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**Experimental Validation of a Microextruder
and In-line Rheological Characterization of
Polymeric Systems for FDM**

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Trabalho efetuado sob a orientação de:

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Resumo

Anteriormente, a tecnologia de Fused Deposition Modelling (FDM) era predominantemente utilizada para criar modelos e protótipos. No entanto, o crescente interesse nesta tecnologia para aplicações finais levou à realização de trabalhos de investigação focados no desenvolvimento de novos materiais para a produção de filamentos, uma vez que estes são a principal matéria-prima utilizada na maioria das impressoras 3D encontradas em vários ambientes mundialmente.

As propriedades reológicas dos materiais a ser utilizados em FDM influenciam a qualidade das peças impressas, uma vez que tem impacto sobre a capacidade da extrusão do material e deste manter a sua forma durante a impressão. Por isso, a determinação das propriedades reológicas do material poderão ajudar a otimização dos parâmetros de impressão e, assim, melhorar a qualidade das peças produzidas.

Acoplar fieiras, capilares ou fendas, instrumentadas a extrusoras permite a determinação das características reológicas a taxas de corte relativamente altas, isto é, na gama tipicamente obtida no processamento por extrusão (acima de 10 s^{-1}), o que faz dos métodos de caracterização em linha de grande interesse para a caracterização de polímeros fundidos, para a previsão da sua processabilidade e para fornecer a ligação entre as propriedades dos polímeros, os parâmetros de processamento e as características do produto final.

O principal objetivo deste trabalho é validar uma linha de microextrusão para a produção de filamentos para FDM e, também, um micro-reómetro com capacidade para a caracterização reológica em linha. Isto permitirá o desenvolvimento e produção de novos materiais para FDM, mas também a capacidade de caracterizar o comportamento reológico de sistemas poliméricos complexos.

Nesta contribuição, é apresentado o design e a construção do micro-reómetro e da linha de microextrusão. São realizadas experiências para definir a janela operacional da linha de extrusão. No que diz respeito ao micro-reómetro, dois sensores piezoelétricos, já validados para a reometria de fenda em linha, são montados ao longo da fenda para medir o gradiente de pressão e, assim, permitir a obtenção de curvas de fluxo de polietileno de baixa densidade (LDPE) e copolímero de olefina cíclica (COC). Os resultados são comparados com reómetros off-line (rotacional e capilar). Após a validação do micro-reómetro, são produzidos filamentos de COC e caracterizados dimensionalmente. Por fim, os filamentos são validados numa impressora 3D, e posteriormente, as peças impressas são caracterizadas mecanicamente, através de ensaios de tração.

Palavras-chave:

fused deposition modelling; extrusão; produção de filamentos; reometria de fenda em linha; sensores piezoelétricos.

Abstract

Previously, Fused Deposition Modelling (FDM) technology was predominantly utilized for creating models and prototypes. However, the growing interest in this technology for end-use applications has led to a surge in research works focused on developing new filament materials, since these are the primary feedstock used in the majority of printers found in various settings worldwide.

The rheological properties of the material being used in FDM can affect the quality of the printed parts, as it can impact the ability to extrude the material and maintain its shape during printing. Therefore, an understanding of the rheological properties of the material can help optimize printing parameters and improve the quality of the printed parts.

Coupling instrumented capillary or slit dies to extruders allows the determination of rheological characteristics at relatively high shear rates, that is, in the region of practical extrusion processing (greater than 10 s^{-1}), which makes in-extrusion characterization methods of great practical interest for the characterization of polymer melts, for the prediction of their processability and to provide the link between polymers properties, processing parameters and final product characteristics.

The main objective of this work is to validate a microextrusion line for filament production for FDM, and also, a microrheometer with capacity for in-line rheological characterization. This will capacitate the research, development and production of new materials for FDM, but, also, the ability to characterize the rheological behaviour of complex polymer systems.

In this contribution, the design and construction of the microrheometer and microextrusion line are presented. Experiments are performed to define the operating window of the extrusion line. Concerning the microrheometer, two piezoelectric sensors, already validated for slit rheometry, are flushed mounted along the microslit to measure the pressure gradient and thus produce flow curves of low density polyethylene (LDPE) and cyclic olefin copolymer (COC). The results are compared with off-line (rotational and capillary) rheometers. After the validation of the microrheometer, COC filaments are produced and dimensionally characterized. Lastly, the filaments are tested in a 3D-printer, with the printed parts being mechanically characterized after.

Keywords: fused deposition modelling; extrusion; filament production; in-line slit rheometry; piezoelectric sensors.

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Nomenclatures

Abbreviations

ABS - Acrylonitrile-butadiene-styrene copolymer

AM - Additive manufacturing

BNC - Bayonet Neill–Concelman connector

CAD - Computer-assisted design

COC - Cyclic olefin copolymer

DMLS - Direct Metal Laser Sintering

FDM - Fused Deposition Modelling

LDPE - Low density polyethylene

PE - Polyethylene

PETG - Polyethylene terephthalate glycol-modified

PID - Proportional-Integral-Derivative

PLA - Poly(lactic acid)

PP - Polypropylene

PMMA - Poly(methyl methacrylate)

PP - Polypropylene

T_g - Glass Transition Temperature

WLF - Williams-Landel-Ferry

Symbols

σ - Shear Stress

$\dot{Q}$ - Volumetric Flow Rate

H - Height

L - Length

W - Width

ΔP - Pressure Gradient

G' - Storage Modulus

$|G^*|$ - Complex Modulus

G'' - Loss Modulus

η - Shear Viscosity

$|\eta^*|$ - Complex Shear Viscosity

$\dot{\gamma}$ - Shear Rate

$\dot{\gamma}_a$ - Apparent Shear Rate

ω - Angular Frequency

K - Flow Consistency Index

n - Power-law constant

η_0 - Viscosity at Zero Shear Rate

η_∞ - Viscosity at Infinite Shear Rate

λ - Relaxation Time

R - Universal gas constant

ΔE - Activation energy

V_c - Volume of C-chamber

r - Radius

S - Screw Pitch length

θ - Flight angle

W_f - Flight Width

Units

min - minutes

MPa - Megapascal

GPa - Gigapascal

Pa - Pascal

V - Volts

mm - milimeters

m - meters

s - seconds

$^\circ$ - Degrees

C - Celsius

CHAPTER 1

Introduction

1.1 Framework and Motivation

Additive Manufacturing

Additive manufacturing (AM) is a popular and massive growing technology defined by the ASTM F42 as the “process of joining materials to make objects from three-dimensional model data, usually layer by layer, as opposed to subtractive manufacturing methodologies” [1]. Introduced to serve the needs of model making and rapid prototyping, AM has emerged as a versatile technology platform for computer-assisted design (CAD) and rapid manufacturing [2], and, for that reason, it became a topic of intensive research and development, in both industry and academia for more than 20 years.

This technology allows the production of customized parts from metals, ceramics, and polymers without the need for molds. The development of AM technologies has the potential to revolutionize computer-assisted fabrication of both complex objects and multifunctional materials systems. Contrarily to conventional fabrication, which is governed by processing constraints related to industrial mass production, AM enables faster turnaround on design and manufacturing of customized objects, tailored to meet the needs of individuals and specific applications [2].

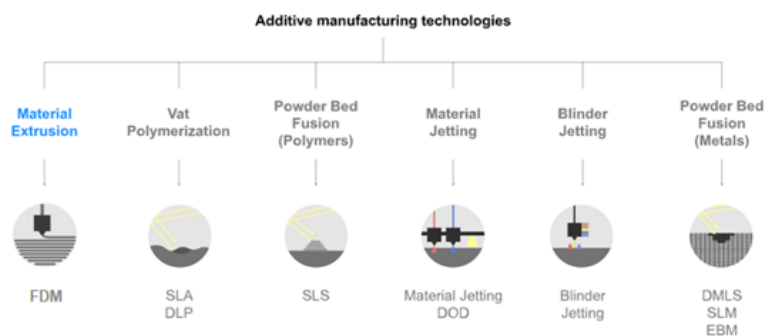


Figure 1.1: Different AM technologies (Adapted from [3]).

Nevertheless, AM technologies differ among themselves in the way the layers are deposited to build parts, in the equipment required and in the physical state of the materials that can be used. For example, in some of these techniques, melts or soften materials are used to obtain the layers, such as selective laser melting (SLM), selective laser sintering (SLS) and fused deposition modelling

(FDM), while others use thermoset materials, such as, for example, stereolithography (SLA). The most relevant AM technologies are shown in Figure 1.1 with the extrusion-based process being highlighted.

Fused Deposition Modelling

In the FDM process, a filament is fed into a machine via a pinch roller mechanism. The feedstock is melted in a heated liquifier with the solid part of the filament acting as a piston to push the melt through a print nozzle. A gantry moves the print nozzle in the horizontal x-y plane as the material is deposited on a build surface that can be moved in the vertical z direction. This enables complex 3D objects to be produced as the melted bead solidifies leaving the nozzle [4]. A representation of the typical used system can be seen on Figure 1.2.

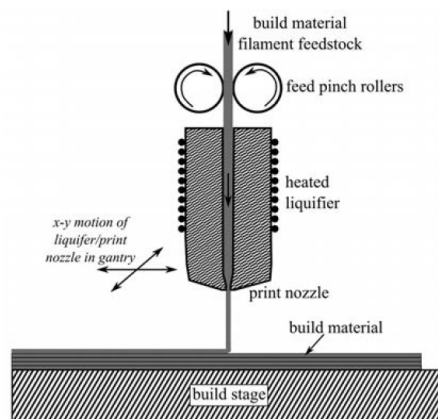


Figure 1.2: Illustration of a typical extrusion-based AM process. Retrieved from [4].

Some of the significant advantages of this technique are its simplicity, reliability, cost-effectiveness, diversity of the compatible materials, and high speed. These aspects make this process a good option for printing multi-functional designs and products, and make it very promising for a wide range of technological applications such as biotechnology, environment, robotics, and aerospace [5, 6]. However, some of the limitations include warping and rough surface finish of the parts, the need for removing supports for any model that overhangs more than 45 degrees and the restrictions of filament properties, since, for example, not all materials can be temperature controlled enough to allow its printing. Another restriction relies on the fact that many of these printable materials cannot be recycled and very few are food safety-approved [6].

Filaments for FDM

Polymeric materials are the most used materials in FDM, from human implants or house appliances to automotive or aerospace applications, since polymers have a unique combination of properties, being the most prominent flexibility, toughness, electrical insulation, lower cost and ease of manufacture [7, 8]. With the growing interest in FDM for end-use applications rather than just models and prototypes, as it was in the beginning, many research works have been done focused on the development of new materials with properties suitable for filaments.

In order to widen the number of suitable materials for this technique, the interest in combining

the properties of different materials, which can be made through polymer blends, reinforced polymers or composites grew steeply. In this scope, it is common to use twin-screw extruders to blend and extrude the filaments, since these machines offer several advantages over single screw extruders, caused by the better feeding and more positive conveying characteristics, which allow good mixing, good heat transfer and the possibility to use modular screw elements [9].

For research and development purposes, it is usual to extrude in smaller scale equipment, since microextrusion has the main principles and functionalities of equivalent industrial lines, although at a much smaller scale [10], which can reduce the amount of material required, making it interesting when small quantities of material are available. Taking a step further, the determination of the shear viscosity at relatively high shear rates, that is, in the region of practical extrusion processing (greater than 10 s^{-1}) becomes accessible by coupling an instrumented die. This is of great practical interest for the characterization of polymer melts and the prediction of their processability and can provide the link between polymers properties, processing parameters and final product characteristics [11].

1.2 Objectives

The main objective of this dissertation is to validate a counter-rotating twin-screw microextruder for filament production for FDM, and, also, with capacity for in-line rheological characterization by coupling a slit microrheometer. This will capacitate the research, development and production of new materials for FDM, but, also, the ability to characterize the rheological behaviour of complex polymer systems, which is essential for understanding the correlation between process parameters and the final properties of the extrudate. In order to accomplish the main objective, the following secondary objectives are outlined:

- Definition of the operating window of the microextrusion line;
- In-line measurement of the rheological properties of materials by coupling a slit microrheometer to the microextruder;
- Validate the in-line microrheometer with off-line (rotational and capillary) rheometers by comparing of the rheological data collected by overlapping the obtained flow curves;
- Validation of the capacity of the microextrusion line in producing suitable filaments for FDM.

1.3 Methodology

Validation of the Microextruder:

The first stage of this work involved the validation of the microextruder. The process will begin with the assembling of all microextruder components followed by system calibration.

To establish the operating window of the microextrusion system, experiments will be carried out to assess the system capacity under a range of parameters such as temperature control, residence time, and constant throughput over time.

Validation of the In-line Rheological Characterization Capacity by the Microrheometer:

In order to achieve this objective, two different materials (a relatively simple homopolymer material (low density polyethylene), followed by a more complex structured material (cyclic olefin copolymer)) will be subjected to experiments using the in-line slit microrheometer. In-line measurements will use a slit die coupled with piezoelectric transducers that enable pressure measurement at various locations on the die. The pressure drop, together with the throughput, enables the determination of material flow curves.

Off-line techniques, such as rotational (steady state and oscillatory) and capillary rheometries are also performed. The results obtained are compared by overlapping the flow curves.

Production and Validation of Polymeric Systems for FDM:

Once the in-line microrheometer is validated, using the microextrusion line, filament production occurred. The research also entails dimensional characterization of the filaments and load of these filaments into an FDM machine to produce test specimens. The produced parts are mechanical characterized.

1.4 Structure of the Dissertation

The Dissertation is subdivided into six chapters.

The Introduction (Chapter 1) will present the framework, the main objectives and the structure of the dissertation.

The goal of Chapter 2 is to present the state-of-the-art of the importance of in-line rheological characterization of materials for FDM.

Chapter 3, will present the materials used, experimental set-ups and other equipments used.

Chapter 4, will present the procedures adopted for performing the experimental work.

Chapter 5, will present and discuss the results obtained, including the validation of the

microextruder, in-line rheological measurements and the use of FDM equipment.

Finally, Chapter 6, will summarize the main Conclusions obtained with this work and will include Suggestions for Future Works.

Appendix, will present the development of a counter-rotating system to adapt in the available mini- twin-screw extruder, including the design of the screw elements and the transmission system and construction of the former.

CHAPTER 2

Importance of In-line Rheometry of Filaments for FDM

The usual approaches in producing parts using FDM are based on trial and error methodologies, which require time, larger quantities of material and originate higher costs of printed parts often lacking dimensional precision [12, 13]. Since FDM is a process of additive manufacturing that involves the deposition of material in a molten state to create 3D structures layer by layer, the rheological properties of the material used can significantly affect the quality and accuracy of the final product [14].

Thus, a careful control of rheological properties is of great importance in order to ensure easy extrusion of the melt through the nozzle. Subsequently, the shape and integrity of the extrudate in the stand-off region between the nozzle exit and print bed, as well as the solidification and adhesion of the deposited extrudate through interlayer polymer chain diffusion are both correlated with the rheological characteristics associated with processing parameters [12, 13].

In sum, the reasons why rheological characterization is important for FDM are [12, 15, 16]:

- **Material Selection:** Different materials exhibit different rheological properties that can affect the FDM process. By understanding the rheological behaviour of different materials, it is possible to determine if a material is suitable for this technique.
- **Print Quality and Speed:** The rheological properties of the material used in FDM can directly affect the quality of the printed object. Thus, determining the rheological properties of the material can help optimize the printing process by adjusting the print speed and temperature to achieve the best quality and accuracy while minimizing the risk of defects or failure, for example, if the material has a high viscosity, it may not flow smoothly through the nozzle, leading to irregularities in the final product.

Usually, the analysis of the rheological properties is conducted using off-line rheometers. Measurements are realized on a sample taken from the raw material or product and transported to the measuring instrument. On account of the need for transporting to the laboratory, but also, sample and rheometer preparation, it originates delays between the moment of the sample collection and the necessary adjustment of the extrusion parameters [17, 18]. A reduction in the time shift is provided by at-line measurements, where the measuring instrument is positioned near the production line. Taking a step further, in-process rheometry refers to the measurement of rheological properties of the material

during its processing using a rheometer that is integrated into the processing equipment [18, 19].

The main advantages of in-process rheometry over off-line rheometry are that it provides more accurate and real-time measurements of the rheological properties of the material being extruded, such as viscosity and normal stress differences. Additionally, in-process rheometry can be used to measure the effects of changes in temperature, pressure, and other extrusion parameters on the material rheological properties [18].

These in-process measurements can be on-line or in-line. Although both these in-process measurements share the same principle, where the melt must be subjected to a controlled deformation rate and the resulting pressure is measured, they differ in the way they perform the measure stage [17, 18].

- On-line devices principle consists in deviating a stream from the main flow channel, pumping it to an instrumented channel, and either returning it to the main flow or not [24]. These devices have their own temperature control, hence the test can be performed at the desired temperature [18].
- In-line data are obtained directly from the main melt stream, typically between extruder and die, or at the die, using flush mounted sensors. In-line measurements cause a short time lag between sampling and results [25]. The mode in which the testing devices are installed enables the determination of the rheological characteristics in the real time [19]. Advanced design solutions employed in the construction of in-line rheometers, also, allow the study of morphology and molecular structure the material by including optical windows along the length of the die [11].

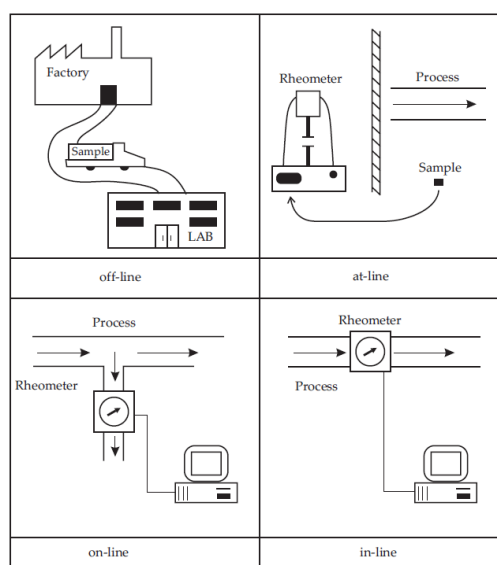


Figure 2.1: Schematic configuration of rheometers relative to the technological process: off-line, at-line, on-line and in-line. Retrieved from [17].

In-line rheometry has several advantages in FDM printing, such as improving the repeatability and reproducibility of the printing process, reducing waste and material costs, and enabling the use of new and complex materials with varying rheological properties. In recent years, there has been a growing interest in developing in-line rheometry systems for FDM printing, and some studies have reported on the design and implementation of such systems [20–22], however, it is still a topic without many research works.

Coogan et al. [20] discussed a method to monitor the rheological behavior of the polymer melt during FDM printing. The authors proposed an in-line measurement technique that uses a pressure sensor and a torque sensor to measure the pressure and torque exerted by the extruder during printing. By measuring these parameters, the melt viscosity of the polymer can be calculated in real-time. The authors demonstrated the effectiveness of this approach by performing experiments with polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) filaments.

Tammaro [22] described a system developed that uses a modified 3D printer to measure the rheological properties of complex fluids, such as viscosity and elasticity, as they are printed. The system is based on the fact that the printing process involves the flow of fluid through a nozzle, which can be used to estimate the rheological properties of the fluid. The author tested this system using a variety of complex fluids, including thixotropic fluids and fluids with shear-thinning behavior. They found that the system was able to accurately measure the rheological properties of these fluids and that the measurements were consistent with those obtained using traditional rheological instruments. The author concludes that their system is a useful tool for characterizing the rheological properties of complex fluids, and that it has the potential to be a low-cost and accessible alternative to traditional rheometers. They suggest that it could be used in a variety of fields, including materials science and biomedical engineering, to study the behavior of complex fluids.

In-line rheometry can be performed using various methods, including in-line slit rheometry and capillary rheometry [18]. Each method has its advantages and disadvantages, and the choice of the method depends on the specific application requirements. Capillary rheometers do not have convenient locations for pressure transducers, in contrast to slit rheometers that have a simple geometry consisting of a flat plate with a narrow gap and are designed to easily accommodate pressure transducers along the length of the channel. The transducers can be located in a variety of positions. For this reason, in this work, only in-line slit rheometry was used and is described here.

In-line slit rheometry, as the name implies, involves the use of a slit die with coupled pressure sensors along the length (See Figure 2.2), that is integrated into a processing line, through which the material flows and its properties are measured. Slit rheometers are often used to determine the viscosity of polymer melts, since they provide the possibility to measure not only the steady shear viscosity but, also, the normal-stress differences, through the pressure-hole method [18, 23, 24]. Other advantages of this type of measuring geometry is that the shear stress is obtained directly from the pressure gradient, with no need to apply the Bagley correction, as in capillary rheometry, low cost and relatively easy to implement in existing processing lines [25, 26].

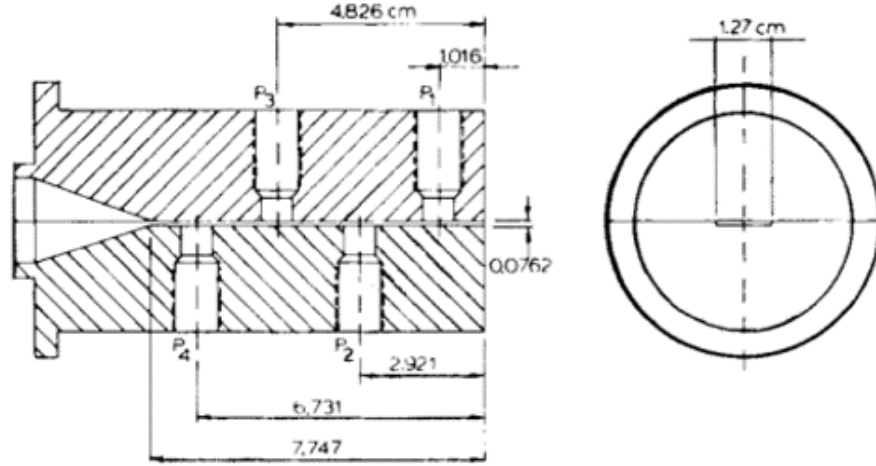


Figure 2.2: In-line Slit die coupled with pressure transducers. Retrieved from [27].

The flow curves are constructed using the following analysis for slit rheometry [27], where the pressure drop, dP , and the volumetric flow rate, $\dot{Q}$, are used to determine the wall shear stress, σ , the shear rate, $\dot{\gamma}$, and viscosity, η , respectively, with the following equations:

$$\sigma = \frac{H}{2(1+H/W)} \frac{dP}{dx} \quad (2.1)$$

where W and H are the width and height of the flow channel respectively, and dx is the distance between the transducers. The apparent shear rate, $\dot{\gamma}_a$, is:

$$\dot{\gamma}_a = \frac{6\dot{Q}}{WH^2} \quad (2.2)$$

where $\dot{Q}$ is obtained in an indirect way by measuring the weight of the extrudate. The apparent shear rate is corrected according to Weißenberg-Rabinowitsch:

$$\dot{\gamma} = \frac{\dot{\gamma}_a}{3} \left(2 + \frac{d \ln \dot{\gamma}_a}{d \ln \sigma} \right) \quad (2.3)$$

and, at last, to determine the viscosity, the equation used is:

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad (2.4)$$

Nonetheless, in-line slit rheometry has a few important disadvantages, such as that coupling a slit die to an extruder to perform rheological measurements prevents the extrusion of products with other cross-sections [25]. Also, in most cases, a single shear rate is obtained, resulting from the extrusion condition. In fact, at each extrusion condition, unless more than two transducers are used, measuring both pressure drop and throughput yields a single point of the shear viscosity versus shear rate curve [18]. In order to generate a range of shear rates to determine a flow curve, the

extruder output has to be changed gradually, either by changing the feed rate, the screw speed or the temperature. However, this proceeding changes the thermomechanical behaviour of the material, which may change the thermal stability, homogeneity and morphology of the polymeric system [18]. Another limitation are the commonly used strain gauge transducers that have large front dimensions (typically a diameter of 7.8 mm) [28, 30], which may impact on the practical possibility of fixing them on small flow channels and have limited sensitivity to lower shear rates and viscosities.

Some other limitations of in-line slit rheometry include difficulty to properly clean the corners of the die and the fact of not attain such high shear rates as capillary rheometry (See Figure 2.3).

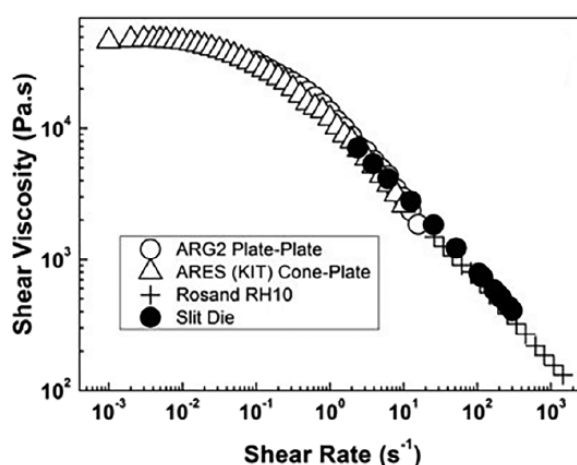


Figure 2.3: Shear viscosity versus shear rate measured on-line (solid symbols) and off-line (open symbols). Retrieved from [18].

Several studies have been performed with slit dies attached to extruders in order to perform in-line rheological measurements aiming to optimize the processes [24, 25, 31].

Various authors proposed slit die designs enabling the acquisition of various points of the flow curve in a single experiment. Pabedinskas et al. [31] used a wedge profile design that increased the strain rate along the length of the slit, but it was subject to errors for polymers with significant elasticity. Horvat et al. [24] developed a multi-step slit die with pressure transducers at different downstream locations, which generated three shear rates spanning one order of magnitude. Coates et al. [32] attached a flow regulating valve to a slit but only achieved low shear rates and moderate agreement with off-line data. Other designs, such as those proposed by Springer et al. [33] and Vergnes et al. [34], involved twin slits and analytical models for power law fluids, respectively. Della Valle et al. [35] successfully used the twin-slit rheological die, but waste of material during measurements was a drawback.

Nevertheless, the twin-slit rheological die approach was found to be advantageous for maintaining total pressure drop while changing shear rate, and was modified to improve practical utility and range of measurements, with one slit suitable for rheo-optical characterization and the other for conventional extrusion and based on that, Teixeira et al. [25] developed a modular double-slit die, that can be

coupled to a miniextruder or to a capillary rheometer. This die has 3 modules, a central main body from where the flow from the extruder or reservoir is sent to the extrusion channel and/or to the measurement channel. The measurement channel has two pressure transducers flush mounted, which allows the determination of the pressure gradient ΔP , and one pressure transducer recess mounted, that permit the determination of the normal stress differences $N_1 - N_2$. The central body also has 2 valves (A and B) located near the entrance of the 2 channels, allowing the control of the flow rate in each channel. This innovative approach allows the generation of a wide range of shear rates without changing the thermomechanical environment inside the extruder [29].

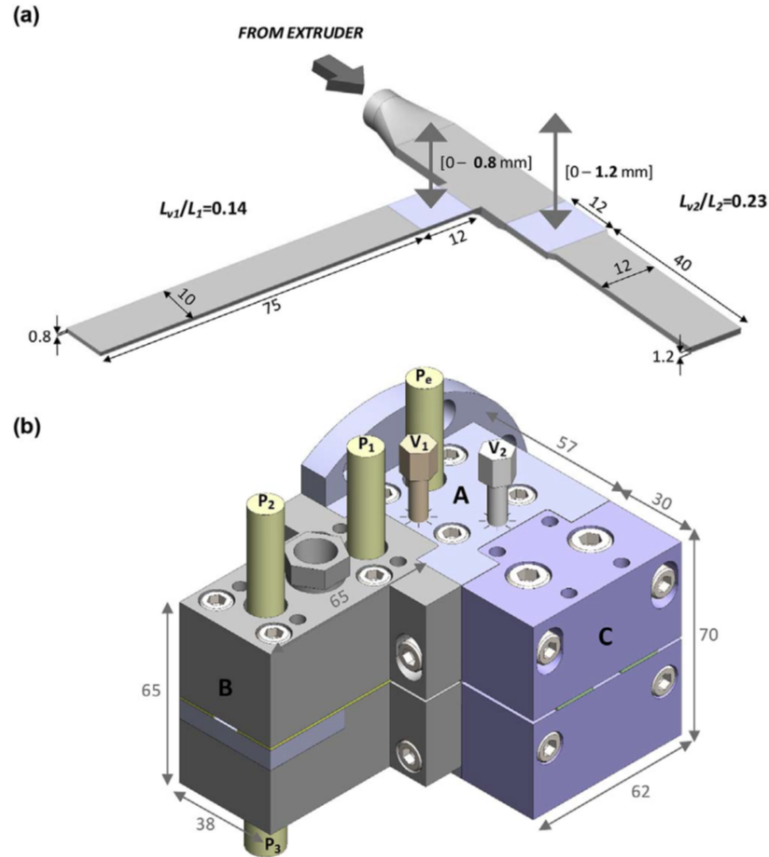


Figure 2.4: Double-slit rheological die. (a) Flow channel configuration and dimensions; the arrows denote the range of vertical aperture of the valves; (b) Die construction: A - main body, B - rheo-optical module with a replaceable lower lip to enable the use of different hole geometries in the hole-pressure method. C - extrusion module. P_1 , P_2 , P_3 and P_e are pressure transducers; V_1 and V_2 are screws controlling the vertical position of the valves. Retrieved from [25].

One of the key components of in-line rheological measurements is, obviously, the pressure measurement devices. These devices are used to accurately measure the pressure of the melt as it flows through the system. The precise measurement of pressure can help optimize their processes and ensure product quality and consistency, making pressure measurement devices an essential tool in in-line rheological measurements.

Pressure Measurement Devices

The conventional sensors to perform measurements are pressure transducers, known as strain gauge, which have two connected diaphragms, one in contact with the melt and the other placed above in contact with the strain gauge. Once the melt contacts with the lower diaphragm, the motion is transmitted to the upper diaphragm causing a mechanical strain, which is proportional to the applied pressure [36]. As mentioned previously, these devices are larger (typically a diameter of 7.8 mm), which could lead to the necessity of designing very long slits to couple several transducers [28]. For this reason, the use of piezoelectric transducers (typically a diameter of 2.5 mm) in rheometry instead of pressure transducers has been studied and validated [28, 30]. These sensors use the piezoelectricity principle to measure the melt pressure. The absence of diaphragm allows these devices to be more robust, making them suitable to withstand higher pressures. Its sensitivity is not affected by its size, but by its geometry and type of piezoelectric material. This way, it is possible to produce very small piezoelectric sensors, which are perfect to be used when space is limited.

These transducers show remarkable sensitivity and faster response times when compared to the conventional pressure transducers. When mounted in miniaturized systems, and implementing oversampling techniques, piezoelectric sensors were used to establish relationships between rapid pressure fluctuations with small amplitudes and distortions found on the surface of the extruded materials [38–40]. Many of the defects on the products of the extrusion process, such as melt fracture and sharkskin, are characterized by periodic distortion of the surface, with high frequency and small amplitude. In capillary rheometry, these instabilities result from compress and decompress cycles with origin in the rheometer reservoir. Since the pressure resolution and the acquisition rate of the conventional transducers are not enough to study these superficial defects, piezoelectric sensors have been used in studies, where the goal was to establish a relationship between the pressure and the extrudate surface distortions. Filipe et al. [37] concluded that the melt instabilities are related with the materials properties. Naue et al. [39] aimed to demonstrate the viability of these sensors in polymer processing and proved that piezoelectric sensors can detect melt instabilities in the extrusion process. Based on this work, Palza et al. [40–42] related the parameters that characterize the melt instabilities with the structural material properties and was able to trace the origin and location of all the melt instabilities range. Kadar et al. [38] coupled piezoelectric sensors in a slit die attached to a capillary rheometer to estimate the first normal stress difference of polymer melts, N_1 , via the pressure hole effect.

Figure 2.5 shows that the acquired signal by the strain gauge is linear, which prevents the visualization of pressure fluctuations. In contrast to that, due to the very high rate of acquisition by the piezoelectric sensors, the level of electronic noise in the acquired signal is also very high. However, this problem can be solved recurring to oversampling techniques, which consist in obtaining an average single point from a fixed number of points between t and $t + \Delta t$. That way, each of these new resulting points have a lower level of electronic noise.

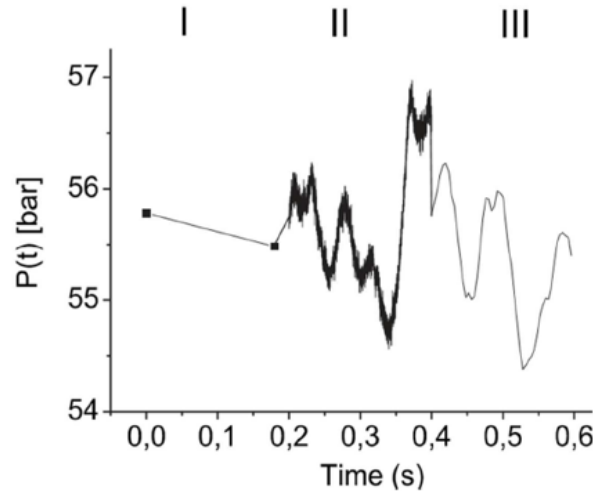


Figure 2.5: Oversampling Technique: Region I - Acquired pressures by a strain gauge transducer, II - Acquired pressures by a piezoelectric sensor, III - Acquired pressures by a piezoelectric sensor after application of oversampling techniques. Adapted from [43].

However, these devices have some disadvantages, such as exhibiting a drift of the signal with time (See Figure 2.6), which is inherent to both the charge amplification and transducer-to-amplifier cabling. These are needed to convert the transducer signal into volts and, therefore, it is necessary to adopt data treatment procedures to account for the drift of the piezoelectric signal [28]. Another setback of these sensors is the sensitivity to external factors, such as environmental conditions and electronic noise.

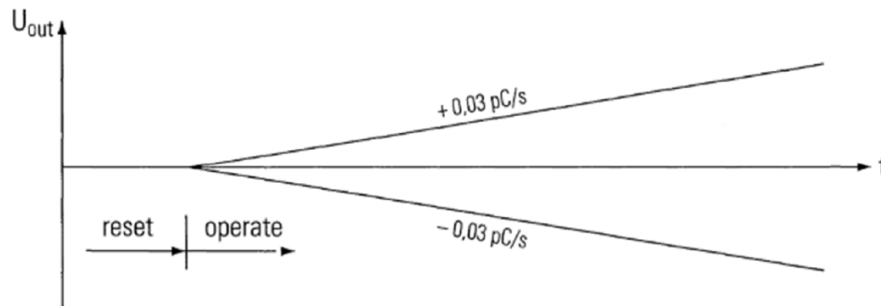


Figure 2.6: Drift. Retrieved from [43].

Kadar et al. [38] determined that the drift in the voltage V_{drift} is assumed to be a linear function of time t ,

$$V_{drift}(t) = V_0 + st, \quad (2.5)$$

where V_0 is the value of the voltage at time 0 defining the start of the recording, and s is the slope that depends on the testing temperature and the pressure applied on the piezoelectric transducer.

On Figure 2.7, the term $p_i(t)$ corresponds to the acquired signal, $p_{drift,i}(t)$ is the inherent

drift used to correct the signal drift recorded during the application of a ramp of steady shear rate steps and $p_i(t) - p_{drift,i}(t)$ is the corrected acquired signal.

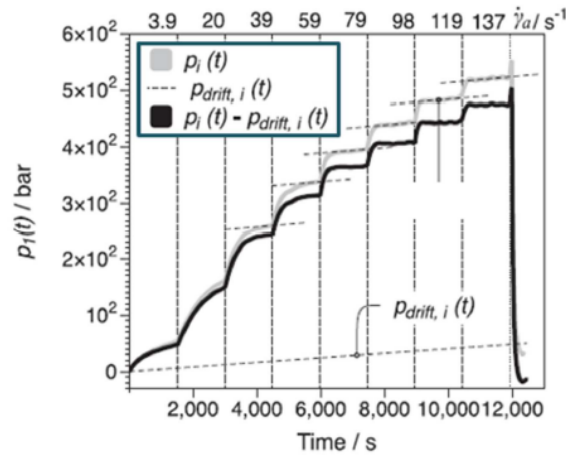


Figure 2.7: Drift Correction. Retrieved from [38].

Recently, Costa et al. [28] assessed the use of piezoelectric sensors for steady melt pressure measurement by directly comparing the flow curves measured with such sensors and with conventional transducers used in capillary rheometry and in polymer extrusion (See Figure 2.8) and the results showed that the drift does not depend on the temperature nor on the pressure. The pressure data acquired with piezoelectric transducers differ from the data returned by conventional transducers, however this difference is acceptable given the 10% error usually reported for viscosities measured either with rotational rheometers or capillary rheometers. Accordingly, the results reported here validate the use of piezoelectric transducers for slit rheometry [28, 30].

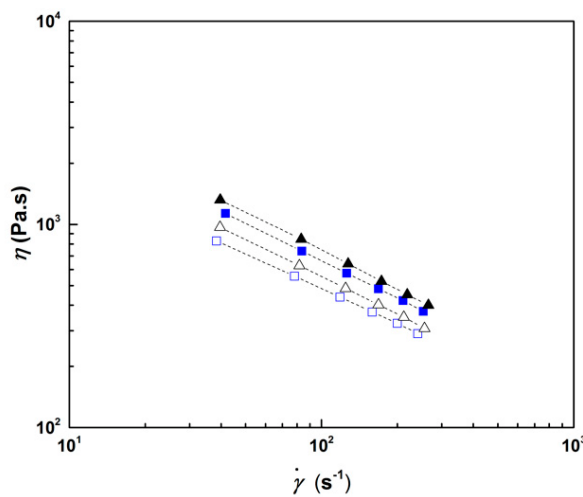


Figure 2.8: Flow curves measured for LDPE at 150 °C (solid symbols) and 180 °C (open symbols) using the piezoelectric (triangles) and the conventional (squares) pressure transducers. Retrieved from [28].

CHAPTER 3

Equipment and Materials

3.1 Microextrusion Line

The microextrusion line (See Figure 3.1) used in this work was developed at the Department of Polymer Engineering, University of Minho. Its main objective, as mentioned previously, is the production of filaments for FDM. The detailed description of each component of this extrusion line is presented in this section.



Figure 3.1: Microextrusion Line: 1 - DC Motor, 2 - Transmission system, 3 - Barrel, 4 - Die, 5 - Volumetric feeder, 6 - Cooling fans, 7 - Haul-off, 8 - Haul-off speed controller, 9 - Screw speed controller, 10 - Temperature controller.

Barrel and Screws

The barrel modular construction and dimensions are presented on Figure 3.2. This type of construction allows that its parts can be replaced, in the event of wear, mal-function or for optimization. Although on Figure 3.2 all sections are made of steel, in the beginning of this work, section B was made of ceramic material, in order to reduce the heat transferred from sections C and D to the feeding

section (A) and, thus preventing the pre-melting of the pellets in this zone.

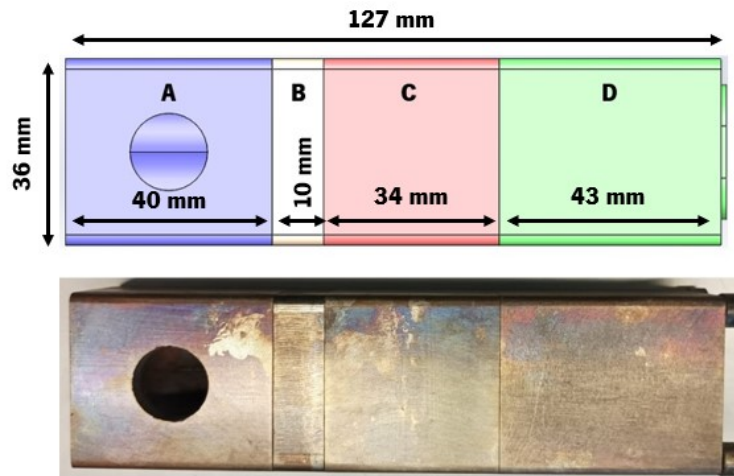


Figure 3.2: Barrel Modular construction.

The design development of the counter-rotating screws is presented in [44]. The counter-rotating screws have a total length of 120 mm, an external diameter of 14 mm and can be subdivided in 4 zones (See Figure 3.3):

- Feeding Zone
- Pre-Heating Zone
- Compression Zone
- Pressure build-up Zone

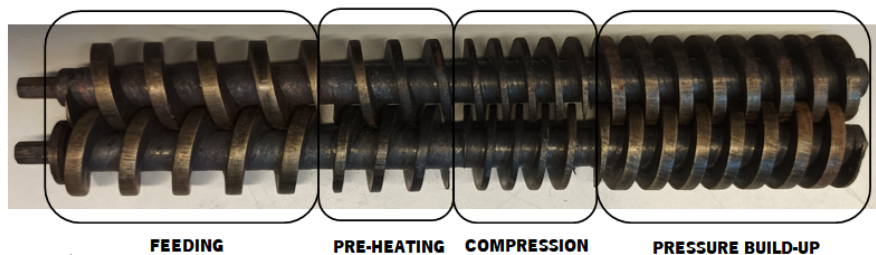


Figure 3.3: Counter-rotating Screws of the Microextruder.

Motor and Transmission System

The motor used was the BLFM230-GFS, Brushless DC Motor (OrientalMotor, Germany) and its maximum velocity is 20 rpm. The velocity was controlled by a BLFDP controller. Both devices are shown in Figure 3.4.

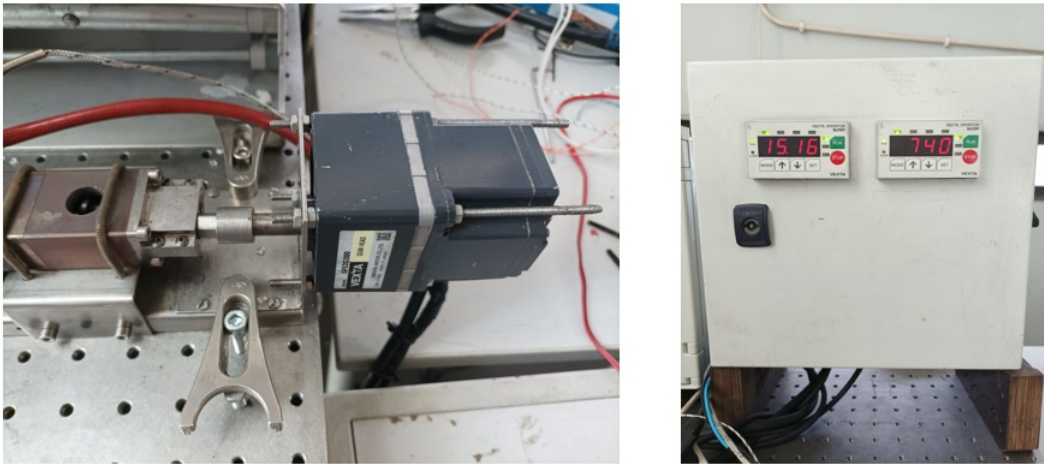


Figure 3.4: Left: BLFM230-GFS Motor; Right: Velocity Controller.

The transmission system of this extrusion line is direct, which means that the motion is directly transmitted from the motor to one of the gears. Only two gears are used, which rotate oppositely (See Figure 3.5). The teeth of the gears are helical, as they are smoother and less noisier during operation, have higher precision and withstand bigger loads when compared to straight gears.

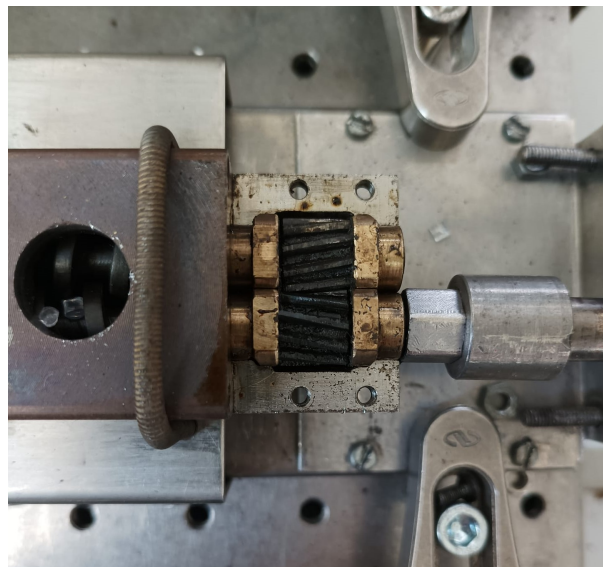


Figure 3.5: Direct transmission system.

Feeder

A volumetric feeder (Piovan MDP1, Italy) was used to supply the granules to the feed hopper. The controller attached allows the variation of the feeder screw speed. Since the granules dimensions and density differ from material to material, measurements were performed to establish the needed screw velocity for the desired feed rates, for each material used.

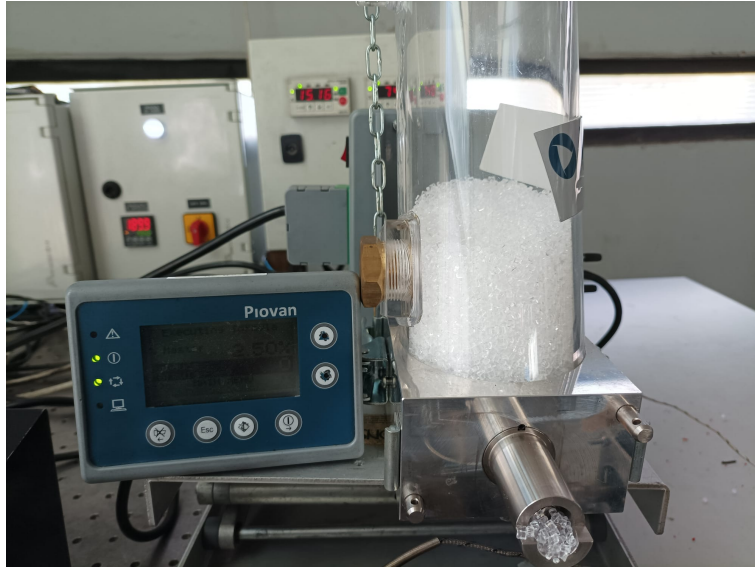


Figure 3.6: Volumetric Feeder Piovan MDP1 and respective controller.

Heating and Temperature Control

In order to heat the barrel, a rectangular heating resistance was used and for temperature measurement a type J thermocouple, with an operation range from $-40\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$, was inserted between the resistance and the barrel. For the temperature setting and control, an Omron E5CB Controller was used in ON-OFF control, a basic control mode that switches a system on or off based on a set point, due to its simplicity, low variability and robustness over other system control methods.

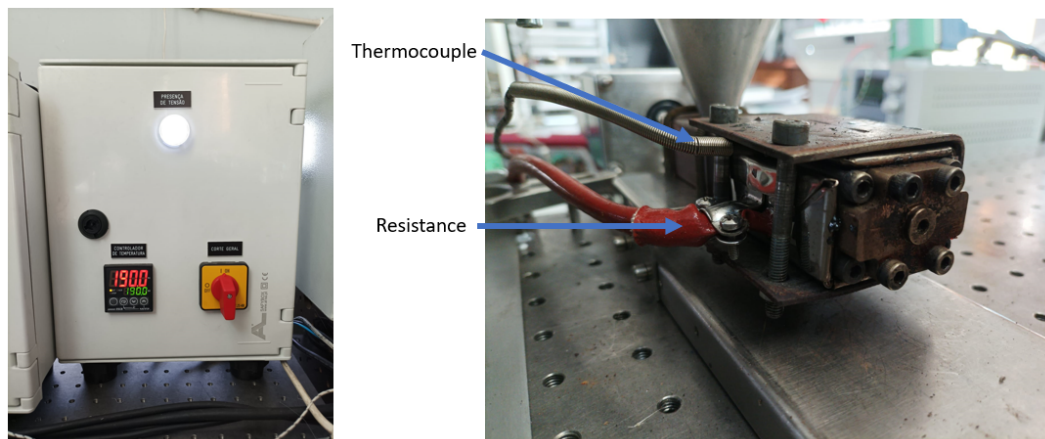


Figure 3.7: Left: Temperature Controller. Right: Thermocouple and Heating Resistance assembled in the barrel.

Die

The circular die converts the flow from the extruder into a annular section with a diameter of 4mm and, although does not have its own temperature control, at such smaller scale and with its location near the resistance band, the temperature is similar to that of the barrel.

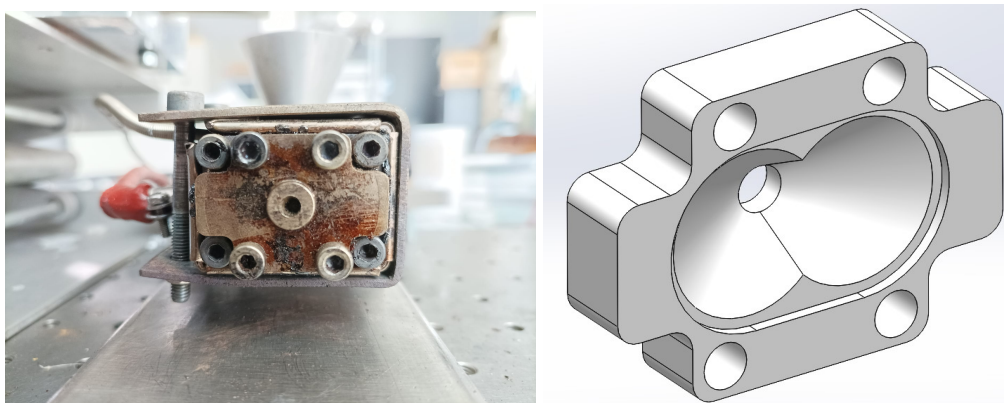


Figure 3.8: Die: Left: Front view of the die coupled to the extruder. Right: Schematic view of the conversion of the flow channel.

Post-extrusion equipment

The cooling of the extrudate occurs through convection heat transfer by means of two fans mounted on a metal plate.

The haul-off unit is powered by a motor capable of a maximum velocity of 4 m/min and its control is performed with a controller similar to that of screw rotation velocity.

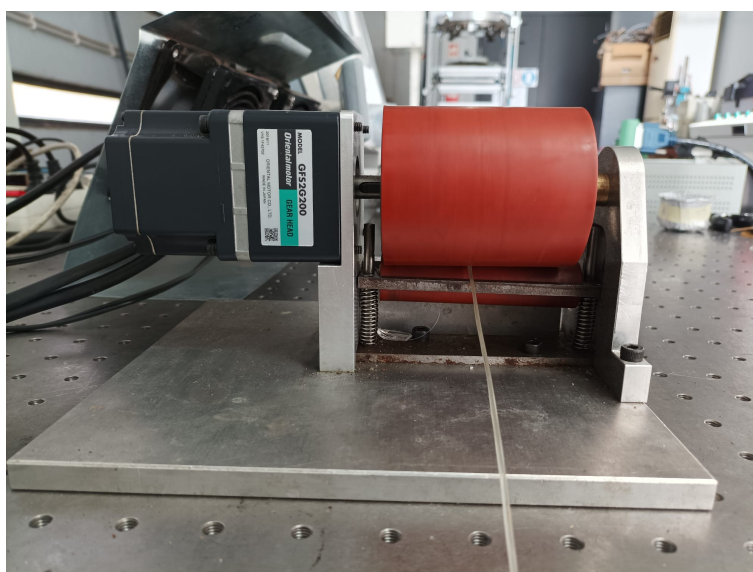


Figure 3.9: Haul-off.

3.2 Rheological Characterization

3.2.1 In-line Slit Rheometry

In order to perform in-line rheological measurements, a microslit die (Figure 3.11) was coupled at the extruder. The experimental set-up used to perform the validation of the capacity of this equipment

in performing rheological measurements is presented on Figure 3.10.



Figure 3.10: In-line Rheological Characterization Set-up: 1 - Microrheometer, 2 - Piezoelectric sensors, 3 - Amplifier, 4 - Power supply, 5 - Terminal block, 6 - Analog-to-digital converter, 7 - Computer, 8 - Temperature controller, 9 - Digital scale.

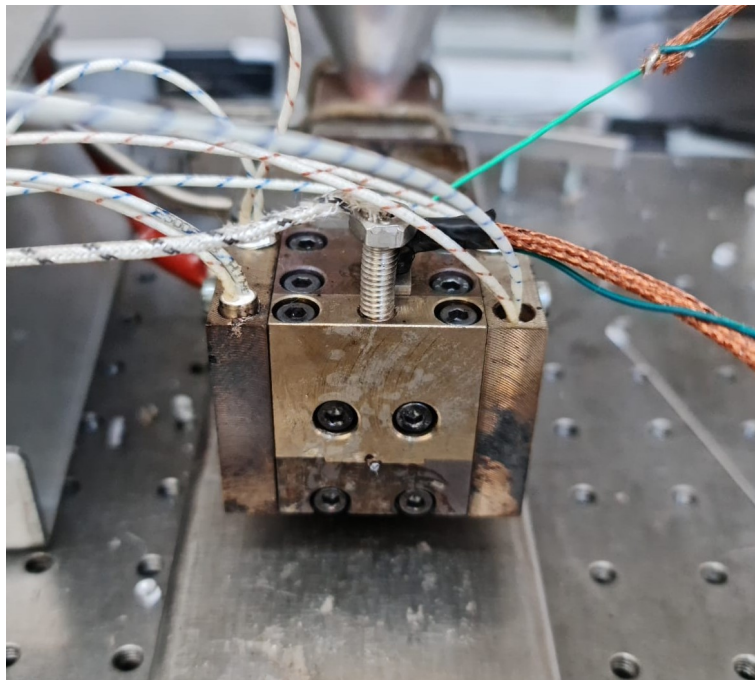


Figure 3.11: Microslit die coupled to the extruder.

This die has modular construction that comprises two main modules, the slit for the rheological measurements, and a shaping die where the slit is converted into a circle with a diameter of 1.5 mm (See Figure 3.12).

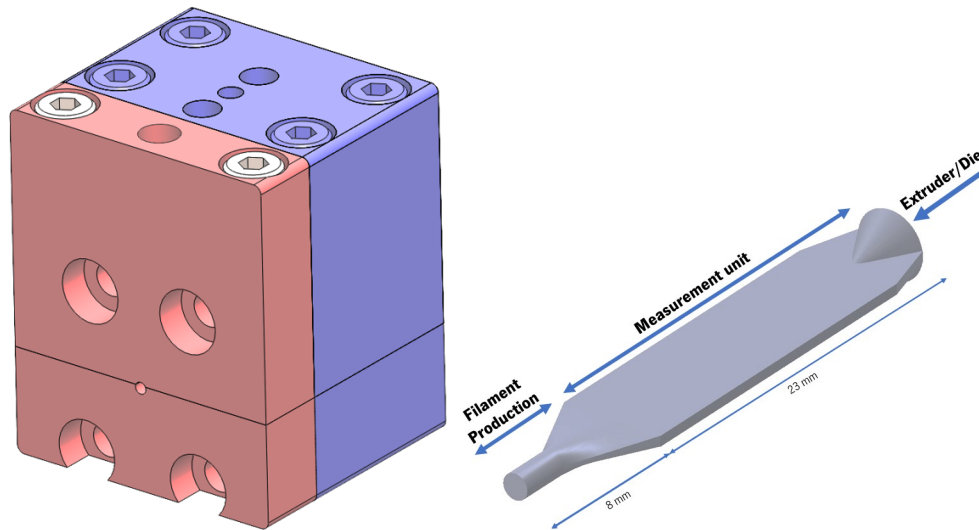


Figure 3.12: Schematics of the Microslit die: Left - Modules of the microslit die: (blue) Measurement unit, (red) filament production unit; Right - Schematics of the flow channel.

The measurement unit has two holes to insert piezoelectric transducers. Two piezoelectric sensors (6182B and 6182C), P1 and P2, are flush mounted to measure the pressure drop along the slit (P1-P2). Both devices have a measurement range from 0 to 20 MPa, a temperature range from 0 to 200 °C and a surface diameter of 2.5 mm. As mentioned before, these devices are very sensitive to electronic noise and environmental conditions and to minimize these effects, copper sleeves served as coatings for the cables of the piezoelectric sensors. The measurement unit also has optical windows, however, since none optical characterization was performed, both upper and lower optical windows were covered with a metal pin during this work.

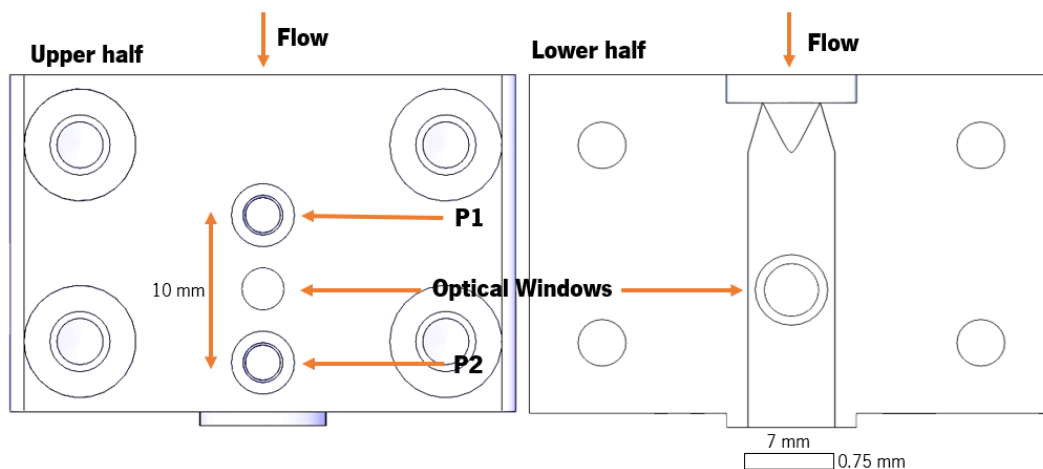


Figure 3.13: Schematics of the measuring channel of the microrheometer. Left: Top view of the upper half. Right: Top view of the lower half.



Figure 3.14: Piezoelectric Transducer Kistler 6189B. Retrieved from [45].

These sensors, however, require some auxiliary equipment, in order to acquire the signal, namely, an amplifier, power supply and a terminal block for each sensor, but also, an analog-to-digital converter and a computer:

- Two amplifiers (Kistler 5155A 22A1 and Kistler 5155A) convert the electric charges of the piezoelectric sensors in proportional voltages. Although these equipments can operate in two range modes, only range II was used to obtain maximum resolution:
 - Range I - Operation range up to 20 000 pC, which corresponds to 10V, and minimum resolution.
 - Range II - Operation range up to 5 000 pC, which corresponds to 10V, and maximum resolution.
- The power supply Matrix MPS-5LK-2 allows to control the energy provided to all the system, which must be fed with a voltage range between 18-30V, and, also, takes over the command functions.
- The DIN-Rail Mount Terminal Block for 25-Pin D-SUB Module is manufactured by National Instruments and has 25 pins. This component works as an interface between the power supply, the amplifier and the analogue to digital converter. The connections are made by single wire cables. The functions attributed to each pin are the following:
 - Pins 7 and 8 - Excitation of the system with 24V;
 - Pins 14, 1 and 2 - Pin 14 works as a reference for the exit signals, Pins 1 and 2, since the signal exit results from the difference between the read signal and the reference point;
 - Pins 18 and 19 - Allow the resetting and the beginning of the measurement, respectively. Pin 18 is the reference point. In order to reset, the Pin 19 is connected to 0V, while when the intention is to start the measurements, this pin must be connected to 5V.
 - Pin 22 - Enables the switch between ranges I and II of the amplifier. When this pin is connected to 0V, range I is on, while when is connected to 5V, the range II mode is on.

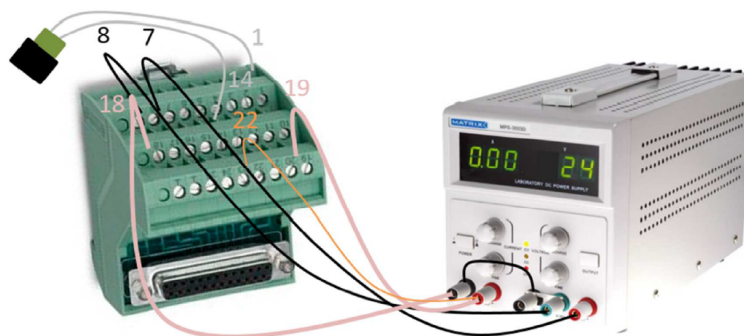


Figure 3.15: Terminal Block (on the left) and Power Supply (on the right).

- The electric signal of the pressure is connected through a BNC cable to a Analogue to Digital Converter from National Instruments with the reference NI 9215. This component is then connected to a computer through an USB cable, where the data are recorded using a script written in LabVIEW.

Heating and Temperature Control

The temperature control of this unit is independent of the extruder and is performed by 4 cartridges flushed in 2 resistance plates (See Figure 3.16). The temperature is read by a type J thermocouple and a Omron E5CB temperature controller was used in ON-OFF control, a basic control mode that switches a system on or off based on a set point, due to its simplicity, low variability and robustness over other system control methods.

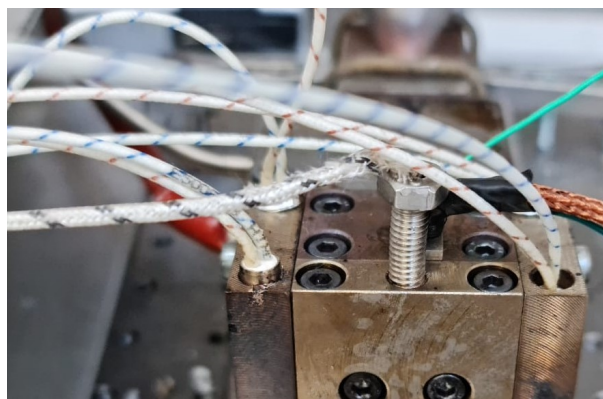


Figure 3.16: Temperature Control of the microrheometer

3.2.2 Rotational Rheometry

A stress-controlled ARG2 rotational rheometer (TA Instruments, New Castle, DE, USA) was used with 25 mm parallel plates. The setting and monitoring of the tests performed in Rheology Advantage software and the analysis of the results in the Data Analysis software, both provided by TA Instruments.

Time sweep tests were performed in the rotational rheometer for both LDPE and COC at 180 and 190 °C, respectively. This test shows the evolution of both storage and loss modulus through time, which determines if a sample is rheologically stable at a certain temperature through time.

3.2.3 Capillary Rheometry

The Davenport capillary rheometer (Daventest Ltd, London, England) was used coupled with a Dynisco PT422A (0–3000 PSI) connected to a Dynisco 1390 strain gauge indicator, with analog re-transmission output accuracy span of $\pm 0.2\%$. The strain gauge indicator is also connected to a data acquisition system NI-9215 from National Instruments and driven by custom-written LabVIEW routines.

3.3 Filament Validation

The 3D-printing of the produced filaments was performed in the Raise3D Serie Pro2 printer (Raise3D, Irvine, CA, USA). This printer has dual extrusion capacity, dimensions of 305×305×300 mm and can operate up to 300 °C.

The mechanical testing of the test specimens manufactured was performed in a universal testing machine, INSTRON 4505.

3.4 Materials

The major restriction in the material selection for this work was the temperature limitation of the piezoelectric sensors (200 °C). Two materials were used during this work. One was the low density polyethylene (LDPE), due to the ease in processing. The other was a cyclic olefin copolymer (COC), which is often used for 3D printing.

An extrusion grade LDPE (ALCUDIA® LDPE 2221FG, from Repsol, Spain) with a density of 0.922 g/cm³, a melt flow index of 2.1 g/10min (190 °C/ 2.16 kg) [46] and a processing temperature range between 150–180 °C was used for the assessment of the characteristics of the microextrusion line and for the first tests in the validation of the microrheometer.

A COC (Topas® COC 8007S, from Topas Advanced Polymers, Germany) with a density of 1.010 g/cm³, a melt flow index of 1.7 g/10min (190 °C/ 2.16 kg) [47] and a processing temperature range between 190–250 °C was used for filament production and validation and the validation of the microrheometer. COC has sufficient melt strength at the processing temperature range for FDM.

The experimental work can be divided in three main stages, as illustrated in Figure 4.1.

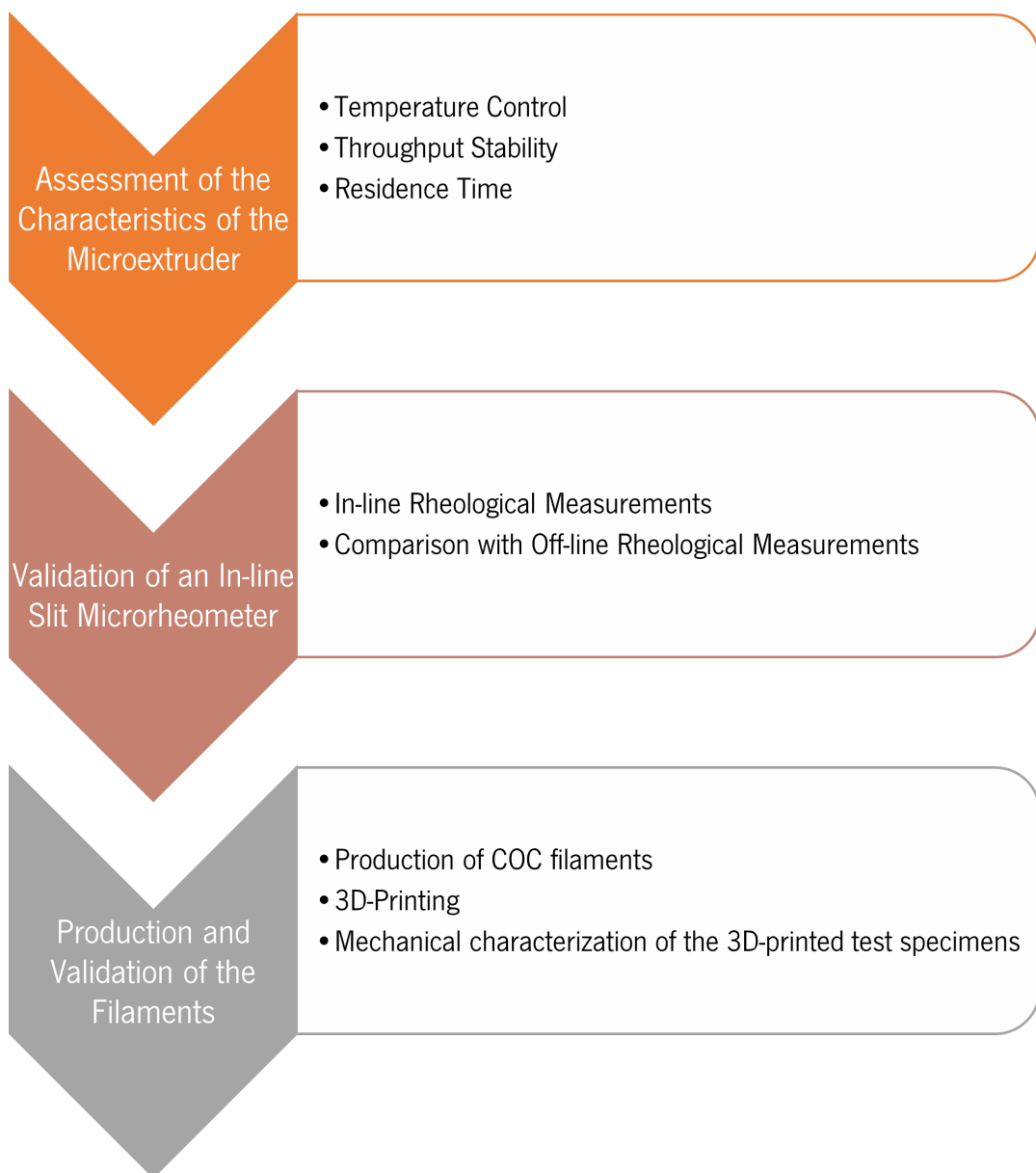


Figure 4.1: Schematics of the experimental work.

4.1 Assessment of the Characteristics of the Microextruder

When developing an extruder, its capacity to control some parameters must be assessed, namely:

- Throughput Stability;
- Temperature Control;
- Residence Time.

In order to evaluate the above parameters, a set of processing conditions were defined and the experiments presented in Table 4.1 were planned.

Table 4.1: Experiments for assessing the microextruder

Test	Changed Parameter	Temperature ($^{\circ}\text{C}$)	Screw Speed (rpm)	Feeder Throughput (g/min)
0	Reference-Conditions	180	15	1.5
1	Temperature	170	15	1.5
2	Temperature	190	15	1.5
3	Screw Rotation	180	10	1.5
4	Screw Rotation	180	20	1.5
5	Throughput	180	15	1.0
6	Throughput	180	15	2

Throughput Stability

For this parameter, tests were performed to evaluate the capacity to maintain a constant throughput at different screw speeds, feeder throughputs and temperatures. Each test performed lasted 15 minutes, with samples being collected after 5-minute periods. In the end, all the samples were weighted and the average masses and respective standard deviations were calculated.

Temperature Control

In order to understand if the temperature in the barrel was equal to the set temperature, a portable temperature reader, was placed at the exit of the die to measure the temperature of the extrudate. Each test performed lasted 15 minutes, with temperature values being collected every minute. In the end, the average temperature difference between the reader and the thermocouple was calculated.

Residence Time

The residence time was determined by introducing a pellet of masterbatch at the feed hopper and measuring the time required for the masterbatch to reach the die (minimum residence time) and the time required for the masterbatch to disappear from the extrudate (maximum residence time).

Due to the high quantity of tests and respective time needed to perform them, only Test 0 in Table 4.1 was repeated 3 times.

4.2 Validation of the In-line Rheological Characterization

4.2.1 Temperature Control of the Microrheometer

The temperature control of the microrheometer is of great importance for a proper rheological characterization, so tests were performed with the microrheometer at 5 different temperatures (150, 160, 170, 180, 190 °C) by placing a portable temperature reader inside the microrheometer and comparing the measured temperature to the set temperature.

4.2.2 Residence Time in the Microrheometer

Coupling the slit microrheometer to the extruder/die system creates an additional residence time. This is an important factor to consider since some materials are thermally and rheologically unstable, which could lead to a wrongful characterization of the material. Therefore, residence time measurements were performed as described in the previous section with the microrheometer coupled.

4.2.3 In-line Slit Rheometry

The whole set-up is switched on at least 30 minutes prior to any measurement to allow for a stabilized temperature in both barrel and slit microrheometer, and to warm up the electronics, therefore reducing the signal drift.

The first test to be performed was the time evolution of the voltage V acquired by the transducers mounted in an empty slit, in order to assess the drift inherent to this measuring system. The signal should present a drift that follows the equation $V_{drift} = V_0 + st$, where V_0 is the initial residual voltage and s is the slope of the signal.

Thus, the voltage $V(t)$ can be corrected to give a flat signal $V_{cor}(t) = V(t) - V_{drift}(t)$. Both V_0 and drift s are due to the closing of the electronic circuit (both amplification and pressure sensing), and as such should be independent of the pressure and temperature at the tip of the sensor [28]. The data acquisition starts and the amplifier is switched on to record the piezoelectric drift $V_{drift}(t)$ over five minutes and the obtained drift signal was used to correct the voltage values obtained during the measurements.

Each measurement lasted 5 minutes and the acquisition rate was 10 points per second. This resulted in each recorded file having 3000 points. In order to perform a measurement, the following procedure was followed:

1. Creation of a LabVIEW file and start of the recording with the setting of 10 points per second for acquisition rate after oversampling;
2. To start the measurement, connection of Pin 19 of the terminal block to 5V in the correspondent power supply, for both piezoelectric sensors;

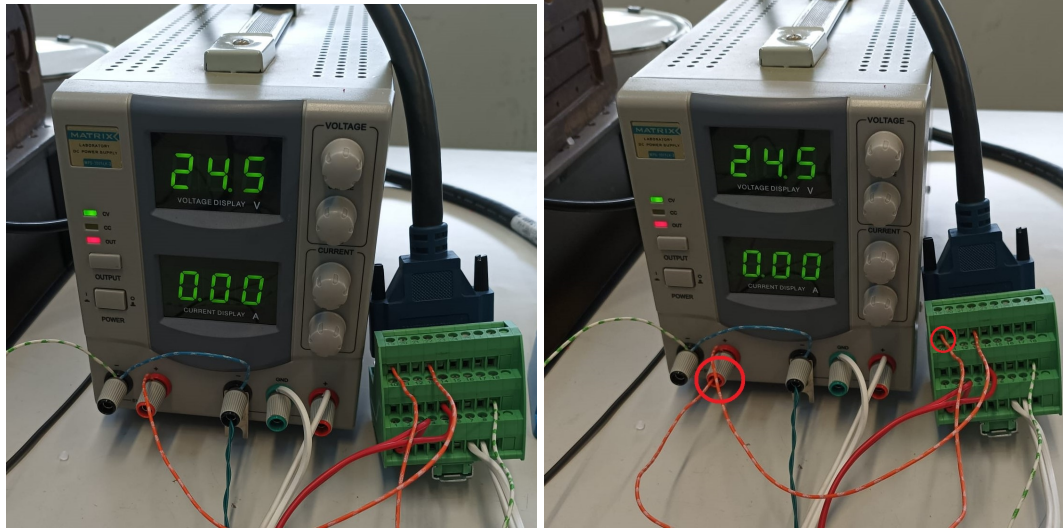


Figure 4.2: Connection of pin 19 (right) to start the measurement.

3. The slit is then fed with melt by setting a constant screw speed and feeder throughput;
4. Once the pressure signal became constant, a timer was started and a sample was retrieved from the extrudate every 30 seconds for a period of 1.5 minutes, resulting in 3 samples.
5. Around 4 minutes after the start of the measurement, the screw speed and feeder throughput were stopped, which resulted in the voltage signal returning to the drift signal inherent to the system.
6. After the 5 minutes are over, the recording is stopped, the retrieved samples are weighted and its average mass and standard deviation are calculated, thus obtaining the volumetric flow rate or throughput.
7. The last stage consists in the data treatment of the LabVIEW file obtained by correcting the signals by subtracting the drift signal inherent to the systems and converting the voltages into pressures, using the following equation provided by the manufacturer, applicable for range II in the amplifier:

$$P = \frac{V \times 200}{9.66} \quad (4.1)$$

, where P is the resulting pressure in MPa. Then the average pressure in P1 and P2 and calculated, resulting in the determination of the pressure gradient.

This procedure is repeated 3 times. However, at each extrusion condition, measuring both pressure drop and throughput yields a single point of the shear viscosity versus shear rate curve. In order to obtain flow curve, at least one parameter has to be varied. For both LDPE and COC, the influence of two parameters was studied separately: the screw speed and the throughput. Tables 4.2 and 4.3 present the range of parameters varied for both LDPE and COC, respectively.

Table 4.2: Different processing conditions used for LDPE characterization. Table on the left: Processing conditions to study the influence of screw speed on the viscosity. Table on the right: Processing conditions to study the influence of throughput on the viscosity.

Processing Conditions			Processing Conditions		
Temperature	Throughput	Screw Speed	Temperature	Throughput	Screw Speed
180 °C	1.5 g/min	10	180 °C	0.75	15 rpm
		15 rpm		1.0	
		17.5		1.5 g/min	
		20		2.0	
				2.5	

Table 4.3: Different processing conditions used for COC characterization. Table on the left: Processing conditions to study the influence of screw speed on the viscosity. Table on the right: Processing conditions to study the influence of throughput on the viscosity.

Processing Conditions			Processing Conditions		
Temperature	Throughput	Screw Speed	Temperature	Throughput	Screw Speed
190 °C	1.5 g/min	10	190 °C	0.75	15 rpm
		12.5		1.0	
		15 rpm		1.5 g/min	
		17.5		2.0	
		20		2.5	

4.2.4 Rotational Rheometry

Production of Disk Samples

In order to use parallel-plate rheometry, small disk samples have to be produced in the hot-press Moore present in the Polymer Engineering Department. To obtain standard samples, a mould with 9 cavities with a diameter and thickness of 25mm and 0.8mm, respectively, was used. Firstly, a teflon sheet is laid on top of a metal plate, then the mould is positioned on top of the sheet and the cavities are filled with pellets of the material (See Figure 4.3) and, lastly, in order to trap the pellets, another teflon sheet and metal plate are laid on top of the pellets.

After the press reached the target temperatures, the prepared set is positioned at the centre of the plates of the press. These plates are brought closer, but still without any pressure applied on the

set, for 2 minutes. After that period, a pressure of 10 tonnes is applied on the set for 8 minutes. At the end of the 8 minutes, the set is removed from the press and let to cool down at room temperature. The last stage includes the demoulding of the samples, using a scissors and a box cutter, obtaining the disks, as shown in Figure 4.3.

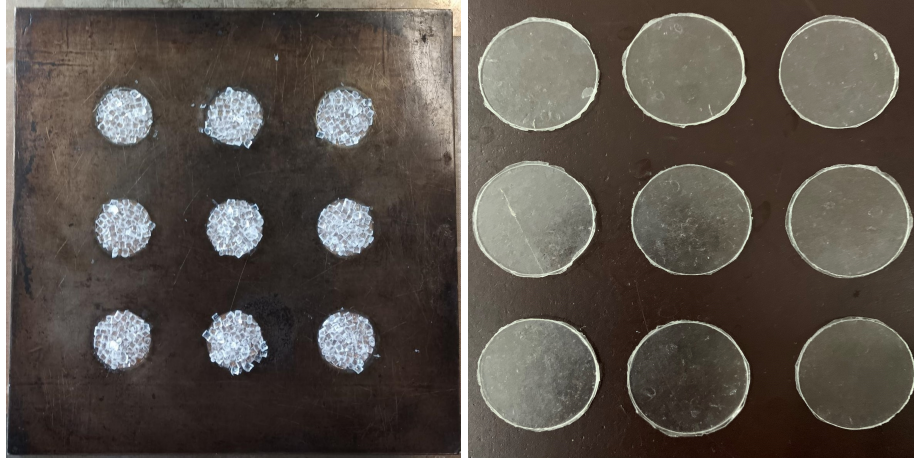


Figure 4.3: Left: Mould filled with granules. Right: Disks obtained through compression moulding.

The temperatures defined to melt the pellets were the following:

Table 4.4: Temperatures defined in the press for LDPE and COC

Material	Temperature Lower Plate ($^{\circ}\text{C}$)	Temperature Upper Plate ($^{\circ}\text{C}$)
LDPE	180	180
COC	190	190

Rheological Tests

Steady shear viscosity and complex shear viscosity measurements of LDPE and COC were performed using the rotational rheometer equipped with a parallel plate geometry with a 25 mm diameter and 0.8 mm gap between plates. Both materials were tested at the same temperatures as the in-line rheometry, that is, the LDPE at 180 $^{\circ}\text{C}$ and COC at 190 $^{\circ}\text{C}$.

In dynamic oscillatory mode the angular velocity is changed and the torque is measured over time. For each sample, two dynamic oscillatory experiments (frequency sweeps) were performed to determine the linear viscoelastic range (LVE) over an angular frequency (ω) from 0.0628 to 628.3 rad s^{-1} . The first test performed with a small strain of 0.01% allows the determination of a mechanical spectrum in LVE, however this strain value lead to higher noise for small frequencies, where a small torque is measured. The second test is performed with a strain of 0.1%, which is used mainly to determine the correct values for for non-linear range due to a higher torque measured. Using the non-linear range values from the higher strain value and the linear range from the lower strain value, it is possible to obtain the mechanical spectrum of the sample. In sum, this test can provide information about the storage modulus, G' , and loss modulus, G'' , which allow the determination of complex

modulus, $|G^*|$, and, consequently, the complex shear viscosity, $|\eta^*|$, of the fluid as a function of frequency.

Contrarily to oscillatory tests, in steady state tests, the angular velocity of the sample was held constant and the torque was measured as a function of the applied shear rate. Readings were obtained while sweeping the steady shear rates from 0.01 s^{-1} up to sample fracture.

4.2.5 Capillary Rheometry

The materials were also characterized by capillary rheometry to access the rheological behaviour at large strain rates, typically between 10 s^{-1} and 10^4 s^{-1} . The experimental procedure involved selecting two dies of the same radius (1 mm) but different lengths L (20 and 10 mm) to perform the Bagley correction. The long die was then mounted in the rheometer and a set of 6 piston speeds was selected (between 12.5 and 25 mm/min). For each piston speed, the total pressure drop for the long die was shown in the pressure controller and the voltage was recorded in a LabVIEW file, as in in-line rheometry. The same procedure was performed for the short die.

Using the Bagley correction, the viscous pressure drop in the capillary is separated from the pressure losses due to entry and exit effects. To determine the inlet-outlet pressure loss, the pressure loss is plotted for different capillaries of the same diameter, but with different lengths and extrapolated to zero, known as the Bagley plot. This extrapolation to zero length allows the determination of ΔP_{entry} , which is the pressure at the entrance of the die, for each piston speed.

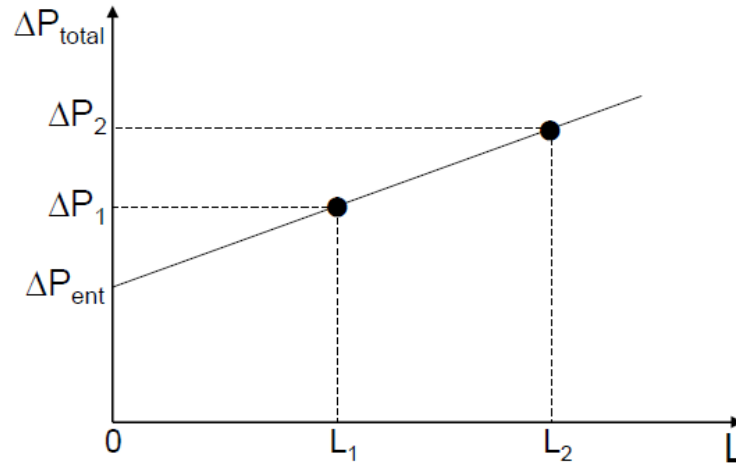


Figure 4.4: Bagley correction.

$$\Delta P_{\text{capillary}} = \Delta P_{\text{total}} - \Delta P_{\text{entry}} \quad (4.2)$$

, where $\Delta P_{\text{capillary}}$ is the real pressure occurring in the capillary, ΔP_{total} is the measured pressure drop, and ΔP_{entry} is the pressure at the entrance of the die, which is determined by the Bagley plot.

The shear stress, σ , which is maximum at the wall and null at the centre, is calculated by

$$\sigma = \frac{P_{capillary}r}{2L} \quad (4.3)$$

, where L and r are the length and the radius of the die.

The apparent shear rate, $\dot{\gamma}_a$, is given by

$$\dot{\gamma}_a = \frac{4Q}{\pi r^3} \quad (4.4)$$

, where $\dot{Q}$ is the volumetric flow rate. The true wall shear rate is calculated using the Weissenberg-Rabinowitsch correction, as a result of shear thinning in real polymer melts with pseudoplastic flow behavior, there is a strong curvature of the velocity profile towards the wall. As a result, shear rates on the wall are increased over the Newtonian medium, especially at higher shear rates:

$$\dot{\gamma} = \frac{\dot{\gamma}_a}{4} \left(3 + \frac{d \ln \dot{\gamma}_a}{d \ln \sigma} \right) \quad (4.5)$$

and, at last, to determine the viscosity, the equation used is:

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad (4.6)$$



Figure 4.5: Experimental Set-up used in Capillary Rheometry.

4.3 Production and Validation of Filaments

Filament Production

After the definition of the operating window of the extruder, the last step in its validation is, precisely, the production of COC filaments to be later used with a FDM printer. Since the rheological characterization temperature had to be lower than 200 °C due to the temperature limitation of the piezoelectric sensors, in order to establish a connection between the rheological characterization and the produced filament, the temperature of the extruder was defined to be 190 °C. The rest of the parameters used were implemented on trial-and-error methodology to define the optimal processing conditions. The initial conditions used are presented in Table 4.5.

Table 4.5: Processing conditions used in the filament extrusion.

Parameter	Value
Extruder/die temperature (°C)	190±1.5
Extruder screw speed (<i>rpm</i>)	15
Haul-off speed (<i>rpm</i>)	5
Feeder Throughput (<i>g/min</i>)	1.5±0.05
Shear Rate (1/s)	22.49

Dimensional Characterization

From the extruded filament, 8 segments of 2 meters were cutted and its diameter was measured. Concerning the filament diameter, which is a very important variable for a good performance in the FDM equipment, 10 measurements of the diameter along the length of each segment were performed using a digital caliper. After the measurements were performed, the average diameter and standard deviation were calculated.

Also regarding dimensional characterization, a visual inspection was performed at the produced filaments to detect possible defects, such as surface roughness, voids, degradation and contaminations.

Filament Printing

The next step consisted in using the produced filaments in the FDM printer. In order to allow the mechanical characterization of the printed parts, the geometry uploaded in the printer was a test specimen with dimensions according to DIN 53504. 6 test specimens were set to be produced and dimensionally measured to assure the part fulfilment of the standard dimensions. The printing strategy implemented was based on trial-and-error methodology to define the optimal processing conditions. The initial conditions used are presented in Table 4.6, with emphasis for the nozzle temperature being 190 °C to establish a relationship with the rheological data obtained for this material at this temperature.

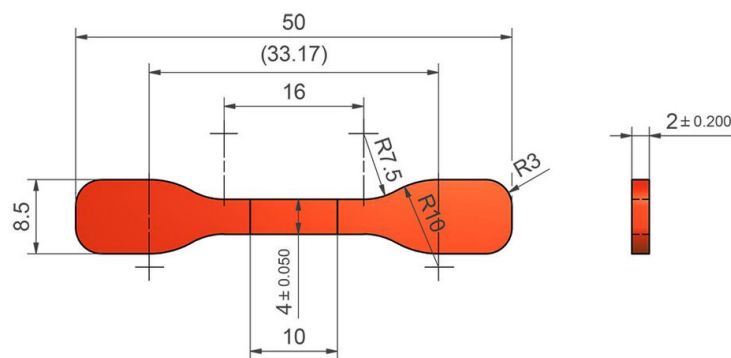


Figure 4.6: Nominal dimensions according to the DIN 53504 standard (mm).

Table 4.6: Initial Processing conditions and printing strategy used in the printing stage.

Parameter	Value
Nozzle temperature (°C)	190
Platform temperature (°C)	90
Printing speed (mm/s)	40
Layer height (mm)	0.2
Layer orientation (°)	±45

Mechanical Characterization of Test Specimens and Filaments

Five printed test specimens were performed in a universal testing machine, INSTRON 4505, at a cross-head speed of 50 mm/min and an initial distance of 25 mm between grips. The tensile strength, strain and Young Modulus were computed.

Due to the lack of appropriate grips for the testing of the filaments, the same procedure as for the mechanical characterization of the printed test specimens was applied.

CHAPTER 5

Results and Discussion

5.1 Assessment of the Characteristics of the Microextruder

Throughput Stability

The results obtained concerning the capacity of the extruder in controlling the throughput are presented in Figure 5.1, which displays the averaged throughputs and error computed from triplicates measured at different processing conditions. As expected, the feeder throughput and extruder throughput are linearly related (See Figure 5.1a), with 3% of average error (Due to the scale, the error bars are not visible). Analyzing the results, it is possible to conclude that the extrusion line is capable of maintaining a constant throughput with changes in temperature and screw speed (See Figures 5.1b and 5.1c), in which the average error is 1.8% and 2.1%, respectively. In all these tests, the small errors calculated can be associated with the volumetric feeder accuracy at lower feed rates, since the feeding of one more pellet leads to significant changes at such smaller feed rates when comparing to bigger feed rates, in which one or two pellets do not cause major variations.

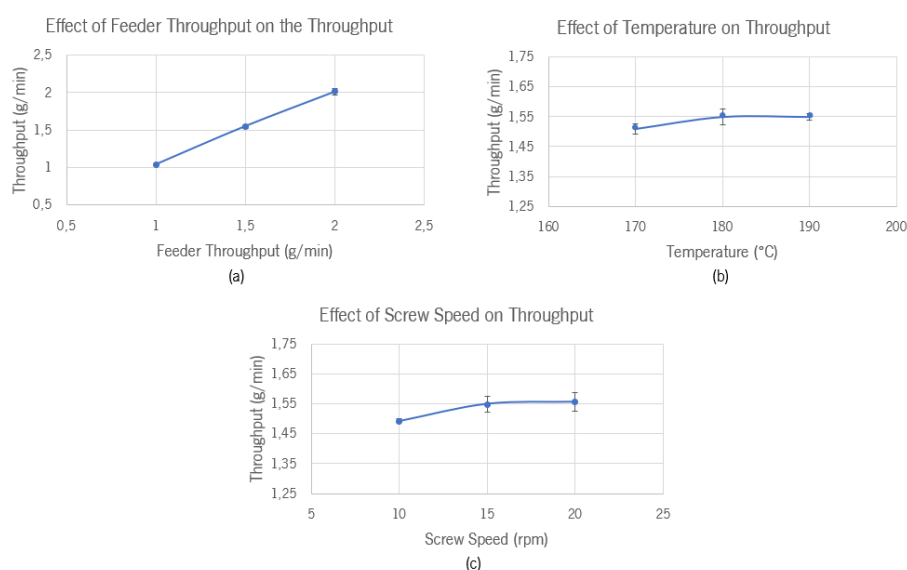


Figure 5.1: Throughput Assessment: (a) Effect of the feeder throughput on the throughput; (b) Effect of temperature on the throughput; (c) Effect of the screw speed on the throughput.

Temperature Control

The results obtained concerning the capacity of the extruder in maintaining the barrel temperature at the set temperature are presented in Figure 5.2 and Table 5.1, where:

$$|\Delta T| = |T_{read} - T_{set}|, \quad (5.1)$$

where T_{read} is the temperature measured with the portable reader and T_{set} is the set temperature. The accuracy of the extrusion line in maintaining the set temperature is relatively good, with the temperature difference between the independent temperature reader and the set temperature being always under 1°C at different processing conditions.

Table 5.1: Average $|\Delta T|$ between temperature reader and the set temperature.

Variable changed	Average $ \Delta T $ ($^\circ\text{C}$)
Temperature	0.71
Screw Speed	0.42
Throughput	0.54

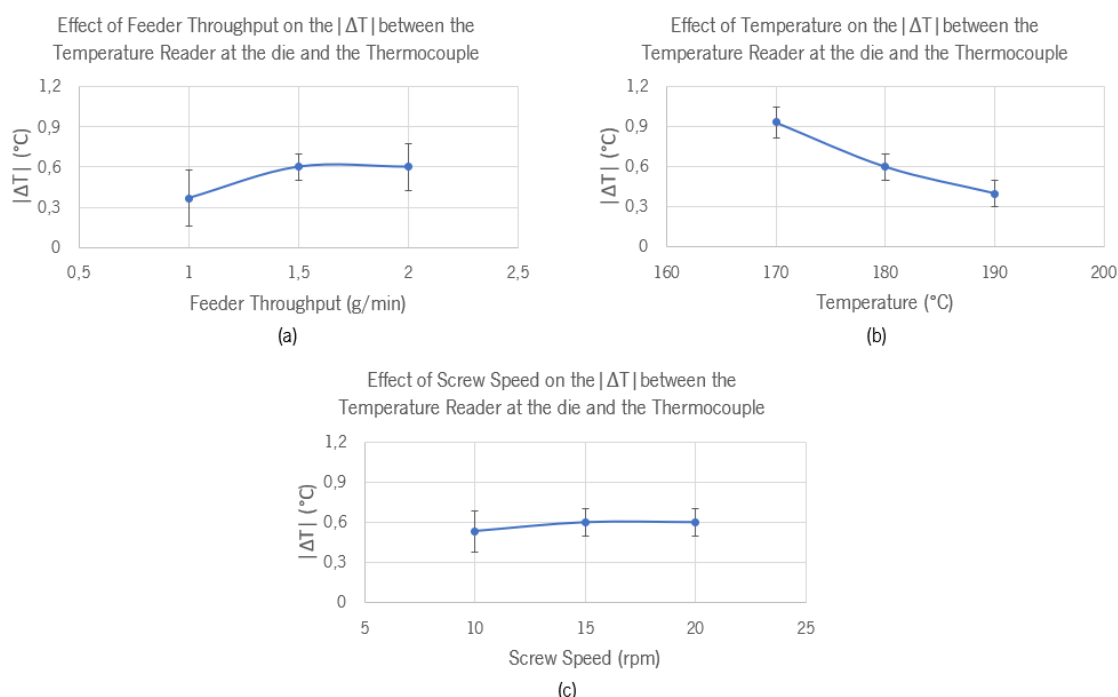


Figure 5.2: Temperature Control Assessment: (a) Effect of the feeder throughput on the temperature control at 180°C ; (b) Effect of temperature on the temperature control; (c) Effect of the screw speed on the temperature control at 180°C .

Even though, as it is possible to see in Figure 5.2, the $|\Delta T|$ shows greater variation in the tests that the temperature is changed, whereas changes in screw speed and feeder throughput do not

cause significant variations in the $|\Delta T|$. These almost constant values obtained by changing the screw speed and throughput can be caused by the viscous heating phenomenon.

Residence Time

The results of the residence time measurements are presented in Figure 5.3, the measured minimum and maximum residence times are reported for different processing conditions.

Concerning the effect of the temperature on the residence time (Figure 5.3a), it is possible to conclude that it is not very significant for the minimum residence time, showing a small decrease caused by the material becoming more fluid, due to lower viscosity, and can flow easily through the die. This means that the material can be extruded more quickly, and therefore the required residence time is decreased. However, concerning the maximum residence time, the effect is opposite, that is, the increasing temperature induces a greater maximum residence time, which might be associated with the difficulty in determining the maximum residence time at the naked eye.

In figure 5.3b, it is possible to conclude that as the feeder throughput is increased, the residence time decreases, that can be explained by the increase in the pressure on the material, which causes the material to flow more quickly through the extruder.

As expected the increase in screw speed leads to the decrease in the residence times, both minimum and maximum (Figure 5.3c), due to the material being conveyed through the extruder at a faster rate, which means that it spends less time in the extruder.

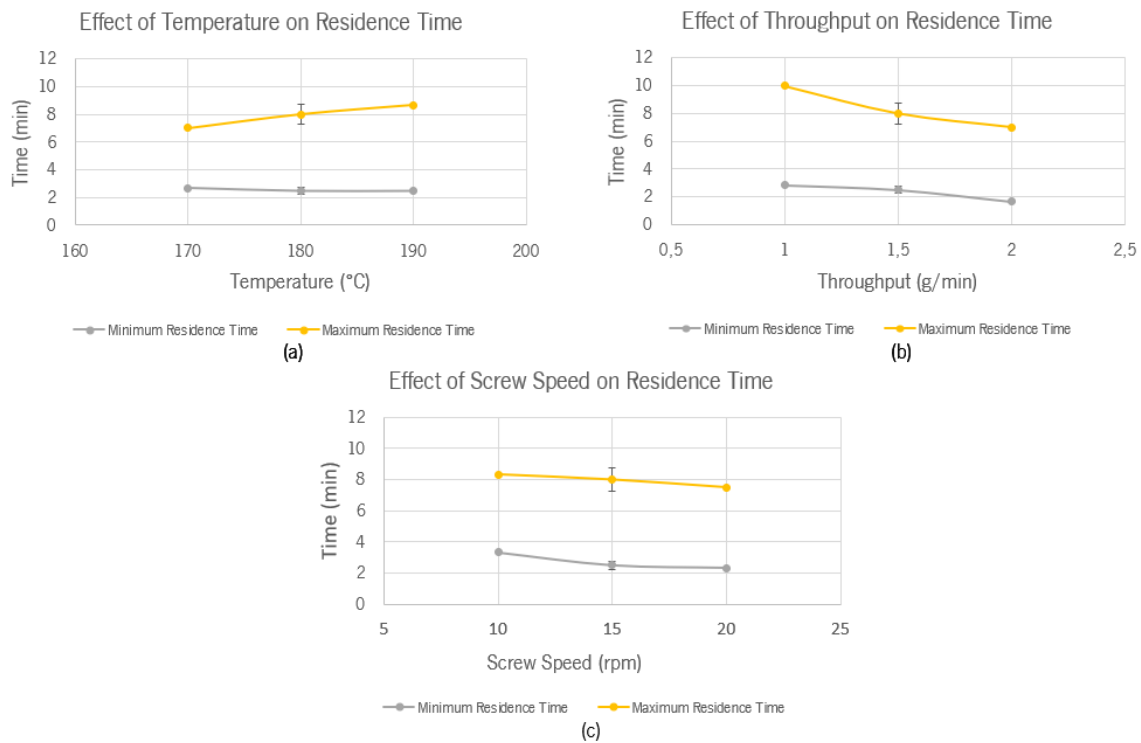


Figure 5.3: Residence Time Assessment: (a) Effect of the feeder throughput on the Residence Time; (b) Effect of temperature on the Residence Time; (c) Effect of the screw speed on the Residence Time.

However, as mentioned above, one important aspect to have in account is the difficulty in determining the maximum residence time, because it is hard to visualize if the residual masterbatch is still in the extrudate or not, which leads to a greater associated error, $\pm 45s$, when compared to the minimum residence time associated error, $\pm 15s$.

During the residence time measurements, one problem was encountered. The ceramic module of the barrel broke, which left a hole in the barrel of the extruder (See Figure 5.4). The origin of this problem was due to the higher thermal expansion coefficient of the steel modules of the barrel when compared to the ceramic material thermal expansion coefficient. This allied to a possible higher grip than necessary when assembling the barrel, may have led to the extreme compression of the ceramic module and thus causing the fracture. At the time, the supplier of the ceramic module was without stock, and that led us to the purchase of a steel module instead of ceramic, in order to allow the experimental work to proceed as scheduled.



Figure 5.4: Broke Ceramic Module.

5.2 Validation of the In-line Rheological Measurements

5.2.1 Temperature Control of the Microrheometer

Immediately after the start of the heating process, it was noticeable the fast increase of temperature of the microrheometer measured by the thermocouple, which led to an overshoot of the temperature by almost 30 °C. This was due to a short response time caused by the fact of having 4 cartridges heating a small volume equipment. To overcome this problem, instead of using the controller in ON-OFF mode, PID (Proportional-Integral-Derivative) mode was implemented, where the proportional term (P) defines a fixed percentage closer to the set point, the integral term (I) closes the gap from the proportional term over time and the derivative term (D) improves the response times. In sum, this mode allows the system to tune itself and, thus, minimizing overshoots as in ON-OFF mode.

Once implemented this control method, the tests to measure the capacity of temperature control of the microrheometer were performed and the results are shown on Figure 5.5. Although the $|\Delta T|$ between the portable temperature reader and the set temperature values are greater when compared to the ones obtained in the assessment of the extruder temperature control (See Figure 5.2), this can be associated to the fact of this system being smaller than the barrel, which leads to short response times because a smaller heating system responds more quickly to changes in temperature, and may not be able to maintain the set temperature as accurately as a larger system with more thermal mass. Also, the location of the thermocouple is different for the 2 systems. For the extruder the thermocouple is placed near the resistance, whereas in the microrheometer, the thermocouple is placed further from the resistances and consequently the temperature is being measured at the furthest point of the 2 resistances, which may explain larger ΔT .

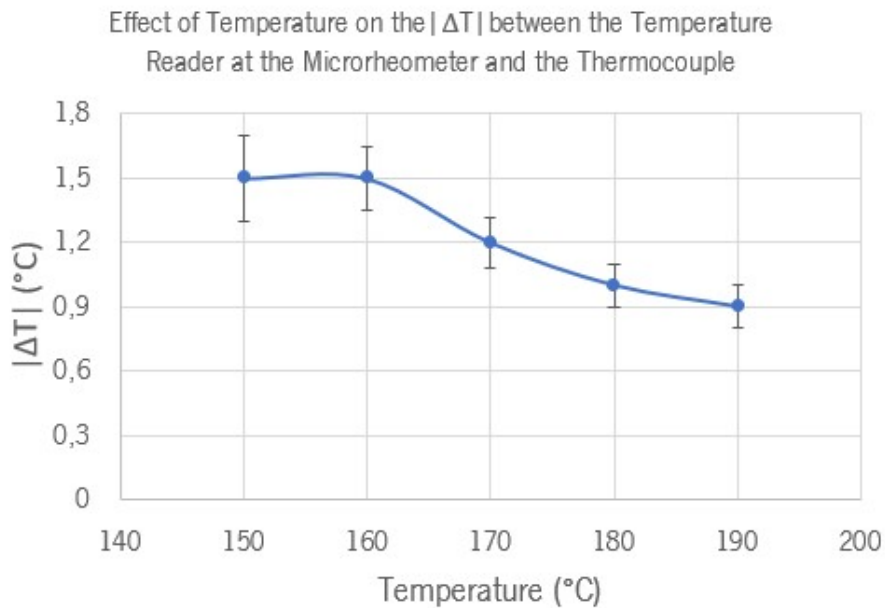


Figure 5.5: Microrheometer temperature control assessment.

5.2.2 Influence of the microrheometer on the residence time

During the measurement of the residence times, the pin that connects the motor to the transmission system broke, was replaced and broke again, which delayed the experimental works for a few weeks. After some time trying to understand what was causing the pin to break, it was determined the problem was due to the microrheometer. The latter implies the successive compression of the material, first into the slit and then to an annular section, which led to material accumulation inside the extruder and, ultimately, the increasing torque delivered by the motor due to the higher resistance of the melt. All this caused the pin to break (See Figure 5.6).

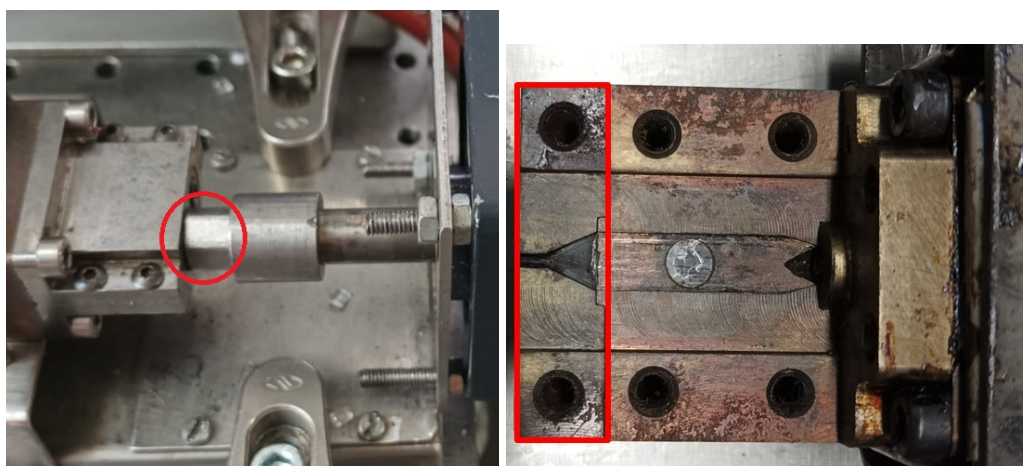


Figure 5.6: On the left: Motor-Transmission system connection pin; On the right: New Microrheometer Set-up.

To overcome this issue, the bottom half of the filament production unit of the microrheometer was removed (Figure 5.7). The major downside of this removal, is that for filament production, the microrheometer should not be coupled.

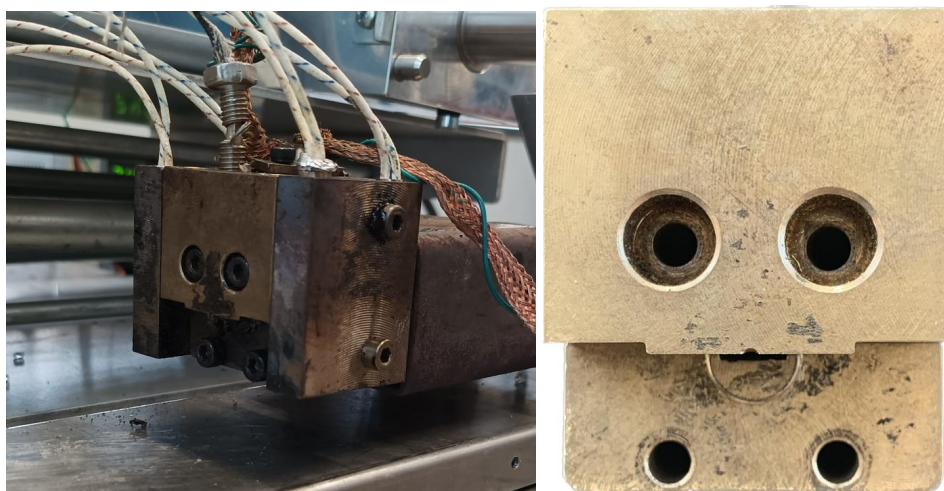


Figure 5.7: On the left: Motor-Transmission system connection pin; On the right: New Microrheometer Set-up.

The results obtained in the study on the influence of the coupling of the microrheometer on the added residence time are shown on Figure 5.8, where are also presented the results obtained on Figure 5.3, in order to provide a better understanding of the added time.

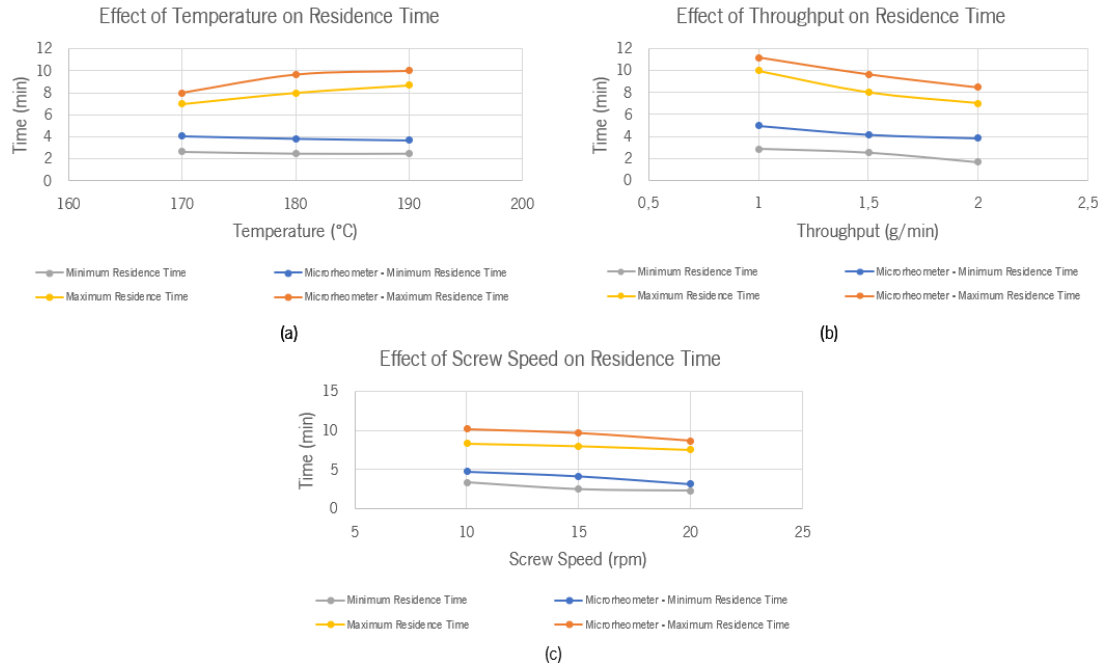


Figure 5.8: Assessment of residence time by coupling of the microrheometer: (a) Effect of the feeder throughput on the added Residence Time; (b) Effect of temperature on the added Residence Time; (c) Effect of the screw speed on the added Residence Time.

Analyzing the collected data, allowed to reach the conclusion, that, in average, coupling the microrheometer adds 1min30s to the time the material is inside the extruder.

The maximum residence time measured was 11min10s, so in order to understand if LDPE and COC withstand this residence time inside the extruder without becoming rheologically unstable, time sweep tests with a duration of 20 minutes (which is more than the maximum residence time in the in-line microrheometer), a strain of 0.5% and a frequency of 1 Hz, which is inside the linear viscoelastic range for these materials, were performed. The results are presented in Figure 5.9.

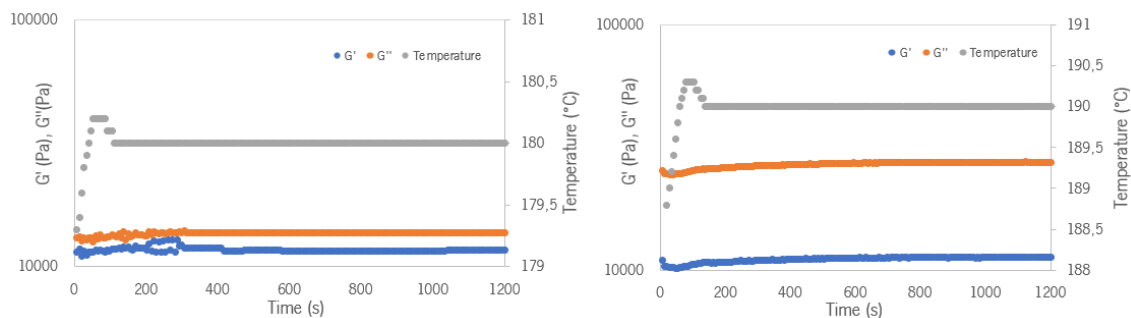


Figure 5.9: Time sweep tests of LDPE(left) and COC(right).

Both materials exhibited stability throughout the test without any major variations in G' and G'' values, which enables both LDPE and COC to be used in the validation of the microrheometer. The minor fluctuations occurring at the beginning of the tests, are associated with the temperature, which is still adjusting for 2 minutes after loading the sample disks and closing the furnace.

5.2.3 LDPE

5.2.3.1 In-line Slit Rheometry

Before the starting of the measurements, the determination of the inherent drift of both piezoelectric sensors was performed by measuring the evolution of the signal through time in an empty slit (Figure 5.10).

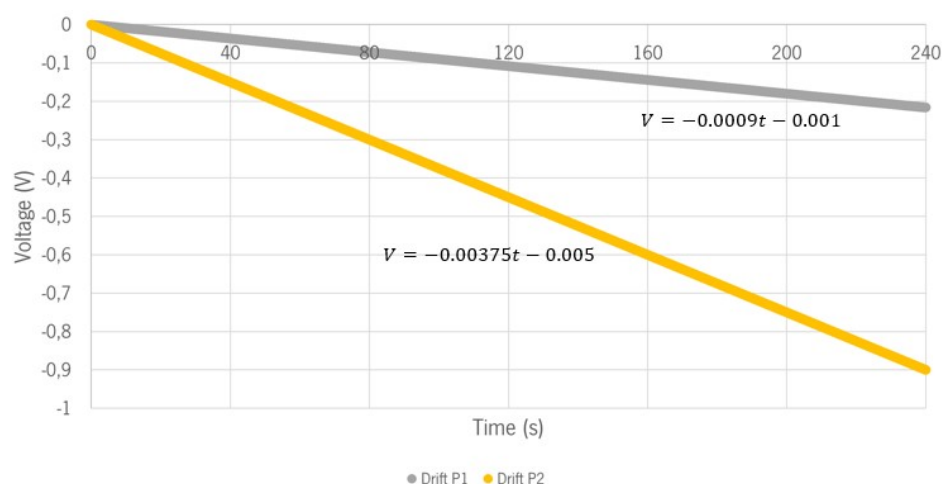


Figure 5.10: Inherent drift of the system for sensors P1 and P2.

After the realization of the planned tests (Table 4.2), the data treatment started. The first stage of the treatment procedure consisted in plotting the raw data in a graph (left side of Figure 5.11) and determine when the signal was reset, i.e., the moment when Pin 19 of the terminal block was connected to 5V, which should be considered Time = 0s. This is shown in the right side of Figure 5.11, where the start of the screw is slightly delayed from the rest time at 0s.

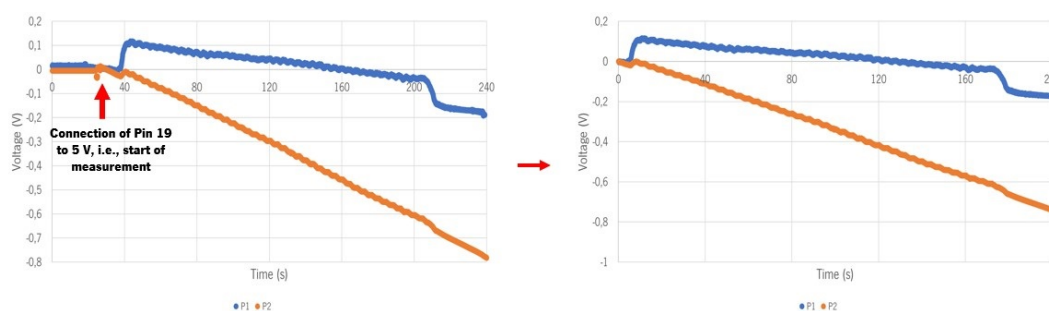


Figure 5.11: Adjustment of the signal so that Time = 0s when pin 19 is connected to 5V.

The second stage was the drift correction, and for that, the drift signal determined earlier was subtracted from the obtained signal to give the corrected signal V_{corr} (See Figure 5.12, right) as detailed in section 4.2.3.

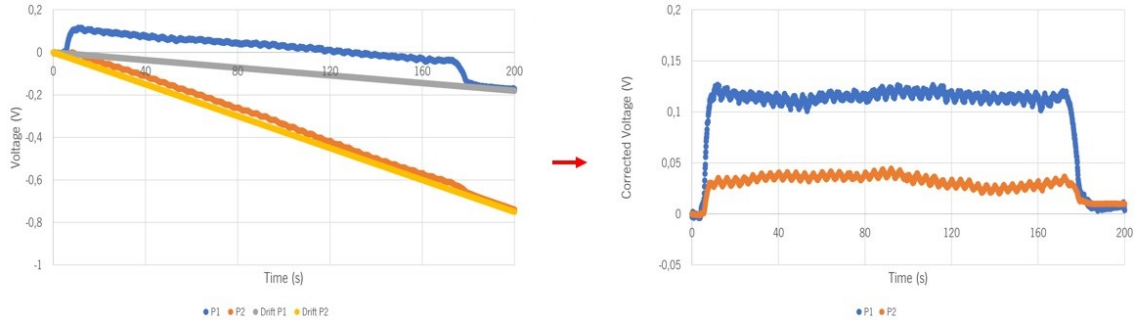


Figure 5.12: Drift correction by subtracting the inherent drift to the obtained signal.

The oscillations present in the obtained signal, which show some periodicity, are caused by the screw rotations frequency. The final stage was simply convert the voltage into pressure by using equation 4.1, and therefore obtaining the pressure values of P1 and P2 over time (Figure 5.13). Then, the average measured pressures were calculated, that allowed the determination of the pressure gradient (P1-P2).

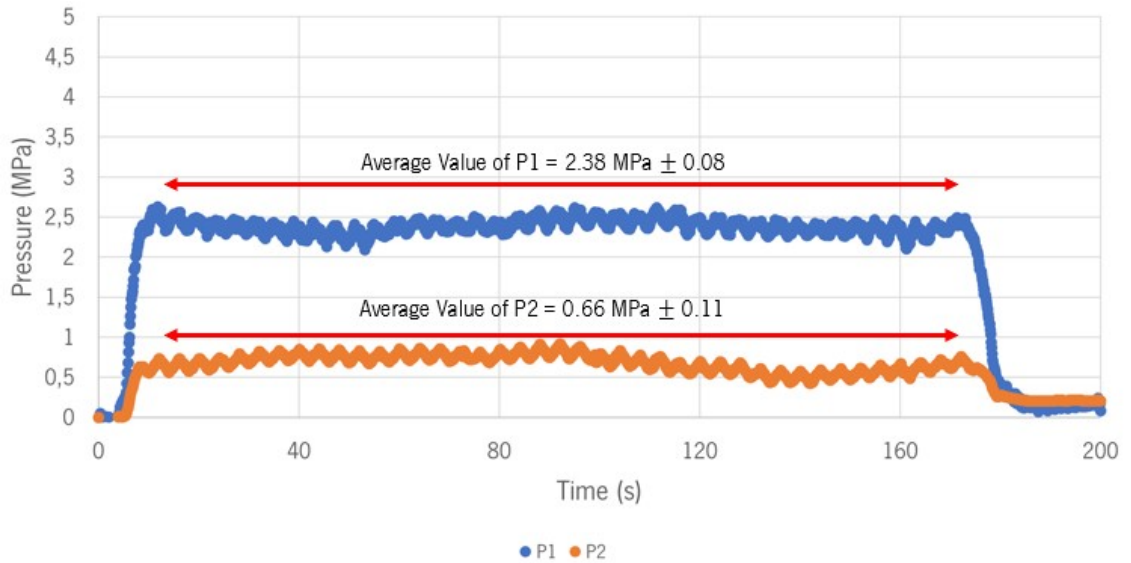


Figure 5.13: Data conversion and oversampling technique application.

Using this data treatment methodology for all tests on Table 4.2, along with the respective measured throughputs, a flow curve is obtained, as illustrated in Figures 5.14 and 5.15, reproducing data measured with different experimental protocols employed to vary the shear rates in the rheological slit. In Tables 5.2 and 5.3, it is possible to see the shear rate and viscosity of each point in the flow curve, but, also, the experimental associated error (too small to be visualized in Figures 5.14 and 5.15) computed from triplicates for each set of processing conditions, which in every test performed is

under 10%, which is the maximum acceptable experimental error for rotational and capillary rheometry [48, 49].

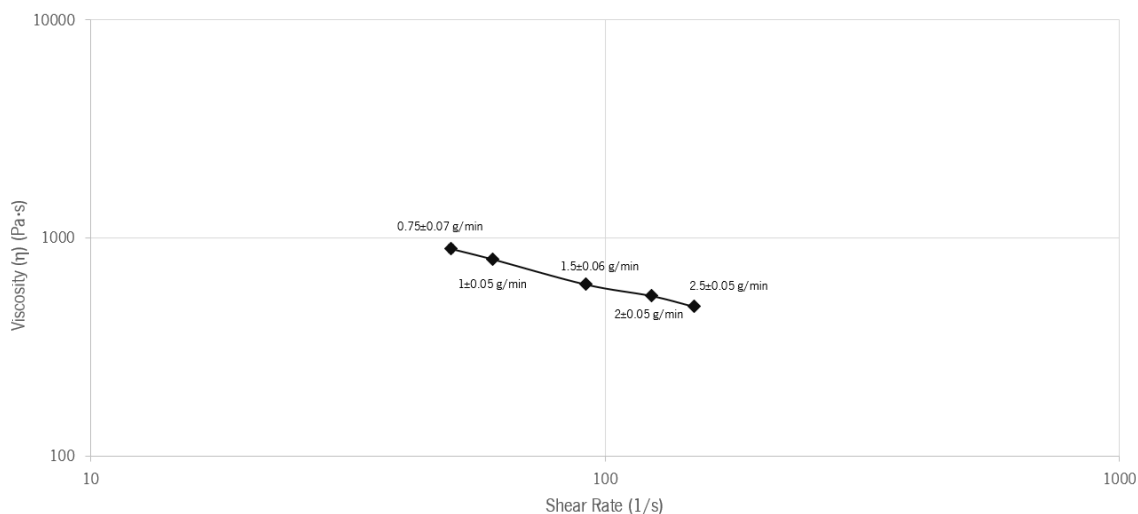


Figure 5.14: Flow Curves of LDPE at 180 °C: Variation of the throughput.

Table 5.2: Data from the obtained LDPE flow curve by changing the throughput

Throughput (g/min)	Shear Rate (s^{-1})	Viscosity (Pa.s)	Experimental Error (%)
0.75	50	892	4.5
1	61	763	1.4
1.5	92	612	3.3
2.0	123	542	2.0
2.5	149	484	2.5

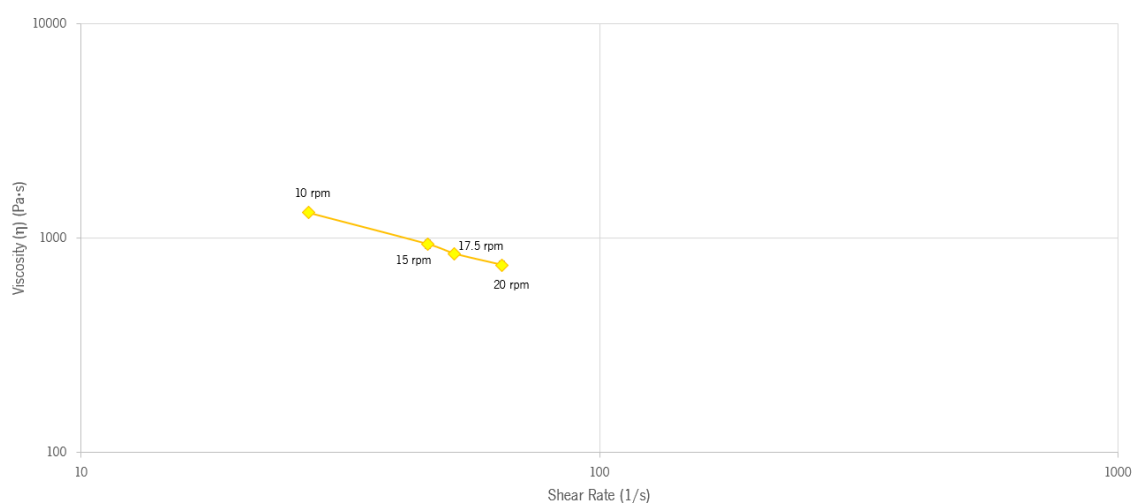


Figure 5.15: Flow Curve of LDPE at 180 °C: Variation of the screw speed.

Table 5.3: Data from the obtained LDPE flow curve by changing the screw speed

Screw Speed (rpm)	Shear Rate (s^{-1})	Viscosity (Pa.s)	Experimental Error (%)
10	27	1310	4.9
15	52	842	5.0
17.5	65	748	3.1
20	67	702	3.4

Merging all the data obtained in in-line slit rheometry and fitting the data with the power-law model (See Figure 5.16), given by the equation:

$$\eta = K \cdot \dot{\gamma}^{(1-n)}, \quad (5.2)$$

where K is the flow consistency index and n is the power law constant, which describes the shear-thinning or shear-thickening behavior of the material.

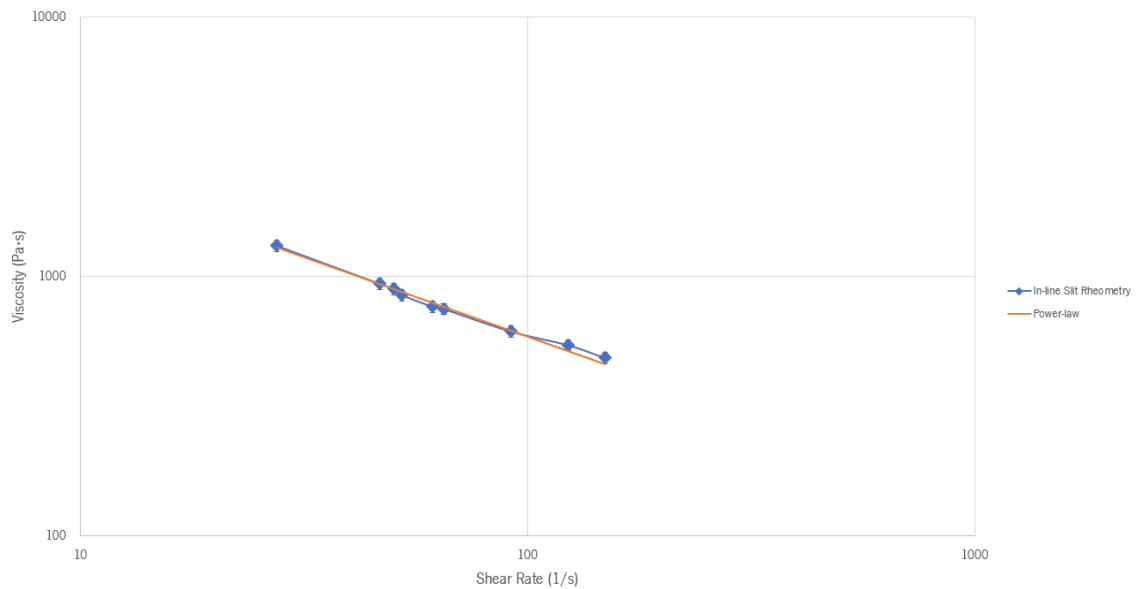


Figure 5.16: Flow Curves of LDPE obtained in in-line slit rheometry.

The resulting model parameters obtained have a R-squared value, R^2 , closer to 1, which indicates a small variance of the experimental value of the viscosity captured by the power-law model and, thus, a good agreement between the data resultant from the different in-line tests performed.

Table 5.4: In-line slit rheometry model fitting through Power-law model

Parameter	Value
K	9797.6853 ± 739.8356
n	0.3880 ± 0.0191
R²	0.9933

5.2.3.2 Rotational Rheometry

The results are presented on Figure 5.17, where is possible to see the overlap of the results of steady shear rate sweeps and frequency sweep tests in rotational rheometry. The experimental associated errors are relatively small, in particular for the steady state test, with an average value of 2.5%. For oscillatory measurements, the associated error is strongly dependent of the angular frequency with errors of 4%, in average, for higher frequencies and 8.7% for lower frequencies, due to the accuracy of the measurements being highly dependent on the sensitivity of the instrument to accurately measure the response of the material.

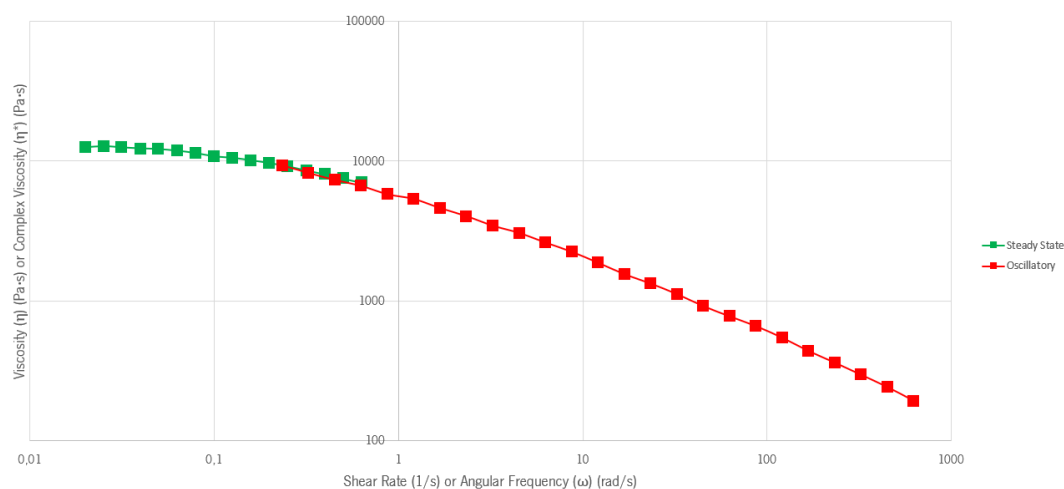


Figure 5.17: Flow Curve of LDPE at 180 °C obtained in rotational rheometry by overlapping steady and oscillatory curves.

Although these two tests have different natures, the validity of Cox-Merz rule, which is an empirical rule assuming equality between the shear rate dependence of the nonlinear steady-state shear viscosity and the angular frequency dependence of the linear complex viscosity, expressed by the equation $\eta(\dot{\gamma}) = \eta^*(\omega)$, for $\dot{\gamma} = \omega$, is verified for the range of overlapping shear rates and angular frequencies tested with LDPE, see Figure 5.15. For most polymers, this rule shows a good overlap between complex and shear viscosity, although some exceptions have been encountered. Nonetheless, as is possible to see on Figure 5.15 by the good overlap between the curves with a small associated error, this grade of LDPE obeys to the rule.

5.2.3.3 Capillary Rheometry

The first stage in the data treatment consisted in converting the voltages registered by LabVIEW into pressure units, as the procedure for in-line rheometry. However, with the pressure transducers used, there is no occurrence of drift in the signal, which means the conversion is performed directly, with the following equation, obtained experimentally by using a calibrator.

$$P(\text{MPa}) = V \times 6.85 - 0.1139 \quad (5.3)$$

Using the Bagley correction, the viscous pressure drop in the capillary is separated from the pressure losses due to entry and exit effects. To determine the inlet-outlet pressure loss, the pressure loss is plotted for different capillaries of the same diameter, but with different lengths and extrapolated to zero, known as the Bagley plot (See Figure 5.18). This extrapolation to zero length allows the determination of ΔP_{entry} , which is the pressure at the entrance of the die, for each piston speed (See Table 5.5).

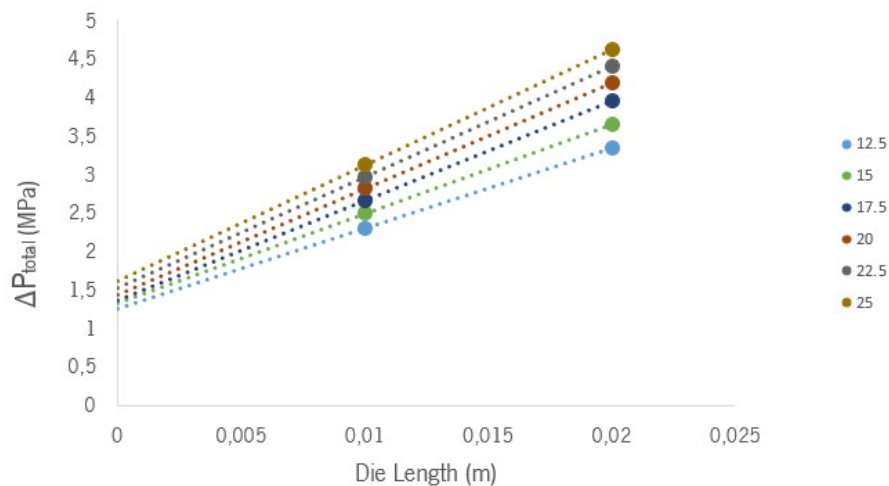


Figure 5.18: Bagley plot of LDPE at 180 °C obtained in capillary rheometry.

Table 5.5: Pressure Gradient and Throughput

Piston speed (mm/min)	ΔP_{entry} (MPa)
12.5	1.2630
15	1.3399
17.5	1.3625
20	1.4485
22.5	1.5254
25	1.6177

Following the rest of the proceeding regarding the data treatment described in Section 4.2.5, the flow curve shown in Figure 5.19 was obtained along with the error computed from triplicates for

each shear rate presented in Table 5.6, which is also in the range of acceptable experimental error. As in the procedure in in-line rheometry, the experimental data obtained was fitted with the power-law model and its parameters were computed.

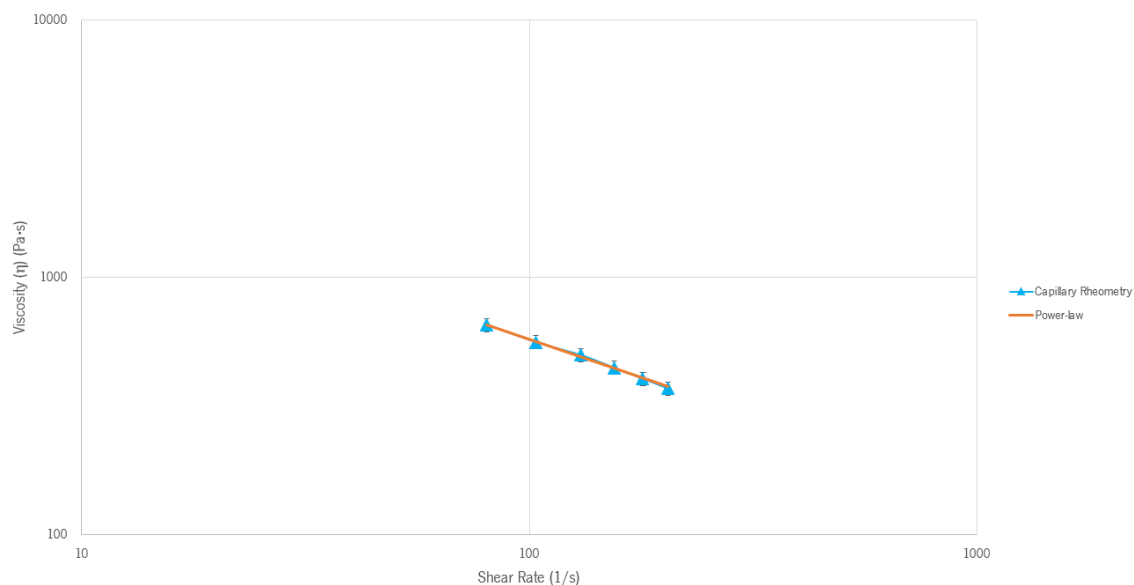


Figure 5.19: Flow Curve of LDPE at 180 °C obtained in capillary rheometry.

Table 5.6: Values obtained through Capillary rheometry.

Piston speed (mm/min)	Shear Rate (s^{-1})	Viscosity (Pa.s)	Experimental Error (%)
12.5	80	653	4.5
15	103	559	6.0
17.5	130	498	4.4
20	155	445	3.6
22.5	179	403	5.4
25	204	369	3.5

The results in Table 5.7 show the K and n values range to be further compared to the other techniques. As in in-line rheometry, the R^2 value is closer to 1, which is good indicator for low variability in the data.

Table 5.7: Power-law model parameters: Capillary Rheometry

Parameter	Capillary Rheometry
K	8951.5198 ± 579.0177
n	0.4032 ± 0.0134
R²	0.9979

5.2.3.4 Comparison between In-line and Off-line Rheometry

The last stage of the validation of the results obtained in in-line rheometry of LDPE consisted in comparing all the curves obtained in the rheological characterization techniques used and fitting the Carreau-Yasuda model (See Figure 5.20), given by:

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty})(1 + (\lambda\dot{\gamma})^a)^{(n-1)/a}, \text{ with } \eta = \eta^* \text{ and } \dot{\gamma} = \omega \quad (5.4)$$

, where η_{∞} is the viscosity at infinite shear rate, η_0 is the viscosity at zero shear rate, n is the power law index, a is a dimensionless parameter and λ is the relaxation time.

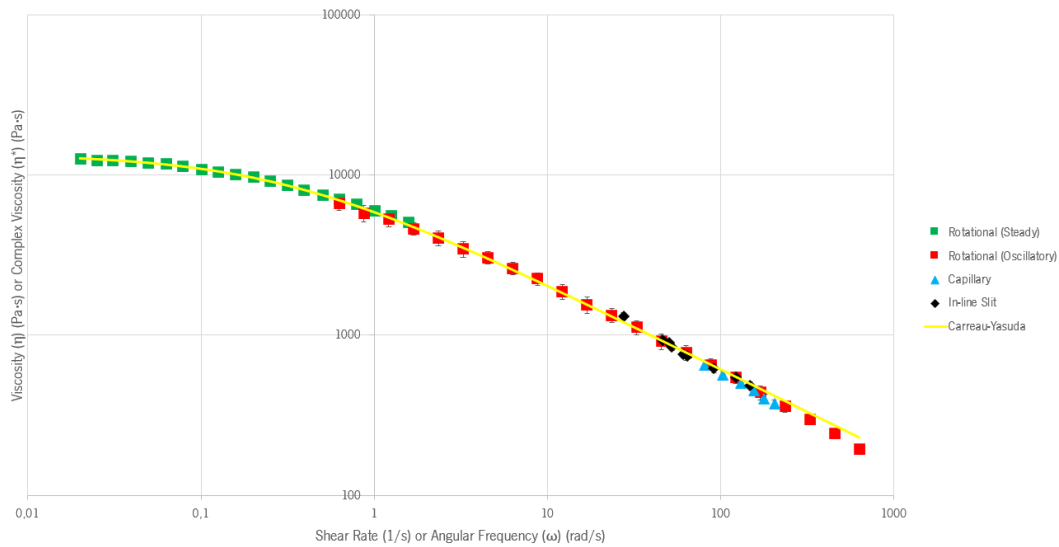


Figure 5.20: Flow Curve of LDPE at 180 °C.

The obtained model parameters presented in Table 5.8 show a relative small variation and the R^2 is almost 1, which indicates a The results showed a very high correlation between the model predictions and the experimental data, and, thus, validating all the experimental data, including the in-line measurements.

Table 5.8: Carreau-Yasuda fitting parameters

Parameter	Value
η_0	$13476.86801 \pm 179.51189$
η_{∞}	0 ± 76.59957
n	0.46675 ± 0.035
a	0.83456 ± 0.05665
λ	3.29145 ± 0.53921
R^2	0.9995

However, with the scale used in Figure 5.20, it is difficult to take final conclusions about the accuracy of the microrheometer in the range of shear rates attained in filament production. Contrarily,

Figure 5.21 shows a smaller range of shear rates. The power-law model was used to compare and fit the rheological data obtained by oscillatory rheometry, capillary rheometry, and in-line slit rheometry and its parameters are presented in Table 5.9. The model provided a good fit to the data with an R^2 value of 0.99557, indicating a high degree of correlation between the predicted values and the experimental results.

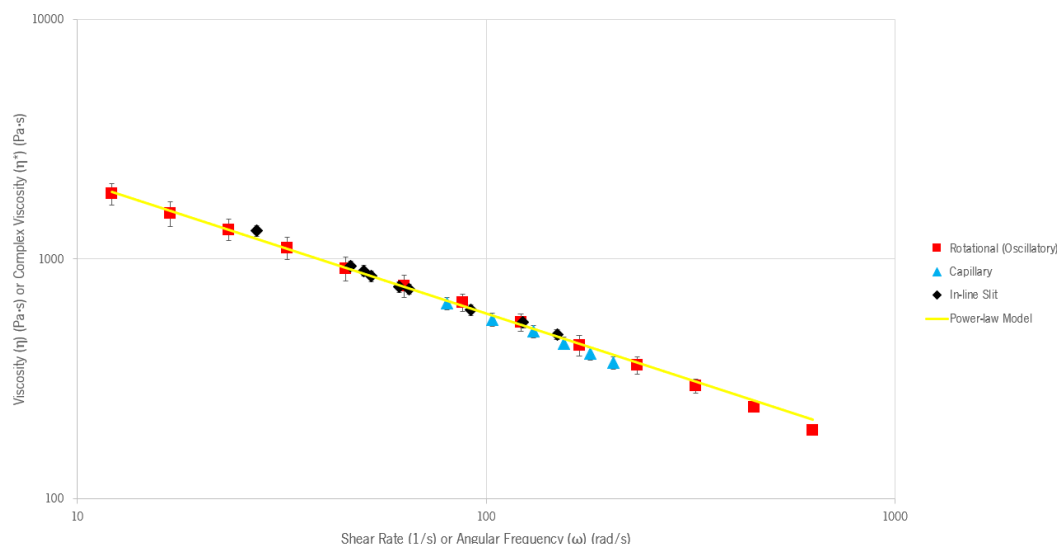


Figure 5.21: Flow Curve of LDPE at 180 °C in the region of practical processing.

Table 5.9: Power-law model parameters: Capillary Rheometry VS In-line Slit Rheometry

Parameter	Oscillatory	Capillary	In-line Slit	Experimental Data
K	7343.190 ± 148.011	8951.519 ± 579.017	9797.685 ± 739.835	7583.873 ± 205.224
n	0.453 ± 0.006	0.403 ± 0.013	0.388 ± 0.019	0.446 ± 0.007
R²	0.9991	0.9979	0.9933	0.99557

These results also allow to conclude that the effect of the wall slip is null for the rheometry techniques used, since the geometries of the channels used are different in each technique.

Concerning the effect of viscous heating, since the temperatures in the rheometers are relatively constant throughout the measurements and there is an overlap of the flow curves, then the effect of viscous heating is either null or similar for all the techniques.

5.2.4 COC

5.2.4.1 In-line Slit Rheometry

The same procedure used for LDPE was used for COC, which allowed to obtain the following flow curves (Figures 5.22 and 5.23 and respective data on Tables 5.10 and 5.11).

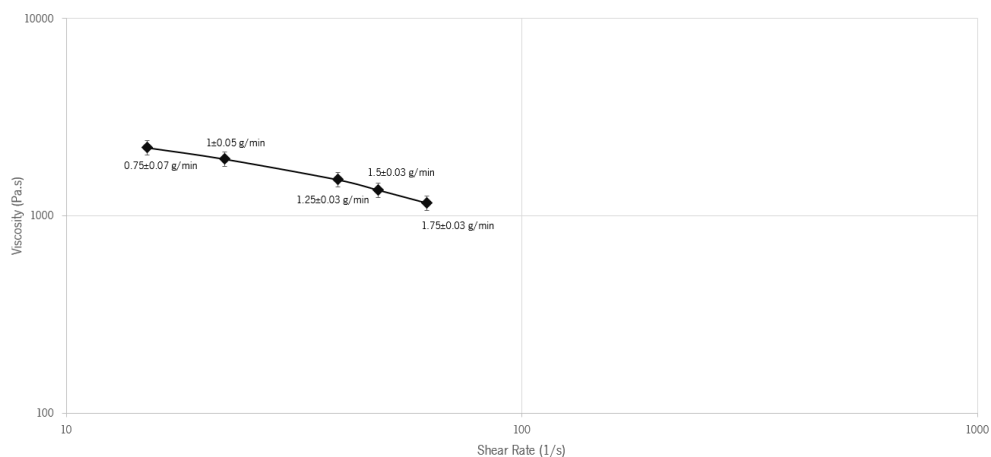


Figure 5.22: Flow Curve of COC by changing the feed rate between 0.75 and 1.75 g/min.

Table 5.10: Pressure Gradient and Throughput

Throughput (g/min)	Shear Rate (s^{-1})	Viscosity (Pa.s)	Experimental Error (%)
0.75	15	2219	7.9
1	22	1942	6.3
1.25	39	1527	4.1
1.5	48	1354	2.0
1.75	62	1163	3.5

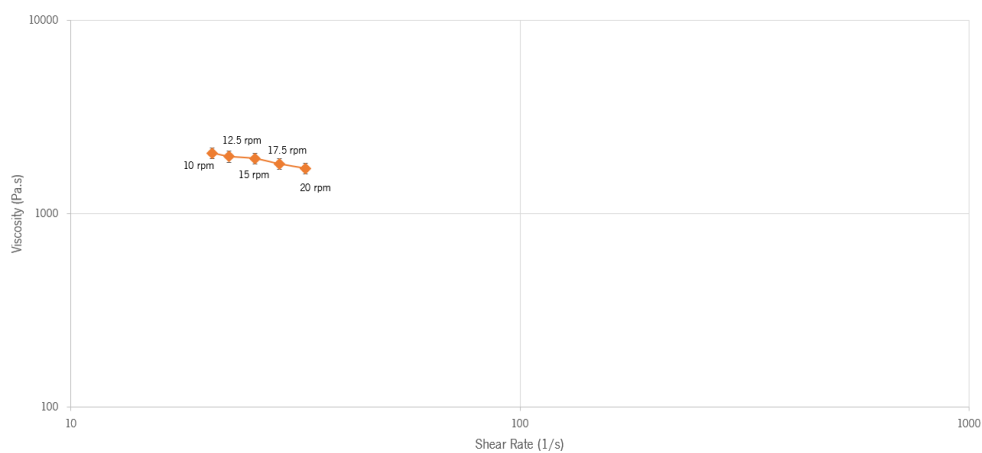


Figure 5.23: Flow Curve of COC by changing the feed rate between 0.75 and 1.75 g/min.

Table 5.11: Pressure Gradient and Throughput

Screw speed (rpm)	Shear Rate (s^{-1})	Viscosity ($Pa.s$)	Experimental Error (%)
10	21	2055	6.5
12.5	23	1974	5.4
15	26	1923	6.3
17.5	29	1807	4.0
20	33	1714	4.5

The results, computed from triplicates, show, in general, a greater experimental associated error for lower shear rates, which may indicate the lower sensitivity of the piezoelectric sensors at smaller shear rates and, consequently, smaller pressure drop values.

Merging all the data obtained in in-line slit rheometry and fitting the data with the power-law model (See Figure 5.24), given by equation 5.2, resulted in R^2 closer to 1 (Table 5.12) with the model parameters obtained, which, as for LDPE, indicates a small variation of the experimental value of the viscosity captured by the power-law model and, thus, a good agreement between the data resultant from the different in-line tests performed.

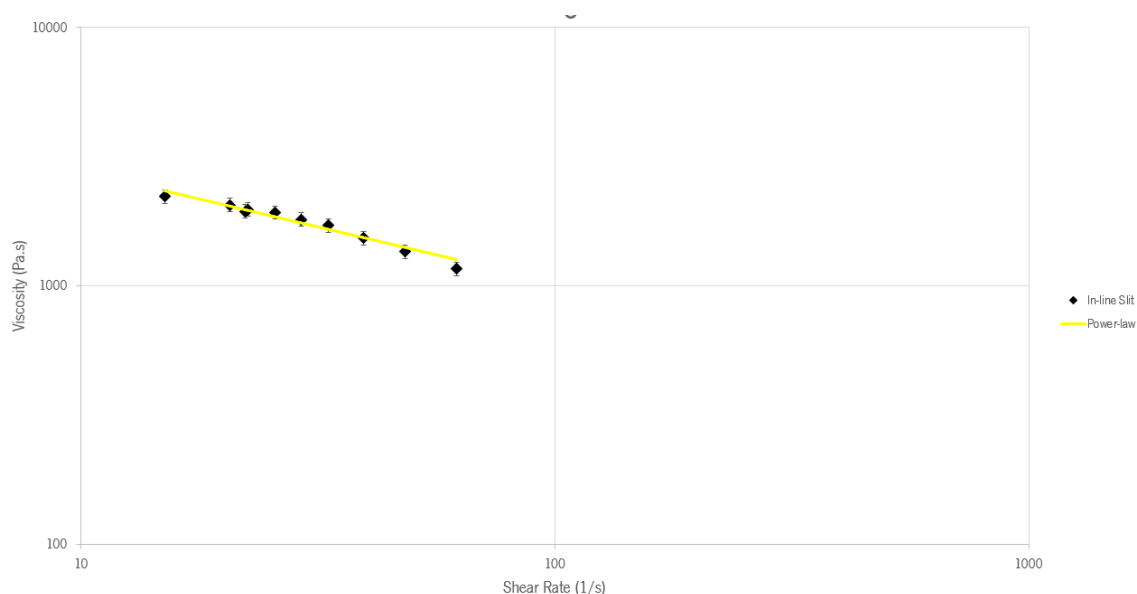
Figure 5.24: Flow Curve of COC by changing the feed rate between 0.75 and 1.75 g/min .

Table 5.12: Power-law model parameters: In-line Slit Rheometry

Parameter	Capillary Rheometry
K	7478.0046 ± 791.0031
n	0.56833 ± 0.03226
R²	0.96065

5.2.4.2 Rotational Rheometry

Figure 5.25 shows the complex viscosity and the shear viscosity measured with COC. However, unlike LDPE, COC did not show a good overlapping between the curves, with $\eta(\dot{\gamma}) < \eta^*(\omega)$, which is the more common failure mode of the Cox-Merz rule [51], often attributed to instabilities such as secondary flow, slip of the polymer on the walls of the geometry, or edge fracture of the sample rather than a disobedience of this purely empirical rule [51].

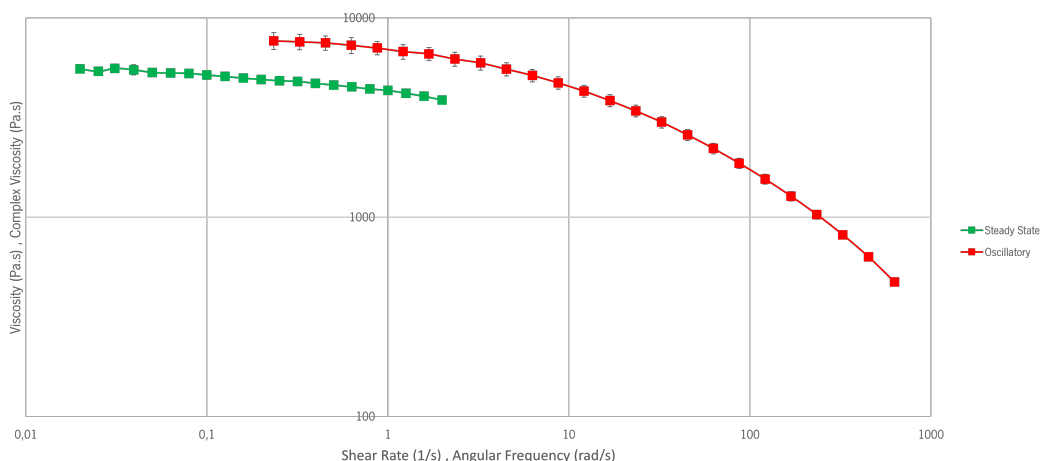


Figure 5.25: Results obtained in rotational rheometry of COC that suggest Cox-Merz Failure.

In order to understand if the failure occurred due to instabilities related to the COC flow in the shearing geometry, additional tests were performed. To rule out the possibility of slippage of the sample during the steady state flow tests, the smoothed surface plates used for all the other tests were replaced with larger and roughed-surface plates (See Figure 5.26). The performed experiments with the different plates gave similar flow curves, see Figure 5.26, right. This leads to affirm that if any experimental error occurred, it was not associated with slip or sample fracture since flow curves are essentially Newtonian for the range of shear rates tested.

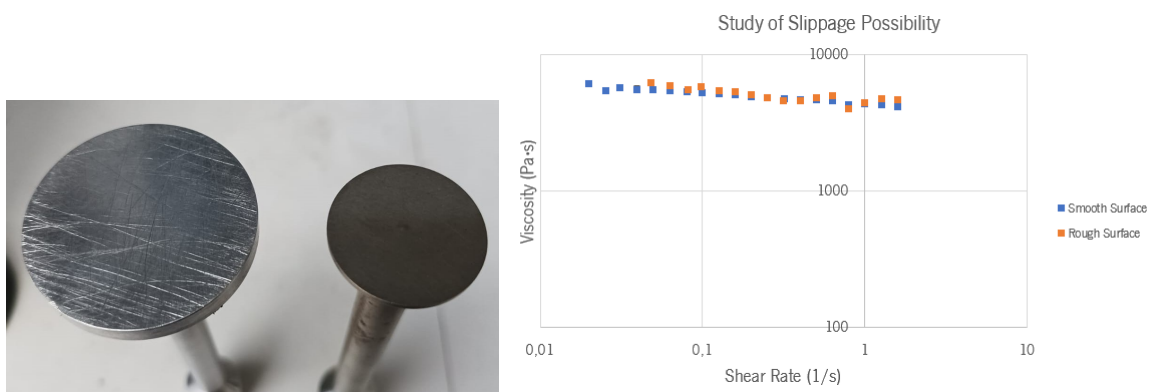


Figure 5.26: Study to determine if slippage occurred during steady state tests: on the left - roughed-surface plate geometry; on the right - flow curves obtained with both geometries.

Regarding the validity of oscillatory measurements, additional frequency sweep tests were

performed, where the strain (0.1% or 0.01%) or the frequency ramp (from 100 Hz to 0.01 Hz or from 0.01 to 100 Hz) were varied. All the additional tests showed good agreement with the oscillatory curve of Figure 5.22, as is possible to see on Figure 5.27. The average experimental error associated with the additional tests is 9.7%, however, none of the tests presented complex viscosity values closer to the shear viscosity values of the steady state tests. Thus, the good reproducibility of the oscillatory testing confirm the absence of COC thermal degradation or nonlinear viscoelastic response during the record of experimental data. Since there is no rheometrical concerns about the experiments, we are left with questioning the intrinsic properties of the COC melt.

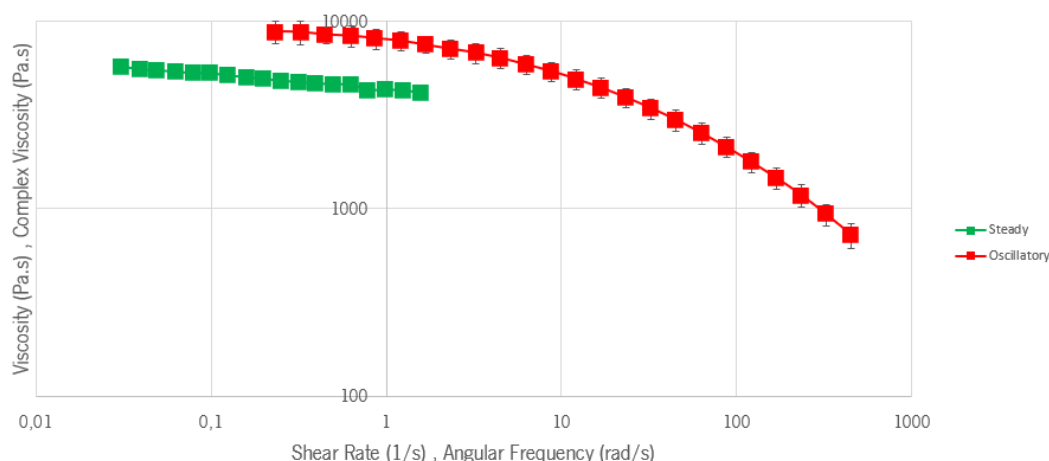


Figure 5.27: Study to determine the reproducibility in the oscillatory testing of COC.

Cyclic olefin copolymer structure, as the name implies, has cyclic side chains in its structure (Figure 5.28), which increases the chain stiffness and might be the reason of the Cox-Merz failure. As mentioned in [51], some polymer chains challenge the validity of the rule with a case of special interest being polymers with high chain stiffness, since the chains are more resistant to bending and stretching, and the polymer may behave more like a solid than a liquid under shear stress. This can lead to an increase in the complex viscosity compared to the shear viscosity, especially at lower shear rates where the polymer has more time to relax and deform.

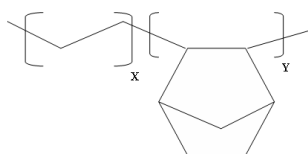


Figure 5.28: Chemical structure of cyclic olefin copolymer (COC). Retrieved from [50].

5.2.4.3 Capillary Rheometry

After the realization of measurements with both short and long dies, the Bagley correction was plotted (See Figure 5.29) and by using equation 4.6, the true pressure that occurred in the capillary was determined.

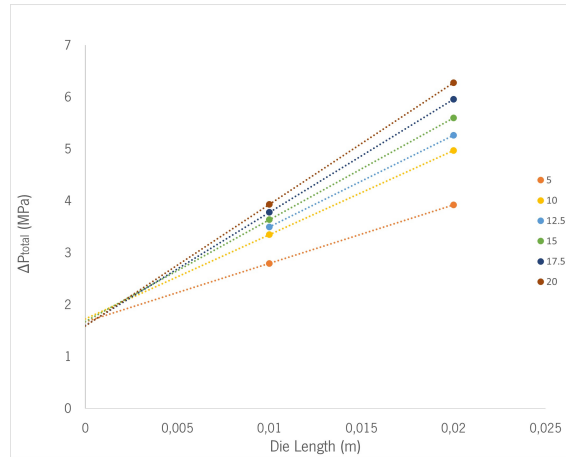


Figure 5.29: Bagley correction of COC at 190 °C obtained in capillary rheometry.

Table 5.13: Pressure Gradient and Throughput

Piston speed (mm/min)	ΔP_{entry} (MPa)
5	1.6687
10	1.7230
12.5	1.7297
15	1.6751
17.5	1.5995
20	1.5822

Following the rest of the procedure regarding the data treatment described in Section 4.2.5, the flow curve shown in Figure 5.30 was obtained along with error computed from triplicates for each shear rate, which inside the range of acceptable experimental error. As in the procedure in in-line rheometry, the experimental data obtained was fitted with the power-law model and its parameters were computed.

Table 5.14: Values obtained through Capillary rheometry.

Piston speed (mm/min)	Shear Rate (s^{-1})	Viscosity (Pa.s)	Experimental Error (%)
5	39	1461	4.3
10	75	1080	4.9
12.5	93	944	2.3
15	111	880	0.9
17.5	129	844	1.2
20	147	798	2.5

The results in Table 5.15 show the K and n values range to be further compared to the other techniques. As in in-line rheometry, the R^2 value is closer to 1.

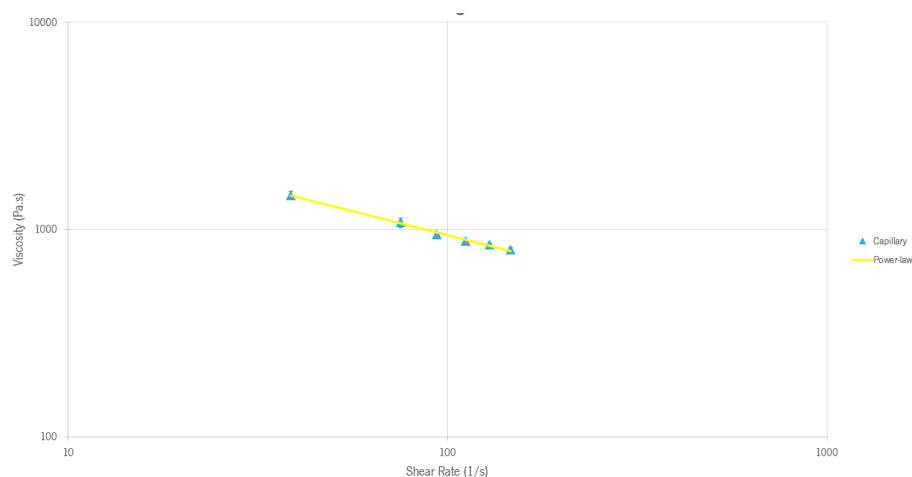


Figure 5.30: Flow Curve of COC at 190 °C obtained in capillary rheometry.

Table 5.15: Power-law model parameters: Capillary Rheometry

Parameter	Capillary Rheometry
k	7907.3099 ± 440.2176
n	0.5370 ± 0.0128
R²	0.9965

5.2.4.4 Comparison between In-line and Off-line Rheometry

The last stage in the characterization of COC consisted in overlapping all the curves obtained in the various rheological characterization techniques used. Figure 5.31 shows the entire range of shear rates measured, however since tests in rotational rheometry suggested that Cox-Merz rule fail for this material, oscillatory measurements cannot be overlapped with steady state tests.

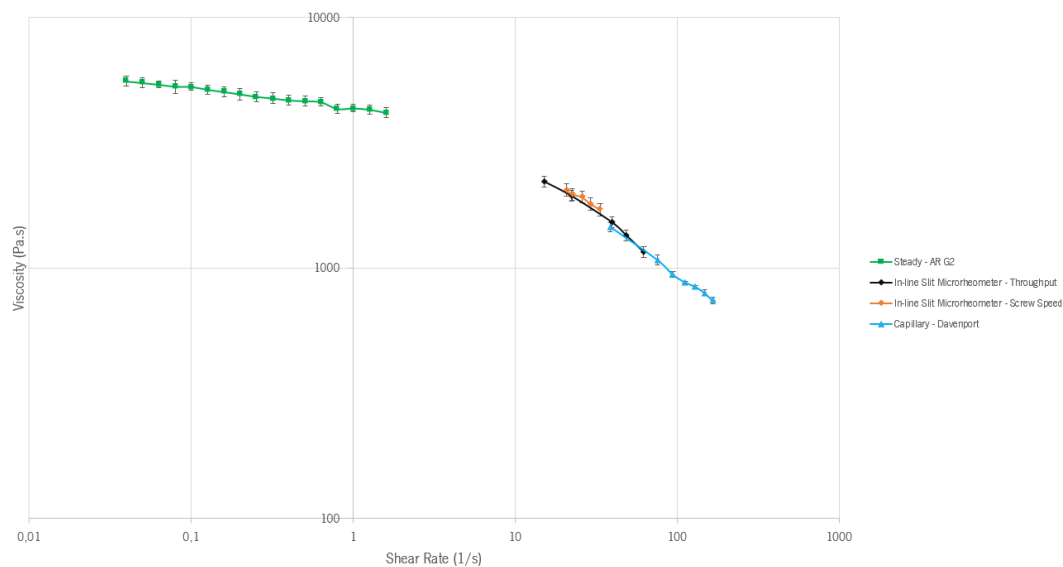


Figure 5.31: Flow Curves of COC experimentally obtained.

Although some points of in-line characterization show good agreement with off-line capillary rheometry, there are still several points without proper validation. This is due to the lack of overlap between tested shear rates in rotational and in-line slit rheometry, and the fact that frequencies cannot be used to fill the gap in shear rates. In this scope, the Carreau-Yasuda model, given by the equation 5.4, was implemented to fit the experimental data. Results presented in Figure 5.32 and Table 5.16, show good agreement between the model and experimental data, with a R^2 of 0.9981 that suggests that there is a very strong relationship with very little unexplained variability.

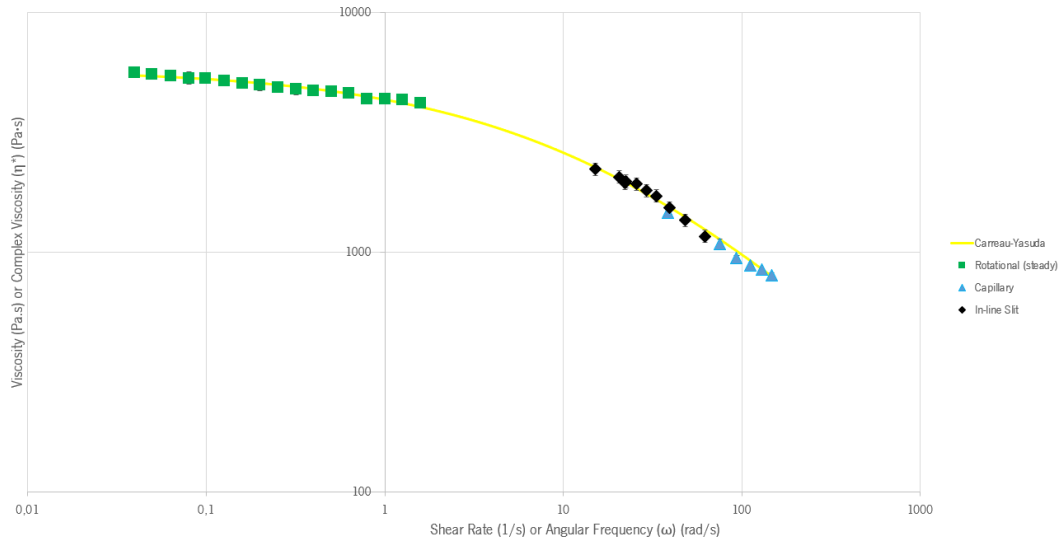


Figure 5.32: Flow Curve of COC by fitting the Cross Model.

Table 5.16: Carreau-Yasuda fitting parameters

Parameter	Value
η_0	5773.67985 ± 208.86409
η_∞	0 ± 1004.80335
n	0.27426 ± 1.14343
a	0.52339 ± 0.15622
λ	0.06248 ± 0.25771
R^2	0.99813

In order to validate the in-line rheological capacity of the microrheometer, it is important to understand if the flow curves obtained in-line successfully overlap off-line obtained curves and with the scale used in Figure 5.32, it is difficult to observe that. Figure 5.33 shows a smaller range of shear rates, which is the typical range attained in filament production, where is possible to see good agreement between in-line slit and off-line capillary data through a power-law model fitting with an R^2 of 0.9844, a very good indicator for correlation between data. These results allow to affirm the validity of the in-line slit microrheometer to characterize more complex structure materials, such as COC, where the Cox-Merz rule cannot be used to infer rheological data from rotational rheometry.

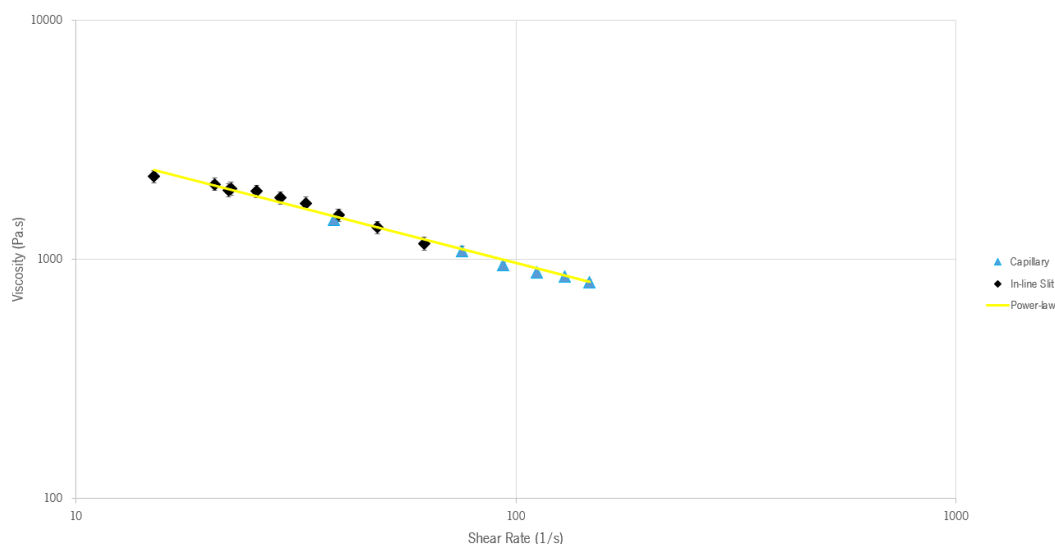


Figure 5.33: Flow Curve of COC at 190 °C in the region of practical processing.

Table 5.17: Power-law model parameters: Capillary Rheometry VS In-line Slit Rheometry

Parameter	Capillary	In-line Slit	Experimental Data
K	7907.310 ± 440.218	7478.005 ± 791.003	8482.568 ± 517.596
n	0.537 ± 0.013	0.568 ± 0.032	0.527 ± 0.018
R²	0.9965	0.9610	0.9844

5.3 Production and Validation of Filaments

Production of COC Filaments

Once concluded the rheological validation, the slit microrheometer was removed from the extruder and then the production of filaments began. Although the extruder without the microrheometer is able to work at higher temperatures than 200 °C and higher feed rates than 2.5 g/min, in order to establish a connection between the rheological characterization performed and the filament produced, the filament production was performed at 190 °C and feed rate of 1.5 g/min. During production, a digital caliper was used from periodically to measure the current diameter of the extrudate and the necessary adjustments were made, mainly to the pulling rolls speed.

Also during production, extrudate swell was monitored by visualization, however, due to the relatively large die diameter, lower throughput and screw speed, which typically results in a lower die pressure and, consequently, reduces the tendency of the polymer melt to swell after leaving the die. All these parameters reduce the resulting shear rate and, consequently, lead to residual extrudate swell. Therefore, due to relatively low throughput and screw speed and a larger die diameter, a minimal extrudate swell was obtained.

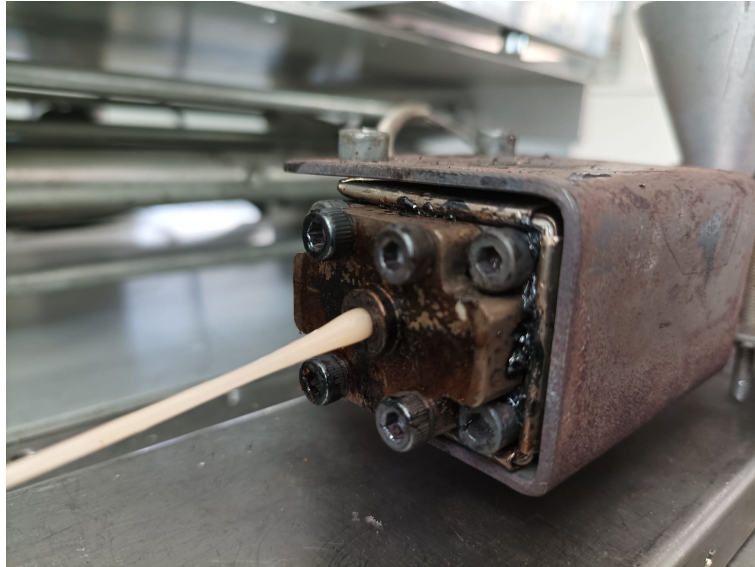


Figure 5.34: Evaluation of extrudate swell.

Around 60 g of COC filaments were produced (Figure 5.35), which are near 24 m of filament (assuming approximately 1.75 mm diameter), which was more than enough to use for dimensional characterization, printing test specimens and to try to perform mechanical characterization of the filaments.



Figure 5.35: COC Filament.

Dimensional Characterization

Dimensions

The results obtained for the dimensional characterization of the 8 filament segments are presented on Table 5.18, which contain the minimum, average, maximum and standard deviation of the 10 measurements performed on each sample. The last column of the table refers to the statistical parameters regarding the 80 measurements performed. As it is possible to observe, the average filament diameter is 1.77 mm, which is a good indicator for the printing tests, since, accounting for the standard deviation, the target-value of 1.75 mm is attained.

Table 5.18: Dimensional Characterization Results.

	Sample								Total
	1	2	3	4	5	6	7	8	
Minimum (mm)	1.72	1.72	1.73	1.72	1.72	1.70	1.70	1.69	1.69
Average (mm)	1.80	1.76	1.79	1.79	1.77	1.79	1.76	1.74	1.77
Maximum (mm)	1.85	1.79	1.88	1.86	1.80	1.86	1.85	1.82	1.88
Standard Deviation	0.04	0.03	0.05	0.04	0.03	0.06	0.05	0.04	0.05

Visual

From the visual inspection performed, no contaminations or locations with surface roughness were encountered. However, at several locations along the length, voids were visible in the COC filaments (Figure 5.36), which can occur in the filament when moisture or other gases are trapped inside during the manufacturing process. These voids can occur due to a variety of reasons such as not drying the feedstock prior to extrusion, improper processing conditions or inconsistent cooling.



Figure 5.36: Filament Voids.

Since the material was dried at 60 °C for 4 hours and has a very low moisture absorption capacity, the reason of the occurrence of the voids was attributed to either the inconsistent cooling,

since air fans were used instead of water cooling, with the latter allowing a more uniform cooling along the diameter or the improper processing conditions, specifically the barrel temperature, that may should have been higher, however, due to the importance of linking the filament production to the rheological characterization, the temperature had to be set at 190 °C.

Printing

COC is a challenging material to 3D print due to its high melting temperature and low viscosity, which can result in poor flow and deposition. In this study, the flow and deposition of cyclic olefin copolymer (COC) filament in 3D printing was investigated. A series of experiments were conducted using different nozzle temperatures and print speeds to determine the optimal printing conditions for this material.

At the start conditions, the filament flowed through the nozzle at this temperature and speed, however, the deposition did not occurred due to the higher printing speed of the nozzle. The printing speed was then lowered to 10 mm/s, and the filament was extruded but kept following the nozzle instead of being deposited. Concerning the printing speed, a last test was performed by lowering the speed to 1 mm/s, which would make the print of a test specimen last 3 hours, and the filament was partially deposited but left large voids in the printed object (Figure 5.37).



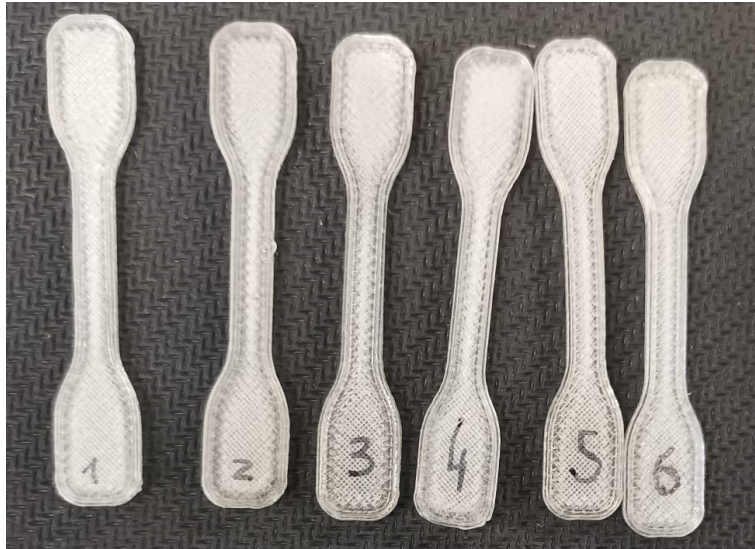
Figure 5.37: On the left: Failed attempt to print at 190 °C. On the right: Some of the printed test specimens.

Concerning the temperature, by increasing the nozzle temperature to 215 °C allowed the filament to flow more easily, however, the deposition problems kept occurring. The optimal nozzle temperature for printing COC filament was 240°C (recommended printing temperature recommended by some manufacturers), which allowed the filament to flow smoothly through the nozzle and being deposited in the platform.

After determining the optimal conditions for the material to flow, concerning the deposition, the gap between the nozzle and platform was optimized, with the optimal gap being near 0.15 mm, using trial-and-error methodologies. The final processing conditions used in the production of the test specimens (Figure 5.38).

Table 5.19: Processing conditions used in the printing stage and averaged dimensions obtained.

Parameter	Value
Nozzle temperature ($^{\circ}\text{C}$)	240
Platform temperature ($^{\circ}\text{C}$)	90
Printing speed (mm/s)	40
Layer height (mm)	0.2
Layer orientation ($^{\circ}$)	± 45

Figure 5.38: On the left: Failed attempt to print at 190°C . On the right: Some of the printed test specimens.

The measurement of 3D printed test specimens is a crucial step in determining if they meet the tolerances specified in DIN 53504. To ensure accuracy, measurements were performed using a reliable and precise measurement tool, namely a digital caliper. The dimensions of the printed specimens were compared to the specifications outlined in the DIN 53504 standard. The dimensions of the printed specimens fall within the specified tolerances, which indicates that the 3D printing process has been successful in producing the desired shape and size of the test specimen (Table 5.20).

Table 5.20: Test specimens averaged dimensions.

Dimension	Averaged Value
Height (mm)	2 ± 0.15
Width of the grip section (mm)	8.5 ± 0.02
Width (central) (mm)	4 ± 0.04
Length (mm)	50 ± 0.1
Mass (g)	0.60 ± 0.05

Relationship between 3D Printing and Rheological Characterization

Once the printing stage were not possible to be performed at the same temperature as the rheological characterization and, since up to the submission date of this work, the rheological characterization at the printing temperature were not able to be performed, attempts to estimate the COC viscosity at 240 °C through mathematical modelling. Three equations were considered:

- **Arrhenius**

$$\eta = Ae^{\frac{\Delta E}{RT}} \quad (5.5)$$

where η is the viscosity, ΔE is the activation energy, R is universal gas constant, A is also a constant which can be determined by experiment. In Arrhenius equation, only when the temperature is at least 200 °C higher than T_g can this equation be applied. For polymers with relatively low glass transition temperature, Arrhenius equation is applicable for describing temperature sensitivity of viscosity of those polymers [54]. But this equation seems inappropriate for polymers with high glass transition temperature, such as PMMA and COC, because processing temperature of polymers with high T_g cannot meet the conditions for applying Arrhenius equation.

- **Williams-Landel-Ferry (WLF)**

$$\log(\alpha_T) = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (5.6)$$

with C_1 and C_2 being the fitting parameters and T_0 the reference temperature. The WLF equation is valid at temperatures ranging from T_g to $T_g + 100$ °C for amorphous polymers [55].

- **Vogel**

$$\eta = Ae^{\frac{1}{\alpha(T - T_0)}} \quad (5.7)$$

where A , α , T_0 are all empirical constants which can be ascertained by experiments. With introducing of T_0 , Vogel equation can explain the abrupt change of viscosity of polymers near glass transition temperature [54].

There is a lack of studies regarding the rheological characterization mathematical modelling of COC behaviour. However, in [55], where the same grade of COC is used, the rheological curves shown in the article may not accurately represent the behaviour of the fluid in equilibrium, especially since the material is close to its glass transition temperature. At this temperature range, the material has a more complex response, leading to significant variations in viscosity with respect to temperature. Therefore, it is possible that the rheological curves presented in the article do not accurately represent the behaviour of the material at equilibrium, which may limit the interpretation of the results and

the applicability of the data for modeling or predicting the behaviour of the material under different conditions.

Since the desired characterization temperature is 240 °C, which is 162 °C higher than its T_g, this prevents the utilization of Arrhenius equation, only suitable for T > T_g+200 °C, and WLF equation, only suitable for temperatures ranging from T_g to T_g+100 °C. In [54], visco-temperature sensitivity of COC was characterized by a logarithmic linearization of Vogel equation.

$$\ln \eta = (1/\alpha) [1/(T - T_0)] + \ln A \quad (5.8)$$

However, the grade of COC used in this paper is significantly different, since its chemical composition is different [56], which may lead to different thermal dependency of the viscosity and, thus, could prevent the usage of the parameters determined in the study, namely the (1/α) value. Nevertheless, attempts to estimate the viscosity at 240 °C were performed using the parameter (1/α) for the shear rate of interest of 3D Printing, which was circa 225 s⁻¹, based on the volumetric flow rate obtained. The results yielded an estimated viscosity of 29.5 Pa·s, which demonstrates the impossibility in using the parameters of the other COC grade.

Without any additional bibliographic data and due to time limitations for the realization and writing of this dissertation, the best extrapolation possible is the one shown in the the paragraph above.

Mechanical Characterization of Test Specimens and Filaments

The mechanical characterization of the test specimens was performed successfully, without any occurrence of slippage or breakage of the test specimen near the grips (See Figure 5.39). On the other hand, the mechanical characterization of the filaments was not successful, not only due to the lack of proper grips for filament tensile testing which caused the fracture to occur by the grips, but also due to the high brittleness of the filaments that in some attempts to load the filaments in the machine caused fractures.

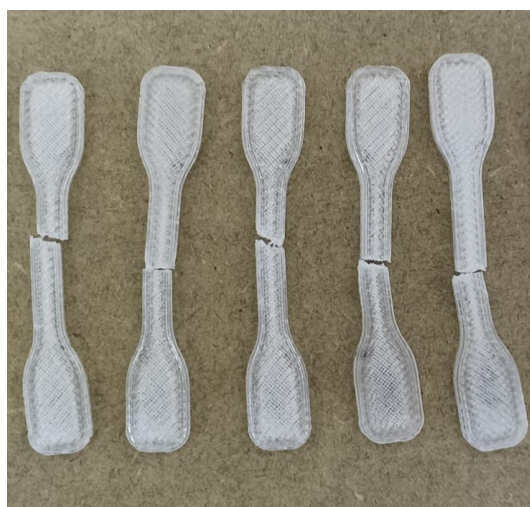


Figure 5.39: Test specimens after mechanical testing.

The results obtained are presented in Figure 5.40 and Table 5.21. As mentioned in the literature [53], this amorphous material showed the expected brittle behaviour, since rupture occurred without any plastic deformation.

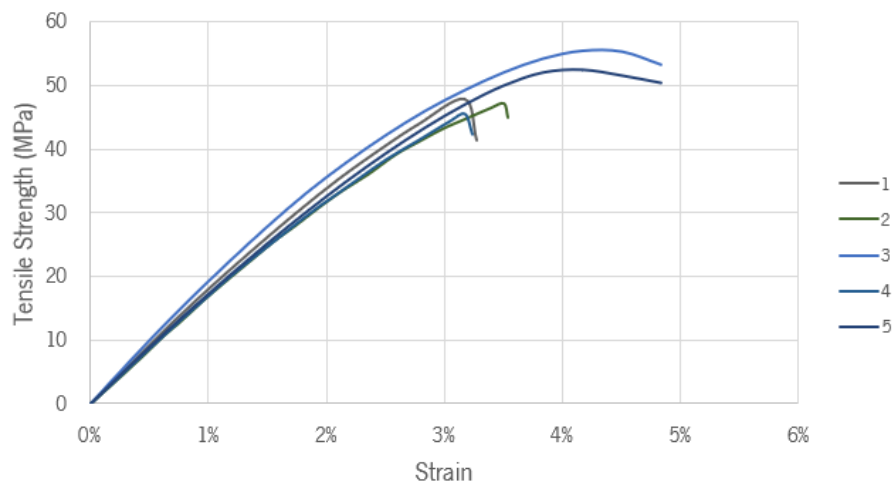


Figure 5.40: Stress-strain curves.

Table 5.21: Tensile Test Results.

	Sample					Total	
	1	2	3	4	5	Average	Standard Deviation
Tensile Strength at yield (MPa)	48.94	47.16	57.18	49.82	54.14	51.45	3.67
Tensile Strain at yield (%)	3.50	3.20	4.17	3.17	4.17	3.64	0.45
Young Modulus (GPa)	1.77	1.73	1.95	1.89	1.75	1.82	0.09

The results obtained were, as expected, lower than the mechanical properties values provided by the manufacturer (Table 5.22), mainly due to weaker interlayer bonding and interlayer porosity when compared to test specimens obtained by injection moulding. However, these results still validate the capacity of the extrusion line in produce filaments suitable for FDM applications, since when compared to other printed materials tested at the same conditions, the values obtained for COC are in the same range as other materials.

Table 5.22: Comparison of test results with datasheet information

	COC Injection Moulding [57]	COC FDM	PP [6]	PETG [58]	ABS [59]	PLA [60]
Tensile Strength at yield (MPa)	63.00	51.45	27.50	35.40	38.13	56.50
Tensile Strain at yield (%)	4.50	3.64	—	4.25	—	3.50
Young Modulus (GPa)	2.60	1.82	1.05	—	2.30	1.85

In conclusion, this work successfully developed and validated a microextrusion line for filament production and a microrheometer for in-line rheological characterization of materials used in FDM technology. The results demonstrated the capability of the microextrusion line to produce high-quality filaments of COC and the microrheometer to provide valuable information on the rheological behavior of materials. This work has the potential to advance the development of new materials and processes for FDM technology and can be expanded upon for other applications beyond FDM.

The first tests performed allowed the assessment of the microextrusion line ability to control several critical parameters such as throughput and temperature, as well as determining the average residence times at different processing conditions. The results obtained from these tests confirmed that the microextrusion line can effectively control its temperature and throughput, leading to consistent filament production.

Concerning the validation of an in-line slit microrheometer, results showed good agreement with off-line rheological measurements, both rotational and capillary rheometry, with experimental errors under 10% for all the techniques used. The other technique planned to be used for validation of the microrheometer was the double-slit die coupled to a co-rotating miniextruder [25], however, since this machine has a different screw configuration in comparison to the counter-rotating microextruder, it will yield different rheological results due to the different thermomechanical history of the material caused by different screw configurations. This factor led to the necessity of adaptation of the miniextruder system from co-rotating to counter-rotating configuration (See Appendix). Although, the screw elements and the transmission system were designed, due to delays in the production of the transmission system by an external company, only screw elements were produced and, thus, the measurements were not performed within the timeline dedicated to the dissertation.

In the rheological characterization of LDPE, the flow curves obtained by in-line slit rheometry, capillary rheometry and rotational rheometry (both steady state and oscillatory tests, implying this material obeys the empirical Cox-Merz rule) showed good agreement. Regarding COC, during rotational rheometry tests, values of shear viscosity and complex viscosity values demonstrated a considerable discrepancy among them, suggesting a special case of Cox-Merz rule failure. This limited the set of experimental data points and led to the implementation of Cross Model fitting, in order to validate

some points attained in in-line rheometry at lower shear rates that did not coincide with shear rates provided by capillary and rotational rheometries. Once implemented the model, it was possible to validate the entire range of shear rates attained by in-line rheometry. Thus, this study proved the capacity of the microrheometer in performing accurate rheological measurements.

After the rheological validation, the work proceeded to the filament production, where COC filaments were produced and dimensionally characterized, showing a diameter value very close to the target FDM value of 1.75mm. The filaments were then loaded to an FDM printer. The printing stage was successful, thus proving the ability of the microextruder in producing suitable filaments for FDM. The major setback during printing tests was the incapacity in printing at a temperature similar to the one used in rheological characterization (190°C), instead values known to function (240°C) were used.

Test specimens were produced by FDM and later mechanically characterized, in which the results proved that, even though the mechanical properties are lower than the values mentioned in the datasheet of the material, due to weaker interlayer bonding and interlayer porosity, the values obtained are similar to other materials under similar printing and testing parameters, thus finalizing the validation of the capacity of the microextrusion line to produce FDM filaments.

Suggestions for Future Work

- Validation of the microextrusion line and microrheometer with the miniextruder and the double-slit die capable of rheological measurements and filament production. This would also include the validation of the counter-rotating system developed for the miniextrusion line.
- Validation of the microrheometer capacity in performing optical measurements through its optical windows.
- Acquisition and validation of pressure sensors for the microrheometer that withstand temperatures higher than 200°C , in order to allow the characterization of a wider range of materials.
- Creation of a LabVIEW routine that instantaneously reports the flow curve, as in commercial rheometers. This would include the connection to a programmed Excel spreadsheet.
- Addition of an FDM printer at the end of the miniextrusion line, which would enable the 3D printing of the filament immediately after its extrusion and cooling.

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Appendix A - Development of a Counter-rotating System

In order to validate the in-line microrheometer, the initial plan also included the use of an already validated in-line double-slit die coupled to a miniextruder [25]. However, since this miniextruder has a co-rotating configuration, contrarily to the counter-rotating configuration of the microextruder, this would yield different thermomechanical history of the material and, thus, lead to different rheological results. In order to overcome this, the work-plan included the development and adaptation of a counter-rotating configuration in the miniextruder.

Adapting a co-rotating extruder to a counter-rotating configuration involves its modification, which involves replacing the existing screw elements with new counter-rotating screw elements and modifying the gearbox to accommodate the new configuration. The modifications need to be carefully designed to ensure that the counter-rotating configuration functions properly.

A.1 Screw Modules

Modular screws are commonly used in twin-screw extrusion as they offer a number of benefits over conventional, non-modular screws [9]. Modular screws are designed in sections, allowing for easy replacement and modification of specific sections as needed. This modular design allows for greater flexibility in the extrusion process, as operators can easily adjust the screw configuration to suit the specific needs of the material being extruded, since it is possible to adjust the amount of shear, compression and mixing applied to the material [61].

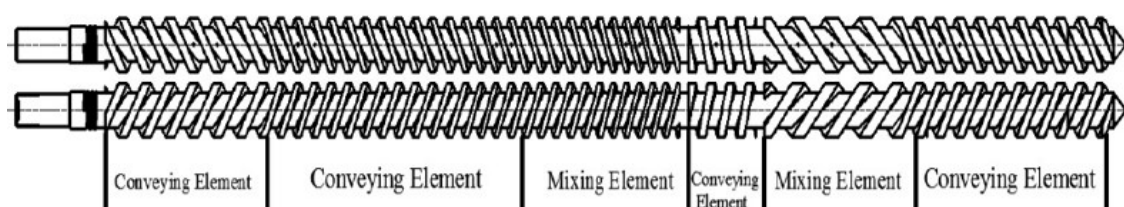


Figure A.1.1: Schematic View of an example of a modular counter-rotating screws configuration. Top: Left Hand Screw; Bottom: Right Hand Screw. Retrieved from [61].

Developing counter-rotating screw modules involves several steps, including design, production,

and testing. In this work, three screw configurations were planned, designed and produced.

Design

The design of counter-rotating extruders can vary depending on the specific application, with factors such as screw diameter, screw pitch, and screw element geometry all playing a role in determining the performance of the extruder [62]. The first step is to design the screw modules using computer-aided design (CAD) software SolidWorks. This involves creating a 3D model of the screw module, including all of its features, such as the screw thread, flights, and mixing elements.

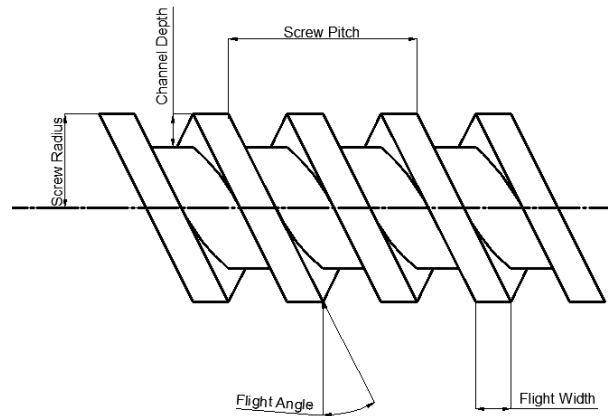


Figure A.1.2: Geometrical Parameters for Simple Model of Theoretical Output. Retrieved from [61]

The external diameter of the screw modules is typically related to the dimensions of the extruder barrel. The screw modules are designed to fit tightly within the barrel and to rotate smoothly, which requires careful consideration of the dimensions of both the screw modules and the barrel. In general, the diameter of the screw modules should be slightly smaller than the inside diameter of the extruder barrel, in order to allow for a small clearance between the two components, allowing for smooth rotation.

Maintaining a constant external diameter, by changing the internal diameter value, the channel depth also changes. In terms of the feeding zone channel depth, it is common to design this zone with a larger channel depth compared to the following zones in order to accommodate the pellets and prevent them from melting due to the high shear and temperature in the feeding zone. This larger channel depth allows the pellets to be transported through the screw module without being excessively compressed or heated, which can lead to melting, degradation, or other processing issues [62].

The screw pitch is the distance between the threads on the screw. A larger pitch generally results in higher throughput, but can also lead to higher shear rates and more thermal energy input. A smaller pitch can reduce shear and thermal energy input, but may result in lower throughput. The specific application will dictate the appropriate pitch, based on the desired balance between throughput and shear/thermal energy input [9].

The geometry of the screw elements, including the number and shape of the flights, will affect

the flow and mixing of the material being processed [61, 62]. Counter-rotating screws typically have intermeshing flights that work together to move the material through the barrel [9]. The specific application will dictate the appropriate element geometry, based on the desired mixing and shear characteristics.

Janssen [63] mentioned that the C-shaped chamber volume can be calculated by subtracting the volume of a given length of screw from the same length of the empty barrel. The volume, V_1 , of one side of the inner barrel bore over one flight pitch length was calculated as:

$$V_1 = \left\{ \left(\pi - \frac{\alpha}{2} \right) R^2 + \left(R - \frac{H}{2} \right) \sqrt{\left(RH - \frac{H^2}{2} \right)} \right\} S \quad (6.1)$$

where R is the external radius, H is the channel depth and S is the pitch length. α is defined as the overlapping angle in radians. It is given by the formula:

$$\alpha = 2 \tan^{-1} \left[\frac{\sqrt{(RH - H^2/4)}}{R - H/2} \right] \quad (6.2)$$

The volume, V_2 , of the screw root over one pitch length is:

$$V_2 = \pi (R - H)^2 S \quad (6.3)$$

The volume, V_3 , of one screw flight is:

$$V_3 = 2\pi \left\{ \left(RH - H^2/2 \right) W_f + \left(RH^2 - \frac{2}{3} H^3 \right) \tan(\theta) \right\} \quad (6.4)$$

where W_f is the flight width and θ is the flight angle. The total volume of C-shaped chamber V_c is:

$$V_c = \frac{V_1 - V_2 - iV_3}{i} \quad (6.5)$$

, where i is the number of entries in the screw module.

The different elements designed and presented in Figure A.1.3 have the same length, at exception of the mixing modules, to allow more interchangeability between configurations. By using the same length for most of the screw elements, it becomes easier to swap out different modules as needed, since there will be less need for adjustments. This can save time and effort during equipment setup and maintenance, as well as providing more flexibility in terms of modifying the screw configuration for different processing needs.

Module	Length (mm)	Flight Thickness W_f (mm)	Pitch S (mm)	Radius R (mm)	Channel Depth H (mm)	C-chamber Volume V_c (mm ³)
	50	4	14.30	Outer: 6.25 Inner: 3.75	3.50	764
	50	3.5	12.85	Outer: 6.25 Inner: 3.75	3.50	489
	50	8	15.99	Outer: 6.25 Inner: 5.25	1	282
	50	5.75	11.35	Outer: 6.25 Inner: 5.25	1	201
	15	—	—	Outer: 6.25 Inner: 5.00	1.25	185
	50	3.6	7.45	Outer: 6.25 Inner: 5.25	1	143

Figure A.1.3: Geometrical Parameters of the designed modules for Simple Model of Theoretical Output.

The twin-extrusion counter-rotating screw modules were designed with different screw geometries to meet the specific requirements of the extrusion process. Two different configurations were planned. Both configurations 1 and 2 aim to process pellets, which requires that they have higher channel depths, around 3 to 4 mm (size of general pellet) in the feeding zone than throughout the rest of the screw length.

• Configuration 1

The simplest configuration, mainly consisting in solids conveying, compression and pressure relaxation modules (See FigureA.1.4). The first configuration consisted of three modules with a channel depth of 3.5 mm in the first 3 modules to facilitate the transport of the pellets, and a channel depth of 1 mm in the remaining modules consisting in compression and pressure relaxation modules to melt and homogenize the polymer. The final module was designed for pressure build-up for the extrusion through the die.

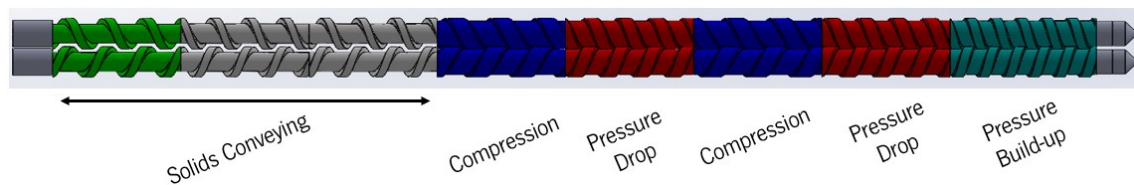


Figure A.1.4: Configuration 1.

• Configuration 2

The second configuration was similar to the first configuration but included mixing elements to promote better mixing and dispersion of the materials. The mixing elements consisted of specially designed profiles that created turbulence and shear forces to improve the dispersion of additives and fillers in the polymer matrix.

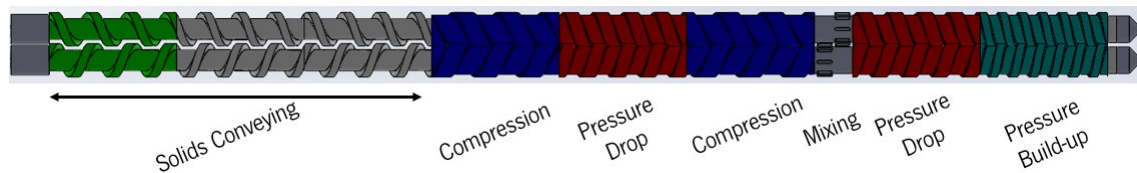


Figure A.1.5: Configuration 2.

Production

Once the design is finalized, the screw modules designs were converted to an STL format and the resulting files were uploaded in the direct metal laser sintering (DMLS) machine (Concept Laser M2 Cusing, GE Additive, Ohio, United States). DMLS is an AM technology that uses a high-powered laser to melt and fuse metal powder together to create a solid object. The DMLS process is carried out layer by layer, with each layer being fused to the previous one until the final object is produced [64]. The use of DMLS to manufacture the screw modules was an innovative approach that demonstrated the application of advanced manufacturing technologies in the development of new extrusion systems and also allows for rapid prototyping and production, which can significantly reduce lead times and costs compared to traditional manufacturing methods. However, when comparing these aluminum modules with traditional steel modules, the accuracy and precision of parts produced using DMLS technology may be lower than those produced using conventional machining methods [64]. This is because the DMLS process involves melting and fusing metal powder particles together, which can result in some degree of shrinkage, warping, or distortion during the cooling process. Also, the surface finish of parts produced using DMLS technology is rougher than those produced using conventional machining methods. This is because the DMLS process involves melting and fusing metal powder particles together, which can result in a surface finish that is not as smooth as those produced using machining methods.

Table A.1.1: Processing conditions used in the modules production.

Parameter	Value
Laser Power (W)	370
Scanning speed (mm/s)	1400
Hatching spacing (μm)	112
Spot size (μm)	190
Support layer thickness (μm)	50
Platform Temperature ($^{\circ}\text{C}$)	200

In order to set the building layout and the parameters, the software Magics was used. The laser sintered islands of $5 \times 5 \text{ mm}$ separated by 1 mm in both X and Y-axis and rotated 45° in each layer. Overall, the production volume was 221.6 cm^3 and Production height: 59 mm

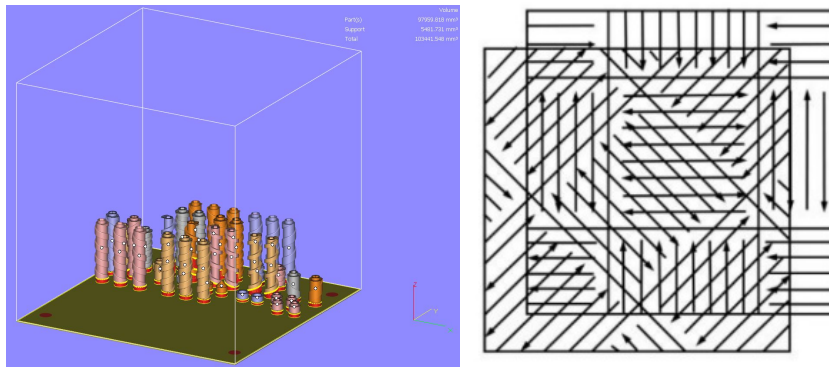


Figure A.1.8: left: Layout of the modules for the production; right: production strategy.

Post-processing

During the DMLS process, excess powder remained on the surface of the part after printing. This residue caused the surface of the part to be rough. Thus, after the screw modules were produced, they required post-processing to remove any excess metal powder and smooth the surfaces. Although this can be done using various methods, such as sandblasting or chemical treatments, this stage was performed manually with a rasp.

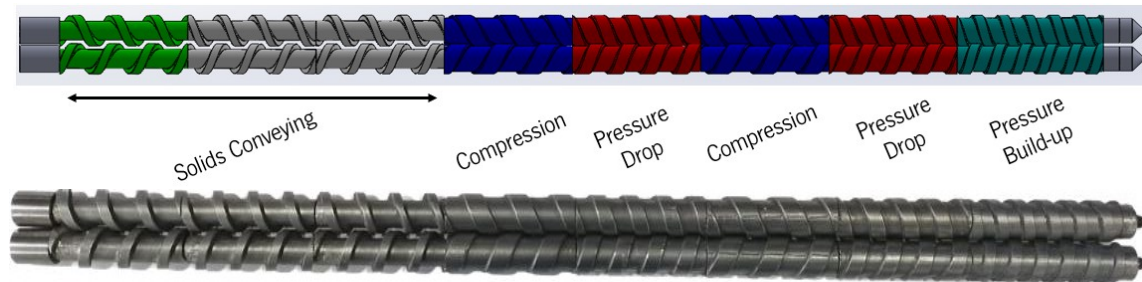


Figure A.1.9: Module after production.

Assembly

Once the screw modules have been post-processed, they can be assembled into counter-rotating screw extruders. This involved fitting the screw modules into a spindle and would include inserting into the extruder cylinders and finally connecting them to the gearbox.

• Configuration 1



A.1.10: Configuration 1.

• Configuration 2

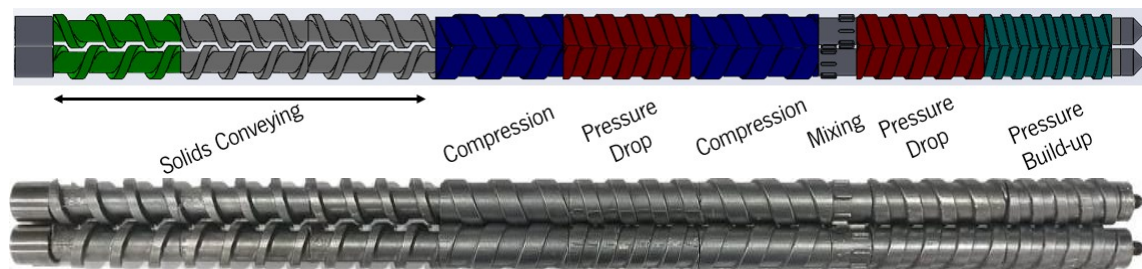


Figure A.1.11: Configuration 2.

In sum, developing counter-rotating screw modules involves a multi-step process that includes design, production, post-processing (when using direct metal laser sintering), assembly, and testing. This procedure can result in high-quality and rapid production screw modules that offer processing capabilities for a wide range of materials.

A.2 Motion Transmission System

Developing a motion transmission system for a counter-rotating extrusion system involves the design and implementation of a system that can transmit rotational motion between two rotating screws that are rotating in opposite directions. The motion transmission system must be precise, efficient, and reliable to ensure a consistent output and minimize downtime. The design process involves careful consideration of factors such as gear selection and type of transmission system, in order to ensure the system optimal performance [65, 66].

In order to perform a good design of the transmission system, it is important to, first, select the best type of gear and respective dimensions for this application. There are various criteria to classify the types of gears, however the main three criteria are the relative position of the driven axis, the relative position of the rotation centres and the shape of the teeth [66].

Concerning the relative position of the driven axis, the gears can be cylindrical, conical or worm. The difference between them, as shown in Figure A.2.1, is the relative position between the axis. In cylindrical gears, the rotation axis are parallel, in conical gears, the rotation axis are perpendicular and, lastly, in worm gears, the rotation axis are in different planes. Since in the extrusion process, both axis of the motor and screws are parallel, the chosen gear in the design was cylindrical.



Figure A.2.1: Position of the driven axis. Retrieved from [65].

In terms of the second criterion, the relative position of the rotation centres, the cylindrical gears can be exterior or interior, as shown in Figure A.2.2. However, once this transmission system is for a counter-rotating extruder, the only possible option is the exterior cylindrical gears, as the interior option only allows the motion to be in the same direction for both gears, which makes it suitable for co-rotating extruders.



Figure A.2.2: Position of the rotation center. Retrieved from [65].

The last criterion is the shape of the teeth of the gear. Cylindrical gears can either have straight or helical teeth (See Figure A.2.3), both with high efficiency rates. Straight teeth gears, also known as spur gears, are cheaper, since it requires less advanced equipment to manufacture them and are easier to couple, however, during operation, they exhibit a smaller contact area and can be noisier when compared to helical gears. The latter are smoother and less noisier during operation, demonstrate higher precision and withstand bigger loads, since the teeth is wider due to the diagonal position along the length of the gear, but are more expensive, mostly due to the fact of the type of advanced machinery required to produced them, such as 5-axis CNC machines.



Figure A.2.3: Shape of the gear teeth. Retrieved from [65].

The process of definition of the gear module was done in collaboration with the company responsible for the manufacturing of the gearbox. The gear module is defined as the ratio of the pitch diameter to the number of teeth of a gear, and it is expressed in millimeters. To select the appropriate gear module, the company used a software that chooses the best gear module for the application in question, based on the distance between the gears, which is an established parameter for the extrusion system in question, with a value of 11.50 mm.

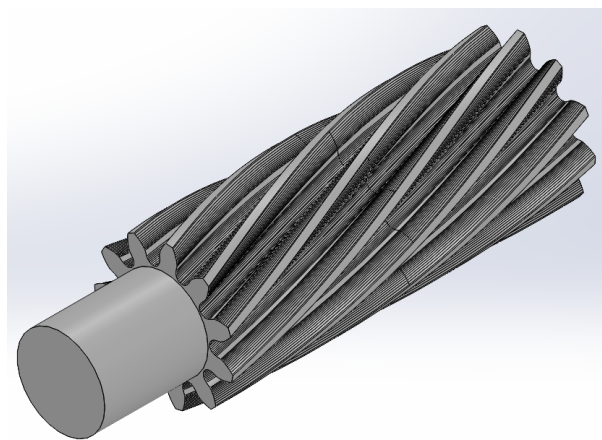


Figure A.2.4: Selected gear.

The selected gear has a module of 1, presenting 11 teeth and an helix angle of 16° . After that,

the next step was to define the type of transmission, that is, if the transmission is direct, where only two gears are used and the motion is directly transmitted from the motor to one of the gears, that consequently transmits the motion to the other gear, making them rotate in opposite directions at the same speed and frequency (See Figure A.2.5, right), or if the transmission has a torque reducer, in order to strengthen the system, making them less likely to break, since it uses three gears, where a upper-central gear directly connected to the motor transmits the motion to the two lower gears, that are connected to the screws, which causes a reduction on torque (See Figure A.2.5, left). Nonetheless, this alternative, also, increases the cost of manufacturing.

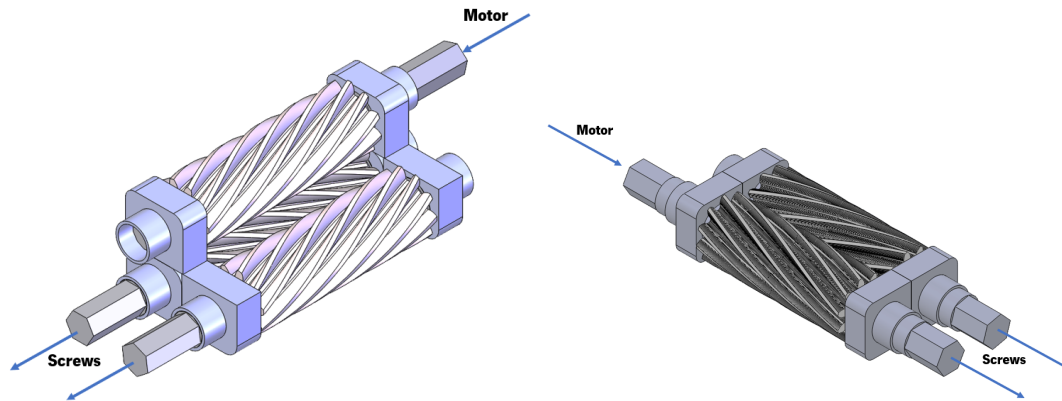


Figure A.2.5: Types of transmission: left: torque reducer; right: direct transmission.

In this case, the more appropriate choice is a direct transmission system, since is more efficient, reliable, and cost-effective solution for twin-screw extruders than one with a torque reducer.

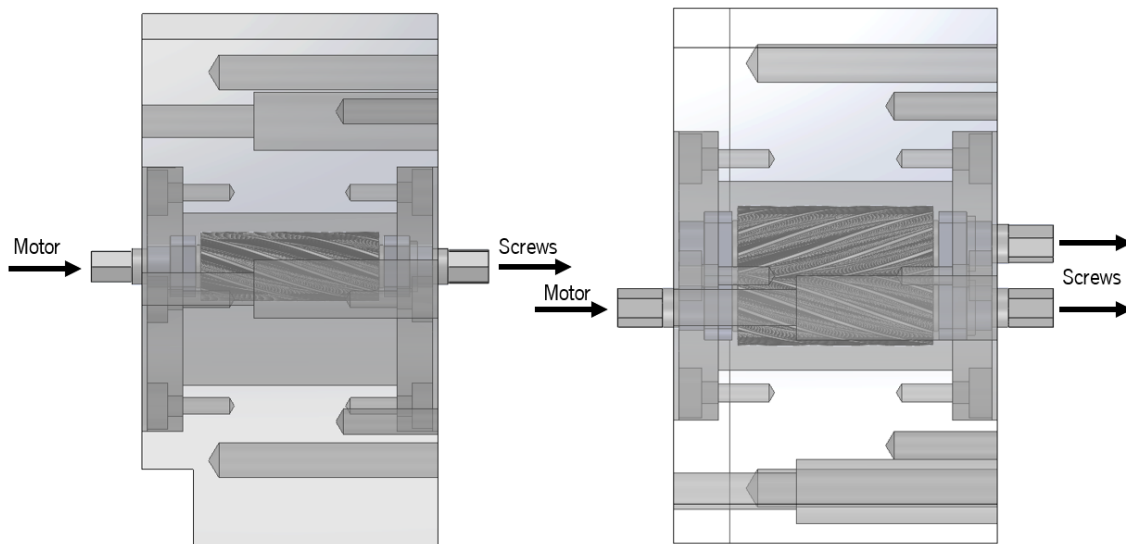


Figure A.2.6: Gearbox: left: Side view; right: Top view.

Regarding the gearbox, the design and dimensions were based on the current gearbox of the miniextruder. The final design is presented in Figure A.2.7.

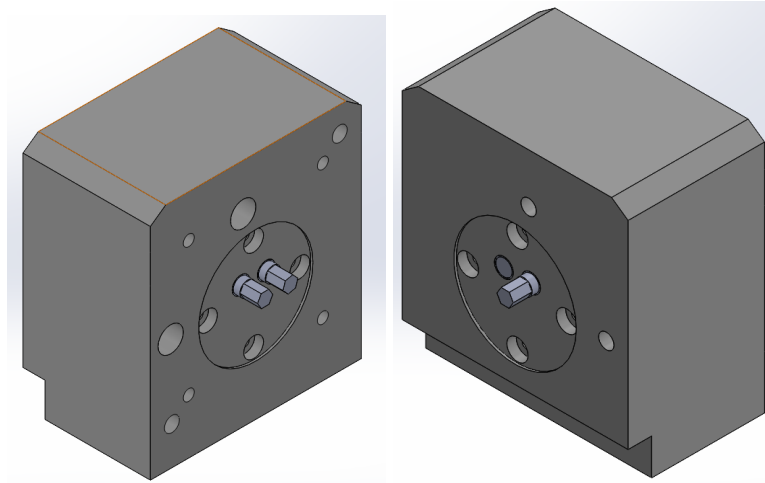


Figure A.2.7: Final Gearbox design.

Once the design is finalized, the gearbox components were set to be produced using various machining processes, however, due to administrative and external factors, the production of the gearbox was delayed up to the moment of the finalization of the present thesis.

