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Isabela da Conceição Evangelista

Development of functional materials for the additive manufacturing, by means of material extrusion, of an interaction object

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Dissertação de Mestrado
Mestrado Integrado em Engenharia de Polímeros

Trabalho efetuado sob a orientação do
Doutora Cátia Samanta Ribeiro da Silva
Professor Doutor António José Vilela Pontes

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Thank you for everything!

STATEMENT OF INTEGRITY

I hereby declare having conducted this academic work with integrity. I confirm that I have not used plagiarism or any form of undue use of information or falsification of results along the process leading to its elaboration.

I further declare that I have fully acknowledged the Code of Ethical Conduct of the University of Minho.

ABSTRACT

In line with the inherent technological advances, the need to quickly obtain functional parts, suitable for the evaluation of final parts, as well as the production of prototype parts becomes crucial in the present, hence making the branch of additive manufacturing of extreme importance.

Thus, this dissertation focusses the study and development of a functional material directed to the production of interaction parts, by using additive manufacturing technologies, specifically material extrusion. The topic of study, an interaction product, emerges from the need to improve products interaction with users. In this context, colour change is an approach that can provide useful information to the user. Currently, products which are informative to the user are in constant growth, from temperature indicators for food safety to baby spoon burns prevention, or even security labels used in safety protocols. With this, it was developed a functional material that would retain particular information of the user's hand. A posterior production was in a filament form made in order to produce prototypes to study the given feature in the material extrusion technique.

The investigation results allowed to conclude that the produced filaments are suitable for the material extrusion additive manufacturing technique, and also present the thermochromic feature. Conclusively, it was possible to manufacture a responsive prototype to various temperatures, based on the developed functional material. This feature is rather useful and suitable for interaction products.

KEYWORDS: Additive Manufacturing, Compounding, Extrusion, Functional Materials, Fused Deposition Modeling, Thermochromism.

RESUMO

Em consonância com os avanços tecnológicos inerentes, a necessidade de obter rapidamente peças funcionais, adequadas à avaliação das peças finais, bem como a produção de peças protótipo torna-se crucial no presente, tornando assim o ramo de fabrico aditivo de extrema importância.

Assim, esta dissertação foca o estudo e desenvolvimento de um material funcional dirigido à produção de peças de interação, utilizando tecnologias de fabrico aditivo, especificamente extrusão de material. O tema de estudo, um produto de interação, emerge da necessidade de melhorar a interação dos produtos com os utilizadores. Neste contexto, a mudança de cor é uma abordagem que pode fornecer informações úteis para o utilizador. Atualmente, os produtos que são informativos para o utilizador estão em constante crescimento, desde indicadores de temperatura para segurança alimentar até à prevenção de queimaduras de colheres para bebé, ou mesmo rótulos de segurança utilizados em protocolos de segurança. Com isto, foi desenvolvido um material funcional que reteria informação particular da mão do utilizador. Uma produção posterior foi feita sob a forma de filamento para produzir protótipos de forma a estudar a característica adquirida através da técnica de extrusão de material.

Posteriormente, foi definido um caso de estudo para o fabrico de uma peça para inferir como o material funciona com as flutuações de temperatura.

Os resultados da investigação permitiram concluir que os filamentos produzidos são adequados para a técnica de fabrico aditivo para extrusão de material, e também apresentam a característica termocrómica. Concluindo, foi possível fabricar um protótipo reativo a várias temperaturas, com base no material funcional desenvolvido. Esta característica é bastante útil e sendo também adequada para produtos de interação.

PALAVRAS-CHAVE: Fabrico Aditivo, Composição, Extrusão, Materiais Funcionais, Fused Deposition Modeling, Termocromismo.

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Abbreviation	**Meaning**
3D	Three-Dimensional
ABS	Acrylonitrile butadiene styrene
AM	Additive Manufacturing
ASTM	American Society for Testing and Materials
ATRP	Atom transfer radical polymerization
CAD	Computer Aided Design
DSC	Differential Scanning Calorimetry
FDM	Fused Deposition Modelling
FFF	Fused Filament Fabrication
IR	Infrared
ISO	International Organization for Standardization
LCP	Liquid Crystalline Polymers
MFI	Melt Flow Index
PLA	Polylactic Acid
SMM	Shape Memory Material
STL	Standard Triangulation Language
TGA	Thermogravimetric Analysis
UV	Ultraviolet

1. Introduction

This first chapter has intended to describe the introductory path for the development of this dissertation. Contextualization and motivation are the first topics to be exposed; a brief description of the laboratory is also present. Finally, the objectives for this project and the general dissertation structure are described.

1.1. Contextualization and motivation for the development of this dissertation

Over time, the computerization of the industry and the search for new and increasingly innovative technologies has become a constant reality in the science field. Since the beginning of times, materials have always been a present reality in the surrounding world. From prehistory to the present era, they are an essential resource for the survival of the human being. Their importance is so crucial, that periods are characterized by them, as for example the stone age. With the evolution of time, it was possible to divide materials into three great families: ceramics, polymers and metals. Polymers were the last material to employ as we understand today. The first example documented was in 1830 by Henri Braconnot, Christian Schonbein and others, described the development of semi-synthetic materials from cellulose [1]. Nevertheless, one of the most well-known discoveries in the polymer industry was the vulcanized rubber. Charles Goodyear and Thomas Hancock were the leading inventors in the transforming of the natural rubber into vulcanized rubber, for the use in product manufacturing [2]. Over time polymers and other materials needed to evolve in order to keep up the technological advances. Nowadays, materials need to have something more to add to the product besides the mechanical and aesthetic performance. Functional materials appear as a response to this need. These materials usually present responsive features which distinguishes them from common materials, the most used in the industry. The responsive behaviour to environmental stimuli, makes the utilization more appealing to the industry community, increasing the potential of a specific product [3].

In comparison with everyday materials, the use of functional materials is still quite recent. The first functional material emerged at the beginning of the 20th century, when the common processing technologies used were mainly conventional. However, new technologies, such as additive manufacturing techniques, are starting to rise as a valid alternative for the manufacturing of products aggregating the material features [4].

The manufacturing of products by means of additive manufacturing is increasing. In this process, the design freedom is more prominent, when compared to the conventional technologies. Besides, the fast-leading times allows the production of complex geometries, in short periods. Material extrusion technology, although it is not the oldest technology of additive manufacturing, is one of the most common and commercially used. As in every additive manufacturing process, a CAD file is transformed in a three-dimensional (3D) object. In this case, the material is initially is heated and then is deposited in a first layer. The overall fabrication of the product consists in the deposition of several layers, until the final geometry is achieved [5].

Accompanying the technological advances, additive manufacturing process is slowly becoming a new trend in the product manufacturing, since it allows a higher design freedom and faster leading times. Aggregating the benefits of this technology with functional materials is what this dissertation is based. Products with increased capabilities and more interaction with the user-environment are the future of the technology, by enabling new applications and improving the previous ones.

1.2. Introduction to DONE Lab

DONE Lab – Advanced Manufacturing of Product and Tools, is a laboratory created at the University of Minho in 2016. The laboratory emerged from a partnership between University of Minho and Bosch Car Multimedia Portugal aiming the research & innovation in the field of additive manufacturing, in order to give support to companies to enhance the innovation and time production of products [6].

DONE
Lab
ADVANCED MANUFACTURING
OF PRODUCTS AND TOOLS
Manufatura Avançada de Produtos e Ferramentas

Figure 1.1 – DONE Lab logo.

1.3. Objectives

With the development of this dissertation, the main objectives to be answered at its conclusion are:

- Material characterization of the polymeric matrix and masterbatch by thermal, physical and microstructural tests;
- Definition of a material compounding methodology to produce functional materials;
- Production of filament with the raw polymer matrix and production of filaments of materials with added functionality, based in the previously defined compounding procedures;
- Material characterization of the filaments produced by thermal; physical, microstructural, tensile and stimulation tests;
- Comparison analysis between of the properties of the composite materials and the original polymeric matrix;
- Definition of a case-study, for production based in extrusion-based additive manufacturing;
- Analysis of the influence of additive manufacturing process parameterization in the quality of the produced parts;
- Test and evaluate the performance of the case-study parts, based in the developed functional materials, with different temperature stimuli.

1.4. Organization of the dissertation

This dissertation is divided into five chapters. This approach was taken into account by considering the work necessary to proceed to a clear and understandable project. Chapter 1 presents the initial part of the project, a general introduction, a brief contextualization of the project, and a description of the objectives. Then, Chapter 2 contains the state of the art concerning the developed work. A theoretical background regarding functional materials and all the processes necessary for the completion of the project are described. Chapter 3 describes the experimental component. Component in which is described material selection, respective compounding, as well as the characterization tests performed. Filament production is also presented along with the characterization of filament testing. Chapter 4 is referent to the case-study development and testing. In this chapter, the process parametrization influence over the quality of the parts is shown. Also, we conduct the performance evaluation of the parts, obtained with the optimized processing parameters, when stimulated by different temperatures. Chapter 5 is the concluding mark in this dissertation and exposes the required future work.

2. State of the art

In this chapter the most relevant theoretical concepts for project development are described. An overview of functional materials is covered, which is followed by the definition and history of thermochromism. In terms of thermoplastic compounding, general aspects are described alongside with processes description of compounding thermochromic materials. For additive manufacturing, the main technologies are reported with main focus on material extrusion. Lastly, functional materials in additive manufacturing are also analysed.

2.1. Overview of functional materials

In order to accompany the industrial and technological evolution through time, a new era of materials emerged, enhancing the interaction between products and user. Aligned with the inspiration of interactive systems present in nature, researchers have started to produce materials that presented responsive features to a physical, thermal or chemical stimulus. In this order, functional materials emerged as a new generation of materials, presenting the possibility of adding new properties to the product and improving optical and thermal properties. Regarding mechanical properties, common structural materials, which are the most used in the industry, present better mechanical properties than functional materials [7], [8].

One of the first documented functional materials with a responsive feature consisted in a discovery by a German chemist, Diesbach. This material consisted in an inorganic compound which presented the colour change feature once an electrical field was applied. It was only in 1824, that studies proceeded to minerals with piezoelectric capabilities, resulting in the observation of the piezoelectric phenomena [9]. Since then, the searching path has continued, providing functional materials in every material class: ceramic, polymers and metals.

Another important factor in functional materials is the misunderstanding with the concept of smart material. Smart materials display intrinsic changes without having an external artificial stimulus, the change occurs only from environmental fluctuations. Thus, they belong to a subclass of functional materials. Further, in this dissertation, will smart materials be explored, yet in this phase, the concept exposure will include the general functional materials [10].

For functional materials, a general observation is the often verification of compounds between the material matrix, which provides the responsive feature. This typical approach results in materials presenting the compound features. Anyhow, there is a possibility to use materials that are intrinsically responsive, although they are not as frequent when comparing with the typical approach. Considering ceramic materials, the fabrication process consists of a structure base material, connected with a ceramic substrate, resulting in a layer formation. A practical example is a film which detects gases via changes in electrical resistance. For this film, it is verified an increase in the electrical conductivity of the device when the ceramic materials (e.g. SnO_2, WO_3, and ZnO) absorb the combustible gas and the air present in the environment (beyond oxygen). This combustible gas reacts with the oxygen ion, releasing electrons in the conductive band, which provides the sensitive feature [11]. In majority, ceramic films are integrated into electronic applications, for microsystems in a layer-by-layer system. However, functional crystals, battery materials, and high-temperature superconductive ceramics are also other possible applications for this class of material [12]. Regarding the polymer family, besides physical mixing and solvent blending methods, the fabrication process can also be approached in terms of chemical methods. Commonly, the process consists in the addition of functional molecules into polymeric systems. The formulation and type of polymerization are established, considering the intended feature and application. For instance, spiropyran, an organic compound, has frequently been used to induce a colour change in polymeric materials. The polymerization process can occur in several forms, but, the most usual is the radical polymerization and atom transfer radical polymerization (ATRP) [13]. In the case of functional metals, inorganic compounds are typically added. The fabrication process is similar to polymer materials, in which a compound is added to the matrix in order to obtain a desired effect [14].

As explained, functional materials are available in different forms and used for variable applications. Therefore, a division between the responsivity versus the stimulus is explicitly exposed for the materials presenting the most importance for this dissertation (see Table 2.1) [15].

Table 2.1 – Types of functional materials based in stimulus and response [14].

Response / Stimulus	Optical	Mechanical	Electrical
Optical	Photochromic	-	Photoconductor
Mechanical	Mecanochromic/ Piezochromic	Negative Poisson Ratio	Piezoelectric Electroresistive
Electrical	Electrochromic Electroluminescent Electro-optic	Electroresistive	-
Thermal	Thermochromic Thermoluminescent	Shape memory	Thermoelectric

Concerning the optical response, the colour change is a response to an environmental condition, resulting of an optical, mechanical, electrical or thermal stimulus. According to Marinella Ferrara, *"the principle by which these materials function can be explained by an alteration in the equilibrium of electrons caused by the stimulus, with a consequent modification of optical properties, such as reflectance, absorption, emission, or transmission "* [16]. The optical properties of materials are critical for a correct interpretation of colour by the human eye; thus, every object is exposed to a light source. In this particularity, materials need to contain compounds capable of absorbing, reflect or scatter the exposed light, along with features which will change through stimulus implementation [17]. During temperature exposure, thermochromic and thermoluminescent materials change the object colour and transparency, respectively. Consequently, the most common application for these types of materials is related to products that provide information about temperature. Coffee mugs, baby spoons, and cups are some examples of products presenting dual-colour change to assure user safety by providing visual information and therefore preventing burning [18]–[20].

In the case of photochromic materials, the use is often for accessories decoration or in sunglasses ; however, recently, the utilization is emerging in traffic signs. The ink applied in the road for signposting glow during the night, after absorption of the sunlight during the day. Submitting the material to any light exposure, from electromagnetic radiation until infrared (IR) light, promotes a higher state of excitation of electrons in photochromic materials. Photochromic materials may be organic or inorganic, being the most employed and therefore, commercially available, the organic type, namely T-type and P-Type materials [21]. The changing feature, in T-type material, consists in the modification of the material's colour, when exposed to visible or ultraviolet (UV) light. The returning to the original state occurs by removing the material from the light. Straight after, is observed a gradual transition until the reaching of the original colour. Similar to T-Type, P-Type materials do not return to the original state through the non-exposure to visible light. In this case, it is necessary to expose the material to electromagnetic radiation of different wavelengths, when compared with what was used to initiate the reaction [22]. The most common application for P-Type materials are the eyeglasses, sensitive do light (see in Figure 2.1). Following the same mechanism, glasses for windows which darkness with the sunlight, are in constant growth, being an option for energy efficiency in houses. In another aspect, photochromic materials are applied for security sensors; authenticity control is observed when a mark appears through UV light exposure. This application is used for controlling branding of clothes until counterfeit passports [23].

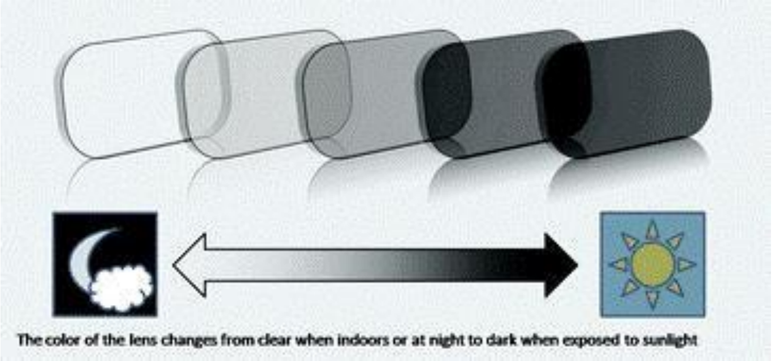


Figure 2.1 – Solar radiation effect on photochromic lens[24].

Mecanochromic materials, which also have optical responses, are stimulated by mechanical stress, stretching, or grinding. The mechanical stimulus creates a chemical reaction that leads to bond breaking, or conformational changes. Affecting the structure geometry, this alterations, on a molecular level, are rotations in the molecular chains around the covalent bonds, which will allow an adjustment of the bond angles [25]. For this type, the changeable mechanism is irreversible; sensorial applications are the natural approach, however, are not used yet due to the difficulty of development of the optimum polymer blend on a large scale [26].

An example of the mechanochromic effect is observable in Figure 2.2, where a mechanical stress is inputted originating a bondage cleavage forming a different colour.

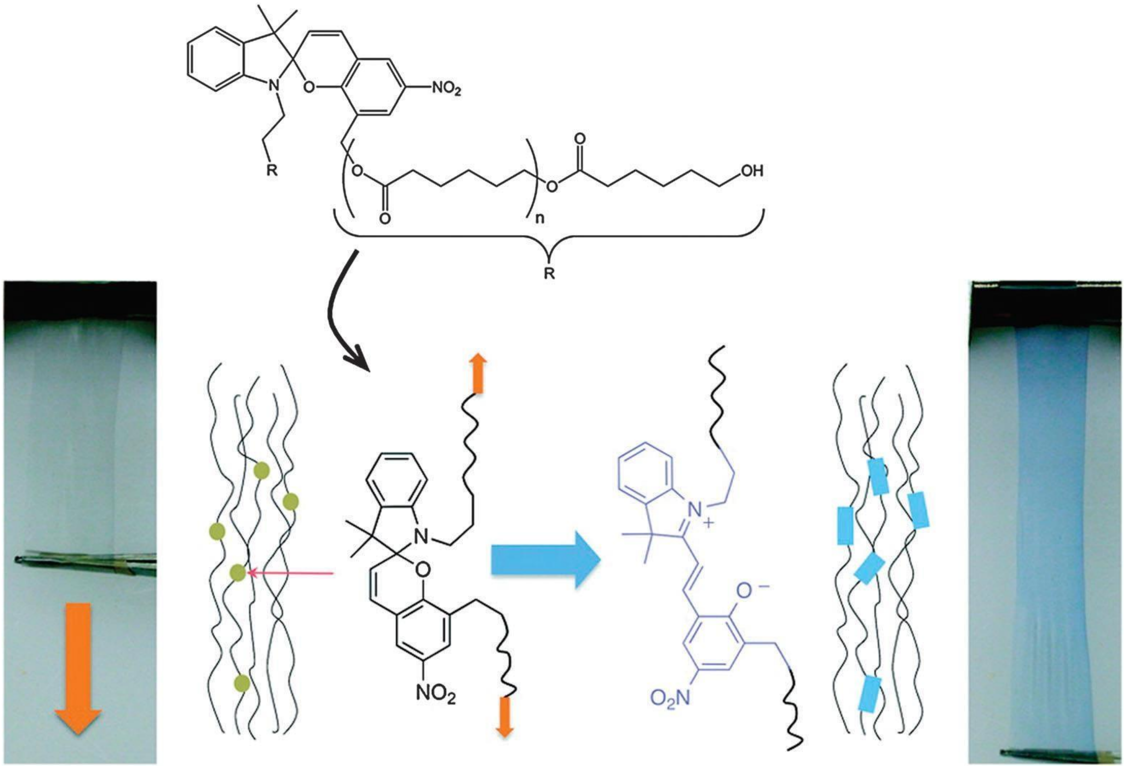


Figure 2.2 – “Mechanically induced bond cleavage of indolinospiropyran-poly(ε-caprolactone) films. Reprinted with permission from ref. 53. Copyright (2010) American”[25].

Piezochromic materials are also stimulated by mechanical stress varying in the type of mechanical input. In this case, a hydrostatic compression or a mechanical grinding/shearing below 1 bar gives the result [27]. During pressure application, it was observed an alteration in the molecular geometry along with intermolecular interaction, which is responsible for the optical feature. Since the stimulus applied in this case is low pressure, the applications directed at this type of material are related to pressure sensors. Detection of a specific mechanical behaviour in experimental tests, visual colour alteration as detection of impacts in the packaging transport, or for industrial applications are some of the most common applications [28].

Lastly, electrochromic materials also present an optical response although, in this case, the stimulus is based on the application of a low electrical potential, which generates the colour change. After the removal of the current, this shifting is held. The changing process consists of a series of chemical reactions, based on an induced oxidation-reduction reaction, leading to a gain or loss of electron [29]. Used as coating in the so-called smart windows, electrochromic materials are chosen above photochromic material. This choice occurs due to a major radiation approach, including the infrared region. The utilization of these windows prevents the overheating in buildings, diminishing the energy consumption for cooling [30].

After the optical response, the mechanical response has the most types of functional materials; in this case, mechanical behaviour is changed when compared to the phase before the stimulus application. Regarding shape-memory materials (SMM), research is constantly evolving thought the years. The associated feature is the shape alteration from a specific temporary deformed shape to a "previously" programmed shape. Usually, this effect is recognized as the shape memory effect. Typically, a stimulus is imposed activating the memory feature ability, which could be temperature change, stress input, a magnetic or electric filed, pH alterations or even UV light. Depending on the trigger, the shape change presents a strong dependence on the programming and recovery conditions, in terms of deformation temperature, deformation quantity, loading rate, cooling rate, and heating rate [31].

In terms of electrical response, several materials are included in these categories. In photoconductive materials, the electric response is observed when there is exposure to light in the infrared, visible or ultraviolet light range. In practical terms, every material is sensitive to light; thus, there is a generation of current carries due to the correct wavelength exposure, which is not always detectable commonly. The photoconductor materials with the most use according to Gregory E. Stillman, *"…are characterized by comparatively long lifetimes and low dark currents, have most of their charge carriers immobile (in the dark)."* [32]. Usually, they are incorporated into other materials. A typical example is the darkness observed when exposing the cell phone displays to light. In general, systems with broad light control have incorporated these materials [33].

Considering piezoelectric and thermoelectric materials, the difference between them is the stimulus imposed. Both are materials entirely used in the electronic field as in the technological advances [34], [35].

In short, functional materials became essential in the production of products so assure that they can keep pace with the time evolution. With the continuous development, the use of functional materials will undoubtedly be more common in structures and applications with higher safety needs.

2.2. Thermochromism

At this stage, the history and definition of thermochromism are exposed. For better understanding, thermochromism is addressed in polymeric materials along with the inherent synthesizing techniques. Finally, the types of materials present and subsequent applications are noted.

2.2.1. History

In 1871, Professor Edwin James Houston carried out one of the first studies on chemical compounds demonstrating colour changes. He carried the investigation focusing on the behaviour of inorganic compounds when exposed to heat, which would indicate the presence of reversible and irreversible colour variations [36]. Nonetheless, it was only in the 1960s that the first practical applications, with liquid crystals, were approached with the appearance of the digital watches, opening this way the door for thermochromic materials [37].

2.2.2. Definition

Thermochromism is the process of colour change to temperature exposure, which it is observed in single inorganic or organic compounds, the use and combination of them with other materials is what confers the effect. For inorganic compounds thermochromism is observed, in solids and solution compounds, structural changes are observed as modification of the crystalline phase, leading to different wave length absorptions originating different colours. Regarding the organic compounds, the process appears also as chemical arrangements, acid-base reactions, keto-ethanol rearrangement and lactim-lactam equilibria are some of examples of molecular structure alteration [38].

Besides the compounds mentioned before, one of the best-known examples that can be found in nature is the behaviour of the colour change of a chameleon. The observation of this process is still in research, however the thermochromism effect is easily observed by the naked eye. The observation of the colour shift is still a great inspiration for plenty application purposes [39].

2.2.3. Thermochromic effect on polymers

Briefly, the molecular structure change is what induces different levels of absorption and reflection of light, which results in colour shifting. In terms of molecular alteration, change varies according to the type of material involved, which means different optical responses [40]. In Figure 2.3 is possible to see a molecular structure change which infers colour change.

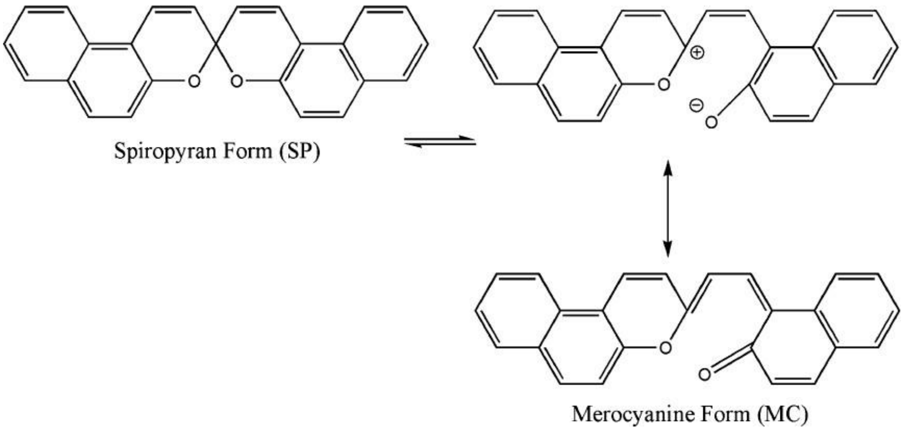


Figure 2.3 – "Mechanism of the ring-opening reaction in the spiropyran di-βnaphythopyran. Cleavage of the spiro carbon-oxygen bond yields a structure with greater planarity and extended π-conjugation. The compound becomes colored due to this extended conjugation."[41].

For liquid crystalline polymers (LCP) presenting the thermochromic effect, in general, two different groups are observed. The first group presents inherent helical superstructures while for the second group, the development of the helical superstructures occurs by stimulation through the addition of chiral dopants. Typically, at the shifting temperature, the helical structure length pitch changes, resulting in a different light reflection in the visible range. In Figure 2.4 an illustrative representation of the effect of colour according with the different pitch is observed. The wavelength reflected when the thermochromic effect is verified needs to satisfies the Bragg Law. In this case, the non-reflected light is either absorbed or transmitted. Concerning a better outcome of the shifting effect, the use of a material matrix presenting black colour, prevents the wavelength interfering.

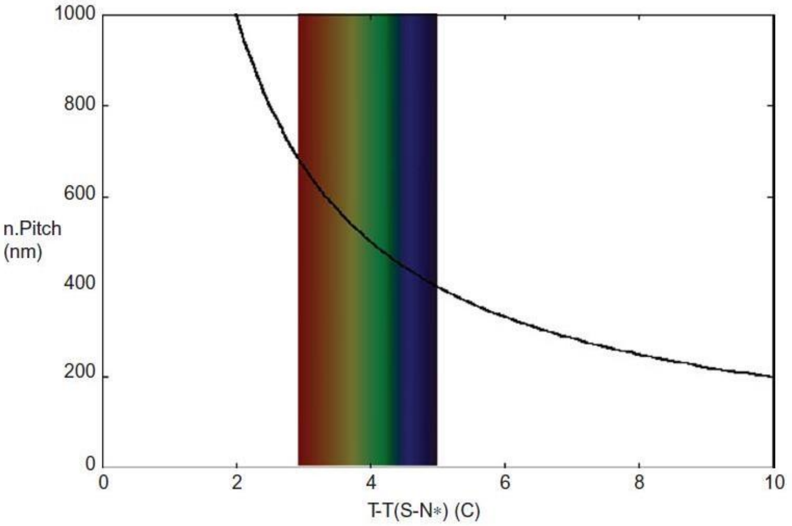


Figure 2.4 – Representative diagram of the pitch length change and the corresponding colour of a chiral nematic phase liquid crystal above the S-N*transition [42].

For crystalline colloidal arrays added to the polymeric matrix, when accomplishing the shifting colour, different reflections are also observed. Regarding organic thermochromic mixtures, two-component mixtures and three-component mixtures are also present in the material category which changes the perception of the wavelength [43]. Leuco dyes, which are responsible for the colour change, do not present thermochromic capabilities without stimulus. The colour-shifting happens due to a change in the pH of the solution. With the presence of the colour developer in the two-component mixture or with the developer plus solvent, the thermochromism effect is achieved (see Figure 2.5). Shortly, the activation temperature changes the equilibrium position of the molecular organization [44].

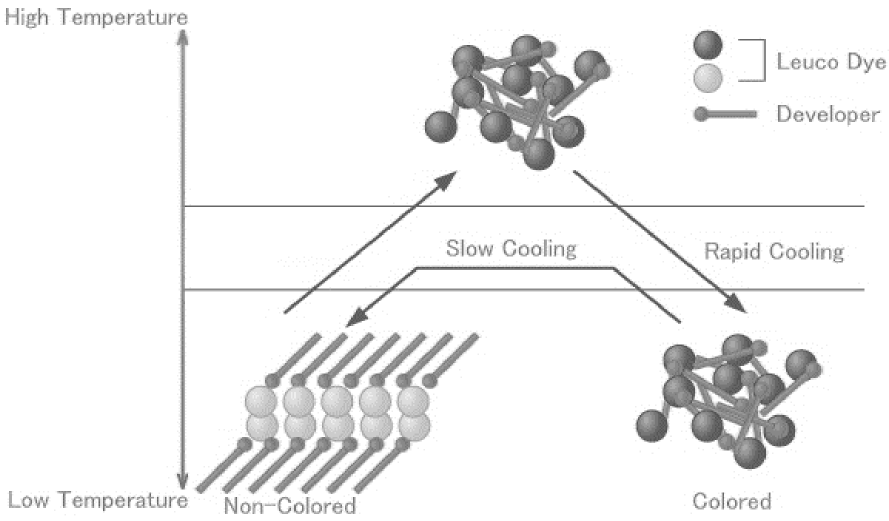


Figure 2.5 – Schematic representation of the synthesizing process of three component mixtures [45].

Besides wavelength distortion, structural changes, resulting in a different wavelength absorption, are also a resulting effect on light. This response is observed for conjugated polymers. Also, in some inorganic compounds involved in polymeric matrixes, and in general, systems that use thermochromic dyes or conjugation of them with developers, the responses are also the same. The conjugated concept, when applied to polymers, is referring to the structural organization of the chain, which is observed as an exchange of single and double bonds thought the chain. This bonding alteration creates a system of de-localize electrons enabling the sharing between several atoms, resulting in a possible movement of the electron through the chain [46]. Here, a change in the wavelength absorption of the light exists when the temperature increases. Consequently, a conformational change occurs, causing order-disorder transition in side-chain groups, differing from the original conformation. Apart from changes in the chromophore zones, thermochromism in inorganic materials may also be originated from an alteration in the bandgap energy, phase transitions or changes in the reflection properties [47]. Figure 2.6 shows an example of thermochromism of an inorganic compound.

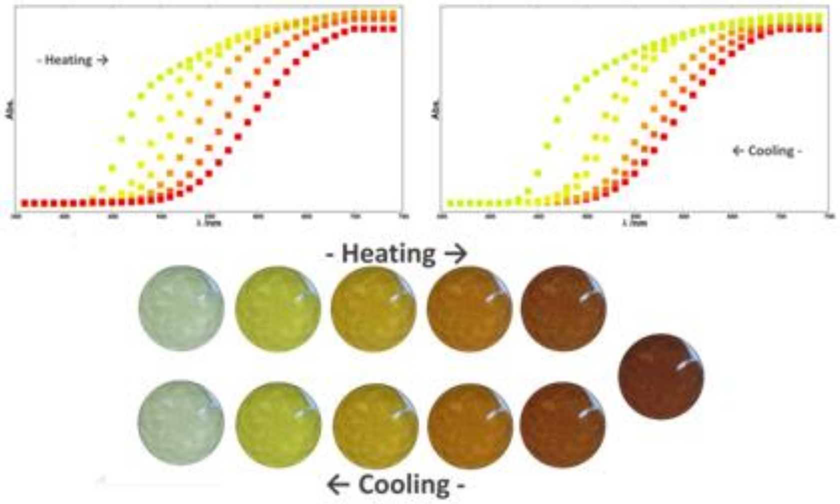


Figure 2.6 – Representation of the thermochromism present in a metal oxide (inorganic compound) monitored by UV-Vis spectroscopy and microscopy [48].

2.2.4. Synthesizing techniques

Synthesizing techniques are specific according to materials' differences/family. Considering this project, the study and development will be focused on thermochromic polymers. It is possible to synthesize polymers that have inherent thermochromic properties. For processing purposes, a combination with other materials is the most common use. Regarding organic substances, conjugated polymers are the only polymers that present intrinsic thermochromic characteristics. There are two main processes for its synthesis, chemical oxidation or electrochemical polymerization. The choice of which process to use is dependent on the final purpose. It was observed chemical polymerization when conjugated monomers are mixed with a suitable oxidant for the solvent, requiring constant stirring. In electrochemical polymerization, a potential is applied to oxidize the monomer solution. The solution contains monomer solvent and the electrolyte facilitating this process. In the end of the process, a pre-doped material is obtained. As an example, polythiophenes present both fabrication process possibilities: oxidative polymerization into the corresponding thiophenes may be conducted and, besides this, a preparation in non-aqueous solution also can occur by electrochemical polymerization [49].

In the same context, liquid crystals that contain a helical structure are another form to provide the thermochromic effect in polymers when combined with the polymer matrix. Thermotropic liquid crystals depending on nature can assume two different types: sterol derivatives and non-sterol derivatives. Sterol derivatives were the first to be discovered and are commonly known as cholesteric liquid crystals, while the non-sterol derivatives assumed the name of chiral nematic crystals. Currently, a combination of both is very used for a better retain of the best advantages of the two. In Figure 2.7 it is possible to see an example of the integration of a thermochromic liquid crystal for a label construction, usually, these products are used to inform specific temperatures.

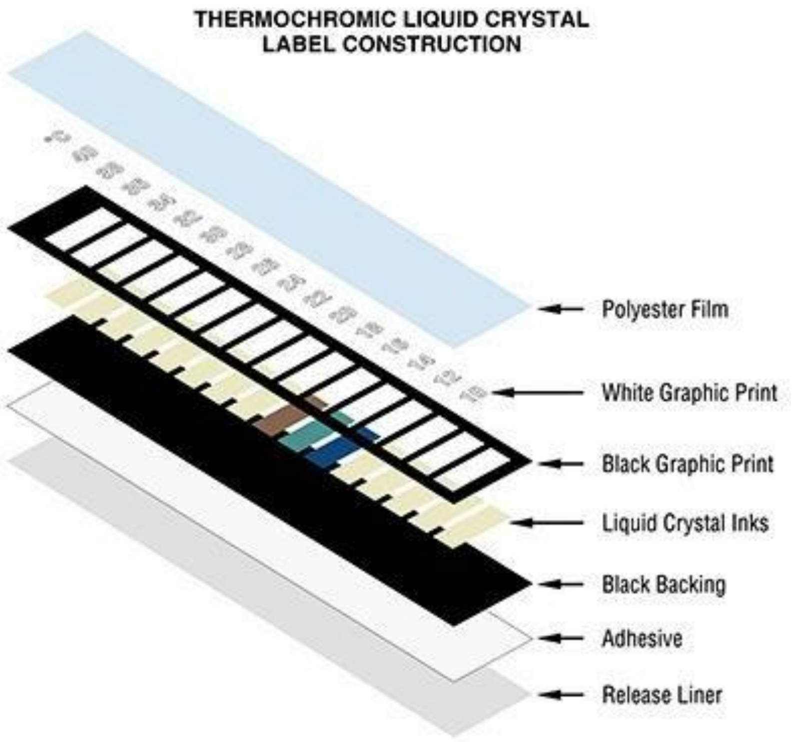


Figure 2.7 – Thermochromic liquid crystal label construction [50].

Another critical aspect of liquid crystals is the specific sensitiveness to several environmental conditions such as light, common solvents, fats, and organic chemicals. The integration by microencapsulation has become a crucial part of the synthesizing process. In general, a coating process involves small quantities of matter. This process provides decreased degradation, therefore increasing lifetime and the ability of mixtures with several materials, allowing as well, the mixing between the several liquid crystals [51], [52].

For leuco-dye-developer systems, the encapsulation also occurs, however, these systems are not used in large quantities for polymer processing due to the sensitivity to high temperatures and by presenting poor shear stability [51]. A representation of leuco-dye-developer systems is represented in the following Figure 2.8.

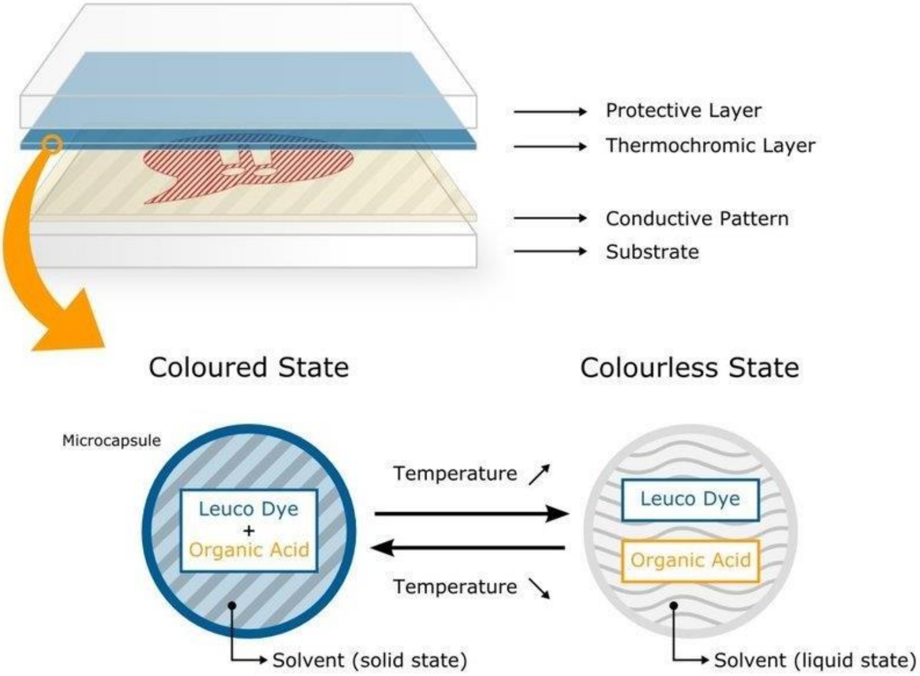


Figure 2.8 – " Schematic illustration of the operation principle of a leuco dye-based thermochromic display."[53].

In summary, for the integration of the thermochromic feature in thermoplastics, microencapsulation of inorganic pigments is commonly employed to generate the most adequate masterbatch for the best result.

2.2.5. Material types and applications

As mentioned before, a wide variety of polymer materials can present thermochromism. Often, thermochromic materials are used as temperature indicators for the majority of the applications, in Figure 2.9 a thermochromic label is used to control at which temperature the tomatoes need to be. However, with technological advances, different purposes are starting to emerge.

Figure 2.9 – Representation of a thermochromic label use for temperature control [54].

It is possible to say that leuco dyes and liquid crystals are still the most prevalent type of materials, due to the several applications. Considering leuco dyes, one of the most common applications is the thermal paper. The thermal paper was first introduced in the market in 1965 for thermal printers. This paper contains a microencapsulated three mixture component which, upon activation by temperature, changes colour. The printer head heats the paper, in specific zones, according to the image to print. Although the faster leading times of printing, the process is cheaper and very precise overcoming the ordinary ink printing when, for example, for printing barcodes. This process is irreversible, however, it is inserted in the thermochromic application [55]. Besides thermal paper, leuco dyes are also used in paints, inks and compositions for polymer composites (see Figure 2.10).

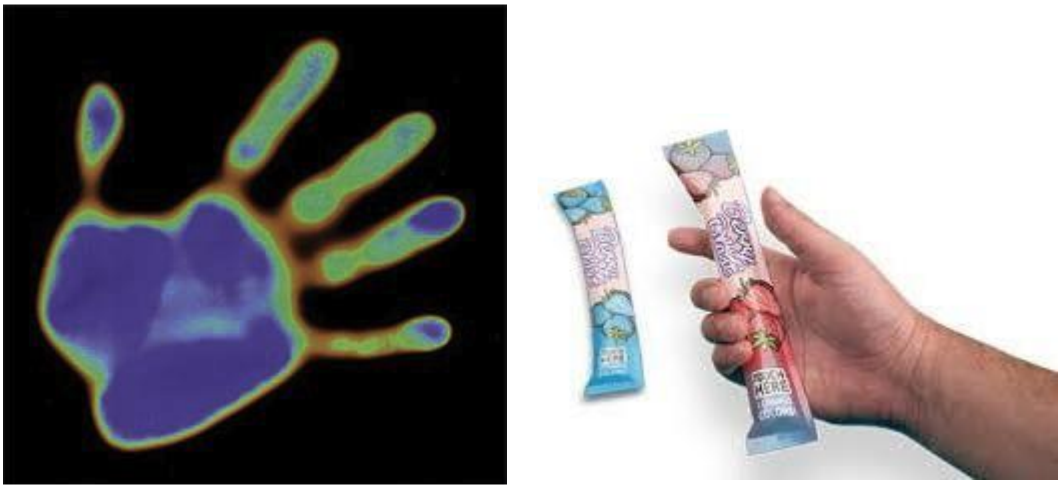


Figure 2.10 – Thermochromic liquid crystal ink representation [56] (left), colour change – Printing package (right)[57].

Similar to leuco dyes microencapsulated, liquid crystals (example in Figure 2.10) can also be used in inks and paints. In the textile industry, liquid crystals are used for dyes in smart clothing or for fashion aspects. K.R. Karpagam et al., developed smart clothing for military purpose (see Figure 2.11). Through a set of changeable colours, it was provided camouflage clothe at a room temperature which, in the case of higher temperatures, would turn into brown colours, mimicking the desert colour [58].

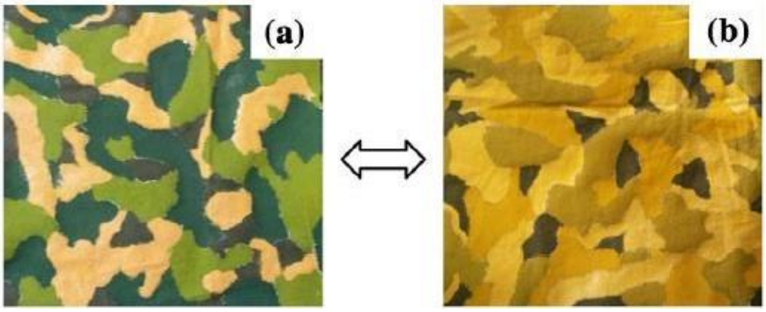


Figure 2.11 – “Reversible colour change of camouflage printed fabric (a) without heating, (b) with heating at 60 °C for 2 min.”[58].

In addition, liquid crystals inks are also applied for athlete clothes in order to have an optical monitor of the body temperature, since professional athletes usually train for several hours’ straight. This solution would be a more effective way to prevent physical exhaustion [59]. Also, in the aerospace industry, thermochromic paints are used to change the emissivity of surfaces under a thermal effect.

Regarding conjugated polymers, polythiophenes and polydiacetylenes derivatives are widely employed. For polyhiophenes, the most common use is as conducting layers in electronic devices. Besides the colour change, due to the electric properties, it is quite used in various application.

An example of application of another material type is in the medical industry. It was developed a thermochromic based system, which is able to detect an interruption of the cold chain of blood bags. In this case, an irreversible change is observed in the material when the blood bags exceed the critical temperature, preventing this way, the incorrect use on a patient [60].

A wide variety of applications exist resourcing to mixtures presenting inorganic compounds. For example, smart windows presenting coatings in the glasses with vanadium oxide, a transition metal compound, enable the regulation of the light amount absorbed. This material presents a reversible transition on the optical properties, due to alterations in the infrared region. Consequently, the glass will present less transparency, when a temperature rise is verified. The use of this coating allows a better management of the energy consumption of a building, promoting this way, more sustainability and fewer costs [61]. In regarding to safety aspects, baby bottles and child spoon containing thermochromic compounds help to prevent burns when sifting colour at the burning temperature. Mugs and pots are also examples of similar applications (see Figure 2.12) [18], [19], [62].

Figure 2.12 – Examples of products with thermochromic feature (left) [63], (right) baby bottle example [19].

2.3. Thermoplastic compounding

At this phase a general overview with the most important aspect regarding thermoplastic and colour compounding are observed.

Compounding operations are characterized by the obtaining of materials with specific behaviour during and after the processing. The involved processes are chosen according to the wanted polymer properties, jointly with its final use. Compounding is an essential process in the industry field, since it allows to introduce and improve the characteristics of raw materials. Also, it reduces processing times through the process optimization [64].

In thermoplastic compounding, the modification and incorporation of additives usually occur in raw polymers, which include mixing and melting as some of the primary operation [65].

2.3.1. Process aspects

Mixing of materials with additives or mixing between different materials initiates the compounding process, in which a physical or a chemical process can occur. Mixing can be divided into two types, dispersive and distributive mixing. Dispersive or intensive mixing is, as the name indicates, the most intense mixing process. In this case, the mixed material is subjected to a combination of forces inherent to the process, diminishing the formed agglomerates and breaking the molecular structures. On the contrary, distributive mixing is referent to as an extensive mixing, since a homogeneous spatial distribution occurs between the components, thus increasing randomness of the spatial component distribution. Distributive mixing is often used for the mixture of colour compounds with a polymeric matrix, while for other compounds, dispersive mixing is preferred. One interesting fact is that distributive mixing will always occur during dispersive mixing, but the opposite only happens when the stresses on polymer compounding increases [66].

For an excellent compounding operation, it is also essential to understand the involved equipment, such as batch and continuous mixers, which are chosen according to the type of material finality, formulation or mixture homogeneity. Batch processing is a mixing operation commonly used for mixtures with controlled mix composition and/or with mixtures that require controlled mix times. In this process, the material and compounds are inserted as a whole in the batch mixer. Afterwards, the mixture proceeds until the accomplishment of the desired homogeneity. There are several types of batch mixers; however, it is possible to admit a division between them. First, there are non-plasticating batches which are aimed for solid and liquid mixtures and present less rotation speed. These characteristics can result in component segregation originating formulation problems. Therefore, these batches are often used for small productions. Lastly, there are plasticating batches destined for the demand of melting and mixing polymers, which have a two-roll mill and internal mixers, as some of the equipment. Opposite to non-plasticating batches, in the case of internal mixers, the rotation speeds involved are higher, thus influencing directly the heat generated in the mixture. This factor results in a better compounding and makes these mixers more suitable for the pre-mixing of polymer formulations.

As previously mentioned, continuous mixing is another type of process present in the compounding operations which, in this case, the process occurs without interruptions and the materials are loaded continuously in the extruded equipment, resulting in a faster and easier process [67].

Compounding extrusion is responsible for the mix and melting of materials in a solid or liquid state. The process has several variants however, one of the most important aspects is the selection between a single or twin-screw extruder. This decision is similar to the reason for the selection between different batch mixers, which is the direct dependent on the material properties, formulations aspects and final use. In general, the extruder principle relies on mixing and melting materials. Single-screw extruders were first in the thermoplastic and thermoset industry, introduced in the 1870s. Nevertheless, it was only at the beginning of the 20th century, that this technology was used to continuous mixing. Before this time, this equipment was only used for pumping material. The often use of this technology, besides compounding, is related to the production of plastic parts, such as filaments, pipes, and sheets. A typical single-extruder is shown in Figure 2.13, the drive system is composed by the gearbox and the drive motor which is responsible for power generation. This energy is used to induce a rotation movement in the screw, thus enabling the material mixing and drag flow with a pre-defined speed. The feed system is composed by the hopper, feed throat and screw feed section. The hopper and the feed throat must be connected entirely and without any leaks in order to prevent possible defects that are inherent to the process as, for instance, build-up material which can originate contaminations in further compounding. Mixing and melting are ensured by a combination of barrel heaters and screw. The screw in combination with the barrel is responsible for the material dragging, resulting from the involved pressures that are present. This combination also has homogenization and mixture are also other features.

Typical screws in single-screw extrusion have three main sections: feed zone, compression zone and metering zone.

- **Feed zone:** responsible for the material carrying from the feed throat, which is situated right under the feed system and, is characterized by the deep flights along with the constant depth. Usually is 50 % of the length;
- **Compression zone:** also named as transition zone. Here, the material starts the transition from the solid to the melted state. The full melted state is only accomplished between the compression and metering zone. This section is about 30% of the length of the screw and is characterized by the presence of a diameter increase through the zone. Also, the depth of the flights is decreased, presenting a shallow surface;
- **Metering zone:** in this zone is present a fully melted material. Therefore, this zone is responsible for providing the necessary pressure for a good material flow through the die. In this case, the diameter screw is constant and the flight depth is the smallest.

The radical changes in the screw designs are only effectuated when the presented screw zones do not correspond to the required specifications. For example, changes can be done to improve mixing aspects or having better temperature control in the process. Compression ratio, which is the reason between the depth feed zone and the depth in the metering zone, is a crucial factor when evaluating new designs. This is mainly because, by measuring the involved pressures, it is possible to have a better comprehension of a good mixture and a consequently good dragging. Other essential accessories present in the extruder are the controllable heaters attached to the barrel. They provide sufficient energy and heat for the correct melting throughout the process, since reasonable temperature control is crucial for preventing material degradation. Lastly, the die is responsible for imposing a specific transversal section to the melting material [67].

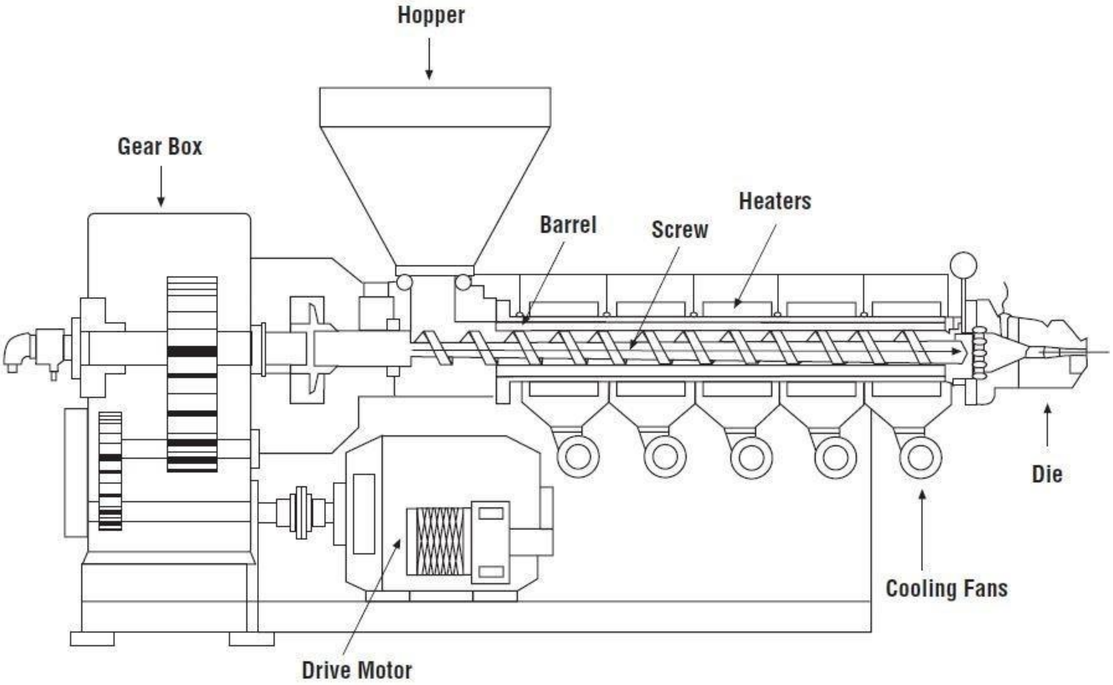


Figure 2.13 – Representation of a typical extruder system [68].

For compounding materials, besides the screw design mentioned, barrier flight screws and the pinned stirring-type extruders are also common approaches. Regarding twin-screws extruders, when comparing to single-screw extruders, as the name indicates, in the barrel are present two parallel screws instead of one screw. They can assume three movements, co-rotation, counter-rotation with intermeshing or non-intermeshing configurations. The movements, aligned with the possible different screw designs, allow the capability of having different degrees of mixing and melting. Existing in several designs, and allowing different mixing ratios, co-rotating twin-screw machines usually have modular configurations and, are thus quite flexible for adapting to changing tasks and material properties. Well-founded knowledge of machines, processes and material behaviour is in order to design twin-screw extruders required for economically successful operations [65], [69].

The processes described above are the general aspects of the extrusion method; for compounding materials, there are screws preferably used.

2.3.2. Colour compounding

Colouring thermoplastics is a specific branch of the compounding process. Similar to every compounding process, some principles and parameters need to be optimized and controlled to assure a superior final finishing.

The colouring plastic materials are mainly used for aesthetic and information purposes, and, it is done by using colour concentrate or masterbatches [38]. Solid masterbatches are the additives most used for colouring thermoplastics, due to the feasibility of processing and colour achievement. Normally, masterbatches are constituted by a polymeric matrix similar or compatible with the primary polymer to process. However, it can also have a universal carrier. In the mixture aspect, the mixture can occur in line or off-line. In line, the mixing occurs in the mixer and is performed upon the extruder. The blending process occurs simultaneously with the extrusion process. On the other side, off-line blending happens before the extrusion process with the materials being mixed in a suitable mixer [70], [71]. For colouring, the process must be optimized as it is crucial to ensure a high degree of homogeneity through a good dispersive and distributive mixing [38].

Regarding the colour concentrates, powder or liquid forms are available yet, are less used due to the difficult dosing maintenance through the process, along with colour differences.

2.4. Compounding of thermochromic materials

Considering the compounding process of thermochromic materials, it was concluded that the compounding process of thermochromic materials is similar to the thermoplastics colouring. The thermochromic feature is a colour change which is conferred to a specific material, whereas the addition is the same as the compounding aspect, including the same mixers and extruders, as mentioned before. Thermochromic materials can be found as standard colours in solid or liquid masterbatches. Regarding the thermochromic effect on polymers, there are polymers that present thermochromism intrinsically, and polymers that have the thermochromic feature added. The addition of a thermochromic feature through the chemical process was previously explained.

Regarding the use of masterbatch, the process also relies on the pre-mixing before the addition in the feed hopper. For example, the production of a hairbrush with thermochromic filaments is an example of how is incorporated this feature. In this case, the filaments are produced independently to the body of the brush due to the thermochromic aspect. A pre-preparation of the thermochromic compound occurs via dye mixing and respective binders. Later, this compound and the polymer matrix are mixed inside the extrusion equipment, and then, pushed to the extruder die, resulting in the thermochromic wires [72].

2.5. Additive Manufacturing

The technological production of parts, layer-by-layer, formed based on a 3D model data, is called Additive Manufacturing (AM). The first appearance of this concept was in 1987, with the emerging of a processing technique consisting of the layer-by-layer deposition and posterior cure of a thin liquid UV sensitive polymer, which would result in the desired part. This process is named stereolithography (SL). This emerging process resulted in the production of the first commercial equipment – Stereolithography apparatus, which was determinant for the growth of additive manufacturing. Up until this event, the only manufacturing technologies existents were traditional subtractive manufacturing and formative manufacturing methodologies [73].

The geometry of the desired part is produced through a CAD software model, being posteriorly converted into a STL file. This conversion is crucial for the interpretation of the production equipment. The conversion is responsible for the transformation of the solid model into a set of transversal layers that will be read by the pre-configured equipment to the desired needs.

AM technologies are interesting production technologies due to the design freedom, fastest producing times, along with a series of different techniques which include rapid prototyping and 3D printing. These aspects make AM stand out when compared to the traditional manufacturing process, increasing its industrial use [74].

2.5.1. Technics & Materials

According to the standard norm ISO/ASTM 52900:2015, AM comprises seven different process categories: **(i) vat polymerization**; **(ii) material extrusion**; **(iii) material jetting**; **(iv) binder jetting**; **(v) powder bed fusion**; **(vi) direct energy deposition**; and **(vii) sheet lamination technique** [75].

Briefly, the **vat polymerization** production process relies in the use of a liquid material, containing suitable light sensibility, which will be cured in a selective manner, forming the 3D part. **Material extrusion** appears as a process that uses material in a filament form that is selectively deposited through a nozzle. In regarding to **material jetting**, droplets of the liquid material are selectively jetted, being then cured with UV light. **Binder jetting** also resources to liquid material that is deposited over powder material layers, and functions as a binder hence, the name of the process. **Powder bed fusion** is a process in which layers of powder material are selectively sintered by a laser beam. In the **direct energy deposition** process, the material is melted simultaneous to the deposition. Finally, the **sheet lamination technique** consists of a bonding process of material sheets to form a part [75], [76].

For this dissertation, the chosen technique is material extrusion. This approach focuses on the fact that it presents itself as an appealing and stimulating prototyping technique for developing the case study. Following the content presentation will be entirely focus on this technique.

2.5.2. Material extrusion

Technological approaches for AM are still recent. Material extrusion is the technology with the vastest number of equipment in the market. It was only in 1988 that the first concept of a material extrusion technique appeared, and S. Scott Crump was the first person to introduce this process. The purpose was to fabricate a toy for his daughter through an easy and faster process. To do so, he used a hot glue gun and formed with the melted material a small part with several layers. He later took his invention to Stratasys Ltd. in Minnesota USA, which was the first company to patent and manufacture equipment for material extrusion. Fused deposition modelling (FDM), fused filament fabrication (FFF) or melted extrusion fabrication, started to spread across the world, becoming the most used method for the production of rapid prototype parts [77] .

i. Process Sequence

The production of a part using material extrusion became simple with time and technological advances. Nowadays, almost any person can design a small part, in proper software design, and then proceed to the fabrication using a FDM equipment.

Concerning the piece to produce, the creation of the CAD model is crucial. The file is posteriorly converted into an STL format. This conversion is essential for a correct reading by the equipment. Briefly, it consists in a transformation of the solid model into a series of slices for the posterior layer deposition. Once the model is defined, it is important to determine the material and the appropriate processing conditions (e.g. building orientation, infill type, deposition speed). In general, these parameters are standard, yet, depending on the equipment, there can be more variants. Figure 2.14 depicts the process sequence.

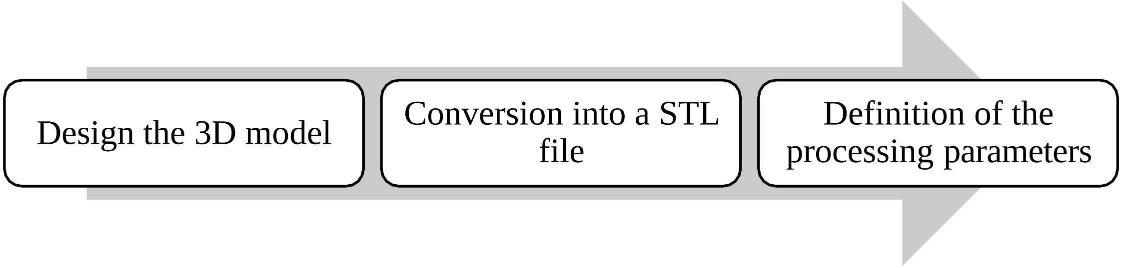


Figure 2.14 – Process sequence for the material extrusion technique.

In the FDM process (see Figure 2.15), the filament of thermoplastic material is transported by drive wheels until the nozzle. At the nozzle, the material is subjected to a heating process until melting. Then, it is extruded over the building platform creating a pre-defined pattern [78].

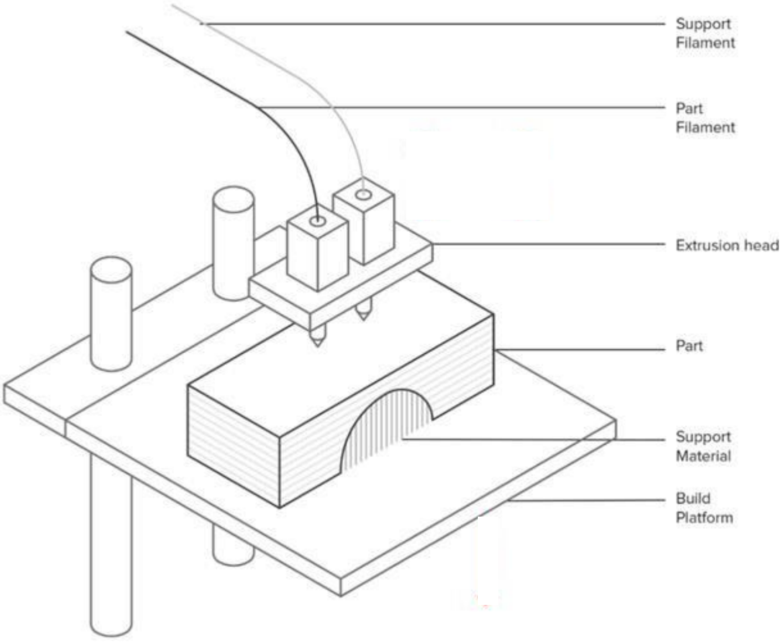


Figure 2.15 – FDM process scheme (adapted from [63]).

It is important to notice in this process the existence of the support material, which can be a weaker material or the same as the building material. For the process, this material is deposited in pre-defined locations to sustain critical areas of the part to build. Typically, the support material is extruded, in the first phase, to give a base between the part and the heated building platform. The support location and configuration typically are optimized by resourcing to specific software or by adequate the part design. Once the part is complete, it has left to cool for a short amount of time to solidify completely [79].

ii. Parameters

When processing a part employing FDM, it is necessary to adequately define the process control parameters in order to accomplish a part with good quality. Several studies related to process parameters and respective optimization are available in the literature [80]–[82].

Temperature parameters mainly include the nozzle and building platform temperature, nevertheless for some equipment's building temperature is also a variable. The establishing of these values considers the material properties, such as for example, melting and glass transition temperature and viscosity. Another important aspect is the diameter of the nozzle tip, typical values are 1,75 mm and 2,85 mm. Other parameters are directly responsible for the part geometry quality and mechanical performance, including layer height, contour width, air gaps, raster angle, number of contours, among others. Layers consist of the slices that were previously converted by the STL file. The layer height is a controlled aspect that affects the quality surface and the building time. For instance, a thicker layer decreases the total building time, the surface quality in the finish decreases, contrarily, a thinner layer potentiates an improved finishing, requiring a longer building time. The control of the deposition process of layers is divided by the orientation of the model, the path orientation of the layers, and building orientation (X, Y, and Z axes of the building platform). Normally, these parameters are widely studied for process optimization [83]. Between layers, it is possible to control the air gap, which indicates the space within each raster tool path. Larger air gaps usually decrease the mechanical properties of the part. Additionally, raster width and raster angle are often misunderstood due to the apparent similarity of nomenclature. Raster angle refers to the angle of the raster pattern concerning the axis of the building plate. Raster width is referent to the thickness of the material, which depends directly on the inherent nozzle tip. Infill density and style (e.g. linear, hexagonal) are also of great influence in the structure of the part since, the filling of the part directly affects the mechanical properties. The combining of these parameters, results in an adequate part, responding to the manufacture desires enable the construction of prototypes testing [84]–[88]. A broad summary of them are observable in the following figure (see Figure 2.16).

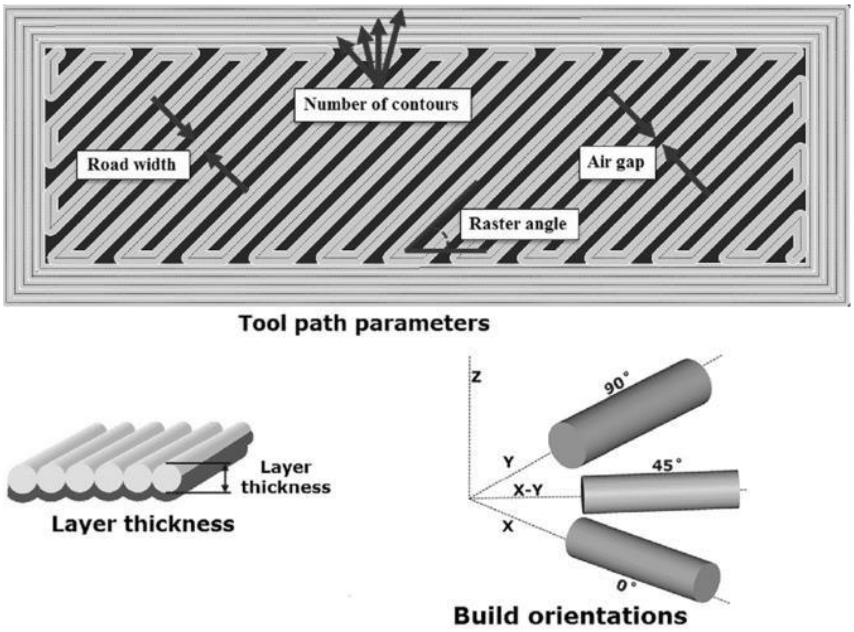


Figure 2.16 – Process parameters in FDM [89].

iii. Materials

For FDM, there is a set of specifications that the material must correspond, in order to guarantee a successful fabrication process and the obtaining of quality parts. The most important properties include: (i) typology; (ii) viscosity; (iii) dimensional stability; (iv) crystallinity; (iv) thermal conductivity; (v) heat resistance; and (vi) mechanical properties. Materials with amorphous structures are the most employed; however, semicrystalline are also used. Historically the most used materials are Acrylonitrile butadiene styrene (ABS), amorphous structure and Polyacid lactic (PLA), semicrystalline structure [90].

In terms of typology, FDM resorts to filaments of materials to build parts. The filament diameter, as previously stated, ranges between 1,75 mm and 2,85 mm. When using larger diameters, a higher temperature is necessary to assure a complete melt [91]. Considering that the filament passes through a nozzle tip with a specific dimension, the dimensional tolerance of the filament is crucial. The dimensional tolerance affects the process and, consequently, the quality of the part. Typical dimensional tolerance values range between ± 0,05 mm and ± 0,1 mm [92].

Similar to other processing technologies for thermoplastic materials, the viscosity is an important property for the printing process. A lower viscosity may promote adhesion through molecular diffusion resulting in parts with improved mechanical properties. Also, as the material becomes more fluid, the passage of material through the nozzle is easier. It is important to consider that, when decreasing the viscosity by incrementing temperature, one must be careful to avoid possible material degradation [93], [94]. Although a lower viscosity presents benefits to the building process, a minimum extensional viscosity is required for the production of filaments by extrusion. Therefore, the viscosity of the material must be balanced in order to take into account these two effects.

The dimensional stability (variation of dimensions caused by exposure to temperature fluctuations) of parts, in any production process, is of major importance. Polymeric based parts manufactured by material extrusion are prone to the occurrence of warpage and residual stress [95], [96]. The crystallinity of the building material also influences the dimensional stability of the resultant part. The building material for FDM should present higher mechanical properties than those intended for the final part, in order to assure that the final part withstands the demands, when in service conditions [79]. Semi-crystalline polymers present better mechanical behaviour and chemical resistance, being suitable for demanding applications [93], [97]. A balance between the properties must be achieved as they are interdependent.

iv. Applications

FDM is a technology used mostly, by the industry, for the production of rapid prototypes. These prototypes have an increased value, due to its similarity to the original product, enabling pre-functional tests before the actual production. Jigs and features are also an application, in substitution to the standard metals, providing weight reduction, customization, and easy handling, at the production floor [98]. Additionally, final products are also commercialized, the use of this approach is in constant growing, for instance, the use in aerospace industry provides critical and non-critical aircrafts parts [99].

Summarily, almost in every industry the presence of material extrusion is starting to be a usual presence, from medical devices and supplies, to automotive industry and much more [100], [101].

v. Advantages & Drawbacks

One of the many advantages of the material extrusion technology includes the cost-effectiveness of the fabrication of customized products and prototypes presenting shorter lead times and design freedom. Also, when referent to plastic materials, a wide range of thermoplastic materials are available for manufacturing, since common purpose to high performance. Whereas, it is a process that, when compared to other AM techniques, provides the lowest dimensional accuracy, resulting in a weaker resolution. In some cases, the support material is soluble while in other cases the support material is the same as the building material and therefore, after removal, it is noticeable the areas where the support material was attached, which inevitably, decreases the aesthetical aspect alongside could also affect the final purpose of the part [84], [102].

2.6. Functional materials for additive manufacturing technologies – material extrusion

Typically, the functional materials available for material extrusion are materials that change colour depending on a temperature stimulus or a light stimulus. This colour change is usually reversible but only between two colours, the main one and the one representing the stimulus-response. Usually, this material is used commercially for playful purposes. However, more and more functional materials have emerged for technical purposes, such as conductive inks for printing conductive electronic circuits or, for example, materials with a shape memory form[103]–[105].

3. Experimental Component

In this chapter it is described in detail all the experimental framework used for development and study the most suitable functional material for material extrusion. For a better comprehension of every material phase, each of its steps, like material development and filament production, will be presented.

3.1. Material Selection

Polyacid lactic (PLA) was the immediate choice for the compounding of the functional material. PLA is one of the commercial materials most commonly used, due to its ease of handling in the process, and by not presenting toxicity. Also, it presents appealing mechanical properties and the relative affordable price are also crucial factors for the permanent choice. Purchased in AGI – Augusto Guimarães e Irmão, Lda, PLA Ercros Bio LL 712 (see Figure 3.1) becomes the polymer matrix of the desired mixture. With the need to develop a functional material, the thermochromic behaviour was the crucial feature chosen for this mixture. For this, it was purchased a thermochromic masterbatch compatible with a polymer matrix to the company Donna Polymer, TCMB-PLA-22FDA Series (see Figure 3.1). The selection of the masterbatch compound was based in the activation temperatures which were defined according to the average human temperature. This way, the material could easily be stimulated by touch, among other types of stimulations. Thus, the activation temperatures were 20 °C and 31 °C, i.e. below 20°C the material is purple, between 20 °C and 31 °C assumes the red colour and above 31 °C it assumes the colour of the polymeric matrix. Both technical datasheets are presented in APPENDICES (1. and 1.A)

Figure 3.1 – Granular thermochromic masterbatch (left), granular polymeric matrix of PLA (right).

3.2. Methods and technics

For the development of a functional material for additive manufacturing, besides theoretical research, it is necessary to do a series of steps to accomplish the suitable material for the correct production of the part. Since the technique used will be material extrusion, the material needs to have a filament form with the correct diameter suitable to the machine.

Thus, characterization technics were introduced firstly in order to understand the material behaviour based on thermal and physical properties. This knowledge enables a better definition of the processing parameters to ensure a proper and correct development of filaments. Characterization in the produced filaments was also ensured for an understanding of the material behaviour based on the integration of the thermochromic filler, and also to evaluate which mixing ratio presents the most suitable performance for the application purpose. Figure 3.2 shows the main steps defined to achieve the case-study while Table 3.1 and Table 3.2 summarize the characterization tests for the raw material and developed filaments, respectively.

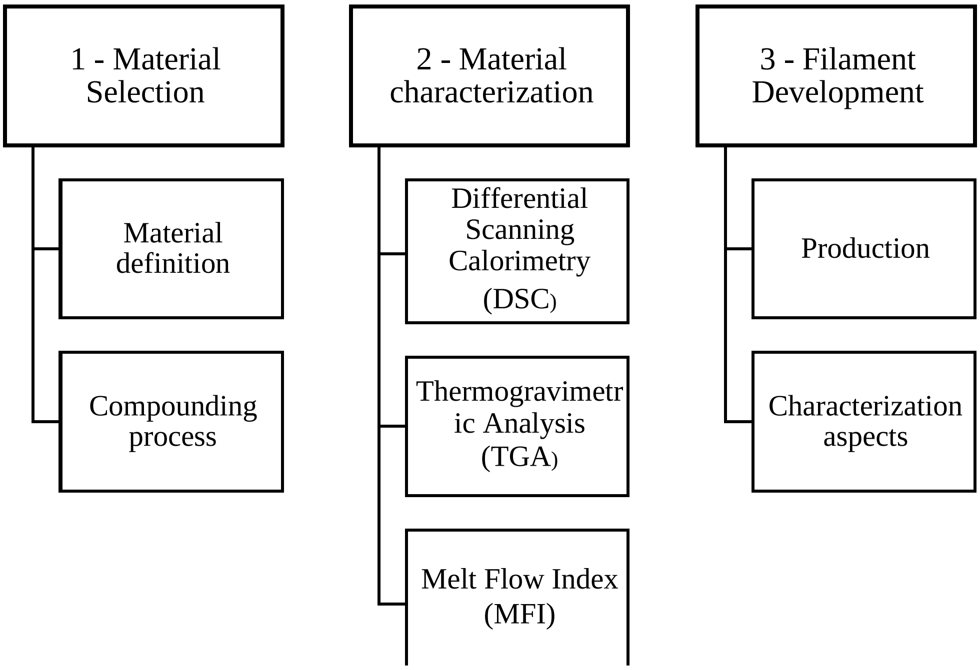


Figure 3.2 – Scheme representing the needed steps to accomplish the correct case-study.

- Materials

Table 3.1 – Characterization tests for the raw material and thermochromic masterbatch, previous to filament production.

Test	**Proceeding description**
Differential Scanning Calorimetry (DSC)	DSC test was performed to understand the melting and crystallization behaviour of the materials in the study. Based on this test, it was possible to obtain information regarding the thermal properties, including: the degree of crystallinity, thermal transitions temperatures, and associated enthalpies. The degree of crystallinity is calculated by the following equation: $$D_c = \frac{\Delta h_f}{\Delta h_c} \times 100\% \qquad (1)$$ Where D_c corresponds to the degree of crystallinity; Δh_f corresponds to the heat of fusion at the melting temperature; and Δh_c is the heat of fusion of the purely crystalline material, Δh_c PLA = 93 J/g [106] (1). For each material, two tests were performed, under a nitrogen atmosphere, with the *Netzsch DSC 200 F3 Maia* equipment and according to ISO 11357. The tests considered a first heating cycle, with a temperature range from 0 °C to 220 °C at a heating rate of 10 °C/min, in order to erase the thermal history of the samples. Next, a cooling step took place (from 220 °C to 0 °C at a heating rate of 10 °C /min), followed by a second heating cycle (from 0 °C to 220 °C at a heating rate of 10 °C/min) to record the melting thermogram. This analysis enables the evaluation of the thermal behaviour between the granular PLA and the respective additive. The samples mass assumed were 13,13 mg and 15,24 mg for the polymeric matrix and masterbatch respectively.

Thermogravimetric Analysis (TGA)	Thermogravimetric analysis was performed to evaluate the weight loss of the samples, as a function of a temperature increment, at a specific heating rate. It also allows us to understand the amount of inorganic compounds present in the material. The test was performed with a *TA Q500* equipment from *TA Instruments*. Testing conditions include an inert atmosphere based in nitrogen pumped with a flow rate of 60 mL/min for the sample and 40 mL/min for the balance). A heating rate of 10 °C/min with a temperature range from 30 °C up to 700 °C was considered for both material samples.
Melt Flow Index (MFI)	Melt flow index test was performed to evaluate the processing properties of the polymeric matrix. The MFI test was performed with resources to an MFI *Daventest* equipment and in accordance with the international standard test norm ISO 1133-1:2011(E). The material was previously dried for 5 hours at 85 °C to remove moisture content and, an average of 10 mg was used for the test. Briefly, the principle of this test consists on the extrusion of material through a capillary, with specifying length and diameter and under defined temperature and load. In this case, the load considered for the extrusion process was 2,16 kg, and the processing temperature was 210 °C (value established considering the technical data sheet indicated by the fabricant). Samples rate collection was at each 5 s until the piston accomplished the final mark.

- Filament

Table 3.2 – Characterization tests for the developed filaments.

Test	Proceeding description
Dimensional tolerance	To infer if the production of filaments occurred without significant changes in regarding to the diameter dimension, it was performed a series of measurements with a digital calliper to evaluate the diameters' uniformity along the filaments' length. Fifty measurements of the filaments' section were performed at each 10 mm, and an average was calculated.

Differential Scanning Calorimetry (DSC)	DSC test was performed to understand the melting and crystallization behaviour of the different produced filaments and to compare the obtained information in regarding to thermal properties (e.g. degree of crystallinity, thermal transitions temperatures, and associated enthalpies) with the original material (polymer matrix and masterbatch). The degree of crystallinity was calculated by using equation 1, presented in the previous table. For each filament, two tests were performed, under a nitrogen atmosphere, with the *Netzsch DSC 200 F3 Maia* equipment and according to ISO 11357. Additionally, all the samples pre-dried at 85ºC for 5 hours. The tests considered a first heating cycle, with a temperature range from 0 °C to 220 °C at a heating rate of 10 °C/min, to erase the thermal history of the samples. Next, a cooling step took place (from 220 °C to 0 °C at a heating rate of 10 °C /min), followed by a second heating cycle (from 0 °C to 220 °C at a heating rate of 10 °C/min) to record the melting thermogram. This analysis enables the evaluation of the thermal behaviour between several filaments. The sample mass for filaments were for the *"Neat Formulation"* 11,72 mg, for the "*Manufacturer Suggestion"* 11,10 mg and for the *"New Approach"* filament 12,10 mg.
Thermogravimetric Analysis (TGA)	Thermogravimetric analysis was performed to evaluate the weight loss of the samples, as a function of a temperature increment, at a specific heating rate. The TGA also allows to infer the amount of fillers that are in the composition of the filaments and enable its functionality. The test was performed with a *TA Q500* equipment from *TA Instruments*, a pre-dry was done at 85 °C for 5 hours. Testing conditions include an inert atmosphere based in nitrogen pumped with a flow rate of 60 mL/min for the sample and 40 mL/min for the balance). A heating rate of 10 °C/min with a temperature range from 30 °C up to 700 °C was considered for both filament samples.

Melt Flow Index (MFI)	An MFI test was performed to evaluate the processing properties of the filaments. The MFI test was performed with resources to an MFI Daventest equipment and in accordance with the international standard test norm 1133-1:2011(E). The produced filaments were first prepared into 5 mm length granules, and then pre-dried at 85 °C for 5 hours, previous to the test. Briefly, the principle of this test consists of the extrusion of material samples through a capillary, with specifying length and diameter and under defined temperature and load. In this case, the load considered for the extrusion process was 2,16 kg, and the processing temperature was 210 °C (value established considering the characterization tests previously done to the polymeric matrix). Samples rate collection was at each 5 s until the piston accomplished the final mark.
Tensile Test	Tensile testing was performed on the filaments. The test was performed with an *Instron 5969* Dual Column Tabletop Testing System, without extensometer, and in accordance with the test norm ASTM D638-1. Testing conditions include testing speeds of 5 mm/s; a load cell of 50 kN; and 45 mm of the gauge length. The test was performed at 23 °C, for seven samples for each filament.
Optical Analysis (transmission microscopy)	An analysis of the filament morphology was performed with a transmission microscope *Olympus BH2*. The analysis proceeded with two magnifications 10x2,5 and 20x2,5. The sample was first prepared with the aid of a glass knife along with the microtome, to have a film with 10 µm of thickness. The knife cut was made transversally. Next, the sample was embedded in *Canada balsam* to improve the optical quality of the sample for the microscopic analysis. This characterization is important for the understanding of the filler (from the masterbatch) distribution along the filament.

Stimulation Testing	One filament sample for each mixing ratio with the thermochromic feature were prepared for the stimulation test presenting 50 mm length. Filaments were subjected to a freezer in order to accomplish the lowest temperature possible for 2 min. They were then removed from it and their colour development was recorded, in a room temperature environment, using a thermographic camera *FLIR* and a common photographic recording camera. The colour registration was done every 10 seconds .

3.3. Material Development

3.3.1. Compounding Definition

Considering the primary purpose of this work, the development of a functional material for additive manufacturing, for a better comprehension of the thermochromic effect, a compounding strategy was defined. Two different mixing ratios were defined between the polymer matrix and the thermochromic masterbatch. Both mixing ratios are observable in Table 3.3.

The first approach for the initial mixing was decided according to the masterbatch manufacturer's suggestion. For the second mixing, an increasing to the double was considered in regarding to the thermochromic masterbatch.

Additionally, a third ratio was also defined, only with the raw material matrix. This way, it is possible to evaluate and compare the effect of the addition of thermochromic material based on the polymer matrix material.

The compounding process occurs in a volumetric dispenser attached to the extruder hopper, which was pre-programmed with the pre-defined mixing ratios.

Table 3.3 – Nomenclature definition for each mixing ratio pre-defined.

Nomenclature Definition	**Ratio (wt % :wt %) (Polymeric matrix : additive)**
"Manufacturer Suggestion"	88,5 : 11,5
"New Approach"	76 : 24
"Neat formulation"	100 : 0

3.4. Material characterization

In this phase, it is exposed a set of results and further discussion regarding to the material characterization. Thermal, physical and morphologic characterizations of both raw PLA and thermochromic masterbatch are presented and analysed.

3.4.1. Differential Scanning Calorimetry (DSC)

The DSC curve provided by the experimental test enables the observation of the melting thermograms for the material of the polymeric matrix and for the thermochromic additive used for the posterior mixtures. Figure 3.3 presents the DSC thermogram corresponding to the second heating cycle, which is representative of the thermal behaviour of the samples without the effects of processing. The first cycle erases the processing history, and the second cycle provides information about the thermal behaviour without external effects.

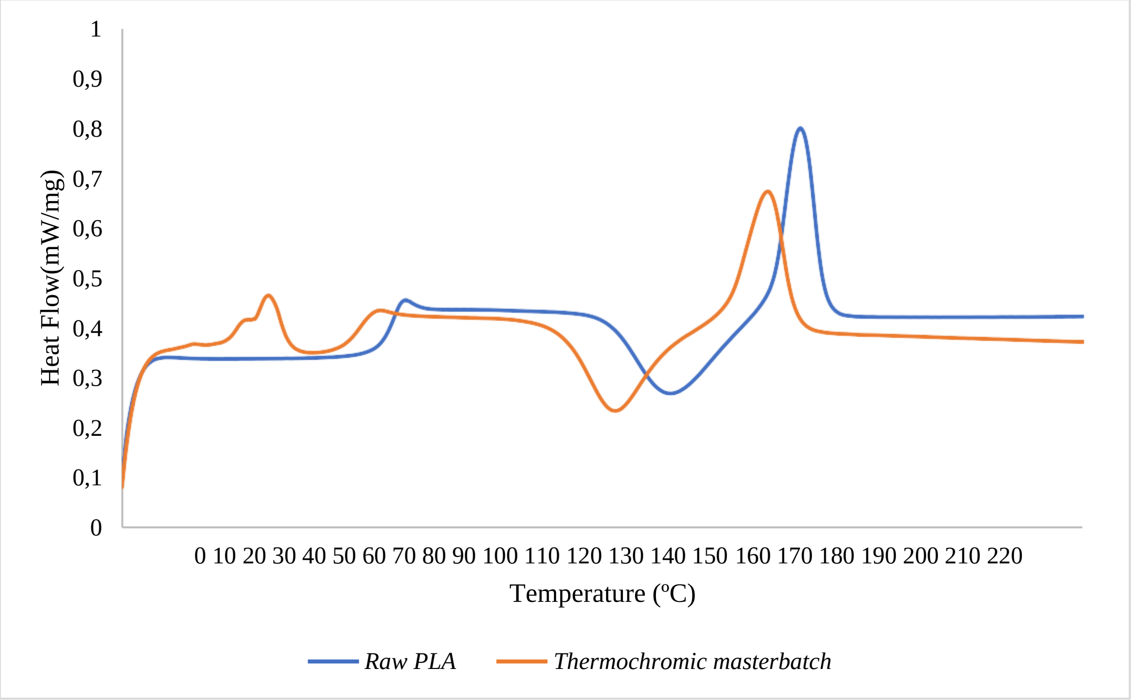


Figure 3.3 – DSC thermogram regarding the materials in study.

In the curve corresponding to the thermochromic masterbatch, considering the first phase of the cycle, in the first transition order zone, it is observable some peaks in the temperature range of 20 °C and 40 °C. This could indicate the presence of a molecular loss form related to the presence of the pigments in the polymer matrix, once that the temperature range observed is the same where is possible to observe the colour transitions due to the temperature variation. Comparing with the raw material, in the curve are not presented peaks at the beginning of the second heating cycle, overall, the curve appears to be a typical semi-crystalline material.

Regarding the temperature at which occurs the most significant molecular mobility, the melting temperature, it is noticeable a higher value for the temperature on the neat material 155,4 °C. The melting temperature of the thermochromic additive is 147,9 °C. It may be inferred that the PLA matrix from the masterbatch is different from the raw PLA (see Table 3.4).

Table 3.4 – DSC results.

Material Samples	**Glass Transition Temperature (°C)**	**Melting Temperature (°C)**	**Degree of crystallization (%)**
Raw PLA	61,2	155,4	19,56
Thermochromic masterbatch	54,8	147,9	18,03

3.4.2. Thermogravimetric Analysis (TGA)

From the following graphic (see Figure 3.4), it is shown a single step degradation curve, with an earlier weight loss sample is noticed between 150°C and 300 °C. Typically, in this temperature range, the mass loss verified is due to a loss of components of low molecular weight presents in the polymer, such as, volatile components, residual solvents or additives with low molecular mass.

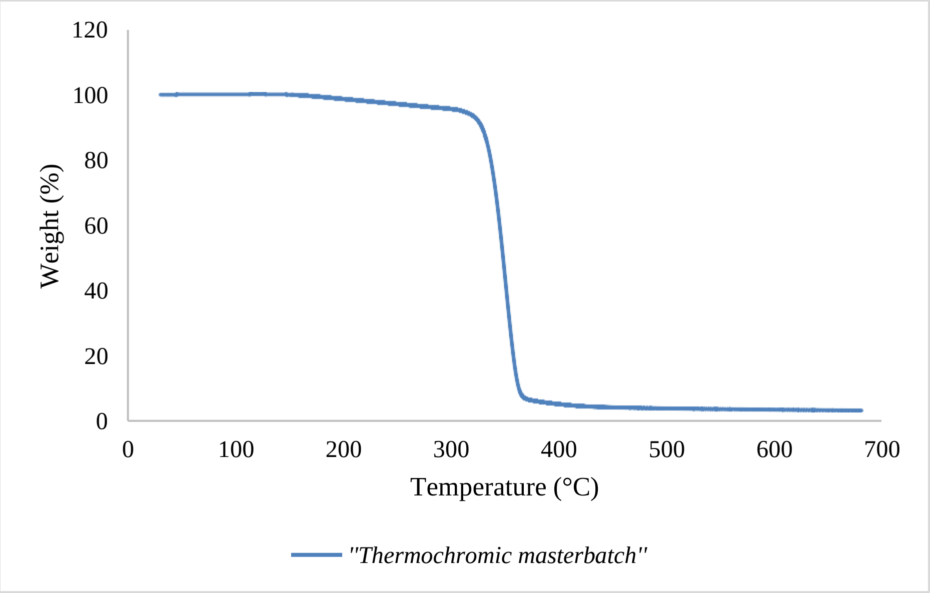


Figure 3.4 – TGA Thermogram for the thermochromic masterbatch.

The thermochromic masterbatch shows a value of 96,84 % for the weight loss, in this case only the masterbatch is observed, indicating a left-out residue originated from the degradation of the material which the constitution is different (see Table 3.5).

Table 3.5 – TGA results for the thermochromic masterbatch.

	Onset Temperature °C	**1st Derivative Peak Temperature °C**	**Total Weight Loss %**	**Total Residue %**
Thermochromic masterbatch	334,81	351,16	96,84	3,16

3.4.3. Melt Flow Index (MFI)

The MFI experimental results, in Table 3.6, present a significant difference when compared with the datasheet value, provided by the manufacture. This may be explained by an error in the experimental conditions and considerations. Besides the dehumidification of the material, an average of six trials were done to validate the value showed next.

Table 3.6 – Obtained results regarding the MFI of the raw PLA.

Datasheet value	8 g/10min
Experimental value	15,09 ± 0,6 g/10min

3.5. Filament Development

3.5.1. Equipment and processing aspects

Filament extrusion was the process used for the correct filament development. The equipment used for this production was the *Coperion ZSK 26 extruder* presenting a twin-screw with a co-rotational movement. Equipment specifications are presented in more detail in the APPENDICES (2).

The process parameters used for the filament production were the optimised values based in a pre-production experiment. This first experiment was to obtain a filament carried out with a diameter suitable for the material extrusion technique. Thus, the expected filament diameter should be 1,75 ± 0,02 mm. However, some parameters are defined initially, which are typical for all the processes independently of the filament diameter, as shown in Table 3.7. Both materials were pre-dried in order to remove moisture content.

Table 3.7 – Process parameters for the filament extrusion process.

	Condition (unit)	Value
Material	Drying time (h)	5 – 6
	Drying temperature (°C)	85
Equipment	Screw Speed (rpm)	180
	Die Temperature (°C)	180
	Heaters temperature (°C)	170
	L/D	40
	Colling zone temperature (°C)	15

3.5.2. Filament production

The production of the three mixtures - *"Manufacturer Suggestion"*, *"New Approach"* and *"Neat Formulation"* was proceeded with the processing parameter mentioned before. For the process parameters affecting the diameter and ovality of the filament dimensions, an optimization of the rollers' speeds at the cooling zone was necessary. Figure 3.5 shows the extrusion machine, on the left, and, on the right, presents the respective cooling zone with two roller speeds.

Figure 3.5 – Extrusion machine (left), cooling zone (right).

For the initial optimization, *"Neat Formulation"* (based in raw PLA), was the first filament to be produced. Around 10 measurements were made with an interval of 1 minute in order to observe the roundness of the filament and the respective diameter. The best relation between diameter versus roundness was accomplished with a first roller speed of 30,00 rpm and a second roller speed of 26,49 rpm. The same conditions were used for the filament production of the mixture "*Manufacturer Suggestion"*, obtaining similar diameter results. In regarding to the mixture *"New Approach"*, the diameter obtained at the same conditions was significantly lower, which lead to a new optimization of the roller speeds, with a result of 25,22 rpm for the first roller and 21,54 rpm for the second one. Produced Filaments are showed in Figure 3.6.

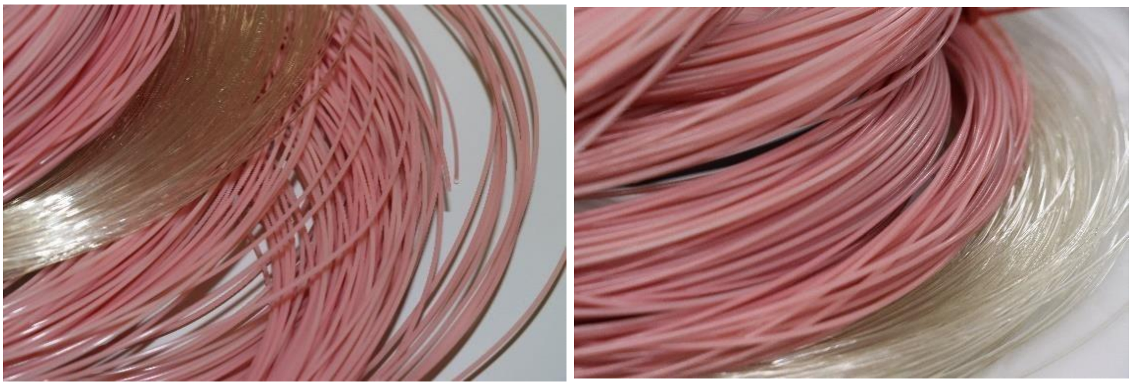


Figure 3.6 – Produced Filaments.

Due to the way the cooling zone was set up, the filament diameter already suffers alterations on a geometry level, because the material does not contact at the same time in all of the surface in the water bath. This condition caused a filament with an oval geometry instead of a circular one by defect, not being possible to accomplish the same diameter through the transversal section of the filament. In Figure 3.7, it is possible to see the filament geometry with more detail. Nevertheless, the defect mentioned before is not entirely observable; a better perception is possible when measured the dimensions with a calliper. Besides the produced filaments presented in the next figure, a commercial filament is also present. The commercial filament is present to enable a visual comparison of the filament geometry. Figure 3.8 shows the filament extrusion in detail.

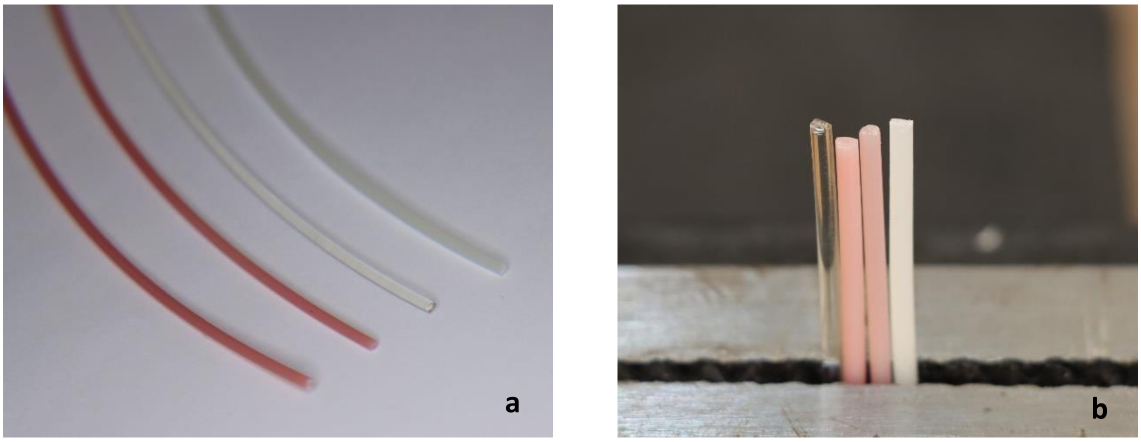


Figure 3.7 – Filament geometry: a) from left to right, 1st filament (*"Manufacturer Suggestion"*), 2nd filament (*"New Approach"*), 3rd filament (*"Neat Formulation"*), 4th filament (*"Commercial comparison"*) | b) from left to right, 1st filament (*"Neat Formulation"*), 2nd filament (*"New Approach"*), 3rd filament (*"Manufacturer Suggestion"*), 4th filament (*"Commercial comparison"*).

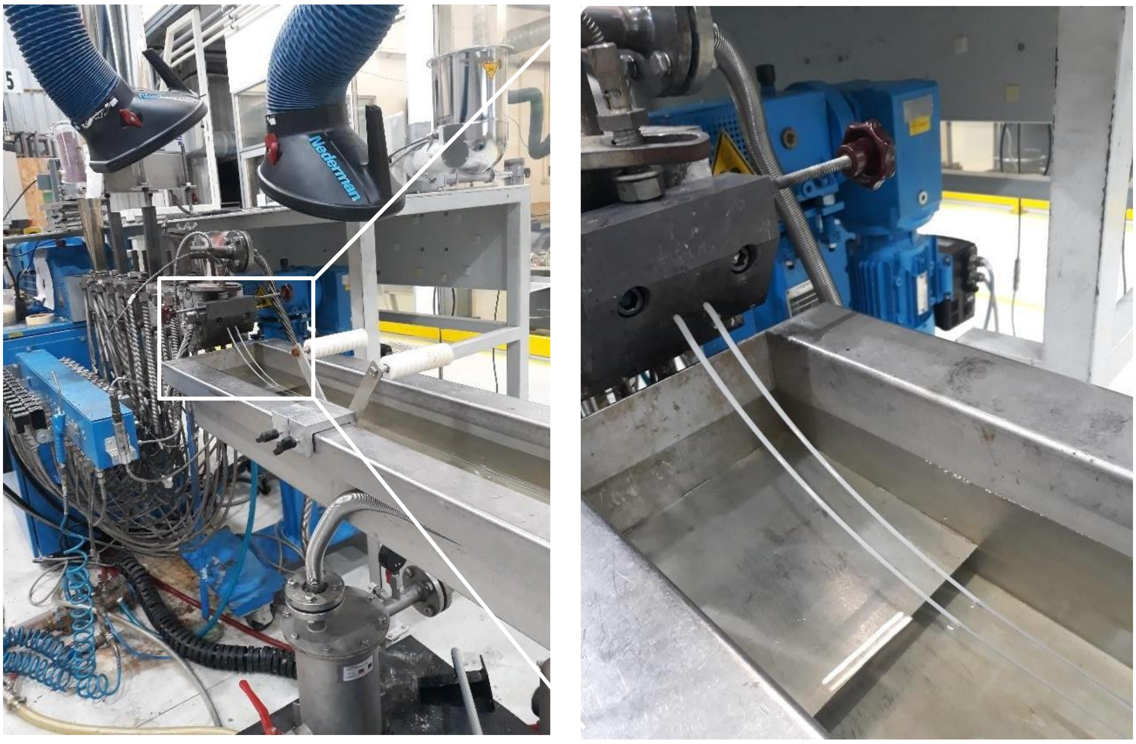


Figure 3.8 – Filament extrusion with detail of the extrusion die.

3.5.3. Characterization of the filaments

Regarding the filaments' characterization, the objective was to study the properties of the mixtures, and also to evaluate the influence of the masterbatch integration in the polymeric matrix.

i. Dimensional control

As mentioned in the topic Filament production, the dimensional control of the filament diameter was not accomplished as expected. It was decided to control the filament geometry as close as a diameter of 1,75 ± 0,05 mm.

Following, the dimensional control was carried out by obtaining two dimensions in the transversal section of the filament, D1 being the largest and D2 the smallest (see Figure 3.9). In the diagram below it is possible to observe the location of these two dimensions.

Where:

- D1 is the dimension represented by ↔
- D2 is the dimension represented by ↔

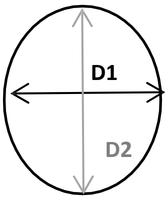


Figure 3.9 – Schematic representation of the transversal section of the produced filament.

In Figure 3.10 it is observable a practical example showing how the measures were proceeded through the filament.

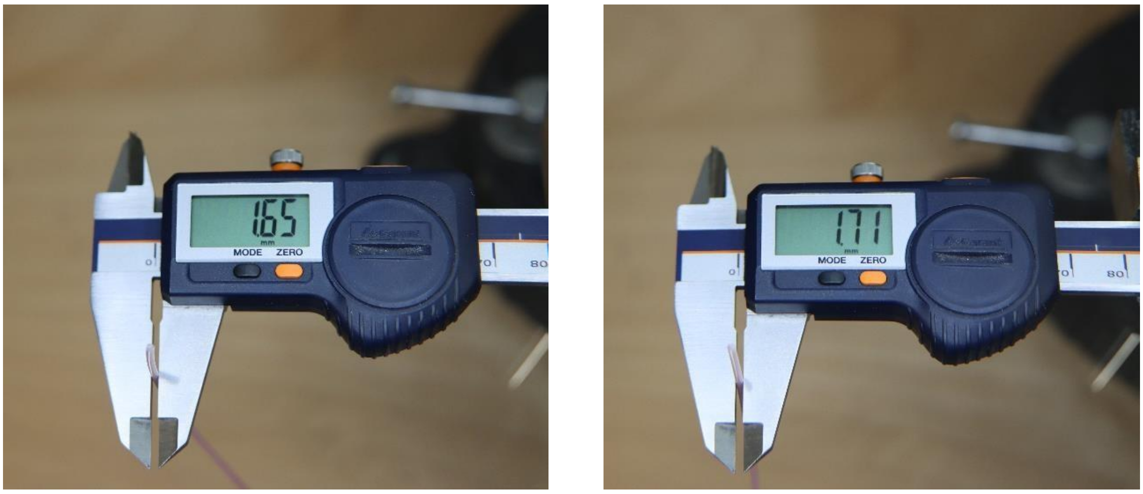


Figure 3.10 – Measurement of the dimensional filament control, (left – D1), (right – D2).

Observing the average values presented in Table 3.8, for the filaments with the thermochromic masterbatch, values of 1,66 ± 0,04 – 1,60 ± 0,04 mm were obtained for the *"Manufacturer Suggestion"* and 1,66 ± 0,06 – 1,63 ± 0,04 mm for the *"New Approach"*. The measured values' average and standard deviation appears to be similar. A more evident difference is observed for the filament dimension corresponding to the *"Neat Formulation"* with average values of 1,73 ± 0,02 – 1,65 ± 0,04 mm. From this analysis, it is possible to notice the average transversal dimension's influence when adding the thermochromic masterbatch to the polymeric matrix, indicating a diminishing in the average material per section, thus the smaller dimensions. Table 3.8 presents the average values of the dimensional control.

Table 3.8 – Filament average dimensions and standard deviation for the filament samples manufactured.

Filament samples	**Dimensions (mm)** **(D1 – D2)**
“Manufacturer Suggestion”	1,66 ± 0,04 – 1,60 ± 0,04
“New Approach”	1,66 ± 0,06 – 1,63 ± 0,04
“Neat Formulation”	1,73 ± 0,02 – 1,65 ± 0,04

ii. Differential Scanning Calorimetry (DSC)

Regarding the DSC thermogram (see Figure 3.11), for the filament samples, the plot curves present the same shape and similar peaks. After the transformation of the raw PLA in a filament form, glass transition temperature remains the same, and a 2 °C difference is observed regarding the melting temperature. The reprocessing of the material did not affect the specific temperatures, however, for the melting enthalpy, a larger area is noticed in the material after the processing which is indicative of a higher degree of crystallinity, pointing to a molecular structure more aligned and regular through the molecular chains. This organization had origin in the second heating process originated by the processing method.

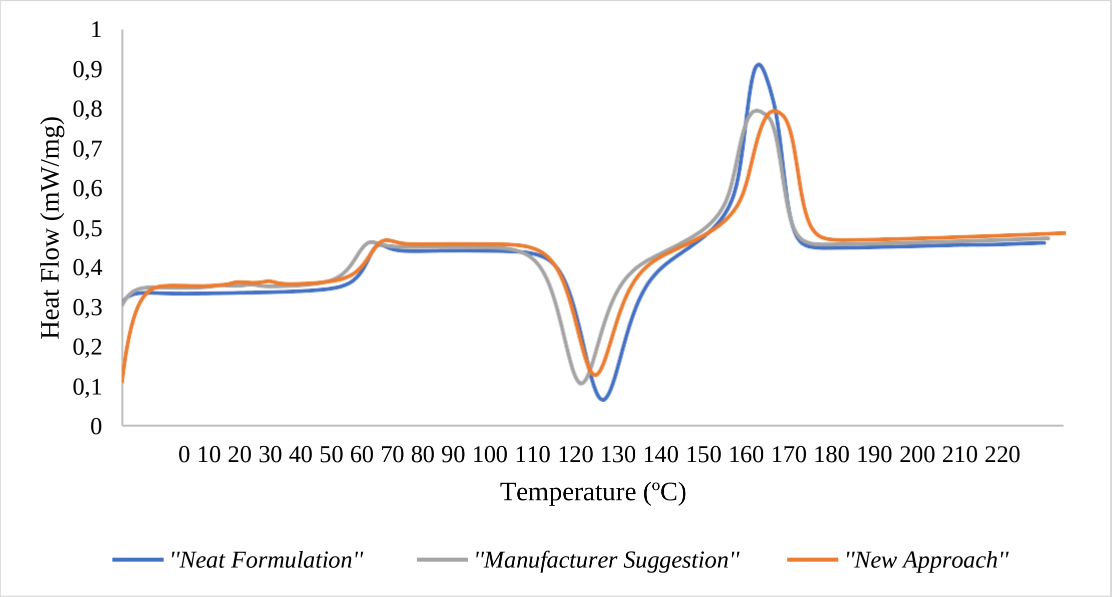


Figure 3.11 – DSC thermogram regarding the produced filaments.

Regarding the filament with the mixture *"Manufacturer Suggestion"*, peaks on the first transition phase, are also observed. Its presence could validate the presence of additives in the molecular structure due to the verification in the granular form, as mentioned before. Regarding the melting enthalpy, both areas above the melting peak are close revelling similar degrees of crystallization, 27,68 % for the mixture "*Manufacturer Suggestion*" and 25,58 % for the mixture "*New Approach*". For the glass transition temperature, a small difference is observed for the different mixtures, 57,6 °C for the "*Manufacturer Suggestion*" mixture and 57 °C for the "*New Approach*". Comparing all the filaments with the addition of masterbatch, the value of the glass transition temperature decreases, which indicates an influence in the chain mobility. In another aspect, for the melting temperature with the addition of the masterbatch, a 1 °C of disturbance is observed, in comparison to the "*Neat formulation*".

Table 3.9 – DSC plot results in regarding to the produced filaments.

Filament Samples	**Glass Transition Temperature (°C)**	**Melting Temperature (°C)**	**Degree of crystallization (%)**
"Neat Formulation"	61,2	153,4	30,41
"Manufacturer Suggestion"	57,6	152,1	27,68
"New Approach"	57	152,3	25,58

iii. Thermogravimetric Analysis (TGA)

Concerning the plot from the graphics, in Figure 3.12, it is observable a single step degradation curve, which differs at the beginning of the samples weight loss.

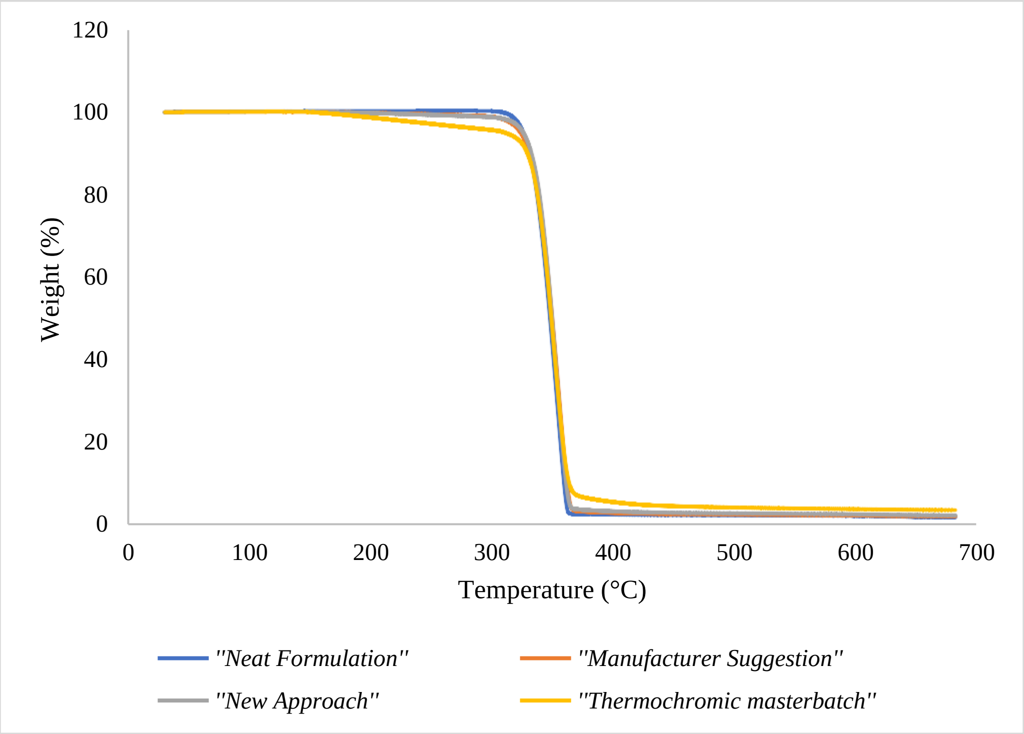


Figure 3.12 - TGA Thermogram.

In respect to the TGA curves, the onset temperature represents the beginning of the thermal degradation. It is noticeable a considerable weight loss from the original mass of material from this point. Comparing the filament samples with the masterbatch addition, the temperature only differs in approximately 1 °C, assuming a value of 335,54 °C for the *"Manufacturer Suggestion"* filament and 336,49 °C for the *"New Approach"* filament. This could be interpreted as a variation in the experimental test, since atmosphere effects or secondary reactions, indicating similar influence when adding a larger quantity of masterbatch. For the *"Neat Formulation"* filament, the beginning of the degradation starts at an early temperature (333,41 °C). Similar behaviour is observed for the masterbatch 334,81 °C. At the end of the test, the weight loss observed for the filaments was larger for the *"Neat formulation"* filament, assuming a value of 98,65 %. Following is the *"Manufacturer Suggestion"* filament with a total weight loss of 98,40 % and the *"New Approach"* filament with 98,12 %. The *"Neat formulation"* filament was the material that presented the largest weight loss and the least left out residue. Since this material has no masterbatch added, in this case, the remaining residue is a product of the rupture of the polymer chains. Commonly, for polymeric materials the degradation occurs until the remaining residue is carbon. However, in this case, it is not possible to identify what composes the residue because the test was all done with an inert atmosphere. For a better quantity analyses a change of the atmosphere should be done at 500 °C. When observing above 600 °C, the presence of material at such high temperature values, for polymeric materials, is usually an indicative of residue. The residue is commonly associated with the presence of inorganic compounds, since the loss of components of low mass component and the volatile products already occurred at lower temperatures. Regarding the filaments with the masterbatch addition, the sample weight lost was lower, 98,40% for the filament "*Manufacturer Suggestion*" and 98,12% for the "*New approach*". Comparing both, the weight lost is lower in the filament which has the increased quantity of masterbatch, indicating a possible presence of more inorganic compounds.

Regarding the DTG curve or the derivative of the TGA curve, presented in the Figure 3.13 it is visible a higher peak, for the "*New Approach*" filament. On the contrary, the lowest peak is represented by the masterbatch sample. The peak for the "*Neat formulation*" filament is observed between the peak corresponding to the filament "*Manufacturer Suggestion*" and the peak corresponding to the thermochromic masterbatch, indicating a beginning of the degradation at a temperature between the two samples.

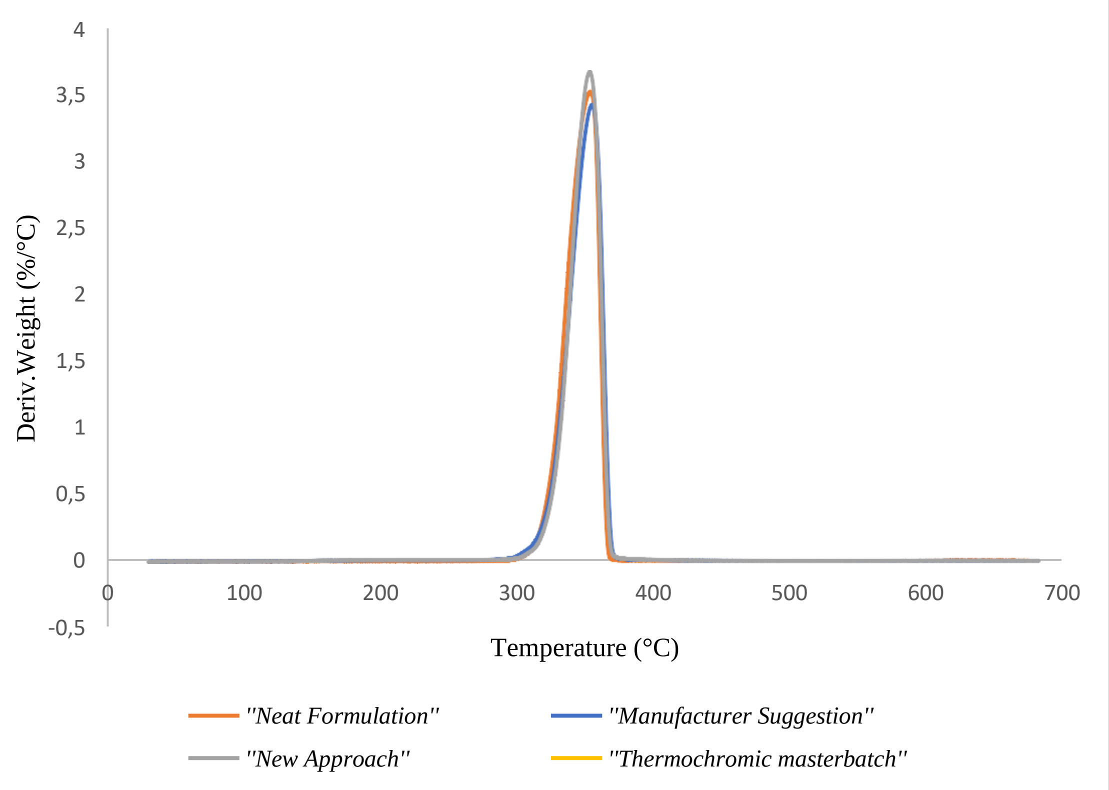


Figure 3.13 – DTA curve.

Table 3.10 – TGA plot results in regarding to filament produced.

Filament Samples	Onset Temp (°C)	1st Derivative Peak Temperature (°C)	Total Weight Loss (%)	Total Residue (%)	Pigment Residue (%)
"Neat Formulation"	333,41	353,83	98,65	1,37	0
"Manufacturer Suggestion"	335,54	354,93	98,40	1,63	0,26
"New Approach"	336,49	353,36	98,12	1,89	0,52

iv. Melt Flow Index (MFI)

The results for the MF test are presented in Figure 3.14. Regarding the results, the produced filaments with the addition of thermochromic masterbatch, present a decrease of the value of MFI, which could indicate that this masterbatch diminishes the molecular mobility. For the *"Neat Formulation"* filament, the value is 11,15 ± 0,01 g/10min. However, increasing the dosage of the masterbatch did not induce a significant difference from the initial value, from 4,91 ± 0,009 g/10min to 4,74 ± 0,004 g/10min.

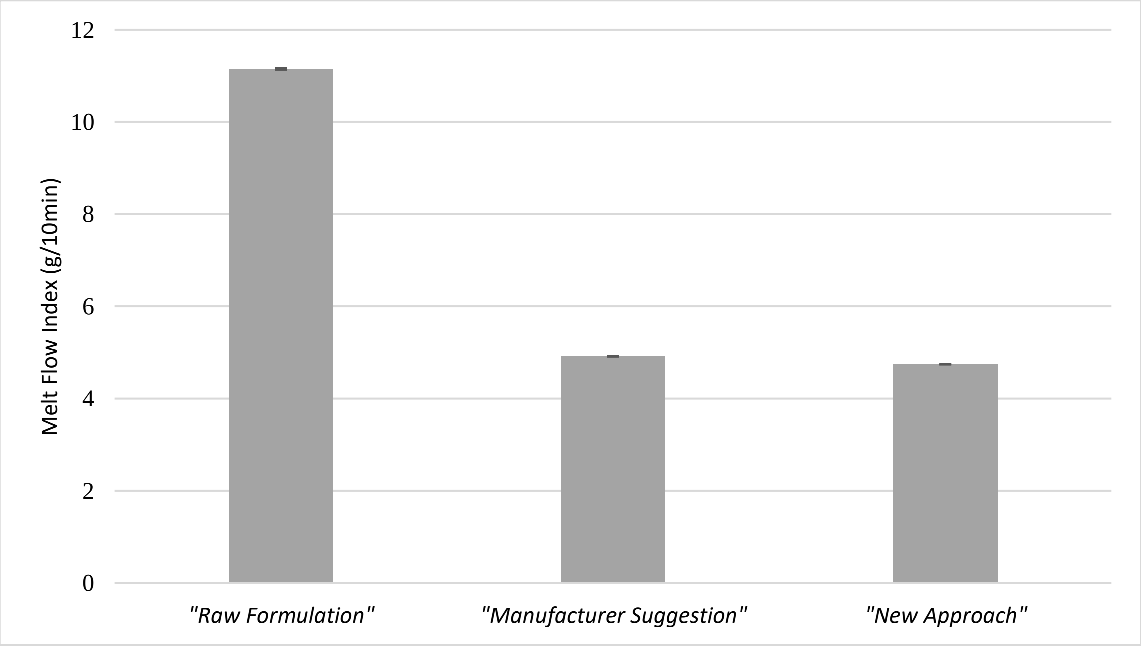


Figure 3.14 – MFI results for the materials in analysis.

v. *Tensile Testing*

For the mechanical testing, filaments were subject to a tensile test for a better evaluation of the processing effect. The tensile curves presented in Figure 3.15 are representative of the seven effectuated experiments, for each filament.

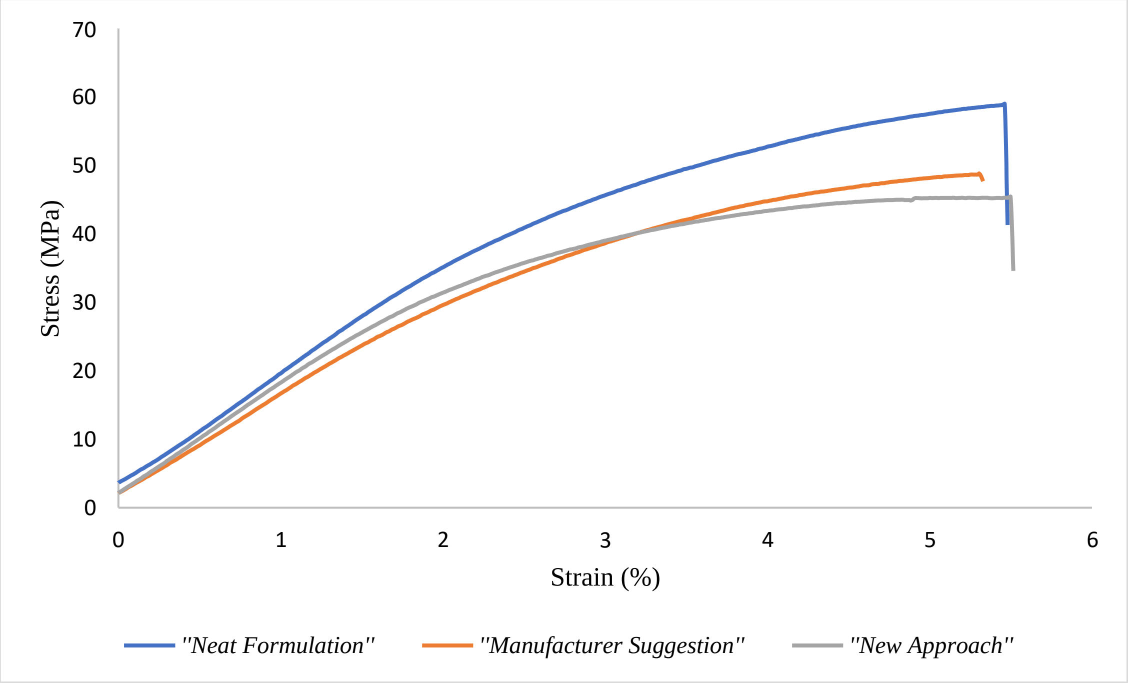


Figure 3.15 – Average Stress-Strain Curve.

In general, differences in the shape of the curve are visible indicating different mechanical properties among the manufactured filaments. The *"New Approach"* filament presents a larger strain before breaking. Contrarily, the filament which has the lowest strain is the "*Manufacturer Suggestion*" filament. Based on the presented chart, it is possible to indicate that the masterbatch addition has an effect on the mechanical behaviour.

Regarding the **Young's modulus** (see Figure 3.16), the values are quite close between all the tested materials. However, the standard deviation appears with higher values indicating a significant discrepancy between the values. The deviation in the Young's modulus may be due to the difficulty of griping the filament edges to the tensile testing machine. Over all it is observed a higher value for the *"New Approach"* filament (1547,12 ± 272,74 MPa), while for the *"Manufacturer Suggestion"* filament a similar value is observed (1525,53 ± 229,98 MPa). These values demonstrate that the masterbatch addition increases, but not significantly, the Young's modulus. Lastly, the

"Neat Formulation" filament has the lowest value, 1478,85 ± 164,65 MPa. Figure 3.16 presents a chart with the average values and standard deviation for each filament material in analysis.

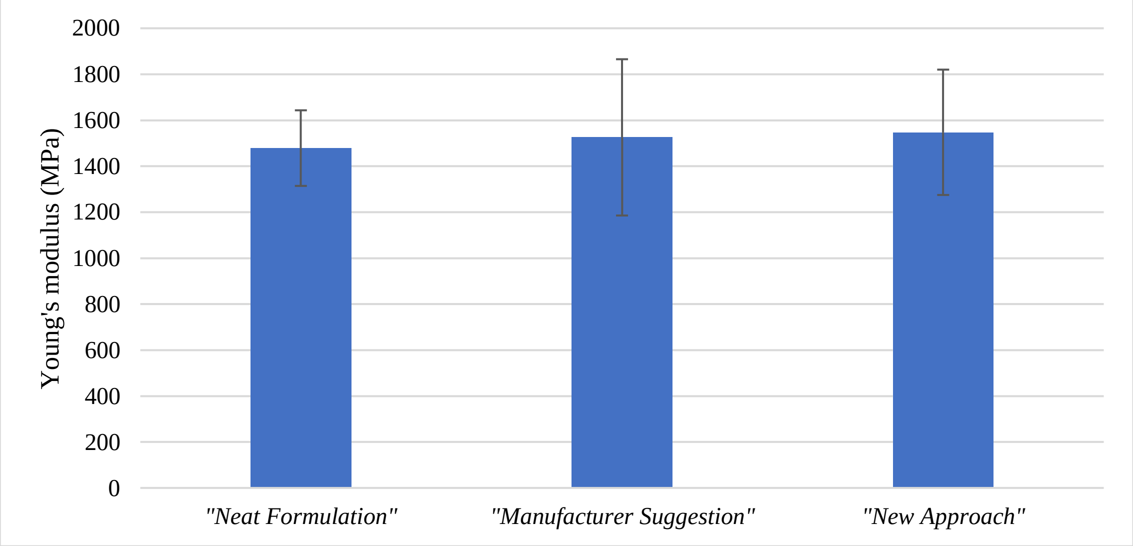


Figure 3.16 – Young's Modulus of produced filaments.

Considering the **yield stress** property, it was verified a decrease when adding the thermochromic masterbatch to the polymeric matrix filament. The *"Neat Formulation"* presented a yield stress of 59,05 ± 0,60 MPa, while the *"Manufacturer Suggestion"* filament presented a value of 47,45 ± 2,17MPa, and finally, the *"New Approach" filament presented a value of* 45,64 ± 0,42 MPa. These values are indicative of an alteration in the material structure, which affects the material mechanical behaviour. There is a decrease in the value when the masterbatch is added, indicating a lower stiffness. Figure 3.17 shows the average and standard deviation for the filaments produces.

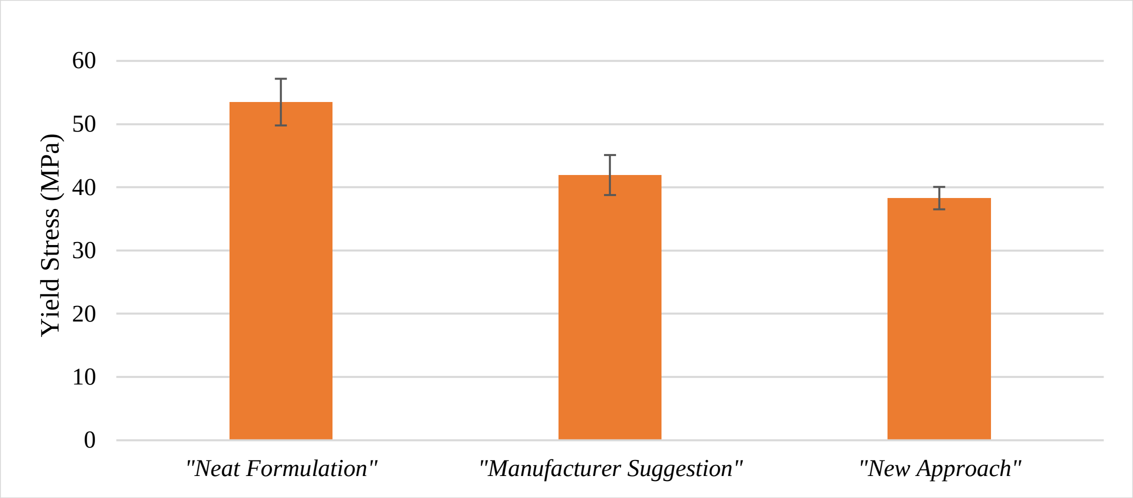


Figure 3.17 – Yield Stress of produced filaments.

Similar values, when it comes to the **tensile strain at yield point,** are observed for the filaments with the thermochromic masterbatch. In general, the tensile strain at yield point is lower for the *"New Approach"* filament (2,9 ± 0,50 %) following the values of the tensile stress at break. "Manufacturer suggestion" filament presents a value of 3,65 ± 0,83 % and the *"Neat Formulation"* filament presents 4,14 ± 0,83 %. Figure 3.18 presents the average tensile strain at yield point for the produced filaments.

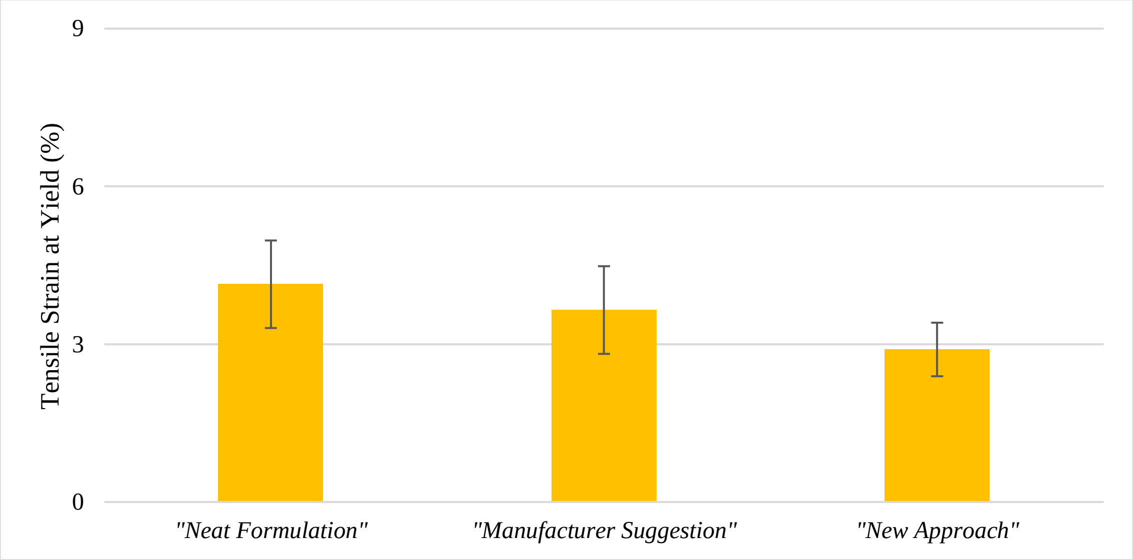


Figure 3.18 – Tensile strain at Yield Point for produced filaments.

In regarding to the **tensile strain at break** (see Figure 3.19), similar results are obtained for the produced filament named *"Manufacturer Suggestion"* (5,00 ± 1,07 %) and "Neat Formulation" with a value of 5,55 ± 0,57 %. However, when adding more thermochromic masterbatch (*"New Approach"* filament), an increase is observed, 5,85 ± 1,08 %, indicating a larger deformation.

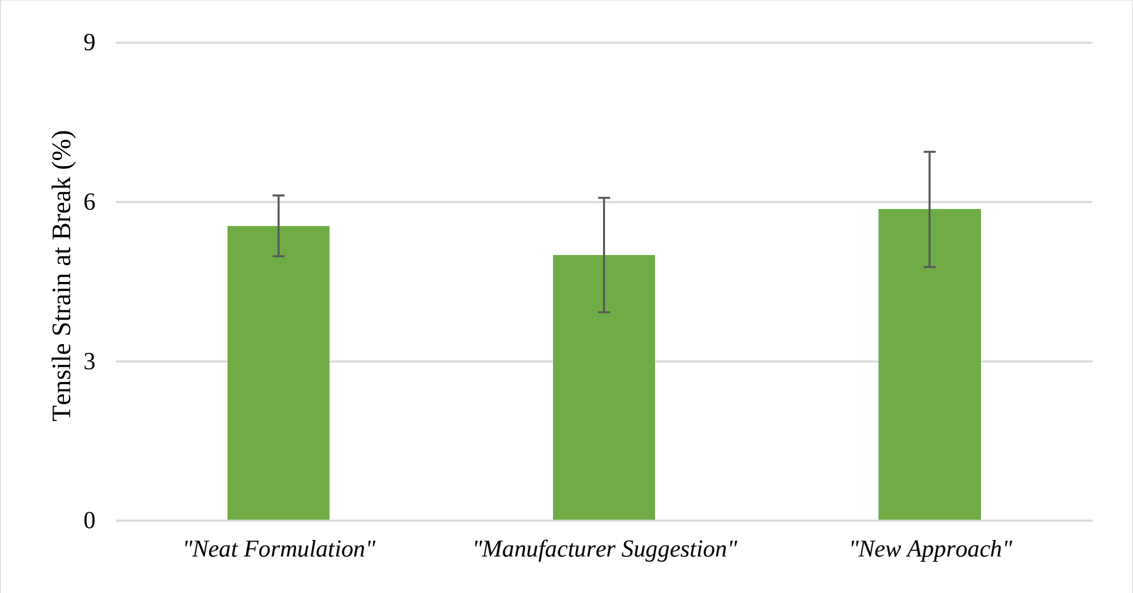


Figure 3.19 – Tensile Strain at Break for the produced filaments.

Lastly, observing the **tensile stress at break**, in Figure 3.20, similar results are obtained for the *"Manufacturer Suggestion"* filament (47,46 ± 2,17 MPa) and for the *"New approach"* filament (45,64 ± 0,42 MPa). These values are lower when comparing with the *"Neat Formulation"* filament (59,04 ± 0,59 MPa), indicating a need of more effort to break the materials.

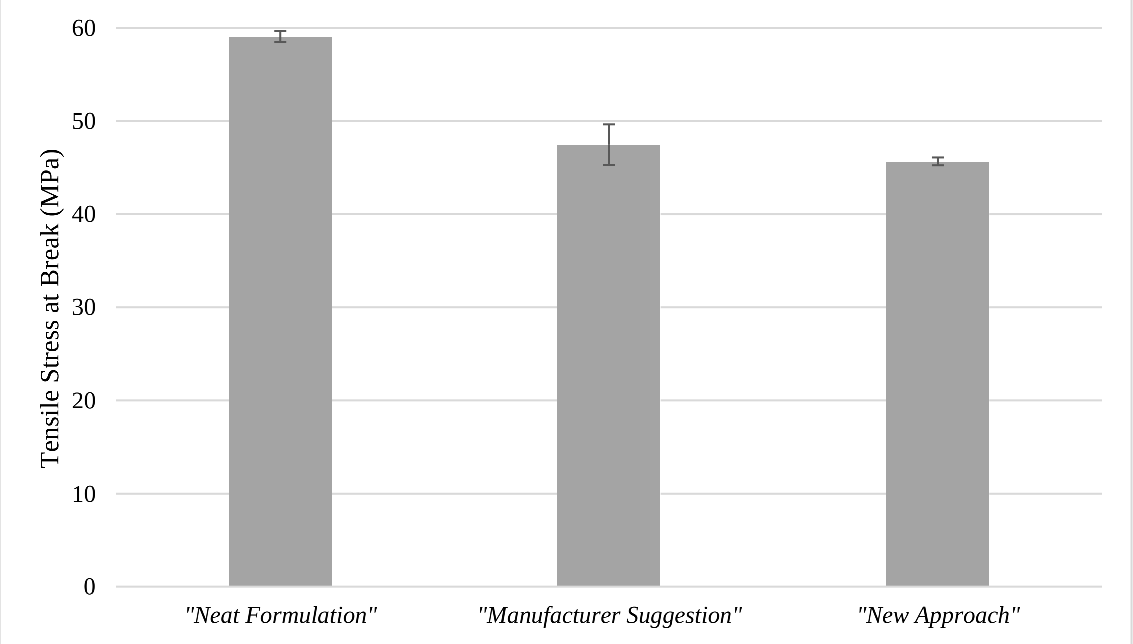
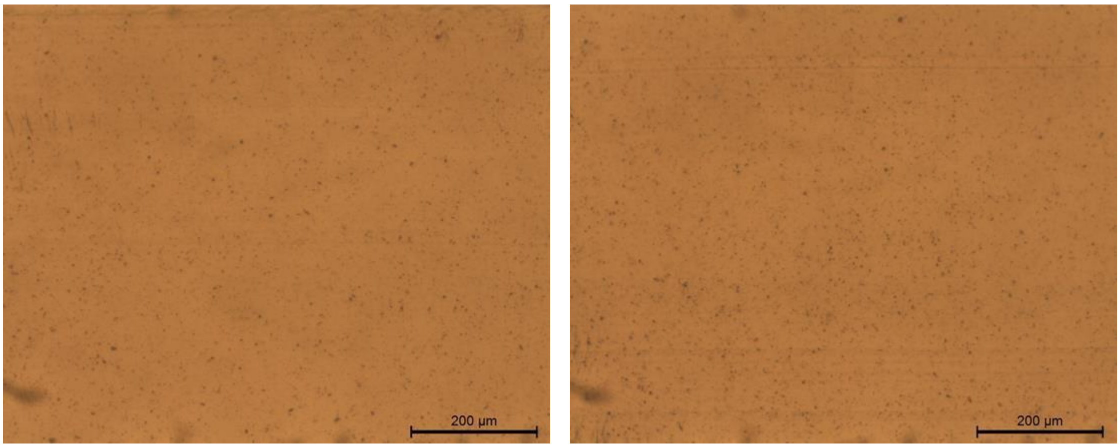


Figure 3.20 – Tensile Stress at Break for produced filaments.

In conclusion, the addition of the masterbatch slightly changes the mechanical properties of the polymeric matrix. However, in regarding to the addition of different amounts of thermochromic masterbatch, the differences are very small.

vi. Microscope Analysis

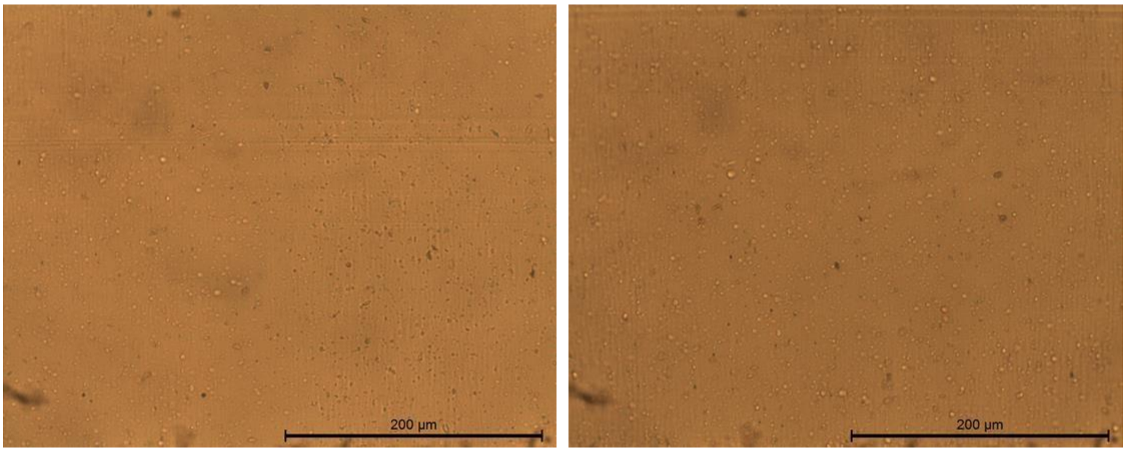
Considering the optical analysis done via an optic microscope, it was observed, for the magnification of 10 x 2,5 µm, a uniform circular disposition of circular dots for the "*Manufacturer Suggestion"* filament (see Figure 3.21). Observing the other filament, "*New Approach"*, the distribution and the dispersion of the circular dots is more homogeneous which could indicate that these dots represent the pigment present in the thermochromic masterbatch.



"Manufacturer suggestion" *"New Approach"*

Figure 3.21 – Microscopic images with a magnification of 10 x 2,5 µm of the produced filaments.

A higher magnification (20 x 2,5 µm) was considered to visualize more precisely the presence and distribution of the dots. Similar to the previous magnification, the distribution and dispersion of the dots are better in the "*New Approach"* filament. From this observation it is possible to indicate that the masterbatch and the polymer matrix mixture occurred without large changes. Figure 3.22 shows the microscopic images with 20 x 2,5 µm as magnification.



"Manufacturer Suggestion" *"New Approach"*

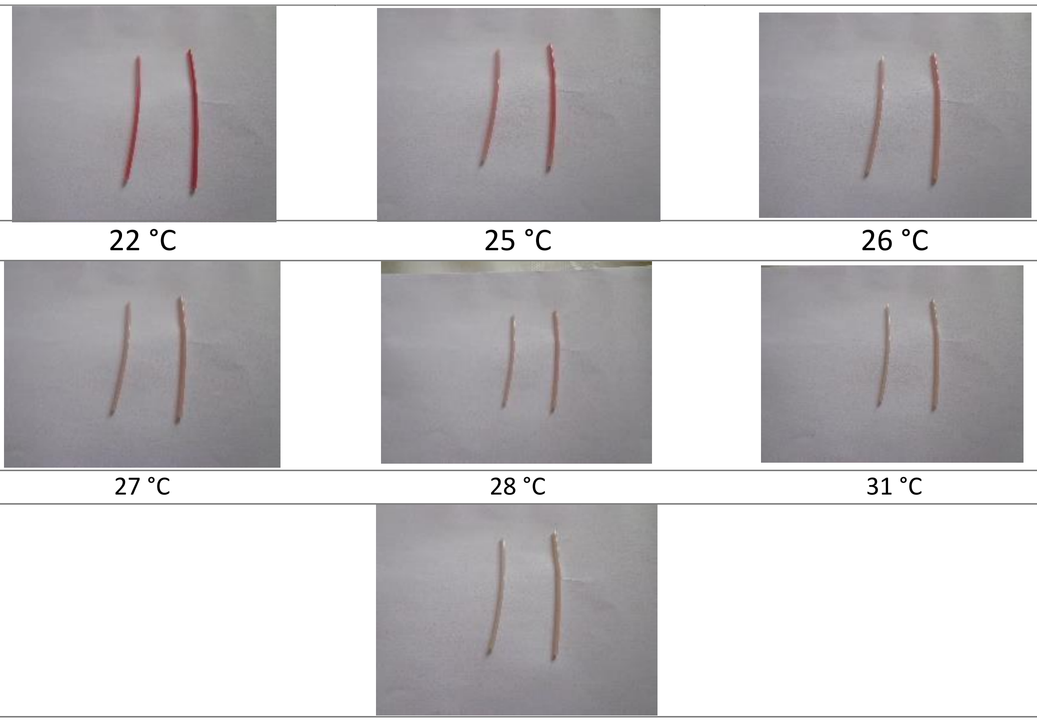
Figure 3.22 – Microscopic images with a magnification of 20 x 2,5 µm of the produced filaments.

vii. Stimulation testing

The evaluation of the colour change proceeded in this experimental phase; colour changes occur when there is an increase in the material temperature above or below the activation temperature. With this particular masterbatch integration, the material presents three colour changes. A transition from a reddish colour to white colour for temperatures between 20 and 45 °C, another particularity is when submitting the material to low temperatures, i.e. 15 °C, the colour comes back to purple. The colour changes as revertible conditions, due to the dual change that happens when altering the colour several times.

Figure 3.23 shows a series of images that represent the recording cycle of pictures, with an interval of 10s, with a thermographic camera and a common camera. In each image, two filaments are presented. The first filament (left) corresponds to the "*Manufacturer Suggestion"* mixture*,* while the second filament (right) corresponds to the "*New Approach"* mixture.

Filament samples		
		
15 °C	17 °C	21 °C



22 °C 25 °C 26 °C

27 °C 28 °C 31 °C

32 °C

Figure 3.23 – Photographic registry of the colour change with temperature variation, for the produced filaments.

In general, for both filaments, the increase of the colour masterbatch does not alter significantly the process of colour change. When the temperature range is identical, the colour observed also is. However, the duration of colour appears to be more precise when the additive is increased. These tests were done at the same conditions of temperature and humidity but, in the case of the "*New Approach"* filament, the heating distribution in the material appears more evident resulting in larger colour duration when comparing to the "*Manufacturer Suggestion*" filament.

4. Case Study – Prototype Development

This chapter presents a case study which focuses the development and production of a prototype in parallel with testing procedures. The case study is crucial to better understand functional features on a post-production part for material extrusion technique.

4.1. Part geometry – Definition & Design

The geometry selected for this case study is a cup sleeve which has the purpose of enabling the understanding on how the material behaves with the user contact and other situations that generate temperature alterations. It is crucial to analyse the **colour propagation, fastness of colour change (speed of response) and part quality** since it is one of the primary purposes of this dissertation. Therefore, the geometry defined was a cup sleeve that would be around a standard glass cup. The cup was chosen with the purpose of insertion of a liquid which would transfer its temperature to the sleeve around it, being possible the study of the temperature influence on the part. The geometry part, presented in Figure 4.1, has the following dimensions: 10 mm of height, 55 mm of diameter and a thickness of 2 mm. The technical drawing is available in APPENDICES (3).

Figure 4.1 – Geometry representation of the sleeve to produce (left image) for the selected cup (right image).

4.2. Fabrication aspects

Before the fabrication process, it was necessary to define what equipment would be used for the additive manufacturing process along with the decision of what would be the most suitable process parameters to correspond to the needs. This study was done in order to understand what is used in the field of material extrusion, specifically for PLA, because it is the polymeric matrix of the functional materials previously developed.

4.2.1. Equipment & Processing parameters

For the production of the parts to study, the equipment used was the *Roboze One +400 extreme* with the *Simplify 3D* software. The choice was made considering equipment availability, and also by being an open-source system.

Since the purpose of this production is to study the behaviour of the material to temperature fluctuations, as well as the optimization of the production process, the processing parameters choice needed to meet these requirements. In material extrusion, factors related to extrusion of the material, such as chamber, extruder and deposition aspects are crucial to achieve a part with the intended quality. However, as there are many factors affecting the properties of a part produced by material extrusion, it was necessary to select only three factors for study development so that the experiments would be more specific and targeted.

Extrusion temperature, **infill density** and **extruder speed** were the chosen parameters to study and optimized through the evaluation of the part. To minimize the number of experiments it was considered an experimental design approach, namely, Taguchi method, where a minimum orthogonal array was selected – L9. This specific array culminates the understanding of the effect of three factors independently chosen, which for this case would be extrusion temperature, infill density and extruder speed, with three different levels associated. In the end, are a set of 9 experiments made for each of the previously produced filaments [107].

For **extrusion temperature**, the values assumed included 190 °C for the lowest level. This value was 10 °C higher from the one considering the extrusion temperature of the PLA material, recommended by the manufacturer of the AM equipment. In the middle level, the defined temperature was 210 °C, since it is a standard extrusion temperature for PLA filaments commercially available. Lastly, for the upper level an increase of 10 °C was made in order to have an extremer value.

Considering the **infill density**, the level choice was made in order to understand if the part would have a significant influence in the temperature transmission through the geometry density; thus 25 %, 50% and 100 % as infill density were the defined values.

Finally, for the extrusion speed head, the values decided were only closed according to with the production of the parts. Pre-tests were done considering 20 mm/s, 40 mm/s and 60 mm/s as extrusion speed and, according to the results, an optimization could or not be made for new levels as 40 mm/s, 60 mm/s, and 80 mm/s.

The set of factors and respective levels according to the array L9 from the Taguchi's Diagram, generates the experimental plans presented in Table 4.2.

Table 4.2 – Experimental plan considering the second approach.

Condition	Extrusion Temperature (°C)	Infill density (%)	Speed of the extruder head (mm/s)
1	190	25	40
2	190	50	60
3	190	100	80
4	210	25	60
5	210	50	80
6	210	100	40
7	220	25	80
8	220	50	40
9	220	100	60

In regarding to the process parameters that were considered fixed values, its definition was made considering literature review. In Table 4.3, are presented the most relevant process parameters considered.

Table 4.3 – Process parameters for part production process.

	Conditions	
Software program	*Simplify 3D*	
Material	Drying time (h)	2
	Drying temperature (°C)	40
Equipment	Nozzle Diameter (mm)	0,40
	Support	No support
	Raft	No raft
	Fill Pattern	Rectilinear
	Bed Temperature (°C)	30

4.2.2. Part production

Part production occurred after the transformation of the 3D design into a STL file. All the parts were predisposed in the production sheet as showed in Figure 4.2. The first line corresponds to the parts with an extrusion temperature of 190 °C. The following line corresponds to an extrusion temperature of 210 °C and, finally, the last line of parts corresponds to the extrusion temperature of 220 °C. Notice that the following figure only aims to present in which position of the building sheet and building chamber the parts were manufactured, for each particular temperature building processing.

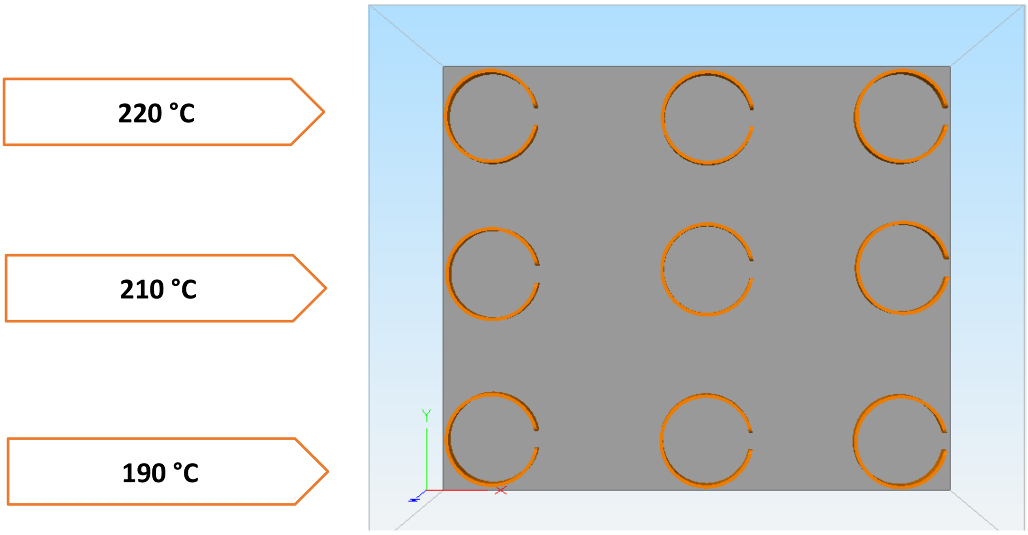


Figure 4.2 – Building plate of the Simplifier 3D software.

Considering the first experimental approach, the part produced at 20 mm/s independently of the other factors, it was noticed that the production was not adequate. It was observed that the extruder head would deposit material as droplets, not being able to form a concise layer. Before abandoning this processing parameter, a verification of the extruder head and an equipment calibration were taken into account since the defects could be due to other factors.

Experimental approach number 2 occurred without significant fluctuations; the problem verified through the production was that the equipment indicated the detection of *broken filament* in every filament. However, after visual verification, it was noticed that the filament was not broken. The variation in terms of filament diameter across its length could be the possible cause for such notification.

It is also important to notice that every filament had the same dehumidification conditions (time and temperature) previous to the production. Regarding the filament *"Neat Formulation"*, after the initial purge it was still verified the presence of bubbles. This factor is common when the material is not adequately dried. Therefore, more time in the dehumidification oven was considered, since 1 to 2 hours at 40 °C, until the purge appeared with a filament without significant bubbles.

Finally, considering the temperature parameters and the infill percentage, it was not verified any alteration through the process of part production that influenced these parameters.

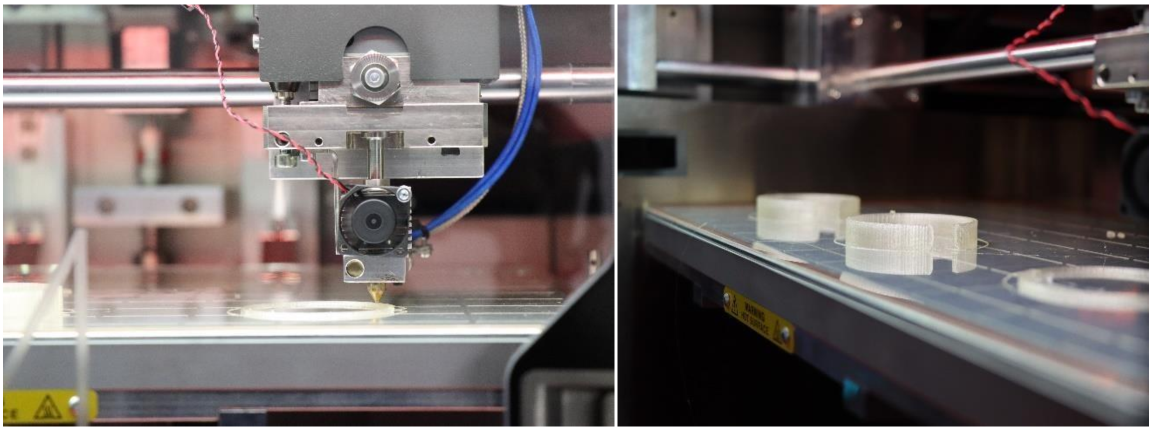


Figure 4.3 – Prototype production: detail of the extrusion head (left image) and manufactured parts still attach to the building sheet inside the machine (right image).

4.3. Prototype Study

In this phase, it is presented the study of the material thermochromic feature, and also an investigation around the processing parameters influences on the surface quality of the part and, consequent adhesion between layers.

Stimulation testing was first made with both cold and hot end temperatures in order to understand colour propagation, in terms of speed and intensity, along with a comparison between the different mixtures: *"Manufacturer Suggestion"* and *"New Approach"*. The visual evaluation of the surface of the part provides useful information for the process of part production optimization, as well as, the verification of possible defects.

4.3.1. Stimulation testing

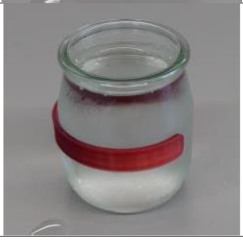
As mentioned before, in this phase, it will be evaluated colour propagation, fastness and change, along with a comparison between the different mixtures, in regarding to the produced parts. A cold environment was used, utilizing the liquid at 15 °C and a hot environment was used to test a condition with higher temperatures with a liquid at 35 °C. The surface observation will enable to understand how parameters affect the part performance and provide useful information for the optimization of processing parameters.

Considering the first extrusion temperature, 190 °C (see Table 4.4), the most intense purple colour observed was verified for the part with 50 % of infill and 60 mm/s of head extrusion speed for the *"Manufacturer Suggestion"* filament. Considering the

“New Approach” filament, the most evident purple colour corresponds to the conditions of 100 % of infill and 80 mm/s of head

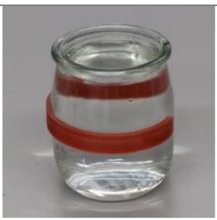
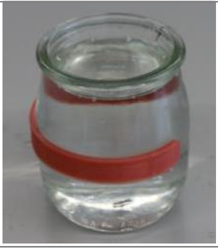
extrusion speed. Colour spreading from video observation appears to be the same for all the parts.

Table 4.4 – Photographic registry of the stimulation testing for the parts obtained with an extrusion temperature of 190 °C.

		Processing conditions		
	Time (s)	*190 °C 25 % 40 mm/s*	*190 °C 50 % 60 mm/s*	*190 °C 100 % 80 mm/s*
“ Manufacturer Suggestion” Filament	0			
	60			
	120			
“ New Approach” Filament	0			
	60			
	120			

Considering the produced parts with an extrusion temperature of 210 °C, presented in Table 4.5, for the first filament used, the colour change speed, spreading and intensity appears to be the same. No significant changes were noticed. Following the *“New Approach”* filament, it is observed a spreading and fastness much lower when comparing the colour change. The final colour at the 120 seconds instant is more reddish than the colour observed in the filament “*Manufacturer Suggestion”,* which may indicate different material temperature, not accomplishing the temperature of 15 °C at that time. Considering the condition 50 % as infill and 80 mm/s as extrusion speed, for the *“New approach”* filament, the resulting part appears to gain a purple colour at the geometry extremities, at the 120 s instant, indicating a possible fastness of colour change when comparing with the others where is not observed this colour at the extremities.

Table 4.5 – Photographic registry of the stimulation testing for the parts obtained with an extrusion temperature of 210 °C.

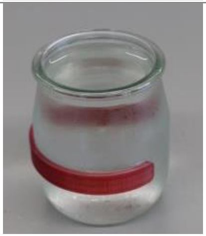
		Processing conditions		
	Time (s)	*210 °C 25 % 60 mm/s*	*210 °C 50 % 80 mm/s*	*210 °C 100 % 40 mm/s*
“ Manufacturer Suggestion” Filament	0			
	60			
	120			
“	0			

60			
120			

For the extrusion temperature with the highest value, 220 °C, the results are presented in Table 4.6. The speed of colour change was greatest for the processing conditions of 50 % infill and 40 mm/s as extrusion speed. In regarding to the other parts, the colour intensity is similar. It was verified that, for both cases, a more prominent line in the middle part of the geometry, spreading also happened equally. For the *New Approach”* filament, in general, it appears with a less intense colour during the whole experiment. Colour change spread and speed occurs faster at the middle processing conditions (*220 °C, 50 %, 40 mm/s)*, and the final colour is more intense. Following the part with the most evident colour change t is the part with the processing conditions of 25 % of infill and 80 mm/s as extrusion speed.

Table 4.6 – Photographic registry of the stimulation testing for parts obtained with an extrusion temperature of 220 °C.

		Processing conditions		
	Time (s)	*220 °C 25 % 80 mm/s*	*220 °C 50 % 40 mm/s*	*220 °C 100 % 60 mm/s*
“ Manufacturer	0			
	60			

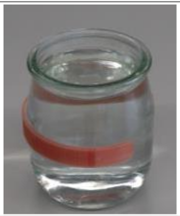
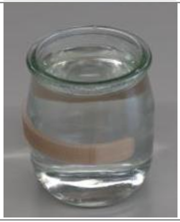
	120			
"New Approach"	0			
	60			
	120			

After the testing for the lowest temperature (15 °C), the experiments with higher temperature (35 °C) took place at the same environmental conditions than the previous. In this case, the colour change occurs faster so the window of time observation is diminished.

Regarding the 190 °C, as extrusion temperature (see Table 4.7), both filament approaches present the same colour change speed and spreading. Comparing both filaments, the colour showed after the transition, for the "New Approach" filament, appears with a slightly darker colour. Correlating the colours between the same time for different colour conditions, a similarity is observed.

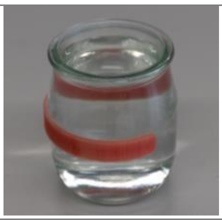
Table 4.7 – Photographic registry of the stimulation testing for the parts obtained with an extrusion temperature of 190 °C, higher temperature testing.

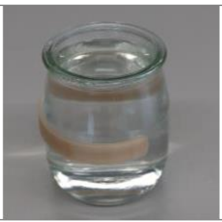
	Processing conditions		
Time (s)	*190 °C 25 % 40 mm/s*	*190 °C 50 % 60 mm/s*	*190 °C 100 % 80 mm/s*

“ Manufacturer Suggestion”	0			
	30			
“ New Approach”	0			
	30			

Considering the middle temperature level, presented in Table 4.8, colour transition and speed is the same between both filament types, thus the colour is similar between them. It was observed a darker colour at 30 s for the third processing conditions. Equally, at the same time, it was also verified a similar behaviour for the filament *“New Approach”.*

Table 4.8 – Photographic registry of the stimulation testing for the parts obtained with an extrusion temperature of 210 °C, highest temperature.

		Processing conditions		
	Time (s)	*210 °C 25 % 60 mm/s*	*210 °C 50 % 80 mm/s*	*210 °C 100 % 40 mm/s*
“ Manufacturer	0			

	30			
“ New Approach”	0			
	30			

Lastly, analysing the processing conditions for the last temperature level (see Table 4.9), colour change speed is similar for both filament types. A darker colour was observed at 30 s of time, when comparing the parts made with the *“New Approach”* filament with the parts made with the “Manufacturer Suggestion” filament. In general, the colour is more evident at a zone with a specific line which would possible be to the more material presence once is where the extruder head stops to go to the other zone of the geometry part.

Table 4.9 – Photographic registry of the stimulation testing for the parts obtained with an extrusion temperature of 220 °C, highest temperature.

		Processing conditions		
	Time (s)	*220 °C 25 % 80 mm/s*	*220°C 50 % 40 mm/s*	*220 °C 100 % 60 mm/s*
“ Manufacturer Suggestion”	0			
	30			

“ New Approach”	0			
	30			

4.3.2. Surface analysis

To have a better understanding of the best conditions, for the obtaining of a part with good quality and corresponding to the wanted features, an observation of the part surface was performed by using a *stereoscopic Leica magnifier DMS 1000*. The part observation was done at two magnifications 0,75x and 1,25x. For every produced part, besides the observation, a comparison between them was made which will be presented next. In every piece, it was observed a prominent line in the superior level. This line is the transversal observation of the building sheet, where the geometry is produced. Although the efforts, it was not possible to entirely remove the building sheet in all parts without compromising the final finishing.

In a general observation of the filaments with the masterbatch addition, no significant changes were noticed on a surface level. However, a change was noticed corresponding to a different colour pattern between the parts.

In Figure 4.4 it is visible that the part colour is more intense in the lower section of the part. Filament adhesion and deposition appear to be uniform.

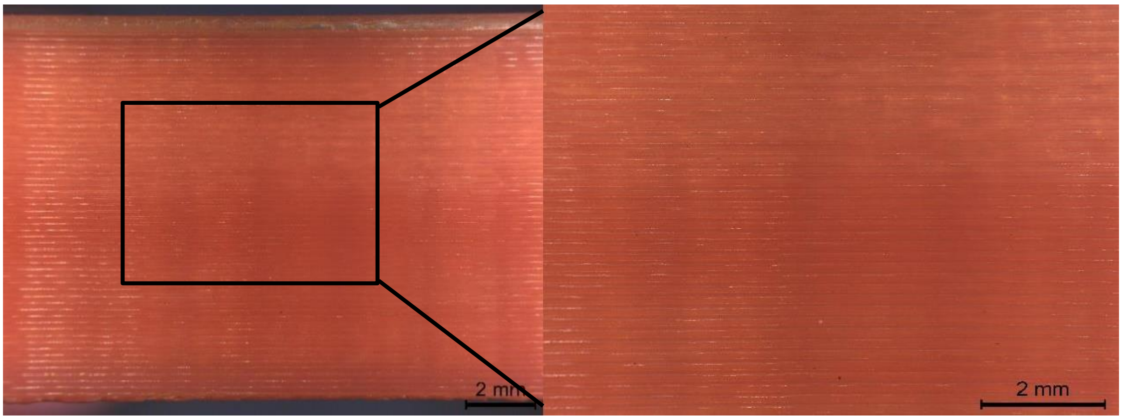


Figure 4.4 - Part produced at 190 °C of extrusion temperature, density infill of 25 % and an extruder head speed of 40 mm/s. Magnifications: 0,75x left and 1,25x right.

In regarding to the part with 50 % of infill and an extruder head speed of 60 mm/s, presented in Figure 4.5, the deposition and adhesion appear uniform, as well as, the colour distribution. A more evident section is observed thought the part length, which is associated to the path that the extruder head does during the part production.

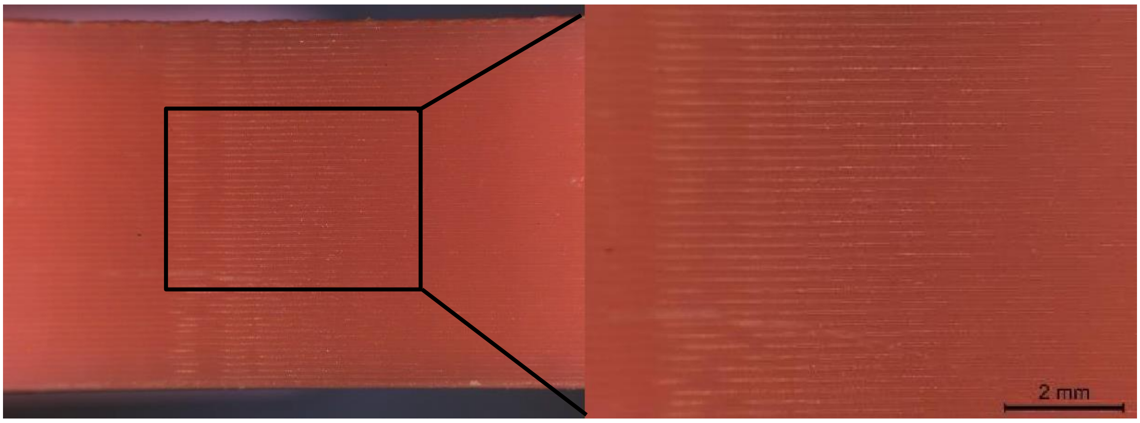


Figure 4.5 - Part produced at 190 °C of extrusion temperature, density infill 50 % and an extruder head speed of 60 mm/s. Magnifications: 0,75x left and 1,25x right.

The last produced part (Figure 4.6), with an extrusion temperature of 190 °C, presents a colour gradient more evident, when compared to the first part analysed.

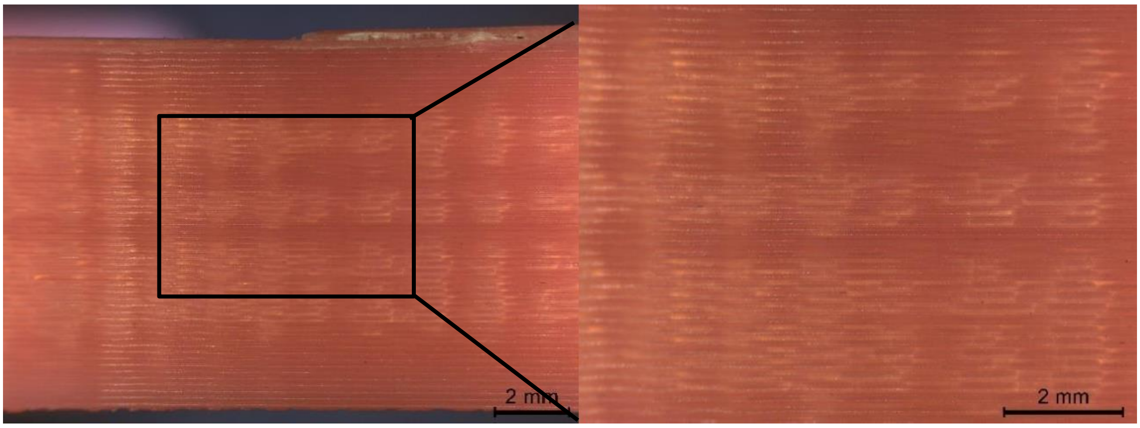


Figure 4.6 – Part produced with 190 °C of extrusion temperature, density infill of 100 % and an extruder head speed of 80 mm/s. Magnifications: 0,75x left and 1,25x right.

At 210 °C, in the first condition, presented in Figure 4.7, the part appears to present a uniform adhesion and deposition. It also presents a significant glow that could be do due moisture presence.

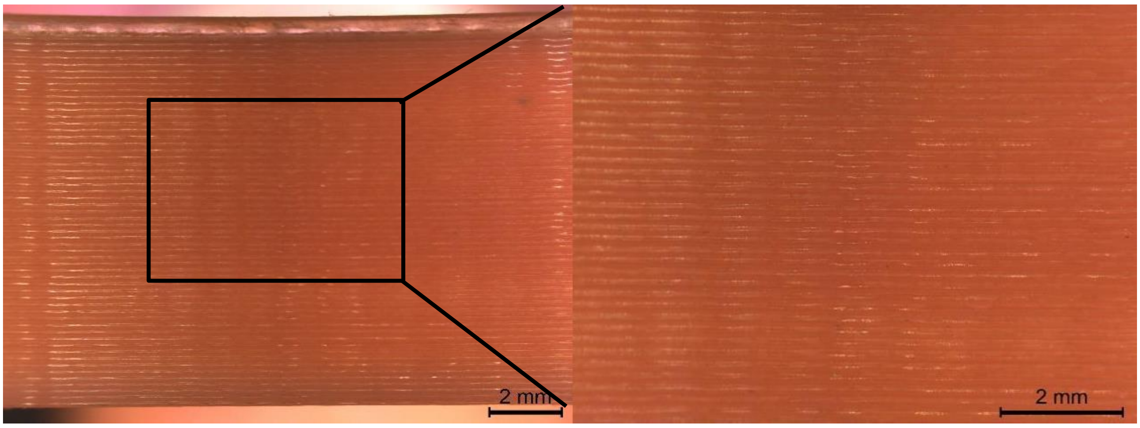


Figure 4.7 – Part produced at 210 °C of extrusion temperature, density infill 25 % and an extruder head speed of 60 mm/s. Magnifications: 0,75x left and 1,25x right.

In Figure 4.8, it can be noticed that adhesion and deposition are also uniform however, in this part, it is also observed a clear part with different adhesion and deposition that represents the zone where the extruder head stops for a small fraction of time in every layer formation, returning after for another layer formation.

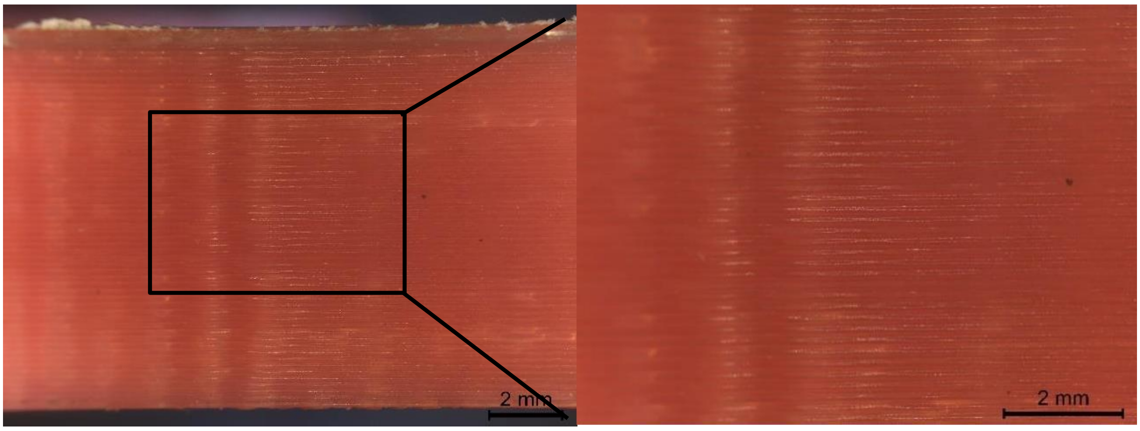


Figure 4.8 – Part produced 210 °C of extrusion temperature, density infill of 50 % and an extruder head speed of 80 mm/s. Magnifications: 0,75x left and 1,25x right.

Regarding the part presented in Figure 4.9, in terms of adhesion and layer deposition, the appearance is good. The only aspect that is detectable is the extra visible glow which could be due to moisture presence.

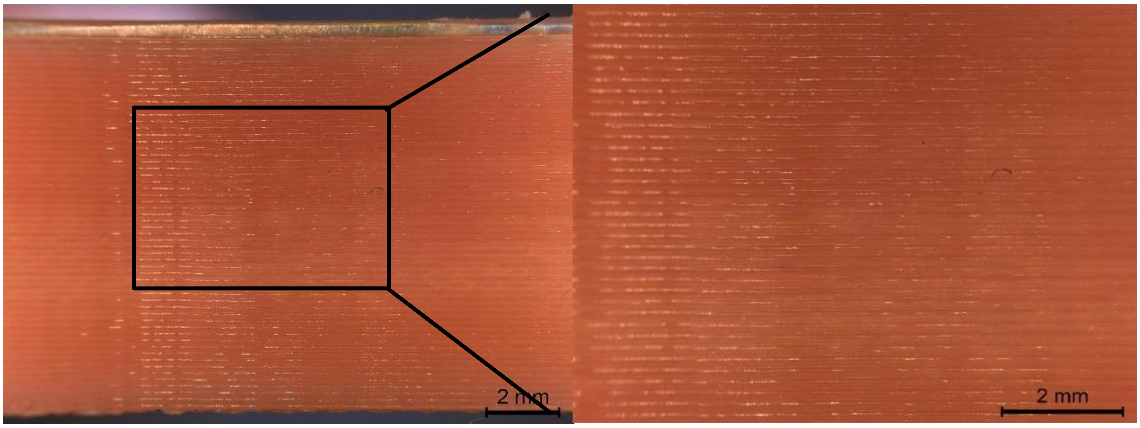


Figure 4.9 – Part produced at 210 °C of extrusion temperature, density infill 100 % and a extruder head speed of 40 mm/s. Magnifications: 0,75x left and 1,25x right.

Increasing the extrusion temperature and the extruder head speed (see Figure 4.10), it is also observed a colour gradient. Deposition of filament appears to be uniform however, the adhesion between the layers does not appear to have the same quality as for the other parts.

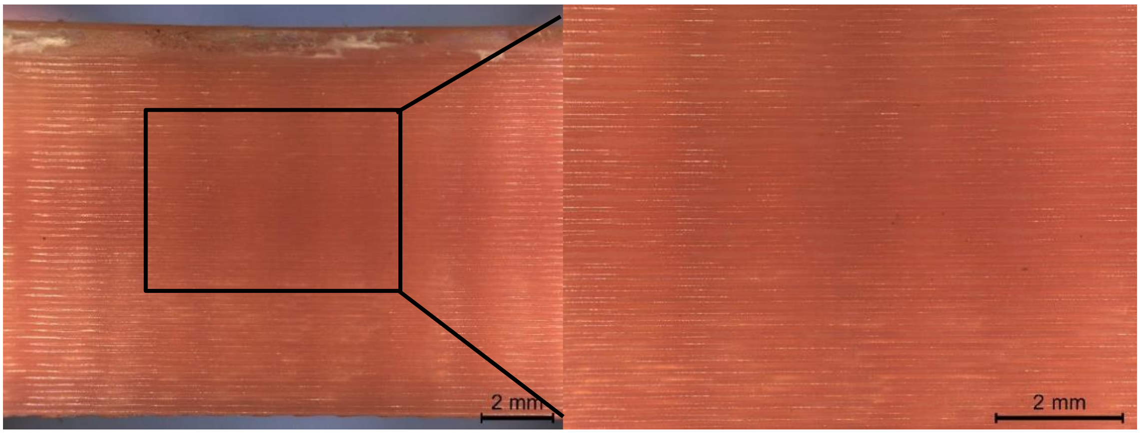


Figure 4.10 – Part produced with 220 °C of extrusion temperature, density infill of 25 % and an extruder head speed of 80 mm/s. Magnifications: 0,75x left and 1,25x right.

In Figure 4.11, it is also visible a significant colour gradient and a specific glow. In terms of filament deposition and adhesion apparently is good when comparing with the other produced parts.

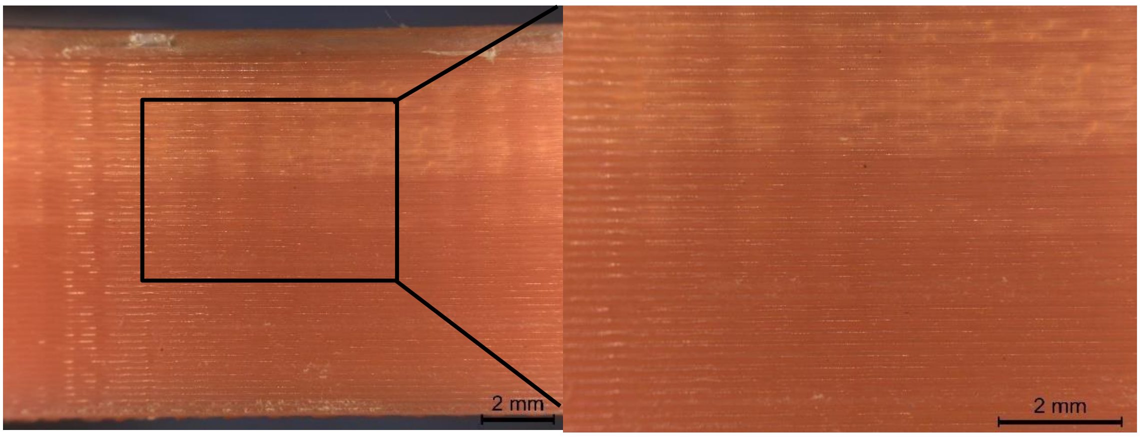


Figure 4.11 – Part produced with 220 °C of extrusion temperature, density infill of 50 % and an extruder head speed of 40 mm/s. Magnifications: 0,75x left and 1,25x right.

In the part presented in Figure 4.12 it is also possible to verify the glow that could be due to moisture content and a colour gradient, between the upper and the lower section.

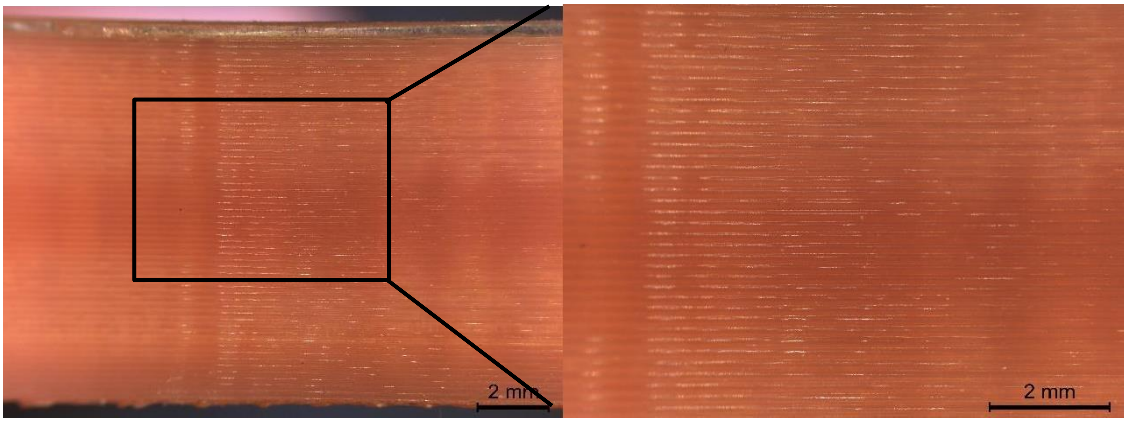


Figure 4.12 – Part produced with 220 °C of extrusion temperature, density infill of 100 % and an extruder head speed of 60 mm/s. Magnifications: 0,75x left and 1,25x right.

Considering the parts produced with *"New Approach"* filament, the analysis is exposed in the following figures. All the samples were observed at the same temperature conditions as the previous ones.

In Figure 4.13, the colour gradient is not so evident when compared with the part with the other filament type. However, at the same conditions, but with the other filament type this colour change are not verified. Filament deposition and adhesion between layers present to be similar and are good.

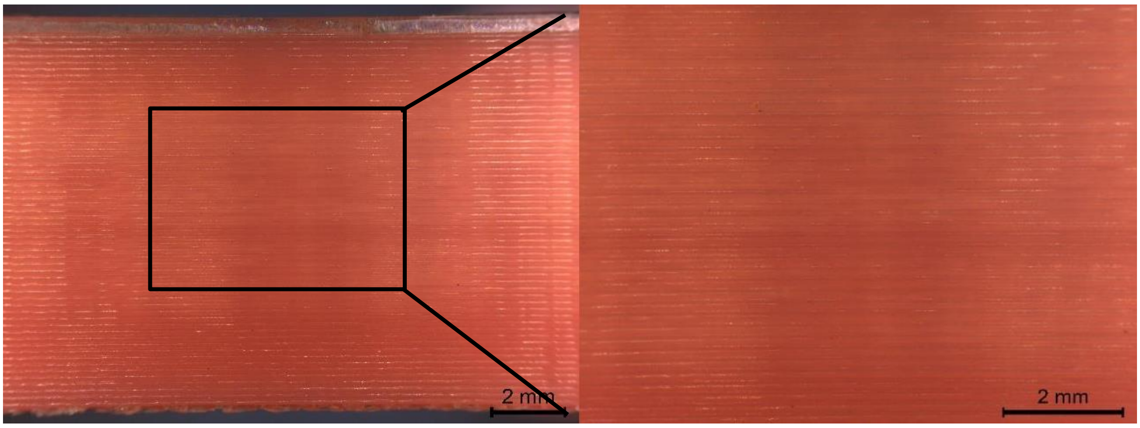


Figure 4.13 – Part produced with 190 °C of extrusion temperature, density infill of 25 % and an extruder head speed of 40 mm/s. Magnifications: 0,75x left and 1,25x right.

Regarding Figure 4.14, the dots observed possibly are impurities that were present in the filament at the time production. Regarding adhesion and deposition, the behaviour is the same, when compared to the part at the same processing conditions but with the *"Manufacturer Suggestion"* filament. Colour gradient and glow appears to be more evident in the presented part.

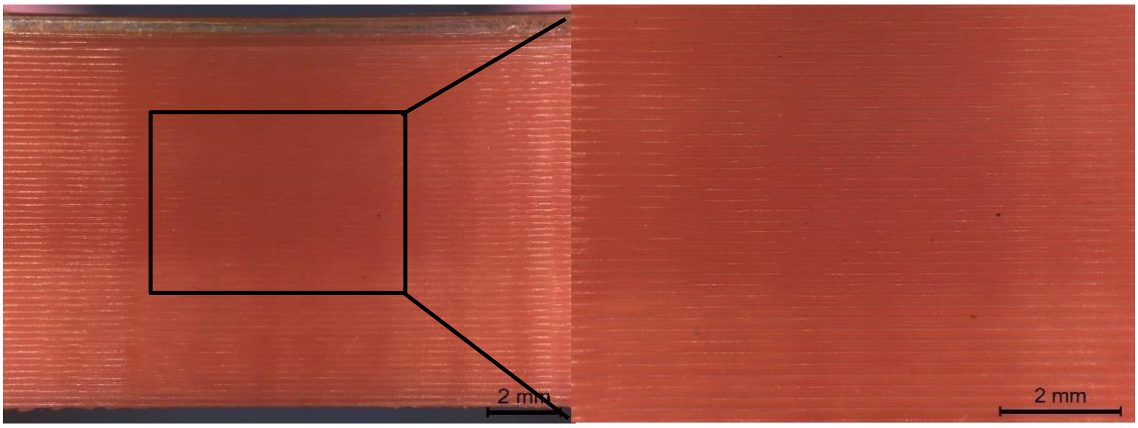


Figure 4.14 – Part produced with 190 °C of extrusion temperature, density infill of 50 % and an extruder head speed of 60 mm/s. Magnifications: 0,75x left and 1,25x right.

For the part (see Figure 4.15) with the highest infill percentage (100 %) and extruder head speed (80 mm/s), it is visible a colour gradient more evident in one zone. In this case, the part does not present a smooth surface, when comparing with the other parts, which could indicate poor deposition layer and adhesion.

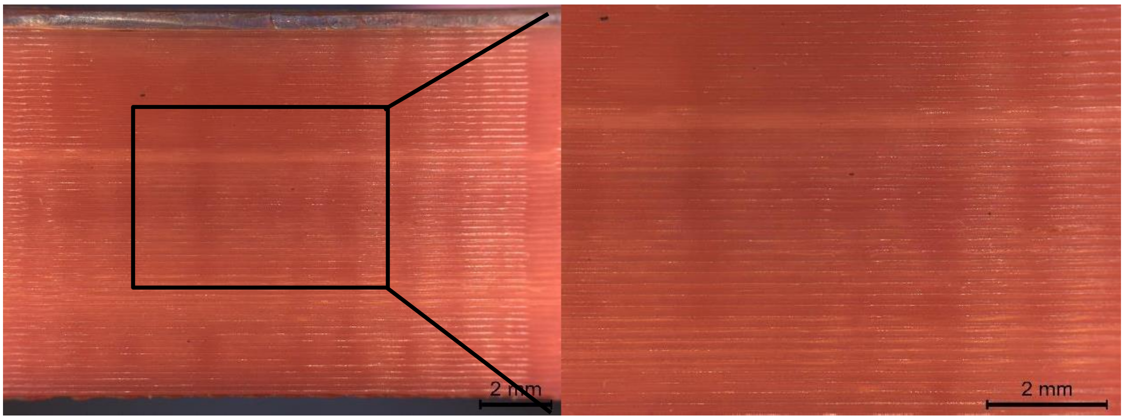


Figure 4.15 – Part produced with 190 °C of extrusion temperature, density infill of 100 % and an extruder head speed of 80 mm/s. Magnifications: 0,75x left and 1,25x right.

In this case (see Figure 4.16), the part does not present an evident colour gradient, when compared with the other part, at the same process conditions, with the

"Manufacturer Suggestion" filament. In terms of layer deposition and adhesion, it appears to be the same. It also presents a visible a glow moisture.

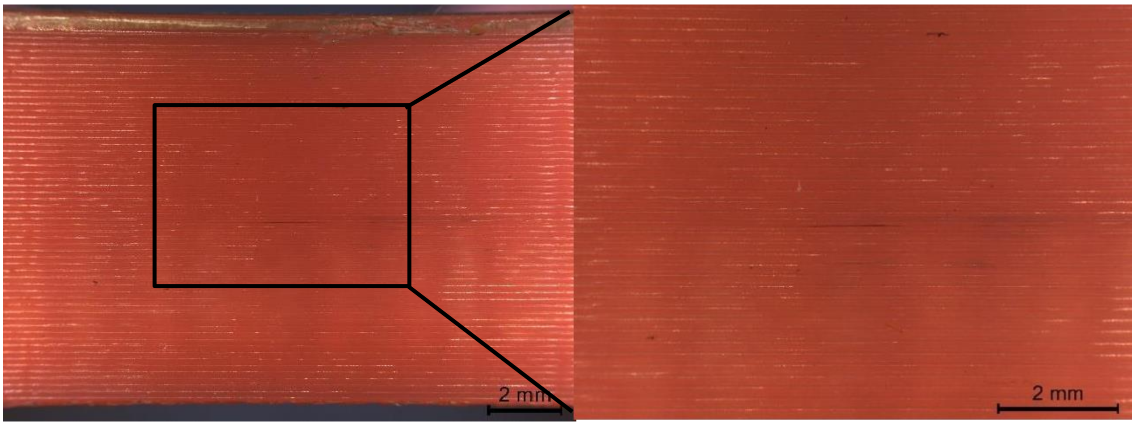


Figure 4.16 – Part produced with 210 °C of extrusion temperature, density infill of 25 % and an extruder head speed of 60 mm/s. Magnifications: 0,75x left and 1,25x right.

Considering the part with the highest extruder head speed, in Figure 4.17, the glow is also observed along with a little gradient of colour that is visible at the lower middle area.

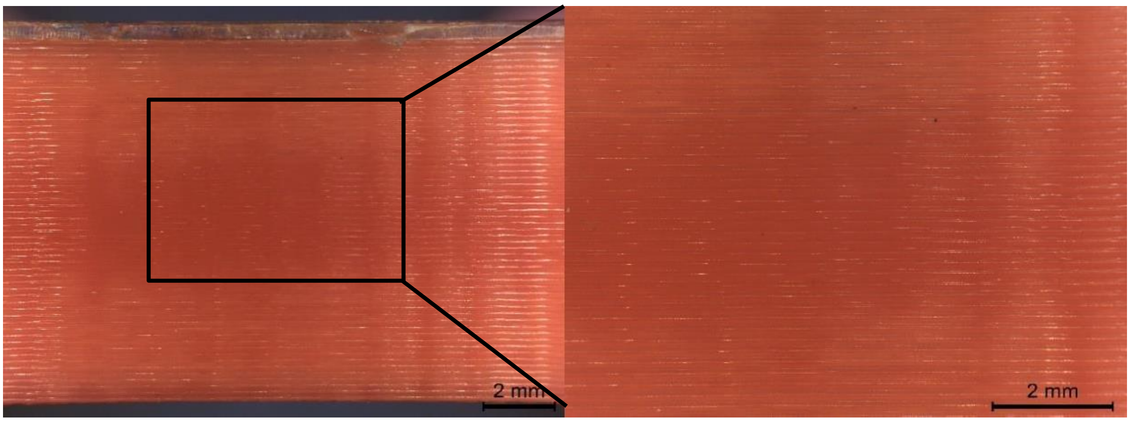


Figure 4.17 – Part produced at 210 °C of extrusion temperature, density infill 50 % and a extruder head speed of 80 mm/s. Magnifications: 0,75x left and 1,25x right.

In regarding to the part presented in Figure 4.18, layer deposition and adhesion appear to be of quality. A small impurity and a little colour gradient were also verified.

The colour gradient is not so evident when compared to the filament *"Manufacturer Suggestion"*

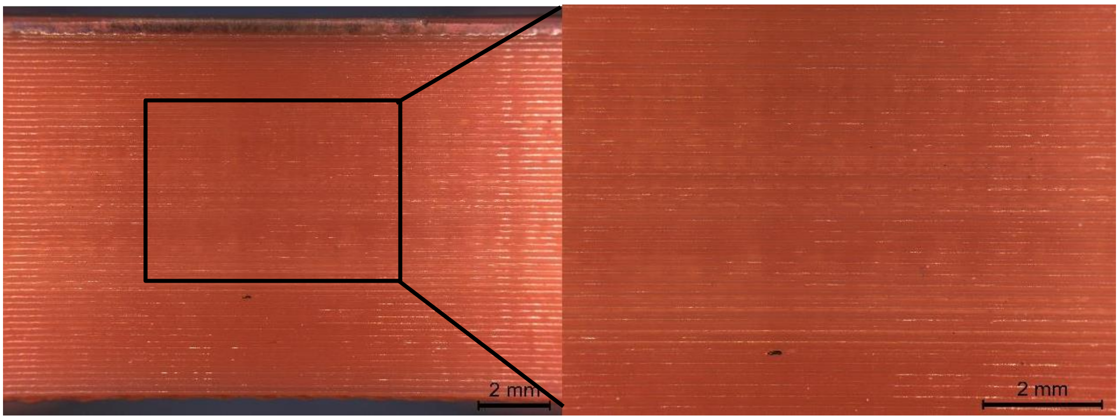


Figure 4.18 – Part produced with 210 °C of extrusion temperature, density infill of 100 % and an extruder head speed of 40 mm/s.

Considering the part obtained with the highest extrusion temperature (220 °C), the colour gradient presented in Figure 4.19 is less intense and a little glow is observed. Also, an area with less colour uniformity is also noticeable.

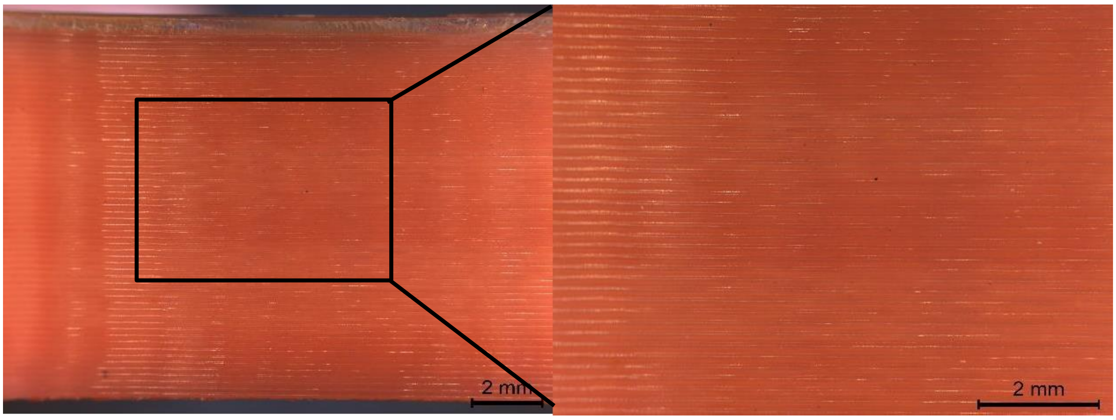


Figure 4.19 – Part produced at 220 °C of extrusion temperature, density infill 25 % and an extruder head speed of 80 mm/s. Magnifications: 0,75x left and 1,25x right.

Regarding Figure 4.20, the colour alteration is more evident in the middle section and glow is also observed. In terms of comparison this part appears to have more uniformity in an overall view regarding *"Manufacturer Suggestion"* filament.

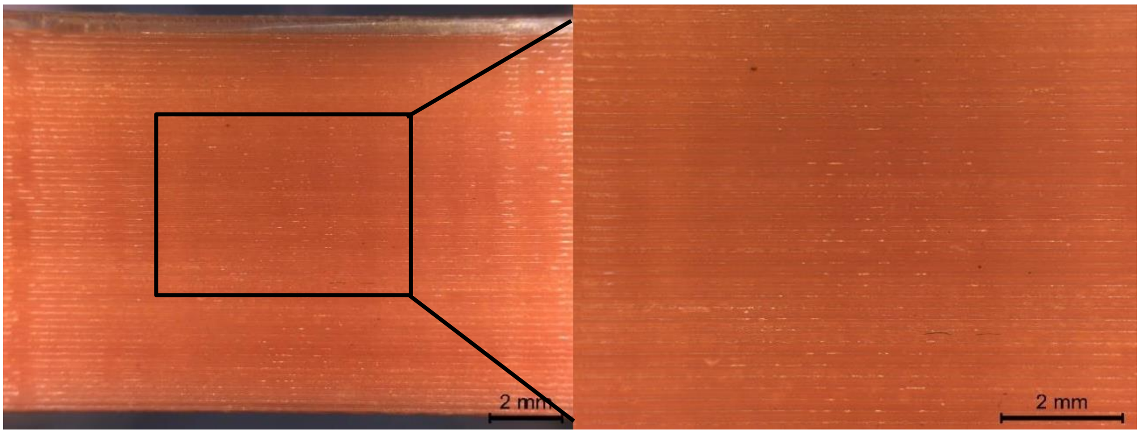


Figure 4.20 – Part produced with 220 °C of extrusion temperature, density infill of 50 % and an extruder head speed of 40 mm/s. Magnifications: 0,75x left and 1,25x right.

For the part, in Figure 4.21, with highest infill, the colour gradient observed is not that present, however, glow is verified similar to the part at the same test conditions, but with a different filament mixture.

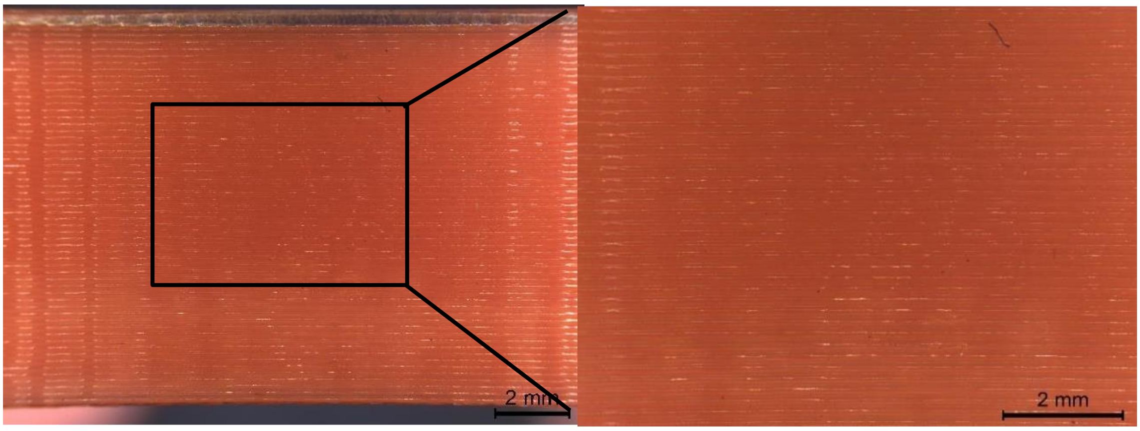


Figure 4.21 – Part produced at 220 °C of extrusion temperature, density infill 100 % and an extruder head speed of 60 mm/s. Magnifications: 0,75x left and 1,25x right.

Regarding the parts with the *"Neat Formulation"* filament, which are composed by only PLA and no masterbatch, all parts present moisture thus, with the higher magnification, little circular forms between the layers are visible. It is important to notice that, in this case, the parts were not subject to the stimulation testing thus, the presence of moisture is not related to the test.

For the lowest extrusion temperature filament, in Figure 4.22, the adhesion between layers is not so evident. Little gaps may be observed and colour gradient is not evident.

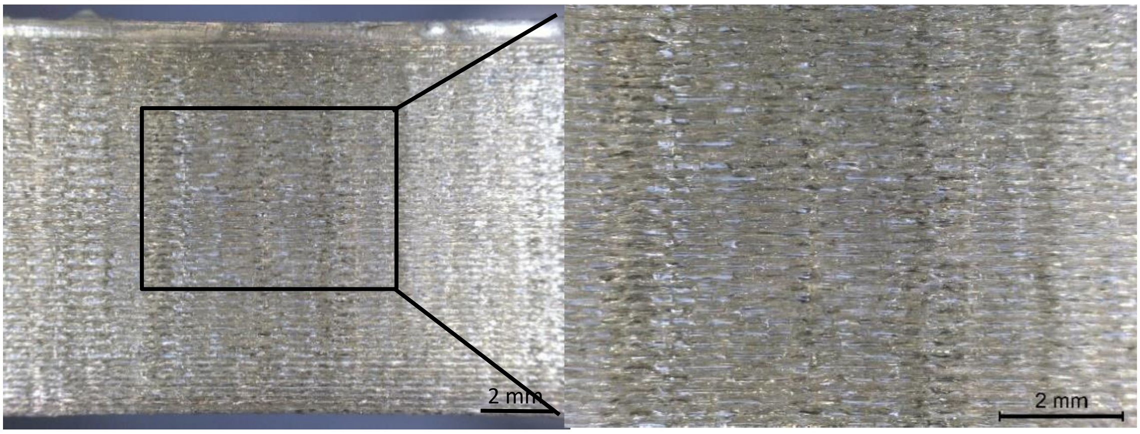


Figure 4.22 – Part produced with 190 °C of extrusion temperature, density infill of 25 % and an extruder head speed of 40 mm/s. Magnifications: 0,75x left and 1,25x right.

Considering 50 % of infill density, in a small upper section, the adhesion between layers is less precise. With a higher magnification it is possible to notice the presence of gaps (see Figure 4.23).

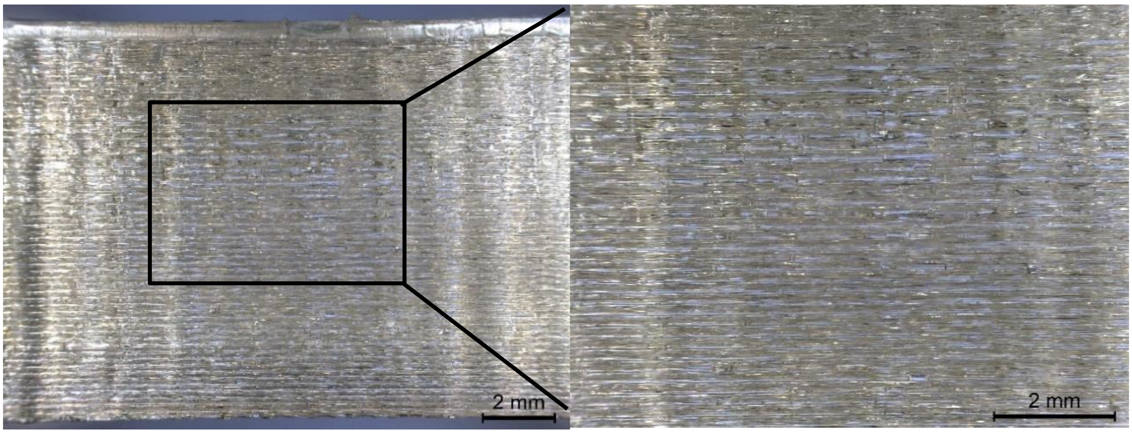


Figure 4.23 – Part produced at 190 °C of extrusion temperature, density infill 50 % and an extruder head speed of 60 mm/s. Magnifications: 0,75x left and 1,25x right.

Considering Figure 4.24, it is observable a good layer deposition. In regarding to the colour gradient, the middle section of the part appears to be have more transparency.

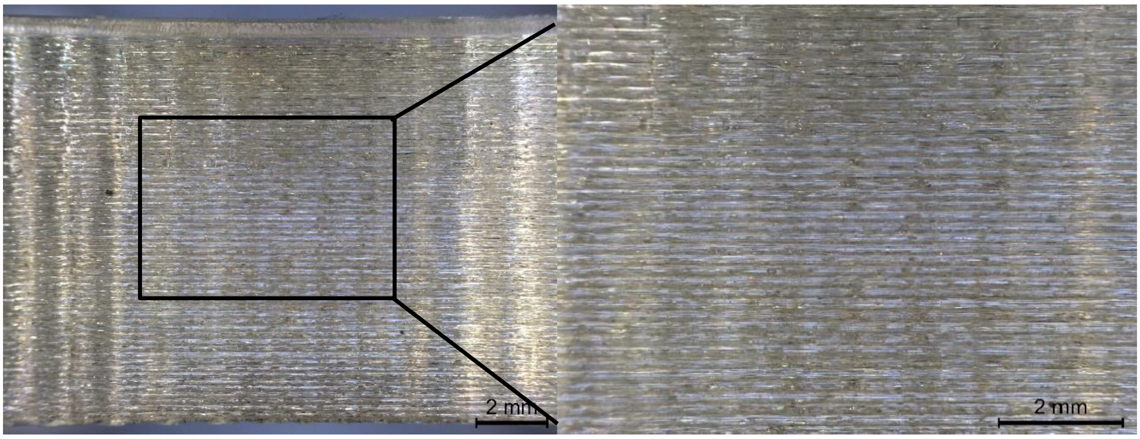


Figure 4.24 – Part produced with 190 °C of extrusion temperature, density infill of 100 % and an extruder head speed of 80 mm/s. Magnifications: 0,75x left and 1,25x right.

Considering the extrusion temperature of 210 °C (see Figure 4.25), the layer appears to be more concise in the upper section, however, small gaps are visible, especially in the middle section.

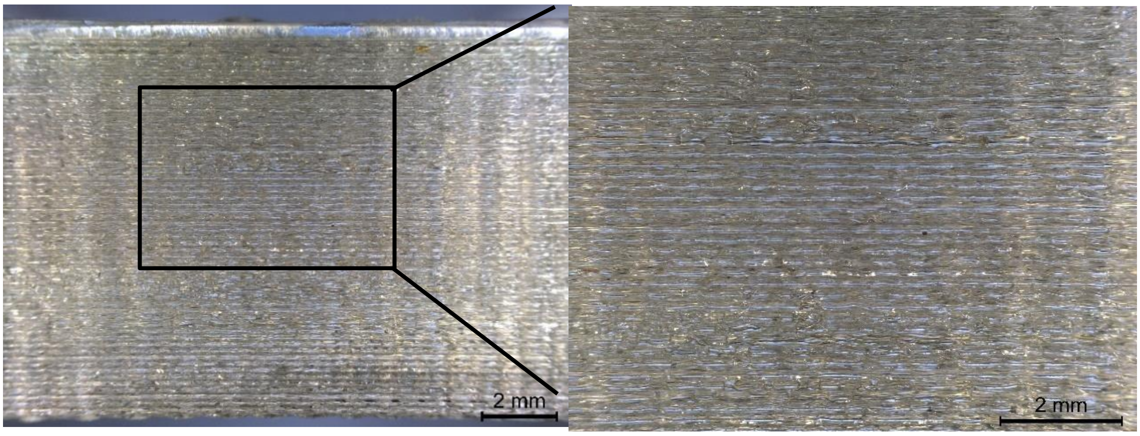


Figure 4.25 – Part produced with 210 °C of extrusion temperature, density infill of 100 % and an extruder head speed of 40 mm/s. Magnifications: 0,75x left and 1,25x right.

For this temperature (see Figure 4.26) it is observed larger points in the middle of the layers. In this case, it was difficult to focus the image due to the reflection and the shape of the part.

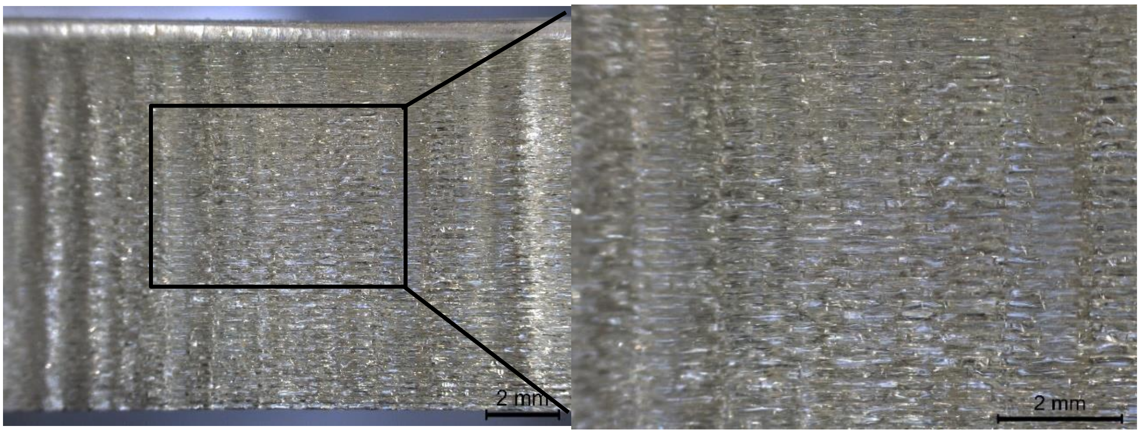


Figure 4.26 – Part produced with 210 °C of extrusion temperature, density infill of 25 % and an extruder head speed of 60 mm/s. Magnifications: 0,75x left and 1,25x right.

In Figure 4.27, the gaps between layers are more evident in the lower section of the part. A darker colour is more prominent in the middle section of the figure with larger magnification.

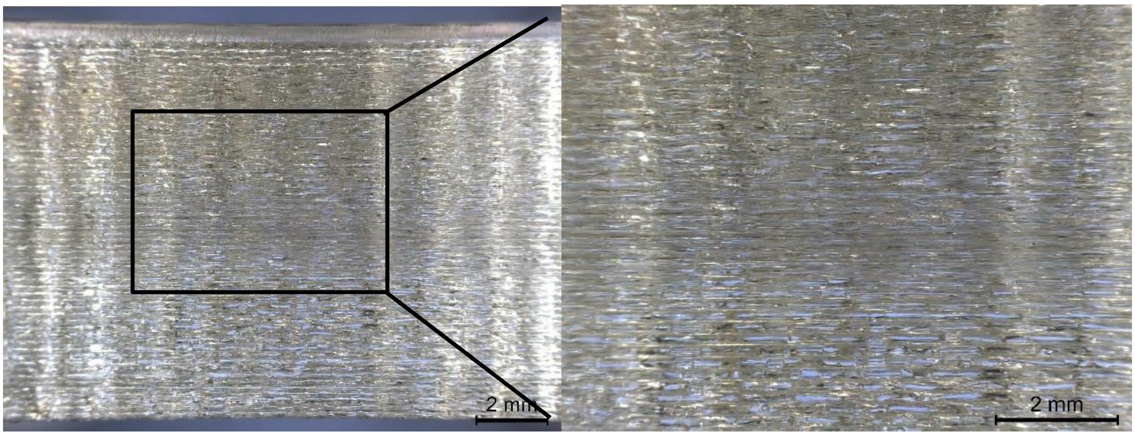


Figure 4.27 – Part produced with 210 °C of extrusion temperature, density infill of 50 % and an extruder head speed of 80 mm/s. Magnifications: 0,75x left and 1,25x right.

Considering the higher extrusion temperature, 220 °C, in Figure 4.28, gaps between layers are evident. This aspect is an indicative of a poor adhesion between filaments.

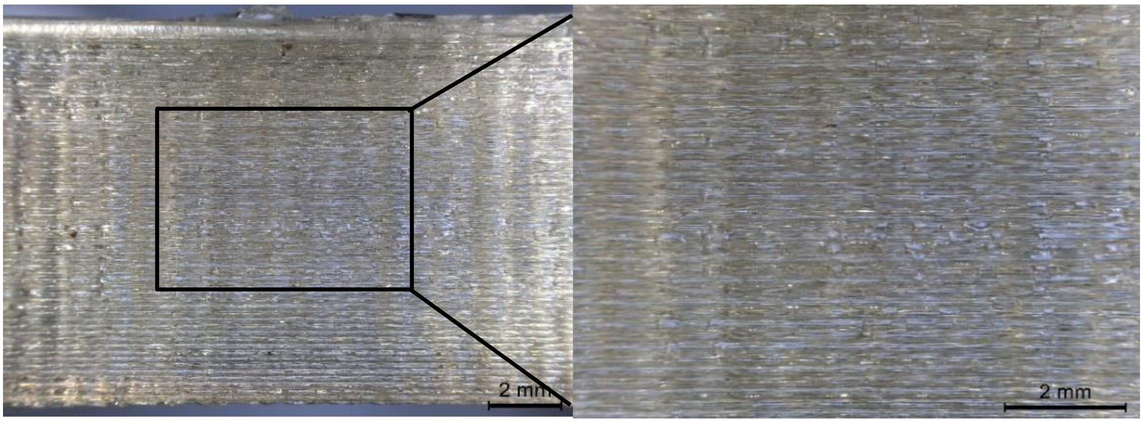


Figure 4.28 – Part produced with 220 °C of extrusion temperature, density infill of 50 % and an extruder head speed of 40 mm/s. Magnifications: 0,75x left and 1,25x right.

In Figure 4.29, moisture content is observable in the lower section of the part. Transparency is also observable in the middle section of the part. Adhesion between layers is better in the upper section.

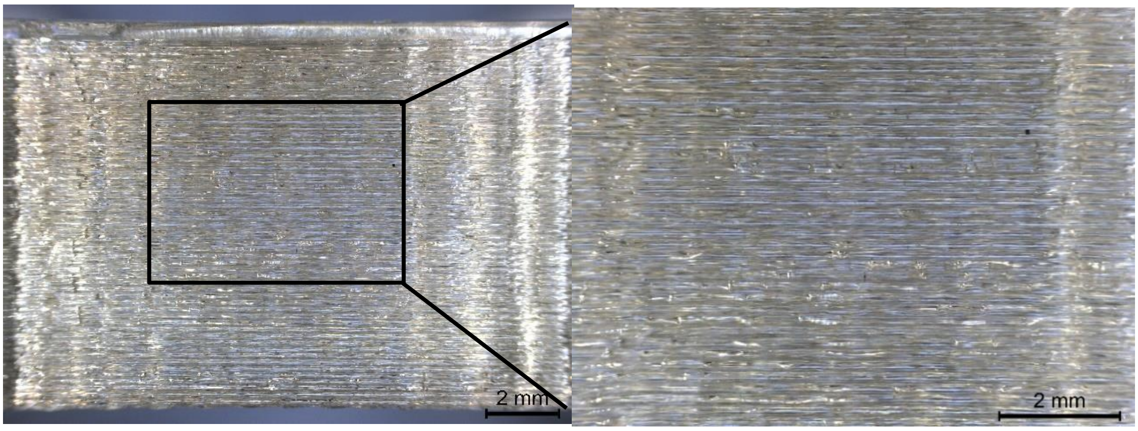


Figure 4.29 – Part produced with 220 °C of extrusion temperature, density infill of 100 % and an extruder head speed of 60 mm/s. Magnifications: 0,75x left and 1,25x right.

Considering every part produced at 220 °C, in this case Figure 4.30, the adhesion between layers appears better since the presence of gaps is lower, however, moisture is still present. Colour gradient shown in *Figure 4.30* is more uniform however, the surface does not present smoothness when comparing with the other parts presented in Figure 4.28 and Figure 4.29.

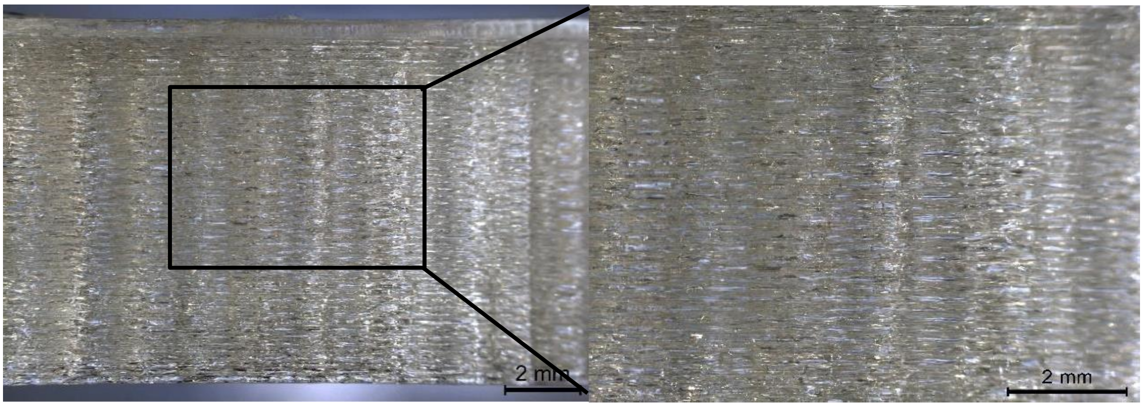


Figure 4.30 – Part produced with 220 °C of extrusion temperature, density infill of 25 % and an extruder head speed of 80 mm/s. Magnifications: 0,75x left and 1,25x right.

5. Conclusion and Future Work

Through this dissertation it was possible to develop a functional material to be used in additive manufacturing technology, in particular material extrusion, and for the posterior development of the case study.

The selection of the functional material was accomplished after an intense market and theoretical investigation, resulting in a material additive that would present thermochromic properties and a PLA polymer matrix to the compound. This masterbatch purchase to Donna Polymer was presented as a material, compatible with PLA, which presents colour changes. At low temperatures, from 15 °C, the material assumes a purple colour while at higher temperatures, between 20 °C and 31 °C, the material presents a red colour. Above this last temperature, the masterbatch assumes the colour of the polymeric matrix used. In order to understand the material thermal and physical properties, DSC, TGA and MFI were the tests performed. Thermal analysis indicates a higher degree of crystallinity for the neat material comparatively to the thermochromic masterbatch, 19,56 % and 18,03 %, respectively. DSC tests also show similar glass transition temperature of 61,2 °C – 54,8 °C and melting temperatures of 155,4 °C – 147,9 °C, respectively. Considering the physical properties tested, by melt flow index analysis, the experimental value obtained for purchased PLA was 15,09 g/10min, which is a value considerably higher for a material used for extrusion. The results obtained were considered for filaments production.

Considering the filament production for AM, the process occurred without significant problems. However, although the rollers' speed was optimized during compound process, the obtained diameter presented significant fluctuations which did not correspond to the expected tolerance 1,75 mm ± 0,05 mm. The cooling process of the extruded filament had significant influence once the filament was not cooled at the same time. Rollers present in the line also affected, since the calibration was not the best. It has also verified an increase in the viscosity when producing the filament with a higher amount of masterbatch.

Regarding the characterization methods done to the produced filaments, for thermal properties, similar glass transition and melting temperatures are noticed. For the filaments with the thermochromic feature, the degree of crystallization is higher for the *"Manufacturer Suggestion"* filament. Considering TGA analysis, filler content is higher for the filament with the more considerable amount of masterbatch as expected. Concerning degradation temperatures, values appear to be similar between the produced filaments.

The mechanical properties of the polymeric matrix are not much affected by the masterbatch addition, however a rigidity increase was noticed in the *"Manufacturer Suggestion"* filament, when compared with the *"Neat Formulation"* filament. In another aspect, the addition of more masterbatch increased the mechanical properties when compared with the *"Manufacturer Suggestion"* mixture.

Microscope analysis indicated an even distribution between the dots that appeared to be thermochromic masterbatch. More quantity in the transversal cut is observed, regarding the filament with the *"New Approach"* formulation.

Finally, to finish the characterization study from the produced filaments, stimulation tests were performed. The results confirmed the colour shifting at the specific temperatures and also there is not much influence on the increasing of masterbatch in terms of colour spreading or higher pigmentation. It is only observed by thermogravimetric record a significant capacity from the *"New Approach"* filament to maintain the acquired colour which could indicate a better retain of the temperature. After the investigation made regarding the obtained material, a prototype part was produced by material extrusion AM technique for the evaluation of the thermochromic feature in a post-production part and a process optimization was made.

Considering stimulation testing, more significant alterations were demonstrated in the "cold" experiments. For part produced with *"Manufacturer Suggestion"* filament, the part with the most pigmentation for every extrusion temperature were with the following processing conditions: 190 °C – 50 % – 60 mm/s, 210 °C – 100 % – 40 mm/s, 220 °C – 50 % – 40 mm/s. Considering the *"New Approach"* filament the processing conditions were: 190 °C – 100 % – 80 mm/s, 210 °C – 25% – 60 mm/s and 220 °C – 50% – 40 %. The parts mentioned before appear to present a faster response to colour change. For "hot" experiences the final colour, for the two higher temperatures, is darker (especially for 220 ° C). However, the colour shifting and stabilization occurs apparently at the same time.

In relation to surface analysis, almost in every material is observed moisture, however is more evident in the material with the *"Neat Formulation"* indicating a possible permeabilization as a characteristic form the thermochromic masterbatch. In respect to the parts with a more uniform surface, for each extrusion temperature are, respectively for *"Manufacturer Suggestion"* filament; 190 °C – 50 % – 60 mm/s, 210 °C – 25 % – 60 mm/s. Considering *"New Approach"* filament the parts were: 190 °C – 50% – 60 mm/s, 210 °C – 25% – 60 mm/s, 220 °C – 100 % – 60 mm/s. Finally, for the *"Neat Formulation"*; 190 °C – 100 % – 80 mm/s, 210 °C – 100 % – 60mm/s and 220 °C – 100% – 60 mm/s.

Regarding process optimization, the part which presents the purple colour with more intensity and, the best surface appearance is the part presenting the *"Manufacture Filament"* with the processing conditions: 190 °C – 50 % – 60 mm/s. In general, the parts produced at 60 mm/s at the 190 °C and 210 °C extrusion temperature were the most interesting parts for both filament testing and surface analysis.

Finally, considering the user interaction purpose of this work in general, it was possible to accomplish a part that would detect a user interaction with a product at a real-time, with absolute accuracy. The material developed is material extrusion suitable, allowing the production of prototypes to study the design approach before the real production avoiding unnecessariness costs.

- ✓ **Future Work**

For future work, in regarding to this project, an analysis of more experiments focused in the process conditions defined would be relevant, in order to validate what processing parameter in the equipment has significant influence in the thermochromic feature activation. In the aspect of parameter optimization, an analysis of the surface roughness and colour would validate the process and will give more information about adhesion and layer deposition.

Considering the ratio mixing selection a decreasing of the amount of masterbatch when compared to the manufacturer suggestion would also be interesting to understand how much influence has in the thermochromic feature the amount of material, since increasing the amount does not affect much.

Finally, a real test should be employed in the design improvement of an object to understand the effect in a real-time situation.

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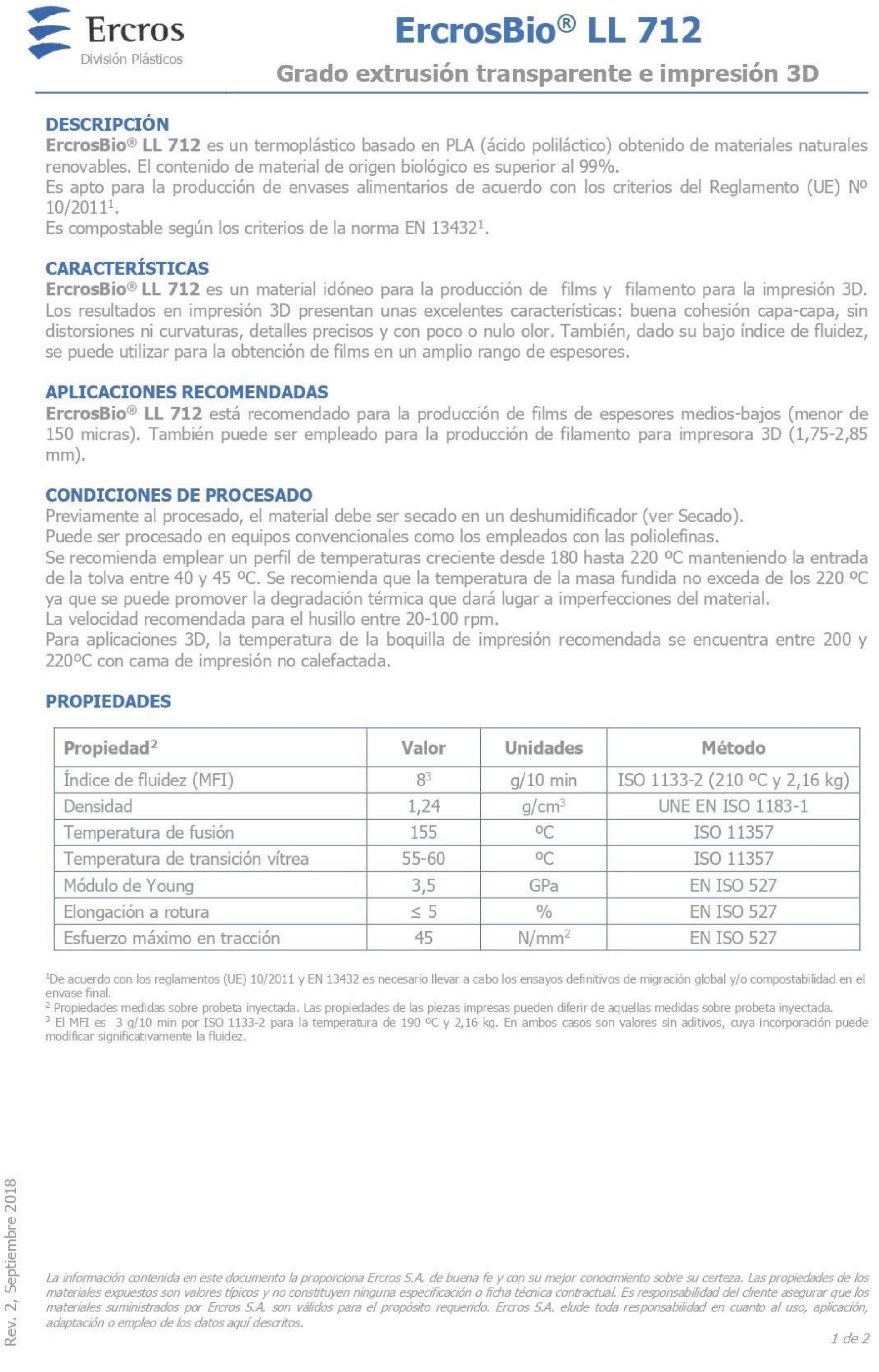
APPENDICES

APPENDIX 1: Technical data sheet from the polymeric matrix



Ercros
División Plásticos

ErcrosBio® LL 712

Grado extrusión transparente e impresión 3D

DESCRIPCIÓN

ErcrosBio® LL 712 es un termoplástico basado en PLA (ácido poliláctico) obtenido de materiales naturales renovables. El contenido de material de origen biológico es superior al 99%.
Es apto para la producción de envases alimentarios de acuerdo con los criterios del Reglamento (UE) Nº 10/2011[1].
Es compostable según los criterios de la norma EN 13432[1].

CARACTERÍSTICAS

ErcrosBio® LL 712 es un material idóneo para la producción de films y filamento para la impresión 3D. Los resultados en impresión 3D presentan unas excelentes características: buena cohesión capa-capa, sin distorsiones ni curvaturas, detalles precisos y con poco o nulo olor. También, dado su bajo índice de fluidez, se puede utilizar para la obtención de films en un amplio rango de espesores.

APLICACIONES RECOMENDADAS

ErcrosBio® LL 712 está recomendado para la producción de films de espesores medios-bajos (menor de 150 micras). También puede ser empleado para la producción de filamento para impresora 3D (1,75-2,85 mm).

CONDICIONES DE PROCESADO

Previamente al procesado, el material debe ser secado en un deshumidificador (ver Secado).
Puede ser procesado en equipos convencionales como los empleados con las poliolefinas.
Se recomienda emplear un perfil de temperaturas creciente desde 180 hasta 220 ºC manteniendo la entrada de la tolva entre 40 y 45 ºC. Se recomienda que la temperatura de la masa fundida no exceda de los 220 ºC ya que se puede promover la degradación térmica que dará lugar a imperfecciones del material.
La velocidad recomendada para el husillo entre 20-100 rpm.
Para aplicaciones 3D, la temperatura de la boquilla de impresión recomendada se encuentra entre 200 y 220ºC con cama de impresión no calefactada.

PROPIEDADES

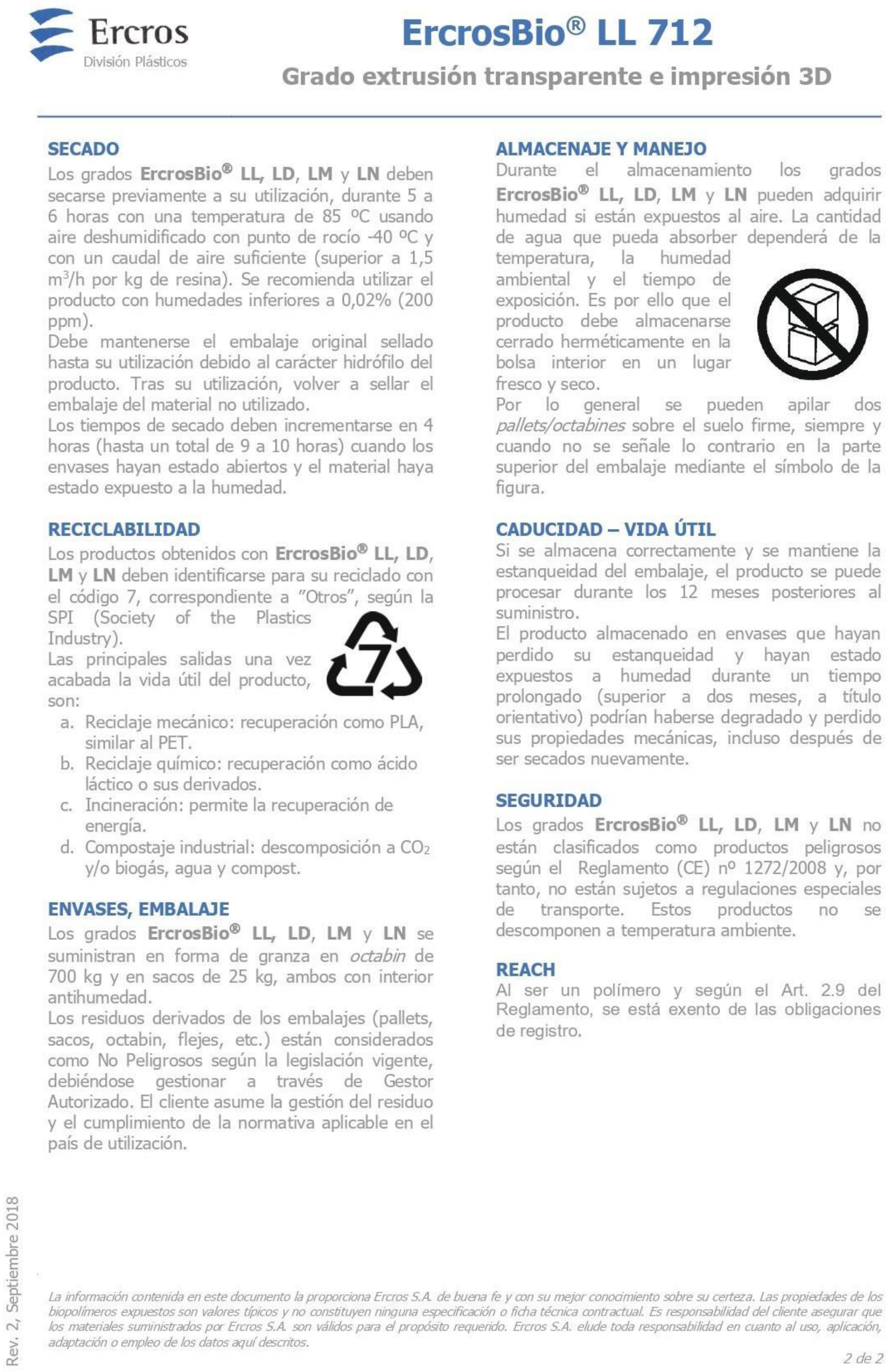
Propiedad[2]	Valor	Unidades	Método
Índice de fluidez (MFI)	8[3]	g/10 min	ISO 1133-2 (210 ºC y 2,16 kg)
Densidad	1,24	g/cm^3	UNE EN ISO 1183-1
Temperatura de fusión	155	ºC	ISO 11357
Temperatura de transición vítrea	55-60	ºC	ISO 11357
Módulo de Young	3,5	GPa	EN ISO 527
Elongación a rotura	≤ 5	%	EN ISO 527
Esfuerzo máximo en tracción	45	N/mm^2	EN ISO 527

[1] De acuerdo con los reglamentos (UE) 10/2011 y EN 13432 es necesario llevar a cabo los ensayos definitivos de migración global y/o compostabilidad en el envase final.

[2] Propiedades medidas sobre probeta inyectada. Las propiedades de las piezas impresas pueden diferir de aquellas medidas sobre probeta inyectada.

[3] El MFI es 3 g/10 min por ISO 1133-2 para la temperatura de 190 ºC y 2,16 kg. En ambos casos son valores sin aditivos, cuya incorporación puede modificar significativamente la fluidez.

Rev. 2, Septiembre 2018



Ercros
División Plásticos

ErcrosBio® LL 712

Grado extrusión transparente e impresión 3D

SECADO

Los grados **ErcrosBio® LL, LD, LM** y **LN** deben secarse previamente a su utilización, durante 5 a 6 horas con una temperatura de 85 ºC usando aire deshumidificado con punto de rocío -40 ºC y con un caudal de aire suficiente (superior a 1,5 m^3/h por kg de resina). Se recomienda utilizar el producto con humedades inferiores a 0,02% (200 ppm).

Debe mantenerse el embalaje original sellado hasta su utilización debido al carácter hidrófilo del producto. Tras su utilización, volver a sellar el embalaje del material no utilizado.

Los tiempos de secado deben incrementarse en 4 horas (hasta un total de 9 a 10 horas) cuando los envases hayan estado abiertos y el material haya estado expuesto a la humedad.

RECICLABILIDAD

Los productos obtenidos con **ErcrosBio® LL, LD, LM** y **LN** deben identificarse para su reciclado con el código 7, correspondiente a "Otros", según la SPI (Society of the Plastics Industry).

Las principales salidas una vez acabada la vida útil del producto, son:

a. Reciclaje mecánico: recuperación como PLA, similar al PET.
b. Reciclaje químico: recuperación como ácido láctico o sus derivados.
c. Incineración: permite la recuperación de energía.
d. Compostaje industrial: descomposición a CO_2 y/o biogás, agua y compost.

ENVASES, EMBALAJE

Los grados **ErcrosBio® LL, LD, LM** y **LN** se suministran en forma de granza en *octabin* de 700 kg y en sacos de 25 kg, ambos con interior antihumedad.

Los residuos derivados de los embalajes (pallets, sacos, octabin, flejes, etc.) están considerados como No Peligrosos según la legislación vigente, debiéndose gestionar a través de Gestor Autorizado. El cliente asume la gestión del residuo y el cumplimiento de la normativa aplicable en el país de utilización.

ALMACENAJE Y MANEJO

Durante el almacenamiento los grados **ErcrosBio® LL, LD, LM** y **LN** pueden adquirir humedad si están expuestos al aire. La cantidad de agua que pueda absorber dependerá de la temperatura, la humedad ambiental y el tiempo de exposición. Es por ello que el producto debe almacenarse cerrado herméticamente en la bolsa interior en un lugar fresco y seco.

Por lo general se pueden apilar dos *pallets/octabines* sobre el suelo firme, siempre y cuando no se señale lo contrario en la parte superior del embalaje mediante el símbolo de la figura.

CADUCIDAD – VIDA ÚTIL

Si se almacena correctamente y se mantiene la estanqueidad del embalaje, el producto se puede procesar durante los 12 meses posteriores al suministro.

El producto almacenado en envases que hayan perdido su estanqueidad y hayan estado expuestos a humedad durante un tiempo prolongado (superior a dos meses, a título orientativo) podrían haberse degradado y perdido sus propiedades mecánicas, incluso después de ser secados nuevamente.

SEGURIDAD

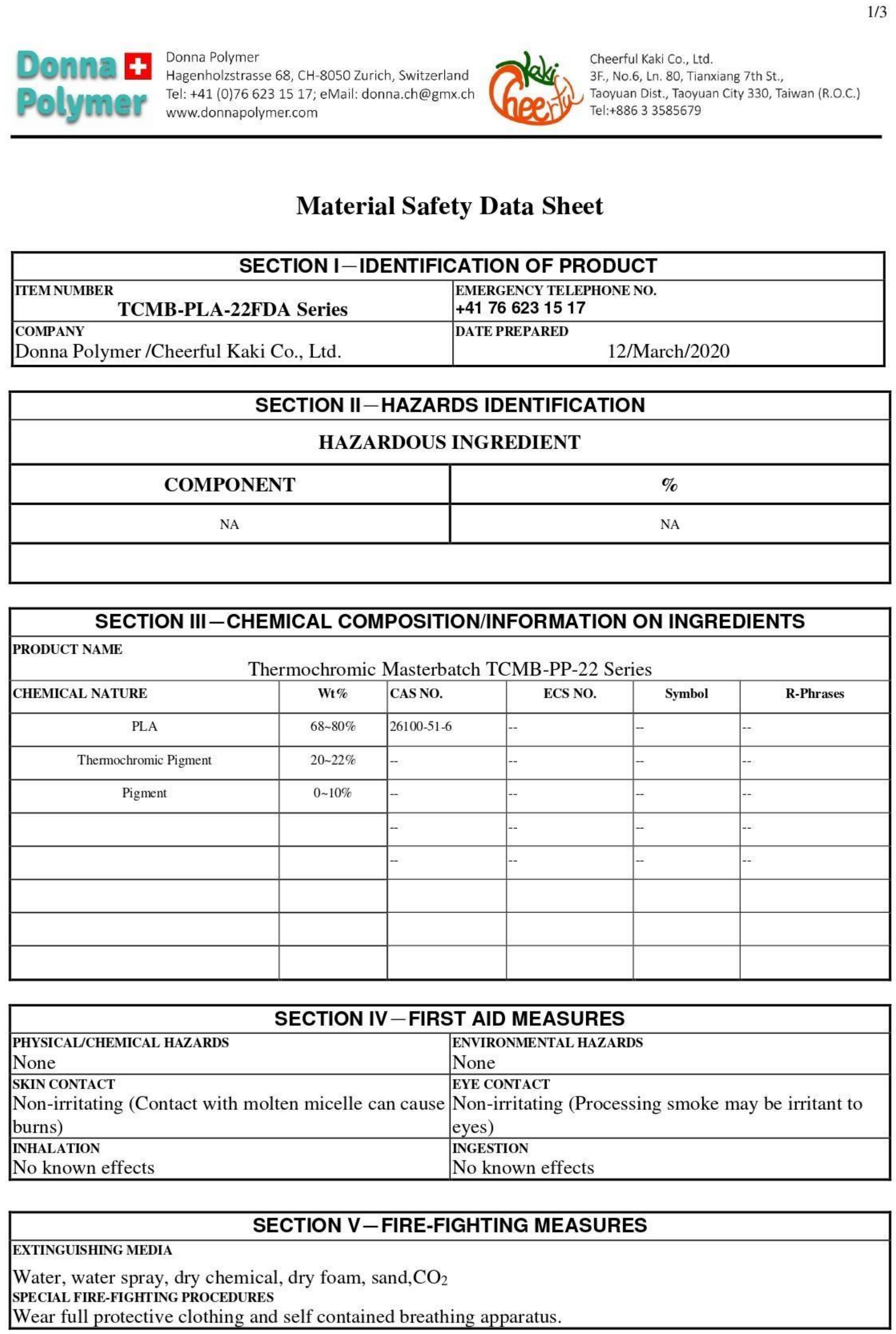
Los grados **ErcrosBio® LL, LD, LM** y **LN** no están clasificados como productos peligrosos según el Reglamento (CE) nº 1272/2008 y, por tanto, no están sujetos a regulaciones especiales de transporte. Estos productos no se descomponen a temperatura ambiente.

REACH

Al ser un polímero y según el Art. 2.9 del Reglamento, se está exento de las obligaciones de registro.

Rev. 2, Septiembre 2018

APPENDIX 1.A Technical data sheet for the thermochromic masterbatch



1/3

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Cheerful Kaki Co., Ltd.
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Taoyuan Dist., Taoyuan City 330, Taiwan (R.O.C.)
Tel:+886 3 3585679

Material Safety Data Sheet

SECTION I—IDENTIFICATION OF PRODUCT

ITEM NUMBER **TCMB-PLA-22FDA Series**	EMERGENCY TELEPHONE NO. **+41 76 623 15 17**
COMPANY Donna Polymer /Cheerful Kaki Co., Ltd.	DATE PREPARED 12/March/2020

SECTION II—HAZARDS IDENTIFICATION

HAZARDOUS INGREDIENT

COMPONENT	**%**
NA	NA

SECTION III—CHEMICAL COMPOSITION/INFORMATION ON INGREDIENTS

PRODUCT NAME

Thermochromic Masterbatch TCMB-PP-22 Series

CHEMICAL NATURE	**Wt%**	**CAS NO.**	**ECS NO.**	**Symbol**	**R-Phrases**
PLA	68~80%	26100-51-6	--	--	--
Thermochromic Pigment	20~22%	--	--	--	--
Pigment	0~10%	--	--	--	--
		--	--	--	--
		--	--	--	--

SECTION IV—FIRST AID MEASURES

PHYSICAL/CHEMICAL HAZARDS None	ENVIRONMENTAL HAZARDS None
SKIN CONTACT Non-irritating (Contact with molten micelle can cause burns)	EYE CONTACT Non-irritating (Processing smoke may be irritant to eyes)
INHALATION No known effects	INGESTION No known effects

SECTION V—FIRE-FIGHTING MEASURES

EXTINGUISHING MEDIA

Water, water spray, dry chemical, dry foam, sand,CO_2

SPECIAL FIRE-FIGHTING PROCEDURES

Wear full protective clothing and self contained breathing apparatus.

SECTION VI—ACCIDENTAL RELEASE MEASURES

Wear respirator, chemical safety goggles, rubber boots and heavy rubber gloves. Sweep up, place in a bag and hold for waste disposal. Avoid raising dust. Ventilate area and wash spill site after material pickup is complete.

SECTION VII—HANDLING AND STORAGE

HANDLING

For molding work, effective means for local exhaust are required to discharge gases generated by melt processing. Avoid retaining hot colloid in the processing machines for many hours. Micelle spilled on the floor is likely to cause slipping. Remove such spillage at any time.

STORAGE

Store in clean and dry cool condition. Material shall not be stored near to flammable material.

SECTION VIII—EXPOSURE CONTROLS/PERSONAL PROTECTION

TECHNICAL PROTECTIVE

Practice good personal hygiene.

PERSONAL PROTECTIVE EQUIPMENT

Wear a dust-proof mask. Wear protective glasses or goggles. Wear heat-resisting gloves against burns, when handling molten Polymer. Wear long sleeve clothes against burns, when handling molten polymer.

INDUSTRIAL HYGIENE

Always clean protective equipment and workplace.

PROTECTION AGAINST FIRE AND EXPLOSION

N/A

SECTION IX—PHYSICAL AND CHEMICAL PROPERTIES

FORM	Pellets	**ODOUR**	Odorless
COLOUR	All colours	**pH**	Not applicable
BOILING POINT（DEGREES CELSIUS）	Not applicable	**SPECIFIC GRAVITY（WATER=1）**	0.66
VAPOR PRESSURE（mm. OF MERCURY）	Not applicable	**PERCENT VOLATILITY（BY VOLUME）**	Not applicable
VAPOR DENSITY（AIR=1）	Not applicable	**EVAPORATION RATE（ETHYL ETHER=1）**	Not applicable
SOLUBILITY IN WATER	Insoluble	**EVAPORATION RATE（BUTYL ACETATE=1）**	Not applicable

SECTION X—STABILITY AND REACTIVITY

THERMAL DECOMPOSITION	＞250 ℃	**DANGEROUS REACTION**	N/A

SECTION XI—TOXICOLOGY INFORMATION

ACUTE ORAL TOXICITY	N/A
SKIN IRRITATION	Non-irritating
EYE IRRATATION	Non-irritating

SECTION XII—ECOLOGICAL INFORMATION

ELIMINABILITY	N/A

SECTION XIII—DISPOSAL CONSIDERATIONS

DISPOSAL

Check possibilities to recycle products. When disposed by incineration, use the well controlled incinerators in accordance with the Wastes Disposal Law, Air Pollution Control Law and Water Pollution Prevention Law.

SECTION XIV—TRANSPORT INFORMATION

GENERAL PRECAUTIONS

Keep this material dry during transport.

SPECIAL PRECAUTIONS

Secure the container firmly so at not to cause collapsing.

SECTION XV—REGULATORY INFORMATION

APPLICABLE REGULATION

Wastes Disposal Law designates it as waste plastics among Industrial wastes.

SECTION XVI—OTHER INFORMATION

Recommended used and restrictions

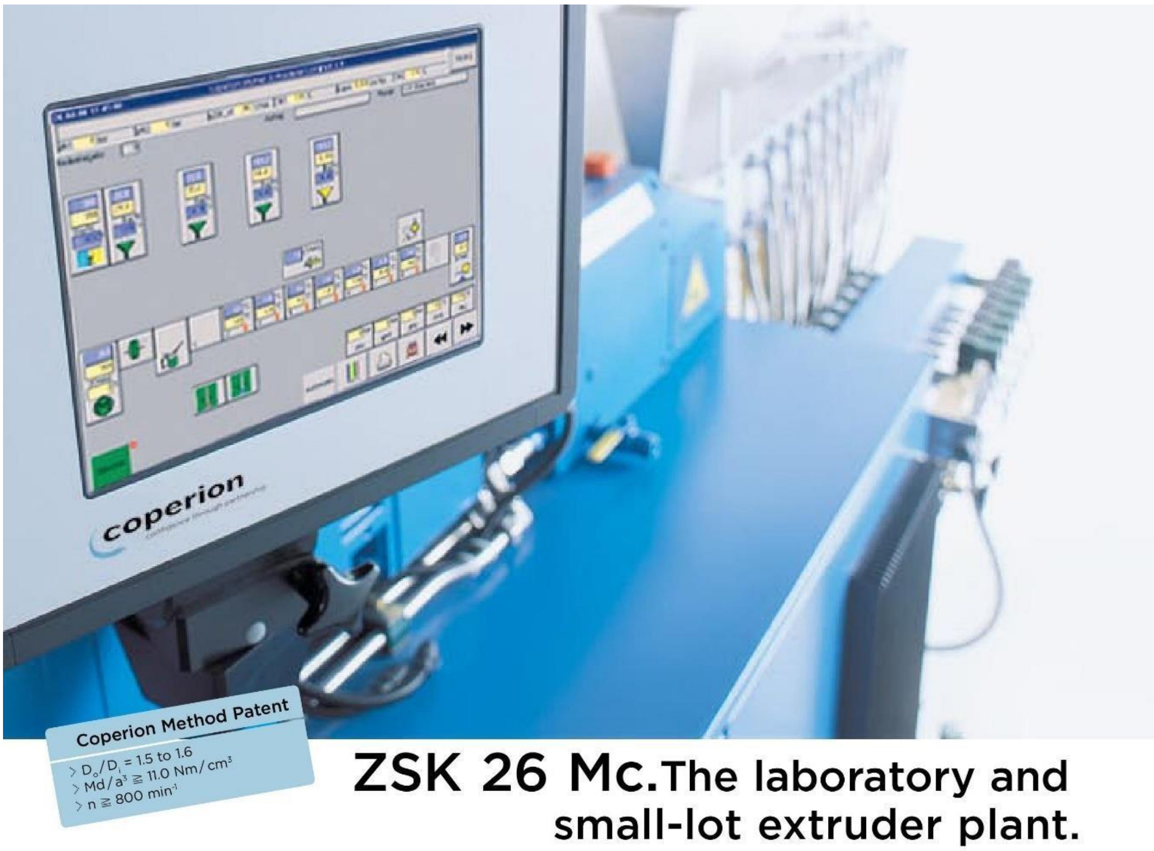
None

DISCLAIMER of LIABILITY

The information in this MSDS was obtained from sources which we believe are reliable. However, the information is provided without any warranty, express or implied, regarding its correctness. The conditions or methods of handling, storage, use or disposal of the product are beyond our control and maybe beyond our knowledge. For this and other reasons, we do not assume responsibility and expressly disclaim liability for loss, damage or expense arising out of or in any way connected with the handling, storage, use or disposal of the product. This MSDS was prepared and is to be used only for this product. If the product is used as a component in other product, this MSDS information may not be applicable.

APPENDIX 2: Technical datasheet from the laboratory twin-screw extruder

Coperion ZSK 26



Coperion Method Patent

- > $D_o/D_i = 1.5$ to 1.6
- > $Md/a^3 \geqq 11.0$ Nm/cm^3
- > $n \geqq 800$ min^{-1}

ZSK 26 Mc. The laboratory and small-lot extruder plant.

> MAXIMUM PERFORMANCE. SMALLEST PRODUCT QUANTITIES.
PERFECT FOR LABORATORY APPLICATIONS. <

Confidence Through Partnership

coperion
werner & pfleiderer

ZSK 26 Mc – More performance, more torque and more volume.

image 1	**Pre-configured connections for plug-and-play.**
image 2	**Option: Side Feeder.**
image 3	**Option: Compact Strand Pelletizer.**
image 4	**Standard Feature: Die head on bail.**
image 5	**Touch-screen.**

Advantages at a glance:

- Immediately ready for operation
- Production of smallest product quantities (1 kg)
- Throughput rates up to 200 kg/h
- Compact dimensions with plug-and-play attachments
- The Coperion Method Patent EP 0 852 533 B2
- Integrated control system CScompact

Technical Data

Screw diameter		mm	25.5
Diameter ratio	D_o/D_i		1.55
Flight depth		mm	4.55
Length per barrel segment	1 L	mm	100
(open or closed)	2 L	mm	200
Max. length of processing section			56 D
Torque per shaft	0-1,200 rpm	Nm	106
	1,200-1,800 rpm	Nm	76
Drive power at screw speed	N = 1,200 rpm	kW	27
	N = 1,800 rpm	kW	29
Permissible operating pressure	max	bar	180

Electric heating power

Screw barrel section	1 L	kW	2x0.6
(open or closed)	2 L	kW	4x0.6
	Die head	kW	0.6

Dimensions

Main dimensions, approx. LxWxH (at processing section length 36 D)		mm	2,550x800x1,800
Weight, approx. (at 36 D)		kg	900
Screw shaft height		mm	1,100

Compact strand pelletizer

Main dimensions, approx. LxWxH		mm	4,700x1,408x1,800
Intake height		mm	1,145
Draw-in speed range	min	m/min	20
	max	m/min	80
Number of strands	max		4
Lengh of water bath		m	2-4

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APPENDIX 3. Technical drawing of the case-study