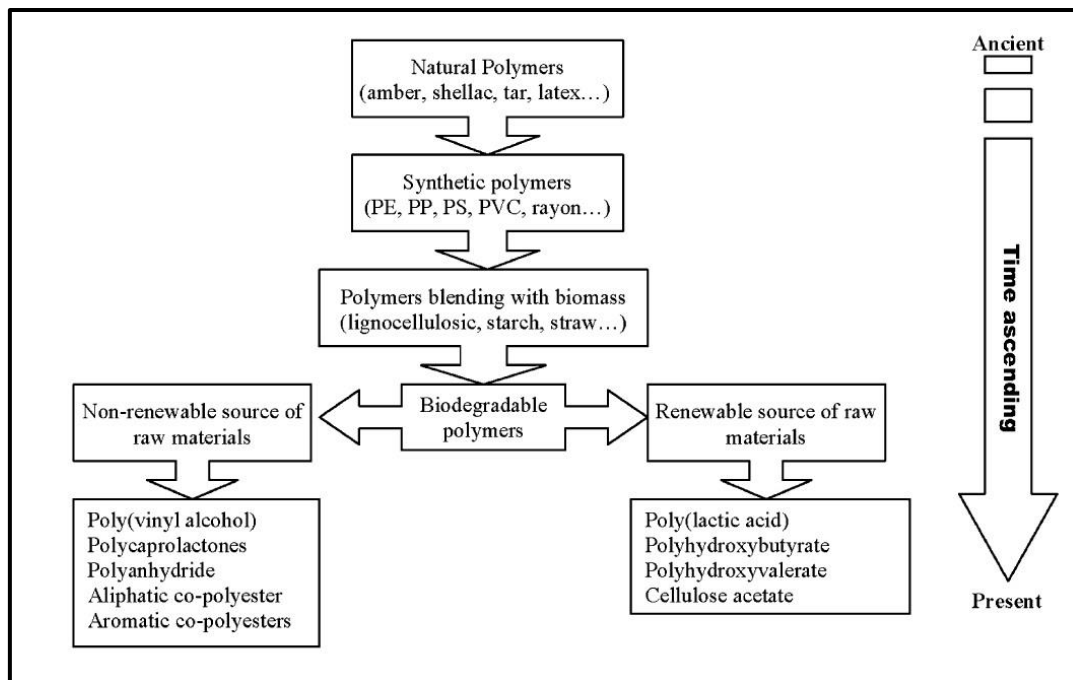


Figure 1 - Trends in polymer development [1].

### 2.1.1 Polymers: semi-crystalline and amorphous

Polymers are macromolecules constituted by the repetition of smaller structural units called monomers, usually linked by covalent bonds. Polymerization is the given name to the process that makes this polymer formation [4]. Thermoplastics are polymers with the ability to soften and flow when subjected to an increase of temperature and pressure. When these conditions are removed, the polymer solidifies into a product with defined shapes. Their characteristics make these materials widely used in almost all walks of life with specific properties: low density, low cost, good thermal/electrical insulation properties and high resistance to corrosion [3].

The solid-state structure of a thermoplastic is characterized by the way in which the molecular chains are organized. If the chains are messed up it's called the amorphous phase. If the chain is ordered, regular and repetitive the polymer is considered semi-crystalline (Figure 2) [3].

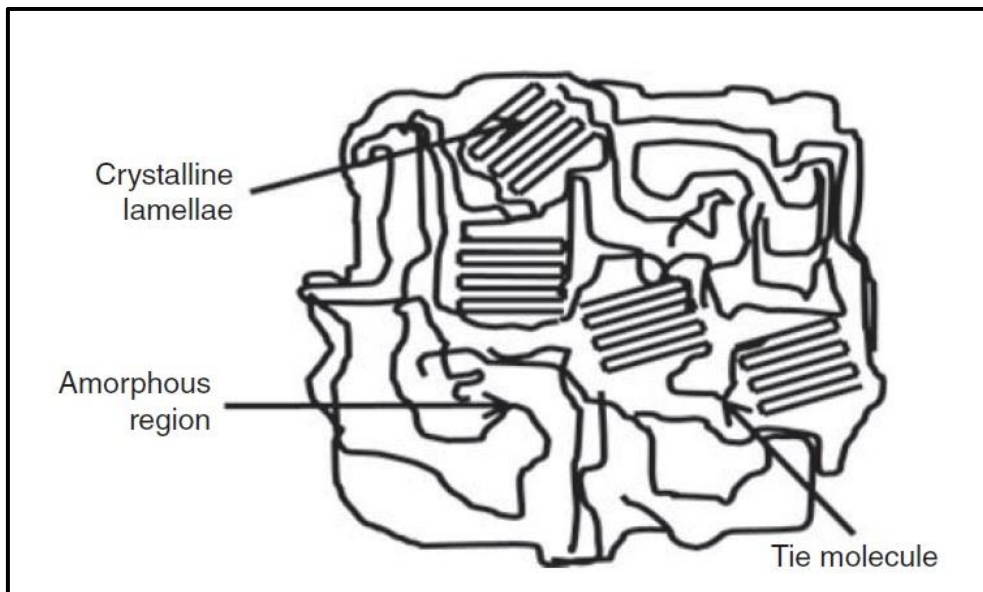


Figure 2 - Semi-Crystalline Polymer [5].

Most physical, mechanical, and thermodynamic properties of semi-crystalline polymer depend on the degree of crystallinity and the morphology of the crystalline regions. If a polymer has a high degree of crystallinity, it's considered rigid with a high melting point, high crystalline melting temperature ( $T_m$ ) and high glass transition temperature ( $T_g$ ). On the other hand, amorphous polymers are classified as soft with lower melting points [3].

### 2.1.2 Temperatures

The thermal properties play a big role in the behaviour of polymers since they strongly affect the mechanical properties and cause them to react in different ways. Generally, polymers can have at least three types of temperatures that define their own thermal properties: glass transition temperature ( $T_G$ ) crystalline melting temperature ( $T_M$ ) and crystallization temperature ( $T_C$ ) [5].

#### Glass Transition Temperature ( $T_G$ )

Polymers are an important group of materials with a defined glass transition temperature. This temperature is the average value of temperature range that, during the heating of a polymeric material from a very low temperature to a higher one, allows the polymeric chains the possibility of changing their conformation [5].

The glass transition temperature is influenced by the cooling rate.  $T_G$  will be higher if the melt is cooled down quickly whereas there will be no glass transition temperature if the cooling is very slow. Below the  $T_G$  the polymer does not have enough internal energy to allow the displacement of a chain. The glass transition temperature directly affects on many of the properties of polymeric materials, including modulus of elasticity, coefficient of thermal expansion, refractive index, specific heat, etc [6].

Below the  $T_g$  the polymer does not have enough internal energy to allow the displacement of a chain. The glass transition temperature directly affects on many of the properties of polymeric materials, including: the modulus of elasticity, coefficient of expansion, refractive index, special heat, etc [5]. Table 2 shows some polymer's glass transition temperatures.

Table 2 - Glass Transition Temperatures of some Polymers [5] (adapted).

| Polymer                                    | $T_g$ [°C] |
|--------------------------------------------|------------|
| Polypropylene (PP)                         | +100       |
| Polystyrene (PS)                           | +90        |
| Poly(methyl methacrylate) (atactic) (PMMA) | +100       |
| Polycarbonate (PC)                         | +150       |
| Poly(vinyl acetate) (PVAc)                 | +28        |
| Poly(ethylene terephthalate) (PET)         | +69        |

### Crystalline melting temperature ( $T_M$ )

This temperature is the average value of temperature range in which, during the heating, crystal regions disappear with the fusion of crystallites. At this point, the energy needed to overcome the intermolecular forces between the chains is reached which allows the transition from the rubbery state to the viscous state. This transition only occurs in the crystalline phase, therefore, it only makes sense if applied to semi-crystalline polymers [3].

### Crystallization temperature ( $T_C$ )

The transition from the amorphous liquid state of the melt to the crystalline state is called crystallization. It is a kinetically controlled process and depends primarily on nucleation. As so, the crystallization temperature is always below the thermodynamically controlled melting temperature [3].

In conclusion, thermal properties such as crystallization temperature, melting temperature and glass transition temperature play a key role to characterize a polymeric material. In Table 3 there're some thermal properties of different types of polymers.

Table 3 - Thermal Properties of different materials for 3D printing [54].

| Polymer | Chemical Formula                                                                                             | $T_G$<br>(°C) | $T_M$<br>(°C) | Density<br>(kg·m <sup>-3</sup> ) | Specific<br>Heat (J·Kg <sup>-1</sup><br>·K <sup>-1</sup> ) | Thermal<br>Conductivity<br>(W·m <sup>-1</sup> ·K <sup>-1</sup> ) |
|---------|--------------------------------------------------------------------------------------------------------------|---------------|---------------|----------------------------------|------------------------------------------------------------|------------------------------------------------------------------|
| ABS     | (C <sub>8</sub> H <sub>8</sub> ·C <sub>4</sub> H <sub>6</sub> ·C <sub>3</sub> H <sub>3</sub> N) <sub>n</sub> | 105           | n/a           | 1060 - 1080                      | 1260 –<br>1675                                             | 0.24                                                             |
| PET     | (C <sub>10</sub> H <sub>8</sub> O <sub>4</sub> ) <sub>n</sub>                                                | 75            | 255           | 1370 - 1455                      | 1040 –<br>1050                                             | 0.24                                                             |
| PLA     | (C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>n</sub>                                                 | n/a           | 150           | 1210 - 1430                      | n/a                                                        | n/a                                                              |
| PP      | (C <sub>3</sub> H <sub>6</sub> ) <sub>n</sub>                                                                | -10           | 165           | 855 - 946                        | 1930 - 2000                                                | 0.12 – 0.22                                                      |

#### 2.1.3 Mechanical Properties

Like in any field of engineering, it's very important to be familiar with the basic mechanical properties of any material that's going to be used. These properties are characterized by how these materials respond to the applied mechanical requests [3]. The nature of this response depends on the chemical structure, temperature, time, and the history of polymer processing [3][5].

To characterize the mechanical properties of a polymer there are many tests that can be applied to evaluate them such as static test, dynamic tests, destructive and non-destructive, short-term, or long-term test, etc. Most of the results of these tests can be shown through a stress vs strain chart as in Figure 3 [7].

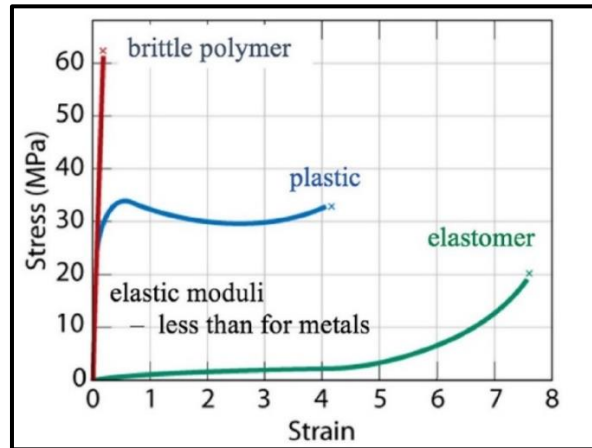


Figure 3 - Mechanical Behaviour of Polymers [7].

There are several parameters that can be evaluated during a mechanical test. These can include [5]:

- **Strength:** is the stress required to break the sample. The most common types of strength are tensile, compressional, flexural, torsional, impact and so on.
- **Percent Elongation to Break:** This strain measures the percentage change in the length of the material before fracture. It's also a measure of ductility.
- **Young's Modulus:** it's the ratio of stress to the strain in the linearly elastic region
- **Toughness:** measures the energy absorbed by the material before it breaks thus providing a measure of its overall stiffness.
- **Viscoelasticity:** polymers have a combined behaviour of elastic and plastic deformation. If an intermediate temperature is applied there is a combined behaviour of both elastic and plastic deformation and therefore the polymer is considered viscoelastic.

All these parameters can be influenced by many internal properties or external factors. The internal properties are related to the structural characteristics of the polymer such as crystallinity, presence of polar groups, molar mass, polymerization, etc. On the other hand, the external factors may include the presence of a plasticizer, an

elastomer, a residual monomer or even fiber reinforcement. To understand the impact of all these parameters on the mechanical behaviour of a polymer, a more in-depth discussion about each one of them will follow.

**Crystallinity:** in the early stages of degradation the polymer property that is more affected is crystallinity. Consequently, the value of young's modulus and strength of a polymer can increase. However, during the later stages of degradation, the dominant factor is molecular weight and both young's modulus and strength reduce to zero [6].

**Molecular Weight:** this property has proved, according to many experiments, to have a major impact on the Young's modulus. However, the variation observed in these experiments as shown that it's not easy that simple to establish a relationship between Young's modulus and molecular weight. Despite all this, it's possible to establish relationship between them. As can be seen in Figure 4, the relationship is non-linear because the Young's modulus only starts to drop significantly after the molecular weight is reduced by over 50% [6].

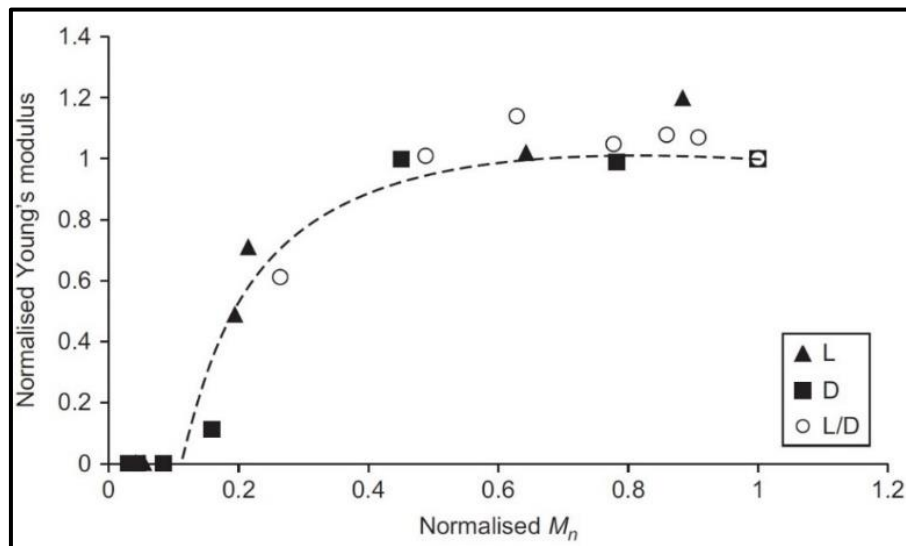


Figure 4 – A plot of Young's modulus versus molecular weight [6].

There are many factors that can affect the degradation of molecular weight such as:

- Sample size and shape;
- Processing techniques such as polymerization or sterilisation;
- Temperature;

Another important factor that can affect the molecular weight of a polymer is the glass transition temperature ( $T_G$ ) which can increase if the molecular weight increases as well. This increase can be accentuated for polymers with lower molecular mass, but it stabilizes as the molar mass reaches a critical value [3].

### **Viscoelasticity**

The phenomenon known as viscoelasticity is a thermally activated mechanism that can occur in many types of materials, especially plastics [8]. The science behind this phenomenon is related with the complexity of a polymer behaviour and is basically a combination of molecular structure and fluid mechanics. When subjected to stress, the elastic materials deform, and this deformation is fully recovered when the loads are removed which means the element stores energy and therefore can give it back to the system if the loads are removed. In other hand, the viscous materials deform permanently when a load is applied. Such deformation is not recoverable since the energy is lost to the system [9].

Most fluids and gases are considered as Newtonian which means their strain-stress response is linear as shown in Figure 5. However, if this response is non-linear then the fluid will be considered as non-Newtonian. An extra kind of fluids shown in Figure 5 are the Bingham plastics. These plastics are neither considered solid or liquid and are the type of fluids that behave as a solid at low stresses but flow as viscous fluid at high stress [10].

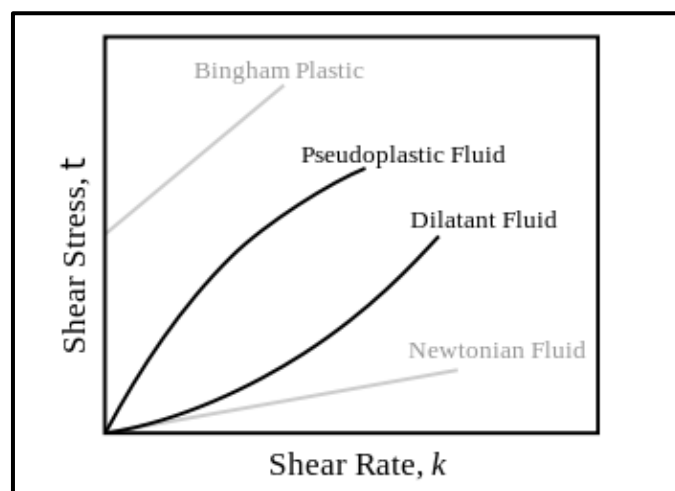


Figure 5 – Classification of Non Newtonian Fluids [11].

There are many viscoelastic materials which can include amorphous polymers, semicrystalline polymers or even biopolymers. A polymer viscoelasticity is strongly dependant on its chemical structure since this property is achieved through molecular chain rearrangements when a stress-strain process takes place [12]. This change of position by the chains is known as creep [8].

A polymeric material is considered viscoelastic at all temperatures which in turn have a great impact in the mechanical behaviour. At lower temperatures the elastic characteristics will be prominent whereas at higher temperatures a more viscous behaviour will be detected (Figure 6) [12]. For example, if the molecular weight of a polymer is very low, the glass transition temperature is mainly dependant of it. Above this temperature any mechanical perturbation that may occur involve a molecular rearrangement [8].

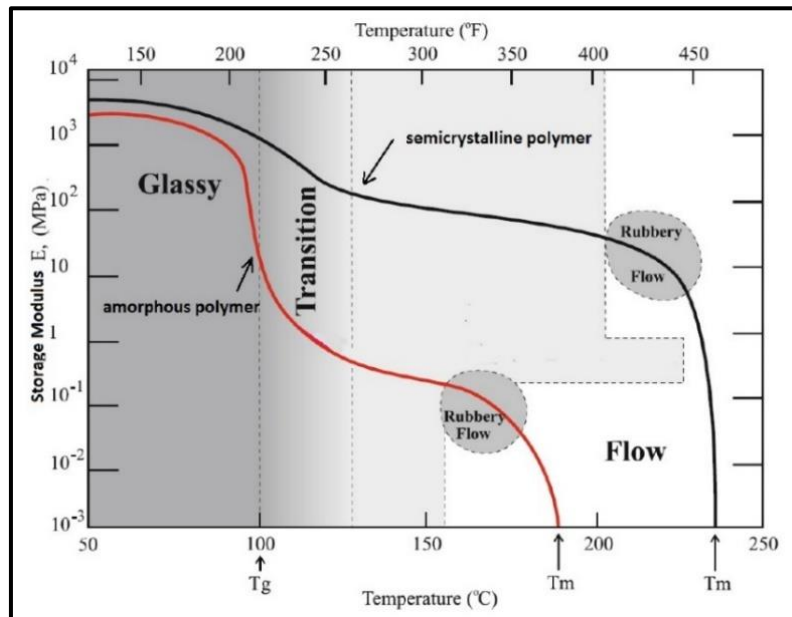


Figure 6 – Temperature dependent behaviour of polymers [13].

#### 2.1.4 Crystallinity

The crystallinity of a given polymer mass is mainly influenced by three types of factors: processing conditions, molecular structure, or the presence of a second molecule. When it comes to increase the order or the special regularity of the molecule, it favours the formation of crystallites and consequently the crystallinity [3]. The crystallinity can be calculated by the following formula — Eq. (1) — [3]:

$$X_t(\%) = \left( \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \right) \cdot 100 \quad \text{Eq. (1)}$$

Where:

- $X_t$ : degree of crystallinity;
- $\rho_c$ : density of the completely crystalline polymer;
- $\rho_a$ : density of the completely amorphous polymer;
- $\rho_s$ : density of the sample.

The polymer will be considered amorphous if the percentage of crystalline is 0% and highly crystalline if the %crystallinity is  $> 90\%$  [3]. Table 4 shows some characteristic values of some of the most used polymers.

Table 4 – Characteristic values of the crystallization parameters of some polymers [3].

| Polymer            | Max. Degree of Crystallinity (%) | Maximum Grow Rate ( $\mu\text{m/s}$ ) | Melting Temperature $T_M$ ( $^{\circ}\text{C}$ ) |
|--------------------|----------------------------------|---------------------------------------|--------------------------------------------------|
| Polyethylene       | 90                               | 33                                    | 141                                              |
| Nylon 6.6          | 70                               | 20                                    | 267                                              |
| Nylon 6            | 35                               | 3                                     | 229                                              |
| Polypropylene (PP) | 65                               | 0.33                                  | 183                                              |
| PET                | 50                               | 0.12                                  | 270                                              |
| Polystyrene (PS)   | 35                               | 0.0042                                | 240                                              |
| Polycarbonate (PC) | 25                               | 0.0002                                | 267                                              |

The second most experimentally used property is the enthalpy which can be obtained using a very common equipment known calorimeter (DSC). Table 5 shows the fusion enthalpy values of some polymers [3].

Table 5 – Fusion Enthalpy of some polymers [3](adapted).

| Polymer                          | Fusion Enthalpy [J/g] |
|----------------------------------|-----------------------|
| Polyethylene Terephthalate (PET) | 140                   |
| Polycarbonate (PC)               | 145                   |
| Polyether ether ketone (PEEK)    | 130                   |
| Polyethylene                     | 290                   |
| Polyamide 11                     | 224                   |

### 2.1.5 Additives

Polymers are the raw material used in a widespread range of products including in the production of thermoplastic filaments used in 3D printing. However, the physical/chemical properties of these materials may not suit the final product demands [14].

As a result, there are some chemicals, better known as additives, that can be mixed with the base polymer. Each one of these additives has its own composition and purpose as shown in Table 6. Their common goal is to improve processability, give colour, and prolong life span of the polymer so that the final product achieves the desired physical and chemical properties [14].

Table 6 - Main types of additives used in polymers and their respective functions [14] (adapted).

| <b>Additive</b>                  | <b>Role</b>                                                                                                                                                                         |
|----------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Expansion agents</b>          | It provides a foam formation through the release of gases from chemical reactions or physical transformations.                                                                      |
| <b>Crosslinking agents</b>       | Cross-link polymer molecules to improve properties such as stiffness.                                                                                                               |
| <b>Antistatics</b>               | Assisting in the dissipation of static charges present on the surface of an elastic part or product through electrical conductivity and preventing electrical discharges or shocks. |
| <b>Loads</b>                     | Add volume to a polymer, increasing its rigidity and surface hardness.                                                                                                              |
| <b>Colorants (pigments/dyes)</b> | Change the appearance of a polymeric product, providing the necessary dyeing of the material for the desired application.                                                           |
| <b>Stabilizers</b>               | Act by slowing down the degradation of polymers or preventing the start of the degradation process during the product's useful life.                                                |
| <b>Lubricants</b>                | Assist the polymer processing, increasing the fluidity of the material without significantly changing its final properties.                                                         |
| <b>Impact modifiers</b>          | Increase the impact resistance of polymers that have brittle behavior, changing their structure to achieve the desired resistance.                                                  |
| <b>Nucleants</b>                 | Promote the increase of polymer crystallinity, facilitating the formation of nucleus for crystal growth.                                                                            |
| <b>Plasticizers</b>              | Increase the flexibility of polymers through the ease of molecular movement caused by their industrial application.                                                                 |
| <b>Reinforcements</b>            | Increase the mechanical strength of polymers, using short or long fibers and spheres.                                                                                               |
| <b>Flame retardants</b>          | Difficult the burning of a polymer by ignition inhibiting, by promoting self-extinguishment of the flame or decreasing the burning rate.                                            |

## **Pigments**

Pigments are natural and synthetic particles that can be added to the polymer base to improve its properties or give a specific colour. They can be categorized based on their chemical composition: organic and inorganic. Both types of pigments can have either good or bad effects on the thermal, chemical, and mechanical properties of a polymer. There also other pigment families such as: aluminium pigments, special effect pigments, and other pigments [15][16].

### **Organic Pigments**

Organic pigments are chemically unstable and thus not suitable for long term applications or processing at high temperature. They can be very hard to disperse and tend to form agglomerates of pigment particles. Yet they provide the most brightly opaque colours available [15].

### **Inorganic Pigments**

Inorganic pigments are based on metal oxides and sulphides. Unlike the organic pigments, these ones are more easily dispersed. These types of pigments are divided in three main classes: white pigments, black pigments, and coloured pigments [15].

White pigments are mostly based on Titanium dioxide ( $\text{TiO}_2$ ). When incorporated into polymers formulation they are known for improving their weatherability and durability mostly because of the ability to absorb UV light energy. Moreover, the use of these pigments improves the efficiency in scattering visible light and to create opacity. The carbon black is by far the most important black pigment in thermoplastics. It's chemically pure and thus can also be used in other kinds of plastics such as elastomers. Moreover, thanks to its chemical stability black pigments can serve as radicals attenuator formed by photodecomposition. Depending on the size and shape of these pigment they can also influence other performance attributes such as UV abortion, conductivity, ease of dispersion, viscosity, etc [15].

### **Aluminium Pigments**

These types of pigments have many different grades and can be used in many types of polymers. If provided in the form of dust, the aluminium powder can easily be airborne and burn explosively if in contact with any source of ignition [16].

### Special Effect Pigments

They can be organic or inorganic compounds and when implemented into polymers can provide quality, attractiveness, and durability. These effects can be accomplished by the following special effects pigments [15][16]:

- Coloured glass;
- Fluorescent pigments;
- Pearlescent pigments;
- Metallic pigments;

### Other Pigments

There are other pigments beyond the one previously mentioned that can be added to the polymers base [16]:

- Fluorescent pigments – pigments with light collecting properties that will produce a brilliant glow-in-the-dark effect;
- Photochromic pigments – organic pigments that have excellent coloration;
- Thermochromic pigments – these pigments can, at a specific transition temperature range, reverse its colours;

#### 2.1.6 Degradation Mechanisms in polymeric materials

The degradation of a polymeric material is a crucial yet complex process that needs to be monitored and studied. Usually, it not only depends on the characteristics of the parts (molecular weight, sample morphology, degree of crystallinity) but also on the surrounding environment (temperature, acidity, presence of oxygen, microorganisms, etc) [17]. It's an unwanted process since it reduces the mechanical, physical, and chemical properties of a polymer by changes in its chemical links thus reducing its lifetime [18]. The degradation rate can vary significantly. Some polymers can take decades to decompose whereas others can completely do it in a few hours. As it shown in Figure 7 there are several major factors that can cause degradation: chemical, thermal, biological, radiolytic, mechanical photodegradation, etc. Each one of these mechanisms will be addressed with more detail below in this section.

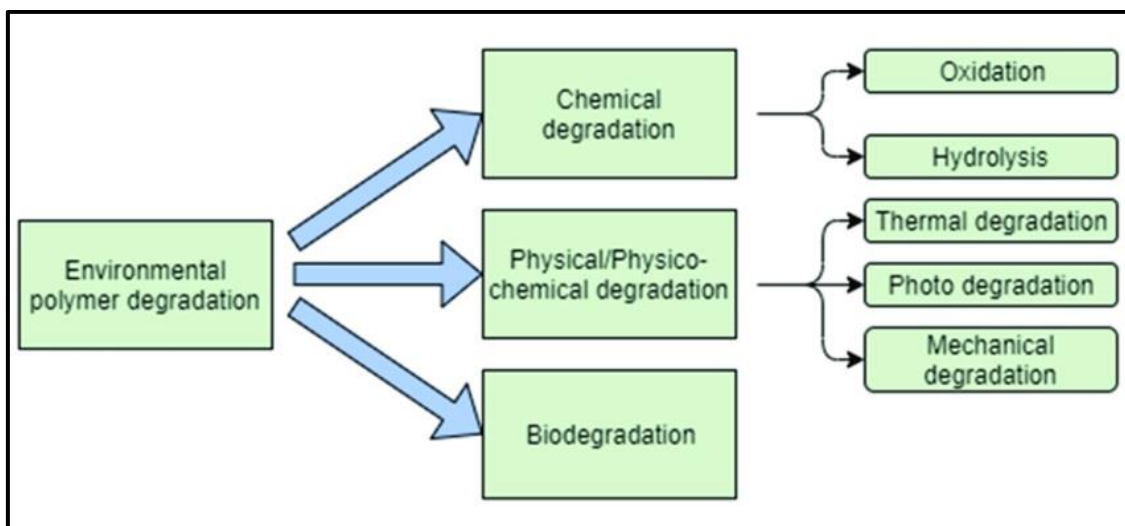


Figure 7 – Schematic presentation of polymer degradation [19].

### Thermal degradation

The thermal degradation mechanism occurs through the absorption of thermal energy by the polymer chemical bonds. This phenomenon will cause the bonds to break off and to free some radicals that are extremely active. These radicals will, in turn, react with the molecules around and thus more chains can be further broken and create oligomers with different molecular weight. As a result, properties like thermal or mechanical behaviour can be changed dramatically [20][17].

According to many scientific papers, thermal degradation has been studied with and without the presence of oxygen. Despite being almost impossible to ignore the influence of oxygen in the polymer's chemical chains, the investigation in this area has proved to be vital because many heat treatments are performed under oxygen free conditions [20].

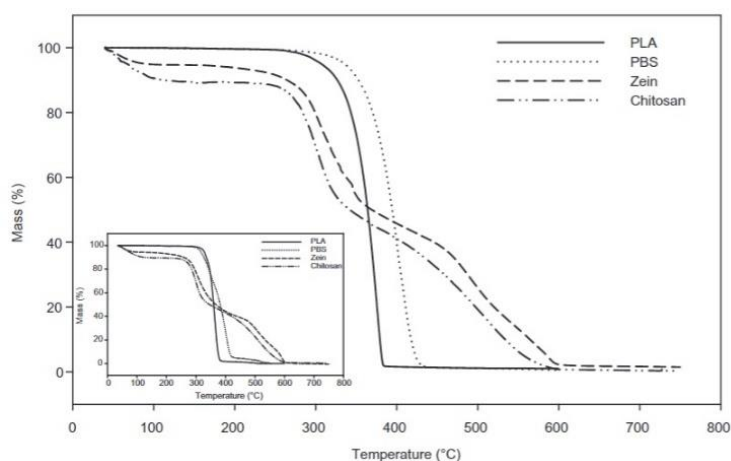


Figure 8 – TG scans of some of some biodegradable polymers [21].

### Thermal Degradation without oxygen

Even in the absence of air any polymer can degrade if heated high enough. Concerning the temperatures at which structural changes may occur, thermal degradation can start at  $T_m$  which is the temperature a polymer is transformed from solid to viscous liquid. When it comes to PLA polymer, it was studied that the lower the molecular weight, the lower will be the temperature at which decomposition starts [17]. There are three types of thermal degradation mechanisms [20].

- Depolymerization
- Random chain-breaking
- Side group elimination

### Thermal-oxidative degradation

The main difference between the previous oxygen free degradation process and the oxidative degradation is that this last can take place at less elevated temperatures. As it was exposed before in this section, if a molecular chain breaks up it will free radicals that will react with oxygen. This phenomenon will induce a molecular chain scission mechanism which will prevent the formation of polymer molecular chains again. As a result, this will increase the polymer degradation rate. Moreover, a chain scission will cause changes in the molecular weight and will consequently decrease in the  $T_g$  and an increase in the degree of crystallinity [17].

### **Photochemical degradation**

Photodegradation is a phenomenon that occurs when a polymer molecule absorbs photons due to being exposed to wavelengths found in infrared, visible light and especially ultraviolet (UV) radiation. The electrons will therefore be excited and a chain breaking reaction may follow. As a result, some properties of the polymer such as mechanical or chemical properties will gradually change [20][22].

There two main types of “chemical degradation” that should be distinguished. The first, occurs in the absence of oxygen (photodegradation) and the second takes place when oxygen is involved (photooxidative) [22].

The photodegradation can be direct or indirect. In the direct degradation the polymer molecular chains can be broken due to absorbed photons and its molecular

weight can decrease. On the other hand, during an indirect degradation the photons energy that is responsible for breaking the molecular chains is firstly absorbed by a substance in the environment.

The photooxidative degradation is mainly induced by UV radiation [22]. It's also possible to occur with longer wavelengths such as infrared or visible light if oxygen is present. This degradation process goes through three main steps as shown in Figure 9.

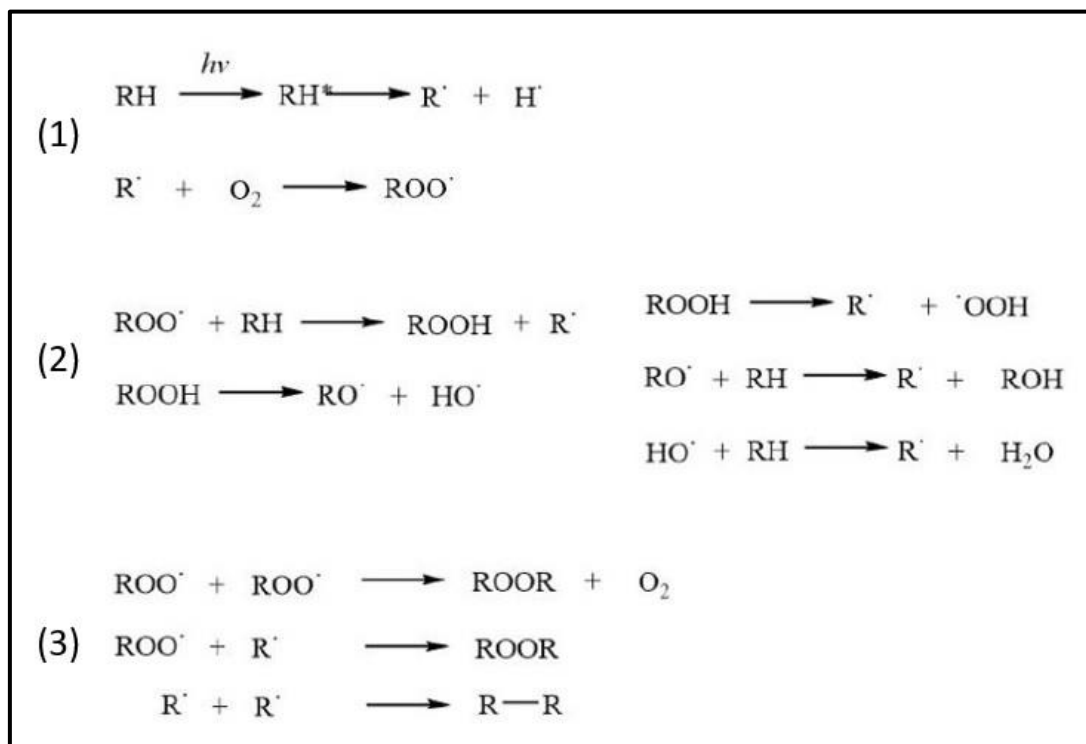


Figure 9 – Reaction Mechanism of photo-oxidative degradation (1) Mechanism-initiation; (2) Mechanism-propagation; (3) Mechanism-termination [20].

#### 2.1.7 Characterization Techniques of polymeric materials

The characterization of polymers is a very important task within the process of creation/implementation of polymeric materials. There are multiple approaches for polymer characterization such as the molecular analysis (FTIR), thermal analysis (DSC, TGA & DMA) and physical analysis (tensile, flexural and compression testing).

##### Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectrometer uses the Michelson interferometer as the working principle, and it is relatively faster, more accurate, reproducible, and more affordable. This spectrometer consists of a radiation source, an interferometer, a sample

compartment, and an infrared radiation detector. The elements of an FTIR spectrometer vary according to the infrared regions under observation. Typical commercial devices operate in a single region (MIR), and its components are appropriate and fixed, but some spectrometers used in research are more versatile allowing the replacement of some components according to a specific region. There are three regions of the infrared: FIR, MIR and NIR [23]. In Figure 10 it's represented an optical scheme of a FTIR spectrometer.

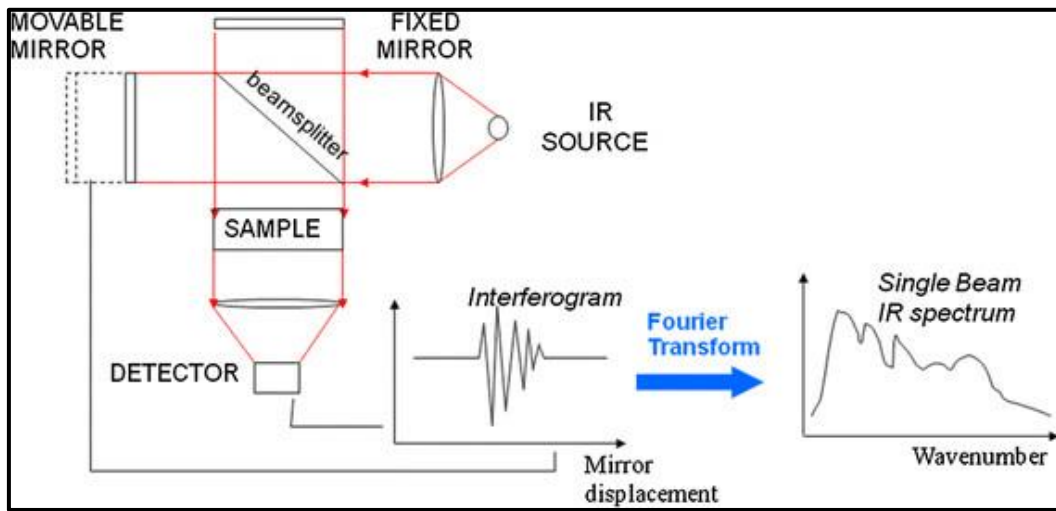


Figure 10 - Optical Scheme of an FTIR Spectrometer [24].

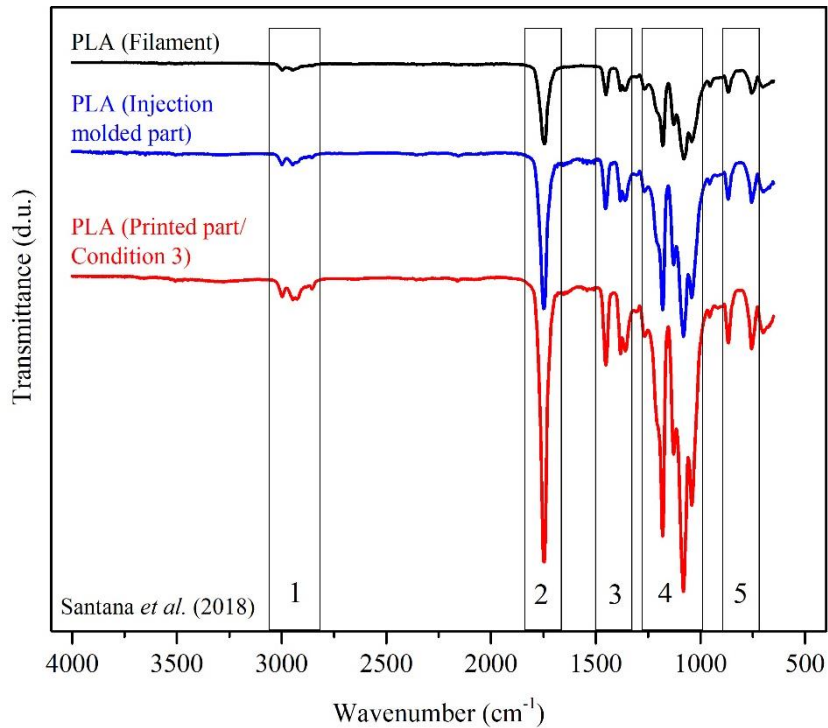


Figure 11 – Example of PLA FTIR Curves [25](adapted).

## Thermal Analysis

There is a branch of materials science where the properties of materials are studied with the change of its temperature. To make this study there are several methods that are commonly used, with each one of them distinguished from one another by the property which is measured.

### Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermos-analytical technique that is widely used in polymers to determine their thermal transitions such as the glass transition temperature ( $T_g$ ), the crystallization temperature ( $T_c$ ) and the melting temperature ( $T_m$ ) [4]. In Figure 12 there's a schematic of how a DSC machine works. There are two main measurement methods:

- **Heat Flux** – the sample unit and the reference material are heated at the same rate from a single heating source. The temperature difference between the sample and the reference material is measured according of temperature.
- **Power Compensated** – unlike the previous method, the sample and reference are heated separately and not next to each other. As soon as the temperature of both chambers is matched, the electrical power that is required to obtain and remain at this state is then recorded [26].

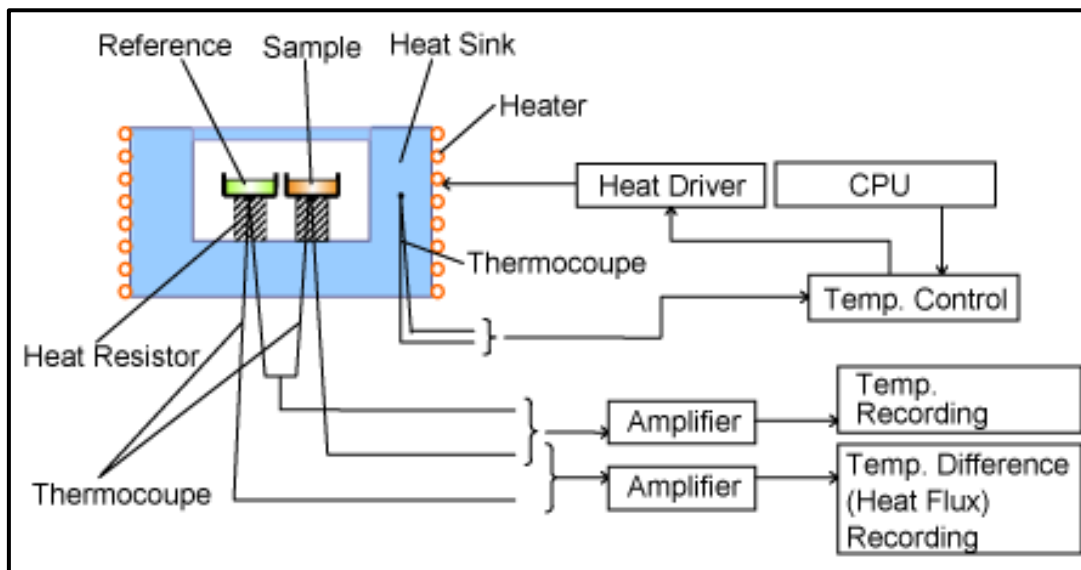


Figure 12 - Block Diagram of Heat Flux DSC [26].

### Thermogravimetric analysis (TGA)

The Thermogravimetric Analysis is a method in which the mass of a substance is measured inside a furnace by a precision balance over time as the temperature changes. The atmosphere inside the furnace is controlled by a gas that can be either inert or reactive. There are three types of thermogravimetry:

- Isothermal thermogravimetry: the sample mass is recorded according to time at a constant temperature.
- Quasistatic thermogravimetry: the sample temperature is raised in multiple intervals and held at those intervals for a specific time until the mass stabilizes.
- Dynamic thermogravimetry: the temperature is linearly raised over time as the mass is recorded.



Figure 13 - A typical TGA system.

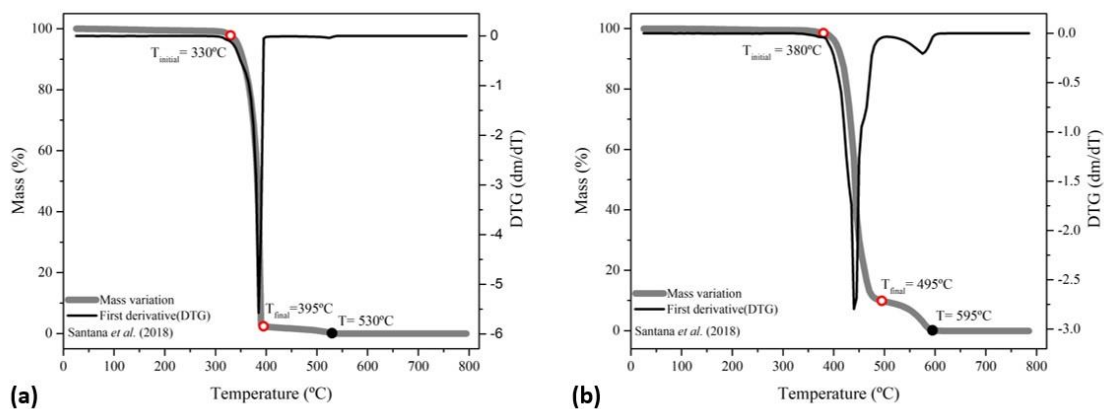


Figure 14 – Example of TGA curves: PLA (a) and PETG (b) [25](adapted).

### Dynamic Mechanical Analysis (DMA)

This technique is used to measure viscoelastic changes as a function of periodic changes in the stress, temperature, or time. Despite being used to investigate many physical properties of a polymer, this technique is more commonly used to accurately evaluate the glass transition temperature ( $T_g$ ). It can also be used to identify secondary transitions corresponding to molecular motions [27].

A DMA test can be measured in terms of storage modulus ( $E'$ ) loss ( $E''$ ), loss factor ( $\tan \delta$ ), etc. The module  $E'$  correspond to the energy absorbed and recovered by the elastic response in each cycle of load application, while  $E''$  represents the energy lost – dissipated in the form of heat – due to viscous responses throughout the cycles. A simple example to define  $E'$  and  $E''$  is to drop a viscoelastic ball onto a surface as shown in Figure 15. Furthermore, in Figure 16 there's a schematic of a DMA machine.

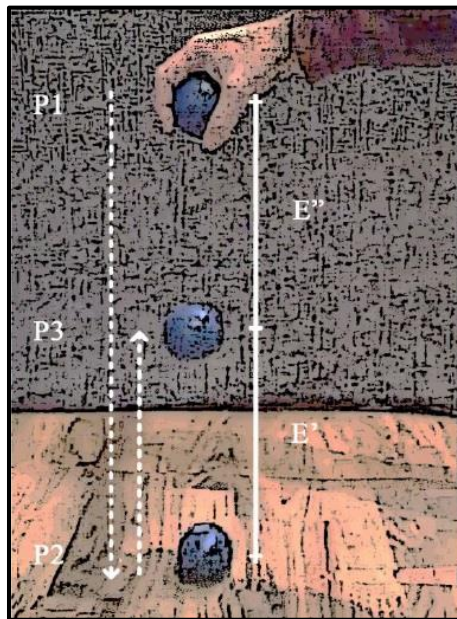


Figure 15 – Practical representation of the storage ( $E'$ ) and loss ( $E''$ ) modulus [9].

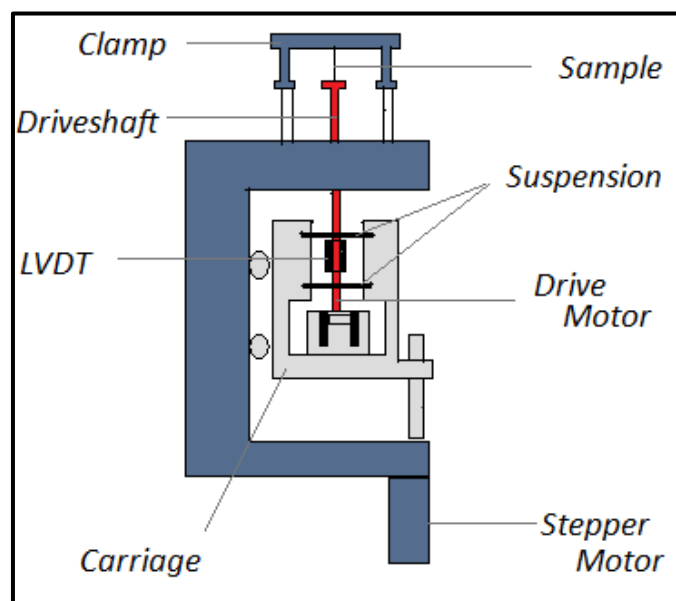


Figure 16 – General schematic of a DMA instrument [28].

## 2.2 Additive Manufacturing (AM)

### Historical Contextualization

It was only in 1987 that the world's first Stereolithographic Apparatus (SLA), capable to fabricate complex parts layer by layer, was released. Thereafter, AM started to show its true potential with the development of new materials in multiple new additive processes such as: Selective Laser Sintering (SLS), Fused Deposition Modelling (FDM), Laminated Object Manufacturing (LOM) and many others [29].

Today, additive manufacturing is a technology revolution towards the 4<sup>th</sup> industrial revolution and it's still on its infancy. However, the innovations that have been made throughout the years have had a big impact in our society and culture. Thanks to its potential to completely change the way our products are made, this technology has grown into a worldwide multi-billion-dollar industry [30].

Regarding the future, the global market of AM is expected to grow 17% annually and will be worth 51 billion dollars by 2030. All the industries will benefit from the grow of 3D printing but the ones that will take the biggest advantage of AM are the aerospace and medical industries. This last one is expected to be capable of bioprinting human tissues in a few years thus contributing to regenerative medicine [29]. In Figure 17 there's a graphic that forecasts the growth of the AM market in the next decade.

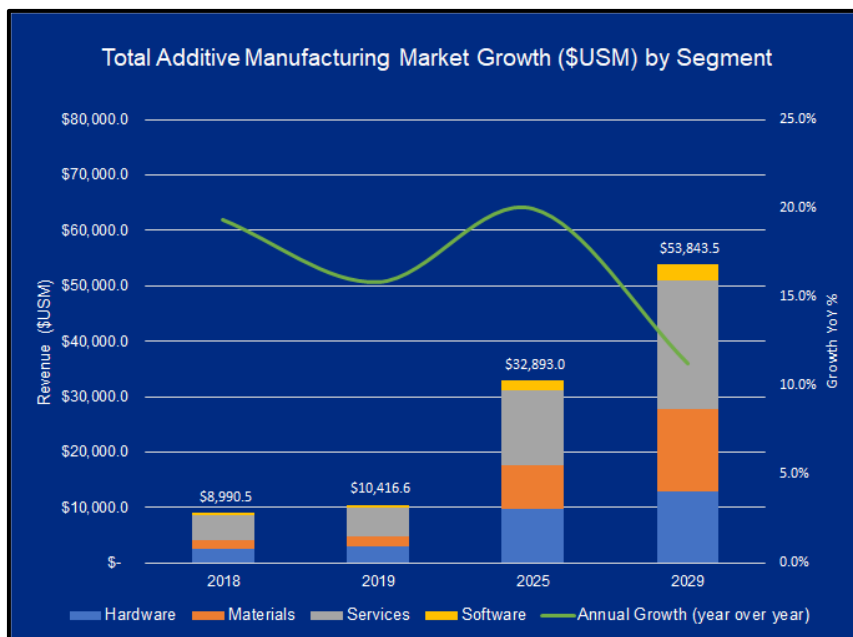


Figure 17 – Additive Manufacturing Market Growth [31].

### 2.2.1 Definition and Classes

Additive manufacturing is an umbrella term used to cover all type of production processes where a part is printed layer-by-layer using a digital 3D model designed in CAD software. These models can be either designed by the user or obtained via 3D scanning (reverse engineering). After the part is designed, the digital prototype is sliced into individual layers, and a toolpath code is generated for a 3D printer as shown in Figure 18 [32][33].

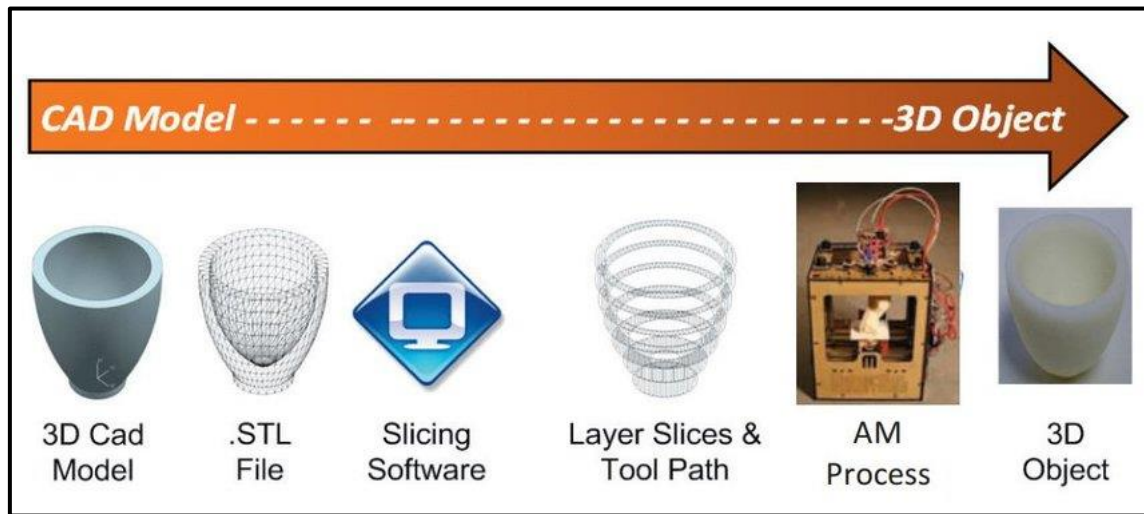


Figure 18 – Generic process of CAD to part, showing all eight stages [9].

In general, AM technologies can be differentiated under four aspects: initial state of the raw material, energy source, method used for the formation of the layers, and the conditions in which the parts are manufactured [9]. According to norm ISO/ASTM 52900-15, AM is composed of seven different categories. Each one of them has its own advantages and drawbacks and are exposed with more detail in Table 7.

Table 7 – Different categories of additive manufacturing according to ISO/ASTM 52900 [32][34](adapted).

| Category               | Description                                                                                                                                       |
|------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| Material Extrusion     | Process where the material is extruded through a fixed diameter orifice, commonly designated as nozzle, if it is presented in a semi-fluid state. |
| Material Jetting       | Process where small particles of construction material coupled with support material are deposited in specific areas of a build plate.            |
| Binder Jetting         | Process where a mixture of granulate and binding materials are selectively deposited to form a solid structure.                                   |
| <i>To be continued</i> |                                                                                                                                                   |

| <i>Continuation</i>        |                                                                                                                      |
|----------------------------|----------------------------------------------------------------------------------------------------------------------|
| Sheet Lamination           | Process where there is successive deposition and bonding of sheets of material with defined sections.                |
| VAT Photopolymerization    | Process where there is a cure phenomenon of photocurable resins by resorting to fixed wavelength radiation exposure. |
| Powder Bed Fusion          | It's a process where an energy source is directed to a bed of powder to heat the particles until they melt together. |
| Directed Energy Deposition | Process where materials are gradually deposited and the fused together by focused thermal energy.                    |

### 2.2.2 AM Applications and Advantages

Over the last few years, AM has improved so much that some companies around the world are starting to use this technology as a viable production process [35] (Figure 19). Generally, there are five key advantages that AM has over conventional manufacturing processes: [36].

- Cost of entry is becoming more affordable;
- It opens the possibility of producing multiple versions of a single design;
- Training programs are becoming more available and affordable at all levels;
- Waste production reduction;
- Savings on energy costs;

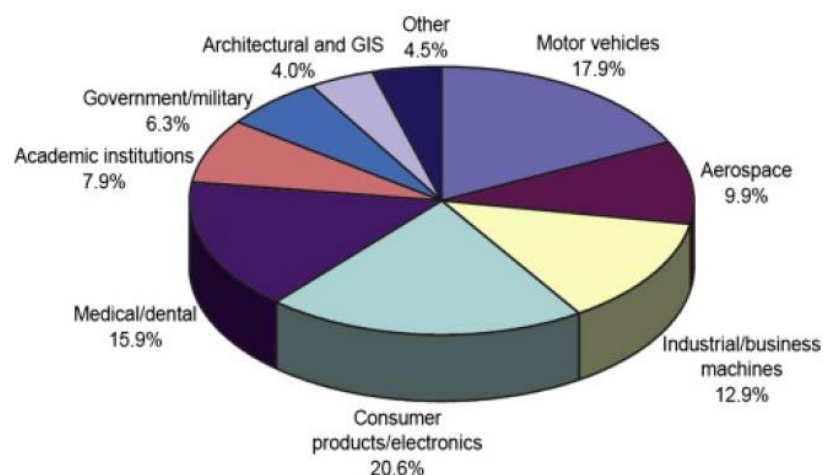


Figure 19 – Industries using additive manufacturing [35].

The data shown in Figure 19 proves that AM is experiencing a widespread use across almost all types of industries. Although the applications will continue to grow in the upcoming years, this graphic also shows that AM have already vastly transformed some industries.

### 2.2.3 3D Printing of Polymer Matrix Composites

Multiple printing techniques aimed to fabricate polymer composites are already established and available on the market. Each one of them has its own advantages and limitations and their selection depends on the physical requirements of the final part. These requirements can be the starting materials, surface resolution, mechanical behaviour, etc [33] Each one of these printing techniques are exposed in Table 8. In Figure 20 there's a graphic that shows the market share of each composite-based printing technology.

Table 8 - A summary of established prototyping techniques [33].

| Technique | State of starting materials | Working Principle                                      | Resolution (Z direction, $\mu\text{m}$ ) |
|-----------|-----------------------------|--------------------------------------------------------|------------------------------------------|
| FDM       | Filament                    | Thermoplastics such as PC, ABS, PLA, and nylon         | 50 - 200                                 |
| SLA       | Liquid photo-polymer Powder | Photocurable resin (epoxy or acrylate-based resin)     | 10                                       |
| SLS       | Powder                      | PLC and Polyamide powder                               | 80                                       |
| 3DP       | Powder                      | Any materials can be supplied as powder, binder needed | 100 – 250                                |
| 3D        | Liquid or plotting past     | PLC, PLA, hydrogel                                     | 5 - 200                                  |

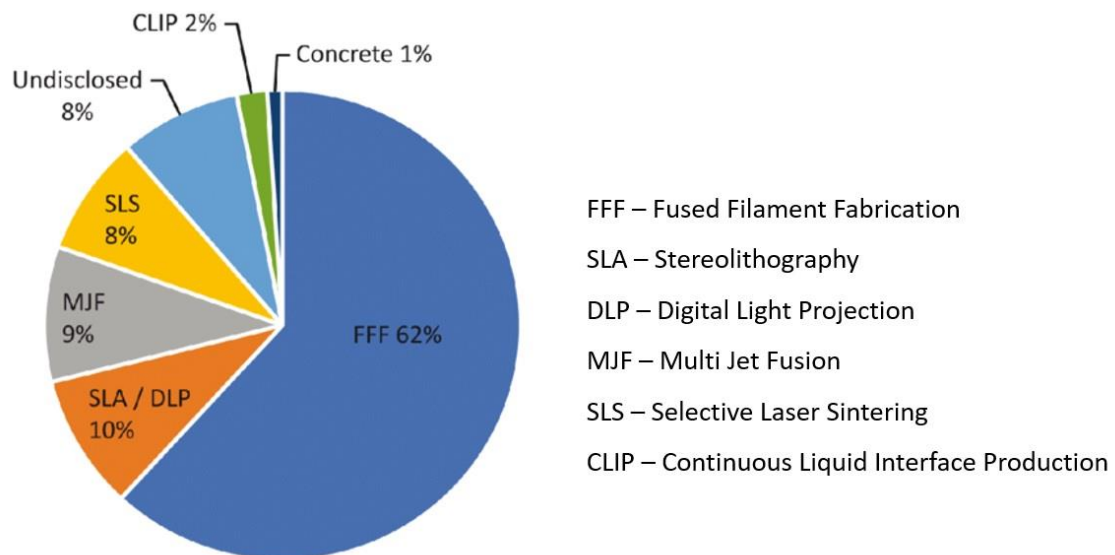


Figure 20 - 3D printing technologies used in projects [37].

## 2.3 Extrusion Based Additive Manufacturing

### 2.3.1 Fused Filament Fabrication (FFF)

Fused Deposition Modelling (FDM) was invented in the late 1980s, but it only began to be commercialized in the 1990s by Stratasys, Inc. The patent of this technology expired in 2009 ever since then companies around the world started to develop and deploy new variants of this technology on the market. Nowadays, Fused Filament Fabrication (FFF) is the most widely used technology thanks to its countless applications in many types of industries including pharmaceutical, automobile, biomedical and many others. The percentage market share of some of these manufacturing sectors are shown in Figure 21. Moreover, because FFF is the most budget-friendly and popular 3D printing technology, more than 70% of users are utilizing this technology in house [38].

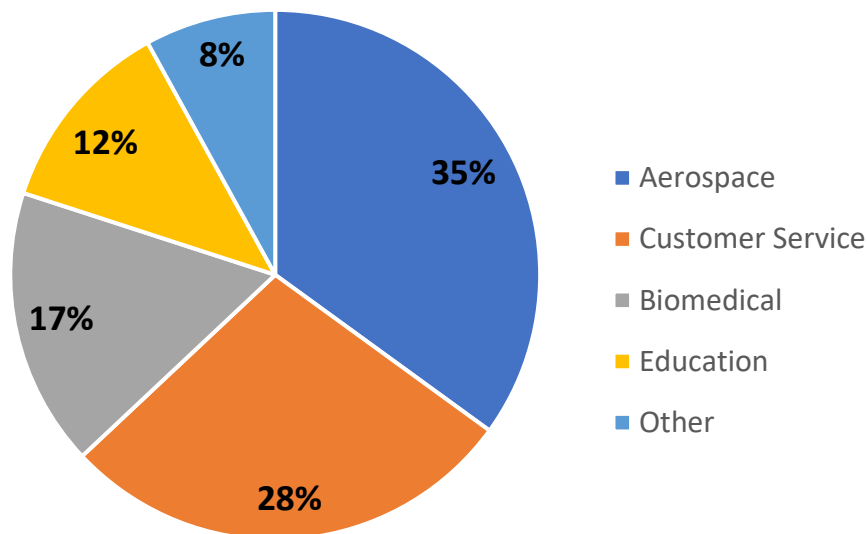


Figure 21 – Percentage Share of FFF [39](adapted).

#### How does it work

Mechanically, the filaments are driven into the extruder by means of two grip-wheels and then transformed into a semi-liquid state before being extruded through a nozzle of the printer. The extruder will continuously deposit the material layer by layer onto a heated building platform according to a G-code until the designed product form and shape are achieved [40].

As it was mentioned this additive manufacture method uses thermoplastics filaments as raw material. PLA is the most common material for its unique properties and will be addressed with more detail in section 2.4. Other materials may also be used in FFF, and these include Acrylonitrile Butadiene Styrene (ABS), Polypropylene (PC), Polyethylene (PE), etc. All these materials are trade by many different brands in the form of filament wires. Each brand has its own way of manufacturing the filaments and these will differ according to the material thermal and mechanical properties and chemical composition [39][40].

In addition to the type of material that is used, FFF has a set of multiple printing parameters that are specified on the slicing software where the G-code is created. These parameters can have a great influence in the quality of the final product and will be addressed with more detail in section 2.3.4. The combination of both machine and material parameters, as shown in Figure 22, will define the properties of the final product [39][40].

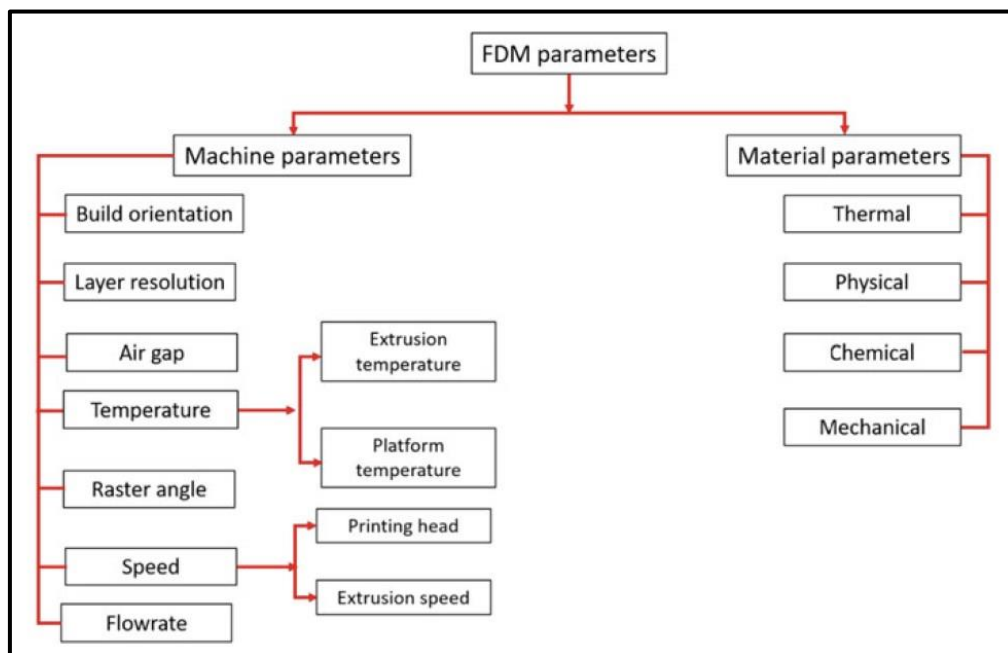


Figure 22 – Parameters that influence the FFF process [40].

### 2.3.2 Types of FFF 3D Printers

There are four main types of FFF 3D Printers: Cartesian, Delta, Polar and Scara 3D printers. To differentiate FFF printers the two most important aspects to consider are coordinate system and the mechanical nature [41].

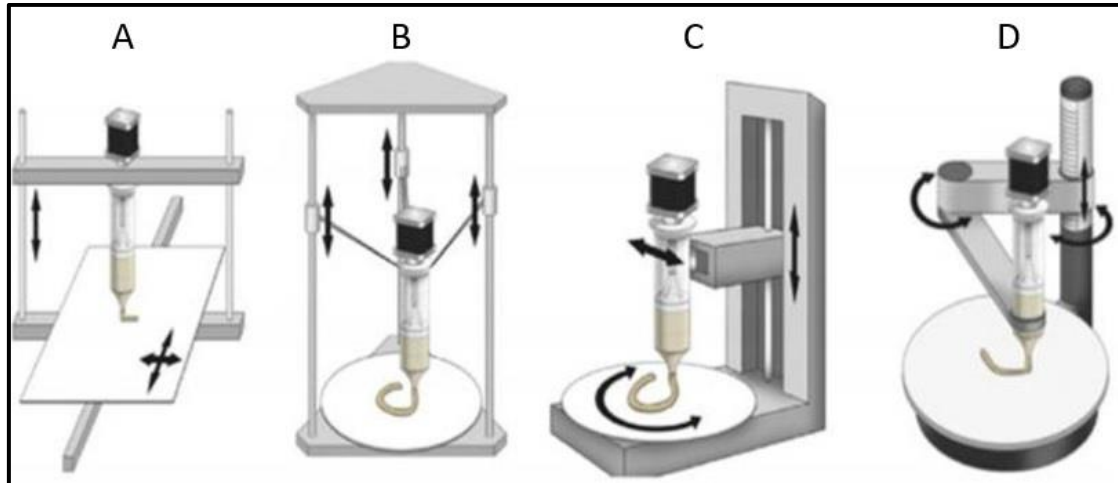


Figure 23 - Structural configurations of major 3D printers: A-Cartesian B-Delta C-Polar and D-SCARA [41].

### Cartesian FDM 3D printer

This type of printers is the most common across the FDM Printer market. In a simple way, the print head moves across a cartesian coordinate system defined by the X, Y and Z axes (Figure 24). The X and Y axis represent the lateral and the longitudinal position while the Z axis defines the elevation. The print bed usually only moves on the Y axis. It's also composed by a total of four motors: one for X axis, one for Y axis and two motors for symmetry in Z axis. Despite being very popular, this kind of printer has the most limited architecture, lower printing speed and more vibration [42][43].

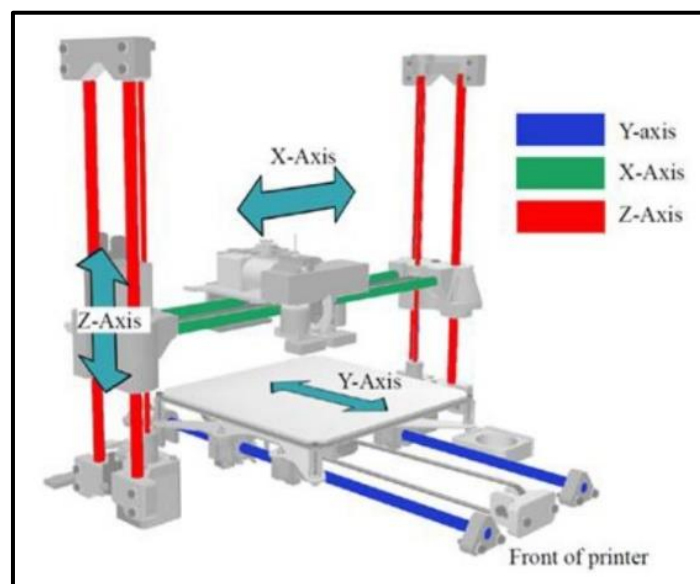


Figure 24 - Cartesian Printer [44].

### Delta FDM printers

The Delta FDM printers are the second most popular type of FDM 3D printers. Its main advantage compared to the cartesian printer is the high speed of printing. Each one of the axes X, Y or Z is controlled by a single motor which a total of three motors (Figure 25). Because the extruder itself doesn't have to carry the weight of a stepper motor the extruder speed can be increased. Another advantage is the structure which happens to be the simplest and enables a much higher Z axis. However, this architecture is the most difficult to calibrate and cannot be used with specific extruders such as the Bowden extruder [44][43].

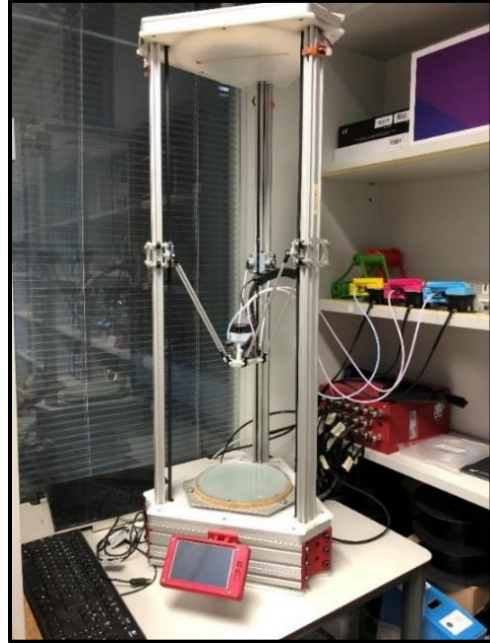


Figure 25 - Delta 3D Printer (LDPS – FEUP).

### Polar 3D FDM Printers

Instead of using a cartesian system, in the polar 3D Printers the positioning is determined by an angle and length. Whereas the previous systems need at least 3 engines to work properly, the polar printer only need two engines which leads to great energy efficiency [42][45].

### SCARA 3D Printer

The Selective Compliance Assembly Robot Arm offers as main advantage greater freedom and flexibility when printing. This printer also uses a cartesian coordinate system but use a different mechanical setup. Unlike the previous printers, the SCARA printer is not limited to a build platform/plate making it possible for the mechanical arm to move in all possible directions which allows to print much more geometrically complex parts [45].

### 2.3.3 Types of Extruders

A 3D printer extruder is a part of a 3D printer and its most complex mechanism. It's responsible for drawing and pushing out the filament. It is composed of several pieces of assembly such as motors, gears, heater block, nozzle, etc (Figure 26).

Normally, the extrusion system is the key to any improvement of the FFF process specially when it comes to multicolour/multi-material functionality. Most extruders have a single nozzle due to its simplicity, lower cost, and effectiveness. However, this type of extruders has its own limitations since it does not allow to print two different filaments simultaneously with different melting temperatures. To solve this problem, dual extruders can be used even though these extruders still need to be further developed to achieve the quality standards of a single 3D printer extruder [46].

#### Description of an extruder head of an FDM 3D printer

The extruders have two main parts: the cold end and the hot end. The cold end is the upper part of the extruder where the filament is fed. On the other hand, the hot end is where the filament is melted, and latter squirted out [46].

- **Cold end** – its composed by an extruder motor, a toothed gear mounted to the motor's shaft and a spring loader idler to hold the filament;
- **Hot end** – its composed by a heated chamber where the filament transitions from solid to liquid and latter squirted out from the nozzle.

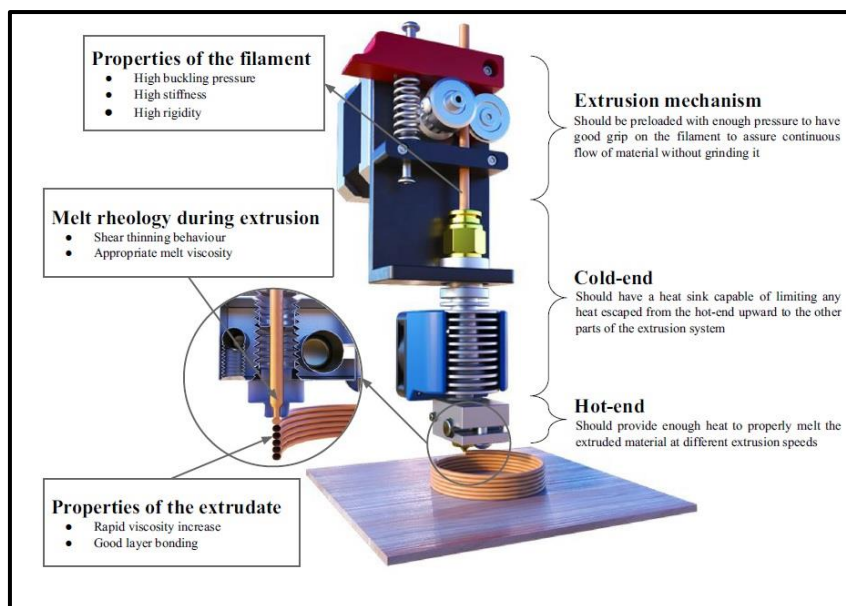


Figure 26 - Cut-away of 3D Printer Extruder [46].

### Types of Extruders

There are two main types of extruders that are widely used in filament 3D printers depending on the type of drive (Figure 27).

- **Direct Extruders** – the extruder motor is placed directly on top of the hot end and the filament is pushed directly from the cog of the extruder to the hot end. The main advantage is the greater control over the flow of filament into the hot end and the main disadvantage is the considerable inertia in the axis through which the extruder and the Hot End moves [47].
- **Bowden Extruders** – mechanically they are very similar to the direct extruders. The main difference though is that the stepper motor is not mounted directly over the hot end. The filament must pass through a PTFE tube which connects the extruder to the hot end. The main benefit of this system is that the hot end is lighter and can move faster and accurately. However, with filaments of bigger diameters, it's not possible to keep the pressure in the filament constant along the PTFE tube [47].

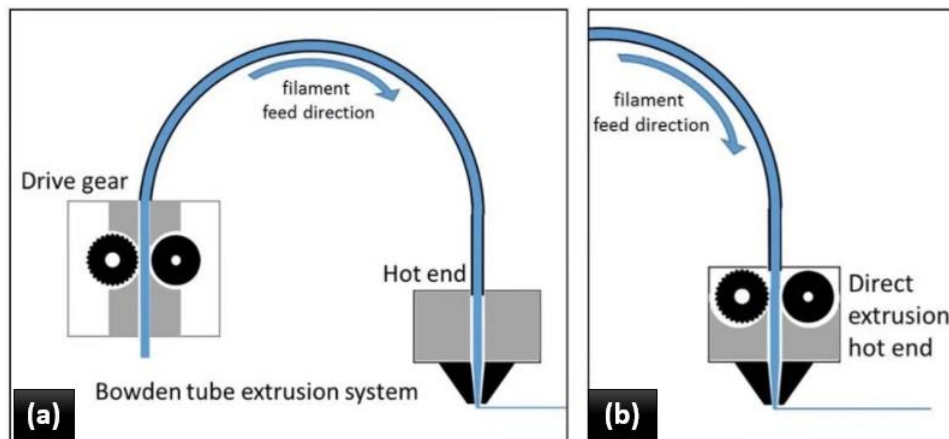


Figure 27 - The difference between the direct drive (b) and the Bowden 3D printer extruder (a)[47].

### 2.3.4 Process Parameters

The FFF process is a process that is used to fabricate geometrically complex shaped parts. However, the quality of these parts is relatively poor, with low dimensional accuracy and mechanical properties. Thus, it's very important to identify and analyse multiple key parameters which affect the before mentioned properties. The optimum setting of these parameters can improve a lot the quality of the parts and reduce the post-production work [51].

There are two main parameters categories in FFF: the 3D printer machine parameters and the printing parameters. The first are entered into the 3D printer and the second ones are inputted in the slicing software. The machine parameters are, for example, bed temperature and nozzle diameter. On the other hand, the printing parameters can be layer thickness, road width, build orientation raster angle, etc [48]. In Figure 28 there a representation of these parameters on an ASTM D638 model.

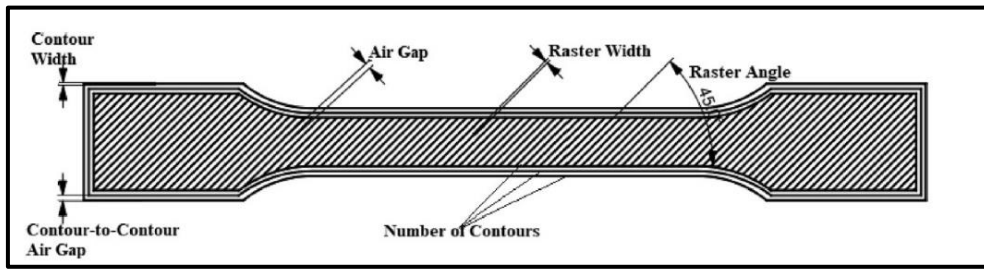


Figure 28 - FDM process parameters related to tool path shown for ASTM D638 model [48].

**Air gap:** it's the distance between two adjacent tool paths on a single deposited layer. Generally, by default, a value of zero is assigned to this parameter to guarantee that the deposited filaments only touch each other. If a positive value is applied means that the scans will be farther apart. At the same time, the use of a negative value indicates that the deposited filaments can overlap resulting in a denser structure and with a longer printing time (Figure 29)[9].

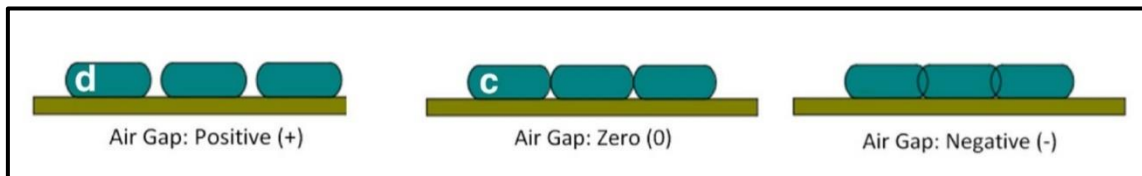


Figure 29 – Different types of air gaps [49].

**Number of perimeters (contours):** this parameter is characterized by the number of printed perimeters, internally and externally, around the part (Figure 30)[48].

**Contours:** this parameter sets a raster that is deposited along the edges of the part defining its geometry. The number of contours can vary and are unlimited but typically at least one is used. The tensile load of resistance will increase if a high number of contours is used due to high number of fibres along the solicitation direction (Figure 30) [9].

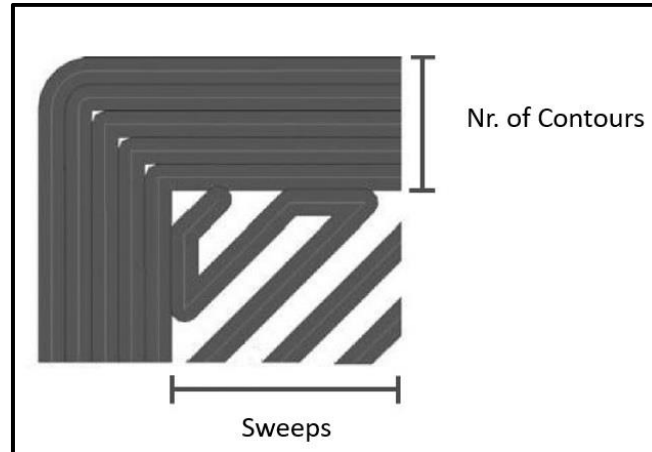


Figure 30 – Graphical representation of the number of contours [50].

**Build orientation:** it represents how the part is placed on the build platform, considering the X, Y, and Z axes as well as the angle at which the part will be produced (Figure 31). It can assume a wide range of settings depending on the solicitations the printed part will be subjected to. This parameter has a big impact on the mechanical properties of FDM manufactured parts because depending on the direction of an external solicitation, the placement of the fibres should be as well as on printing time [51].

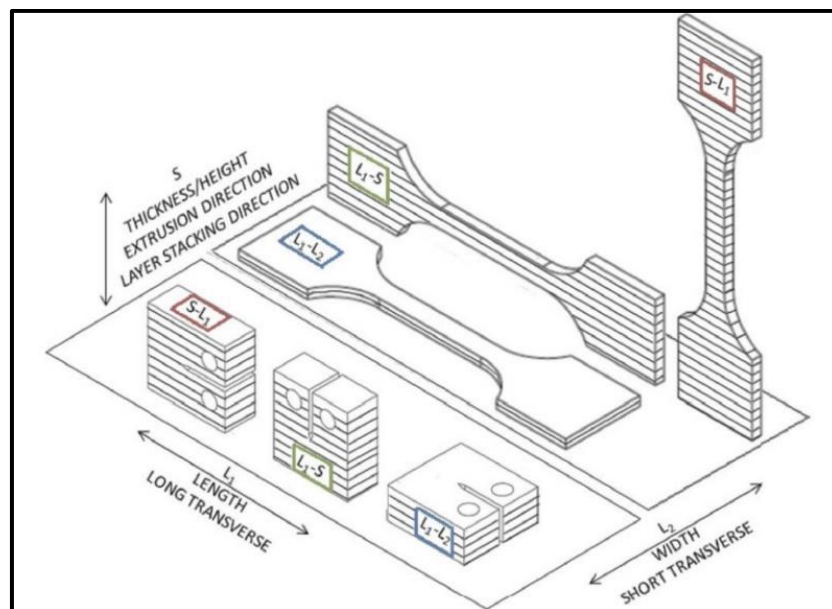


Figure 31 – Various build orientation at which different test samples can be printed [52].

**Bed temperature:** this temperature has an important role in reducing deformations in parts manufactured by FDM since it facilitates the relaxation of tensions in the deposited filaments. It also contributes to the adhesion between the deposited layers [48][53].

**Extrusion temperature:** it's basically the temperature at which the thermoplastic filament is heated just before extrusion. This temperature affects the viscosity of the material. If temperature is too low, then there's a high risk that the material doesn't flow correctly through the nozzle and therefore the layers do not fuse properly. This can generate an effect of delamination or separation of the layers. On the other hand, if the temperature is too high then the material can lose the ability to cool down properly between layers, thus damaging the print. Moreover, the thermal gradients can become larger thus leading to accumulation of inner stresses in the fibres. If the temperature surpasses a maximum limit the material can degrade which can generate a burnt appearance [9].

**Extrusion multiplier:** the adjustment of this variable affects the dimensional quality, surfaces, mechanical behaviour, and porosity of printed parts. It is responsible for controlling the flow of material through the printhead. By default, it is set to 1. Values above generate denser parts, however, if far too above, they can cause excess material deposition thus impacting dimensional distortions. On the other and, settings below 1 can result in printed parts with amounts of material lower than necessary to obtain good mechanical properties [9].

**Infill pattern:** there are a lot of different infill patterns than can be used in FDM 3D printing. These patterns can have shapes like diamond, cross, honeycomb and linear [53]. In Figure 32 are represented three types on infill patten than can be used.

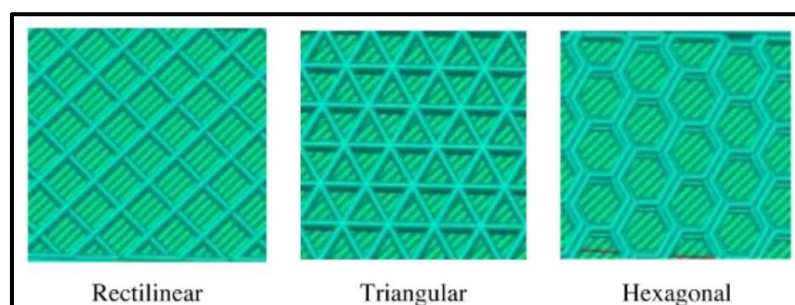


Figure 32 – Infill patterns commonly used and studied by Alafaghani and Qattawi [54].

**Infill density:** it's the percentage of infill volume with filament material to create the internal structure also known as the infill. A value of 100% in this parameter means that the material density inside the component is maximum, while a percentage of 0%

corresponds to a hollow part. The infill density is also a parameter that must be adjusted according to the application of the part to be manufactured. Wider fills print much faster than denser parts, but the strength tends to decrease [9][48][53]. The effects on the variation of the infill percentage is shown in Figure 33.

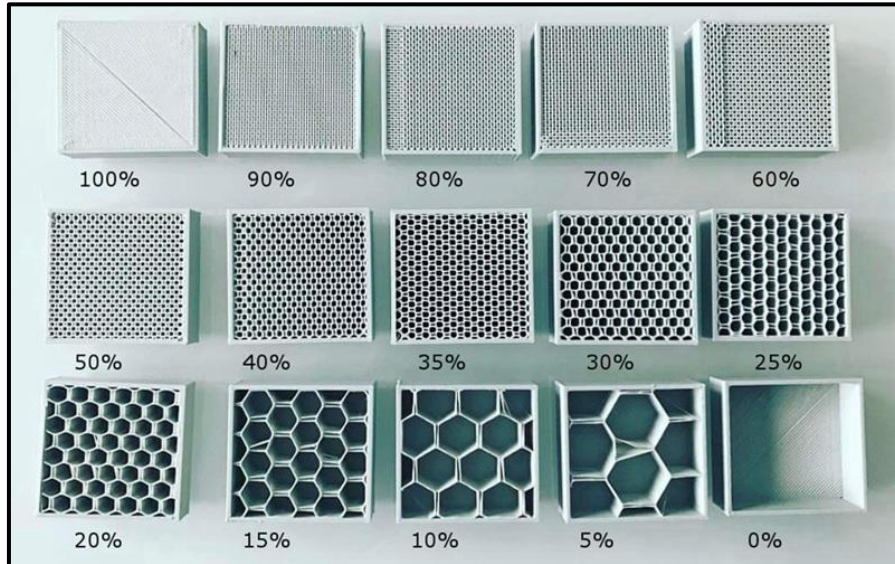


Figure 33 - Variation of infill percentage [55].

**Layer thickness:** it's the thickness of the deposited layers along the Z axis and is responsible for the resolution of the printed parts. The height of the layers depends on the material and the extruder tip diameter and therefore the layers height is always smaller than the diameter of the nozzle.

Smaller thicknesses help to improve the adhesion between layers as they increase the surface contact between the deposited filaments, benefiting the heat transfer. On the other hand, a bigger layer thickness reduces manufacturing time, and the printing surface will show more horizontal lines favouring the appearance of the “*staircase effect*” as shown in Figure 34 [9][48][53].

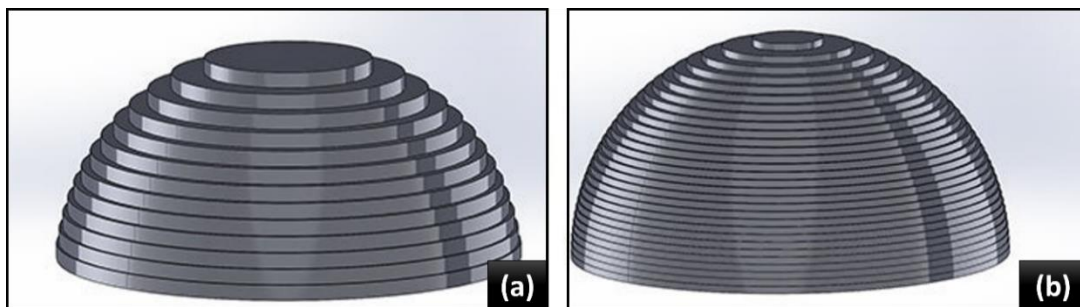


Figure 34 - Layer thickness visual effects – (a) 0.1mm; (b) 0.05mm [56].

Regarding the effects on mechanical properties, Chacón et al. (2017) stated that for lower values of layer thickness it was possible to obtain higher tensile strength. This phenomenon is mainly explained by the fact that for lower layer heights, the air gaps are smaller and the bonding areas between the layers are bigger.

**Raster angle:** it's the angle of the deposition bed according to X direction of the build platform. This angle can vary from 0 to 90 degrees. In Figure 35 there's a graphical representation of this parameter.

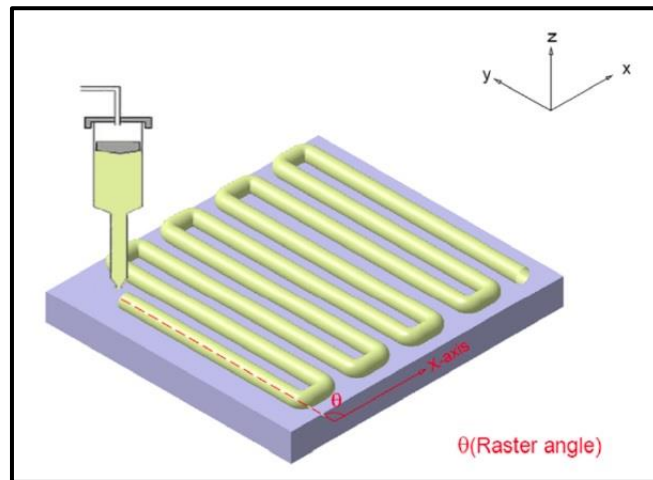


Figure 35 – Graphical definition of raster angle [57].

**Raster width (road width):** this parameter depends on the nozzle tip diameter, and it's defined as the width of the deposition beds;

**Print speed:** it's the speed of the extruder head across the XY plan during the material deposition when building the layers, measured in mm/s. The printing speed can affect the quality of the printed part and must be properly configured depending on the material flow. A low speed usually increases the print quality but if it's far too low, the print area can be overloaded [58].

Ning *et al.* (2017) showed that for higher printing speeds, the tensile and flexural resistance of the printed parts may decrease. His justification was that thanks to shorter deposition times, the porosity increased and the bonding between the layers was weaker.

### 2.3.5 Filament Quality

There are many different filament producers around the world that are increasingly flooding the market with new types of filaments. However, a large proportion of these alternatives use low quality bends and are not suitable for 3D printing. As result, the printers used with these filaments may stall and the quality of the final product may be affected. Therefore, it's very important to accomplish with the thermal, morphological, and structural characterization of commercially available filaments.

#### Filament Pigmentation

The use of filament pigmentation is an influential factor and is somehow connected to the properties of the final parts. The light-coloured filaments that use translucent or transparent pigmentation, like grey or transparent, have a more pronounced ability to adhere on the surface of a solid. At the same time, the use of colours the are brighter and opaquer will improve the tensile strength of the final part [59]

On the other hand, materials without pigmentation tend to have greater viscosity which improves the surface quality of the printed parts. Moreover, the dimensional accuracy of the final parts is much better when pigments are not used [59].

#### Storage Conditions

When it comes to material degradation, some studies have proved that the storage conditions in which the polymeric filaments are kept are more important than temperature or pigments. Because some types of filaments are characterized by their hygroscopic properties, the presence of moisture in their storage place makes them very susceptible of material degradation. Thanks to the action of water, when a filament is being used for extrusion, the temperature in the nozzle will cause water boiling thus forming part bubbles. The accumulation of these bubbles will cause the propagation of cracks when a mechanical test is performed. Contrary, in dry atmospheric conditions the material becomes less tenacious, and a more fragile break may occur but unlike humidity, this doesn't happen because of defects in the material structure [59].

### Diameter Tolerance

A very common problem while extruding FDM filaments is the possible variations of the filament diameter. If the filament diameter is too small, then the lack of tension created by the grip-wheels will cause failures in the extruder. On the other hand, if the diameter is too wide then the filament will not be able to fit in gap of the nozzle and therefore the material will not be deposited properly [60]. If these variances are too significant it can influence the final part quality since the presence of irregularities in the filament will not be compensated by the printer. The standard tolerance across the filament industry is  $\pm 0.05\text{mm}$ . The severity of these issues relies also in the type of 3D printer that's being used [61].

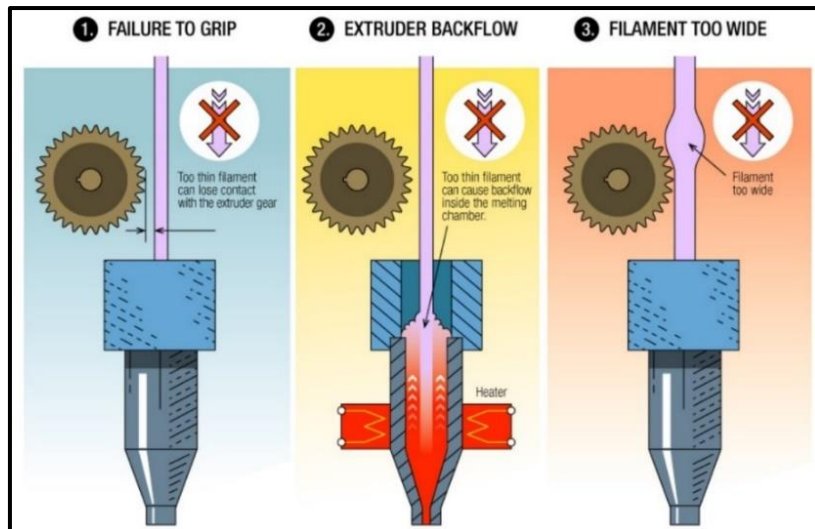


Figure 36 – Schematic representation of filament diameter related issues [62].

It has also been studied that the presence of porosity in filaments may lead to weaker printed parts and the presence of inclusions can lead to nozzle blockages [63].

#### 2.3.6 Mechanical Properties of FFF Printed Parts

Before being economically viable and used in a wide range of applications, AM technology was originally used to fabricate prototypes without high mechanical properties. However, with the development of this technology and the emergence of new materials it is possible now to fabricate end-use components with a good quality and, of course, good mechanical specifications.

## Printing Parameters

The printing parameters can be divided in two main groups: manufacturing and structural. The manufacturing parameters includes extrusion temperature, build platform temperature and printing speed whereas the structural parameters include filament separation, printing orientation, filament rasters, etc. What has been observed whatsoever, is that the structural parameters have a greater influence than the printing ones on the mechanical properties of FFF parts. To understand the relation between the print material, the structural and the manufacture parameters, the Ishikawa Diagram represented in Figure 37 summarizes their influence.

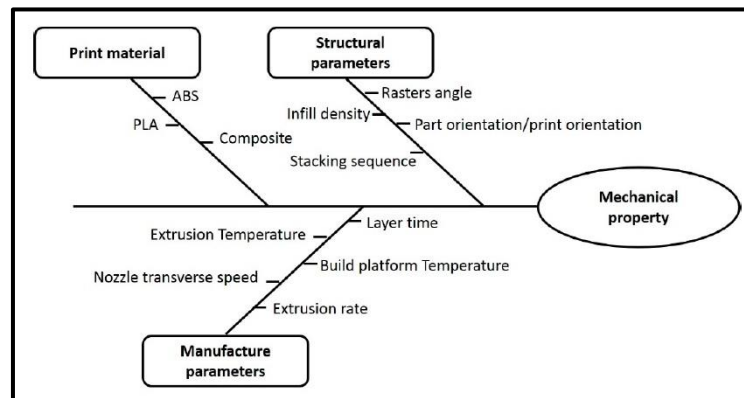


Figure 37 - Ishikawa Diagram [64].

## Material Parameters

The FFF can be used with a broad range of materials such as Acrylonitrile Butadiene Styrene (ABS), Poly (lactic acid) (PLA), Polyoxymethylene (POM), High Impact Polystyrene (HIPS), and Polyamides (PA). There are also the high-performance materials such as Poly(ether-etherketone) (PEEK) and Polyvinylidene fluoride (PVDF). In Table 9 there's a comparison between the proprieties of HIPS, PLA, and ABS [9][65][66].

Table 9 - Properties of HIPS, PLA, and ABS polymers [65].

| Polymers                          | HIPS              |      |              | ABS              |      |              | PLA              |      |              |
|-----------------------------------|-------------------|------|--------------|------------------|------|--------------|------------------|------|--------------|
|                                   | OV                | SD   | SE $\bar{x}$ | OV               | SD   | SE $\bar{x}$ | OV               | SD   | SE $\bar{x}$ |
| MFI (g/10 min)                    | 7.5 $\pm$ 0.20    | 0.16 | 0.11         | 8.76 $\pm$ 0.16  | 0.13 | 0.09         | 13.52 $\pm$ 0.11 | 0.09 | 0.06         |
| Young's modulus (MPa)             | 112.5 $\pm$ 0.12  | 0.09 | 0.06         | 175 $\pm$ 0.11   | 0.09 | 0.06         | 47.9 $\pm$ 0.10  | 0.08 | 0.05         |
| Yield stress (MPa)                | 3.44 $\pm$ 0.21   | 0.17 | 0.12         | 0.49 $\pm$ 0.21  | 0.17 | 0.12         | 0.27 $\pm$ 0.16  | 0.13 | 0.09         |
| Glass transition temp (°C)        | 100.41 $\pm$ 0.16 | 0.13 | 0.09         | 109.76 $\pm$ 0.2 | 0.16 | 0.11         | 62.57 $\pm$ 0.21 | 0.17 | 0.12         |
| Peak load (N)                     | 80.8 $\pm$ 0.11   | 0.08 | 0.06         | 207 $\pm$ 0.2    | 0.16 | 0.11         | 282.4 $\pm$ 0.20 | 0.16 | 0.11         |
| Peak strength (MPa)               | 4.21 $\pm$ 0.16   | 0.13 | 0.09         | 10.78 $\pm$ 0.11 | 0.09 | 0.06         | 14.71 $\pm$ 0.16 | 0.13 | 0.09         |
| Peak elongation (mm)              | 1.9 $\pm$ 0.20    | 0.16 | 0.11         | 4.75 $\pm$ 0.16  | 0.13 | 0.09         | 5.13 $\pm$ 0.16  | 0.13 | 0.09         |
| Percentage elongation at peak (%) | 3.0 $\pm$ 0.11    | 0.09 | 0.06         | 6.0 $\pm$ 0.15   | 0.12 | 0.08         | 7.0 $\pm$ 0.10   | 0.08 | 0.05         |

Note: OV = Observed value, SD = standard deviation, SE $\bar{x}$  = Standard error of mean.

### 2.3.7 Degradation in FFF Printed Parts

There are several degradation mechanisms that have been studied regarding 3D printed parts using thermoplastics, especially PLA's. However, in this section the focus will be only on three of those degradation processes since these are the ones that are planned to be experimentally tested.

#### Landfill Degradation

In the context of this work, landfills are terrestrial ecosystems that provide a great habitat for vegetation establishment and colonization of faunal communities. However, despite the biological activities that take place under these mixtures of soil, their environmental factors are quite hostile mostly because of limited oxygen conditions (anaerobic), humidity and microbiological conditions [67][68].

Theoretically, PLA is a biodegradable polymer which means it's environmentally friendly and therefore can be easily dumped into sanitary landfills without converting itself into toxic substances. However, there is limited information about how this polymer degradation behaves under landfill conditions and how FFF parts made from it will be affected in terms of mechanical properties such as tensile and flexural strength or even mass [62].

To test the influence on the physical and chemical properties by the previously mentioned factors on a FFF PLA printed part, some experimental tests have been performed. One of them, for example, printed five ASTM D790 tensile plates and buried them for 90 days at a thermophilic temperature of 60°C. As the testing time had passed, the samples were weighted and placed under Scanning Electron Microscopy (SEM) [64].

The results had shown that the mass of each sample had been reduced by 10% due to disintegration of PLA. The disintegration was mainly caused by hydrolytic processes and microorganisms. Within the 90 days, it was also observed that the pH had ranged from 5 to 7.3. There were also some physical appearance changes that suggested that the colour aspect had changed from clear to opaque. This phenomenon was mainly attributed to hydrolysis. The surface morphology changes that had been evaluated by SEM throughout the experimental period reported a lot of small micropores and irregular roughness. Finally the FTIR spectroscopy graphic showed that the percentage of carbon from the molecular structure had decreased [69].

### Humidity Degradation

Despite its many advantages such as biodegradability, lower cost, recyclable nature, PLA is high in hygroscopicity. Although there are few references regarding the effects of moisture environments on biopolymers, it is known that the presence of moisture in the polymeric chains accelerates the decomposition rate. Generally, this phenomenon happens mostly because the molecular chains become more susceptible of rearrangements (specially for temperatures above  $T_G$ ) [70].

During a printing process, humidity in filaments can cause big trouble. The nozzle can either break or jam as the filament can swallow. Moreover, because a printer extruder usually works at temperatures beyond 200°C, the presence of moisture in the filament can boil and generate micro bubbles. After solidification, these bubbles will turn into voids in the final part structure which results in weaker mechanical properties [65].

### Salt Solution Degradation

Thanks to the evolution of FFF printing technologies, the spectrum of applications is becoming wider. Amongst new industries there's, for example, the maritime industry which have been considering the use of polymeric materials. In this context, there's an emerging concern on understanding how the mechanical properties might be affected if the materials are exposed to salty water. Thus, understanding how these polymers behave under these external factors has been motivating a lot of research in this area [70].

To better understand the effects of salty water on FFF printed parts, an experimental study where specimens were immersed in fully saturated water for 10 weeks, was carried out by [70]. The PLA filaments had a diameter of 1.75mm, were natural coloured and had a density of 1.24 g/cm<sup>3</sup>. A total of 30 specimens with square-shaped forms of 30mm×30mm×3mm were immersed in two different solutions: distilled water and fully saturated water (15 specimens per solution). The salt solution was based on a proportion of 39g of salt for every 100mL at 20°C.

When it comes to water absorption, all the samples were weighted every week and it was observed that in general the main absorption took place in the first 3 days. The distilled water samples stabilized in weight after 8 weeks whereas the salt solution

samples stabilized after 3 weeks but there were variations 2 or 3 weeks later. These variations might have been caused by open gaps caused by hydrolysis processes that can dissolve the external layers of the samples. It is important to keep in mind that the PLA's organic nature allows sudden changes in the absorption rates. Regarding colour changes, these occurred most likely because of hydrolysis (water molecules break carbon hydrogen bonds). Moreover, it has been determined that transparency-opaque transitions might occur due to modifications of crystallinity yet further investigations had to be performed to confirm this [70].

## 2.4 Poli (lactic acid) (PLA)

### 2.4.1 General Properties

Because of the ease of its printing, glossiness, and multicolour appearance, PLA is the most widely used polymer in FFF. Beyond that, PLA is a bioplastic that is fabricated from fully renewable sources and therefore it's an eco-friendly that degrades into non-poisonous gases even when its incinerated [40]. Another major attribute about these thermoplastics is that they can be heated to their melting point, cooled, and reheated again without significant degradation. This allows them to be easily injection moulded and then subsequently recycled. In Table 10 there's a comparison between the thermal and mechanical properties of both PLA and another commonly used thermoplastic, the ABS. In Figure 38 it's shown a representation of the before mentioned eco-friendly cycle of PLA.

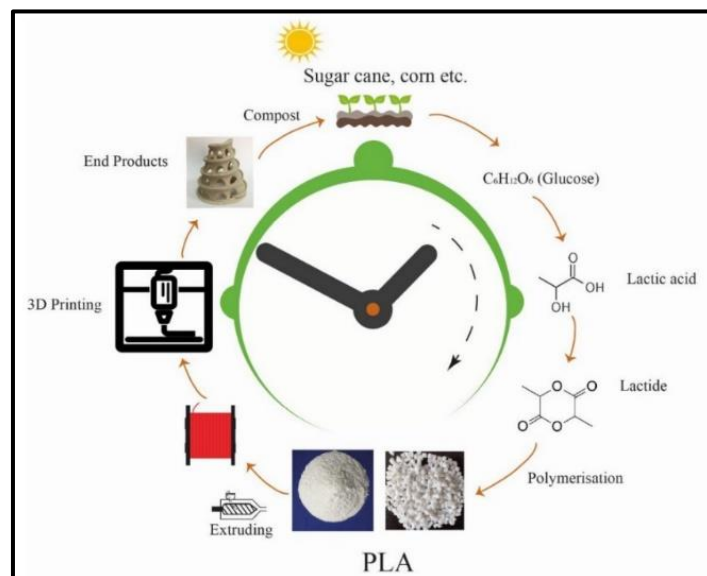


Figure 38 - Environmentally friendly polylactic acid (PLA) cycle [71].

Table 10 - Properties of polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS)[71].

| Property                        | PLA       | ABS                 |
|---------------------------------|-----------|---------------------|
| Printing temperature (°C)       | 180 - 230 | 210 - 250           |
| Build platform temperature (°C) | 20 - 60   | 80 - 110            |
| Raft                            | Optional  | Mandatory           |
| Strenght                        | High      | Medium              |
| Flexibility                     | Brittle   | Moderately flexible |
| Heat resistance                 | Low       | Moderate            |
| Biodegradability                | Yes       | No                  |
| Moisture absorption             | Yes       | Yes                 |

#### 2.4.2 Synthesis and Stereochemistry of PLA

Most plastics are derived from polymerization of non-renewable petroleum reserves. However, PLA is a bioplastic that is produced with materials sourced from renewable biomass products such as sugar cane, corn, wheat, rice, etc. These sources make PLA a biodegradable plastic with vast array of applications which will be exposed further in this section [66].

As it was studied in section 2.1, polymers are macromolecules constituted by the repetition of structural units called monomers which are linked by covalent bonds. The monomer that is used in a PLA polymer is Lactic acid (LA) which exists in two enantiomeric forms as shown in Figure 39 [66].

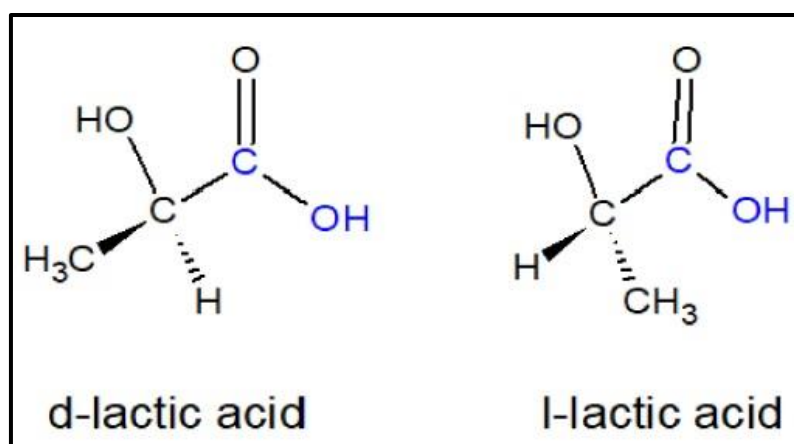


Figure 39 - Lactic acid stereoisomers [71].

As it was mentioned before PLA is produced by condensation or polymerization of LA. During these processes factors such as temperature (condensation) or the concentration of the catalysts (polymerization) enable the control of the molecular weight and the ratio of D- and L-lactic acid units in the final PLA polymer. The distribution

of these stereoisomers within the polymer molecular chains will determine the crystallinity and the mechanical, thermal and biodegradation characteristics of the final PLA [66].

Based on the stereoregularity, if a PLA is composed entirely of L-lactic monomers then is called a **PLLA** (semi-crystalline). In the opposite, if a PLA consists entirely of D-lactic monomer is called a **PDLA** (amorphous). A fully amorphous polymer can be obtained when the D- content is larger than 20% whereas highly crystalline structure can be obtained if the L- content is larger than 90%. When it comes to commercial PLA a blend of higher amount of L-lactide and a lower amount of D-lactide is the most used ratio [72]. Other PLA characteristics such as the degree of crystallinity, the glass transition temperature ( $T_G$ ) and the melting temperature ( $T_M$ ) will decrease if either the D-isomer increases or if the L-isomer decreases [71].

#### 2.4.3 Crystalline Structure

Among biodegradable polymers, PLA is the one with the greatest potential for replacing petroleum-based polymers in industry. However, one of its main weaknesses is its low thermal stability and complex crystallization behaviour [73].

First, to understand the effects of annealing, the heat deflection temperature (HDT) is a key factor. Basically, the HDT is the temperature at which a polymer starts to soften when exposed to a specific load. Under these circumstances, recrystallized PLAs have an advantage compared to the amorphous ones since these last have an HDT of 50 °C whereas semi-crystalline PLAs have an HDT of 130 °C [72].

The structure of a polymer is defined in terms of crystallinity. As it was mentioned in section 2.4.2 commercial PLAs used in FFF are semi-crystalline. However, while printing a part, depending on temperature and cooling rate, recrystallization of the PLA may occur and will result in one of four crystalline forms ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ ) [73]. The  $\alpha$  crystallite form is the most likely to be developed and is also the most stable form. To achieve this form the PLA must be cooled down from the melt in a very slow rate. If the cooling rate is too high, then there's a high risk of crystallization into a less ordered form called  $\alpha'$  (also called  $\delta$ ) with worse mechanical properties. For a PLA, the formation of  $\alpha'$  crystals takes place at temperatures below than 100 °C whereas the  $\alpha$  crystals only crystalize above 130 - 140 °C [74]. If a  $\alpha'$  form is melted and recrystallized, then a  $\alpha - \alpha'$

transition may occur. Moreover, the lower the molecular mass of a PLA, the lower the temperature transition of the  $\alpha - \alpha'$  will be [72]. The  $\beta$  crystalline phase can be obtained by the deformation of the  $\alpha$  crystals under elevated temperatures and the orthorhombic  $\gamma$  form is obtained by epitaxial crystallization [73][74]. In Figure 40 there's the transition temperatures of the metastable phases of an amorphous PLA.

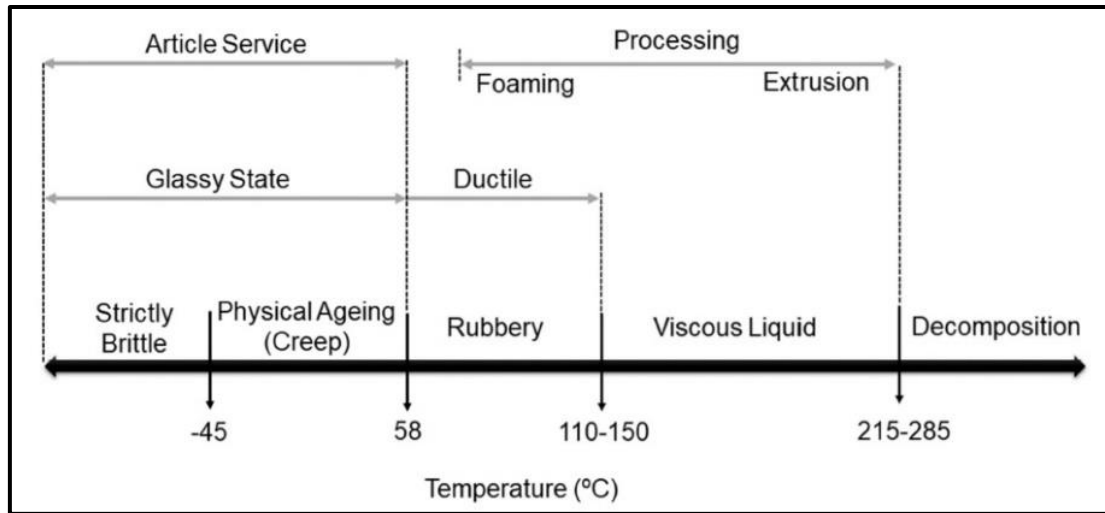


Figure 40 - Metastable phases of an amorphous PLA [17].

### 3. Materials and Methods

In this chapter, the methodological procedures, equipment, and materials used to carry out this master's dissertation will be presented. Figure 41 shows a schematic with the main experimental and research steps.

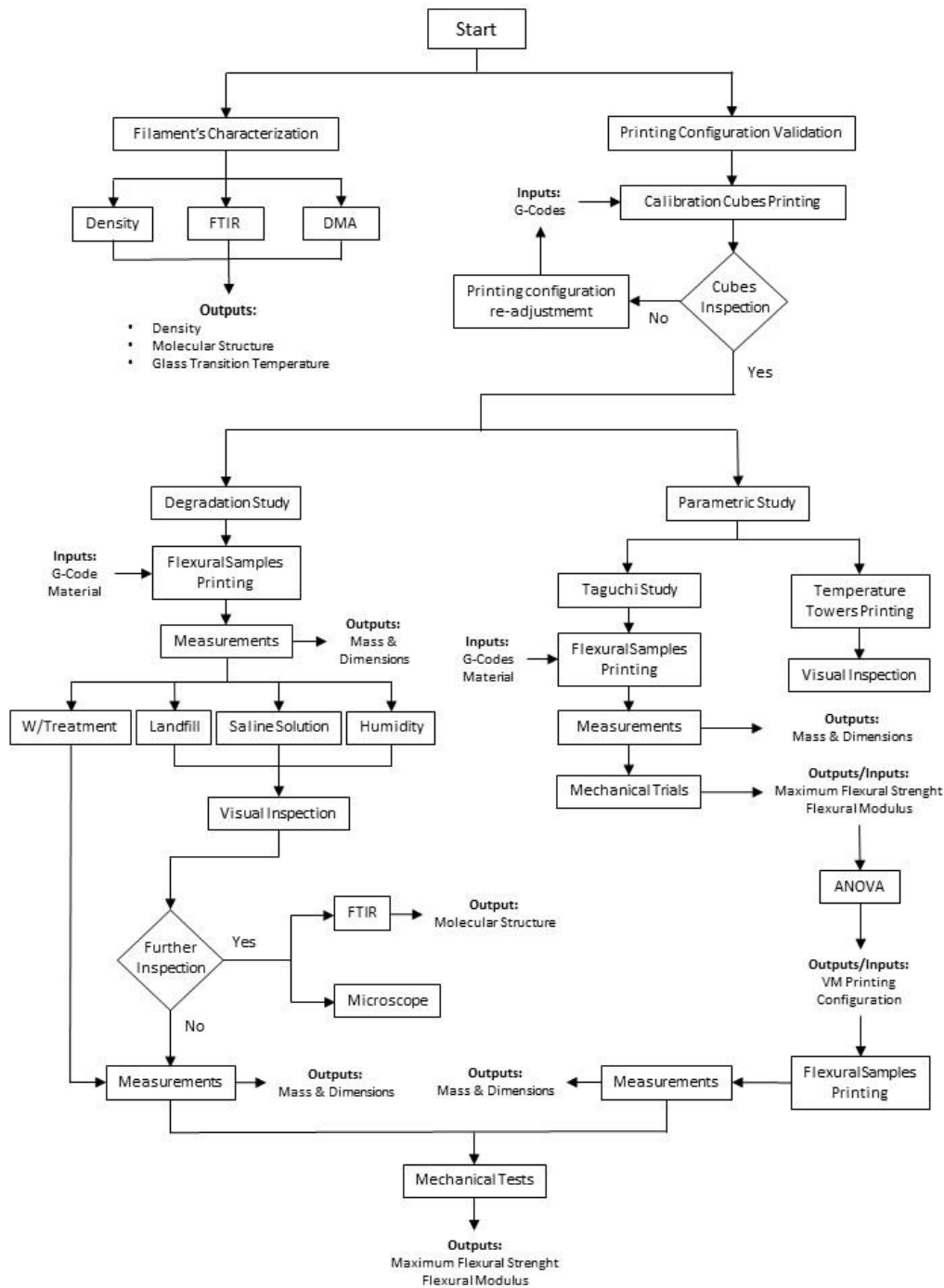


Figure 41 – Schematic of the experimental procedures.

### 3.1 Materials

This study is a continuation of Castro [75] master thesis, previously carried out at LPDS/FEUP. During that work, PLA filaments of four different colours (white, blue, orange, and red) from the same supplier more specifically from the *Filament PM™* brand, were evaluated. The author identified the red material as the most critical case, which motivated a second phase of investigation of this pigment. Therefore, the main goal of the present master research is to explore the influence of different red PLA manufacturers on the quality of printed parts.

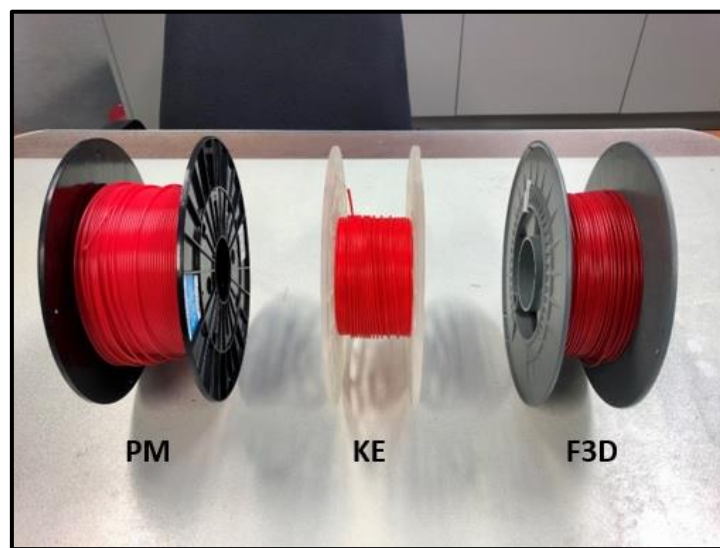


Figure 42 - Filament rolls from PM, KE and Fil3D (source: Author).

To achieve this goal, three different suppliers were evaluated: *Filament PM™*, *Kexcelled™*, and *Fil3D™*. The filament rolls that were supplied for this work are represented Figure 42. Throughout this work, according to its manufacturer, the filaments will be always mentioned by PM (*Filament PM™*), KE (*Kexcelled™*), and F3D (*Fil3D™*). The technical specifications of the three filaments are presented in Table 11. The F3D filament uses the grade 3D850 which has faster crystallization rates. This grade says that the glass transition temperature of this PLA ranges between 55°C and 60°C.

Because many samples were printed with these 3 filament suppliers, identification codes were generated according to a nomenclature that will be further explained in section 3.4.

Table 11 – PLA filament's technical characteristics [76][77][78][79].

| Properties/Parameters             | Suppliers            |             |                      |
|-----------------------------------|----------------------|-------------|----------------------|
|                                   | <i>PM™</i>           | <i>KE™</i>  | <i>Fil3D™</i>        |
| Filament diameter (mm)            | 1.75 ± 0.05          | 1.75± 0.03  | 1.75± 0.08           |
| Density (g/cm³)                   | 1.24                 | 1.23 ~ 1.26 | 1.24                 |
| Melt Flow Index (g/10min)         | 6                    | 7~15*       | 7~9 ***              |
| Glass transition temperature (°C) | <i>Not available</i> | ≈ 60        | <i>Not available</i> |
| Melt temperature (°C)             | <i>Not available</i> | ≈ 160       | <i>Not available</i> |
| Printing temperature (°C)         | 200 – 230            | 205±15      | 210±20               |
| Printing bed temperature (°C)     | 20 – 60              | 30 – 60     | 60±10                |
| Flexural modulus (MPa)            | 3500                 | 3200~3400** | <i>Not available</i> |

### 3.2 Materials' characterization

To characterize the PLA filaments three different techniques were used: (i) density measurement, (ii) Fourier-Transform Infrared Spectroscopy (FTIR) and (iii) Dynamic Mechanical Analysis (DMA).

#### 3.2.1 Density measurement

The density measurement was done at LabMat from the Federal University of Santa Catarina in Brazil. The equipment used was a Mettler Toledo balance model XS205 with a setup dedicated to density measurement by Archimedes method. The liquid used was distilled water at 22°C. For each filament supplier, five 3 cm long samples (1.75 mm diameter) were used making a total of 15 tested samples. The before mentioned balance is shown in Figure 43.



Figure 43 – Mettler Toledo XS205 Dual Range balance.

### 3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

This test was performed at Faculty of Engineering of University of Porto (FEUP) at the Lubricants Laboratory (CETRIB/INEGI). The equipment used was a Cary 630 FTIR from Agilent Technologies as shown in Figure 44. A sample filament from each brand (PM, KE & F3D) was analysed for spectrum identification with a wavelength ranging from 4000 to 650  $\text{cm}^{-1}$ .

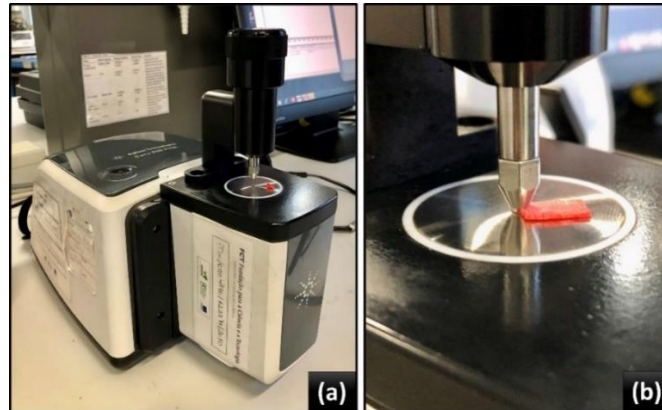


Figure 44 – (a) Cary 630 FTIR; (b) PM Sample about to be tested.

### 3.2.3 Dynamic Mechanical Analysis (DMA)

The DMA analysis was done at LabMat from the Federal University of Santa Catarina (Brazil) to measure the glass transition temperature of red PLA from different suppliers. To successfully perform this test, specimens with rectangular profile and dimensions of (35x5x1.3) mm (Figure 48) were printed, following the design guidelines by Santana [9]. For each PLA brand, five samples were built with the same printing configuration of the degradation flexural samples (section 3.3), making a total of 15 test samples. The equipment used for this characterization test was a DMA 242E Artemis (Netzsch™) (Figure 46). The test was carried out in tensile mode, with temperature range from 25°C to 90°C and heating rate of 3K/min. Procedure was made under atmospheric air, amplitude of 60  $\mu\text{m}$ , and frequency of 1Hz.

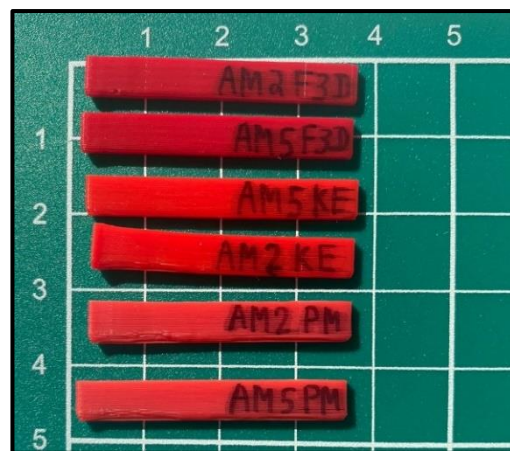


Figure 45 - Samples that were used in the DMA test.

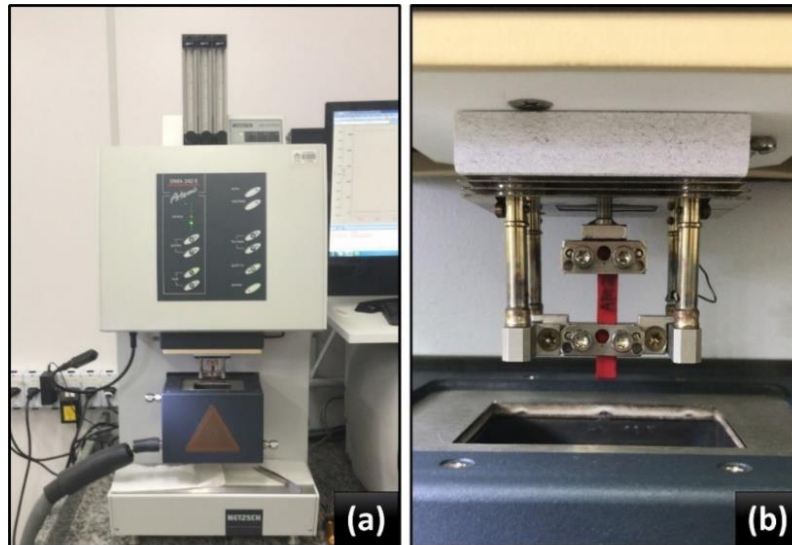


Figure 46 – (a) DMA equipment; (b) setup for tensile test.

### 3.3 3D Printing system

#### 3.3.1 Software

To print the calibration cubes and the flexural test specimens, the required files (G-codes) need to be created. To do so, a slicer software that allows the importation of STL files, and the manipulation of the printing parameters, was used. For this project the PrusaSlicer (version 2.3.3) (Figure 47) software was used.

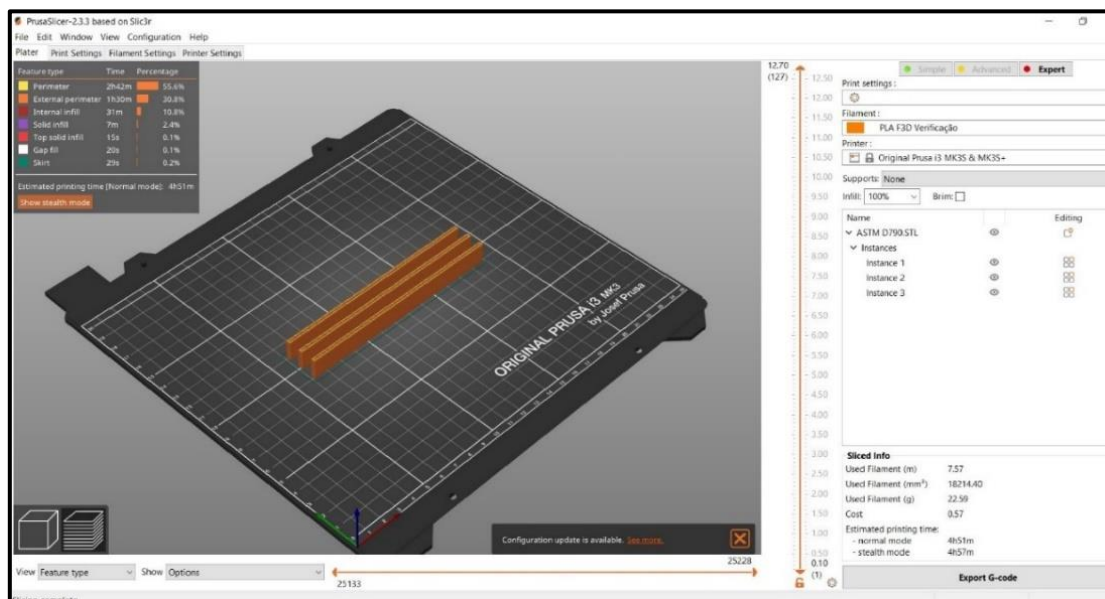


Figure 47 - PrusaSlicer Software.

### 3.3.2 3D Printers

In this work two 3D Printers were used to print all the flexural samples and the calibration cubes. The main printer was a Prusa i3 MK3S as shown in Figure 48. The second printer was also a Prusa i3 MK3S but with an improved hotend extruder that will be addressed with more detail in section 3.2.4. The technical specifications of the printer represented in Figure 48 are shown in Table 12.

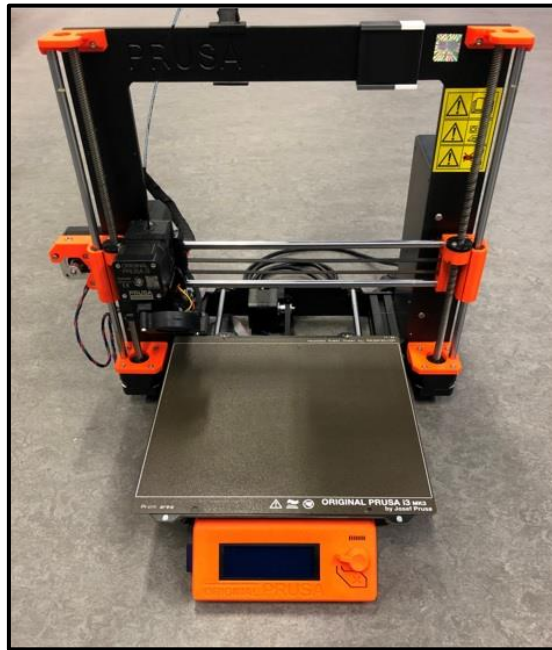


Figure 48 – Prusa i3 MK3S Printer.

Table 12 - Prusa i3 MK3S Technical Parameters.

| Parameter               | Technical Data Values                                                                                                                                                                                |
|-------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Build Volume            | 25×21×21 cm                                                                                                                                                                                          |
| Layer height            | 0.05 – 0.35 mm                                                                                                                                                                                       |
| Nozzle                  | 0.4mm default, wide range of other diameters/nozzles supported                                                                                                                                       |
| Filament diameter       | 1.75 mm                                                                                                                                                                                              |
| Supported Materials     | Wide range of thermoplastics, including PLA, PETG, ASA, ABS, PC (Polycarbonate), CPE, PVA/BVOH, PVB, HIPS, PP (Polypropylene), Flex, nGen Nylon, Carbon filled, Woodfill and other filled materials. |
| Max travel speed        | 200+ mm/s                                                                                                                                                                                            |
| Max nozzle temperature  | 300 °C                                                                                                                                                                                               |
| Max heatbed temperature | 120 °C                                                                                                                                                                                               |
| Extruder                | Direct Drive, Bondtech gears, E3D V6 hot end                                                                                                                                                         |
| Print Surface           | Removable magnetic steel sheets with different surface finishes, heated with cold corners compensation                                                                                               |
| Printer dimensions      | 7 Kg, 50×55×40 cm; 19.6×21.6×15.7 in (X×Y×Z)                                                                                                                                                         |
| Power consumption       | PLA stings: 80W / ABS settings: 120W                                                                                                                                                                 |

### 3.3.3 Equipment calibration procedure and printing parameters

Before printing the flexural samples, the printing parameters that were going to be used throughout this work had to be settled. The starting point came from a previous configuration that first emerged from a series of works [80][25][81][82]. Afterwards, this configuration was adjusted by Castro [75] for PLA parts as shown in Table 13.

Table 13 - Printing parameters [75].

| Parameters                                              | Values          |
|---------------------------------------------------------|-----------------|
| Number of perimeters                                    | 3               |
| Seam                                                    | Aligned         |
| Perimeter Printing Speed                                | 20 mm/s         |
| Fill Printing Speed                                     | 40 mm/s         |
| Overlapping adjacent lines                              | 27%             |
| Extrusion Temperature (1 <sup>st</sup> layer/following) | 215 °C / 210 °C |
| Bed Temperature                                         | 60 °C           |
| Extrusion Multiplier                                    | 1               |
| Fill type                                               | Concentric      |
| Fill percentage                                         | 100%            |
| Layer Height                                            | 0.2 mm          |
| Retraction Length                                       | 1 mm            |
| Retraction Speed                                        | 30 mm/s         |

To check if his configuration was suitable to print the ASTM D790 flexural samples, a calibration study was performed to validate them. Therefore, five PM cubes as shown in Figure 49 were printed and were evaluated according to two types of analysis: qualitatively and quantitatively. The quality analysis serves to identify multiple defects that can occur in the geometry and on the surface of the parts. On the other hand, the quantity analysis evaluates the dimensional response and the mass variance between each cube, and it will be explained with more detail later in this section.



Figure 49 - Calibration Cubes.

When it comes to FFF printing methods there are several factors that can affect the print quality such as:

1. Over extrusion;
2. Under extrusion;
3. Warping;
4. Elephant foot formation;
5. Delamination between layers;
6. Detachment between infill and perimeters;
7. Oozing;
8. Formation of bubbles on the surface;
9. Distortions in the corners;
10. Overheating and deposition of degraded material;

To ensure that none of the previous mentioned defects had occurred, each single cube has been visually assessed. In Figure 50 there's an example of one of the five printed cubes. From this example, it's possible to observe that apparently there aren't any significant printing defects. Since any of the other four cubes haven't shown defects, it's possible to conclude that the quality analysis was successful and therefore the only analysis that remains to validate the printing configuration of Castro [75] is the quantitative analysis.



Figure 50 - Calibration Cube.

The quantitative analysis is evaluated, as mentioned before, by two main features: dimensional quality and mass measurement.

On one hand, the quantity analysis was based on the mass measurement of each cube on a balance described in section 3.2, and its values are shown in Table 14. The results confirm that the coefficients of variance (CV) are far below 10% and therefore this requirement is checked.

Finally, the dimensional analysis was made through the measurement of each axis (X, Y and Z) from every single cube. Each axe was measured three times to homogenize the values and an average axe length was calculated. To measure the axes a calliper from *Mitutoyo*<sup>TM</sup> with a resolution of  $\pm 0.05\text{mm}$ , as shown in Figure 51, was used. The specifications of this instrument are fully described in section 3.4.



Figure 51 - Test cube being measured with a *Mitutoyo*<sup>TM</sup> caliper.

In this study, two criteria were established to seek a good dimensional quality of the parts: (i) dimensional variations in the centesimal place, in relation to the nominal dimensions of the cube (15x15x15 mm), and (ii) a statistical coefficient of variation (CV) below 10%. All the results of each axe length and respective standard deviation and coefficient of variance are shown in Table 14.

Table 14 - Average Dimensions and mass of calibration cubes.

| Cube direction | Average dimensions [mm] | CV (%) | Mass [g]         | CV (%) |
|----------------|-------------------------|--------|------------------|--------|
| x              | 15.03 $\pm$ 0.05        | 0.32   | 15.03 $\pm$ 0.05 | 0.32   |
| y              | 14.97 $\pm$ 0.04        | 0.27   | 14.97 $\pm$ 0.04 | 0.27   |
| z              | 15.06 $\pm$ 0.04        | 0.30   | 15.06 $\pm$ 0.04 | 0.3    |

These results further confirm that all the parameters established for the calibration procedure are fulfilled. As a result, the printing parameters set by Castro [75] shown in Table 13 doesn't need any change and are ready to be applied in the printing of the ASTM D790 flexural samples.

### 3.3.4 Mosquito System

Initially, this work had only planned the use of the Prusa i3 MK3S Printer equipped with the original Direct Drive Extruder with an E3D V6 hot end. However, it was observed that, while using F3D filaments with low printing temperatures (215°C) this filament, at some point was being crushed by the extruder gears and swollen on its tip as shown in Figure 52.

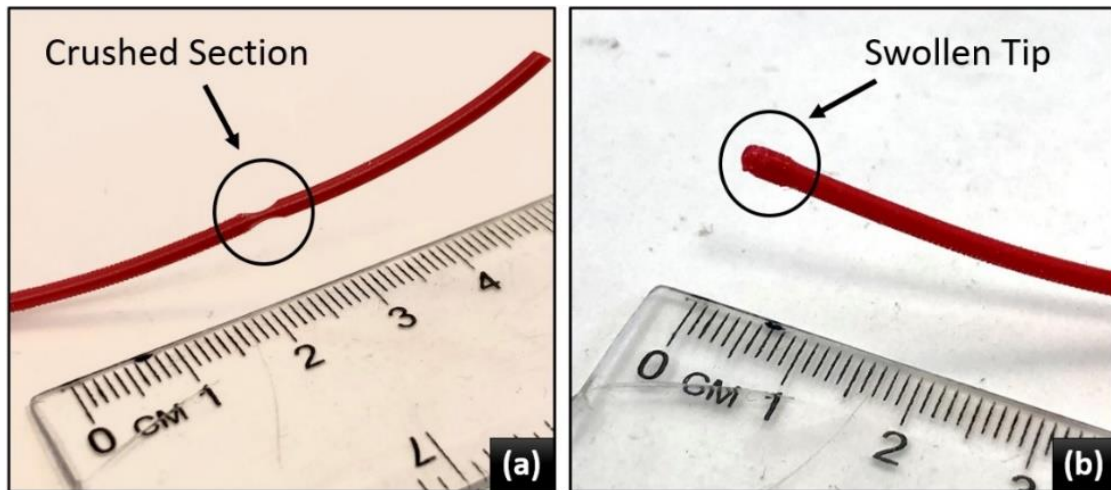


Figure 52 - (a) Crushed Section; (b) Swollen Section.

To solve this problem, another printer with an improved extruder from BondTech had to be used instead to print F3D filaments. This extruder has a “mosquito” hot end from Slice Engineering. This hot end, shown in Figure 53, is composed by a composite heat break which allows a steep temperature gradient that reduces the likelihood of jamming. Furthermore, this hot end allows for temperatures up to 450°C.

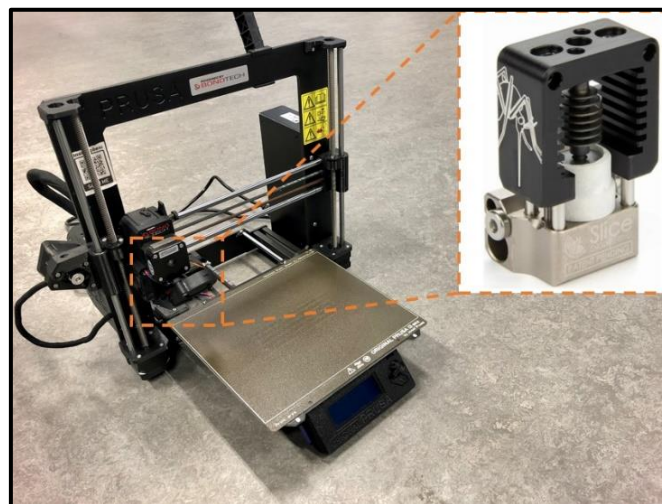


Figure 53 - Original Prusa i3 MK3S with a “mosquito” extruder and its hot end on the right.

### 3.4 Case study 1: degradation of printed parts

Polymers of the polylactic acid (PLA) have been synthesized for many years but their sensitivity to heat and water has precluded them for many industrial applications since durability is one of the most valuable assets in the market. As so, a study where the degradation rate of these PLA parts can be assessed is necessary.

To carry out this study flexural samples were designed following ASTM D790 and printed according to the configuration exposed in Table 13.

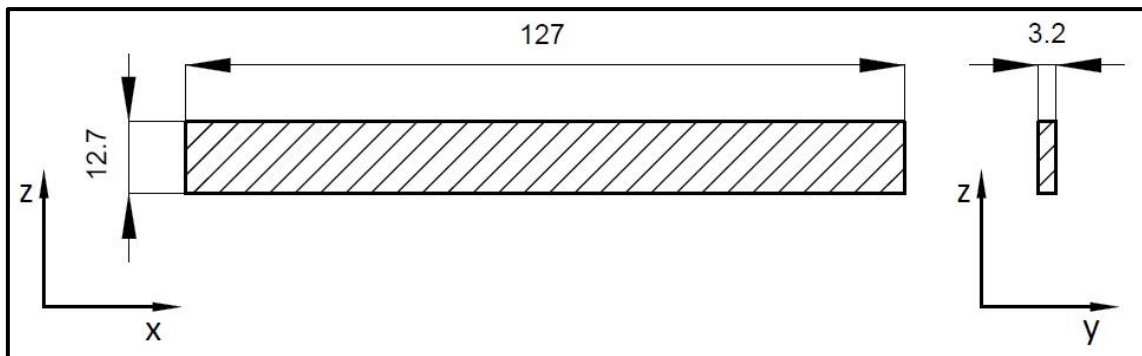


Figure 54 - Dimensions of the test samples according to ASTM D790 (All the dimensions are in millimeters).

The degradation study consists of three different external adverse conditions at which slots of printed test samples have been submitted:

- Landfill study;
- Humidity study;
- Saline solution study;

To analyse the impact of these adverse conditions on the flexural sample's mechanical properties, an extra slot of samples, also known as "w/treatment", will be printed, and tested. The mechanical results obtained with these samples will serve as a reference while analysing the results obtained by the degraded samples.

To test the effects of these three degradations mechanisms on the three PLA filament suppliers (PM, KE and F3D) with red colour, a total of 72 flexural samples were printed. To print the flexural parts a lateral building orientation as shown in Figure 55 was used since it is studied that the highest mechanical properties are obtained when the deposition direction coincides with the tensile load section (4).

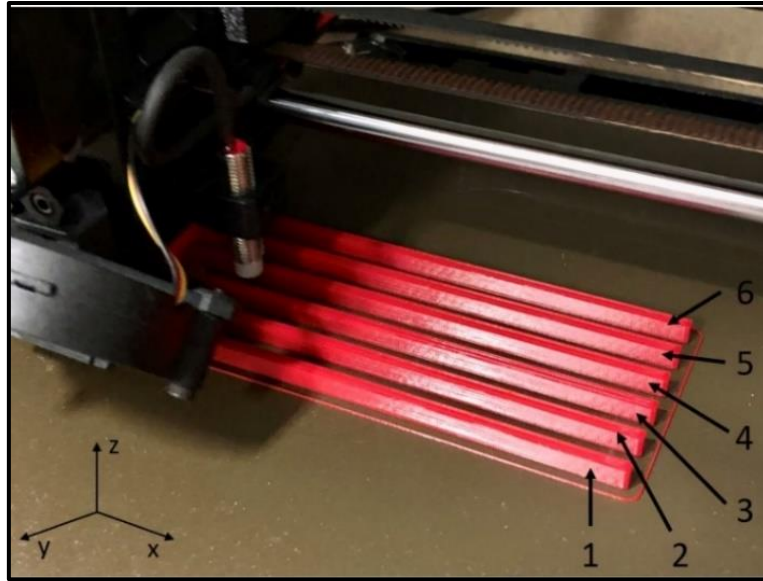


Figure 55 – Slot of 6 ASTM D790 flexural samples being printed on a lateral building orientation.

Because there were four degradation studies to carry out, 24 flexural samples (6×4) per filament supplier had to be printed. To distinguish each one of these samples an identification code was created according to the nomenclature shown in Figure 56. In Figure 57 there's a set of printed samples along with their respective identification code.

Table 15 - Number of samples per condition/supplier (Degradation Study).

| Condition       | PM                 | KE                 | Fill3D             | Total     |
|-----------------|--------------------|--------------------|--------------------|-----------|
|                 | <i>Nr. samples</i> | <i>Nr. samples</i> | <i>Nr. samples</i> |           |
| After Printing  | 6                  | 6                  | 6                  | 18        |
| Landfill        | 6                  | 6                  | 6                  | 18        |
| Humidity        | 6                  | 6                  | 6                  | 18        |
| Saline Solution | 6                  | 6                  | 6                  | 18        |
| <b>Total</b>    | <b>24</b>          | <b>24</b>          | <b>24</b>          | <b>72</b> |

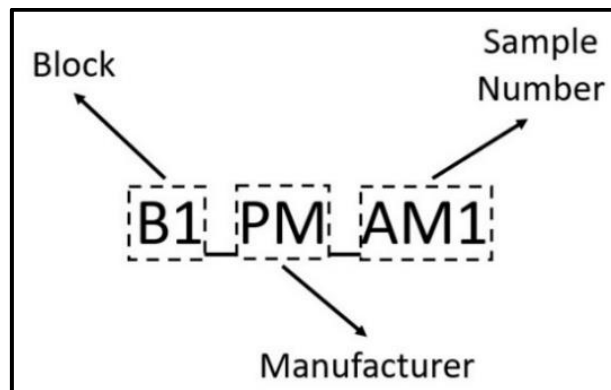


Figure 56 - Identification code nomenclature.

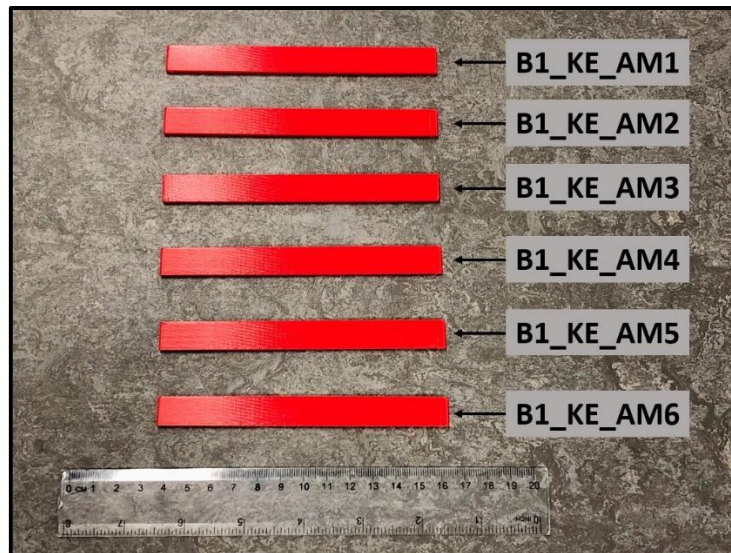


Figure 57 – B1\_KE flexural sample after being printed.

To characterize the samples that were submitted to a degradation mechanism, a set of analysis, which will be explained with more detail in this section, were applied to every single sample by the following order: mass measurement, dimensional measurement, and mechanical tests.

From each one of the nine slots that were placed under degradation conditions (landfill, humidity, and salt solution), one test sample was spared. These spared samples were then broken in half and a slice from one of its cores was removed and submitted to a FTIR spectroscopy to confirm that no molecule has disappeared. The other half samples were placed under microscopic observation as shown in Figure 59. The slices were also placed under microscopic observation to analyse its surface and to detect the presence of inclusions, dirt or even any loss of material.

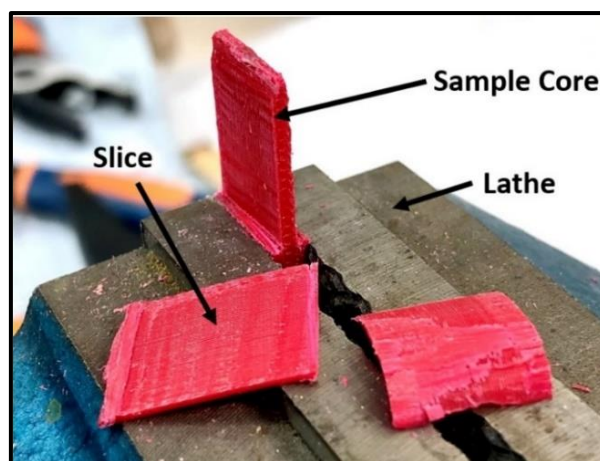


Figure 58 – Flexural sample being carved.

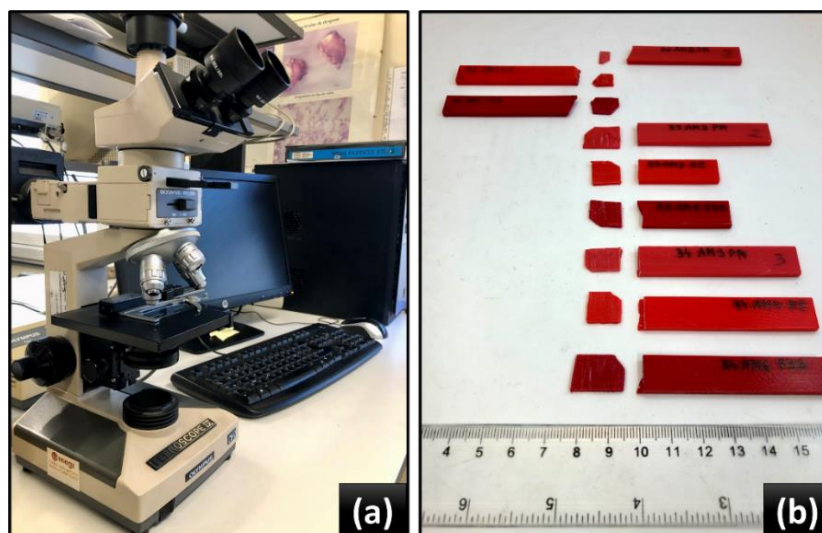


Figure 59 - (a) Ferroscope IV Microscope from Olympus; (b) Slices used for the FTIR test with their respective half flexural sample used for microscopic observation.

# 1. Mass Measurement

The mass measurement of the samples was done on a *Scale House HLD300* digital balance with a resolution of  $\pm 0.05\text{g}$  as shown in Figure 60.

The mass of all the degradation samples was measured before and after the degradation period. The main objective was to verify if there was any water absorption, or eventual losses of matter, induced by the effects of the degradation mechanisms to which the polymers were submitted.



Figure 60 – Digital Balance Scale House HLD300.

An additional procedure was performed to assist the analysis of the water absorption by the samples due to the degradation conditions. For this, the parts were submitted to drying after the flexural tests. Therefore, this process required two additional mass measurements of the samples. The first was done right after the mechanical test to consider the possible loss of fragments in case of total fracture. The second measurement was done after the drying process to determinate how much humidity was removed from the samples. With that data it was possible to calculate the percentage of absorbed water during the degradation test.

## 2. Dimensional Measurement

The length, thickness, and width of each sample were measured using a digital Calliper from *Mitutoyo*<sup>TM</sup> (Figure 63) with a resolution of  $\pm 0.05\text{mm}$ .



Figure 61 - Digital Calliper from *Mitutoyo*<sup>TM</sup>.

The dimensional measurement of the printed samples was carried out at three different points in each direction (length, width, and thickness) as shown in Figure 62. The length is measured across the x-axis, the thickness across the y-axis and the finally the width is measured across the z-axis. For the degradation study, five points were used instead for every single direction. Afterwards, an average measure for each axe was calculated to homogenize the values and to calculate the cross-section area of each sample. Every degradation sample was measured one time before the degradation test and two times after to study the effects on dimensional variations and the hygroscopic properties of each part.

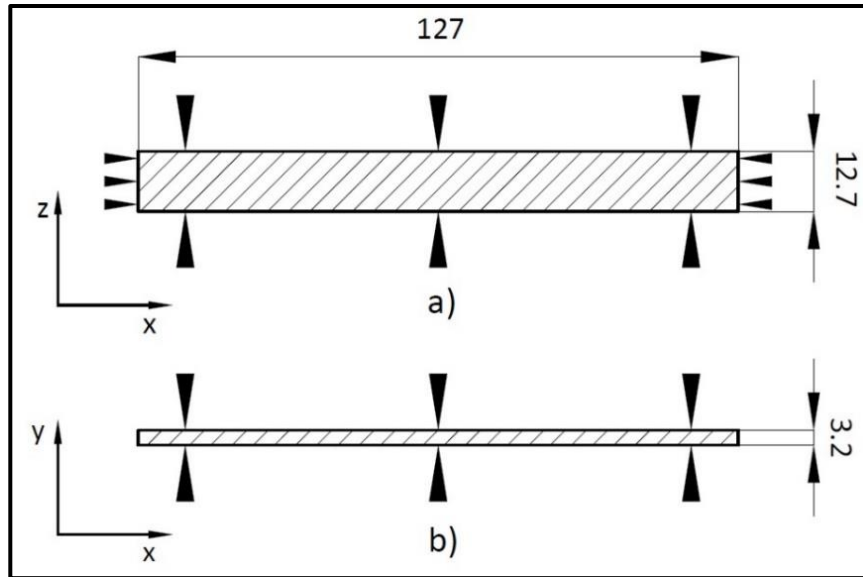


Figure 62 - Measuring points for length (a) and width (b) thickness (Parametric Study) (all measures are in millimeters).

### 3. Mechanical Tests

Each flexural test is based on a three-point loading system where the load is applied from one point and the part acts as supported beam. These mechanical flexural tests were carried out in an equipment composed of a dynamometer with a load cell of 2.5 kN – AFG (Advanced Force Gauge) 2500N – coupled to a displacement column model Multitest 2.5 – Dv (Displacement resolution of 0.001mm) from the Mecmesin brand. The tests were performed at a speed of 5 mm/s. This setup is shown in Figure 63.



Figure 63 – (a) Bending Test Machine in LPDS; (b) Bending test on a flexural sample.

#### 4. Drying process

To dry the flexural samples, in the degradation study, after the flexural tests, a SLW 53 STD Pol-Eko-Aparatura SP. J oven, shown on Figure 64, was used to perform this task. The PLA drying condition was 40°C during 4h. After the drying program was finished, the samples were kept inside the oven for some time to let the inside temperature almost equalize the outside ambient temperature. After this, the samples were removed and weighed to calculate the percentage of evaporated water from each sample. The technical specifications of the oven are shown on Table 16.

Table 16 – Oven Technical Specifications.

|                            |              |
|----------------------------|--------------|
| <b>Power Supply</b>        | 230V 50-60Hz |
| <b>Nominal Power</b>       | 1700 W       |
| <b>Chamber Capacity</b>    | 56L          |
| <b>Maximum Temperature</b> | 300 °C       |

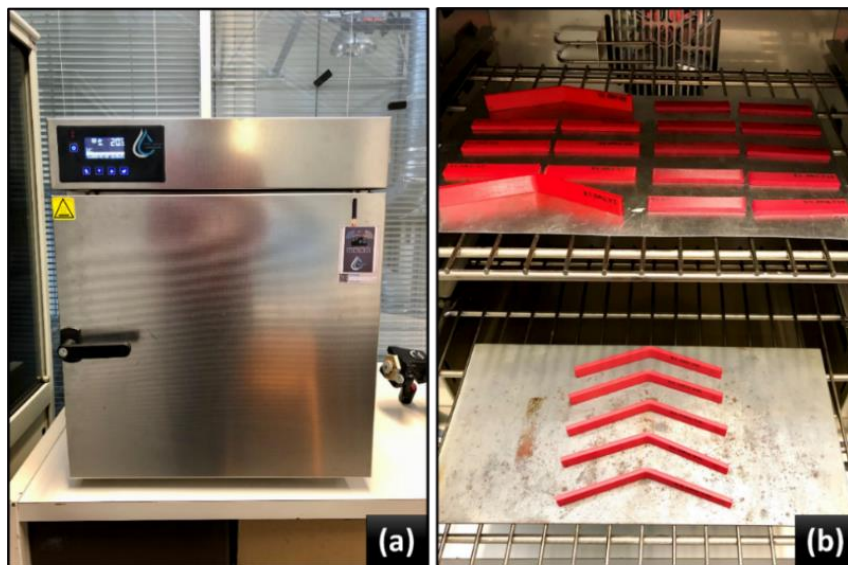


Figure 64 - (a) Oven; (b) Samples about to be enclosed inside the oven.

##### 3.4.1 After Printing Study

The main goal of after printing study is to test the mechanical properties of the flexural samples right after the printing process. The parameters used to print these samples were the same as described in Table 13. The experimental methodology applied to each one of these samples can be resumed in two main procedures:

With this data it was possible to establish a term of comparison between these results and the ones obtained after the degradation mechanisms. Therefore, it was later possible to check if the degraded flexural samples really suffered any loss (or gain) of mass and mechanical properties.

### 3.4.2 Landfill Study

The aim of the landfill study is to activate degradation mechanisms on the polymers caused by some of the soil's characteristics: variation of temperature, humidity, acidity or even the presence of dirtiness, and microorganisms. To accomplish this study, three (3) blocks of six (6) flexural samples each from three different suppliers (PM, KE and F3D) were buried in a domestic garden as shown in Figure 66.

The flexural samples were buried from 10/27/2021 to 01/27/2022. During this period, the land conditions were monitored once and every single day through a S-2 *Soonda* soil tester, as shown in Figure 65.



Figure 65 – Soil Tester characteristics.

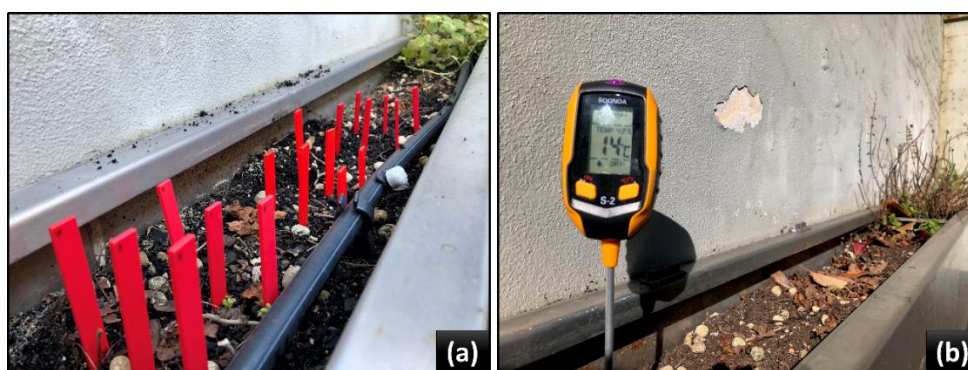


Figure 66 – (a) Flexural Samples before being fully buried; (b) Fully buried samples with the *Soonda* soil tester on the left.

### 3.4.3 Humidity Study

The main goal of the humidity study is to evaluate the hygroscopic behaviour of each filament supplier and its effect on the mechanical properties. To perform this study, an apparatus (Figure 68) was developed to provide the humidity and the enclosure needed. It is basically based on a domestic humidifier (Orbegozo model HU 2031 capable of producing a flow of 250ml/h), plastic box and a set of sensors to monitor the humidity inside the box. Six flexural samples from each supplier (PM, KE & Fill3D) were exposed to humidity for three months, more precisely from 10/29/2021 to 01/29/2022. Because the samples must be vertically positioned to allow the steam to circulate through all samples' corners, three black supports were designed and printed in PLA as shown in Figure 67.



Figure 67 - Support used inside the humidity box.

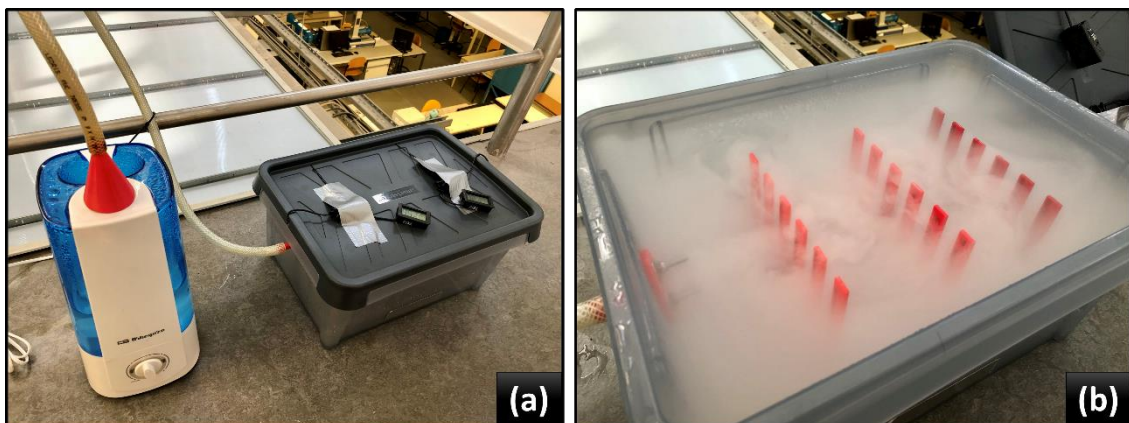


Figure 68 – Humidification System: (a) Humidifier + Box; (b) Steam Flow.

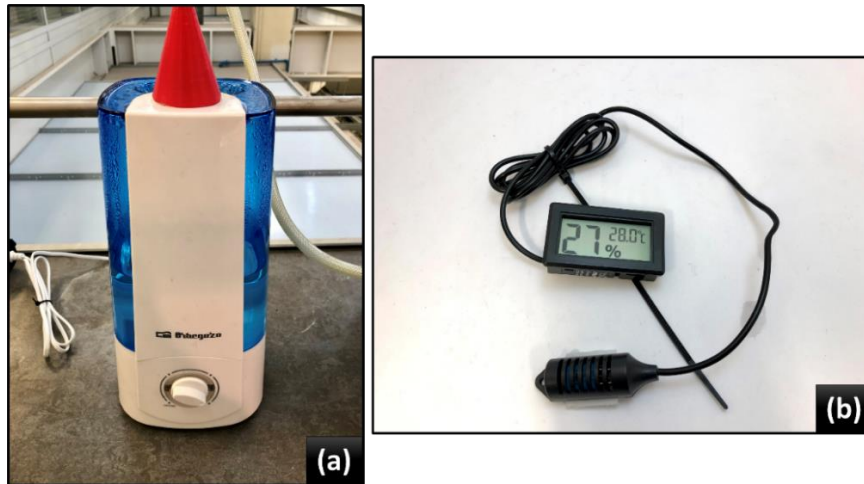


Figure 69 – a) Humidifier model HU 2031 from Orbegozo; b) Humidity Sensor from *Aquario Eletrônica*.

During this experiment, twice a week (Monday and Friday), the mass of each sample was measured, the data was stored on an excel sheet and the percentual mass difference from the first measure (after printing) was calculated. This calculation served as way of monitoring the quantity of absorbed humidity of each material between each measuring day. The formula used to calculate the percentage of absorbed water can be seen on Figure 70.

$$\text{Absorption (\%)} = \frac{(\text{Measured Mass} - \text{Initial Mass}) \times 100}{\text{Initial Mass}}$$

Figure 70 – Percentage of absorbed water formula.

#### 3.4.4 Salt Solution Study

The saline solution is an experiment where a solution of salt water is created to simulate the same concentration of salt of the ocean which happens to be approximately 35g of table salt (5) (sodium chloride – NaCl) per 1000g of total solution (water plus salt) [83][84].

To perform this experiment, three plastic bottles were filled with the mixture and each slot of six (6) printed samples from each supplier were labelled and submerged as shown in Figure 71. The samples were kept submerged from 10/28/2021 to 01/28/2022. After the conclusion of the degradation period the same experimental procedure applied to the samples that were submitted to landfill and humidity degradation mechanisms, was implemented to check the effects of the saline solution on both microscopic and mechanical properties.

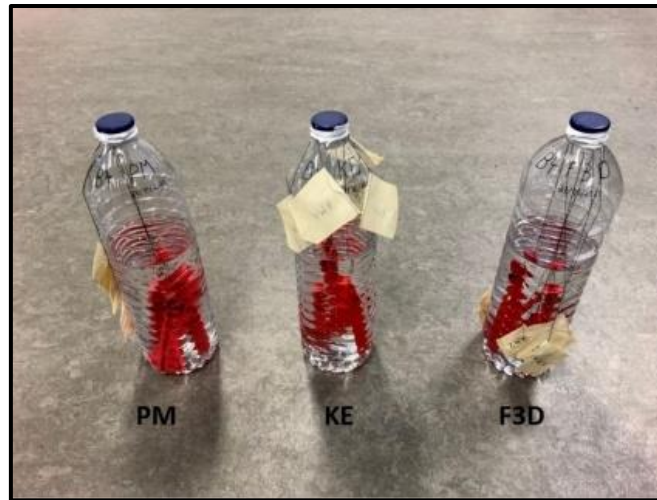


Figure 71 - Bottles containing the saline solution and the labelled samples.

### 3.5 Case Study 2: Parametric analysis (Taguchi DOE)

The parametric study carried out in this work is a sequence of a previous work from Castro [75]. During that work a set of printing parameters was fixed to print multi-coloured PLA ASTM D790 flexural samples using just one filament supplier (PM). The colours used to print those samples were blue, white, orange and red. It turned out that colour variation in PLA filaments has been a significant factor in mechanical properties especially when the red pigment was used. As result, there was an opportunity to develop a study in which the colour factor is fixed (red), and the influence of three filament suppliers on several responses is assessed through a parametric analysis.

The Taguchi experiment aimed to study the effects of four factors on three average responses: maximum flexural strength (MFS), flexural modulus (FM) and mass. The factors (printing parameters) that were varied throughout the experiment were:

- Extrusion temperature;
- Layer thickness;
- Printing speed;
- Extrusion multiplier;

For each factor, three levels have been assigned (Table 17) and the combination between the factors and their respective values, were determined from the application of a Taguchi L9 orthogonal array (Table 18). For each condition, three samples were printed thus generating 27 printed samples. Since this work addresses three filament suppliers it makes a global total of 81 flexural samples.

Table 17 – Levels assigned to each factor.

| Factors                               | Level (1) | Level (2) | Level (3) |
|---------------------------------------|-----------|-----------|-----------|
| Extrusion temperature (°C) ( $E_t$ )  | 215       | 225       | 235       |
| Layer thickness (mm) ( $L_t$ )        | 0.1       | 0.2       | 0.3       |
| Print speed (mm/s) ( $P_s$ )          | 40        | 60        | 80        |
| Extrusion multiplier (d.u.) ( $E_m$ ) | 0.9       | 1.0       | 1.1       |

Table 18 - L9 Taguchi orthogonal array: parametric study.

| Conditions | $E_t$ (°C) | $L_t$ (mm) | $P_s$ (mm/s) | $E_m$ (d.u.) |
|------------|------------|------------|--------------|--------------|
| <b>T1</b>  | 215        | 0.1        | 40           | 0.9          |
| <b>T2</b>  | 215        | 0.2        | 60           | 1            |
| <b>T3</b>  | 215        | 0.3        | 80           | 1.1          |
| <b>T4</b>  | 225        | 0.1        | 40           | 1.1          |
| <b>T5</b>  | 225        | 0.2        | 60           | 0.9          |
| <b>T6</b>  | 225        | 0.3        | 80           | 1            |
| <b>T7</b>  | 235        | 0.1        | 40           | 1            |
| <b>T8</b>  | 235        | 0.2        | 60           | 1.1          |
| <b>T9</b>  | 235        | 0.3        | 80           | 0.9          |

During the printing, all parameters not mentioned in Table 17 were fixed as shown in Table 13. To identify every single sample an identification code nomenclature was also applied as shown in Figure 72. The printing of the samples was also based on a lateral building orientation as shown in Figure 73.

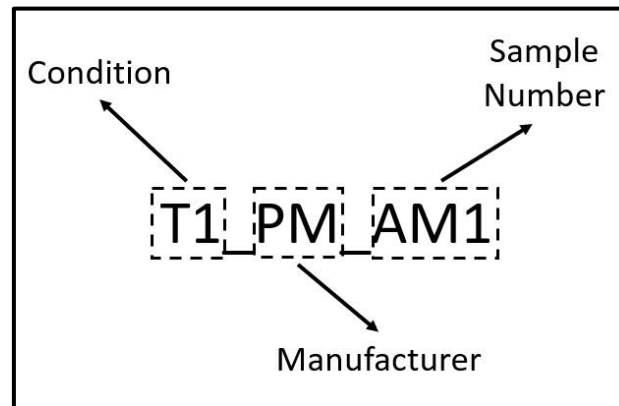


Figure 72 - Identification code nomenclature used in the parametric study.

After printing the slots, every single flexural sample was submitted to mass measurement, dimensional analysis, and flexural tests. The mass measurement, the dimensional analysis and the flexural tests of each sample were carried out following the same experimental procedure exposed in section 3.4.

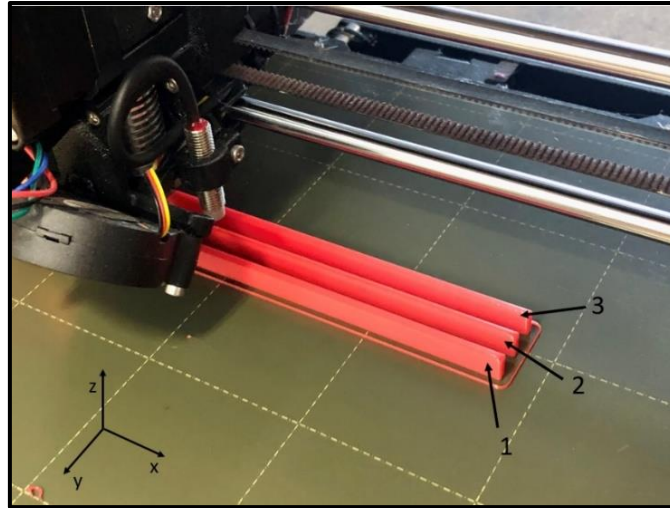


Figure 73 - T9\_PM slot being printed.

To study the influence of the four factors on the three responses, an analysis of variance (ANOVA) was implemented. This statistical analyse allows to verify if for a specific response, one factor is significant or not. To be significant, the P-Value of that factor must be lower than 0.05. After the application of ANOVA, every significant factor is submitted to a post-hoc test. In this case, a Tukey's test was carried out to make a multiple comparison between the average levels from one factor and to group them (A, B or C) according to their statistical similarity. If the two average levels from one factor are very similar, then they will be placed in the same group whereas statically different levels will be placed in different groups.

### 3.5.1 Verification Models

The main goal of the verification model is to create a printing configuration for each filament supplier that maximizes the responses of the printed PLA flexural samples. The creation of the verification models is a direct yet complex process that will be introduced in this section and further discussed in section 4.3.4.

The first step was to apply ANOVA to identify the significant parameters for each response. Then, a post-hoc test (Tukey test) was used to statically differ the average levels of each significant factor. From there, the best levels for each factor were sorted out and organized in a table. In this table, each column corresponds to one response (MFS, FM, and mass) whereas each line corresponds to one factor ( $E_t$ ,  $L_t$ ,  $P_s$ ,  $E_m$ ).

Afterwards, an analysis of agreement was carried out between the best levels of each response to set up a global printing configuration, more precisely, the "Verification

Model". To better understand how the VM levels have been sorted out, in Figure 74 there's an example. The green levels for each factor were selected to be applied to the verification model. The levels highlighted in red were discarded.

| Factors                               | Best level responses |    |      | VM |
|---------------------------------------|----------------------|----|------|----|
|                                       | MFS                  | FM | Mass |    |
| Extrusion temperature (°C) ( $E_t$ )  | 2                    | 2  | 3    | 2  |
| Layer thickness (mm) ( $L_t$ )        | 1                    | 2  | 1    | 1  |
| Print speed (mm/s) ( $P_s$ )          | 1                    | 1  | 1    | 1  |
| Extrusion multiplier (d.u.) ( $E_m$ ) | 1                    | 2  | 2    | 2  |

Best levels by response

Selection of the best levels

Figure 74 - PM Verification Model best level responses.

First, to be directly chosen for the final MV configuration, a level must be the best one for at least two different responses. For example, as it can be seen in Figure 74, for the extrusion temperature the level two (green) has proved to be the best for two different responses and therefore was directly chosen for the VM. To provide a clearer example, for the print speed, level one was the best for every single response and as a result was chosen for the final configuration. However, in some situations the before mentioned criteria was not enough to select a level and a more complex analysis was therefore necessary. These situations will be addressed with more detail in section 4.3.4. The final printing configuration obtained for each supplier is shown in Table 19.

Table 19 - Printing Parameters of the Verification Models.

| Supplier | Extrusion Temperature [°C] | Layer Thickness [mm] | Print Speed [mm/s] | Extrusion Multiplier [u.a.] |
|----------|----------------------------|----------------------|--------------------|-----------------------------|
| PM       | 235                        | 0.1                  | 60                 | 1                           |
| KE       | 235                        | 0.1                  | 60                 | 1.1                         |
| Fill3D   | 225                        | 0.1                  | 60                 | 1.1                         |

These printing setups were used to print three sets of six flexural samples each making a total of 18 manufactured samples. The experimental procedures applied to these samples (mass measurement, dimensional analysis, and flexural tests) were the same one applied to samples printed for the Taguchi study (section 3.5). The statistical analyse of the responses will be addressed in section 4.3. and the results will be compared with the responses obtained by Castro [75].

### 3.5.2 Temperature Towers

The printing of temperature towers made it possible to visually evaluate the best temperature value for each parameters/supplier in study. This calibration model is traditionally used by FFF enthusiasts and is widely referenced in the main knowledge platforms about the technology, among which Thingiverse2. The temperatures used to print these towers ranged from 215°C to 235°C as shown in Figure 75.

The visual analysis of this print consists of evaluating the quality of the suspended parts of the print. Each floor of the tower corresponds to a temperature value. The stage that presents the best printing result, that is, without geometric distortions, corresponds to the best extrusion temperature of the material in question.

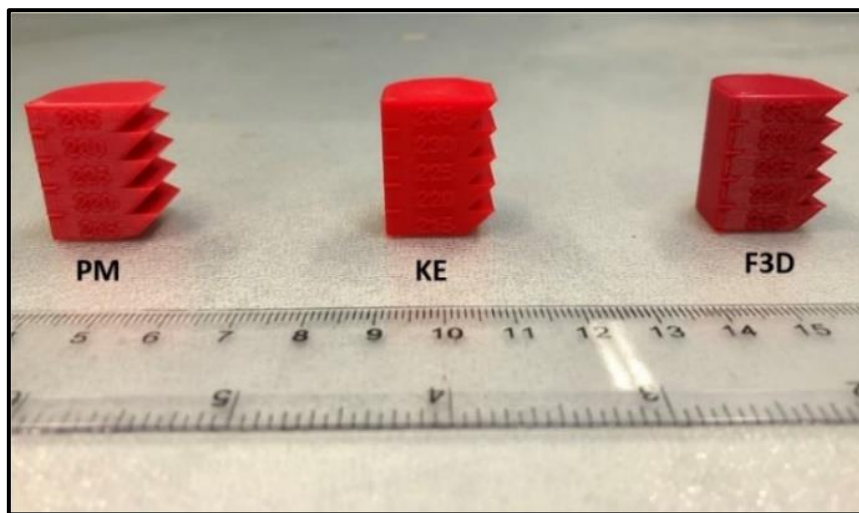


Figure 75 – Temperature Towers.



## 4. Analysis and comparison of the results

### 4.1 Filament Characterization Results

This chapter will address the results obtained from the characterization methods which were: Density Measurement, Fourier Transform Infrared Spectroscopy (FTIR) and Dynamic Mechanical Analysis (DMA).

#### 4.1.1 Density

The density measurement results for each sample, the average density values for each supplier and the claim filament density by the manufacturers are shown in Table 20.

Table 20 – Density results of each of the three filament suppliers.

|                       | Density [g/cm <sup>3</sup> ] |                    |             |
|-----------------------|------------------------------|--------------------|-------------|
|                       | PM                           | KE                 | F3D         |
| <b>Average</b>        | 1.25                         | 1.24               | 1.25        |
| <b>Std. Deviation</b> | 0.004                        | 0.008              | 0.017       |
| <b>CV (%)</b>         | 0.35                         | 0.6                | 1.35        |
| <b>Manufacturers</b>  | <b>1.24</b>                  | <b>1.23 ~ 1.26</b> | <b>1.24</b> |

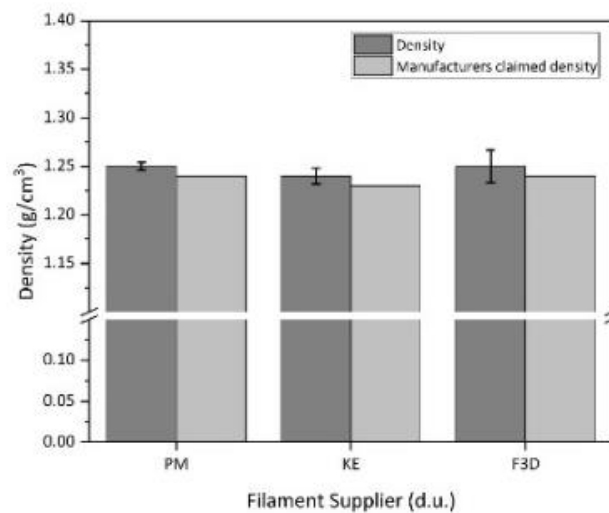


Figure 76 –Density measurements (dark grey) related with manufacturers claim value (light grey).

Overall, the average density values are very similar to those claimed by the filament manufacturers (Figure 76). Beyond that, the average value obtained for the PM supplier is very to the values obtained by Santana [9] and Castro [75]. The fact that the KE supplier has a slightly lower density (1.24 g/cm<sup>3</sup>) might have been influenced by the balance precision and the calculation process itself.

#### 4.1.2 FTIR

To analyse the molecular composition of each PLA filament supplier (PM, KE, and F3D) a FTIR spectroscopy was performed. Afterwards, the results obtained were compared with similar materials analysed in the literature to determine if the FTIR, in fact, corresponds to a PLA polymer. The test parameters used in these tests, as well as the analysis equipment, are presented in section 3.3.2.

The curves obtained for each filament supplier can be seen in Figure 77 – FTIR analysis curves from PM, KE, F3D and PM from Castro (2021). There is also an extra curve represented by the pink dashed line (PLA PM – Castro [75]) which is the curve obtained by Castro [75]. Each curve is characterized by its peaks, which are delimited by one of the five highlighted regions (I, II, III, IV, and V). Each one of these peaks is associated to a molecular functional group that will be further discussed in this section.

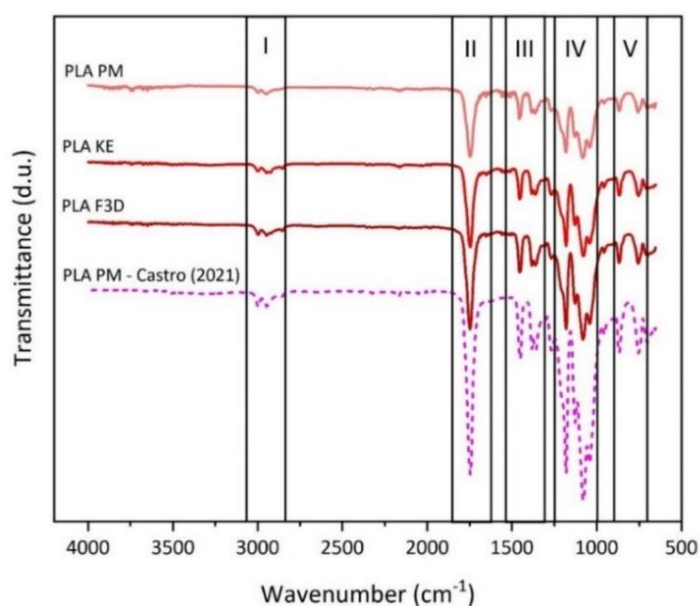


Figure 77 – FTIR analysis curves from PM, KE, F3D and PM from Castro (2021).

To complement the presentation of the results shown in Figure 77, the Table 21 provides the main peaks and wave numbers, identified in the spectroscopy test, and represented in the regions delimited by the rectangles (I to V) (Figure 77). All regions are defined by two or three peaks except for zone II which is defined by only one peak. To help the interpretation of the curves resulting from the FTIR spectroscopy, test studies on the composition of PLAs will be used. To summarize the main chemical elements found on a specific band, table 20 was created to help in the interpretation of the FTIR results.

Table 21 – Results of FTIR analysis by regions delimited in the curves.

| Filament          | Wave Number (cm <sup>-1</sup> ) |         |                |                |         |
|-------------------|---------------------------------|---------|----------------|----------------|---------|
|                   | Zone I                          | Zone II | Zone III       | Zone IV        | Zone V  |
| PM                | 2998;2949                       | 1749    | 1456;1383;1363 | 1182;1081;1042 | 867;757 |
| KE                | 2998;2947                       | 1744    | 1452;1381;1363 | 1180;1078      | 867;753 |
| F3D               | 2998;2947                       | 1747    | 1456;1381;1363 | 1180;1081;1042 | 867;755 |
| PM [Castro, 2021] | 2998;2947                       | 1745    | 1452;1381;1359 | 1180;1079      | 867;755 |

Table 22 – Relationship between the number of waves (cm<sup>-1</sup>) and the functional group [85][86][87](adapted).

| Wave Number (cm <sup>-1</sup> ) | Functional Group       |
|---------------------------------|------------------------|
| 2400 - 3400                     | -OH (COOH)             |
| 2850 – 3000                     | -CH (CH <sub>3</sub> ) |
| 1650 – 1750                     | -C=O                   |
| 1450 – 1500                     | C-H                    |
| 1345 - 1450                     | -CH <sub>3</sub>       |
| 1000 – 1300                     | -C-O (COOH)            |
| 754 - 800                       | C-H                    |

The FTIR results obtained in Table 21 indicate that all filaments' suppliers have a similar molecular structure to that described in the literature as it is in the work of (L. Santana, J. Alves, et al. 2018), which makes a broad analysis of the PLA spectra.

The peaks in region I of the graph in Figure 77 (2947 to 2998 cm<sup>-1</sup>) correspond to the stretching -CH group [25][88]. The bands in region II (1744 to 1749 cm<sup>-1</sup>) are associated with the -C=O stretching of the ester group, which belongs to the polylactic acid chain [88]. In region III there are two peaks that correspond to the -CH<sub>3</sub> stretching whereas the other peaks are associated with the C-H [88]. In region IV are found spectra classified as C-O-C stretching [88]. Finally, region V features a band at 755 cm<sup>-1</sup> which represents the crystalline portion of PLA, and another band at 867 cm<sup>-1</sup> associated with the amorphous portions of PLA [88].

In summary, the filaments correspond to PLAs polymers and did not suffer any significantly change in their molecular structure neither as no unconventional band has been identified. This also proves that the pigments that have been used to manufacture these filaments haven't had any influence on the molecular structure. Moreover, this characterization study revealed that the filaments are semi-crystalline as the peaks from zone V confirm. Consequently, the printed samples might be sensitive to thermal variations caused by the printing process itself.

#### 4.1.3 DMA

The glass transition temperature obtained for the three materials (PM, KE, F3D) is shown in Table 23 and were obtained via the designing of the DMA curves shown in Figure 78.

Table 23 – Glass transition temperatures obtained by the filament materials.

| Materials | T <sub>g</sub> (°C) |                |
|-----------|---------------------|----------------|
|           | E'' (1Hz)           | TanDelta (1Hz) |
| PM        | 69.2                | 75.5           |
| KE        | 70.3                | 75.7           |
| F3D       | 69.6                | 75.7           |

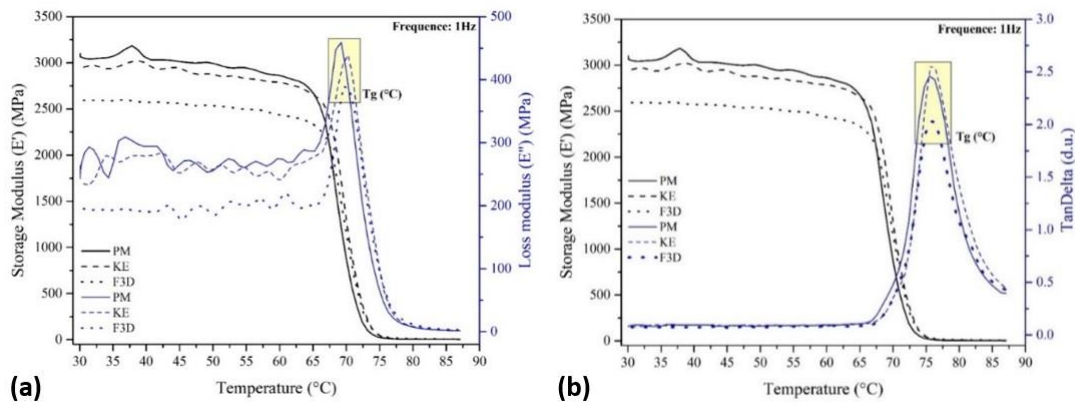


Figure 78 – DMA Curves (a) E' and E''; (b) E' and tan (δ).

All the T<sub>G</sub> values have fell within the temperature range claimed by the literature on PLA's glass transition temperature [1]. As a result, it's possible to confirm that the materials used throughout this work are and will thermically behave as they are supposed to.

## 4.2 Degradation Study

In this section, the influence of four conditions (W/Treatment<sup>1</sup>, Landfill, Saline Solution, and Humidity) on three major responses (Mass, MFS, and FM) will be addressed. In each one of the following sub sections the results obtained by each filament supplier will be discussed.

### 4.2.1 PM

#### Mass

To study of the influence of the three degradation mechanisms on the variation of mass the first step was to calculate the average mass, standard deviation, and coefficient of variance at four different timings at it was explained in section 3.4. The mass measurements obtained by all degradation mechanisms are shown in Table 24.

Table 24 – PM Conditions mass measurement.

|               | After-Printing | After-Degradation | After-Testing | After-Drying |
|---------------|----------------|-------------------|---------------|--------------|
| Landfill      |                |                   |               |              |
| Mean [g]      | 6.20           | 6.22              | 6.22          | 6.20         |
| Std. Dev.     | 0.004          | 0.00              | 0.00          | 0.00         |
| CV (%)        | 0.072          | 0.04              | 0.04          | 0.06         |
| Salt Solution |                |                   |               |              |
| Mean [g]      | 6.20           | 6.23              | 6.22          | 6.20         |
| Std. Dev.     | 0.002          | 0.004             | 0.01          | 0.01         |
| CV (%)        | 0.036          | 0.067             | 0.09          | 0.09         |
| Humidity      |                |                   |               |              |
| Mean [g]      | 6.20           | 6.23              | 6.22          | 6.21         |
| Std. Dev.     | 0.004          | 0.00              | 0.00          | 0.00         |
| CV (%)        | 0.068          | 0.04              | 0.07          | 0.07         |

Overall, the samples absorbed humidity after going through to their respective condition, thus proving the hygroscopic properties of the PM supplier. The after-testing results show that some samples particles might have been lost during the flexural tests after breaking in half. Finally, the after-drying results show the amount of humidity that has been possible to extract from the samples.

The after-degradation results were then evaluated through the statistical analysis of variance (ANOVA). According to the p-Values (Table 25), it was confirmed that at least one degradation mechanisms is significant. The graphic in Figure 79 shows

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<sup>1</sup> After-Printing Condition

the average mass values by condition as well as a comparison between the average responses that has been carried out through a Tukey's test. The statistical differences between each condition are represented by the letters A, B or C. If two conditions are statistically equal then both will be placed in the same group, that is, will show the same letter. In table 23, it's possible to check the results of the analyse of variance parameters.

Table 25 – Degradation study PM Mass Analysis of Variance ( $\alpha=95\%$ ).

| Source    | DF | Adj SS   | Adj MS   | F-Value | p-Value |
|-----------|----|----------|----------|---------|---------|
| Condition | 3  | 0.002474 | 0.000825 | 41.23   | 0.000   |
| Error     | 16 | 0.000320 | 0.00020  |         |         |
| Total     | 19 | 0.002794 |          |         |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

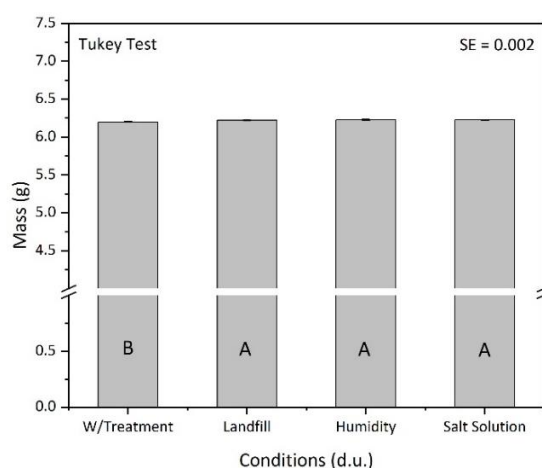


Figure 79 - Average mass related with the degradation mechanisms (PM).

The graphic from Figure 79 shows that without treatment (after printing) the average mass tends to be statistically lower. This result was expected since at this stage the samples haven't absorbed any amount of humidity, a key factor in the remaining conditions that will be further addressed.

As so, the remaining three conditions show that regardless of the condition the samples are submitted to, the average mass values have increased and are statically equal between them. However, this increase is overall lower than 1% compared with the w/treatment condition's mass. Because the samples were submitted to these conditions for such a short period of time (approx. 2 months) and the increase is so small, it may be related to the measurement equipment precision. However, had the samples been exposed for a much longer period, the increase of mass would be mainly caused by the three conditions' common environmental factor: moisture; and therefore,

the increase of mass itself would have been explained by the multi-layered construction of FFF printed parts which can produce a lot of internal voids where moisture can fit [70]. Consequently, these voids combined with the hygroscopic properties of the PM filament may increase the absorption of humidity and the overall mass of each sample.

To complement this analysis, the landfill condition parameters such as the pH, temperature, and humidity (%) were monitored and recorded as the graphic of Figure 80 shows. From there, it can be observed that the maximum humidity absorption percentage was of **84%** registered on the 77<sup>th</sup> day while the lowest temperature of **8°C** was registered on the 89<sup>th</sup> day of exposure. As for the pH it has remained stable and neutral throughout the entire burial period. This graphic should also be taken in consideration in the analysis of the KE and the F3D suppliers in sections 4.2.2 and 4.2.3, respectively.

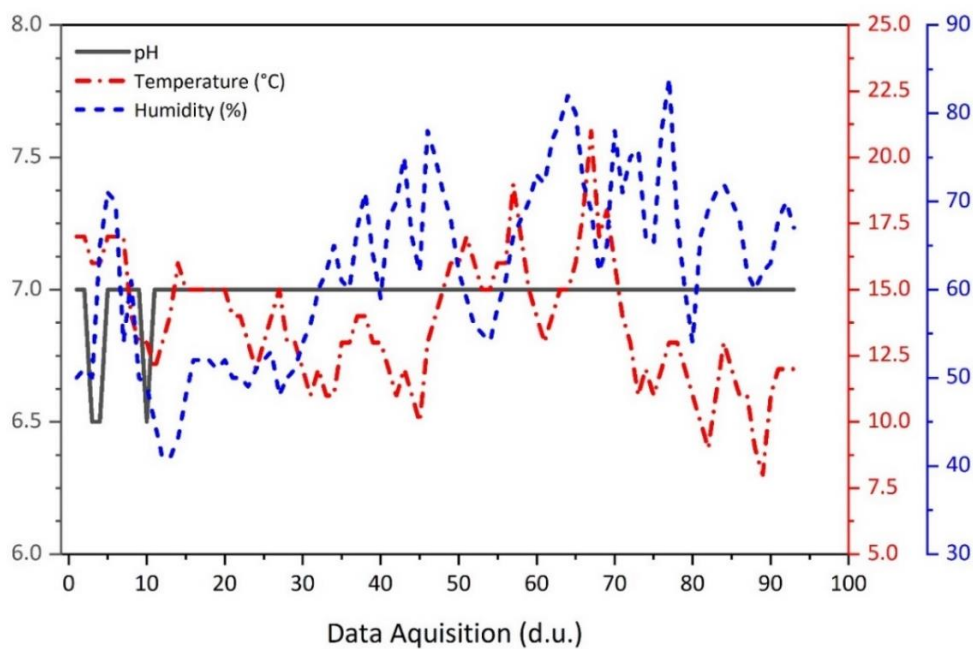


Figure 80 – Landfill condition parameters evolution.

Moreover, the variation of absorbed humidity within the humidity condition was also recorded and is represented by the graphic of Figure 81. According to this graphic, the maximum percentual of humidity absorption has been of **1.33%** and was registered on the 3<sup>rd</sup> day of exposure, more precisely, on the 29<sup>th</sup> of November. It's also worth mentioning that the average mass percentage of absorbed water per day was of **0.6%**. Moreover, from the 10<sup>th</sup> to the 14<sup>th</sup> and on the 18<sup>th</sup> exposure days, there were no measurements.

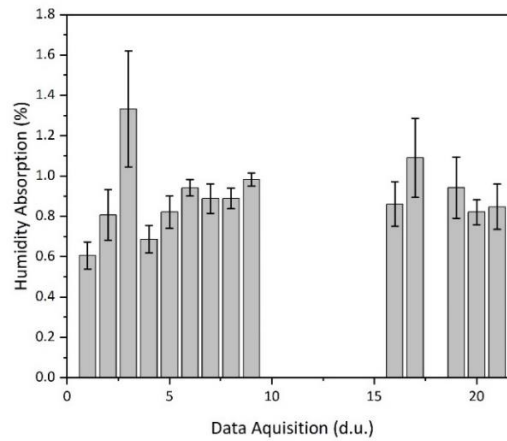


Figure 81 – Humidity condition – variation of %humidity per day (PM).

A comparison between a PM ASTM D790 theoretical mass and the remaining mass measurements per condition has also been carried out. The theoretical mass value and the remaining average mass measurements per condition are shown in Table 26.

Table 26 - Comparison between a sample's theoretical mass and the after-degradation measurements.

|          | Theoretical | W/Treatment | Landfill | Humidity | Salt Solution |
|----------|-------------|-------------|----------|----------|---------------|
| Mass [g] | 6.43        | 6.20        | 6.22     | 6.23     | 6.23          |

The theoretical mass was calculated through the multiplication of the theoretical volume of an ASTM D790 specimen with the PM density obtained in section 4.1.1. The results confirm a decrease of approximately **4%** between the theoretical mass and the after-printing sample's mass. Considering the isoparametric nature of the degradation study, this phenomenon is related with the printing configuration which has already been exposed in Table 13. The most likely reason for this decrease of mass is the presence of voids between the deposited layers (Figure 82). Nieto et al [70], for example, have studied that the multi-layered construction of FFF printed parts creates internal voids which are consequently left unfilled with material thus decreasing the overall mass of a sample.

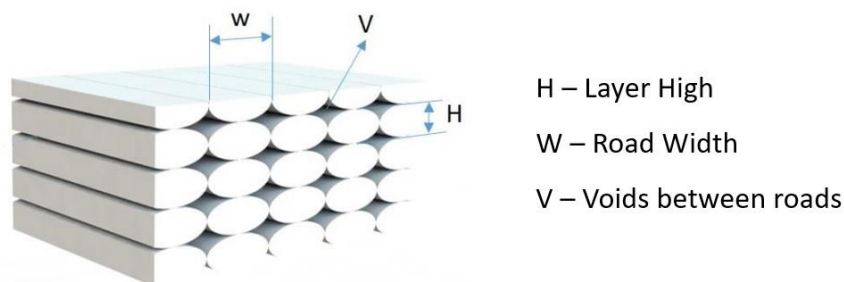


Figure 82 – Schematic of the deposited layers of a 3D printed part [70](adapted).

### MFS and FM results analysis

To achieve analyse the influence on the MFS and the FM responses, it was necessary to calculate its average responses, standard deviation, and coefficient of variance for each condition (Table 27).

Table 27 - Results of the flexural tests of the PM samples.

| Sample                                                                                            | Landfill     |             | Humidity     |             | Salt Solution |             |
|---------------------------------------------------------------------------------------------------|--------------|-------------|--------------|-------------|---------------|-------------|
|                                                                                                   | MFS (MPa)    | FM (GPa)    | MFS (MPa)    | FM (GPa)    | MFS (MPa)     | FM (GPa)    |
| <b>Mean</b>                                                                                       | <b>91,58</b> | <b>3,34</b> | <b>90,60</b> | <b>3,34</b> | <b>91,31</b>  | <b>2,28</b> |
| <b>Std. Dev.</b>                                                                                  | 0,72         | 0,07        | 0,56         | 0,05        | 4,63          | 0,02        |
| <b>CV (%)</b>                                                                                     | 0,79         | 2,15        | 0,62         | 1,36        | 5,07          | 0,87        |
| <b>Note:</b> MFS – Maximum Flexural Strength; FM – Flexural Modulus; CV – Coefficient of Variance |              |             |              |             |               |             |

The mean results exposed in Table 27 were evaluated through the statistical analysis (ANOVA). According to Table 28 it was verified at least one condition is significant since all the p-Values are below 0.05. The graphic in Figure 83 shows the average MFS and FM values by condition as well as a statistical comparison between the condition's average values that was carried out through a Tukey's test.

Table 28 – PM Degradation study: MFS&FM Analysis of Variance ( $\alpha=95\%$ ).

|                                                                              | Source    | DF | Adj SS  | Adj MS  | F-Value | p-Value |
|------------------------------------------------------------------------------|-----------|----|---------|---------|---------|---------|
| <b>MFS</b>                                                                   | Condition | 3  | 245.33  | 81.778  | 14.44   | 0.000   |
|                                                                              | Error     | 16 | 90.64   | 5.665   |         |         |
|                                                                              | Total     | 19 | 335.98  |         |         |         |
| <b>FM</b>                                                                    | Condition | 3  | 3.93388 | 1.31129 | 647.64  | 0.000   |
|                                                                              | Error     | 16 | 0.03240 | 0.00202 |         |         |
|                                                                              | Total     | 19 | 3.96627 |         |         |         |
| <b>Note:</b> DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares |           |    |         |         |         |         |

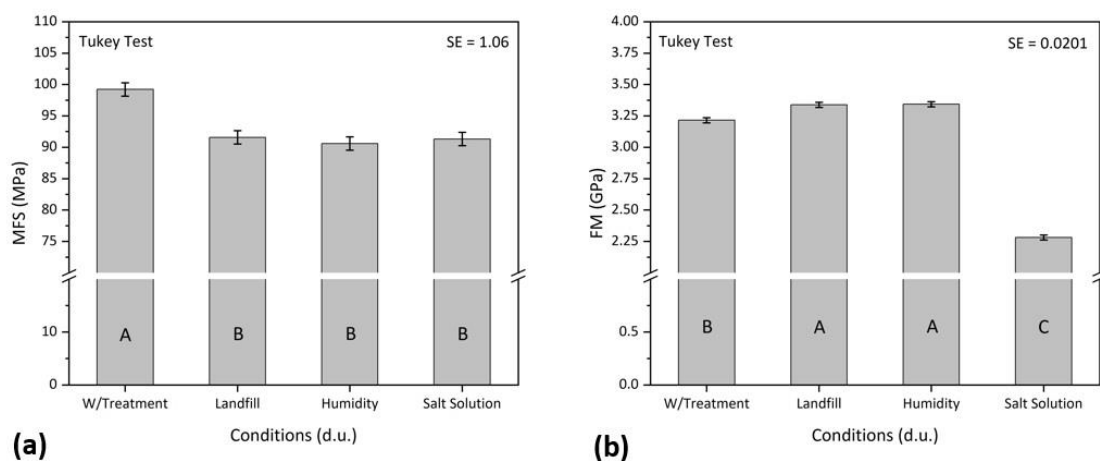


Figure 83 - The Average Maximum Flexural Strength and the Average Flexural Modulus related with the degradation mechanisms (PM).

Overall, the fall of the average MFS responses is quite significant compared with the W/Treatment condition response. When it comes to the FM responses, apart from the salt solution condition, the average modulus has, curiously, gone up. The only condition that has made the flexural modulus to decrease was the salt solution. Another important aspect to take into consideration is the fact that the presence of moisture was the main reason of multiple degradation mechanisms that might have occurred. This analysis will be further extended in the following topics.

### MFS Analysis

As it was expected, it seems that the average responses tend to decrease when the samples are submitted to a treatment condition. The graphic also show that the average responses of landfill, humidity and salt solution are statically equal and on average all of them have dropped approximately **8%**. These results suggests that, apart from moisture, no condition's specific characteristics such as microorganisms, had a significant impact on the MFS responses. In the particular case of the landfill condition, this scenario had been forecasted because the degradation of the PLA in soil is very slow and takes at least 100 days for the molecules to start to disintegrate [89].

### FM Analysis

Generally, the graphic (b) shows that, apart from the salt solution, the FM average responses tend to increase, and the Tukey's test shows the statistical similarity between the landfill and humidity conditions. For example, Vasile et al [89] studied that the burial of PLA parts can cause the FM to increase significantly due to the bio-composites present in the polymeric chain among which chitosan is the main responsible for the increase of this response.

Because moisture absorption was the main cause of degradation in the flexural samples, another plausible explanation for the increase of the flexural modulus is the fact that, as Banjo et al [90] have studied, water first penetrates the amorphous regions while its diffusion in the crystalline phase is slightly harder. As a result, had the samples been left exposed to moisture for a longer period of time (at least 100 days), the FM response of landfill and humidity conditions would have dropped quite significantly [89].

On the other hand, the saline solution condition has caused the average FM response to considerably decrease by just over **29%**. This result highlights once again

the impact of the salt water on the molecular structure of the PLA and thus prove that a higher degradation rate has occurred under this condition.

### FTIR analyse

To ensure that the molecular structure hasn't suffered any significant change that could affect the responses, a FTIR spectroscopy was performed. The four curves designed for every condition are shown in Figure 84 and the peaks of each zone are presented in Table 29.

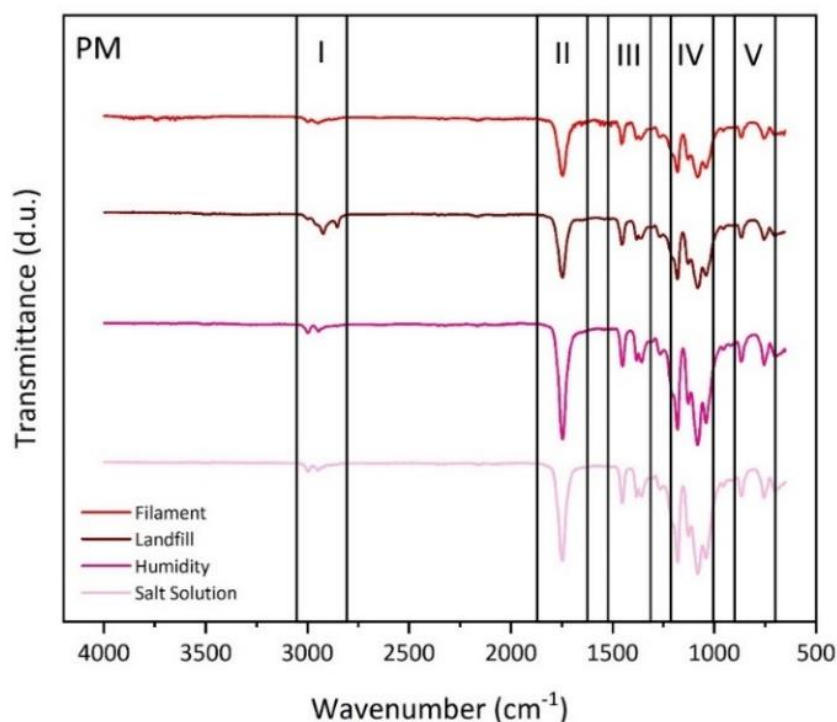


Figure 84 – FTIR Curves of PM flexural samples before and after being submitted to the degradation mechanisms.

Table 29 – PM FTIR Peaks by Zone.

| Degradation Mechanism | Wave Number (cm <sup>-1</sup> ) |         |                |                |         |
|-----------------------|---------------------------------|---------|----------------|----------------|---------|
|                       | Zone I                          | Zone II | Zone III       | Zone IV        | Zone V  |
| Filament              | 2998;2949                       | 1749    | 1456;1383;1363 | 1182;1081;1042 | 867;757 |
| Landfill              | 2923;2854                       | 1747    | 1454;1381;1360 | 1181;1081;1042 | 867;755 |
| Humidity              | 2998;2947                       | 1747    | 1450;1381;1357 | 1182;1083;1040 | 867;755 |
| Salt Solution         | 2998;2947                       | 1747    | 1452;1383;1357 | 1180;1081;1040 | 867;757 |

From Table 29 it's possible to confirm that the results did not suffer any significantly change in their molecular structure and no unconventional band have been identified. Therefore, the chemical structure of the filaments hasn't had a significant impact on the responses and no further conclusions can be drawn.

#### 4.2.2 KE

##### Mass

The next step in the degradation study is to evaluate the influence of the four conditions on the variation of the three responses, this time, for the KE filament supplier. The results obtained for each condition are shown in Table 30.

Table 30 – KE Conditions mass measurements.

|                        | After Printing | After-Degradation | After-Testing | After-Drying |
|------------------------|----------------|-------------------|---------------|--------------|
| <b>Landfill</b>        |                |                   |               |              |
| <b>Mean [g]</b>        | <b>6.09</b>    | <b>6.15</b>       | <b>6.14</b>   | <b>6.12</b>  |
| <b>Std. Dev.</b>       | 0.02           | 0.03              | 0.03          | 0.03         |
| <b>CV (%)</b>          | 0.41           | 0.41              | 0.41          | 0.41         |
| <b>Saline Solution</b> |                |                   |               |              |
| <b>Mean [g]</b>        | <b>6.09</b>    | <b>6.14</b>       | <b>6.12</b>   | <b>6.09</b>  |
| <b>Std. Dev.</b>       | 0.01           | 0.01              | 0.01          | 0.01         |
| <b>CV (%)</b>          | 0.18           | 0.20              | 0.20          | 0.13         |
| <b>Humidity</b>        |                |                   |               |              |
| <b>Mean [g]</b>        | <b>6.09</b>    | <b>6.12</b>       | <b>6.10</b>   | <b>6.08</b>  |
| <b>Std. Dev.</b>       | 0.00           | 0.00              | 0.00          | 0.00         |
| <b>CV (%)</b>          | 0.0            | 0.06              | 0.07          | 0.07         |

Overall, it's possible to conclude that the samples, after going through their respective condition, have absorbed an average amount of **0.05g** of water. This result is higher than the amount of water mass absorbed by the samples made of PM filament. This suggests that the KE supplier seems to be more hygroscopic than the PM supplier. Finally, the after-drying results prove that an average mass of **0.04g** of evaporated water has been removed from the samples (0.02g more compared with the PM material).

The after-degradation results were then evaluated through the statistical analysis of variance (ANOVA). According to the p-Values (Table 31), it was confirmed that at least one degradation mechanisms is significant. The graphic in Figure 85 shows the average mass values by condition as well as a comparison between the average responses that has been carried out through a Tukey's test.

Table 31 – Degradation study KE Mass Analysis of Variance ( $\alpha=95\%$ ).

| Source                                                                       | DF | Adj SS   | Adj MS   | F-Value | p-Value |
|------------------------------------------------------------------------------|----|----------|----------|---------|---------|
| <b>Conditions</b>                                                            | 3  | 0.012245 | 0.004082 | 18.93   | 0.000   |
| <b>Error</b>                                                                 | 16 | 0.003450 | 0.000216 |         |         |
| <b>Total</b>                                                                 | 19 | 0.015695 |          |         |         |
| <b>Note:</b> DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares |    |          |          |         |         |

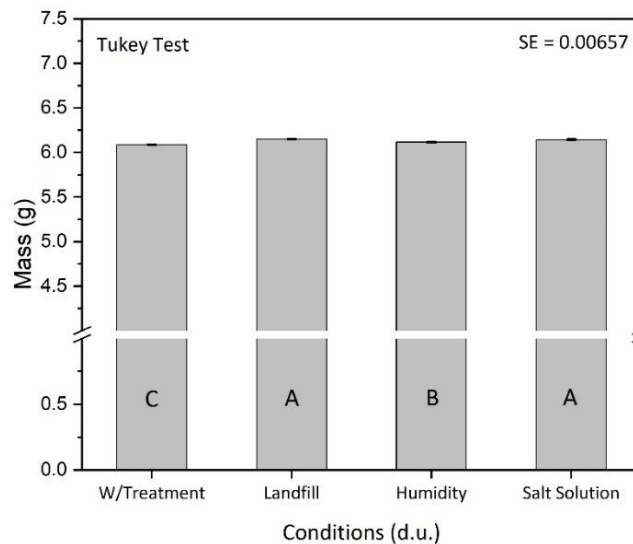


Figure 85 - Average mass related with the degradation mechanisms (KE).

The graphic from Figure 85 shows that without treatment (after printing) the average mass tends to be statistically lower, as expected.

Regarding the remaining three mechanisms, it's possible to conclude that the average mass tends to increase slightly. Once again, the increase is so small that this difference might be explained by the balance calibration yet when a sample is submitted to the humidity condition, the increase is not that pronounced as the Tukey's test confirm. D. Banjo et al [90] have studied that the variation on the mass is mostly related to the supplier's material unique hygroscopic nature and molecular structure. As result, the variation of the humidity condition is most likely related with a combination between the measurement equipment precision and the material's own characteristics.

To further study the variation of absorbed humidity in the humidity condition the percentage of absorbed water was recorded and is represented in the graphic of Figure 86. According to this graphic, it's possible to observe that the maximum humidity absorption of **1.71%** was registered on the 9<sup>th</sup> day of exposure, more precisely, on the 20<sup>th</sup> of December. Just like the PM samples. from the 10<sup>th</sup> to the 14<sup>th</sup> and on the 18<sup>th</sup> exposure days, there were no measurements. Finally, the average mass percentage of absorbed water per day was of **0.92%** which happens to be the highest average water absorption rate from the three suppliers. This result suggests that the KE is the most hygroscopic material.

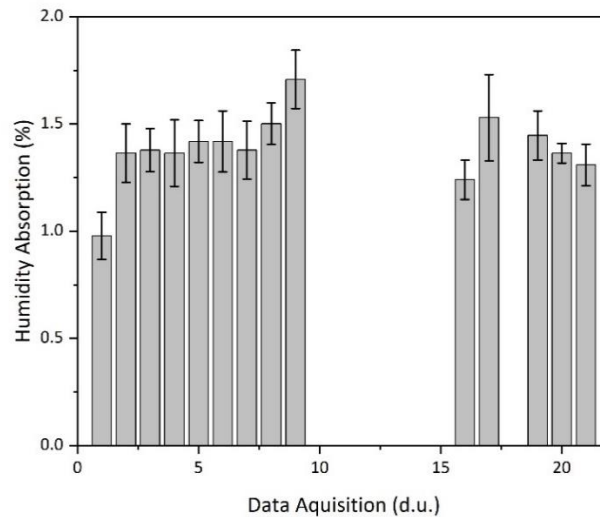


Figure 86 - Humidity condition – variation of %humidity per day (KE).

Just like what has been done for the PM samples, a comparison between a KE ASTM D790 theoretical mass and the remaining mass measurements per condition has also been carried out. The theoretical mass value and the remaining average mass measurements per condition are shown in Table 32.

Table 32 - Comparison between a KE sample theoretical mass and the KE degraded samples.

|          | Theoretical | W/Treatment | Landfill | Humidity | Salt Solution |
|----------|-------------|-------------|----------|----------|---------------|
| Mass [g] | 6.48        | 6.09        | 6.15     | 6.12     | 6.14          |

From the table above it's possible to compare theoretical mass of one KE sample with the average mass measurements of every single condition. The theoretical mass was calculated through the multiplication of the volume of an ASTM D790 with the KE density obtained in section 4.1.1. As expected, the results confirm a decrease of **6%** between the theoretical mass and the sample's mass without treatment (after printing). Had a smaller layer thickness have been used instead, the overall decrease of mass wouldn't probably be that considerable [70].

#### MFS and FM results analysis

The analysis regarding the significance of the four conditions on MFS and FM average responses begins the next stage in the KE degradation analysis. The average responses, standard deviation, and coefficient of variance of the two responses for each condition are shown in Table 33.

Table 33 - Results of the flexural tests of the KE samples.

| Sample           | Degradation Mechanisms |             |              |             |               |             |
|------------------|------------------------|-------------|--------------|-------------|---------------|-------------|
|                  | Landfill               |             | Humidity     |             | Salt Solution |             |
|                  | MFS (MPa)              | FM (GPa)    | MFS (MPa)    | FM (GPa)    | MFS (MPa)     | FM (GPa)    |
| <b>Mean [g]</b>  | <b>87,32</b>           | <b>3,25</b> | <b>86,15</b> | <b>3,27</b> | <b>77,82</b>  | <b>2,32</b> |
| <b>Std. Dev.</b> | 1,11                   | 0,02        | 0,90         | 0,03        | 0,55          | 0,03        |
| <b>CV (%)</b>    | 1,28                   | 0,47        | 1,05         | 0,83        | 0,70          | 1,08        |

Note: MFS – Maximum Flexural Strength; FM – Flexural Modulus;

The mean results exposed in Table 33 were evaluated through the statistical analysis (ANOVA). According to Table 34, it was verified at least one condition is significant for its respective response since all the p-Values are below 0.05.

Table 34 – KE Degradation Study: MFS&FM Analysis of Variance ( $\alpha=95\%$ ).

|            | Source    | DF | Adj SS  | Adj MS   | F-Value | p-Value |
|------------|-----------|----|---------|----------|---------|---------|
| <b>MFS</b> | Condition | 3  | 873.11  | 291.038  | 440.58  | 0.000   |
|            | Error     | 16 | 10.57   | 0.661    |         |         |
|            | Total     | 19 | 883.68  |          |         |         |
| <b>FM</b>  | Condition | 3  | 3.13912 | 1.046637 | 1552.45 | 0.000   |
|            | Error     | 16 | 0.01078 | 0.00067  |         |         |
|            | Total     | 19 | 3.14991 |          |         |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

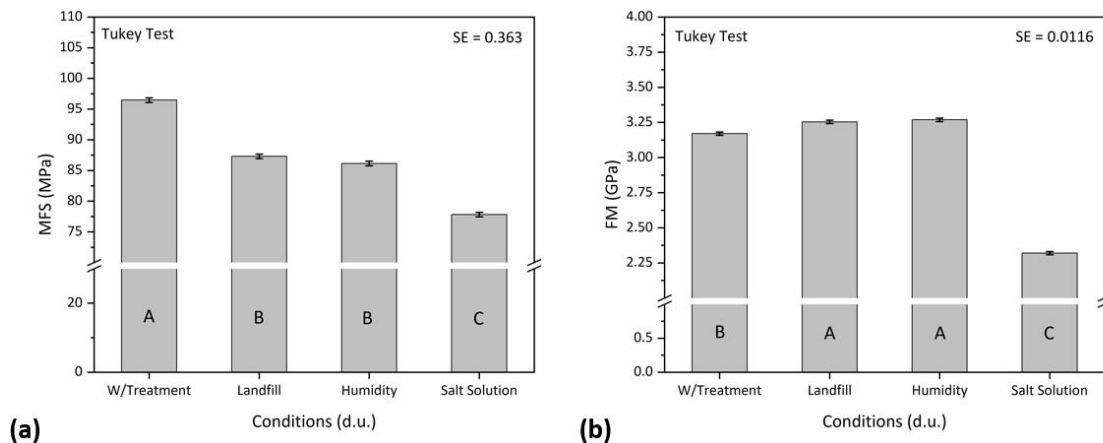


Figure 87 - The Average Maximum Flexural Strength and the Average Flexural Modulus related with the degradation mechanisms (KE).

Compared with the PM supplier, the only difference in the mechanical responses of the KE supplier is the fact that the MFS response has dropped even more in the salt solution. Apart from this situation, the remaining conditions mechanical behaviour is very similar compared with the previous supplier.

### MFS Analysis

The results obtained by this analysis show a decrease of approximately **10%** by both landfill and humidity conditions whereas the salt solution condition made the average mass to drop by almost **20%**. As expected, the reduction of the MFS in all conditions is mainly caused by hydrolytic cleavage caused by the presence of moisture [90]. In the case of the saline solution, the presence of salt seemed to have accelerated the degradation processes of the samples that were submitted to these conditions.

### FM Analysis

Just like what has been observed for the PM filament, the average modulus tends to increase when either landfill or humidity are applied. The exact opposite behaviour has taken over the salt solution whose FM response has decreased almost **27%**. As it was studied from previous works this phenomenon might have been caused by the following theory. Because PLA is a biodegradable thermoplastic, when submitted to water saturated environments the phenomenon of hydrolysis is very likely to occur. If so does happen, the exterior layers will start to disintegrate and a chemistry reaction leading into a formation of an acid compound may take place. The salt by nature is corrosive and therefore seems to have the ability of accelerating the hydrolysis processes on the samples surface [91]. To complement this analysis, in Figure 88 it's possible to observe some salt inclusions on the surface of a KE flexural sample as well as some traces of salt around the bonding lines. This shows that degradation through hydrolysis have in fact occurred and has started to dissolve the external layers thus reducing the FM.

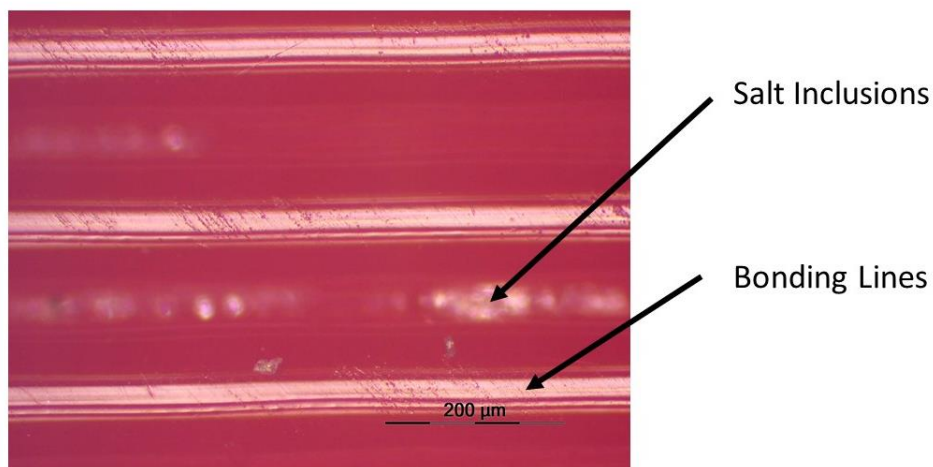


Figure 88 – Microstructure of the surface of a KE sample after being submitted to the saline solution.

## FTIR analyse

Just like what has been done for the PM supplier, a FTIR spectroscopy was performed to ensure that the molecular structure hasn't suffered any significant changes. The four curves obtained by every condition are shown in Figure 89 and the peaks of each zone are presented in Table 35.

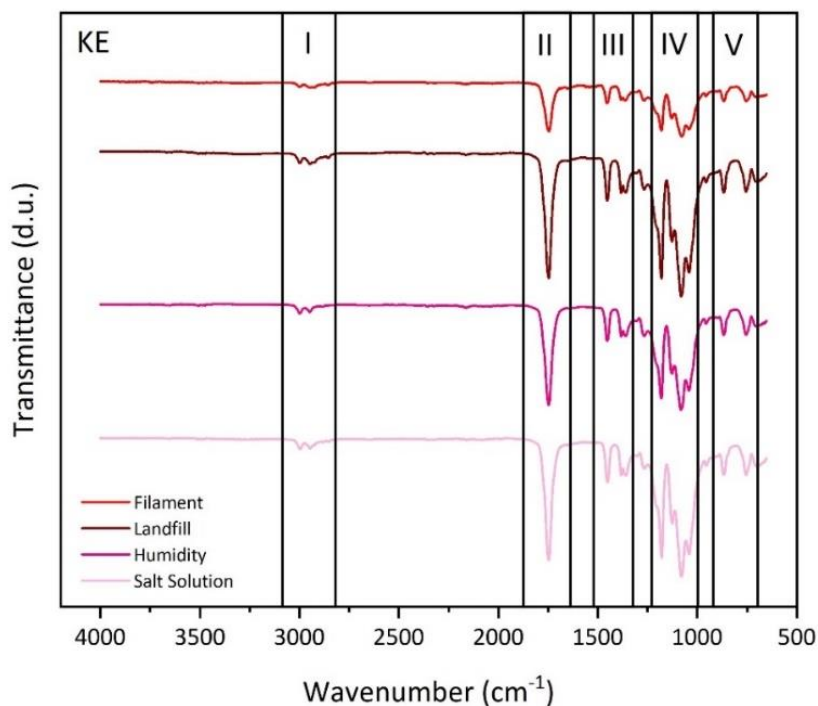


Figure 89 - FTIR Curves of KE flexural samples before and after being submitted to the degradation mechanisms.

Table 35 - KE FTIR Peaks by Zone.

| Degradation Mechanism | Wave Number (cm <sup>-1</sup> ) |         |                |           |         |
|-----------------------|---------------------------------|---------|----------------|-----------|---------|
|                       | Zone I                          | Zone II | Zone III       | Zone IV   | Zone V  |
| Filament              | 2998;2947;2925                  | 1744    | 1452;1381;1363 | 1180;1078 | 867;753 |
| Landfill              | 2998;2947;2927                  | 1747    | 1452;1381;1359 | 1180;1081 | 867;755 |
| Humidity              | 2998;2947                       | 1747    | 1452;1381;1359 | 1182;1081 | 867;755 |
| Salt Solution         | 2996;2945                       | 1747    | 1450;1381;1357 | 1180;1079 | 867;755 |

From Table 35 it's possible to confirm that the results did not suffer any significantly change in their molecular structure and no unconventional band has been identified. Therefore, the chemical structure of the filaments hasn't had a significant impact on the responses.

#### 4.2.3 F3D

The last flexural samples to be analysed in the degradation study are the ones made from F3D filament. As so, the aim of this section is to evaluate the influence of the three degradation mechanisms on the variation of the three average responses (MFS, FM and F3D). It also worth mentioning that these samples were printed through an improved system (“mosquito extruder”) that is characterized by its relatively reduced and more stable thermal gradients.

#### Mass

Just how has been done for the samples made from PM and KE suppliers, a calculation of the average mass, standard deviation, and coefficient of variance for each degradation condition has also been carried out as shown in Table 36.

Table 36 – F3D Conditions mass measurements.

|                        | After-Printing | After-Degradation | After-Testing | After-Drying |
|------------------------|----------------|-------------------|---------------|--------------|
| <b>Landfill</b>        |                |                   |               |              |
| <b>Mean [g]</b>        | <b>6.04</b>    | <b>6.07</b>       | <b>6.08</b>   | <b>6.05</b>  |
| <b>Std. Dev.</b>       | 0.00           | 0.00              | 0.00          | 0.00         |
| <b>CV (%)</b>          | 0.05           | 0.07              | 0.07          | 0.05         |
| <b>Saline Solution</b> |                |                   |               |              |
| <b>Mean [g]</b>        | <b>6.04</b>    | <b>6.09</b>       | <b>6.07</b>   | <b>6.02</b>  |
| <b>Std. Dev.</b>       | 0.00           | 0.02              | 0.02          | 0.00         |
| <b>CV (%)</b>          | 0.06           | 0.31              | 0.26          | 0.06         |
| <b>Humidity</b>        |                |                   |               |              |
| <b>Mean [g]</b>        | <b>6.04</b>    | <b>6.12</b>       | <b>6.11</b>   | <b>6.08</b>  |
| <b>Std. Dev.</b>       | 0.01           | 0.01              | 0.01          | 0.00         |
| <b>CV (%)</b>          | 0.10           | 0.13              | 0.12          | 0.07         |

Generally, just like what has been observed for the PM and KE supplier, the F3D samples have also absorbed water. The amount of absorbed water by sample was on average **0.05g** (very close to KE). However, the humidity condition results have shown that the samples that were submitted to a humidity condition have absorbed, on average, **0.08g** of water. In addition, the after-testing weights confirm what has been observed for the previous suppliers with an average loss of 0.01g of, most likely, micro-particles. Finally, the after-drying results confirm an increase of evaporated water mass with an average of almost **0.04g** per sample.

To help with the assessment on the impact of these conditions in the variance of mass, the results shown in table 34 were evaluated through the statistical analysis of

variance (ANOVA). According to the p-Values (Table 37), it was confirmed that at least one degradation mechanisms is significant. The graphic in Figure 90 shows the average mass values by degradation mechanism as well as a statistical comparison between the averages that was carried out through a Tukey's test. The statistical differences between each condition are represented by the letters A, B or C.

Table 37 – F3D Degradation study: Mass Analysis of Variance ( $\alpha=95\%$ ).

| Source    | DF | Adj SS   | Adj MS   | F-Value | p-Value |
|-----------|----|----------|----------|---------|---------|
| Condition | 3  | 0.013974 | 0.004658 | 40.50   | 0.000   |
| Error     | 16 | 0.001840 | 0.000115 |         |         |
| Total     | 19 | 0.015814 |          |         |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

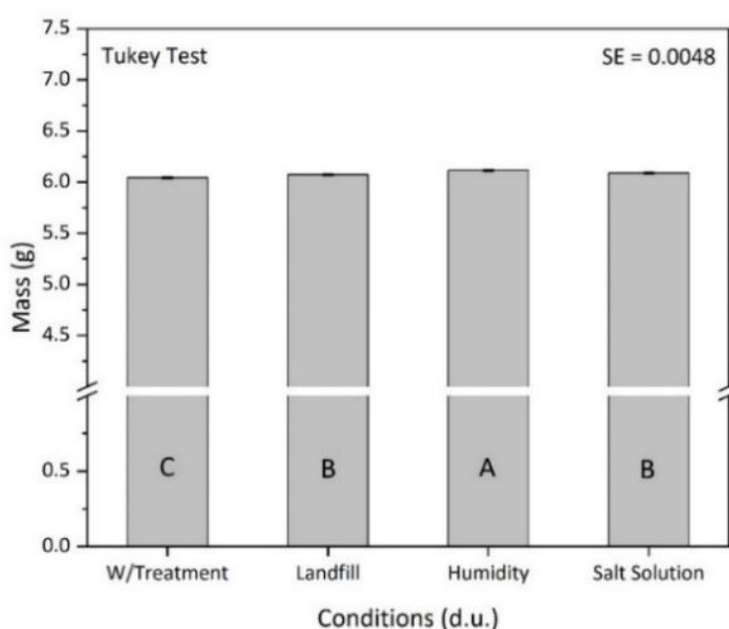


Figure 90 - Average mass related with the degradation mechanisms (F3D).

From the analysis of the graphic from Figure 90, and just like what has been learned from the previous suppliers, it's possible to conclude that the average mass tends to decrease if not submitted to a degradation mechanism. This situation was expected and doesn't need further justification.

On the other hand, as expected, the remaining conditions have shown that the mass tends to increase when exposed to either landfill, humidity, or salt solution. However, the graphic also shows that under moisture saturated environments the average mass tends to increase even more. Taking in consideration the interpretation

that has been made for Table 36, this statistical difference that has been pointed out by the Tukey's test reinforces the status of most hygroscopic material by F3D.

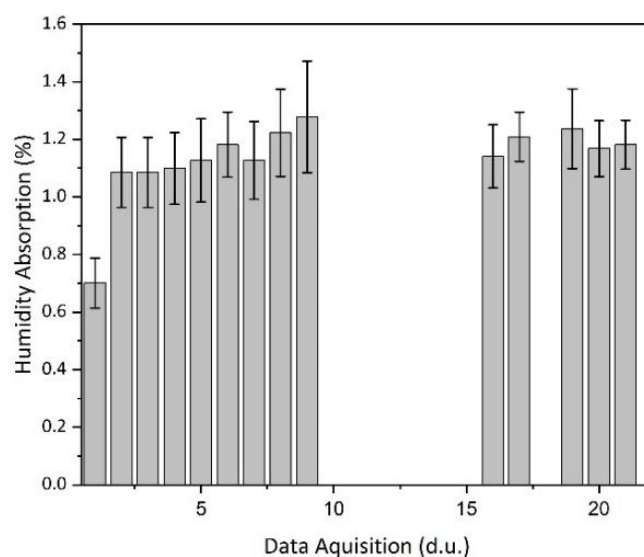


Figure 91 - Humidity condition – variation of %humidity per day (F3D).

To further study the variation of absorbed humidity in the humidity condition the percentage of absorbed water was recorded and is represented in the graphic of Figure 91. According to this graphic, it's possible to conclude that the maximum humidity absorption of **1.28%** was registered on the exact same day the maximum absorption of humidity had been registered by the KE supplier, the 20<sup>th</sup> of December (9<sup>th</sup> day of exposure) Also, from the 10<sup>th</sup> to the 14<sup>th</sup> and on the 18<sup>th</sup> exposure days, there were no measurements. The average mass of absorbed water per day for this supplier was of **0.75%** (this average mass was of 0.6% and of 0.92% for the PM and KE suppliers, respectively).

Now that all the humidity absorption percentages for all suppliers have been analysed, it's worth to point out the unstable character of the PLA. In the study of Nieto et al [70], it was investigated that this random absorption behaviour is normal and is related to the organic nature of the PLA which allows sudden changes in the absorption rates.

To fully understand the average mass results obtained by the F3D supplier, once again a comparison between a F3D ASTM D790 theoretical mass and the remaining mass measurements per condition has also been carried out (Table 38).

Table 38 – Comparison between the theoretical mass and the F3D degraded samples.

|                 | Theoretical | W/Treatment | Landfill | Humidity | Salt Solution |
|-----------------|-------------|-------------|----------|----------|---------------|
| <b>Mass [g]</b> | 6.42        | 6.04        | 6.07     | 6.12     | 6..09         |

The theoretical mass was calculated through the multiplication of the theoretical volume of an ASTM D790 specimen with the F3D density obtained in section 4.1.1. The results confirm a decrease of approximately **6%** between the theoretical mass and the after-printing sample's mass.

Comparing the three filament suppliers, the percentage of mass loss was equal on the KE and F3D suppliers (6%) and was considerably lower in the PM supplier (4%). Because of the overall isoparametric nature of the degradation study, these variations were most likely caused by a combination of the printing parameters (Table 13) and the different additives used by each filament manufacturer which may affect the viscosity of each material's supplier and, consequently, its fluidity.

#### MFS and FM results analysis

The last act of the degradation study is the discussion regarding the impact of the conditions on the MFS and FM F3D samples. The average results obtained for these responses are shown in Table 39 along with their respective standard deviations, and coefficients of variance.

Table 39 - Results of the flexural tests of the F3D samples.

| Sample                                                                                            | Degradation Mechanism |             |              |             |               |             |
|---------------------------------------------------------------------------------------------------|-----------------------|-------------|--------------|-------------|---------------|-------------|
|                                                                                                   | Landfill              |             | Humidity     |             | Salt Solution |             |
|                                                                                                   | MFS (MPa)             | FM (GPa)    | MFS (MPa)    | FM (GPa)    | MFS (MPa)     | FM (GPa)    |
| <b>Mean</b>                                                                                       | <b>88,96</b>          | <b>3,30</b> | <b>86,77</b> | <b>3,32</b> | <b>80,43</b>  | <b>2,40</b> |
| <b>Std. Dev.</b>                                                                                  | 0,54                  | 0,01        | 1,24         | 0,01        | 1,69          | 0,03        |
| <b>CV (%)</b>                                                                                     | 0,61                  | 0,41        | 1,43         | 0,21        | 2,11          | 1,13        |
| <b>Note:</b> MFS – Maximum Flexural Strength; FM – Flexural Modulus; CV – Coefficient of Variance |                       |             |              |             |               |             |

Afterwards, the significance of each condition on these responses were evaluated through a statistical analysis of variance (ANOVA). According to Table 40 it has been verified at least one condition is significant. The graphic in Figure 92 shows the average MFS and FM values by condition as well as a statistical comparison between the condition's average values that was carried out through a Tukey's test. Just like the previous analysis, the statistical differences between each condition are represented by the letters A, B or C.

Table 40 – F3D Degradation study: MFS&FM Analysis of Variance ( $\alpha=95\%$ ).

|            | Source    | DF | Adj SS  | Adj MS   | F-Value | p-Value |
|------------|-----------|----|---------|----------|---------|---------|
| <b>MFS</b> | Condition | 3  | 394.30  | 131.434  | 94.78   | 0.000   |
|            | Error     | 16 | 22.19   | 1.387    |         |         |
|            | Total     | 19 | 416.49  |          |         |         |
| <b>FM</b>  | Condition | 3  | 2.78621 | 0.928737 | 1561.85 | 0.000   |
|            | Error     | 16 | 0.00951 | 0.000595 |         |         |
|            | Total     | 19 | 2.79572 |          |         |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

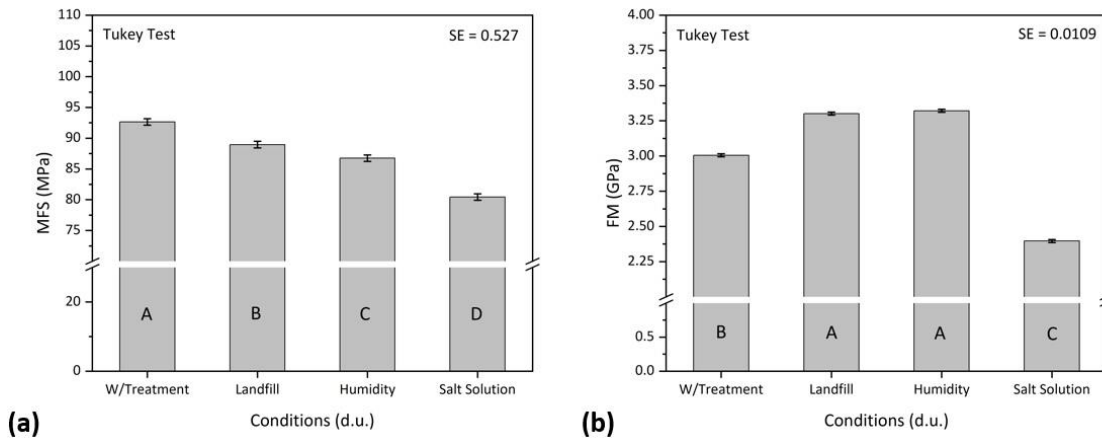


Figure 92 - The Average Maximum Flexural Strength and the Average Flexural Modulus related with the degradation mechanisms (F3D).

Overall, just like what has been observed in the previous suppliers, the immersion in saline substantially changes the mechanical properties of the flexural samples. The behaviour of the remaining conditions for both responses remains once again very similar.

### MFS Analysis

As expected, the graphic (a) from Figure 92 show that the average MFS tends to increase when no treatment is applied. On the other hand, when the samples were submitted to a condition, the MFS tended to gradually decrease and this time, there weren't any statistical equalities between the conditions. When it comes to the landfill and the humidity conditions the decrease may be mainly related with moisture. As Vasile et al [89] has studied, because of the bio origin of the PLA, there's a good chance of the presence of high contents of chitosan which increases hydrophilicity on the sample's surface and therefore favours the action of moisture.

For the first time in this degradation study, one response has fell bellow even further thus being placed in group D by the Tukey's test. Compared with the w/treatment response this was a reduction of **10%** of flexural strength. This result once again suggests the stronger impact of salt water in the chemical structure of the overall samples, yet for the F3D this phenomenon has been reinforced.

#### FM Analysis

Just like what has been observed for the previous fiament suppliers, the average FM tends to increase when a sample is submitted to either landill or humidity conditions.

However, this phenomenom once again has not been observed for the salt water condition where the average FM has decreased by over **20%**. This result, once again proves the harmful effect of the salt on the material's molecular structure as it has been explined in section 4.2.1 and 4.2.2.

#### FTIR Analysis

Just like what has been done for PM and KE supplier, a FTIR spectroscopy was performed to ensure that the chemical structure of the samples made of F3D haven't suffered any significant change. The four curves obtained by every condition are shown in Figure 93 and the peeks of each zone are presented in Table 41.

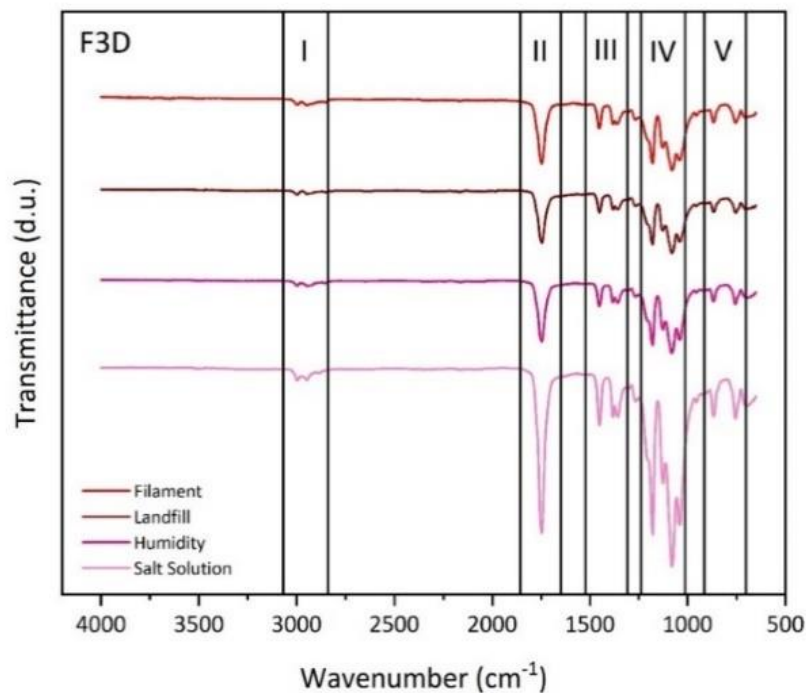


Figure 93 - FTIR Curves of F3D flexural samples before and after being submitted to the degradation mechanisms.

Table 41 – F3D FTIR Peaks by Zone.

| Degradation Mechanism | Wave Number (cm <sup>-1</sup> ) |         |                |                |         |
|-----------------------|---------------------------------|---------|----------------|----------------|---------|
|                       | Zone I                          | Zone II | Zone III       | Zone IV        | Zone V  |
| Filament              | 2998;2947                       | 1747    | 1456;1381;1363 | 1180;1081;1042 | 867;755 |
| Landfill              | 2996;2945                       | 1747    | 1450;1381;1357 | 1180;1081;1040 | 867;755 |
| Humidity              | 2998;2945                       | 1747    | 1452;1383;1357 | 1180;1081;1040 | 869;757 |
| Salt Solution         | 2996;2947                       | 1747    | 1450;1383;1357 | 1180;1081;1040 | 869;757 |

From Table 41 it's possible to confirm that the chemical structure of the F3D flexural samples haven't suffered any significantly change and no unconventional band has been identified. Therefore, the molecular structure of the filaments seems to not have had a significant impact on the three responses.

### 4.3 Parametric Study

In this section, the influence of four factors ( $E_t$ ,  $L_t$ ,  $P_s$ ,  $E_m$ ) on three major responses (Mass, MFS, and FM) that have been obtained by flexural samples made of three filament suppliers (PM, KE and F3D) during the Taguchi experiment will be exposed and discussed.

#### 4.3.1 PM

##### Mass

To study of the influence of the four factors on the variation of mass the first step was to calculate the average mass, standard deviation, and coefficient of variance of each condition of the Taguchi L9 array (Table 42). The experimental procedure that has been followed to measure all the condition's mass is explained in section 3.5.

Table 42 – Mass measurement of Taguchi PM.

| Condition   | T1   | T2   | T3   | T4   | T5   | T6   | T7   | T8   | T9   |
|-------------|------|------|------|------|------|------|------|------|------|
| Average [g] | 5.89 | 6.20 | 6.51 | 6.92 | 5.61 | 5.93 | 6.52 | 6.82 | 5.39 |
| Std.Dev [g] | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 |
| CV (%)      | 0.13 | 0.05 | 0.08 | 0.15 | 0.09 | 0.10 | 0.08 | 0.04 | 0.11 |

The results were then evaluated through the statistical analysis of variance (ANOVA). According to the p-Values (Table 43), it was confirmed that the all the parameters were significant, yet layer thickness and extrusion multiplier were the factors that stood out. The graphic in Figure 94 shows the average mass values by factor

and their respective levels as well as a comparison between the averages that was carried out through a Tukey's test.

Table 43 – Taguchi study PM Mass Analysis of Variance ( $\alpha=95\%$ ).

| Source                | DF | Adj SS  | Adj MS  | F-Value  | p-Value |
|-----------------------|----|---------|---------|----------|---------|
| Extrusion Temperature | 2  | 0.01777 | 0.00889 | 274.20   | 0.00    |
| Layer Thickness       | 2  | 1.10907 | 0.55454 | 17111.40 | 0.00    |
| Print Speed           | 2  | 0.01115 | 0.00558 | 172.03   | 0.00    |
| Extrusion Multiplier  | 2  | 5.27362 | 2.63681 | 81364.46 | 0.00    |
| Error                 | 18 | 0.00058 | 0.00003 |          |         |
| Total                 | 26 | 6.41220 |         |          |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

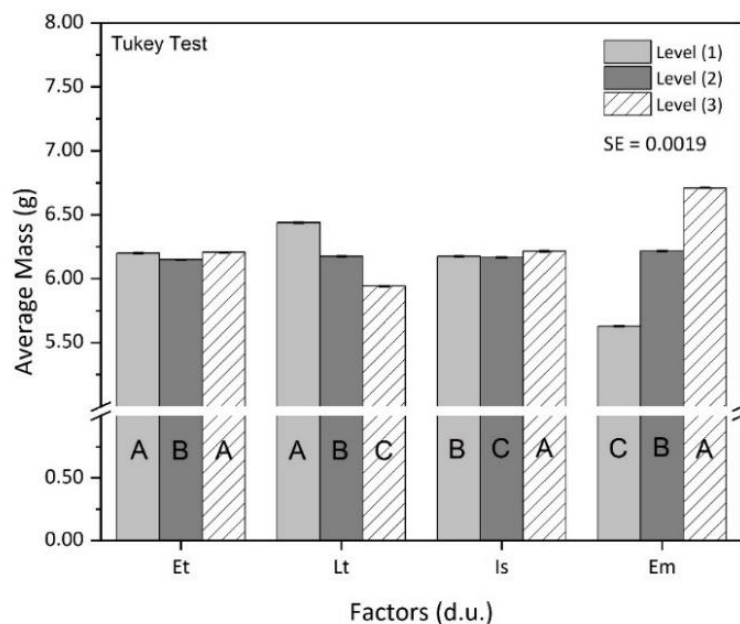


Figure 94 - Average mass related with the significant parameters and levels (PM).

### Extrusion Temperature

From the graphic of Figure 94 it's possible to observe that, overall, the mass hasn't shown a linear behaviour. Yet, the Tukey's test has placed two average mass levels on the same group (A) thus meaning their responses are statistically similar and confirming that the average mass tends to increase when temperatures of 215°C and 235°C are used. From what has been studied from previous works, this pattern confirms that the extrusion temperature had not a significant influence on the average mass. The results themselves may seem more dependent on the material's imperfections and printing process [92].

### Layer Thickness

The analyse of layer thickness shows that for lower values of thickness, the mass tended to increase by **8%**. From what is known from the literature, this phenomenon was expected because when the layer is thinner, a high number of layers is therefore necessary to fulfil the volume. Consequently, the number of voids inside the sample will be reduced and filled with printing material which leads the final part's mass to increase.

### Printing speed

When it comes to the printing speed, the graphic shows that the average mass is higher when a printing speed of 80mm/s is used whereas the use of 60mm/s or 40 mm/s will make the average mass to drop significantly. The results, whatsoever, are very similar and may be justified by the material's characteristics.

### Extrusion multiplier

Finally, the extrusion multiplier proved to be the factor that has a bigger influence on the average mass values. When an extrusion multiplier of 1.1 is used the outcome mass is **19%** higher compared with the use of a 0.9 multiplier. This situation was predictable and went accordingly to what has been exposed in section 2.3.4: the higher the multiplier, the bigger will be the volume of deposited material thus resulting in a denser sample.

To complement this, an analyse of comparison between the best level responses obtained by ANOVA (Table 44) and the theoretical mass value of a flexural sample was carried out. The procedure to calculate the theoretical mass value was based on the calculus of an ASTM D790 sample volume which is then multiplied by the material's density thus resulting in a sample's mass. The value used for density in the calculation of the mass was determined in section 4.1.1 and the results are shown in Table 44.

Table 44 – Comparison between the theoretical mass and the best levels average mass (PM).

| PM ASTM D790              |                              | Mass [g]    |                |                |                |                   |
|---------------------------|------------------------------|-------------|----------------|----------------|----------------|-------------------|
| Volume [cm <sup>3</sup> ] | Density [g/cm <sup>3</sup> ] | Theoretical | E <sub>t</sub> | L <sub>t</sub> | P <sub>s</sub> | (E <sub>m</sub> ) |
| 5.16                      | 1.25                         | <b>6.43</b> | 6.21           | 6.44           | 6.21           | 6.71              |

From what it has been learned from Table 44 the use of 0.1mm of layer thickness almost results in a hundredth approximation of the theoretical value (6.43g). When it

comes to the remaining factors, the use of 235°C of extrusion temperature and a printing speed of 80mm/s resulted in the same average mass and were 3% lower compared to the theoretical value. As expected, the extrusion multiplier achieved the highest average mass value being approximately 4% heavier.

#### MFS and FM results analysis

The next stage in this discussion is the significance of the four factors on MFS and FM responses. The results from Table 45 were obtained following the experimental procedure explained in section 3.5 and were evaluated through a statistical analysis (ANOVA).

Table 45 – Results of the flexural stress analysis by experimental condition (PM).

| Condition                                                           | MFS (MPa)            | CV (%) | FM (GPa)           | CV (%) |
|---------------------------------------------------------------------|----------------------|--------|--------------------|--------|
| T1                                                                  | 96.58 ± 1.29         | 1.3    | 3.29 ± 0.08        | 2.3    |
| T2                                                                  | 98.03 ± 0.39         | 0.4    | 3.35 ± 0.00        | 0.1    |
| T3                                                                  | 85.78 ± 0.56         | 0.7    | 2.59 ± 0.00        | 0.2    |
| T4                                                                  | <b>108.98</b> ± 1.94 | 1.8    | 3.50 ± 0.07        | 1.9    |
| T5                                                                  | 95.64 ± 0.67         | 0.7    | 3.23 ± 0.04        | 1.1    |
| T6                                                                  | 88.11 ± 1.09         | 1.2    | 2.81 ± 0.03        | 1.1    |
| T7                                                                  | 106.58 ± 0.10        | 0.1    | <b>3.56</b> ± 0.03 | 0.9    |
| T8                                                                  | 100.19 ± 0.70        | 0.7    | 3.23 ± 0.04        | 1.4    |
| T9                                                                  | 86.07 ± 0.23         | 0.3    | 2.90 ± 0.04        | 1.5    |
| <b>Note:</b> MFS – Maximum Flexural Strength; FM – Flexural Modulus |                      |        |                    |        |

From Table 45 it can be observed that the maximum flexural stress value was 108.98 MPa and the maximum flexural modulus was 3.56 GPa. In Table 46 and Table 47 it's possible to check the results of the analyse of variance of MFS and FM, respectively. From there it has been verified that all the parameters are significant since all the p-Values are below 0.05.

Table 46 – Taguchi study PM MFS Analysis of Variance ( $\alpha=95\%$ ).

| Source                                                                       | DF | Adj SS  | Adj MS  | F-Value | p-Value |
|------------------------------------------------------------------------------|----|---------|---------|---------|---------|
| Extrusion Temperature                                                        | 2  | 102.38  | 51.190  | 56.98   | 0.00    |
| Layer Thickness                                                              | 2  | 1402.13 | 701.066 | 780.32  | 0.00    |
| Print Speed                                                                  | 2  | 34.31   | 17.153  | 19.09   | 0.00    |
| Extrusion Multiplier                                                         | 2  | 163.76  | 81.879  | 91.14   | 0.00    |
| Error                                                                        | 18 | 16.17   | 0.898   |         |         |
| Total                                                                        | 26 | 1718.75 |         |         |         |
| <b>Note:</b> DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares |    |         |         |         |         |

Table 47 – Taguchi study PM MF Analysis of Variance ( $\alpha=95\%$ ).

| Source                | DF | Adj SS  | Adj MS  | F-Value | p-Value |
|-----------------------|----|---------|---------|---------|---------|
| Extrusion Temperature | 2  | 0.10595 | 0.05297 | 27.65   | 0.00    |
| Layer Thickness       | 2  | 2.23309 | 1.11655 | 582.76  | 0.00    |
| Print Speed           | 2  | 0.10656 | 0.05328 | 27.81   | 0.00    |
| Extrusion Multiplier  | 2  | 0.08579 | 0.04289 | 22.39   | 0.00    |
| Error                 | 18 | 0.03449 | 0.00192 |         |         |
| Total                 | 26 | 2.56588 |         |         |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

These tables couple with the graphic from Figure 95 which shows the average MFS and FM values by factor along with their respective levels as well as a comparison between the average responses that has been carried out through a Tukey's test. The statistical differences between each level are represented by the letters A, B or C.

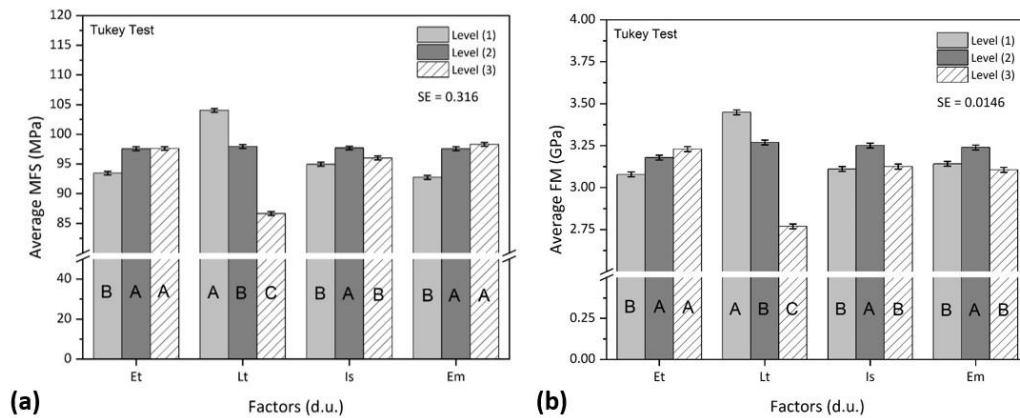


Figure 95 – The Average Maximum Flexural Strength and the Average Flexural Modulus related to the significant parameters and levels (PM).

Overall, unlike what has been observed for the mass response, the MFS and FM responses appeared to have been more significantly influenced by parameter variation. Despite this, the behaviour of one response for one factor is very similar to the other response when affected by the same factor. On one hand, both responses seem to be greatly influenced by the layer thickness. On the other hand, the extrusion multiplier seemed to have followed a different pattern on both responses.

### Extrusion Temperature

In both MFS and FM responses, the average response tends to increase approximately **4%** when the temperature is set higher. This phenomenon can be attributed to larger quantities of thermal energy involved in the extrusion process which contributes to layer bonding.

### Layer Thickness

The analyse of layer thickness shows that for lower values of thickness, the MFS and FM responses tend to increase by **17%** compared to the average response that has been obtained by the use 0.3mm. This increase can be explained by the fact that when lower layer heights are used, the air gaps between the layers become smaller and the bonding areas become larger. Sood et al [92] have studied, for example, that the maximum strength will increase for lower layer heights.

### Print Speed

In this case, the MFS and FM responses tend to increase by approximately **4%** when a printing speed of 60mm/s is used whereas the use of 40mm/s or 80mm/s will make both responses to drop significantly. Since there isn't a linear pattern on both responses it's fair to assume that these variances were caused by either the printing process or the material's properties.

### Extrusion Multiplier

As it was mentioned before, the behaviour of this factor was different between MFS and FM responses. On one hand, the use of an extrusion multiplier either 1.0 or 1.1 has made the average MFS response to increase **6%**. On the other hand, for the FM response the use of an extrusion multiplier of 1.0 seemed to have benefited the average response by **3%** if compared with the use of either 0.9 or 1.1.

In both cases this parameter does not show a linear pattern which makes it harder to link this situation with the literature. Yet, it's possible to observe that the influence of this factor was considerably bigger on the MFS and that use of a 1.0 multiplier has somehow benefited both responses.

### 4.3.2 KE

#### Mass

The next stage in the Taguchi study is to evaluate the influence of the four factors on the variation of the three responses, this time, for the KE filament supplier. The procedure to obtain the mass measurements of every single sample was the same one used for the PM samples. The average mass, standard deviation and coefficient of variance were calculated according to each condition of the Taguchi L9 array (Table 48).

Table 48 – Mass measurements of Taguchi KE.

| Condition          | T1   | T2   | T3   | T4   | T5   | T6   | T7   | T8   | T9   |
|--------------------|------|------|------|------|------|------|------|------|------|
| <b>Average [g]</b> | 5.72 | 6.09 | 6.38 | 6.91 | 5.47 | 5.84 | 6.39 | 6.71 | 5.27 |
| <b>Std.D</b>       | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 |
| <b>CV (%)</b>      | 0.10 | 0.05 | 0.09 | 0.11 | 0.00 | 0.22 | 0.16 | 0.07 | 0.16 |

The results that are shown in Table 48 were evaluated through the statistical analysis of ANOVA. According to the p-Values (Table 49), it was verified that all the parameters were significant. However, just like what has been observed for the PM, the layer thickness and extrusion multiplier are factors that stood out and seemed to have had a bigger influence on the average mass responses.

The graphic in Figure 96 shows the average mass values by factor and their respective levels as well as a comparison between the averages that was carried out through a Tukey's test. The statistical differences between each level are represented by the letters A, B or C. In Table 49 it's possible to check the analyse of variance parameters along with the p-Values which confirm that all factors are significant and therefore are worth of discussion.

Table 49 – Taguchi study KE Mass Analysis of Variance ( $\alpha=95\%$ ).

| Factors                      | DF | Adj SS  | Adj MS  | F-Value  | p-Value |
|------------------------------|----|---------|---------|----------|---------|
| <b>Extrusion Temperature</b> | 2  | 0.01572 | 0.00786 | 61.09    | 0.000   |
| <b>Layer Thickness</b>       | 2  | 1.21940 | 0.60970 | 4737.24  | 0.000   |
| <b>Print Speed</b>           | 2  | 0.00214 | 0.00107 | 8.29     | 0.003   |
| <b>Extrusion Multiplier</b>  | 2  | 6.17026 | 3.08513 | 23970.78 | 0.000   |
| <b>Error</b>                 | 18 | 0.00232 | 0.00013 |          |         |
| <b>Total</b>                 | 26 | 7.40984 |         |          |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

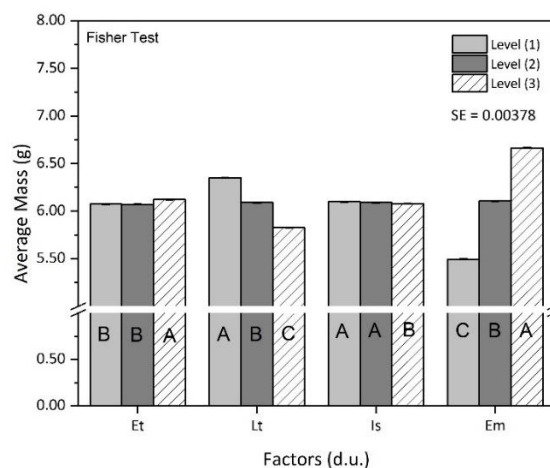


Figure 96 - Average mass related with the significant parameters and levels (KE).

### Extrusion Temperature

For this parameter, it has been noted that for a temperature of 235°C, the average mass tends to increase whereas the use of lower temperatures leads to lower and average weights. Although the results don't show an increasing pattern, the general behaviour went accordingly to what has been reported in section 2.3.4. The fact that the use of the lowest temperature causes a slightly higher average mass than the one obtained using 225°C, can be justified by the overall level 1 printing configuration.

### Layer Thickness

The layer thickness columns show that for lower values of thickness, the mass tends to increase by **9%**. The same phenomenon was observed for the PM supplier and no further justifications beyond the ones that have been appointed before are needed.

### Printing Speed

The graphic shows that the use of printing speeds of either 40mm/s or 60mm/s are equally significant and cause the average mass to increase. However, if a higher speed is used, the average mass tends to decrease. Yet, the overall difference is so small that average mass might have gone down due to either printing process or materials characteristics.

### Extrusion Multiplier

Just like what has been observed for the PM, the extrusion multiplier proved once again to have a bigger influence in the average mass response. In this case, when an extrusion multiplier of 1.1 is used the average mass can increase by approximately **21%** (for PM the increase was of 19%). Since both suppliers have experience almost the same increase of mass for the same multiplier, no further justifications are needed.

Table 50 – Comparison between the theoretical mass and the best levels average mass (KE).

| KE ASTM D790              |                              | Mass [g]    |                |                |                |                |
|---------------------------|------------------------------|-------------|----------------|----------------|----------------|----------------|
| Volume [cm <sup>3</sup> ] | Density [g/cm <sup>3</sup> ] | Theoretical | E <sub>t</sub> | L <sub>t</sub> | P <sub>s</sub> | E <sub>m</sub> |
| 5.16                      | 1.25                         | <b>6.48</b> | 6.12           | 6.35           | 6.10           | 6.67           |

The best average mass levels obtained by each factor are shown in Table 50 along with the value of the theoretical mass of a KE ASTM D790 sample that has been achieved following the same procedure explained in section 4.3.1.

Just like the PM samples, the parameter that achieved the closest average mass value was the layer thickness which was just 2% lighter compared to the theoretical mass. The average mass obtained by the parameters extrusion temperature and print speed were very close to each other and were both approximately 6% lighter than the theoretical value. Finally, the use of an extrusion multiplier of 1.1 obtained, once again, the highest average mass and was the only average mass level above the theoretical mass. This phenomenon was also observed for the PM filament, yet this time the difference was only of **3%**.

#### MFS and FM results analysis

The next step is the discussion on the significance of the four factors on the MFS and FM responses. All the MFS and FM results were obtained following the experimental procedure explained in section 3.5 and their respective standard deviations and coefficients of variance, were calculated according to each condition of the Taguchi L9 array (Table 51).

Table 51 - Results of the flexural stress analysis by experimental condition (KE).

| Condition                                                           | MFS (MPa)            | CV (%) | FM (GPa)           | CV (%) |
|---------------------------------------------------------------------|----------------------|--------|--------------------|--------|
| <b>T1</b>                                                           | 86.41 ± 1.79         | 2.1    | 2.84 ± 0.12        | 4.1    |
| <b>T2</b>                                                           | 95.28 ± 0.11         | 0.1    | 3.11 ± 0.02        | 0.5    |
| <b>T3</b>                                                           | 89.26 ± 0.03         | 0.0    | 2.78 ± 0.03        | 1.1    |
| <b>T4</b>                                                           | 97.64 ± 1.35         | 1.4    | 3.09 ± 0.08        | 2.5    |
| <b>T5</b>                                                           | 90.05 ± 0.10         | 0.1    | 2.98 ± 0.03        | 1.0    |
| <b>T6</b>                                                           | 88.08 ± 1.06         | 1.2    | 2.84 ± 0.06        | 2.2    |
| <b>T7</b>                                                           | <b>101.91 ± 1.08</b> | 1.1    | <b>3.31 ± 0.12</b> | 3.7    |
| <b>T8</b>                                                           | 100.08 ± 1.00        | 1.0    | 3.19 ± 0.02        | 0.6    |
| <b>T9</b>                                                           | 85.45 ± 0.81         | 0.9    | 3.23 ± 0.04        | 1.3    |
| <b>Note:</b> MFS – Maximum Flexural Strength; FM – Flexural Modulus |                      |        |                    |        |

The results obtained show the Taguchi's T7 condition achieved the highest maximum flexural stress (101.91 MPa) and the maximum flexural modulus (3.31 GPa). The average MFS and FM responses were both evaluated through the statistical analysis of ANOVA. When it comes to the MFS response, according to the p-Values (Table 52 and Table 53), it was verified that all the parameters were significant yet this time no factor has stood out from the other ones. On the other hand, the p-Values obtained for the FM response prove that all the factors, except one, were significant. As so, because the p-

Value of the printing speed parameter was well above 0.05, this factor won't be considered in the discussions.

Table 52 – Taguchi study KE MFS Analysis of Variance ( $\alpha=95\%$ ).

| Source                | DF | Adj SS | Adj MS  | F-Value | p-Value |
|-----------------------|----|--------|---------|---------|---------|
| Extrusion Temperature | 2  | 143.78 | 71.890  | 72.13   | 0.000   |
| Layer Thickness       | 2  | 349.80 | 174.900 | 175.47  | 0.000   |
| Print Speed           | 2  | 22.24  | 11.121  | 11.16   | 0.001   |
| Extrusion Multiplier  | 2  | 392.84 | 196.419 | 197.06  | 0.000   |
| Error                 | 18 | 17.94  | 0.997   |         |         |
| Total                 | 26 | 926.60 |         |         |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

Table 53 – Taguchi study KE FM Analysis of Variance ( $\alpha=95\%$ ).

| Source                | DF | Adj SS  | Adj MS   | F-Value | p-Value |
|-----------------------|----|---------|----------|---------|---------|
| Extrusion Temperature | 2  | 0.22839 | 0.114195 | 24.42   | 0.000   |
| Layer Thickness       | 2  | 0.38443 | 0.192216 | 41.10   | 0.000   |
| Print Speed           | 2  | 0.02789 | 0.013944 | 2.98    | 0.076   |
| Extrusion Multiplier  | 2  | 0.16084 | 0.080419 | 17.20   | 0.000   |
| Error                 | 18 | 0.08418 | 0.004677 |         |         |
| Total                 | 26 | 0.88573 |          |         |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

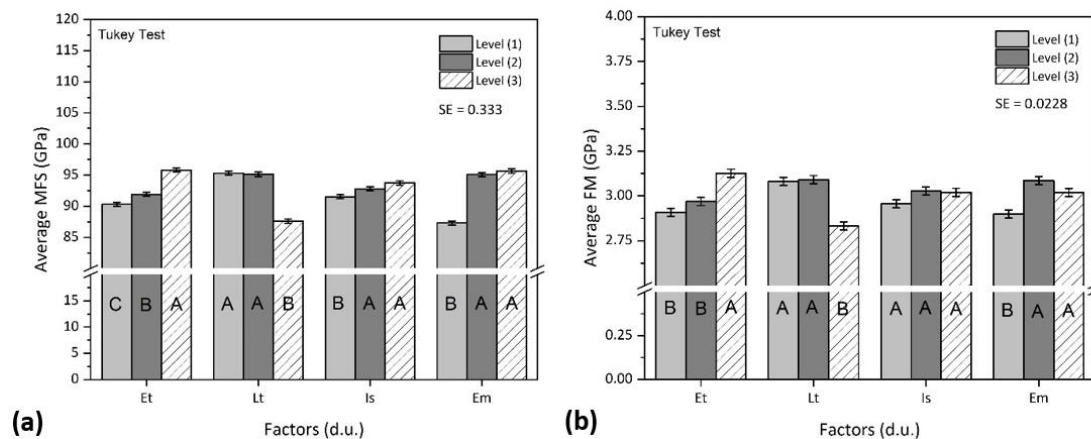


Figure 97 - The Average Maximum Flexural Strength and the Average Flexural Modulus related to the significant parameters and levels (KE).

Overall, the behaviour of both responses when affected by one factor is very similar. Just like the analysis that has been made for the PM supplier the only factor that seemed to haven't had a similar influence is the extrusion multiplier.

### Extrusion Temperature

For both MFS and FM, the average response tends to increase when a temperature of 235°C is used. In case of MFS, the use of 235°C has caused the average

response to increase by **6%** whereas the FM the average response as increase by almost **11%**. This phenomenon was predictable since the higher the temperature, the stronger the bonding between the layers will be.

#### Layer Thickness

The analyse of this parameter has proved that the average MFS and FM responses tend to increase by **8%** when a thickness of either 0.1mm or 0.2mm is used. Despite the reasons for this phenomenon being basically the same ones that have been pointed out for the previous supplier, the patterns here are quite different. First, the impact on one response for using 0.1mm is not that big compared to what has been observed for PM to the point that both thicknesses (0.1mm and 0.2mm) were considered statistically equal on both responses. Second, despite the use of a thickness of 0.1mm causes the FM to-this phenomenon might not have been influenced by the printing parameters and rather been caused by the material's imperfections.

#### Print Speed

The graphic (a) shows that the average response of MFS tends to increase by **2%** when a printing speed of 80mm/s is used. This phenomenon is curious because according to section 2.3.4 the increase of the printing speed might lead to insufficient wetting between the layers and can cause the formation of voids which is harmful for the overall mechanical properties. Taking this theory into consideration, the increase of the average MFS can only be attributed to the material's characteristics.

The graphic (b) shows the FM average responses but as it has been mentioned before, this factor isn't significant and therefore not worth of discussion.

#### Extrusion Multiplier

Just like what has been noted in the PM supplier analysis, the extrusion multiplier has different behaviours between the two responses. On one hand, the average MFS response tends to increase by **9%** when an extrusion multiplier of either 1.0 or 1.1 is used (for the PM the increase was of 6%). This scenario was predictable since a higher multiplier led to higher density of the sample which leads to stronger layer's bonding. On the other hand, the use of an extrusion multiplier of 1.0 seemed to have benefited the FM response by **6%** (for the PM the increase was of 3%). Because there isn't a clear pattern, this observation can only be justified by the material's characteristics.

The overall conclusion is that the KE filament is less dependent of the printing parameters compared with the PM filament.

#### 4.3.3 F3D

The last filament supplier to be analysed is the F3D. Therefore, the aim of this section is to evaluate the influence of the four factors on the variation of the three average responses (MFS, FM and F3D) obtained by the F3D flexural samples.

#### Mass

Just how has been done for PM and KE suppliers, a calculation of the average mass, standard deviation, and coefficient of variance for each condition of Taguchi L9 array was carried out (Table 54). The experimental procedure to obtain the mass measurements was explained in section 3.5.

Table 54 – Mass measurement of Taguchi\_F3D.

| Condition          | T1   | T2   | T3   | T4   | T5   | T6   | T7   | T8   | T9   |
|--------------------|------|------|------|------|------|------|------|------|------|
| <b>Average [g]</b> | 5.79 | 6.09 | 6.39 | 6.92 | 5.42 | 5.82 | 6.35 | 6.65 | 5.24 |
| <b>Std.D [g]</b>   | 0.02 | 0.02 | 0.01 | 0.00 | 0.00 | 0.01 | 0.01 | 0.01 | 0.00 |
| <b>CV (%)</b>      | 0.30 | 0.33 | 0.09 | 0.04 | 0.09 | 0.13 | 0.12 | 0.22 | 0.06 |

The results were evaluated through the statistical analysis of variance (ANOVA) and the analysis parameters are shown in Table 55. According to the p-Values it was confirmed that all the parameters were significant and unlike the previous filament suppliers, the extrusion multiplier was the factor that stood out. The graphic in Figure 98 shows the average mass values by factor along with their respective levels as well as a comparison between the averages that were carried out through a Tukey's test. The statistical differences between each level are represented by the letters A, B or C.

Table 55 – Taguchi study F3D Mass Analysis of Variance ( $\alpha=95\%$ ).

| Source                                                                       | DF | Adj SS  | Adj MS  | F-Value  | p-Value |
|------------------------------------------------------------------------------|----|---------|---------|----------|---------|
| <b>Extrusion Temperature</b>                                                 | 2  | 0.00577 | 0.00289 | 23.44    | 0.000   |
| <b>Layer Thickness</b>                                                       | 2  | 1.32904 | 0.66452 | 5396.10  | 0.000   |
| <b>Print Speed</b>                                                           | 2  | 0.00701 | 0.00350 | 28.44    | 0.000   |
| <b>Extrusion Multiplier</b>                                                  | 2  | 6.10972 | 3.05486 | 24806.37 | 0.000   |
| <b>Error</b>                                                                 | 18 | 5.97    | 0.332   |          |         |
| <b>Total</b>                                                                 | 26 | 1319.59 |         |          |         |
| <b>Note:</b> DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares |    |         |         |          |         |

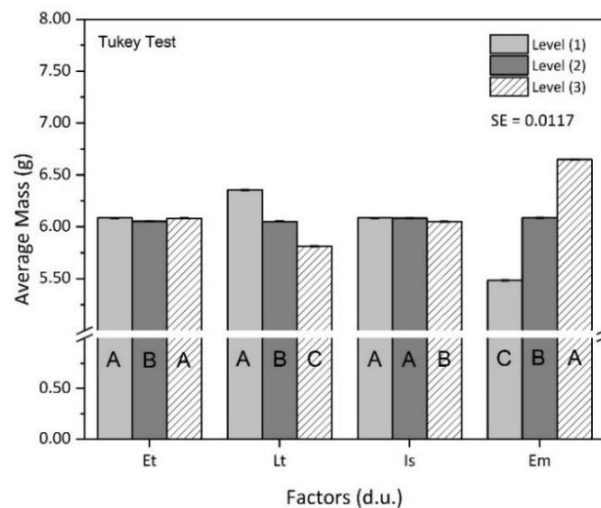


Figure 98 - Average mass related with the significant parameters and levels (Taguchi\_F3D).

### Extrusion Temperature

The analyse of the responses for the extrusion temperature shows that the average mass tends to increase when a temperature of either 215°C or 235°C is used. This nonlinear behaviour has been also observed for the PM suppliers (section 4.3.1). As a result, the F3D is not at all dependent of this factor and these variances may be justified by this material's rheological characteristics.

### Layer Thickness

The layer thickness columns show that for lower values of thickness the mass tends to increase by **9%** the same increase that has been observed on the previous suppliers.

### Printing Speed

According to Tukey's test, the printing speed of 80mm/s causes de average mass to decrease, yet very slightly. On the other hand, the average mass tends to increase if a printing speed of either 40mm/s or 60mm/s is used. Compared with the KE, both behaviours are equal most likely for the same reasons (section 4.3.2).

### Extrusion Multiplier

The last factor shows that the use of an extrusion multiplier of 1.1 causes the average mass to increase by approximately **21%** compared to average mass obtained by using a 0.9 multiplier. Curiously, the same percentual difference has been calculated for the KE supplier which means these two suppliers share the same justification for their

average mass variation. The use of lower extrusion multipliers (0.9 and 1.0) will cause the average response to significantly decrease. In Table 56 it's possible to check the theoretical mass of a F3D flexural sample and the average mass best levels obtained by each factor.

Table 56 - Comparison between the theoretical mass and the best levels average mass (F3D).

| F3D ASTM D790             |                              |             | Factor [g]     |                |                |                |
|---------------------------|------------------------------|-------------|----------------|----------------|----------------|----------------|
| Volume [cm <sup>3</sup> ] | Density [g/cm <sup>3</sup> ] | Theoretical | E <sub>t</sub> | L <sub>t</sub> | P <sub>s</sub> | E <sub>m</sub> |
| 5.16                      | 1.24                         | 6.42        | 6.09           | 6.36           | 6.09           | 6.65           |

Just like the previous filament suppliers the parameter that achieved the closest average mass value was the layer thickness. Just like the KE samples, this average mass fell short by just only 1%. The average mass obtained by the parameters extrusion temperature and print speed were once again equal and both fell approximately 5% below the theoretical value. Finally, as it has been observed for PM and KE, the use of an extrusion multiplier of 1.1 obtained the highest average mass as the samples were on average approximately 4% heavier compared to the theoretical mass.

#### MFS and FM results analysis

To conclude the Taguchi study, the influence of the four factors on MFS and FM average responses must be carried out. Just like how has been done for PM and F3D supplier, the MFS and FM average responses were obtained following the experimental procedure explained in section 3.5 Their respective standard deviations and coefficients of variance were calculated according to each condition of the Taguchi L9 array (Table 57).

Table 57 - Results of the flexural stress analysis by experimental condition (F3D).

| Condition                                                           | MFS (MPa)            | CV (%) | FM (GPa)           | CV (%) |
|---------------------------------------------------------------------|----------------------|--------|--------------------|--------|
| <b>T1</b>                                                           | 94.14 ± 0,55         | 0.6    | 3.05 ± 0.07        | 2.3    |
| <b>T2</b>                                                           | 95.70 ± 0,18         | 0.2    | 3.03 ± 0.04        | 1.3    |
| <b>T3</b>                                                           | 89.04 ± 0,45         | 0.5    | 2.65 ± 0.01        | 0.4    |
| <b>T4</b>                                                           | <b>107.97</b> ± 0,15 | 0.1    | <b>3.53</b> ± 0.01 | 0.4    |
| <b>T5</b>                                                           | 89.39 ± 1,00         | 1.1    | 3.08 ± 0.01        | 0.3    |
| <b>T6</b>                                                           | 84.89 ± 0,38         | 0.4    | 2.69 ± 0.05        | 1.7    |
| <b>T7</b>                                                           | 91.92 ± 0,88         | 1.0    | 2.89 ± 0.03        | 1.1    |
| <b>T8</b>                                                           | 94.04 ± 0,70         | 0.7    | 2.85 ± 0.02        | 0.9    |
| <b>T9</b>                                                           | 82.38 ± 0,13         | 0.2    | 2.79 ± 0.02        | 0.9    |
| <b>Note:</b> MFS – Maximum Flexural Strength; FM – Flexural Modulus |                      |        |                    |        |

From the Table 57 it can be observed that the highest maximum flexural stress (107.97 MPa) and the maximum flexural modulus (3.53 GPa) both belong to the same Taguchi's condition (T4). Exactly how it has been proceeded with the previous suppliers, the average MFS and FM responses were evaluated through the statistical analysis of ANOVA. According to the p-Values (Table 58 and Table 59), it was confirmed that the all the parameters were significant and thus worth of discussion.

Table 58 – Taguchi study F3D MFS Analysis of Variance ( $\alpha=95\%$ ).

| Source                | DF | Adj SS  | Adj MS  | F-Value | p-Value |
|-----------------------|----|---------|---------|---------|---------|
| Extrusion Temperature | 2  | 107.90  | 53.950  | 162.63  | 0.000   |
| Layer Thickness       | 2  | 738.57  | 369.284 | 1113.22 | 0.000   |
| Print Speed           | 2  | 137.56  | 68.780  | 207.34  | 0.000   |
| Extrusion Multiplier  | 2  | 329.59  | 164.794 | 496.78  | 0.000   |
| Error                 | 18 | 0.00222 | 0.00012 |         |         |
| Total                 | 26 | 7.45375 |         |         |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

Table 59 – Taguchi study F3D FM Analysis of Variance ( $\alpha=95\%$ ).

| Source                | DF | Adj SS  | Adj MS   | F-Value | p-Value |
|-----------------------|----|---------|----------|---------|---------|
| Extrusion Temperature | 2  | 0.31792 | 0.158961 | 130.05  | 0.000   |
| Layer Thickness       | 2  | 0.91868 | 0.459339 | 375.79  | 0.000   |
| Print Speed           | 2  | 0.36088 | 0.180040 | 147.29  | 0.000   |
| Extrusion Multiplier  | 2  | 0.08878 | 0.044391 | 147.29  | 0.000   |
| Error                 | 18 | 0.02200 | 0.001222 |         |         |
| Total                 | 26 | 1.70747 |          |         |         |

**Note:** DF – Degrees of Freedom; SS – Sum of Squares; MS – Mean Squares

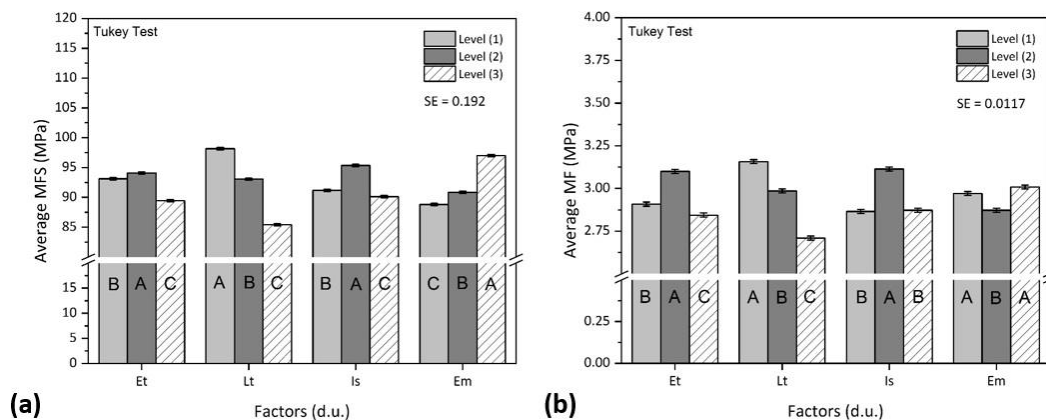


Figure 99 - The Average Maximum Flexural Strength and the Average Flexural Modulus related to the significant parameters and levels (Taguchi\_F3D).

The overall results from the graphics of Figure 99 show a very similar behaviour compared with the PM supplier. Just like what has been observed for that supplier the

layer thickness seems to have the biggest impact on the mechanical properties of the samples. The main differences though seem to have been on the FM responses as the following analysis for each factor will show.

#### Extrusion Multiplier

Both graphics from Figure 99 that a temperature of 225°C has caused the MFS response to increase approximately **5%** whereas the FM response almost increased **9%**. At the same time, both responses tended to decrease when a temperature of 235°C is applied. Combining these results with the theory it seems that for this specific material the benefits of rising the temperature are only worth until approximately 225°C.

#### Layer Thickness

As it has been mentioned, this parameter had the biggest influence on both responses and resembles what has been observed for the PM supplier where both responses have increased by 17% thanks to the use of the lowest layer height. Nonetheless, in this supplier the MFS average response tended to increase by only **13%** whereas the FM average response tended to increase by approximately **17%**.

#### Print Speed

Compared with the previous suppliers, this factor seemed to have had a bigger impact on both MFS and FM responses. Nonetheless, both tend to increase when a printing speed of 60mm/s is used. The average MFS response has increased by **6%** while the FM response has increased by **11%**. Once again, there hasn't been a clear pattern in this factor which would allow a connection between these results and what is already known about this parameter's variation. Focusing on this situation, the chemical and rheological properties of the F3D seemed to have had a bigger influence rather the printing parameter itself.

#### Extrusion Multiplier

Starting with graphic (a), it is shown that for higher extrusion multipliers, the average MFS response tends to increase by **10%** (the increase was of 6% for PM and of 9% for KE). This pattern goes along what has been studied in the literature (section 2.3.4) and to what has been observed for the MFS of previous suppliers.

Contrary, the influence of this factor on the FM average response has proved to be quite different compared to the previous suppliers since the graphic shows that the use of an extrusion multiplier of 1.0 has caused the average FM response to decrease. On the other hand, the use of other extrusion multipliers has made this response to increase approximately by 5%. Once again, no linear pattern can be determined, and the samples mechanical properties aren't greatly influenced by this printing parameter.

#### 4.3.4 Verification Models

This section has two main goals. The first is to explain how the printing parameters for each supplier's "Verification Model" printing configuration were sorted out. The second goal was to compare the average responses obtained with the VM configurations with the average responses obtained with the printing configurations of Castro [75].

##### Selection of the MV printing parameters

The underlying principles that were used to select the parameters that are going to be considered in this analysis are addressed in section 3.5.1. As it has been mentioned in that section, one level to be selected for the final configuration must be the best option for at least two different responses. However, this criterion may not be enough to evaluate every single situation and therefore extra analysis will have to be carried out to determine which levels are selected for the final VM configurations. The path that has been taken to reach the final VM configurations will be fully described in this section.

##### PM Supplier

As it can be seen in Table 60 all responses consider an extrusion temperature of 235°C. Therefore, this will be chosen extrusion temperature for the final VM. When it comes to layer thickness and printing speed both proved to have a level that is statistically better in at least two different responses. As a result, a thickness of 0.1mm and a speed of 60 mm/s are the selected levels. The final factor to be analysed is the extrusion multiplier. From this, it's possible to confirm that an extrusion multiplier of 1 has proved to be the best level for the FM response. Since the MFS also considers this level, the main criterion is fulfilled and therefore 1.0 is the value to be considered for the final PM VM configuration.

Table 60 – PM Verification Model considered levels and final configuration.

| Factors                                                                               | Best level responses |            |            | VM  |
|---------------------------------------------------------------------------------------|----------------------|------------|------------|-----|
|                                                                                       | MFS                  | FM         | Mass       |     |
| Extrusion temperature (°C) ( $E_t$ )                                                  | 225 or 235           | 225 or 235 | 215 or 235 | 235 |
| Layer thickness (mm) ( $L_t$ )                                                        | 0.1                  | 0.1        | 0.1        | 0.1 |
| Print speed (mm/s) ( $P_s$ )                                                          | 60                   | 60         | 80         | 60  |
| Extrusion multiplier (d.u.) ( $E_m$ )                                                 | 1.0 or 1.1           | 1.0        | 1.1        | 1   |
| Note: MFS – maximum flexural strength; FM – flexural modulus; VM – Verification Model |                      |            |            |     |

### KE Supplier

Since the best level for all responses only consider an extrusion temperature of 235°C, this will be chosen extrusion temperature for the final VM. When it comes to layer thickness the average mass response has only considered one level of 0.1mm. Since both MFS and FM responses also consider this thickness, the main criterion is fulfilled and the layer thickness of the final VM will be 0.1mm. The printing speed analysis will only consider the levels of MFS and Mass responses since this factor was not considered significant by ANOVA in FM. As so, because a printing velocity of 60mm/s is considered twice this will be the final print speed. Finally, an extrusion multiplier of 1.1 is considered in every single response and therefore will be selected for the final KE VM configuration.

Table 61 - KE Verification Model considered levels and final configuration.

| Factors                                                                               | Best level responses |            |          | VM  |
|---------------------------------------------------------------------------------------|----------------------|------------|----------|-----|
|                                                                                       | MFS                  | FM         | Mass     |     |
| Extrusion temperature (°C) ( $E_t$ )                                                  | 235                  | 235        | 235      | 235 |
| Layer thickness (mm) ( $L_t$ )                                                        | 0.1 or 0.2           | 0.1 or 0.2 | 0.1      | 0.1 |
| Print speed (mm/s) ( $P_s$ )                                                          | 60 or 80             | Not Sig.   | 40 or 60 | 60  |
| Extrusion multiplier (d.u.) ( $E_m$ )                                                 | 1 or 1.1             | 1 or 1.1   | 1.1      | 1.1 |
| Note: MFS – maximum flexural strength; FM – flexural modulus; VM – Verification Model |                      |            |          |     |

### F3D Supplier

For the F3D supplier, an extrusion temperature of 225°C chosen because it was the only temperature be considered in at least two different responses. When it comes to layer thickness there's no doubt that 0.1mm is selected thickness since this the only level to be considered in every single response. As for the print speed there is only one level that is considered in every single response and therefore the final configuration will have a print speed of 60mm/s. To finish the analysis of the F3D printing configuration

the use of an extrusion multiplier of 1.1 is a level that is not only considered in every single response but is also the best level for MFS and Mass responses. The final F3D VM configuration is shown in Table 62.

Table 62 – F3D Verification Model considered levels and final configuration.

| Factors                                                                               | Best level responses |            |            | VM  |
|---------------------------------------------------------------------------------------|----------------------|------------|------------|-----|
|                                                                                       | MFS                  | FM         | Mass       |     |
| Extrusion temperature (°C) ( $E_t$ )                                                  | 225                  | 225        | 215 or 235 | 225 |
| Layer thickness (mm) ( $L_t$ )                                                        | 0.1                  | 0.1        | 0.1        | 0.1 |
| Print speed (mm/s) ( $P_s$ )                                                          | 60                   | 60         | 40 or 60   | 60  |
| Extrusion multiplier (d.u.) ( $E_m$ )                                                 | 1.1                  | 0.9 or 1.1 | 1.1        | 1.1 |
| Note: MFS – maximum flexural strength; FM – flexural modulus; VM – Verification Model |                      |            |            |     |

#### Response analyses for each supplier

In this part, an analysis of the average responses obtained by the flexural samples printed with the “Verification Model” will be carried out. The results will also be compared with the responses obtained by the samples printed with the configuration of Castro [75](Table 13).

#### Mass

After the samples were printed and weighted, the average mass, standard deviation and coefficient of variance were calculated for every filament supplier as shown in Table 63.

Overall, the graphic from Figure 100 shown an increase of the average mass on every filament supplier when the VM configuration is used. This situation could be mainly explained by the lower layer thickness of the VM models which happens to be of only 0.1mm (Castro [75] configuration uses 0.2mm).

Focusing on the variations of each supplier, the KE and the F3D suppliers have registered an increase of 14% and 15%, respectively whereas the PM had an increase of only 5%. Coincidentally, the bigger increase that has been observed for the average mass of these two suppliers meet their VM extrusion multiplier of 1.1 which has proved to have a major influence on the sample’s mass. The remaining parameters remain almost equal.

Table 63 – Mass measurements obtained by the VM and [Castro, 2021] printing configurations.

|                         | Verification Model |             |             | [Castro, 2021] |             |             |
|-------------------------|--------------------|-------------|-------------|----------------|-------------|-------------|
|                         | PM                 | KE          | F3D         | PM             | KE          | F3D         |
| <b>Average Mass [g]</b> | <b>6.53</b>        | <b>6.97</b> | <b>6.94</b> | <b>6.2</b>     | <b>6.09</b> | <b>6.04</b> |
| <b>Std. Deviation</b>   | 0.01               | 0.01        | 0.02        | 0.01           | 0.01        | 0.00        |
| <b>CV (%)</b>           | 0.09               | 0.23        | 0.29        |                |             |             |

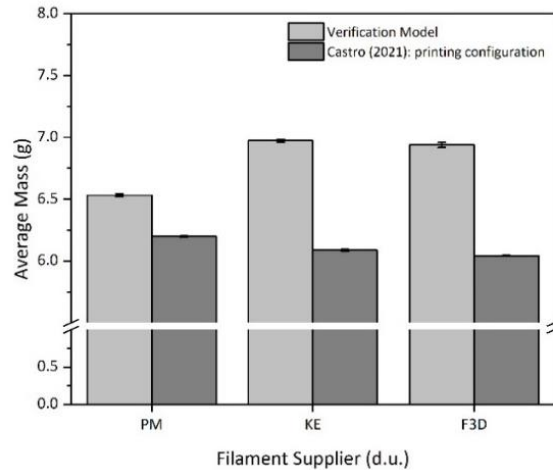


Figure 100 - Average mass related with the significant parameters and levels (Verification Model).

### MFS and FM results analysis

The calculation of the MFS and FM responses followed the same procedure that has been explained in previous sections. The mean, standard deviation, and the coefficient of variance of each response for each supplier is shown in Table 64. Observing the values, it has been observed that the maximum MFS belongs to PM\_VM condition and the maximum FM corresponds to [Castro, 201] \_F3D condition. The values were then coupled with representations of the graphics from Figure 101 which allows for further comparison and characteristics to be outlined.

Table 64 - Results of the flexural tests by filament supplier (Verification Model).

| Sample                                                                                            | "Verification Model" Configuration |             |               |             |               |             |
|---------------------------------------------------------------------------------------------------|------------------------------------|-------------|---------------|-------------|---------------|-------------|
|                                                                                                   | PM                                 |             | KE            |             | F3D           |             |
|                                                                                                   | MFS (MPa)                          | FM (GPa)    | MFS (MPa)     | FM (GPa)    | MFS (MPa)     | FM (GPa)    |
| <b>Mean</b>                                                                                       | <b>102.90</b>                      | <b>3.38</b> | <b>100.95</b> | <b>3.23</b> | <b>101.81</b> | <b>3.14</b> |
| <b>Std. Dev.</b>                                                                                  | 0.52                               | 0.04        | 0.63          | 0.03        | 1.04          | 0.06        |
| <b>CV (%)</b>                                                                                     | 0.51                               | 1.26        | 0.63          | 1.03        | 1.02          | 1.95        |
|                                                                                                   | [Castro, 2021] Configuration       |             |               |             |               |             |
|                                                                                                   |                                    |             |               |             |               |             |
|                                                                                                   |                                    |             |               |             |               |             |
| <b>Mean</b>                                                                                       | <b>99.21</b>                       | <b>3.22</b> | <b>99.10</b>  | <b>3.22</b> | <b>92.57</b>  | <b>2.99</b> |
| <b>Std. Dev.</b>                                                                                  | 0.64                               | 0.02        | 0.63          | 0.03        | 0.84          | 0.05        |
| <b>Note:</b> MFS – Maximum Flexural Strength; FM – Flexural Modulus; CV – Coefficient of Variance |                                    |             |               |             |               |             |

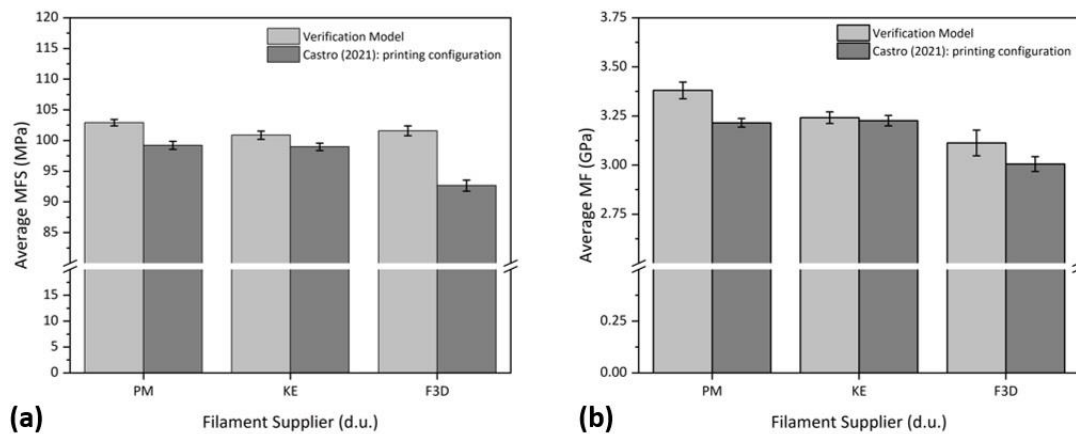


Figure 101 – Average responses obtained by filament supplier with the VM configuration (light grey) and [Castro, 2021] configuration (a) MFS; (b) FM.

Focusing on the maximum flexural strength, as it can be seen in Figure 101 (a), this response has increased for every filament supplier when the VM printing configuration was used. The biggest discrepancy whatsoever, has been observed on the F3D supplier where the average response has increased approximately **10%**. Overall, this phenomenon can be attributed to larger amounts of thermal energy since in all VM configurations the extrusion temperature is at least 10°C higher. This allows for raster diffusion and bonding of the deposited layers.

On the other hand, from the graphic of Figure 101 (b), two main phenomena can be observed. First, the FM average response obtained using the VM configurations is always higher. Secondly, there's a pattern in which both configurations' average FM responses gradually decrease according to the filament supplier. These two observations may suggest that the FM would be more dependent on the material transformations during the printing process rather than the printing parameters.

#### 4.3.5 Temperature Towers

The temperature towers that were printed for each manufacturer are shown in Figure 102. The ideal extrusion temperatures are also marked. Before this analysis can go forward, it's important to take into consideration that the F3D tower was printed through a "mosquito" extruder from BondTech thus following the same experimental procedure that was carried out for this supplier during the parametric study. By analysing each temperature "floor" of each tower it's possible to choose the ideal temperatures for each filament supplier (Table 65).

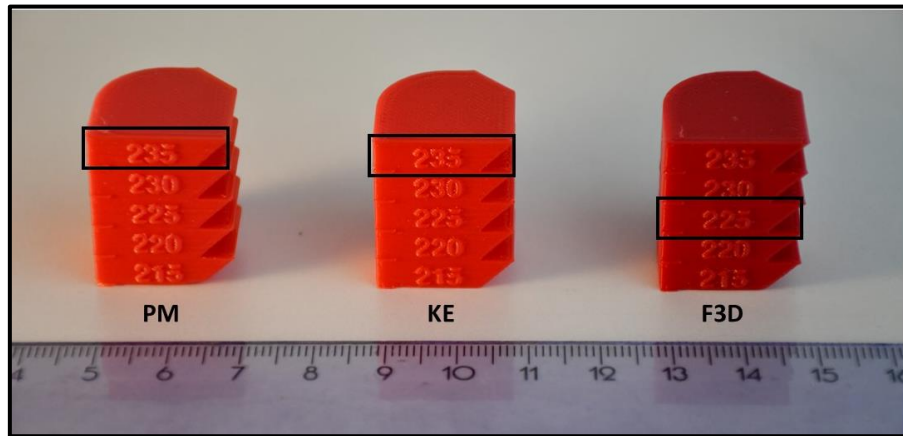


Figure 102 – Temperature towers along with the ideal extrusion temperatures.

Table 65 – Chosen temperatures for each supplier.

| Filament Supplier | Temperature [°C] |
|-------------------|------------------|
| PM                | 235              |
| KE                | 235              |
| F3D               | 225              |

The results in Table 65 show that the F3D is the only supplier to have a lower ideal extrusion temperature of 225°C while the other two suppliers had higher ideal extrusion temperatures of 235°C. These values are within the temperature range claimed by the manufacturers.

From these results, it's possible to conclude that the temperature variation changes the fluidity and stabilizing/cooling ability of the material. These changes in the viscosity of each material proves that this property is somehow affected by the different additives used by each manufacturer. Furthermore, each supplier might require a specific printing configuration to get the best quality by the obtained printed parts.



## 5. Conclusions

This investigation work has allowed the research on a broad and intricate topic such as 3D printing. Although FFF is a technology that allows for entry level users to rapidly become mildly proficient, dealing with abstract phenomenon such as polymer degradation or co-dependency of multiple printing parameters, requires a very high level of knowledge and skill. Yet, the amount of research work that has been laid out throughout this dissertation project, has made it possible to achieve a bird's-eye view over a wide range of topics such as polymer's science, additive manufacturing, and fused filament fabrication technologies. Thanks to this knowledge a deep and more reliable interpretation of the experimental outcomes could be performed.

Starting with the filament characterization techniques, overall, the experimental results corresponded to the data claimed by the filament manufacturers. The Fourier-transform infrared spectroscopy (FTIR) has allowed to conclude that the identified bands corresponded to PLA's. Furthermore, the FTIR analysis of the samples that were submitted to degradation conditions confirmed that no significant molecular changes have occurred. However, due to limitations of these techniques, a more depth analysis on the thermal, chemical, and rheological properties of the polymers through characterization techniques such as Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Chromatography and Measurement of the Fluid Index (MFI) is also recommended.

In general, the analysis on the influence of the degradation mechanisms on the mechanical properties of PLA printed samples have proved to be quite tough and abstract. The existence of few investigations works about the impact of some of these external environments on the mechanical properties of the samples, left a poor starting point for this investigation, yet it has opened new doors for new theories. Overall, regardless of the external condition at which a sample was submitted to, there was always an impact on its responses especially on MFS and FM.

Regarding the degradation study sample's mass, overall, it has been observed that this response tends to increase when a sample is submitted to any kind of adverse condition. The evolution is slightly different in each material, yet this might be justified

by each material's own properties. The overall analysis of the MFS and FM responses have shown that despite the presence of some common patterns, there're still some major differences in the evolution of this responses across the three filament suppliers.

Starting with the major common point which happens to be the salt solution, this condition has proved to be far worst compared to the others when it comes to the degradation rate. Speaking of MFS, the KE supplier has suffered a considerable decrease of 20% which suggest that the additives used in this supplier are strongly affected by the salt water. As for the FM, this condition was the only one that as affected (and in a quite dramatic way) this response by making all supplier's FM to drop an average of 25% compared to the w/treatment condition modulus. These results suggest the higher sensitivity to salt water from the general manufacturers. This sensitivity seems to accelerate the hydrolyse reaction which affects the molecular structural integrity of the material. Another interesting aspect to consider across the FM responses is the fact that for all suppliers, the landfill and humidity conditions cause the FM to increase quite considerably. This phenomenon might be explained by a possible re-crystallization of the polymeric chains caused by these external adverse conditions.

Moving onwards to the parametric study, given the main objective of studying three different filament suppliers by evaluating their influence on three responses trough the variation of some printing parameters, it became clear the importance of a good experiment design for the sake of a successful research. To achieve this, prior to the initial stages of the experimental work, several well-structured guidelines were stablished. Consequently, it was possible to recover a vast amount of information and technical data in a structured manner which has proved to be quite essential for the final stages of the parametric study.

Starting with the influence on the mass, this work as proved that both layer thickness and extrusion multiplier have portrayed a significant role in the variation of this parameter. The layer thickness evolution has shown to be inversely proportional to the increase of mass whereas the use of bigger extrusion multipliers has caused the quantity of deposited material to increase 20% on average.

As for the maximum flexural strength (MFS) and flexural modulus (FM), the determining factor was, in most situations, the layer thickness. As it has been observed

for the average mass, lower values of layer heights have yielded in bigger values of MFS and FM. This phenomenon emphasises with the fact that FFF is multi-layered construction process where typical imperfections like the presence of voids between different rasters can lead to significant differences on mechanical behaviours.

It has also been observed that the evolution of the four parameters across the three filament suppliers have been different. In one hand, the KE supplier, unlike the other two suppliers, was a material that hasn't suffered any major variations on its responses. At the same time, this behaviour is more obvious for the layer thickness factor where the PM and the F3D have suffered variations of 17% whereas the KE has only shown a maximum variation of 8%. This may indicate that the KE is a material that isn't that highly dependent on the printing configurations. Moreover, the evolution pattern of the F3D average responses across the four factors has proved to be quite different from the PM and the KE suppliers. This may be justified by two possible scenarios. The first is the possibility of the chemical and the rheologic properties of this material have played a much more significant role, on the variation of the mechanical properties rather than the variation of the printing parameters. Secondly, it's also possible that the use of a different system (mosquito extruder) has somehow influenced the pattern evolution of the average responses.

Regarding the "verification model" average responses, the overall conclusion is that every result obtained with these configurations has improved compared with the results obtained using the printing configuration of Castro [75]. By taking a deeper look on the evolution of each response, it's possible to observe that the mass has significantly increased for the KE and the F3D whereas for the PM supplier the same behaviour could not been identified. Regarding the MFS, the F3D samples were the ones that have benefited the most whereas for the FM, no VM response has been considerable improved. On the opposite, the FM and the KE supplier have remained almost unchanged.

Finally, it was possible to build a printing configuration model for each filament supplier based on the evidence that has been gathered throughout the parametric study. Although the main and ambitious goal of this type of investigation is to achieve the best mechanical responses by using the lowest possible amounts of material, both

MFS and FM average responses have increased significantly for every single filament supplier.

In conclusion, the ease of access from users and technicians to printing equipment has turned FFF into one of the most popular 3D printing technologies worldwide. However, due to a wide range of available materials from multiple manufacturers, we still have a long way to go to master the influence of the printing parameters configurations on the chemical, thermal and physical properties of a 3D printed part. As a result, the scientific community as to keep searching for innovative solutions to fulfil the demands of an AM skyrocketing market. This work is only a small step in that direction.

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## Appendix

### A – Calibration Cubes Dimensions & Mass

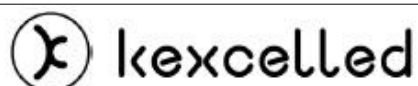
|               |   | Measure 1 [mm] | Measure 2 [mm] | Measure 3 [mm] | Mass [g] |
|---------------|---|----------------|----------------|----------------|----------|
| <b>Cube 1</b> | x | 14,98          | 14,99          | 14,99          | 4.04     |
|               | y | 14,98          | 14,98          | 14,95          |          |
|               | z | 15,11          | 15,09          | 15,08          |          |
| <b>Cube 2</b> | x | 15,11          | 15,11          | 15,08          | 4.02     |
|               | y | 15,04          | 15,04          | 15,03          |          |
|               | z | 15,12          | 15,11          | 15,11          |          |
| <b>Cube 3</b> | x | 15,05          | 15,07          | 15,06          | 4.02     |
|               | y | 14,96          | 14,96          | 14,97          |          |
|               | z | 15,04          | 15,04          | 15,05          |          |
| <b>Cube 4</b> | x | 15,02          | 15,01          | 15,02          | 4.02     |
|               | y | 14,94          | 14,95          | 14,95          |          |
|               | z | 15,04          | 15,03          | 15,04          |          |
| <b>Cube 5</b> | x | 15,00          | 14,99          | 14,99          | 4.01     |
|               | y | 14,93          | 14,93          | 14,93          |          |
|               | z | 15,02          | 15,01          | 15,01          |          |

## B – Filament Technical Data Sheet

### PM Filament Technical Sheet

| PLA FILAMENT         |                                                                                            |            |            |
|----------------------|--------------------------------------------------------------------------------------------|------------|------------|
| Use                  | is a material for the FDM (FFF) 3D printing additive technology                            |            |            |
| Material             | polylactid acid by NatureWork, biodegradabilic material, non petroleum product             |            |            |
| Diameters            | 1,75 or 2,90 mm                                                                            |            |            |
| Tolerance            | ± 0,05 mm                                                                                  |            |            |
| Weight               | 0,5 kg netto ± 5% / 0,7 kg brutto ± 5%                                                     |            |            |
|                      | 1,0 kg netto ± 5% / 1,3 kg brutto ± 5%                                                     |            |            |
|                      | 2,0 kg netto ± 5% / 2,4 kg brutto ± 5%                                                     |            |            |
| Packing              | spool in Vacuum ZIP bag, inserting to paper box, all in LDPE foil                          |            |            |
| Colours              | views on web <a href="https://www.filament-pm.com/pla">https://www.filament-pm.com/pla</a> |            |            |
| Solvents             | 1,2 Dichloroethane, Toluene, Tetrahydrofuran,                                              |            |            |
| Printing Properties: |                                                                                            |            |            |
| Temperature HE       | 200 – 230 °C                                                                               |            |            |
| Temperature HB       | 20-60 °C                                                                                   |            |            |
| Surface bed          | kapton, ultem, PET foil, commons for FDM printing                                          |            |            |
| Cooling print object | YES                                                                                        |            |            |
| Nozzle               | All diameters / for glitter using nozzle min 0,5 mm and more                               |            |            |
| Printer space        | Open / Close                                                                               |            |            |
| Material Properties: |                                                                                            |            |            |
| Thermal              | vicat softening temperature                                                                | ISO 306    | 55 °C      |
|                      | heat deflection temperature                                                                | ISO 75     | 55 °C      |
| Mechanical           | impact strength                                                                            | ISO 179    | 16 kJ/m²   |
|                      | flexural modulus                                                                           | ISO 178    | 3500 MPa   |
| Physical             | Density                                                                                    | ISO 1183/B | 1,24 g/cm³ |
|                      | Melt Flow Index                                                                            | ISO 1133   | 6 g/10 min |

## KE Filament Technical Sheet



### TECHNICAL DATA SHEET

#### KEXCELLED PLA K5

| Product code: | Revision Number: | Revision date: | TDS No.:      |
|---------------|------------------|----------------|---------------|
| PLA K5        | 02               | 2/04/2020      | KT04.012.0121 |

#### CHARACTERISTIC

Environmentally friendly | good interlayer bond | no buckling deformation | high melt flow rate.

#### IDENTIFICATION OF THE MATERIAL

|               |                 |
|---------------|-----------------|
| Trade name    | PLA K5          |
| Chemical name | Polylactic Acid |
| Use           | 3D printing     |
| Origin        | KEXCELLED       |

#### GUIDELINE FOR PRINT SETTINGS

|                    |                        |
|--------------------|------------------------|
| Nozzle temperature | 205±15℃                |
| Bed temperature    | 30~60℃                 |
| Bed modification   | Tape or glue below 60℃ |
| Active cooling fan | ON, 100%               |
| Layer height       | 0.2mm                  |
| Shell thickness    | ≥0.8mm                 |
| Print speed        | 40-80mm/s              |

Settings are based on a 0.4mm nozzle.

#### MATERIAL PROPERTIES

|                                               |                             | Test Method |
|-----------------------------------------------|-----------------------------|-------------|
| Melt temperature                              | ~160℃                       | ISO 11357   |
| Glass transition temperature                  | ~60℃                        | ISO 11357   |
| Melt flow rate (MFR) <sup>1</sup>             | 7~15 g/10min                | ISO 1133    |
| Heat deflection temperature(HDT) <sup>2</sup> | 57℃                         | ISO 75      |
| Vicat softening temperature(VST) <sup>3</sup> | 57℃                         | ISO 306     |
| density                                       | 1.23~1.26 g/cm <sup>3</sup> | ISO 1183    |
| Odor                                          | Odorless                    | /           |

## F3D Filament Technical Sheet

**Fil3D**  
PLA 3D850

**Tucab**  
soluções de fibra e carbono, lda



Impressão 3D

### FICHA TÉCNICA

| Matéria Prima- PLA 3D850                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |       |                 |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|-----------------|
| Propriedade                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Norma | Valores Típicos |
| Índice de Fluidez (210°C /2.16kg)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | D1238 | 7-9 g/10min     |
| Resistência na Deformação                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | D882  | 65.5 MPa        |
| Alongamento na Tração                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | D882  | 4.3%            |
| Densidade                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | D792  | 1,24 g/cc       |
| <ul style="list-style-type: none"> <li>Elevada precisão</li> <li>Não deforma</li> <li>Boa resistência mecânica e térmica</li> <li>Fácil manuseamento</li> <li>Elevada Rigidez</li> <li>Boa Adesão</li> <li>Baixa Probabilidade de <i>Stringing</i></li> <li>Pode ser submetido a um processo de <i>Annealing</i> para aumentar a sua resistência</li> <li>Matéria Prima de acordo com Regulamentação FDA</li> <li>Matéria Prima de Acordo com Regulamento (UE) N.º 10/2011 da Comissão (relativo aos materiais e objetos de matéria plástica destinados a entrar em contacto com os alimentos)</li> </ul> |       |                 |

| Diâmetro do Filmento (mm) | Gama de tolerância (mm) |
|---------------------------|-------------------------|
| 1,75                      | 1,67 a 1,83             |
| 2,85                      | 2,77 a 2,93             |

| Propriedade de Impressão        | Valores Típicos        |
|---------------------------------|------------------------|
| Temperatura de Impressão        | 210±20°C               |
| Mesa (Não Necessita)            | 60±10°C (Se aplicável) |
| Temperatura de <i>Annealing</i> | 80 a 130°C             |
| Temperatura de Fundição         | 210°C                  |

C - Average Flexural Stress/Displacement Curves

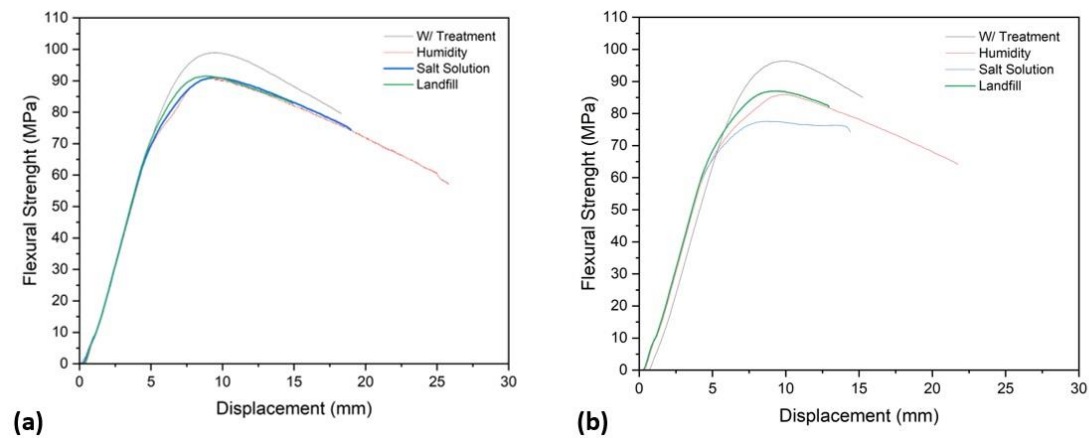


Figure 103 – PM Degradation Study Average Flexural Stress/Displacement Curves.

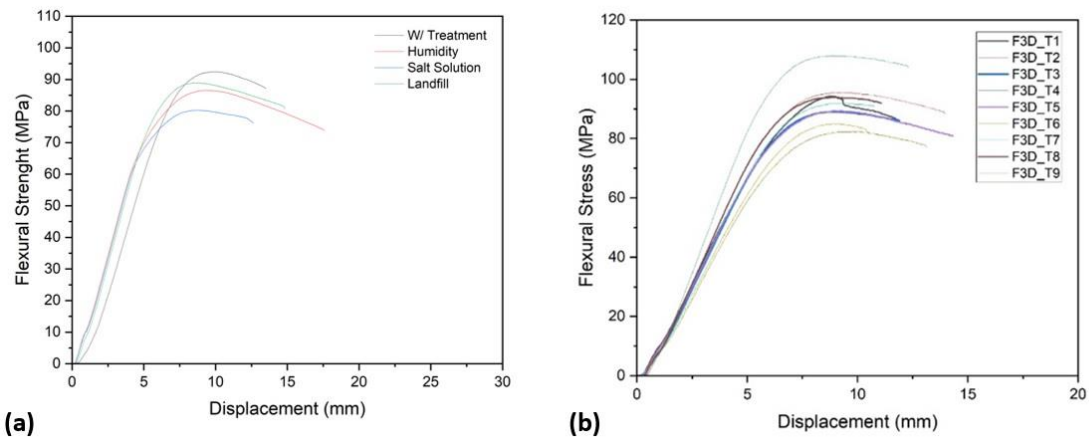


Figure 104 – F3D Degradation & Taguchi Average Flexural Stress/Displacement Curves.

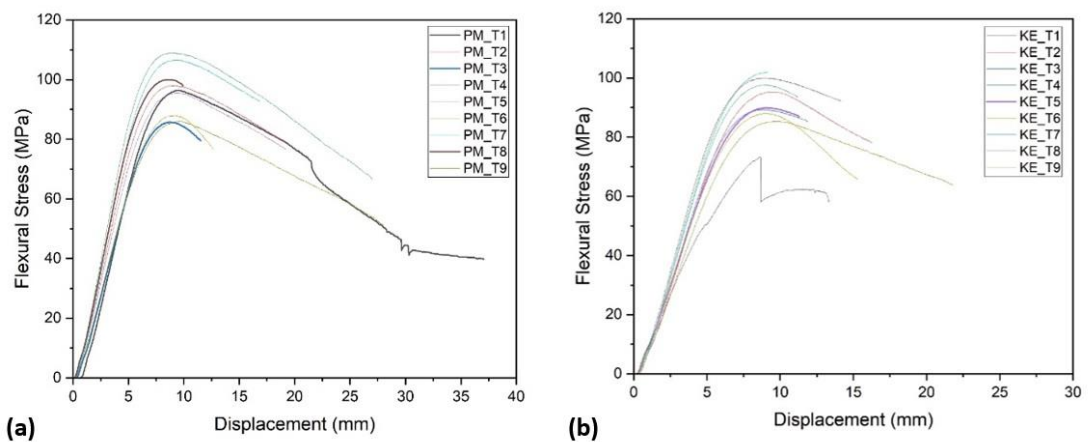


Figure 105 – PM\_KE Taguchi Average Flexural Stress/Displacement Curves.

## D – Microscopic Images

As explained in section 3.4, as a complementary analysis one sample from each filament supplier that has undergone an external adverse condition (landfill, humidity, and salt solution) were not submitted to mechanical trials and were instead placed under microscopical observation.

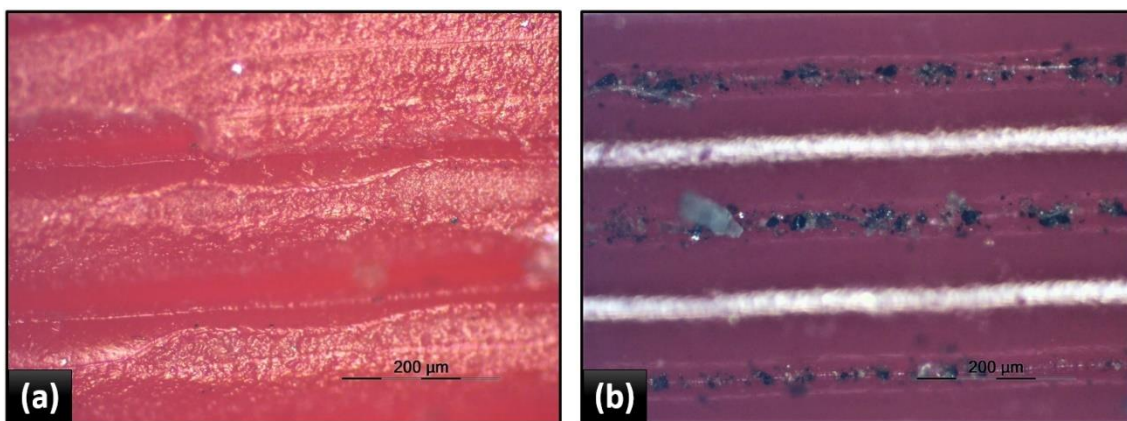


Figure 106 – Microscopical Images of B2\_PM: (a) Sample's Core; (b) Sample's Surface.

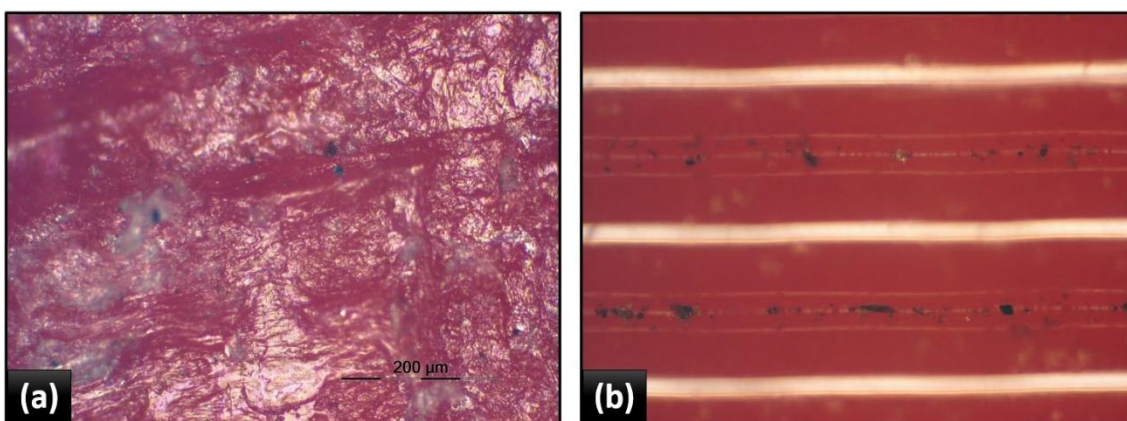


Figure 107 - Microscopical Images of B2\_KE: (a) Sample's Core; (b) Sample's Surface.

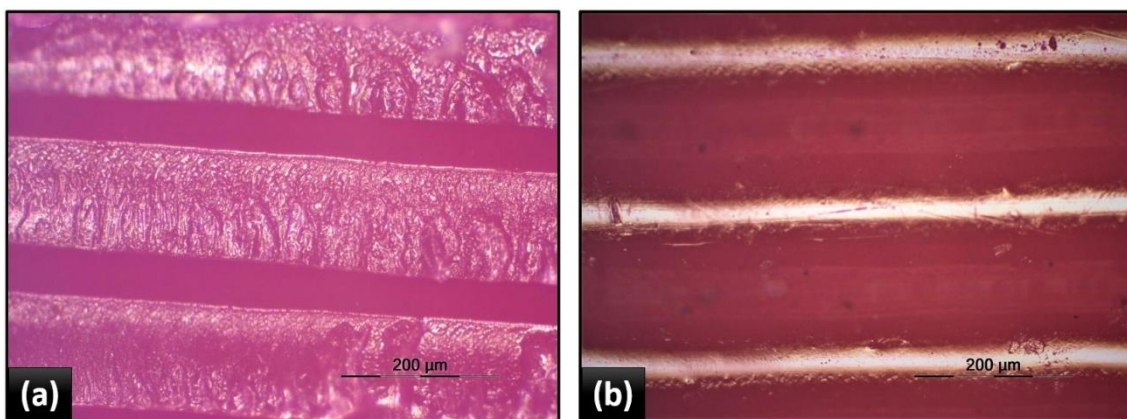


Figure 108 - Microscopical Images of B2\_F3D: (a) Sample's Core; (b) Sample's Surface.

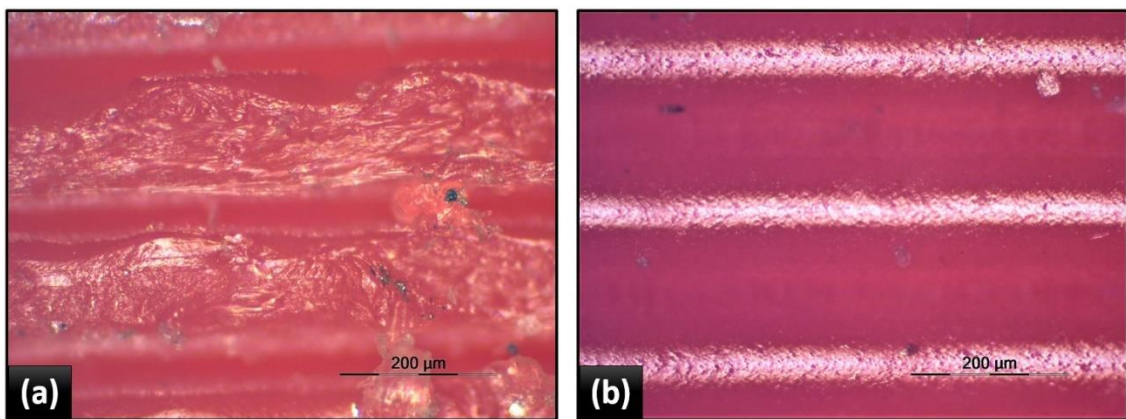


Figure 109 - Microscopical Images of B3\_PM: (a) Sample's Core; (b) Sample's Surface.

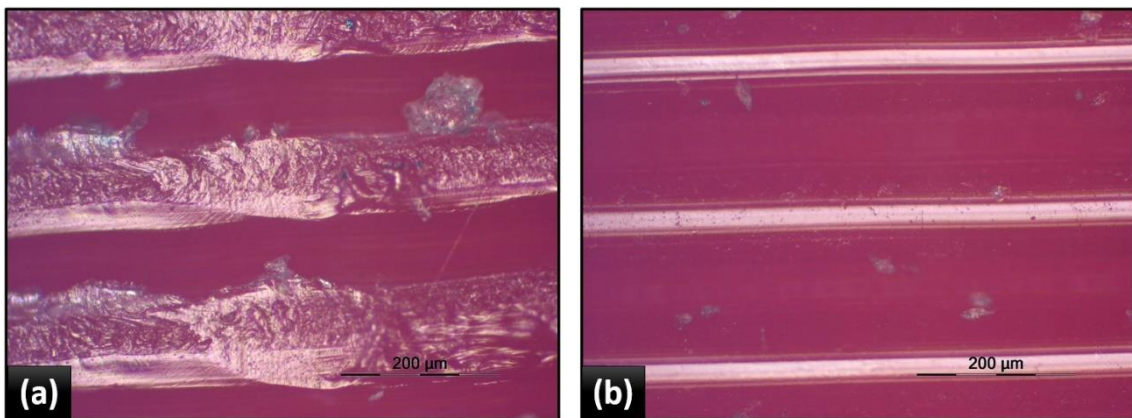


Figure 110 - Microscopical Images of B3\_KE: (a) Sample's Core; (b) Sample's Surface.

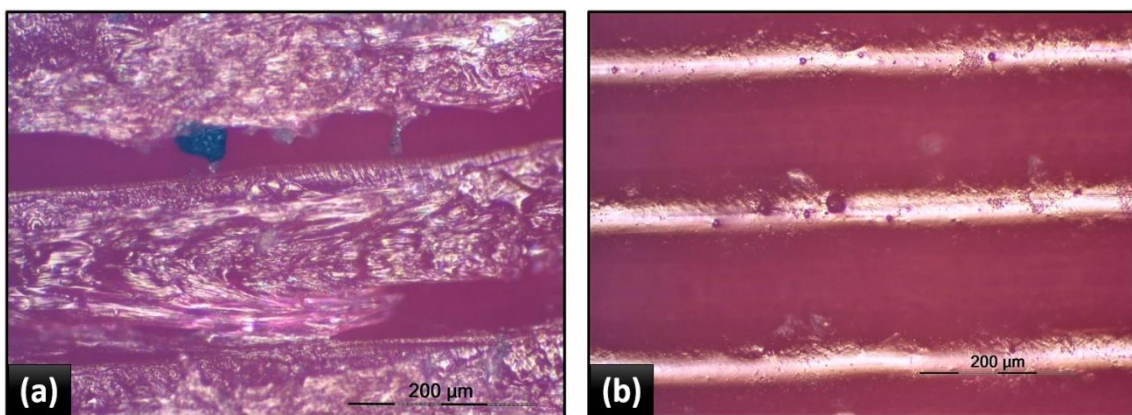


Figure 111 - Microscopical Images of B3\_F3D: (a) Sample's Core; (b) Sample's Surface.

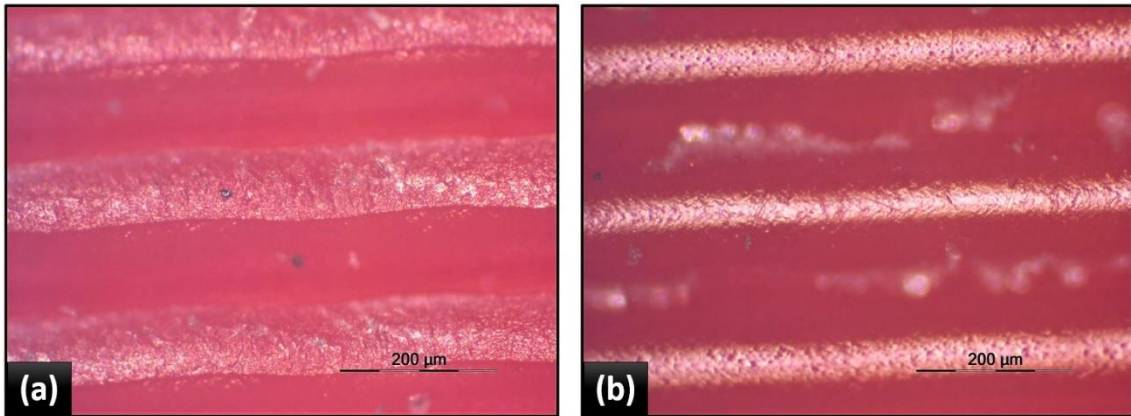


Figure 112 - Microscopical Images of B4\_PM: (a) Sample's Core; (b) Sample's Surface.

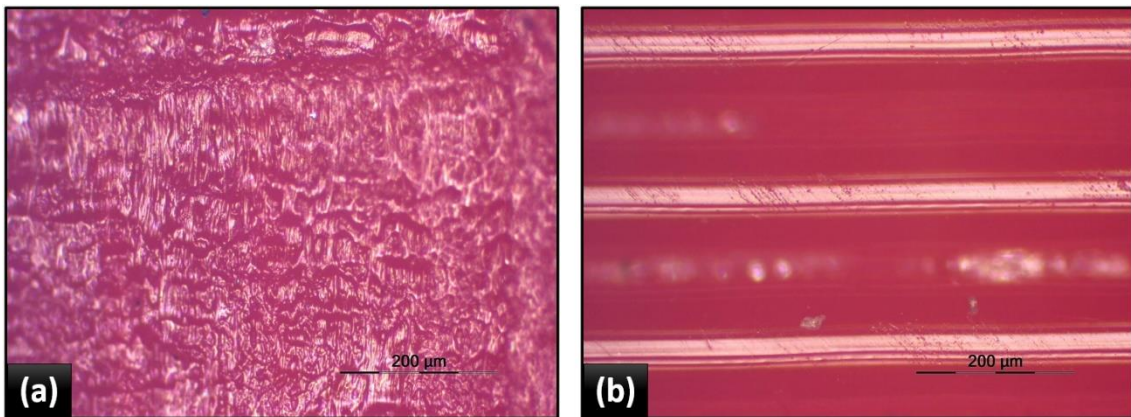


Figure 113 - Microscopical Images of B4\_KE: (a) Sample's Core; (b) Sample's Surface.

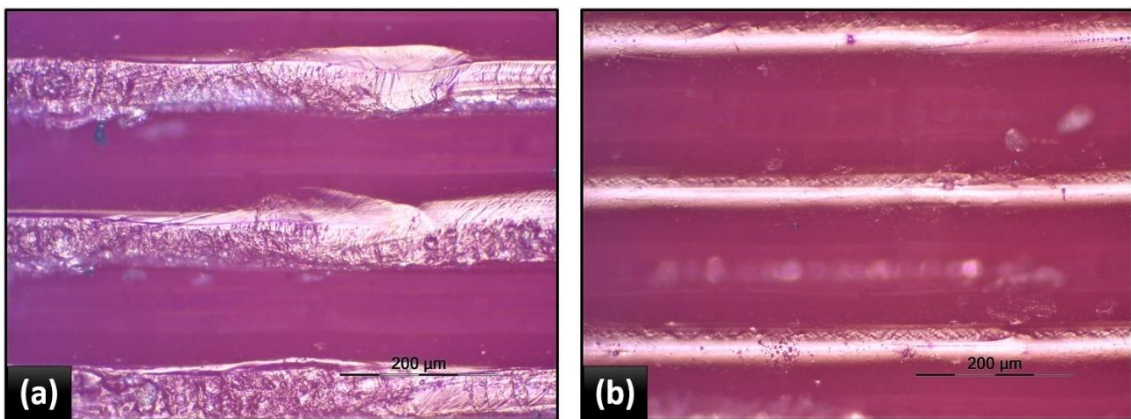


Figure 114 - Microscopical Images of B4\_F3D: (a) Sample's Core; (b) Sample's Surface.

## E – Summary of the mechanical trial results and mass measurements

### Degradation Study - PM

| Sample    | Condition       | TMF (MPa) | MF (GPa) | Massa (g) |
|-----------|-----------------|-----------|----------|-----------|
| B1_AM1_PM | W/Treatment     | 99,79     | 3,20     | 6,200     |
| B1_AM2_PM | W/Treatment     | 99,76     | 3,20     | 6,200     |
| B1_AM3_PM | W/Treatment     | 99,04     | 3,22     | 6,190     |
| B1_AM4_PM | W/Treatment     | 98,23     | 3,20     | 6,200     |
| B1_AM5_PM | W/Treatment     | 99,22     | 3,25     | 6,210     |
| B2_AM1_PM | Landfill        | 90,38     | 3,22     | 6,220     |
| B2_AM3_PM | Landfill        | 91,56     | 3,34     | 6,220     |
| B2_AM4_PM | Landfill        | 91,98     | 3,37     | 6,220     |
| B2_AM5_PM | Landfill        | 92,25     | 3,36     | 6,225     |
| B2_AM6_PM | Landfill        | 91,72     | 3,40     | 6,220     |
| B3_AM1_PM | Humidity        | 91,00     | 3,35     | 6,230     |
| B3_AM3_PM | Humidity        | 89,67     | 3,28     | 6,225     |
| B3_AM4_PM | Humidity        | 90,71     | 3,32     | 6,225     |
| B3_AM5_PM | Humidity        | 91,07     | 3,38     | 6,230     |
| B3_AM6_PM | Humidity        | 90,58     | 3,39     | 6,230     |
| B4_AM1_PM | Saline Solution | 88,91     | 2,30     | 6,225     |
| B4_AM2_PM | Saline Solution | 89,44     | 2,27     | 6,220     |
| B4_AM4_PM | Saline Solution | 99,57     | 2,25     | 6,225     |
| B4_AM5_PM | Saline Solution | 89,69     | 2,29     | 6,230     |
| B4_AM6_PM | Saline Solution | 88,93     | 2,30     | 6,230     |

### Degradation Study – KE

| Sample    | Condition       | TMF (MPa) | MF (GPa) | Massa (g) |
|-----------|-----------------|-----------|----------|-----------|
| B1_AM1_KE | W/Treatment     | 96,07     | 3,20     | 6,09      |
| B1_AM2_KE | W/Treatment     | 96,37     | 3,19     | 6,08      |
| B1_AM3_KE | W/Treatment     | 95,95     | 3,17     | 6,09      |
| B1_AM4_KE | W/Treatment     | 97,31     | 3,11     | 6,09      |
| B1_AM5_KE | W/Treatment     | 96,60     | 3,18     | 6,10      |
| B2_AM1_KE | Landfill        | 86,34     | 3,25     | 6,135     |
| B2_AM3_KE | Landfill        | 88,84     | 3,25     | 6,170     |
| B2_AM4_KE | Landfill        | 87,51     | 3,26     | 6,125     |
| B2_AM5_KE | Landfill        | 87,79     | 3,28     | 6,185     |
| B2_AM6_KE | Landfill        | 86,12     | 3,23     | 6,140     |
| B3_AM1_KE | Humidity        | 86,11     | 3,29     | 6,115     |
| B3_AM3_KE | Humidity        | 86,57     | 3,24     | 6,120     |
| B3_AM4_KE | Humidity        | 84,60     | 3,25     | 6,115     |
| B3_AM5_KE | Humidity        | 86,72     | 3,26     | 6,110     |
| B3_AM6_KE | Humidity        | 86,74     | 3,30     | 6,120     |
| B4_AM1_KE | Saline Solution | 78,21     | 2,34     | 6,14      |
| B4_AM2_KE | Saline Solution | 78,41     | 2,28     | 6,13      |

|           |                 |       |      |      |
|-----------|-----------------|-------|------|------|
| B4_AM4_KE | Saline Solution | 77,75 | 2,33 | 6,15 |
| B4_AM5_KE | Saline Solution | 77,00 | 2,33 | 6,16 |
| B4_AM6_KE | Saline Solution | 77,71 | 2,33 | 6,14 |

#### Degradation Study – F3D

| Sample     | Condition       | TMF (MPa) | MF (GPa) | Massa (g) |
|------------|-----------------|-----------|----------|-----------|
| B1_AM1_F3D | W/Treatment     | 94,18     | 3,05     | 6,04      |
| B1_AM2_F3D | W/Treatment     | 92,46     | 3,00     | 6,04      |
| B1_AM3_F3D | W/Treatment     | 91,83     | 3,01     | 6,05      |
| B1_AM4_F3D | W/Treatment     | 92,67     | 3,02     | 6,04      |
| B1_AM5_F3D | W/Treatment     | 92,12     | 2,95     | 6,04      |
| B2_AM1_F3D | Landfill        | 89,59     | 3,30     | 6,07      |
| B2_AM3_F3D | Landfill        | 88,96     | 3,28     | 6,08      |
| B2_AM4_F3D | Landfill        | 88,64     | 3,32     | 6,08      |
| B2_AM5_F3D | Landfill        | 88,24     | 3,30     | 6,07      |
| B2_AM6_F3D | Landfill        | 89,38     | 3,30     | 6,08      |
| B3_AM1_F3D | Humidity        | 88,07     | 3,31     | 6,11      |
| B3_AM3_F3D | Humidity        | 86,47     | 3,31     | 6,12      |
| B3_AM4_F3D | Humidity        | 84,92     | 3,33     | 6,12      |
| B3_AM5_F3D | Humidity        | 86,62     | 3,32     | 6,13      |
| B3_AM6_F3D | Humidity        | 87,76     | 3,33     | 6,11      |
| B4_AM1_F3D | Saline Solution | 83,11     | 2,44     | 6,06      |
| B4_AM2_F3D | Saline Solution | 78,80     | 2,37     | 6,105     |
| B4_AM4_F3D | Saline Solution | 79,18     | 2,39     | 6,105     |
| B4_AM5_F3D | Saline Solution | 80,32     | 2,38     | 6,09      |
| B4_AM6_F3D | Saline Solution | 80,73     | 2,41     | 6,08      |

#### Taguchi Study - PM

| Samples   | TMF (MPa) | MF (GPa) | Massa (g) |
|-----------|-----------|----------|-----------|
| T1_AM1_PM | 95,39     | 3,21     | 5,90      |
| T2_AM1_PM | 97,58     | 3,35     | 6,21      |
| T3_AM1_PM | 94,45     | 2,85     | 6,53      |
| T4_AM1_PM | 111,22    | 3,57     | 6,90      |
| T5_AM1_PM | 95,66     | 3,20     | 5,61      |
| T6_AM1_PM | 89,85     | 2,95     | 5,99      |
| T7_AM1_PM | 106,70    | 3,55     | 6,53      |
| T8_AM1_PM | 99,38     | 3,18     | 6,71      |
| T9_AM1_PM | 85,84     | 2,85     | 5,39      |
| T1_AM2_PM | 97,95     | 3,36     | 5,89      |
| T2_AM2_PM | 98,31     | 3,35     | 6,21      |
| T3_AM2_PM | 85,33     | 2,52     | 6,53      |
| T4_AM2_PM | 107,76    | 3,47     | 6,91      |
| T5_AM2_PM | 96,30     | 3,27     | 5,62      |

|           |        |      |      |
|-----------|--------|------|------|
| T6_AM2_PM | 92,55  | 3,15 | 5,99 |
| T7_AM2_PM | 106,50 | 3,53 | 6,52 |
| T8_AM2_PM | 100,58 | 3,25 | 6,72 |
| T9_AM2_PM | 86,30  | 2,92 | 5,39 |
| T1_AM3_PM | 96,40  | 3,31 | 5,88 |
| T2_AM3_PM | 98,21  | 3,35 | 6,20 |
| T3_AM3_PM | 93,32  | 2,77 | 6,53 |
| T4_AM3_PM | 107,97 | 3,45 | 6,92 |
| T5_AM3_PM | 94,96  | 3,22 | 5,61 |
| T6_AM3_PM | 90,94  | 3,14 | 5,98 |
| T7_AM3_PM | 106,55 | 3,59 | 6,52 |
| T8_AM3_PM | 100,60 | 3,26 | 6,71 |
| T9_AM3_PM | 86,07  | 2,94 | 5,40 |

### Taguchi Study – KE

| Samples | TMF (MPa) | MF (GPa) | Massa (g) |
|---------|-----------|----------|-----------|
| T1_AM1_ | 92,69     | 2,85     | 5,78      |
| T2_AM1_ | 89,15     | 2,91     | 6,05      |
| T3_AM1_ | 89,29     | 2,76     | 6,38      |
| T4_AM1_ | 98,24     | 3,10     | 6,90      |
| T5_AM1_ | 89,97     | 2,96     | 5,47      |
| T6_AM1_ | 88,79     | 2,45     | 5,82      |
| T7_AM1_ | 97,33     | 3,25     | 6,37      |
| T8_AM1_ | 99,06     | 3,20     | 6,71      |
| T9_AM1_ | 85,66     | 2,86     | 5,28      |
| T1_AM2_ | 86,68     | 2,97     | 5,77      |
| T2_AM2_ | 92,87     | 3,12     | 6,06      |
| T3_AM2_ | 89,23     | 2,81     | 6,39      |
| T4_AM2_ | 98,59     | 3,01     | 6,91      |
| T5_AM2_ | 90,16     | 3,01     | 5,47      |
| T6_AM2_ | 89,73     | 2,98     | 5,86      |
| T7_AM2_ | 93,98     | 3,00     | 6,31      |
| T8_AM2_ | 101,06    | 3,17     | 6,72      |
| T9_AM2_ | 86,12     | 2,92     | 5,28      |
| T1_AM3_ | 84,50     | 2,80     | 5,76      |
| T2_AM3_ | 92,98     | 3,12     | 6,05      |
| T3_AM3_ | 89,26     | 2,76     | 6,38      |
| T4_AM3_ | 96,10     | 3,16     | 6,92      |
| T5_AM3_ | 90,02     | 2,96     | 5,47      |
| T6_AM3_ | 89,00     | 2,90     | 5,80      |
| T7_AM3_ | 95,96     | 3,11     | 6,31      |
| T8_AM3_ | 100,13    | 3,20     | 6,71      |
| T9_AM3_ | 84,55     | 2,86     | 5,26      |

### Taguchi Study – F3D

| Samples | TMF (MPa) | MF (GPa) | Massa (g) |
|---------|-----------|----------|-----------|
| T1_AM1_ | 88,86     | 2,84     | 5,635     |
| T2_AM1_ | 95,50     | 3,04     | 6,07      |
| T3_AM1_ | 88,61     | 2,66     | 6,375     |
| T4_AM1_ | 108,14    | 3,52     | 6,92      |
| T5_AM1_ | 90,44     | 3,07     | 5,415     |
| T6_AM1_ | 107,06    | 3,62     | 5,84      |
| T7_AM1_ | 91,81     | 2,92     | 6,355     |
| T8_AM1_ | 93,29     | 2,85     | 6,67      |
| T9_AM1_ | 82,45     | 2,81     | 5,245     |
| T1_AM2_ | 86,84     | 2,63     | 5,68      |
| T2_AM2_ | 95,74     | 2,99     | 6,11      |
| T3_AM2_ | 89,51     | 2,64     | 6,385     |
| T4_AM2_ | 107,93    | 3,52     | 6,925     |
| T5_AM2_ | 88,45     | 3,07     | 5,425     |
| T6_AM2_ | 87,11     | 2,76     | 5,845     |
| T7_AM2_ | 91,10     | 2,86     | 6,36      |
| T8_AM2_ | 94,69     | 2,83     | 6,64      |
| T9_AM2_ | 82,45     | 2,76     | 5,24      |
| T1_AM3_ | 86,84     | 2,55     | 5,635     |
| T2_AM3_ | 95,86     | 3,06     | 6,085     |
| T3_AM3_ | 89,01     | 2,64     | 6,375     |
| T4_AM3_ | 107,84    | 3,54     | 6,92      |
| T5_AM3_ | 89,27     | 3,09     | 5,42      |
| T6_AM3_ | 89,22     | 2,93     | 5,84      |
| T7_AM3_ | 92,84     | 2,90     | 6,345     |
| T8_AM3_ | 94,13     | 2,88     | 6,64      |
| T9_AM3_ | 82,23     | 2,79     | 5,245     |