Universidade do Minho
Escola de Engenharia

António Eliseu Pereira Abreu

Coextrusion of multifunctional filaments

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UMinho | 2016

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Dissertação de Mestrado
Ciclo de Estudos Integrados Conducentes ao
Grau de Mestre em Engenharia de Polímeros

Trabalho efetuado sob a orientação do
Professor Doutor João Miguel Nóbrega
Engenheiro Mestre Fernando Eblagon

outubro de 2016

DECLARAÇÃO

Nome: António Eliseu Pereira Abreu
Endereço eletrónico: eliseuabreu93@gmail.com Telefone: 912287383
Cartão do Cidadão: 14322527
Título da dissertação: Coextrusion of multifunctional filaments

Orientadores:
Professor Doutor João Miguel Nóbrega
Engenheiro Mestre Fernando Eblagon

Ano de conclusão: 2016
Mestrado Integrado em Engenharia de Polímeros

Universidade do Minho, ____/_____/_____

Assinatura:

ACKNOWLEDGMENT

This space is dedicated to all those who contributed to the success of this project. To all of them my deepest thanks.

Firstly, I would like to express my sincere gratitude to my advisors, Prof. João Miguel Nóbrega and Engineer Fernando Eblagon for the continuous support of my master study and related research, for their patience, motivation, immense knowledge, feedback and support.

I would also like to thank my colleague Bruno Vale for all the team work, friendship and availability.

My sincere thanks to Doctor Sacha Mould for all the kindness and help during the first phase of the project.

I thank all the Lankhorst Euronete team for their availability, knowledge and gaiety during all the project.

I would like to acknowledge all the technical polymer engineering department for their patience and professionalism. A special acknowledge to João Paulo for all the support during the extrusion and coextrusion process.

Last but not the least, I would like to thank my family: my parents and my sister for supporting me spiritually throughout writing this thesis and my life in general.

A huge thank you to all of you!

ABSTRACT

Some commercial filaments are becoming commodities so aiming to increase the market competitiveness producers are looking for alternatives to improve their products performance. A simple material change is not enough, since better performant materials are usually more expensive and can easily be copied by the competition, so new approaches are needed.

The challenge of this project was to improve the properties of a commercial filament using a coextrusion process. The filament that is being studied has good tenacity but poor abrasion resistance, so the goal was to coextrude this filament with a second material in order to increase the abrasion resistance, without affecting negatively the filament tenacity. Two blends (B1 and B2) and one single material (M1), which is known to possess good abrasion resistance and average tensile resistance, were selected for this study.

The methodology of this research project was divided into three steps. Firstly, the materials were characterized rheologically, to identify its main flow properties and guide the definition of processing conditions. Subsequently, monofilaments of each material were extruded separately using different processing conditions, to identify their processing window and to obtain the resultant properties. The results obtained in this phase allowed to select the most promising material combination to test in the next phase of the work. The last step was to produce and characterise the coextruded filaments. Each filament was characterized by their tenacity, elongation and abrasion resistance properties.

After all the data treatment it was possible to identify the best configuration of materials (a coextrusion of B1 and B2) and processing conditions, which, when compared with the commercial filament, yielded an improvement of 35% in abrasion resistance without affecting the mechanical properties.

KEYWORDS: COEXTRUSION, FILAMENT, DENIER, TENACITY, ABRASION RESISTANCE

RESUMO

Alguns filamentos comerciais estão a tornar-se de uso vulgar então, para aumentar a sua competitividade no mercado, os produtores procuram alternativas para melhorar as suas propriedades. Uma simples alteração na matéria-prima utilizada não é suficiente, pois materiais com melhores propriedades são normalmente mais caros e esta alteração pode ser facilmente copiada pela concorrência. Por esta razão, novas abordagens são necessárias.

O desafio deste projeto foi melhorar as propriedades de um filamento comercial através de um processo de co-extrusão. Este filamento apresenta boas propriedades de tenacidade mas pouca resistência à abrasão, então o principal objetivo foi co-extrudir esse mesmo filamento com outro material de forma a manter as propriedades de tenacidade mas aumentando a sua resistência à abrasão. Para este estudo foram selecionadas duas misturas e um material, que é conhecido por ter boa resistência a abrasão e razoáveis propriedades mecânicas.

A metodologia utilizada neste projeto foi dividida em três passos. O primeiro foi a caracterização reológica dos materiais, para identificar as propriedades do escoamento e guiar a definição das condições de processamento. O segundo passo foi extrudir os filamentos de cada material separadamente com diferentes condições de processamento, de forma a obter a janela de processamento e identificar as suas propriedades resultantes. Os resultados obtidos nesta fase permitiram selecionar a combinação de materiais mais promissora para ser testada na fase seguinte. Por último, os filamentos foram co-extrudidos e caracterizados. Cada filamento foi caracterizado ao nível das suas propriedades de tenacidade, alongamento e resistência à abrasão.

Após o tratamento de todos os resultados obtidos, foi possível identificar a melhor combinação de materiais (filamento co-extrudido B2+B1) e as condições de processamento, que, quando comparadas com o filamento comercial, apresentaram uma melhoria de 35% de resistência à abrasão sem afetar as suas propriedades mecânicas.

PALAVRAS-CHAVE: CO-EXTRUSÃO, FILAMENTO, DENIER, TENACIDADE, RESISTÊNCIA À ABRASÃO

CONTENTS

1. INTRODUCTION

Filaments are used in many different applications such as 3D printers for tissues and scaffolds production [1], ropes [2], antistatic and floor coverings [3], textile products [4], fishlines [5] and structural reinforcement [6]. Their use is so wide that some commercial filaments are becoming a commodity, so their development is very important to obtain better properties and increase the competitiveness in an increasingly demanding market.

Increasing the performance of a commercial filament through a coextrusion process was the challenge made by *WireCo* (company leader in market and manufacturing wire and synthetic rope) to University of Minho that resulted into two master's dissertations, this one and another one made by other student [7]. The overall aims are a very demanding task that comprises materials selection, development of a new production technology and identification of the best material system configuration and process conditions. The present work is focused on the materials specification, selection of the most promising combination for the coextruded product and identification of adequate processing conditions.

With the improvement of the filament properties, *WireCo* is seeking to improve the performance of their main products, which are ropes.

1.1 State of art

1.1.1 Fibers and filaments

Fiber is a commercial term used to denominate filaments with a minimum length of at least 100 times its diameter that usually is around 0,1-0,13 mm [8]. A filament is the smallest unit of a fibrous material and its cross section is identified by the denier which is the weight in grams per 9000 m of length [9]. The lower the denier, the finer the filament. There are many plastics used to manufacture filaments, being the most important PP, nylon 66, polyester and PETP [10]. Each family of plastics has different grades that provides different properties to the filaments. The physical properties of filaments are influenced by the morphology and the processing conditions [8].

1.1.2 Filament extrusion

Extrusion is the process used to manufacture products in the form of continuous lengths with a constant cross section such as tubes, films, sheets and filaments [11]. Thermoplastic filaments are produced in adequate extrusion lines, as the one illustrated in Figure 1.

There are three basic methods that are used commercially in filaments manufacturing: wet spinning, dry spinning and melt spinning. In each case, a viscous fluid is extruded through a die, forming a fine diameter filament [12]. The melt spinning technique comprises two manufacturing steps: extrusion of a filament (extruder) and the subsequent thermal and mechanical stretching (water bath, roll systems, heaters and winding) [13]. In the process, molten plastic is forced using an extruder through fine holes in the die. After that, they are immediately cooled, stretched and collected at the end of the line [8].

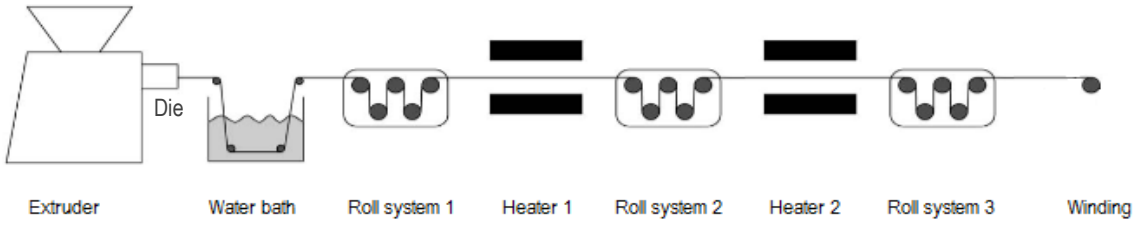

Figure 1 - Filament extrusion line [14]

The standard extruder for monofilament lines is a single screw machine. Inside the extruder, the pellets are transported by one rotating screw [9]. As the polymer is forced forward, it is gradually heated up to the desired melt temperature. At the extruder exit, or discharge zone, the molten material is forced through an extrusion die that shapes the melt into a specified cross-section [11]. In the monofilament die, melted material is filtered and formed into monofilaments. After leaving the die, the monofilaments are cooled in the water bath to a temperature below the crystallite melting point. The cooling medium is normally water which allows a fast cooling speed [10]. The melted material should flow through the water bath without turbulence and should enter always at a constant temperature, since the properties and dimensional precision of the monofilament is affected by them. Usually, the draw zone of a monofilament line consists of a three roll systems and two heaters [9]. The heater is the unit frequently used for heating the monofilaments for drawing, however a water bath can also be used if the drawing temperature is lower than 100ºC [15]. In order to achieve identical properties for all monofilaments produced it is necessary to keep the temperature and air velocity fluctuations as low as possible over the entire width of the heaters [8]. The

monofilament is maintained under tension and drawn during the heat treatment to modify the structure of the filament, since there is an increase of the molecular mobility and an increase of the orientation during the stretch [16]. Following the heat treatment, the monofilament is relaxed to further increase crystallinity and decrease the degree of amorphous orientation, so with the increment of another heater the molecules will be stretched again, resulting in an increase of the degree of amorphous orientation [16]. Depending on the end product, monofilaments are wound either individually or in fibers. Fibers winding is used to monofilaments processed into cord, ropes hawsers and bristles [9].

1.1.3 Processing characteristics

In the die design and manufacture there are exact requirements that have to be met to achieve monofilaments with consistent shape and dimensions. The monofilaments should have the narrowest possible tolerances in relation to each other as well as in the longitudinal direction. A least possible deviation in roundness is also a requirement [10].

In the manufacture of filaments, a relatively isotropic plastic (with properties similar in all directions) is converted into an orthotopic plastic where most of the plastics strength is in the direction of the fiber axis due to the applied shear stress in the melt flow during the extrusion process [17]. This desirable effect provides a certain degree of filament strength in the longitudinal direction, but usually not enough. So the fiber are made stronger by stretch orientation during or after processing. [8] The physical properties of the monofilament, such as tensile strength, elongation, elastic modulus, shrinkage, shape retention, wear resistance and flexibility are determined by the degree of orientation imparted to the macromolecules filament by the drawing process.

The end-user properties of the filaments mainly depend on the degree of crystallinity as determined by the processing conditions [18]. Crystallization is the result of two processes: nucleation and nuclei growth. The rate of both processes depends on the crystallization temperature as well as on the temperature and duration time of the molten polymer state [19]. So, the degree of fiber orientation is controlled by the quenching conditions and drawing ratio [20] and [21].

1.1.4 Coextrusion

Coextrusion is the simultaneous extrusion of two or more polymers through a single die where the polymers are joined to form distinct well-bonded layers, forming a single extrusion product [8]. This process has been applied in film, sheet, tubing, blown film, wire coating, filaments and other types of profile extrusion. Coextrusion of two or more polymers into layered structures is often performed to achieve a desirable mix of end-use characteristics [22]. The layers thicknesses is controlled by the feed ratio of each extruder [23].

When two or more polymers are coextruded, it is important to produce smooth interfaces between the layers, because an irregular interface is detrimental to the quality of the product, as determined by its mechanical and/or optical properties [24]. Some studies have reported that this interfacial instability is influenced by both the viscosity and elasticity ratios of the two fluids being coextruded and the thickness ratio of the two layers [25].

During coextrusion processing it is important that a combination of materials occurs and not a formation of a new one. It is always necessary that the extruded materials are not mixed, so that it is possible to maintain, in an integral way, the unique properties of each material [26]. To prevent mixing between materials, it is necessary that do not combine miscible materials. Moreover, the combination of immiscible materials it is not advantageous, as in that case there would be no adhesion between the different layers causing delamination. The successful selection of materials for coextrusion involves the use of compatible materials [27]. Additionally, the processing temperatures ranges of the materials used must not be very different, since the materials have to flow in the same flow channel.

A solution found in literature to improve the interfacial stability is to decrease the flow rate by decreasing the screw speed [28]. However, this is not a good solution to the industrial level, because there is a decrease of the production rate.

1.1.5 High strength and abrasion resistance filaments

Research on developing new processes that improve tensile properties can be found in the literature [29], [30], [31]. To improve these properties, treatments such as drawing and/or annealing the filaments are required. Some studies have showed that there is a strong relationship between structural development and the spinning conditions of the melt-spinning process. Two important methods of manufacturing high-performance filaments are increasing the cooling rate combined with rapid quenching for extruding filaments and then drawing at

low strain rates with two-stage drawing processes. These methods allow to obtain a filament with high draw ratios [32].

It is also known that molecular weight and molecular weight distribution have great influence on polymer elongational viscosity, degree of crystallinity, strength, modulus, and elongation at break, and some researchers have worked on the effect of these characteristics on fiber performance by correlating them with process conditions [33], [34]. Some studies have shown that increasing the molecular weight in the polypropylene blends increases tenacity and decreases breaking elongation [34].

To increase the filaments performance, researchers have been working on various deformation methods to increase the orientation in amorphous regions and crystallinity percentage [31]. Some important techniques to improve mechanical properties and the dimensional stability are zone-drawing and zone-annealing methods [35], continuous vibrating zone-drawing [36], constant load oven drawing [37], die drawing [38], hot nip drawing [39], gel-spinning technique [40], adding reinforcing agents [41] and using high performance materials [42]. However, many of these methods have not been commercialized because they have some disadvantages. For instance, in general, these methods need larger production areas, require waste recovery systems, consume high amounts of energy, and require the use of solvents. The techniques can be discontinuous and quite expensive. Moreover, the control of filament cross section, higher amount of waste, very low production rate, and the environment impact and human health are some other important concerns [31].

The increase of fiber abrasion properties allows a lifecycle improvement due to the increase of durability [43]. Previous investigators of plastic abrasion related abrasion resistance to the fracture energy and friction. It was possible to obtain a reasonable correlation with a deformation factor that included the friction of the abrasive sand on the plastic and a term that related to the energy required to deform the material plastically. The more easily the material deforms in contact with a particular abrasive, the better the abrasion resistance [44].

This effect is obtained by coating the filament with a high performance material with better abrasion resistance properties [45], [46]. Another method to improve the abrasion resistance is the lamination templating method that was reported to create superhydrophobic polymer surfaces with excellent abrasion resistance and water pressure stability [47].

1.2 Motivation and objectives

Raw materials available for the plastics industry have a wide disparity as regards the costs, when comparing polymer engineering/standard with high-performance polymers and/or active properties. One possible methodology to significantly reduce costs without compromising performance is the design of coextruded products. Being a process commonly used in the industry, the coextrusion of multicomponent filaments continues to be a challenge. There are numerous variables/parameters that affect the process, including: the process conditions and rheological compatibility.

The main objective of this project was to select the best materials to increase the commercial fiber tribological properties and to define the optimum process conditions.

The production of a coextruded filament can be advantageous, since coextrusion is a complex process and it is not easy to be reproduced by other companies on the market, so the products will be more unique. A simple change on the filament material is much more easy to reproduce. The company has a current commercial filament that is made of a polymer blend, that will be nominated as Blend 1 (B1), compounded by Material 1 (M1) and Material 2 (M2). M1 presents the best tenacity and M2 the highest abrasion resistance. This blend presents a good tenacity (7,5 g/den) but unsatisfactory abrasion resistance for high demanding applications. The main goal of the present study was to perform a systematic research work to verify if the filament abrasion resistance can be improved with a coextruded filament, without affecting its mechanical properties. For this purpose, in addition to B1, different setups for the coextruded filament were tested, involving also M1 and a new blend, Blend 2 (B2), that combines M1 and M2 with different percentages.

1.3 Structure and organization of the dissertation

This dissertation is divided into four chapters. Chapter one presents the introduction where a global introduction of the work is presented, state of art where are described the most relevant information of the topic that has been published, the main goal of the project and motivation and the structure and organization of the dissertation. Chapter 2 comprises the material and methods starting by a brief description of the material systems tested followed by the presentation of the characterisation and production process employed, namely: rheometry, extrusion and coextrusion and tensile and abrasion tests. Chapter 3, presents and discusses the main results obtained along the project, while justifying the path followed in the research work.

Chapter 4 summarizes the main conclusions obtained and presents some recommendations for future works.

2. MATERIALS AND METHODS

This chapter comprises the material and methods starting by a brief description of the material systems tested and followed by the presentation of the characterisation (rheometry, microscopy, tensile and abrasion tests) and production process (extrusion and coextrusion) employed.

2.1 Materials

For the present study, two materials were used: Material 1 (M1) and Material 2 (M2). The M1 has density = 0.952 g/cm^3 and melt mass-flow rate = 0.60 g/10min (190ºC/2.16kg). The M2 has density = 0.905 g/cm^3 and melt mass-flow rate = 1.7 g/10min (190ºC/2.16kg). These materials were obtained in granular form and were stored in regular conditions.

There were two blends produced. The Blend 1 (B1) was compounded by 30% of Material 1 (M1) and 70% of Material 2 (M2) and the Blend 2 (B2) was compounded by 70% of material 1 and 30% of Material 2 as presented in Table 1.

Table 1 - Blends composition

	Material 1	**Material 2**
B1	30%	70%
B2	70%	30%

2.2 Rheometry

To compare the material flow it is needed the rheological constants of that fluid. So, the first step of this project was to characterize the polymer blends and M1. M2 was not characterized because it has poor abrasion resistance. To characterize them, two complementary techniques were employed: parallel plate rheometry and capillary rheometry. The parallel plate rheometry technique evaluates the viscosity at low shear rates while the capillary rheometry technique evaluates the viscosity at high values of shear rate, which are tipycal values the processing

range. The plot of both values allows a construction of a complete flow curve, as illustrated in Figure 2, which presented the relation between viscosity and shear rate.

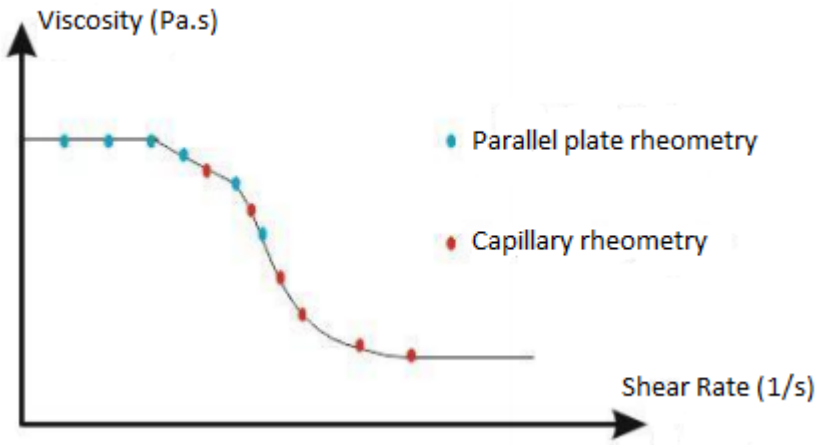

Figure 2 – Example of a flow curve obtained with both parallel plate and capillary rheometry tests [48]

The analyses were carried out at temperatures of 210, 230 and 260 ºC (250 ºC for M1) and to assess reproducibility all tests were performed 3 times. After obtaining the experimental values the best ones were selected to create the flow curve.

Before doing these tests it was needed to blend the materials and produce the samples.

2.2.1 Blend and samples production

The materials were physically pre-mixed and blended in an extrusion line, with Extruder – Periplast, Ltd (D=20 mm, L/D=20) a single screw extruder with the temperature profile of 180/200/230ºC and an extrusion die that allowed the production of a 2mm diameter filament. The extruded filament was cooled in a water bath at 25ºC, dried and cut in pellets form using a granulator (C F SCHEER & CIE, Model D-7000).

The pellets were subsequently used to produce, by compression moulding, the disk samples required for parallel plate rheometry flow tests. The press used to manufacture the sample disks was a Moore – hydraulic, using a temperature of 230ºC. The detailed production procedure is given in Appendix I.

2.2.2 Parallel plate rheometry flow test

The rheological measurements were performed using a shear rheometer (AR G2 - TA Instruments) with stainless steel parallel-plate geometry with a 25 mm diameter. The shear rate varied in ramp mode from 0 to 100 s^{-1} and the gap was set at 2 mm. In Figure 3 is given an example of the results obtained with this test.

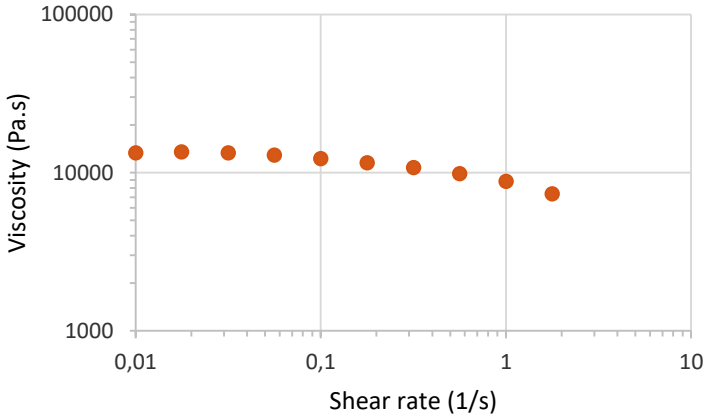

Figure 3 - Example of the parallel plate rheometry results

2.2.3 Capilar rheometry flow test

A twin bore capillary rheometer (RH10 - Malvern Instruments) equipped with two dies with same diameter (2 mm) and different lengths was used. The tested materials were B1, B2 and M1. An initial melting time of 10 min was applied. The instrument was set at constant speed/shear rate mode to a shear rate range of 1 to 1000 s^{-1}.

Both Rabinowitsch-Weissenberg and Bagley corrections were performed as well as the melt viscosity values were calculated by the software FlowMaster®. In Figure 4 is given an example of the results obtained with this test.

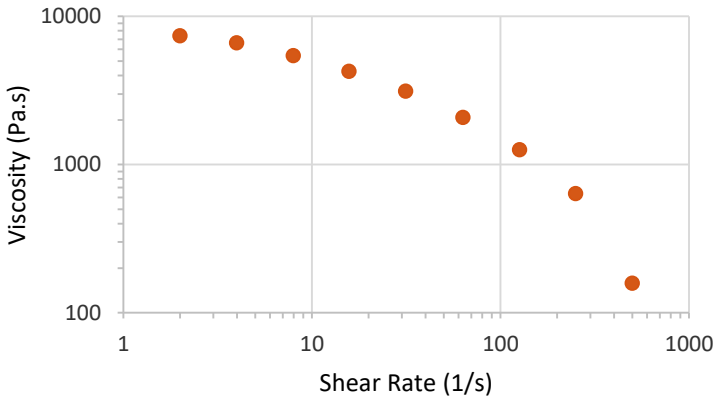

Figure 4 – Example of the capilar rheometry results

2.2.4 Flow curve and rheological model

To obtain the blends flow curves, the time-temperature superposition principle was applied to extend the characterization window of the material, making possible to calculate the viscosity at any temperature from the viscosity at a reference temperature [7]. The model used to fit all the rheological data points were constituted by the Carreau model stated in Equation 1 [7].

$$\eta = \eta_0 a_T [1 + (\lambda a_T \dot{\gamma})^2]^{\frac{n-1}{2}} \quad (1)$$

where $\eta\ (Pa.s)$ is the viscosity, $\eta_0\ (Pa.s)$ is the viscosity at zero shear rate, $\lambda\ (s)$ is the material relaxation time, n is the Power Law index, a_T is the shift factor and $\dot{\gamma}\ (s^{-1})$ is the shear rate.

Using the *Excel* software, the equations mentioned above were applied to the rheological data points for each blend and M1 for the three temperatures used in the rheometry tests. The procedure used to obtain the models rheological constants consist in optimizing the rheological constants using the *Excel* tool *Solver* to minimize the differences between the viscosity values obtained experimentally and by the fitting models. To do so, the *Solver* algorithm was set to use evolutionary methods, thus providing the best possible results. In Figure 5 is given an example of a flow curve with the selected values obtained in the rheometry characterization and the rheological model.

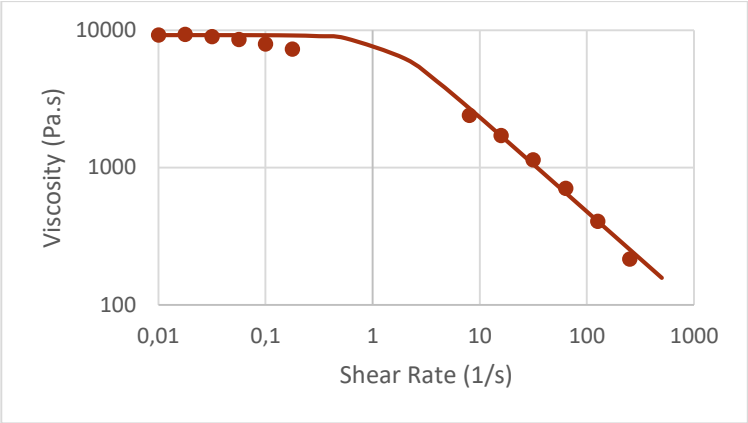

Figure 5 – Fitting of the experimental data with the Carrau model

2.3 Prototype filament extrusion line

In order to obtain the filament properties of each blend and M1, it was necessary to extrude each one separately and characterize it. This subsection presents the methodology used to define the processing conditions of the extruded and coextruded filaments using the prototype filament extrusion line of University of Minho.

2.3.1 Extrusion die

The extrusion line used was a typical line of the filament extrusion with two heaters as shown in Figure 6.

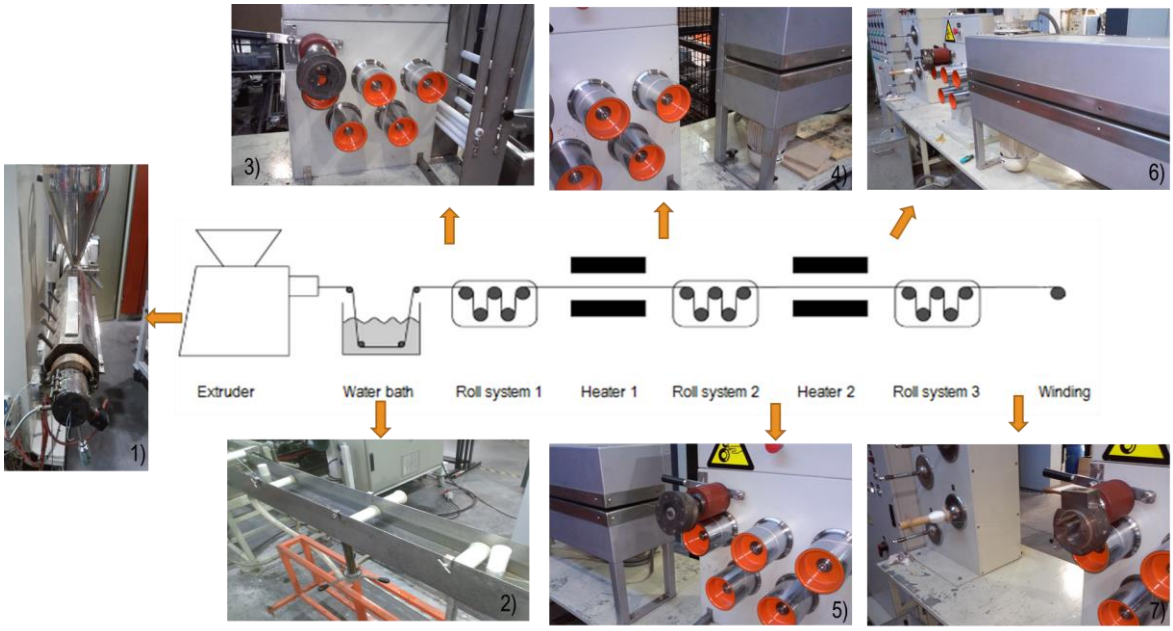

Figure 6 - Scheme of the extrusion line – 1) extruder, 2) cooling system, 3) roll system 1, 4) heater 1 and roll system 2, 5) roll system 2 and heater 2, 6) heater 2, 7) roll system 3 and winding

The filament is extruded and cooled down in a water bath. After that, the filament is guided through the three roll pulling systems where each one has a higher speed than the previous one. For each transition there is a heater responsible to heat the filament. At the end of the line the filament is wrapped.

Filaments were obtained by the extrusion process, performed with Extruder – Periplast, Ltd single screw extruder (D= 25mm, L/D= 25) at a thermal profile of 195/205/230/230ºC, while the screw speed was set at 1,9 rpm. The die temperature was set at 230ºC and the water bath temperature at 25ºC. The Roll System 1 Speed were changed in order to obtain a stretch ratio (difference between the Roll System 1 and Roll System 3 speeds) of 8, 9, 10, 11 and 12. The other process variables (Roll System 2 Speed, Roll System 3 Speed and heaters temperature) were kept constant.

With that set it is possible to obtain filaments with different stretch ratios but with the same denier.

2.3.2 Coextrusion die

In this phase, the main goal was to coextrude two monofilaments with two layers and different stretch ratios and characterize them to compare with the monofilaments extruded before. In both cases, the inner layer was made with B1, but the external layer in one case was composed with B2 and the other one with M1 as illustrated in Figure 7.

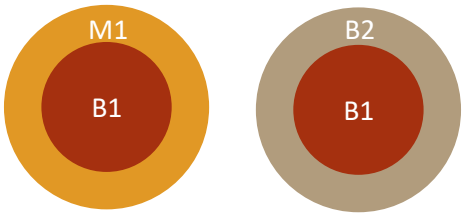

Figure 7 - Scheme of the coextruded filaments. On the left it was used M1 on the external layer and, on the right, B2 on the external layer

Using the simulations produced by another student [7] it was possible to determine that the ideal percentage of each layer in order to the flow on the channel has the same velocity is 33% in the exterior layer and 67% in the inner layer. To obtain these values experimentally it was coextruded filaments with different rotational screw speed and made a microscopy analyses to evaluate the area of each layer. The procedure of this analyses is presented in subsection 2.5.3. Since one of the extruders had a minimum rotational screw speed of 5 rpm it was determined that would be the speed of this extruder in order to keep the process speed slower. So, the variation of rotational screw speed was made just in the other extruder to obtain the percentages of extruded material.

After the rotational screw speed of each extruder was determined, it was possible to start the coextrusion process presented in Figure 8.

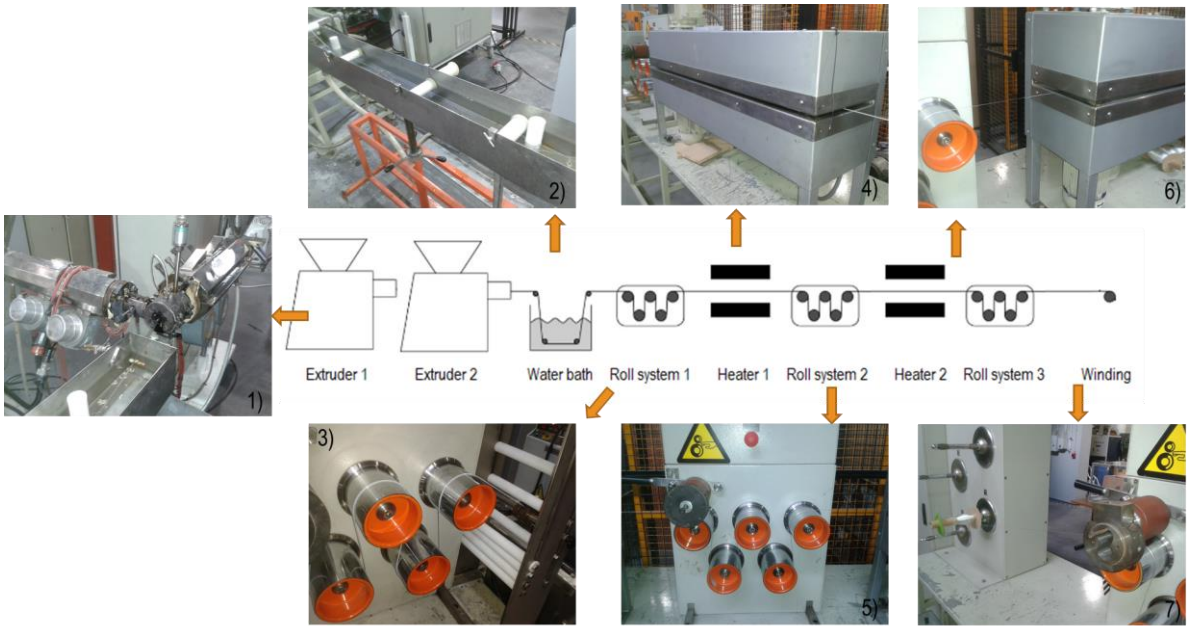

Figure 8 - Scheme of the coextrusion line - 1) two extruders are linked to one die, 2) cooling system, 3) roll system 1, 4) heater 1 and roll system 2, 5) roll system 2 and heater 2, 6) heater 2, 7) roll system 3 and winding

The process is the same as in the filament extrusion, but instead of being just one extruder, there are two extruders feeding a single die.

The filaments were obtained by coextrusion, performed with two single screw extruders (Extruder – Periplast, Ltd (D= 25mm, L/D= 25)) at a thermal profile of 195/205/230/230ºC in each one, while the screw speed was set at the values determined before. The die temperature was set at 230ºC, the water bath temperature at 25ºC. The Roll System 1 Speed were changed in order to obtain a stretch ratio of 9, 10 and 11. The other process variables (Roll System 2 Speed, Roll System 3 Speed and heaters temperature) were kept constant.

2.3.3 Filament extrusion with a coextrusion die

Due to the difference of the diameter between of the die used in the extrusion filament and in the coextrusion one, a big difference on the fiber denier was obtained each made their comparison inadequate. So, it was needed to extrude the monofilaments B1 and B2 again but with a higher diameter. In order to obtain that, it was used the coextrusion line, but with only one extruder working to extrude the filaments.

The filaments were obtained by extrusion, performed with a single screw extruder (Extruder – Periplast, Ltd (D= 25mm, L/D= 25)) at a thermal profile of 195/205/230/230ºC, while the screw speed was set at 7,3 rpm. The die temperature was set at 230ºC, the water bath temperature at 25ºC and the heaters temperature at 140ºC. The Roll System 1 Speed was changed in order to

obtain a stretch ratio of 9, 10 and 11. The other process variables (Roll System 2 Speed and Roll System 3 Speed) were kept constant.

2.4 Semi-industrial filament extrusion line

It was not possible to extrude the M1 in the extrusion line of the university due to the sensibility of the material at any processing variation. The extrusion was horizontal and should be vertical and the heaters were not isolate so the heating was not uniform. Due to that problems, the extrusion of this material was made in the *WireCo* facilities where the process was much more controlled.

The process had the same configuration of the previous one (with two heaters and three roll systems). However, in this case the extrusion was made in vertical position and the heaters were totally isolated as illustrated in Figure 9.

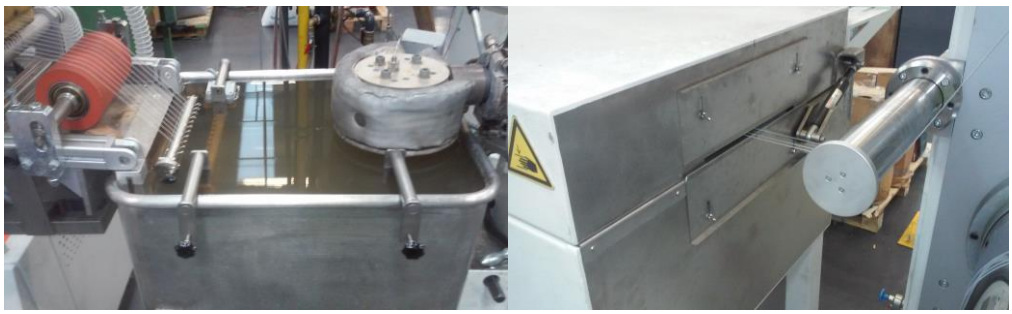

Figure 9 - Company extrusion line. On the left side is presented the vertical extrusion and on the right side the heaters isolation

A vertical extrusion allows the cool down of the filaments immediately after the extrusion, each preserves the small orientation obtained during the die flow. With the horizontal one there is a gap between the extrusion die and the water bath so the molecules have time to relax the orientation suffered. Besides that, the filament will be submitted to the gravity force during that gap which will create stretching zones and a non-uniform filament. A totally covered heater allows that a temperature inside it is the same and, since the polymer viscosity has a significant variation with the temperature, a variation on temperature will result in different viscosities. This variation will result in an earlier filament break when the filament is approaching the limit of the stretching, so the control of the temperature inside the heaters is very important to control the process.

In this case, the filaments were obtained by extrusion, performed with a single screw extruder at a thermal profile of 180/195/205/230/230, while the screw speed was set at 4,3 rpm. The die temperature was set at 230ºC, the water bath temperature at 20ºC and the heaters at 120ºC. The

variable that was changed was the Roll System 3 Speed due to the set up of the extruder. Since it was an automatic process when the stretch ratio was selected (8, 9, 10, 11 and 12) the variables changed automatically.

2.5 Physical characterization

This subsection comprises the methodology used to characterize the filaments tenacity, elongation and abrasion resistance. Microscopy tests were made to characterize the coextruded filaments and to obtain the percentage between layers.

2.5.1 Tenacity

The first step was to calculate the denier of each filament. To obtain that value it was weighted a filament of 9 m and multiplied that value by 1000, in order to obtain the weight corresponding to 9000 m.

The tensile tests were made on a Zwick/Roell Z005 with a specific tool designed for filament tests as observed in Figure 10.

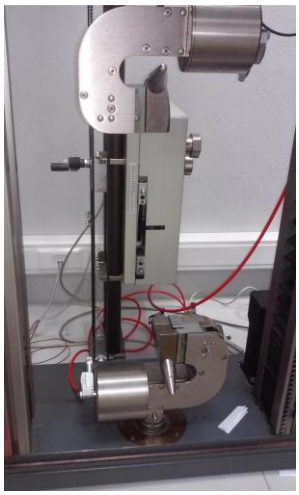

Figure 10 - Tools used in the tensile tests

Before starting the test, it was selected the denier of the fiber on the software that after finishing the test show the results of elasticity modulus, tenacity, elongation and peak strength. All tests were performed 10 times.

2.5.2 Abrasion resistance

The abrasion resistance tests were performed with the installation presented on the Figure 11.

Figure 11 - Abrasion resistance tests installation

The test speed was 70 rpm and the filament was attached to a weight of 3% of the value of peak strength obtained in the tensile test and wrapped around himself for one and a half turns. All tests were performed 5 times.

2.5.3 Microscopy

A sample of filament was coextruded with a selected rotational screw speed and cooled down to room temperature (around 20 ºC). With this filament it was prepared 3 samples of 15 µm in microtome *Leitz* for microscopy observation in the *Olympus BH2*. With the images taken in the microscopy it was possible to measure the area of each layer using the software *Leica Application Suite v.4.4.* and if it was not obtained the percentages needed the rotational screw speed of the extruder changed and this process was repeated until reach that values.

3. RESULTS AND DISCUSSION

This chapter presents and discusses the main results obtained along the project, while justifying the path followed in the present research work. The first subsection is the Rheometry flow tests where the results are presented and discussed. The next subsection, Extrusion, comprises the processing conditions and characterization of the extruded filaments. Coextrusion is the third subsection where is presented the processing conditions and characterization of the coextruded filaments. Extrusion of filaments with higher denier, the fourth subsection, comprises the processing conditions of the extruded filaments using the coextrusion die and a comparison of their properties. The last chapter is the Overall properties comparison, where different filaments are compared to identify the best configuration of material.

3.1 Rheometry flow tests

3.1.1 Parallel plate flow test

During the parallel plate flow test, that had a duration of 35 min, the test samples seem to degrade above certain temperatures. After the tests, the samples were collected and organized by temperature as shown in Figure 12 to 14.

Figure 12 - Parallel plate flow samples of M1

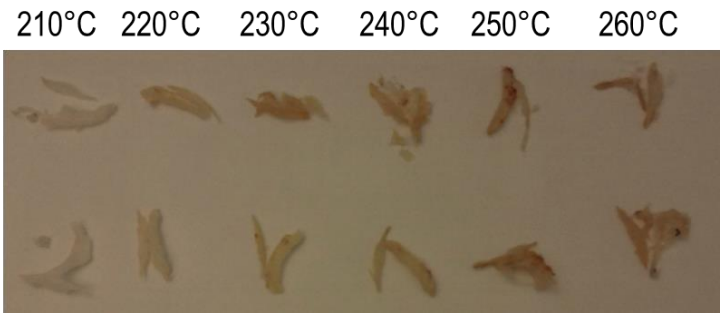

Figure 13 - Parallel plate flow samples of B1

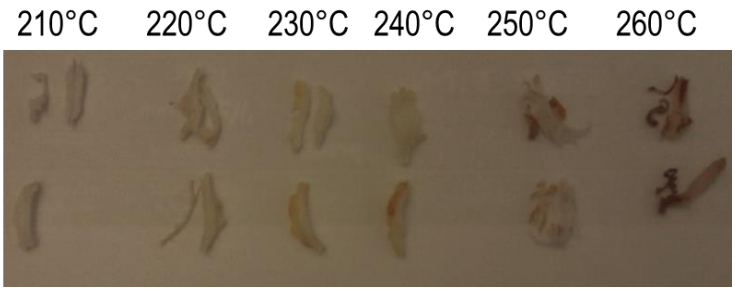

Figure 14 - Parallel plate flow samples of B2

Looking at Figure 13 and 14 there is a small portion of the sample that presents a colour change above 220ºC. This portion was the sample part that was exposed to oxygen during the test, and this effect is becoming more evident with temperature increase. However, above 230ºC there is a colour change in the entire sample. From these results the processing temperature was defined to be 230ºC to avoid material degradation.

3.1.2 Rheometry flow tests

Table 2 shows the rheological constants for the Carreau model of the blends.

Table 2 - Rheological constants for the Carreau model

	$\eta_0\ (Pa.s)$	$\lambda\ (s)$	n	$E\ (J/mol)$
B1	14684	0.50	0.23	20690
B2	9239	0.73	0.31	38734
M1	11416	0.35	0.37	3069

The values obtained were used to plot the selected experimental flow curve experimental data for B1, B2 and M1, which are illustrated in Figures 15 to 17. In Appendix II all the values obtained on the different tests performed are provided.

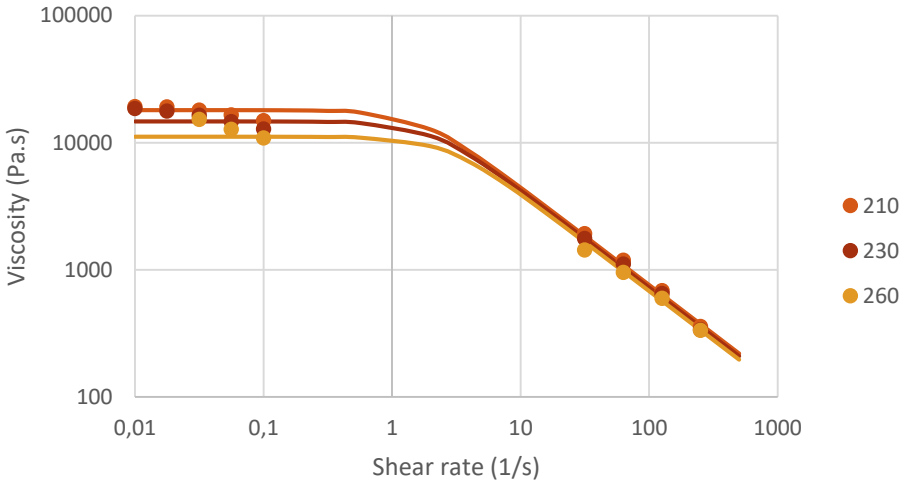

Figure 15 – Flow curve for B2 experimental data and constitutive model fit

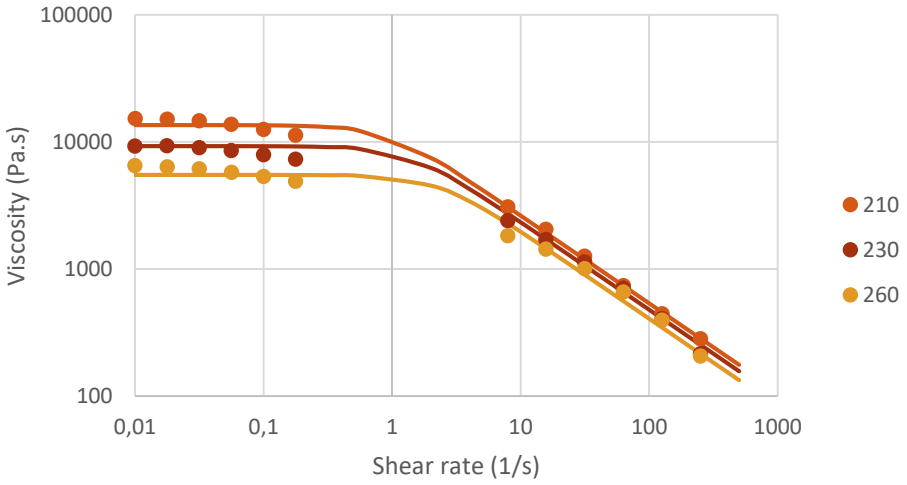

Figure 16 - Flow curve for B1 experimental data and constitutive model fit

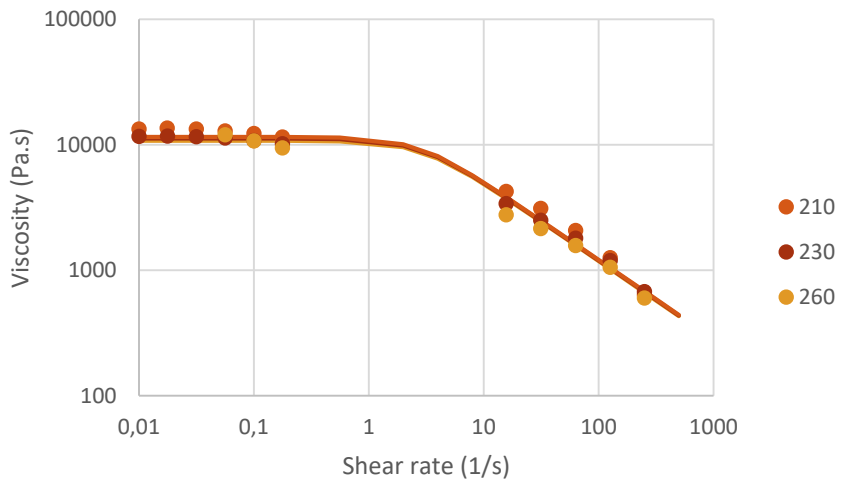

Figure 17 - Flow curve for M1 experimental data and constitutive model fit

The values registered in Figures 15 to 17 for shear rates up to 1 s^{-1} were obtained from parallel plate rheometry while the data for higher shear rates were collected during capilar rheometry. The onset of melt fracture occurred for shear rate values slightly above 500 s^{-1}, for all materials and temperatures, thus the flow curves were built just with shear rate values up to 500 s^{-1}. This happened because in the experimental test the gap between shear rates selected was high so small variations on the shear rate was not detected. This result provides relevant information for the debit to avoid exceeding this limit value, otherwise the same type of rheological defect may appear in the product.

Temperature affects the rheological behaviour of the tested materials, since there is a small decrease of the viscosity with the temperature increase as illustrated in Figures 15 and 16. High temperatures lead to an increase of the free volume, allowing more space for the polymer chain motions and thus reduced friction between them [49]. This increase of molecular mobility results in a decrease of viscosity. It is also evident that the decrease of viscosity with temperature is shear rate dependent. A stronger temperature dependence of viscosity occurs at lower shear rates as presented in Figure 16. As the shear rate increases, the polymer-chains are getting more oriented which results in a more pronounced effect of shear rate resistance even with the temperature increasing. However, these effects are not observed in Figure 17 where the viscosity variation with the temperature increase it is just slightly higher to M1.

With the increase of the percentage of M2 in the blends composition the viscosity decrease, due to the lower viscosity of this material.

3.2 Extrusion

3.2.1 Process setup

The processing conditions provided in the next subsection were obtained after a long trial-and-error process, that allowed to achieve stable processing conditions. The most relevant difficulties during that stage and the respective solutions devised are describer hereafter.

One of the most important issues encountered was the control of the filament lateral displacement out of the die. Since there was no friction between the water bath and the Roll System 1, the filament went moved freely and frequently came out of the rolls. To overcome this problem a tissue cluster was used to increase the tension of the filament between these two places.

Another problem that was observed was the influence of the speed of the Roll System 1. If this speed was too high (more than 5 m/min) the filament was stretched right after exiting the extrusion die, so during the stretch between Roll System1 and 2 the required stretch ratio was not achieved. The solution was to manufacture the filament with a Roll System 1 speed around 3 m/min.

Inhomogeneity in the temperatures in the heaters was also a difficulty that had to be solved to achieve stable process conditions. An increase of the Roll System should be accompanied by an increase in the temperature of the heaters, because the time that the filament spends inside the heaters is reduced. Consequently, for temperatures below 100 ºC and higher than 140ºC the filament could not stand the load imposed and broke with stretch ratios below the target values. This can be explained by the temperature being too low to provide the required molecular mobility in the first case, and, in the second case, the temperature was too high and the filament fully melted inside the heater. So, the temperature was kept between 100ºC and 140ºC.

However, with this processing line was possible to produce B1 and B2 filaments. The processing of M1 was made in the *WireCo* facilities where the process was better controlled since the material shown to be very sensitive and no stable process conditions were obtained.

3.2.2 Monofilament extrusion

After some trial and error process it was possible to obtain the processing conditions of the Blend 1 and Blend 2 presented in Table 3 and Table 4, respectively.

Table 3 – Monofilament B1 processing conditions

Stretch Ratio	Rotational Screw Speed (rpm)	Die Temperature (ºC)	Water Bath Temperature (ºC)	Roll System 1 Speed (m/min)	Roll System 2 Speed (m/min)	Roll System 3 Speed (m/min)	Heater temperature (ºC)
8	1,9	230	25	4,4	33,5	35	125
9	1,9	230	25	3,9	33,5	35	125
10	1,9	230	25	3,5	33,5	35	125
11	1,9	230	25	3,2	33,5	35	125
12	1,9	230	25	2,9	33,5	35	125

Table 4 – Monofilament B2 processing conditions

Stretch Ratio	Rotational Screw Speed (rpm)	Die Temperature (ºC)	Water Bath Temperature (ºC)	Roll System 1 Speed (m/min)	Roll System 2 Speed (m/min)	Roll System 3 Speed (m/min)	Heater temperature (ºC)
8	1,9	230	25	2,8	21	22	120
9	1,9	230	25	2,4	21	22	120
10	1,9	230	25	2,2	21	22	120
11	1,9	230	25	2,0	21	22	120
12	1,9	230	25	1,8	21	22	120

The only variable that changed was the Roll System 1 Speed, because that way it is possible to obtain filaments with different stretch ratios but with the same denier as observed in Table 6.

The processing of the M1 monofilament was made at the *WireCo* facilities with the processing conditions presented in Table 5.

Table 5 – Monofilament M1 processing conditions

Stretch Ratio	Rotational Screw Speed (rpm)	Die Temperature (°C)	Water Bath Temperature (°C)	Roll System 1 Speed (m/min)	Roll System 2 Speed (m/min)	Roll System 3 Speed (m/min)	Heater temperature (°C)
8	4,3	230	20	2,8	15	22,4	120
9	4,3	230	20	2,8	15	25,2	120
10	4,3	230	20	2,8	15	28	120
11	4,3	230	20	2,8	15	30,8	120
12	4,3	230	20	2,8	15	33,6	120

This extrusion line did not allow to control the roll system speeds individually, the adjustable variable was the stretch ratio, which was achieved by a modification of a Roll System 3 Speed thus affecting the filament denier, as indicated in Table 6. This did not happen for both blends filament, since the prototype extrusion line allowed to control independently the roll system speed.

Table 6 – Monofilament denier of the blends and the M1 (g/9000m)

Stretch Ratio	B1	B2	M1
8	485	515	510
9	480	520	460
10	480	530	410
11	475	525	370
12	480	545	340

As observed in Table 6, the change of speed of the Roll System 1 does not have effect on the filament denier as observed to the denier values of monofilament B1 and B2, but a change on speed of the Roll System 3 effect it, as showed in the denier values of monofilament M1. The denier of the produced monofilament depends only on the ratio between the extrudate velocity after leaving the extrusion die and the speed of the last Roll System. Changes on the intermediate speeds do not have any effect on the denier.

3.2.3 Filaments characterization

Two tests were done to characterize the filaments, one for evaluating their tenacity and elongation, and another to quantify the abrasion resistance. The results of this characterization are illustrated in Figures 18 to 20.

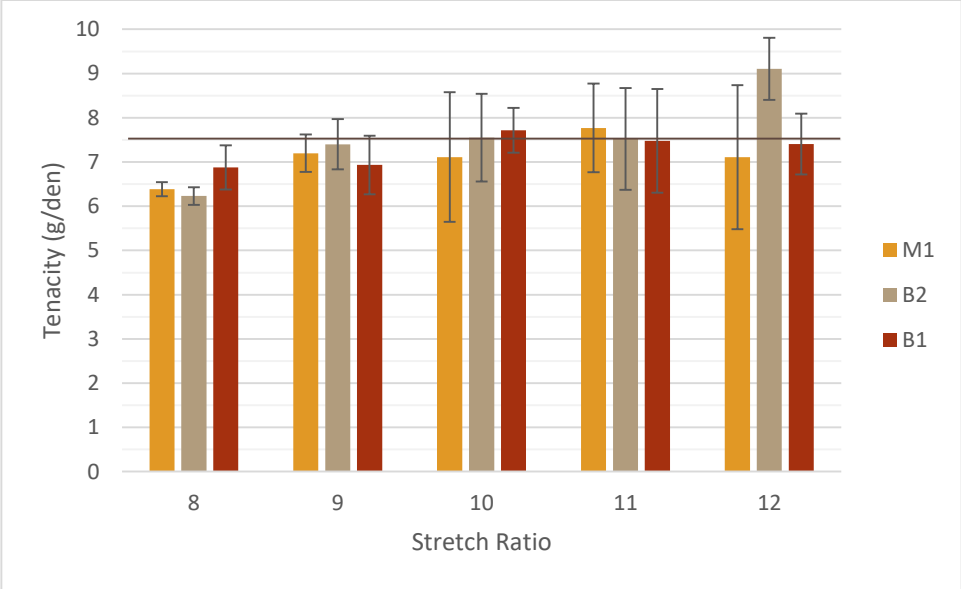

Figure 18 – Tenacity/denier values of the extruded filaments as function of the Stretch Ratio

As shown in Figure 18, with increasing stretch ratio, the molecules are more oriented in the direction of stretching, explaining the slight rise of tenacity values with the stretch ratio.
Looking at the average values, the blends filaments present better properties than M1 filament due to the presence of M2 which has higher tenacity properties. However, considering the standard deviation, the values overlap in most cases, which makes this result inconclusive.
Generally, the M1 does not satisfy the requirement of 7.5 g/den in most cases, but the blends possess values near the requirement, or even slightly above for stretch ratios higher than 10.

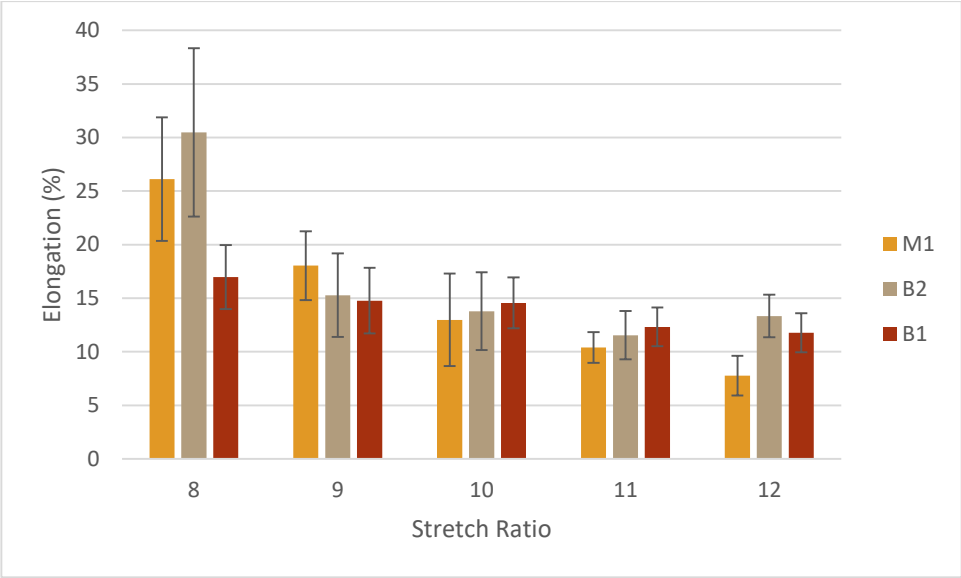

Figure 19 - Elongation values of the extruded filaments as function of the Stretch Ratio

Looking at the elongation results, provided in Figure 19, it can be concluded that there is a decrease in elongation with an increase in stretch ratio. This can be explained by the stretching that is applied to the filament during the extrusion process. With a lower stretch ratio, the filament is not so stretched, so during the tensile test the molecules still have some ability to orient, resulting in higher elongation values. On the opposite side, in filaments with higher stretch ratios, the molecules are already highly oriented, so during tensile tests they cannot stretch much more, resulting in lower elongation values. At stretch ratio values of 11 and 12, the results are very similar which means that the material has reached its maximum elongation capacity.

The elongation values obtained from the blends and M1 are similar, so this property will not affect the material selection for the coextrusion process.

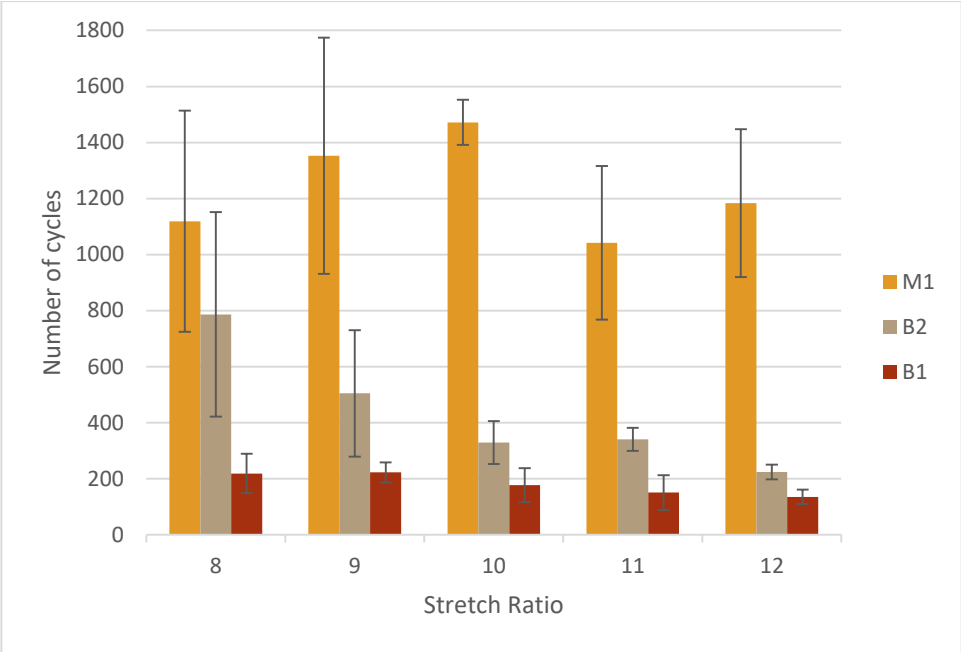

Figure 20 - Abrasion resistance values of the extruded filaments as function of the Stretch Ratio

Concerning the abrasion resistance results, presented in Figure 20, it is clear the higher values of M1 when compared with the blends. The abrasion resistance decreases with increasing of M2 in the blend, an additional proof that M1 has better abrasion resistance properties than M2. It is also observed that the abrasion resistance results in different stretch ratios are similar, showing that variable has no effect on the property.

In an overall analyses, considering all the results studied, M1 filament has the best abrasion resistance, but lowest tenacity, while for B1 filament the conclusions are the opposite. The B2 filament presents a good balance of all the evaluated properties.

Since for value of stretch ratio of 8 none of the filaments satisfy the minimum requirement of 7.5 g/den and to value of 12 the materials are in their limit of elongation properties, it was determined that these two limits of range will not be studied in the subsequent phases. So, the next phase is to coextrude and characterize the filaments M1+B1 and B2+B1 at stretch ratios of 9, 10 and 11.

3.3 Coextrusion

3.3.1 Coextrusion of filaments with B2 in the external layer

Aiming to achieve a percentage of layers of 67%/33%, after performing several tests with different screw rotation speeds combination, it was determined that extruder B2 would work at a screw rotation speed of 5 rpm and the other, extruder B1, at 6.6 rpm to maintain low processing speed. In Figure 21 is illustrated the cross section of a filament manufactured with that conditions. The details of this trial-and-error study are provided Appendix III.

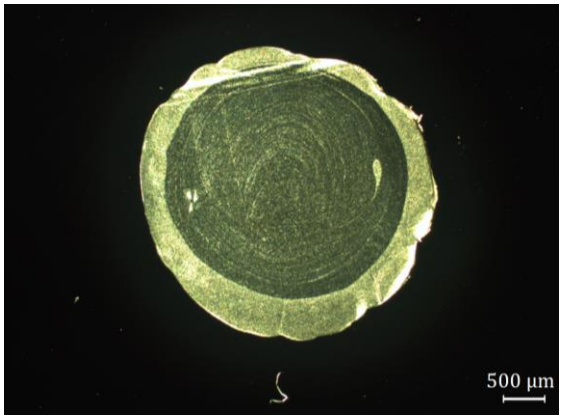

Figure 21 - Microscopy sample of cross-section B2+B1 filament with percentages between layers of 67,6%/32,4%

As shown in Figure 21, the filament outer layer has a non-uniform thickness, and thus eccentricity layers. However, the two layer are well distinguished and there is no formation of a third material which indicates a good interface.

Some filament samples were difficult to prepare for microscopy as stated in section 2.5.3. The sample shown in Figure 22 is one of that examples. During the sample preparation, more precisely when the sample was placed on lamella, the outer layer was delaminated. This result could evidence that the layers bondage is weak, which may influence negatively the filament properties.

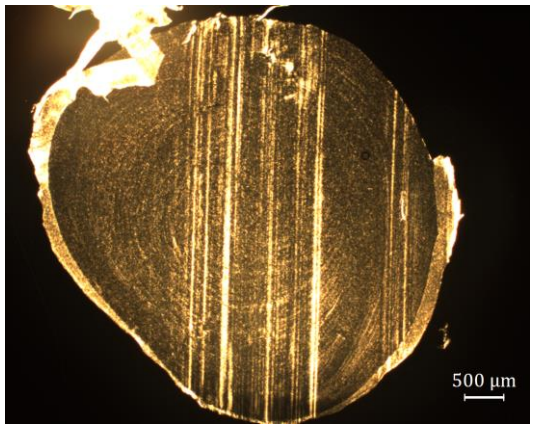

Figure 22 - Microscopy B2+B1 filament sample obtained with a rotational screw speed of 15,3 rpm

On Table 7 the operational conditions of filament coextrusion with B2 in the external layer with stretch ratios of 9,10 and 11 are presented.

Table 7 - Processing conditions of coextrusion of the filament with B2 in the external layer

Stretch Ratio	Rotational Screw Speed of Extruder 1 (rpm)	Rotational Screw Speed of Extruder 2 (rpm)	Die Temperature (ºC)	Water Bath Temperature (ºC)	Roll System 1 Speed (m/min)	Roll System 2 Speed (m/min)	Roll System 3 Speed (m/min)	Heaters temperature (ºC)
9	5	6,6	230	25	6,1	53,1	55	120
10	5	6,6	230	25	5,5	53,1	55	120
11	5	6,6	230	25	5	53,1	55	120

3.3.2 Coextrusion of filaments with M1 in the external layer

A similar procedure to the one presented in the previous section was applied to manufacture the coextruded filament with of M1 in the outer layer. The rotational screw speed obtained for a percentage between layers of 67%/33% was 5 rpm for one extruder and 5.3 rpm for the other one as shown in Figure 23.

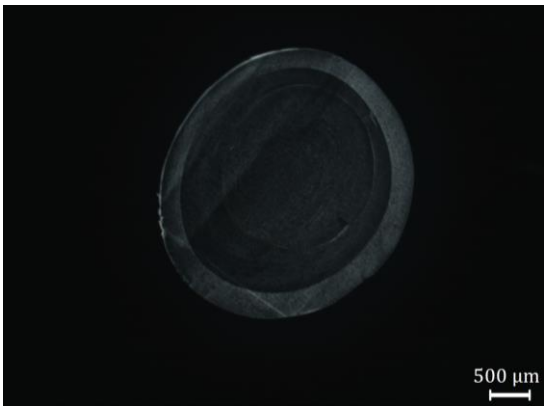

Figure 23 - Microscopy sample of cross-section M1+B1 filament with percentages between layers of 67,5%/32,5%

On the Table 8 are presented the operational conditions of filament coextrusion with M1 in the external layer with stretch ratios of 9,10 and 11.

Table 8 - Processing conditions of coextrusion of the filament with M1 in the external layer

Stretch Ratio	Rotational Screw Speed of Extruder 1 (rpm)	Rotational Screw Speed of Extruder 2 (rpm)	Die Temperature (ºC)	Water Bath Temperature (ºC)	Roll System 1 Speed (m/min)	Roll System 2 Speed (m/min)	Roll System 3 Speed (m/min)	Heaters temperature (ºC)
9	5	5,3	230	25	3,7	30,2	33	155
10	5	5,3	230	25	3,3	30,2	33	155
11	5	5,3	230	25	3	30,2	33	155

3.3.3 Denier comparison of the extruded and coextruded filaments

After weighing the coextruded filaments, the denier was measured and summarized in Table 9.

Table 9 – Denier values of the extruded and coextruded filaments (g/9000m)

Stretch Ratio	B1	B2	M1	M1 B1	B2 B1
8	485	515	510	-	-
9	480	520	460	2830	1860
10	480	530	410	2610	1890
11	475	525	370	2850	1880
12	480	545	340	-	-

Since the coextrusion die diameter was larger than the one of the extrusion die, a significant difference was obtained on the filament denier, between the extruded and the coextruded, so the comparison of theirs properties would be inadequate. For this reason, it was necessary to also extrude the filaments with the coextrusion die to obtain products with comparable deniers.

3.4 Extrusion of filaments with higher denier

To extrude filaments with the coextrusion die, it was used two extruders linked to the same die, but with just one working, since the other one was turned down. Since M1 did not fulfil the client requirement in the previous section it was not studied in this phase.

The identified processing conditions for B1 and B2 filaments are presented in Table 10 and Table 11, respectively.

Table 10 - Processing conditions of the B1 extrusion with the coextrusion die

Stretch Ratio	Rotational Screw Speed (rpm)	Die Temperature (ºC)	Water Bath Temperature (ºC)	Roll System 1 Speed (m/min)	Roll System 2 Speed (m/min)	Roll System 3 Speed (m/min)	Heaters temperature (ºC)
9	7,3	230	25	3,7	30	33	140
10	7,3	230	25	3,3	30	33	140
11	7,3	230	25	3	30	33	140

Table 11 - Processing conditions of the B2 extrusion with the coextrusion die

Stretch Ratio	Rotational Screw Speed (rpm)	Die Temperature (ºC)	Water Bath Temperature (ºC)	Roll System 1 Speed (m/min)	Roll System 2 Speed (m/min)	Roll System 3 Speed (m/min)	Heaters temperature (ºC)
9	7,3	230	25	3,7	30	33	140
10	7,3	230	25	3,3	30	33	140
11	7,3	230	25	3	30	33	140

Again, the only variable that was changed along the different trial was the Roll System 1 speed, to obtain filaments with different stretch ratios, but the same linear mass. The denier obtained for that conditions is given in Table 12.

Table 12 - Denier of the coextruded and extruded filaments with higher diameter (g/9000m)

Stretch Ratio	M1 B1	B2 B1	B1	B2
9				
10	2610	1890	2550	2070
11	2850	1880	2480	1930

With the new setup, it was possible to obtain denier with the same order of magnitude for all the studied filaments. The variation presented in Table 12 between filaments was due to a small variations during the manufacturing of the filaments that was impossible to control.

3.5 Overall comparison of the properties

After extruding all the filaments, a comparative analysis of their properties was carried out.

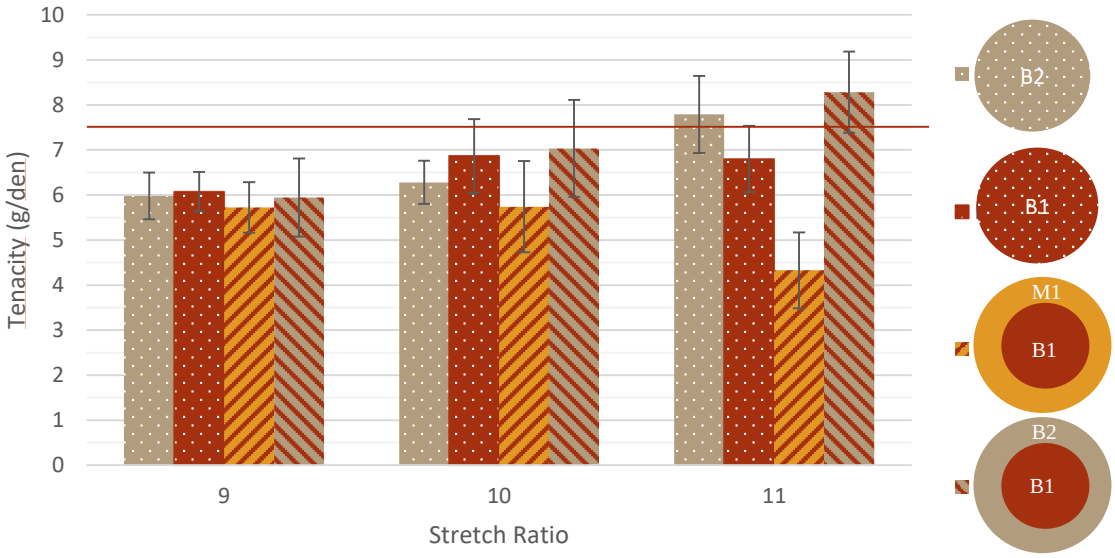

Figure 24 - Comparison of the tenacity values of extruded and coextruded filaments as function of the Stretch Ratio

The results presented in Figure 24 show that only two possibilities accomplish the filament specification of 7.5 g/den for the tenacity. The coextrusion of M1+B1 presents very low tenacity so it cannot be used in this application. However, B2 and B2+B1 filaments fulfil the established

requirement, for a stretch ratio of 11. In fact, the addition of a layer of B2 at the currently commercial filament B1 did not affect tenacity.

The effect of the stretch ratio on tenacity is also evident from the results obtained, since it was only possible to manufacture the required filaments with 11 for the stretch ratio, the highest value tested.

In order to determine which filament is the best, it was necessary to examine all the properties simultaneously. The results shown in Figure 31, were normalized to a range [0-1], where 1 is the best value obtained for each property. Since the M1+B1 filament did not fulfil the tenacity requirement, it was not included in the following analyses.

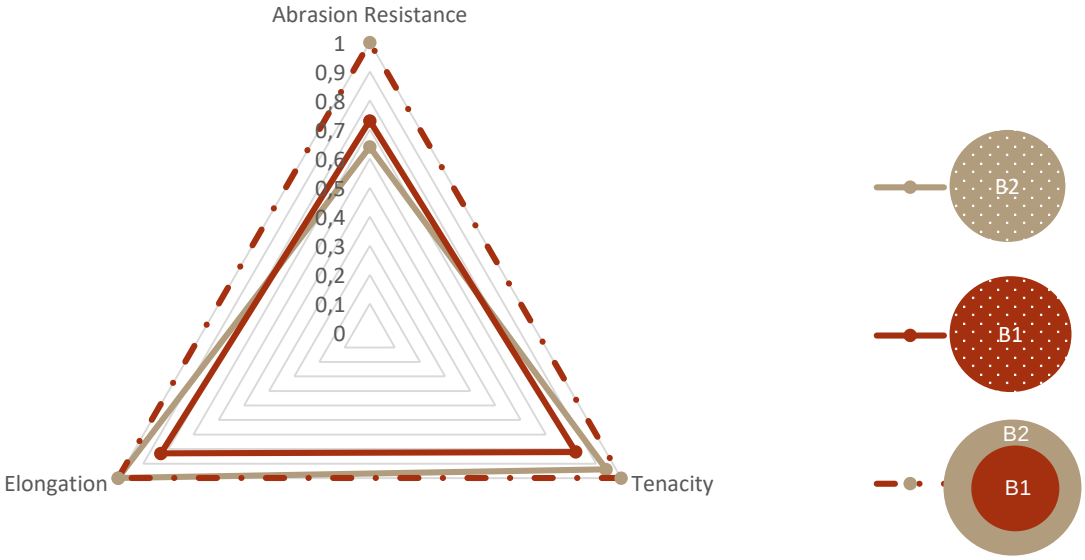

Figure 25 - Properties diagram of the extruded B1, B2 and coextruded B2+B1 filaments

From the plotted results presented in Figure 25, one can easily conclude that the coextruded filament B2+B1 presents the best results for all the evaluated properties. In comparison with the commercial filament is about 15% better in elongation and tenacity, and has 35% higher abrasion resistance. B2 filament has almost the same elongation and tenacity properties, but show a lower abrasion resistance and, since this is the property which is sought to further improve the change of the material is not justified. However, this result was not expected since B2 has a higher percentage of M1, which has higher abrasion resistance. The presence of M2 in lower percentage can act as an impurity, which allows a lower performance of this blend.

Thus, the conclusion is that the co-extruded filament B2+B1 is the best option to improve the currently available commercial filament.

4. CONCLUSION

Concerning to the rheological characterization, the temperature increasing has almost no effect on viscosity variation to M1, but it has on the blends. However, all the tested materials presented a decrease of viscosity with an increase of shear rate.

About the extrusion process there are some conclusions that were registered. In the extrusion line is recommended a vertical extrusion directly to a cool system and a good isolation of the heaters to minimize the instabilities during the process. The heaters temperature should be carefully selected since it has a great effect in the process, the temperature should be enough to provide some mobility to the material molecules to be stretched, but not too much to avoid the filament melting.

About the physical characterization it is possible to conclude that with an increase of stretch ratio there is an increase of tenacity, but a decrease of elongation.

Overall, the option that better fulfil the established specifications is the coextruded B2+B1 filament with Blend 2 in the external layer.

The methodology used in this project was efficient and it can be followed in future works for improving fiber properties through the use of a coextrusion processes. However, it is still needed to use these filaments in the ropes and evaluate their performance to understand if that filament improvement on the abrasion resistance property results in a rope property improvement. That is the next phase of the project.

Other analyses that is recommended to be done in future works is the evaluation of the bondage between the filament layers.

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APPENDIX I – PARALLEL PLATE RHEOMETRY SAMPLE PRODUCTION

The samples production was made following the procedure (Figure 26):

1. Put a Teflon sheet in a metallic board and put the mould on top of that;
2. Fill the mould with pellets of the material or blend that will be characterized;
3. Cover that with another Teflon sheet and metallic board;
4. Pressurize the set in a hydraulic press at 230 ºC during 5 minutes at 20 Pa (in order to melt the pellets). After that, increase the pressure to 50 Pa during more 5 minutes;
5. Cool down the system until reach a temperature of 40 ºC;
6. Take out the system of the press and demould the polymer board;
7. Cut the polymer board into disks form of 25 mm.

This procedure was made to Blend 1, Blend 2 and Material 1.

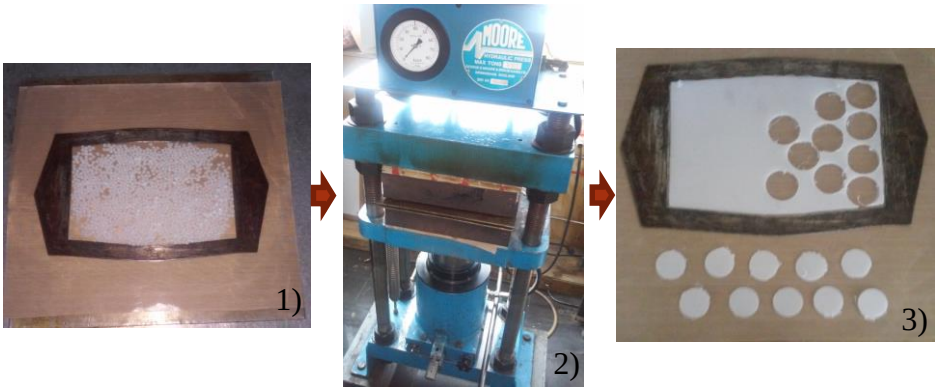

Figure 26 - Samples production – 1) fill the mould on top of a metallic board and teflon sheet, 2) pressurization, 3) demould and samples cut

APPENDIX II – RHEOMETRY TESTS RESULTS

In the following figures is presented the results of the parallel plate and capillary rheometry flow tests of the blends and M1.

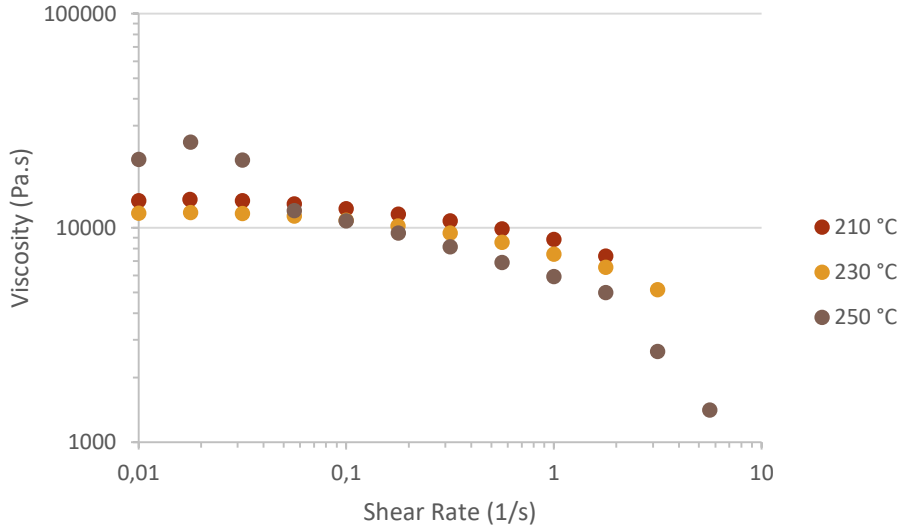

Figure 27 - Parallel plate rheometry flow test - M1 values

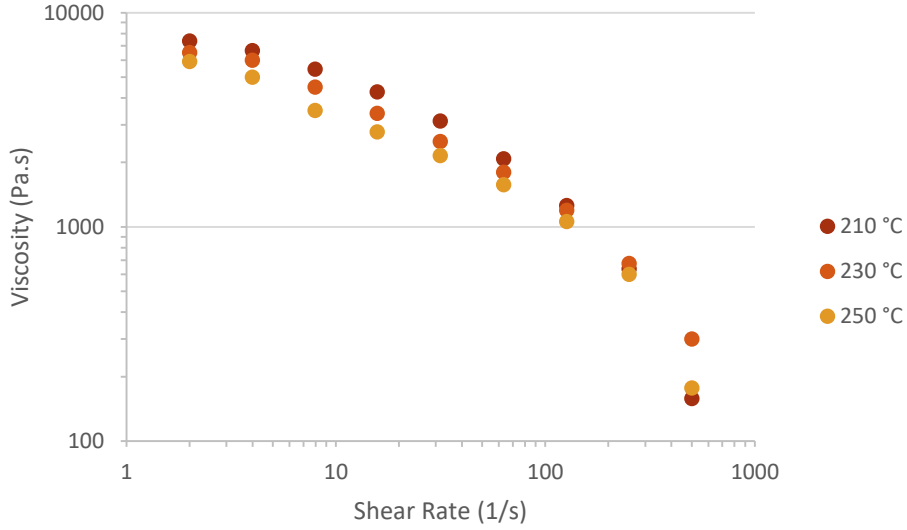

Figure 28 - Capilar rheometry flow test - M1 values

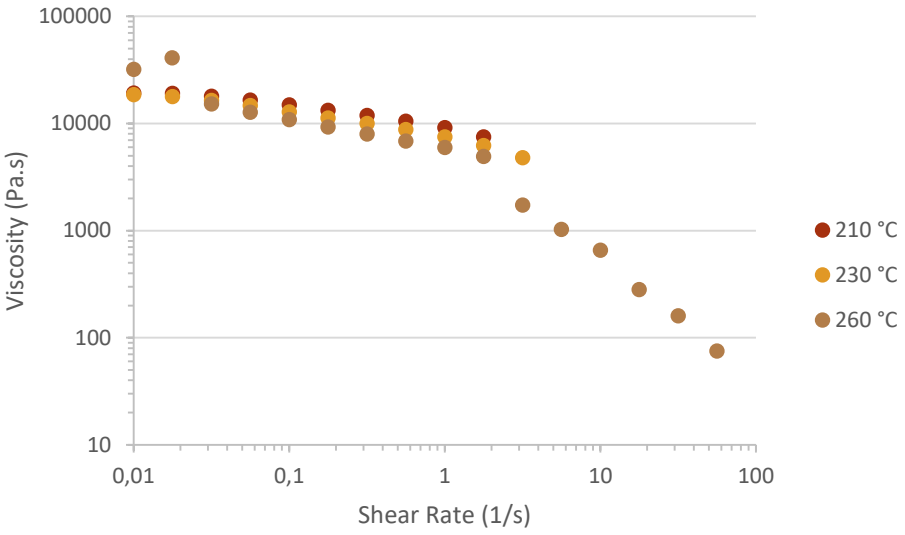

Figure 29 - Parallel plate rheometry flow test – B2 values

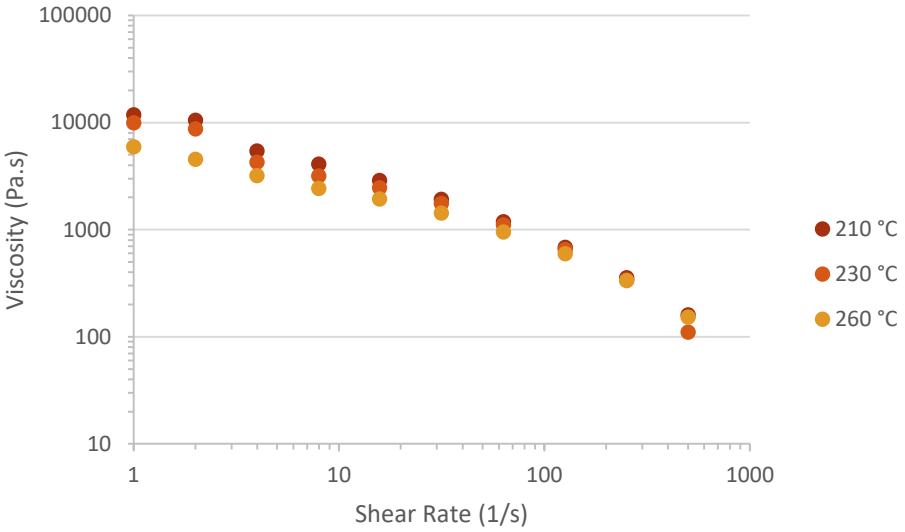

Figure 30 - Capilar rheometry flow test – B2 values

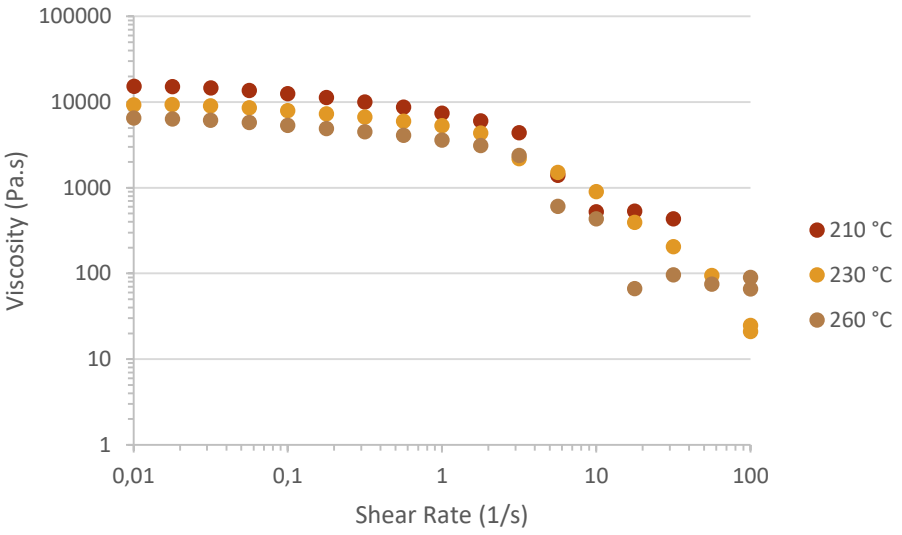

Figure 31 - Parallel plate rheometry flow test – B1 values

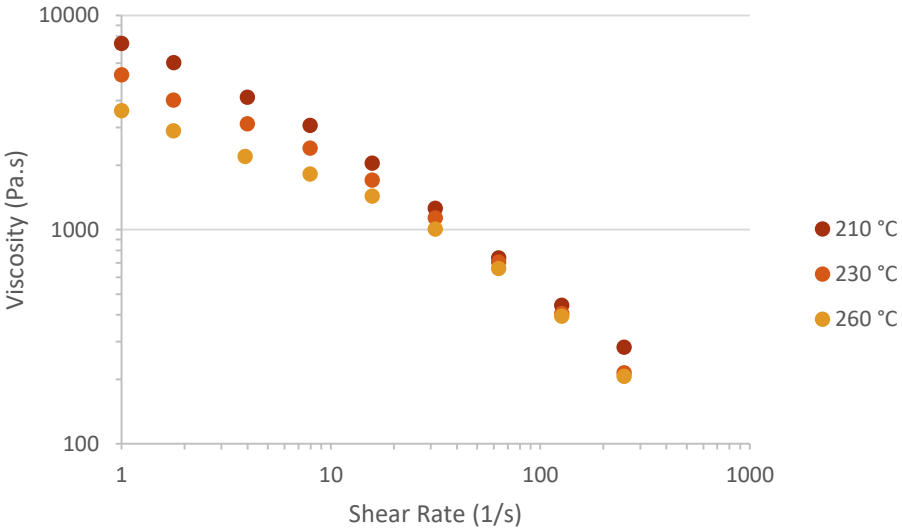

Figure 32 - Capilar rheometry flow test - B1 values

APPENDIX III – MICROSCOPY RESULTS

The coextruded filaments were obtained using two single screw extruders (Extruder – Periplast, Ltd (D= 25mm, L/D= 25)) at a thermal profile of 195/205/230/230ºC in each one, while the die temperature set at 230ºC. In Figures 33 and 34 is presented the coextruded samples of B2 in the external layer at rotational screw speed of 8 and 12.7 rpm and the percentage obtained of the inner layer was respectively 81.5 and 71.2%. These speeds were changed in the extruder of the inner layer since the extruder of the external layer was always kept at 5 rpm.

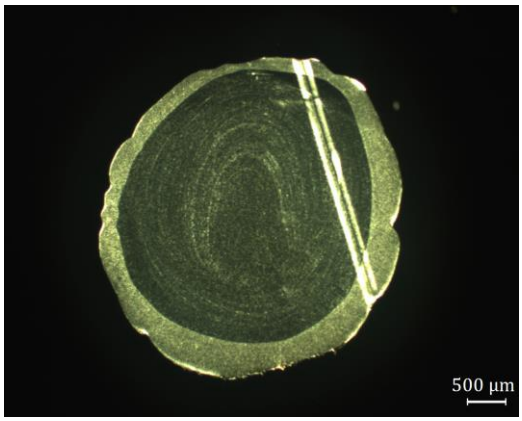

Figure 33 - Microscopy sample obtained with a rotational screw speed of 8 rpm

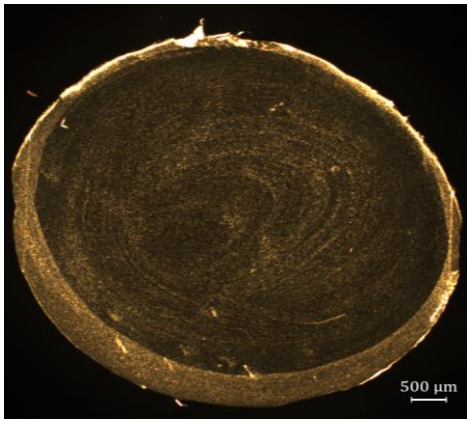

Figure 34 - Microscopy sample obtained with a rotational screw speed of 12,7 rpm

In the Figure 35 and 36 is illustrated the coextruded samples of M1 in the external layer at rotational screw speed of 6.6 and 8 rpm respectively. At a speed of 6.6 rpm the percentage of the internal layer was 72.5% and at a rotational screw speed of 8 rpm was 74.6%. The conditions mentioned before were also used in this case.

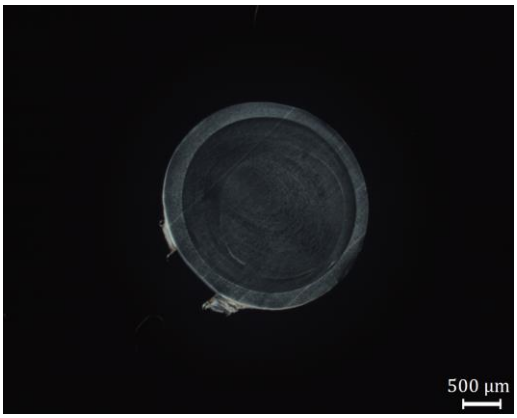

Figure 35 - Microscopy sample obtained with a rotational screw speed of 6,6 rpm

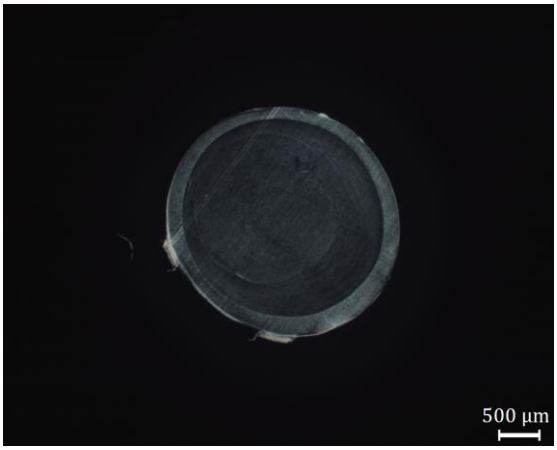

Figure 36 - Microscopy sample obtained with a rotational screw speed of 8 r

APPENDIX IV – INDEX OF FIGURES

APPENDIX V – INDEX OF TABLES