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Produção de Fitas Termoplásticas Pré-impregnadas e Processamento por Pultrusão e por Compressão a Quente

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PRODUCTION OF PRE-IMPREGNATED THERMOPLASTIC TAPES AND PROCESSING BY PULTRUSION AND HEATED COMPRESSION MOULDING

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Dissertação apresentada ao Instituto Superior de Engenharia do Porto para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Mecânica, realizada sob a orientação do Professor Doutor João Francisco Machado Gomes da Silva.

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PALAVRAS-CHAVE

Material Compósito; Matriz Termoplástica; Pré-impregnados; Fibra de Carbono; Pultrusão; Compressão a Quente; Laminado

RESUMO

Os materiais compósitos têm vindo a ser cada vez mais incorporados na indústria, oferecendo boas propriedades mecânicas e químicas, aliadas a uma densidade inferior quando comparados com os materiais tradicionalmente utilizados, tais como os metais. Estes aspetos tornam a utilização de compósitos cada vez mais interessante, substituindo os materiais de engenharia mais comuns, sempre que seja possível e viável.

Os compósitos termoendurecíveis são mais populares comercialmente devido à menor viscosidade apresentada durante o processamento. No entanto, atualmente não é possível, por meios convenientes, reciclar estes compósitos, tornando-os mais impactantes relativamente ao fim de vida das peças produzidas. Além disso, são mais nocivos para o ambiente devido às emissões de estireno durante o processo de endurecimento e também prejudiciais para o bem-estar dos operadores que os manuseiam. Os compósitos termoendurecíveis apresentam também alguns inconvenientes do ponto de vista do comportamento mecânico, apresentando um comportamento mais frágil com níveis de tenacidade inferiores, quando comparados com os de matriz termoplástica.

Pelos razões anteriormente mencionados, os termoendurecíveis têm vindo a ser substituídos por termoplásticos enquanto matriz em materiais compósitos poliméricos. No entanto, os termoplásticos apresentam maior dificuldade na produção de compósitos, estando especialmente associados com a maior viscosidade apresentada durante o processamento. Ao contrário dos termoendurecíveis, os termoplásticos caracterizam-se por serem recicláveis e reprocessáveis, permitindo uma circularidade na utilização do polímero. Além disso, devido à inexistência de emissões químicas, o processamento de compósitos termoplásticos permite ambientes de trabalho mais limpos, para além do melhor comportamento mecânico possibilitado pelas melhores propriedades gerais destes polímeros.

Nesta dissertação pré-impregnados de matriz termoplástica em forma de fita (ou *Tape*) foram produzidos por um processo de imersão de fibra numa solução fundida de polímero. As fibras de carbono foram utilizadas como reforço, combinando-as com três termoplásticos diferentes, nomeadamente o PET, o PA6 e o PC.

O processamento dos pré-impregnados foi realizado pelo processo de pultrusão, que é um processo contínuo caraterizado pelo fabrico de perfis compósitos. A compressão a quente foi também utilizada para o fabrico de laminados compósitos. As caraterísticas de processamento destes foram devidamente descritas, e os compósitos finais submetidos a testes mecânicos como forma de avaliar a qualidade do processamento.

KEYWORDS

Composite Materials; Thermoplastic Matrix; Pre-impregnated; Carbon Fibre; Pultrusion; Heated Compression Moulding; Laminate

ABSTRACT

Composite materials have been increasingly incorporated in industry, offering good mechanical and chemical properties, allied with a lower density when compared to traditionally used materials, such as metals. These aspects make the use of composites increasingly interesting, replacing the most common engineering materials, whenever is possible and feasible.

Thermosetting composites are more popular commercially due to the lower viscosity presented during processing. However, it is not currently possible by convenient means to recycle these composites, making them more impactful regarding the end of life of the parts produced. Moreover, environmentally, these are more harmful due to the styrene emissions during the hardening process and also prejudicial to the well-being of the operators that handle them. Thermosetting composites also present some drawbacks from the point of view of mechanical behaviour, presenting a more fragile behaviour with lower toughness levels, when compared to those of thermoplastic matrix.

For the reasons previously mentioned, thermosets have been replaced by thermoplastic as a matrix in polymeric composite materials. However, thermoplastics present greater difficulties in the production of composites, being especially associated with the higher viscosity presented during processing. Unlike thermosettings, thermoplastics are characterised by being recyclable and reprocessable, allowing a circularity in the polymer usage. Furthermore, due to the inexistence of chemical emissions, thermoplastic composite processing allows cleaner working environments, in addition to the better mechanical behaviour made possible by the better general properties of these polymers.

In this dissertation thermoplastic matrix prepregs in tape form was produced by a process of fibre immersion in a molten solution of polymer. Carbon fibres were used as reinforcement, combined with three different thermoplastics, namely PET, PA6 and PC.

The processing of the prepregs was carried out by the pultrusion process, which is a continuous process characterised by the manufacturing of composite profiles. Heated

compression moulding was also employed for the manufacturing of composite laminates. The processing characteristics of these was duly described, and the final composites were submitted to mechanical tests as a way to evaluate the processing quality.

LIST OF SYMBOLS AND ABRREVIATIONS

List of Abbreviations

BMC	Bulk Moulding Compounds
CF	Carbon Fibre
CFRT	Continuous Fibres Reinforced Thermoplastic
ISEP	Instituto Superior de Engenharia do Porto
LFRT	Long Fibres Reinforced Thermoplastic
min	Minutes
PAN	Polyacrylonitrile Precursors Fibres
PA	Polyamide
PC	Polycarbonate
PEEK	Polyether Ether Ketone
PEI	Polyetherimide
PET	Polyethylene Terephthalate
PLA	Polylactic Acid
PPS	Polyphenylene Sulfide
PP	Polypropylene
PSU	Polysulfone
SMC	Sheet Moulding Compounds
SFRT	Short Fibres Reinforced Thermoplastic
TGA	Thermogravimetric Analysis

List of Units

cm	Centimetre
°C	Degree Celsius
GPa	Gigapascal
g	Gram
kg	Kilogram
kN	Kilonewton
MN	Meganewton
MPa	Megapascal
m	Metre
µm	Micrometre
mm	Millimetre
N	Newton

List of Symbols

A	Cross-Section Area
m_1	Crucible Mass
m_3	Crucible Mass after Incineration
m_2	Crucible Mass with Sample
ρ_{comp}	Density of the Composite
ρ_f	Density of the Fibre
ρ_p	Density of the Polymer
L	Distance Between Ties

v_f	Fibre Volume Fraction
E_f	Flexural Modulus of Elasticity
σ_f	Flexural Strength
u_p	Flow Front Velocity
D_p	Impregnation Distance
m_{linear}	Linear Weight of the Fibre
$\left(\frac{\Delta F}{\Delta s}\right)$	Liner Slope in the Load-Displacement Graph
F	Load
m_{final}	Mass after Incineration
w_f	Mass Content of Fibres
w_{ff}	Mass Fraction of Fibres
w_{fp}	Mass Fraction of Polymer
m_{comp}	Mass of the Sample
s	Maximum Displacement
Nr	Number of Rovings
K	Permeability of the Fibres
η	Polymer Viscosity
dP/dx	Pressure Gradient
ε	Strain in the Outer Surface of the Specimen
h	Thickness of the Specimen
t_{imp}	Time to Impregnate the Reinforcement Completely
b	Width of the Specimen

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INTRODUCTION

1.1 Objectives

1 INTRODUCTION

Composites with polymeric matrixes began to appear in the middle of the 20th century and are now one of the biggest research focus of the modern area. The use of composites initially focused mainly on the automotive, biomedical and electronics industries, however with the technological developments they have been expanded to other areas, including the aeronautical and aerospace industries. The reason for the rapid increase in the use of polymeric composites is due to the fact that these materials offered a very attractive combination of stiffness and toughness with lower density and higher corrosion resistance [1], [2].

A composite material is a combination of two or more distinct materials that have a common interface. Composites are structurally composed by a reinforcing material and a matrix [3], [4]. Existing a huge variety of composites, this dissertation will focus on polymeric composites, more specifically on the subject of thermoplastic matrix composites.

Composite materials consisting of thermosetting matrices are the most commonly used industrially due to their low viscosity, resulting in an easy processing and handling. However, the inability of recycling these materials or even reprocess, leads to an approach for the search of thermoplastics to be used as matrix in composites.

The major inconvenient of thermoplastics is associated with the higher viscosity during processing, which leads to a more difficult processing. Thus, there is a need to find new ways to produce and process thermoplastic composite materials, from prepregs to processing final parts [5], [6].

In this work, a method of producing thermoplastic prepregs in Tape form consisting of carbon fibres and thermoplastic polymers will be studied to evaluate the optimal processing parameters of each. Furthermore, the processing of the Tapes by pultrusion and heated compression moulding will be also assessed to evaluate the processing possibilities.

1.1 OBJECTIVES

The objectives of this work are the production of prepreg Tapes reinforced by carbon fibres, combined with the three polymers already mentioned, namely PET, PA6 and PC. For obtaining results, the following objectives were outlined for this work:

1. Thermal analysis of the carbon fibres and the used thermoplastic polymers, namely PET, PA6 and PC.
2. Production of pre-impregnated tapes reinforced by carbon fibres, using the mentioned thermoplastics.
3. Processing of tapes by pultrusion, with tunning of temperature for improving properties.
4. Processing by heated compression moulding, using the weaved tapes for production of composites laminates.
5. Calcination of carbon fibre reinforced composites by total and partial incineration method.
6. Mechanical and analytical testing of the produced materials for characterisation.

LITERATURE REVIEW

2 LITERATURE REVIEW

2.1 Polymeric Matrix Composites

A composite material is a combination of two or more materials with a common interface and allows to obtain properties that each of the materials individually do not have. At composition level, composites consist of a reinforcement and a matrix. The reinforcement material is responsible for supporting the applied load and for providing the material with rigidity, hardness, and mechanical resistance. When referring to the matrix material, it is important to emphasise that this is not responsible for providing any structural function to the final material. Thus, its main function is to join the reinforcement material, preventing it from leaving their relative position, fill the existent empty spaces between the reinforcement and transmit the loads among the reinforcement [4], [7], [8].

Nowadays, thermosets and thermoplastics are the polymers that are used as a matrix. Thermosets are widely used in the industry, counting with over 90% of the market share due to its low viscosity and easy processing and handling. However, these materials are fragile, impossible to reprocess and hard to recycle which is the main reason why thermosets are being replaced by thermoplastics. On the other hand, thermoplastics are characterised for their ability to melt, reprocess, and offer improved mechanical performance when compared with thermosets. Thus, thermoplastics are characterized by having greater tenacity, fracture resistance and higher tolerance to impact. Its main advantages are the production rates, the possibility of being thermoformed, welded and recyclable. However, thermoplastic have high viscosity during processing, which can be seen as a disadvantage since it imposes the necessity of using advanced technology and high standard scientific knowledge to impregnate continuous fibres. This problem should be considered, as the lack of impregnation of the fibres may lead, in some cases, to the impoverishment of the mechanical properties of the composite material [5], [6], [8].

Despite the use of composite materials have growth in the last decades, there are still a relatively recent material used industrially. The usage of those materials in the present cannot be compared as the use of metallic materials, that continues being the most common material in the high-volume industrial markets [6].

2.2 Pre-impregnated Thermoplastic Materials

A pre-impregnated material, or prepreg, is formed by a reinforcement fibre that has been impregnated by a matrix, in advance, in such a way that the matrix is only partially cured. This material is used to manufacture composites. It is considered a semi-finished product which consists in a mixture between the reinforcing fibres and the polymeric matrix. One way to obtain thermosets pre-impregnated it is necessary to stack the fibres and the polymer, mould them and finally cure them by applying pressure. Those prepreg consist in the use of a saturated reinforcement with resin and during its production it is possible to characterize three different phases. There is the "A-state" when the resin is not cured, the "B-state" which corresponds to the polymerisation of the resin and the "C-state" that is the final of the polymerisation process [9].

Prepregs are a product that present several advantages, such as shorter curing time, and low bulk density which consequently enhances the quality of this product. Additionally, the manufacturing process for prepreg production can be simple and automatized, increasing the final product quality. On the other hand, thermosetting prepregs need to be stored in freezers and as consequence of having a limited workability at room temperature.

There are three types of thermoplastic matrix prepregs which can be divided into short fibres (SFRT), long fibres (LFRT) and continuous fibres (CFRT) [9]–[11].

- Short fibres (SFRT): Normally these fibres are supplied in the form of granules and the fibres are short in length. When compared to unreinforced thermoplastics, these fibres offer better mechanical properties, are easy to fabricate and are cheaper. Moreover, they can be easily moulded by injection or compression moulding. These characteristics boost their use as engineering materials specially in the automotive industry [12], [13].
- Long fibres (LFRT): Long fibre reinforced thermoplastics are composite materials that have in their constitution discontinuous fibres of more than 6 millimetres in length. These materials have seen rapid growth, mainly due to the technology advances in the automotive industry. Compared to SFRT, LFRT offers better mechanical properties combined with ease of processing [14], [15].
- Continuous fibres (CFRT): Continuous fibres have the best mechanical properties when applied to a composite material. Although the high cost associated with impregnating these fibres, they are increasingly being applied in many rigorous uses such as aerospace, aeronautic and military industries [16].

2.2.1 Reinforcement Fibres

In the field of composite materials, glass and carbon fibres are characterised as the most widely used reinforcement fibres, being glass fibres the prevalent choice.

Glass fibres are essentially composed of silica, which is associated with dissimilar oxides that facilitate the melting of the fibres, making it possible to pass it through the die during its manufacture. The main features of these fibres are their mechanical, chemical, and thermal resistance, their low cost, excellent fibre/matrix adhesion and good dielectric properties [7], [17].

When it comes to carbon fibres, they are stiffer compared to glass fibres, however they are less used due to their higher cost. Thus, the use of carbon fibre is limited to high performance components requiring low density and high module. The production of carbon fibres is expensive, time-consuming, and complex. The Pitch carbon fibres can be fabricated through treated petroleum distillation residues while the PAN are made from polyacrylonitrile. The PAN fibres offer better mechanical strength and higher fibre/matrix adhesion while Pitch fibres have a higher elastic module [7], [18].

Aramid fibres are rarely used in comparison to the fibres mentioned above. These fibres are characterized by their considerable strength, low density, high tenacity, and impact resistance. Aramid fibres are being used in some specific applications in the ballistics industry such as helmets and bulletproof components. However, the manufacture of composite materials using aramid fibres as reinforcement, especially with thermoplastic matrices is a major problem because they exhibit poor adhesion properties and therefore the application of aramid fibres is very restricted [19], [20].

Table 1 summarises the main characteristics of the different types of fibres mentioned.

Table 1 – Characteristics of the different types of fibres (Adapted from [7], [21])

Reinforcement Fibres		Glass			Carbon		Aramid
Property	Unit	E	S	R	PAN	Pitch	-
Density	g/cm^3	2.56	2.49	2.58	1.80	2.0	1.44
Tensile Strength	MPa	3600	4500	4400	2800	1500	2800
Elastic Modulus	GPa	76	86	85	270	380	62
Specific Tensile Strength	kNm/kg	1400	1800	1700	1555	750	1944
Specific Elastic Modulus	MNm/kg	29.6	34.5	32.9	150	190	43
Fibre Diameter	µm	3-20	8-13	5-24	7.5	10-11	12

2.2.2 Thermoplastic Matrices

To choose a thermoplastic matrix it is necessary to consider its mechanical performance allied to cost. The polymers that offer the best ratio and are the most widely used are polyamide (PA), polypropylene (PP), polyethylene terephthalate (PET) and polycarbonate (PC).

It is important to choose a thermoplastic with a processing temperature suitable for the type of process that is going to be used. In addition, it is also important to consider toughness, impact behaviour and mechanical strength, where the latter is important to counteract anisotropy in continuous fibre composites.

The use of high-performance thermoplastics is not always desired, as they require higher processing temperatures, leading to a more challenging and costly production. There are many cases where composites are being used at higher temperatures and it is important to consider the thermal properties of the selected thermoplastic as it may

influence the performance of the material. In summary, using the higher thermal performance of the thermoplastic may cause issues in processing, but it should be selected to fulfil the functionality of the composite, at the risk of causing the loss of properties and degradation of the polymer. In extreme cases of temperature, it is normally used high end thermoplastics which are more expensive, but capable of hold high service temperatures. Those thermoplastics normally are polyetherimide (PEI), polysulfone (PSU), polyphenylene sulfide (PPS) and polyether ether ketone (PEEK) [7], [8], [21].

In Table 2 is summarised the principal thermoplastic polymers properties that are used with composite materials.

Table 2 – Principal thermoplastic polymers properties (adapted from[7], [21], [22])

Property	Unit	PA6	PP	PC	PET	PEI	PEEK
Density	g/cm^3	1.10	0.90	1.15	1.30	1.26	1.30
Tensile Strength	MPa	35	33	65	75	70	62
Elastic Modulus	GPa	3.00	1.40	2.80	3.50	3.40	3.60
Melting Temperature	°C	220	165	-	250	-	350
Processing Temperature	°C	230-285	190-230	270	260-310	340-370	340-400
Service Temperature	°C	140	120	120	100	180	260
Relative Price	-	2.30	1.00	4.20	3.00	8.80	49.30

One of the most used thermoplastics nowadays is polypropylene due to its low price, easy recycle and reasonable properties. Additionally, polypropylene is a thermoplastic which is relatively easy to process with the different processing technologies available in the market such as injection, extrusion, thermoforming, rotational moulding, and blow moulding. Other thermoplastics such as PET or PA6 are the most used for

continuous fibre pre-impregnated thermoplastics, due to the better properties presented [7], [22], [23].

2.3 Thermoplastic Matrix Prepregs Production

Achieving a complete impregnation of dry fibres with a thermoplastic matrix is one of the biggest challenges of these polymers. The prepreg quality is directly related with factors like polymer viscosity, fibre length, fibre dispersion, and pressure. The difficulty of impregnating the dry fibres can be explained based on the rheological properties of the molten polymer (high viscosity) and the fluid behaviour in a porous medium [24], [25].

Using Darcy's law Equation 2.1 it is possible to calculate the impregnation speed of flow of a fluid through a porous area in a single direction of impregnation, shown in Figure 1.

$$u_p = \frac{dx}{dt} = \frac{K}{\eta}\frac{dP}{dx} \tag{2.1}$$

Where:

u_p – Flow front velocity

K – Permeability of the fibres

η – Polymer viscosity

$\frac{dP}{dx}$ – Pressure gradient

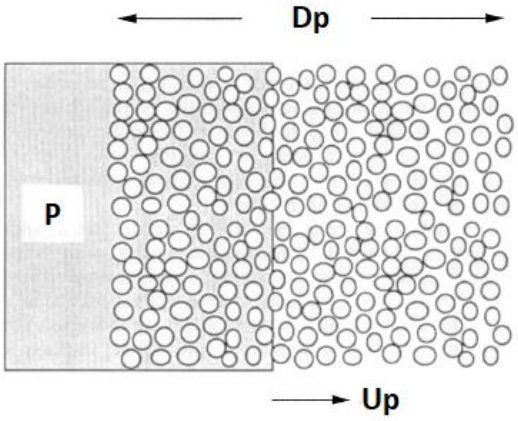

Figure 1 – Fibre impregnation by external pressure, P (adapted from [25])

Assuming that the pressure gradient is constant and using the appropriate frontier conditions it is possible to obtain the equation that provides the required time to impregnate the reinforcement completely. This is obtained by integrating the Equation 2.1 [4], [7].

$$t_{imp} = \frac{\eta D_p^2}{2KP} \quad (2.2)$$

Where:

t_{imp} – Required time

D_p – Impregnation distance

By analysing Equation 2.2 it is possible to conclude which of the terms present in the expression have a greater effect in the impregnation process. Thus, the impregnation distance is the critical effect since it is one squared term and will therefore have a greater impact on the impregnation time, which will increase proportionally as the impregnation distance grows. This is the reason why the main production techniques try to reduce the impregnation distance to achieve the best impregnation time [7], [25].

2.3.1 Impregnation Processes

2.3.1.1 Film Stacking

This impregnation process is a simple process that requires only a heated plate press as equipment. It is a time-consuming process since it is difficult to impregnate the fibres transversally especially with matrix material that has a high viscosity [26].

This process consists of the using fibres which can be unidirectional or woven fabrics, combined with thermoplastic sheets. Consolidation is achieved through pressure and temperature with the help of a heated plate press, which can be seen in Figure 2. The production process consists of three steps [26], [27]:

1. Heat the press to lower the polymer viscosity.
2. Increase the pressure to force the thermoplastic matrix to impregnate the fibre.
3. Cool the press to solidify the laminates.

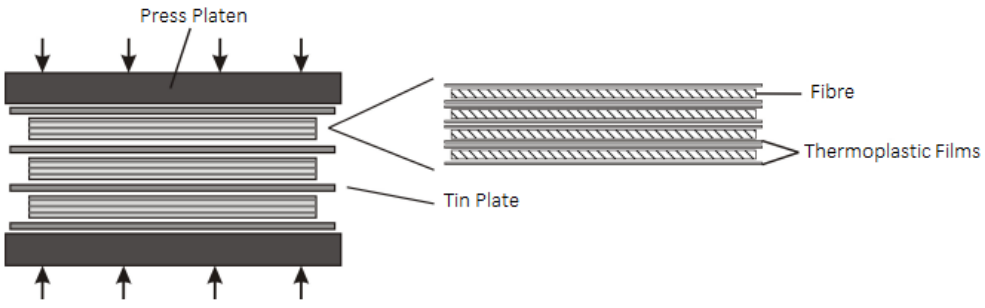

Figure 2 – Film Stacking Process (adapted from[27])

In the film stacking process, the time, pressure, and temperature are the key parameters to control the process. The values of these three parameters depend on the polymer characteristics, not only the melting temperature and viscosity as well as the temperature and the load that the fibre resists [28]. It is noteworthy that it is important to have a good relationship between the dwell time at the melt temperature with the peripheral and core temperature to make sure that the laminate is at the same temperature at all points. This ensures that the centre of the laminate is as well impregnated as the periphery, where the temperature is easily reached [21].

2.3.1.2 Low Viscosity Precursors

As mentioned earlier, thermoplastics have a high viscosity and so there is great complexity in fully impregnating the fibres. One way to avoid the difficulties associated with the impregnation process is to reduce the viscosity of thermoplastics. The method low viscosity precursor impregnation has two variants, one is called polymerisation and chain extension, and the other is the use of solvents and plasticizers [21].

The first method consists of using a low molecular weight thermoplastic which weight can be increased by chain extension. This method can be observed in some thermoplastics, such as PPs, where an increase in temperature is accompanied by increased molecular weight. The other variant of this method consists in the use of a reagent which is applied to the fibres. This reagent, when in contact with the polymer increases its weight [25].

The second method is defined by reducing the viscosity of the thermoplastic polymer during processing with the addition of solvents. These solvents make the impregnation of the fibres easier. However, it is necessary to remove the solvents completely so that no voids appear in the composite. Due to this fact, this type of impregnation is not widely used in industry. Like the use of solvents, plasticisers are not used because it is difficult to remove the material whose volatility after impregnation is limited [25], [29].

2.3.1.3 Solution Impregnation

This impregnation technique is typically used with amorphous polymers such as PEI. It is possible to adjust the polymer concentration and temperature to lower the polymer viscosity which is not possible with melt impregnation. Additionally, it is necessary to dissolve the polymer in organic solvents with high boiling points such as 1-Methyl-2-Pyrrolidinone [30], [31].

The process begins with the unwinding of the fibre roving, which passes through a container that contains a solution with a solvent and a thermoplastic. This can be called polymer solution. After the fibres passes through the solution it is necessary to pass the tow through a solvent evaporation unit which is required to remove the solvent

remaining in the tow. The solvent must be removed before the consolidation step. At the end the tow is rolled into a roll. This method is represented in Figure 3 [31][32].

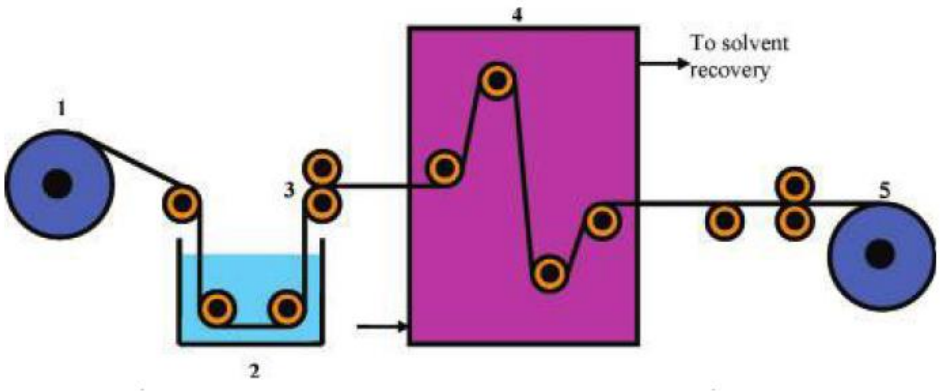

Figure 3 – Solution impregnation method. (1) fabric supply, (2) polymer solution, (3) calendaring rollers, (4) solvent evaporation unit, (5) batch collection [32]

With this technique it is possible to achieve a good quality prepreg, however there are some restrictions that this type of impregnation entails. First, solvents are usually expense, and dangerous. In addition, the removal of the solvent is the critical point for this method since it is undesirable. The solvent directly affects the mechanical properties as it will cause void formation due to the release of volatiles. Another problem lies in the fact that some thermoplastics are not soluble in solvents, which makes it a huge obstacle, as this technique is limited to a certain combination of polymer-solvent [31].

2.3.2 Continuous Fibres Thermoplastic Matrix Prepregs Production

2.3.2.1 Melt Impregnation

Melt impregnation is one of the simplest production techniques still existent when it comes to fibre impregnation. There are two techniques that are used to impregnate the fibres by melt impregnation. The first is called co-extrusion and the second is based on continuous pultrusion [8], [26].

The co-extrusion technique consists of using an extruder which is used to feed a die with molten polymer. The fibre then passes through the die where it is impregnated with the molten thermoplastic. However, this technique is not so satisfactory for continuous production of composites due to the difficulty of impregnating the interior fibres properly and homogeneously [26].

On other hand, the method based on continuous pultrusion is used to circumvent impregnation defects that the co-extrusion technique cannot ensure. Here, the fibre tow is unwound from a feed spool and is lead into a melt pool. The melt pool is filled with melted thermoplastic that is supplied by an extruder. The fibre bundle is guided through

a polymer bath, where it needs to pass over several bars, that are often called spreader pins. The spreader pins are used to increase the permeability of the polymer increasing the physical exposure area of the fibres. Finally, the fibres pass through a die that consolidate the prepreg into the desired shape. The final product obtained through this process is a unidirectional tape that can be applied in many industries. In Figure 4 it is possible to see a type of mechanism used for the impregnation [26], [33], [34].

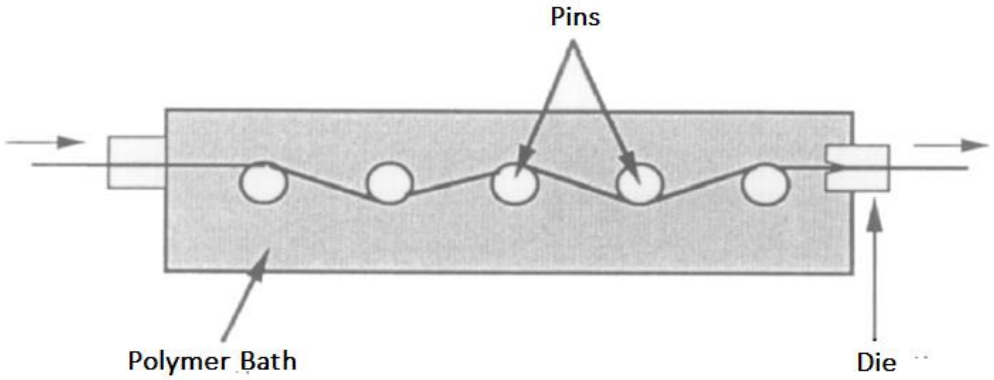

Figure 4 – Melt impregnation process (Adapted from [25])

It is also important to note that pulling the fibre over the impregnation pins while in contact with the viscous polymer, can cause high local shear rates between the bundle and the bars, which results in high shear forces contrary to the pulling force, as shown in Figure 5. The shear forces increase with the increase of the number of bars and speed. It is important to pay attention to these parameters, so that the shear force does not reach the pulling force otherwise the fibre will break or will result in poor impregnation. Increasing the speed not only increases the pulling force but also reduces the impregnation time and quality [33].

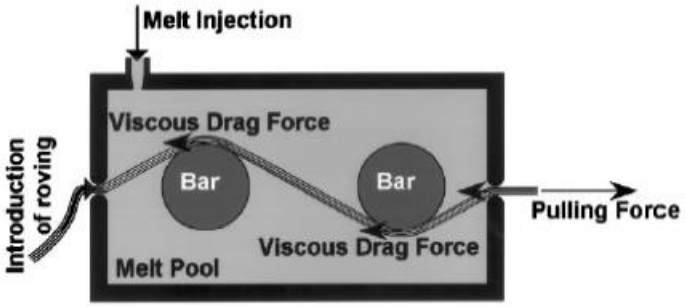

Figure 5 – Melt impregnation forces [33]

The biggest problem associated with this process is the consumption time it takes and the difficulty of optimising it. Therefore, many studies are being carried to reach an ideal solution since it is a cheap process that if optimised achieves a good level of impregnation [34].

2.3.2.2 Fibre Comingling

One technique that has emerged as a cost-effective method to produce complex components is the fibre commingling process [35].

This process can produce flexible prepregs called “commingled fibres”. Firstly, the thermoplastic matrix needs to be processed into fibres. Subsequently, the fibre reinforcement and the thermoplastic fibre are blended where the commingled yarns contain a mixture of fibres that are used as reinforcement, and thermoplastic polymer used as a matrix. In the end a single yarn is obtained, and it is wound into a roving [26], [35], [36]. This system is described in Figure 6.

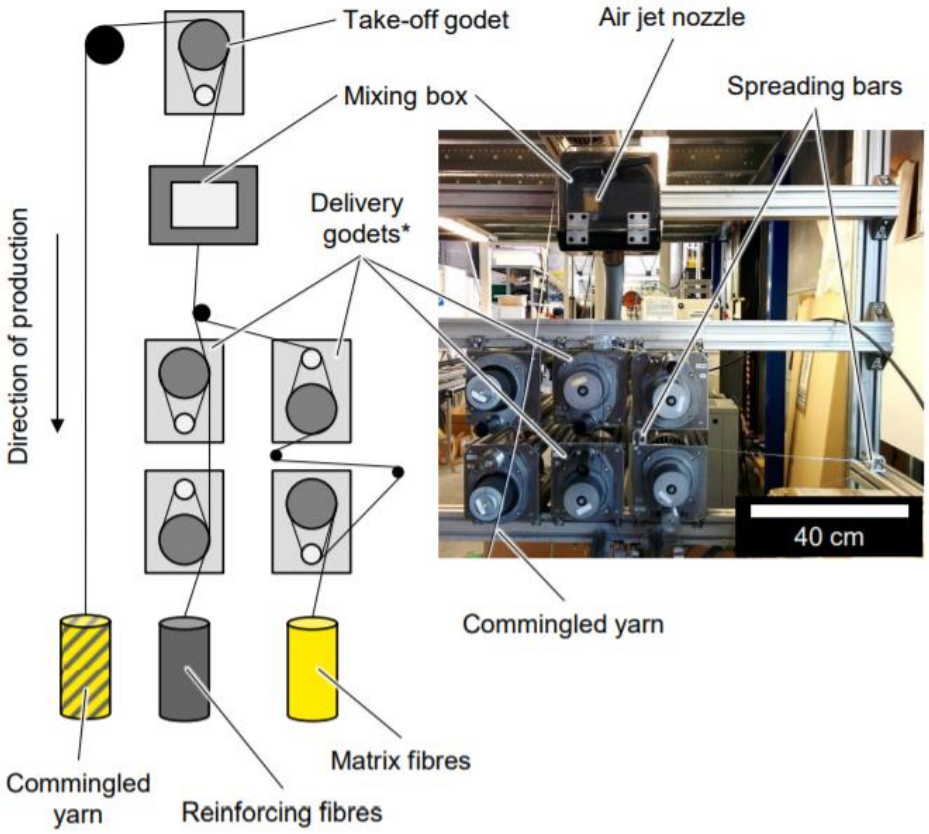

Figure 6 – Traditional commingling process (adapted from [37])

The commingling process represented in Figure 6 is a more traditional type of production, presenting some efficiency problems. Therefore, there is another process capable of producing these fibres and it is represented in Figure 7.

In this method, the polymer is inserted into an extruder, where it is melted. After melting, the polymer is pulled by a spinning pump and a number of yarns are drawn out of the nozzle. While the polymer is being processed into yarns, the fibre yarns are at that moment also making their way to the sizing application where they meet the polymer yarns and commingle. This technique is more advantageous compared with the

traditional commingle process because the mechanical load on the yarn during the commingling is lower and the filament distribution homogeneity is reasonably high [38].

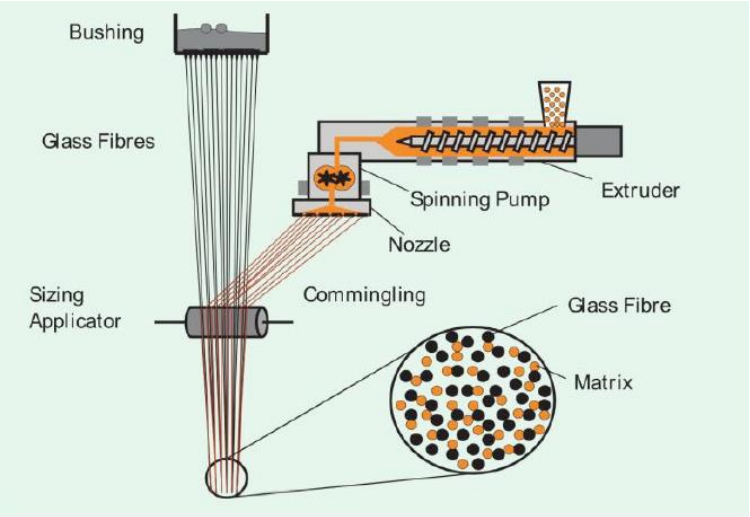

Figure 7 – Commingling process [38]

The main advantage of commingling process lies in the fact that the flow distance of the polymer is reduced when the matrix and the fibres are completely blended. As a result, the impregnation time of the fibres is reduced as well as the need to apply high pressures. It leads to a very competitive manufacture when compared to traditional prepreg production [35].

The final yarn usually has a non-uniform fibre distribution and to combat this struggle it is possible to reduce this effect by using a bath of molten thermoplastic to impregnate the dry fibre bundle prior the commingling. Additionally, it is necessary for the fibre and thermoplastic yarns to have a similar diameter to reduce this problem. Note that the polymers commonly used in this process have a low molecular weight to facilitate the impregnation process [39].

2.3.2.3 Dry Powder Impregnation

Dry powder impregnation is one of the most promising techniques that was developed by Prince in 1973. The main purpose of this type of impregnation is to deposit the dry thermoplastic powder on the fibre [40].

This technique consists of continuously pulling the fibre reinforcement through a recipient containing powdered thermoplastic. Here there are usually some bars or rollers that are used to open spaces between the fibre tow, helping the incorporation of polymers between the fibres [40].

First, it is necessary to transform the thermoplastic polymer into powder form. This powder can coat individual fibres without bulk flow of the polymer. After that, to achieve a good impregnation, it is necessary to open spaces between the fibres, using a

spreader to facilitate the impregnation of the fibres. Then the fibre must be heated in such a way that after passing through the container with the powdered thermoplastic, the polymer is melted and adheres superficially to the fibre. This is called primary adhesion. To ensure the impregnation process, the tow, which is already impregnated, is heated in a consolidation oven. To finish, the tow can be passed through a die to form a consolidated tow, or it can be stored in a roving. This method is shown in Figure 8. The product that is obtained by this process is called towpreg [26], [41].

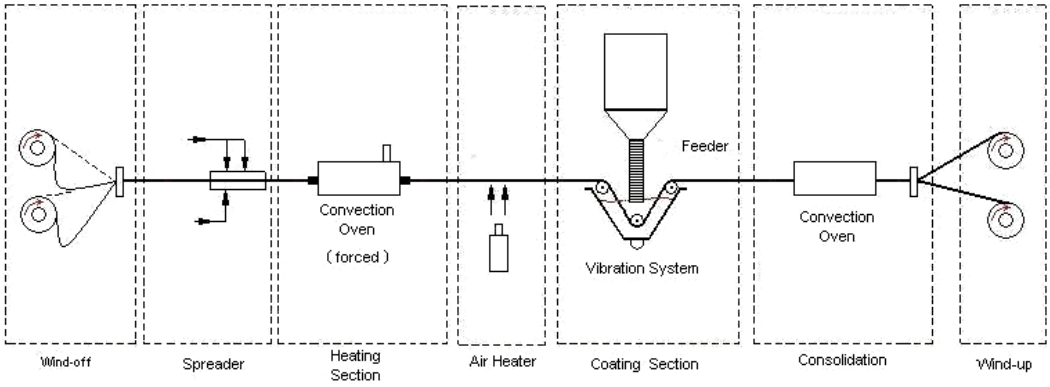

Figure 8 – Dry powder impregnation process (Adapted from [42])

The major advantage of this method lies in the fact that the thermoplastic viscosity is not important for the process, which is a huge problem for thermoplastic impregnation. The obtained prepregs are easy to handle and to cut which is important when preparing the material. The product width and the fibre volume can also be chosen as desired. However, as the fibre are in contact with the polymer powder for a short time without pressure or spreading on the fibres, micro-impregnation does not occur. This means that only the exposed fibres are impregnated which leads to poor impregnation [43].

2.3.3 Fibre Spread Mechanism

In order to achieve good impregnation in thermoplastic composites there has to be a special attention to the impregnation stage of the process. It is established that the spreading of the fibres influences the degree of impregnation of the fibres [44]. The presence of voids, seen through microscopic techniques, as well as thermoplastic blisters result from a deficient impregnation. This can occur when fibres are attached to each other hampering the penetration of the thermoplastic matrix through the fibres. In addition, the melted thermoplastic may not even impregnate the first few layers of fibres, therefore the mechanical characteristics of the composite will be compromised [45]. Taking this into consideration, it is easy to understand that it is necessary to pay attention to the degree of fibre spreading. Regarding the fibres spreading concern there are some techniques that can be implemented.

2.3.3.1 Pneumatic System

Firstly, there are pneumatic systems that impose air pressure into the fibres in order to separate them [45]. In Figure 9 is represented a schematic diagram of the spreading process using airflow. This method consists in a pneumatic system with a regulatory valve and flow controllers.

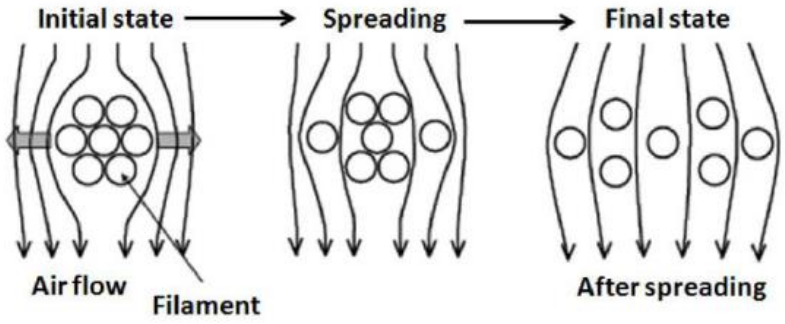

Figure 9 – Schematic diagram of spreading process using air flow [45]

The regulatory valve is responsible for controlling the pressure in the pneumatic system. This valve can either be operated manually or have an automated system. In both configurations the pressure must be sufficient to spread the fibres. Besides that, the pneumatic system can be equipped with flow controllers. These components allow more customization to the pneumatic spreading system. Different fibres have distinct behaviours, so the system adaptability is welcome.

The pressurized air channels are directed perpendicularly to the fibre tow axis, as can be seen in Figure 10 . In turn, the fibres must be accommodated on a rail with variable width, narrow at first and widened at the end. The narrow part concentrates the fibre in the path of the pressurized air so that the fibre bundle spreads transversally by the thrust of airflow [7], [44].

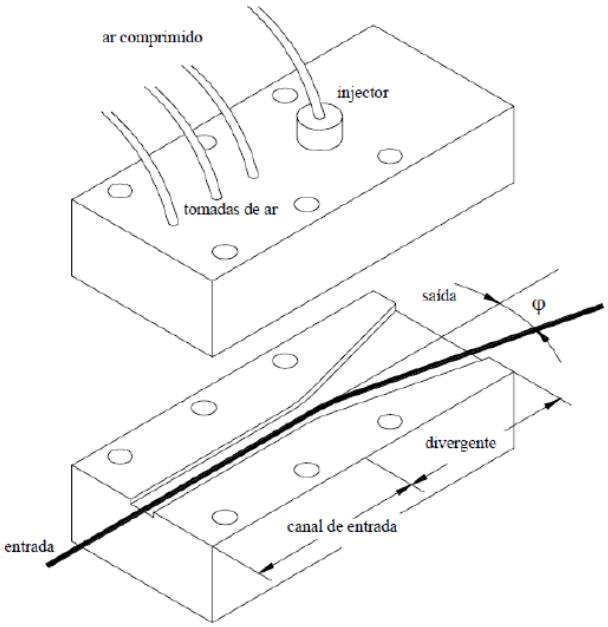

Figure 10 – Pressurized air fibre spreading system [7]

At this stage there can be applied several aired pressure terminals to achieve better separation of the fibres. After that, the rail starts to widen, giving more space to the fibres to spread out. Moreover, the spreading of the fibres is assisted with another pressurized air terminal. Finally, the fibre spreading degree depends not only on the force exercised by the pressurized air but also the tensioning force applied to the fibres [7].

The pneumatic system can be applied with other methods and technologies like the schematic diagram from Figure 11. This system consists in a method which combines pneumatic with a vibrating structure.

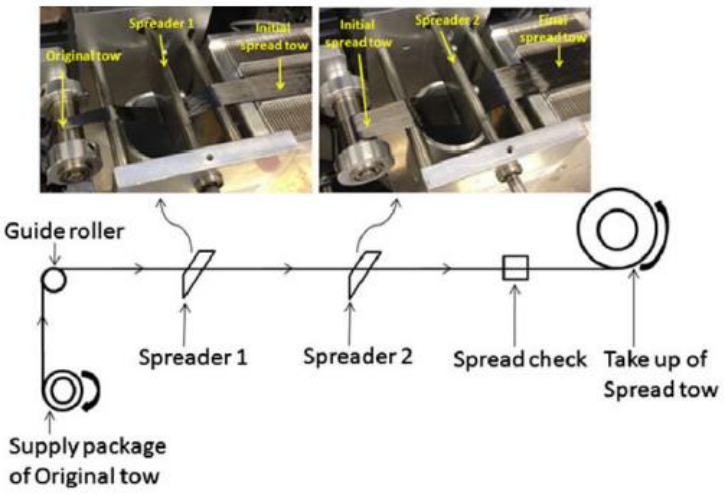

Figure 11 – Pneumatic vibrating spreading system [46]

The pneumatic component works similarly to the one previously described, except that the air flow is vacuumed downward from the tow. This helps the fibre tow to sag and lose tension promoting uniformly fibre spread aided by the back-and-forth vibrating spreaders. The air velocity is controlled by an air flow regulator to avoid damage to the fibres [46].

It was found that a pneumatic spreading system is a promising technology for tow spreading. It enables effective wet-out and impregnation from thermoplastic polymer in the fibres [46].

Although this system presents good results in spreading fibres it is a complex and costly solution. There is another technique worth studying that can be simpler and achieve the same results.

2.3.3.2 Roller System

To achieve fibre spreading it is possible to appeal to a mechanical roller system. This system is characterised for its simplicity. It consists in a set of rollers disposed in certain configuration so that the fibre tow maintains its tension and can spread the fibres. The spreading of the fibre is dependent of the radius of curvature of the pins as well as the height difference between pins [44]. Such method is shown in Figure 12.

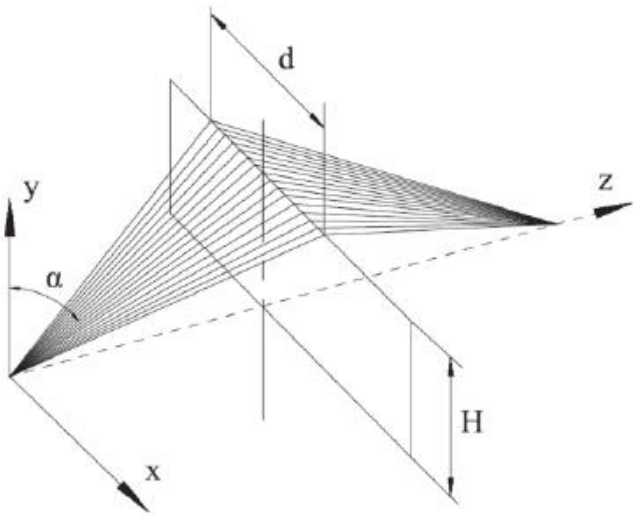

Figure 12 – Spreading model of a fibre bundle [44]

In addition to that, the rollers are not all the same, they must have different profiles. The convexity and the presence of grooves in the rollers play an important role in the effectiveness of fibre spreading. Since the objective of the system is to spread and not compact the fibre, the concavity of the rollers will not be studied.

As previously mentioned, this spreading system is composed by grooved and convex rollers disposed in distinct geometric plans as can be seen in Figure 13.

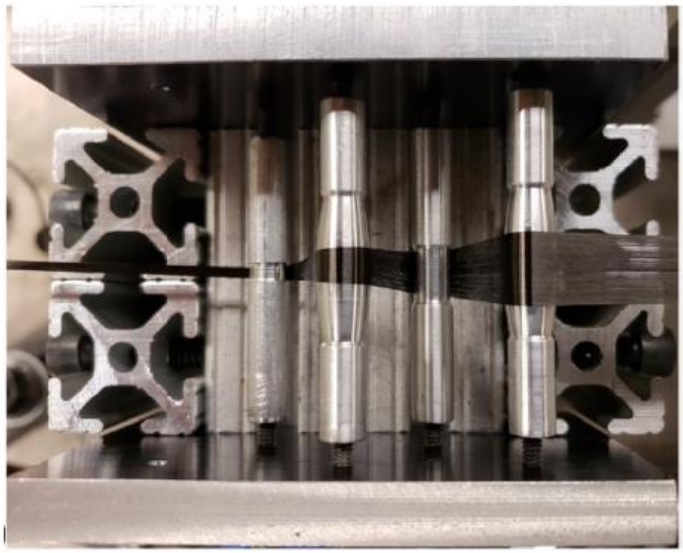

Figure 13 – Roller spreading system [24]

The first roll has a small groove that serves as a guide to stabilise the fibre tow before passing through the first convex roll. Reaching the convex roller, the fibre tow starts to spread due to the tension applied to the tow. After that, there is a third rod with another linear groove, however wider than the first one. This third groove allows realignment of the fibre tow without compromising the spread from the previous rod. Finally, another convex roller enhances the spreading degree of the fibres.

The system previously described has some limitations when it comes to the tension applied to the fibre tow. The fibres spread becomes non uniform, with gaps in the centre of the tow, when pulled with too much upstream tension. Otherwise, this design allows a uniformly distributed fibre tow [24].

As previously described for the pneumatic systems, with mechanical roller systems it is also possible to combine distinct methods and techniques in an attempt to separate the fibres evenly. The combination of mechanical and vibration techniques results in a series of rollers which vibrate as well as rotate. The suggested method might produce a more uniform yarn compared with other methods [47].

There are other variations to this method where the rollers are profiled, for example, rollers that have a sheet made from ball bearings in the surface, and other method involves motorized rollers [47].

2.3.3.3 Commercial Solutions

There are already some devices commercially available as solutions for fibre spreading. US company, Izumi International Inc, focuses on the trade of equipment for carbon fibres and composites industry as well as equipment for factory automation.

Regarding the roller system has a mechanical fibre spreader solution represented in Figure 14.

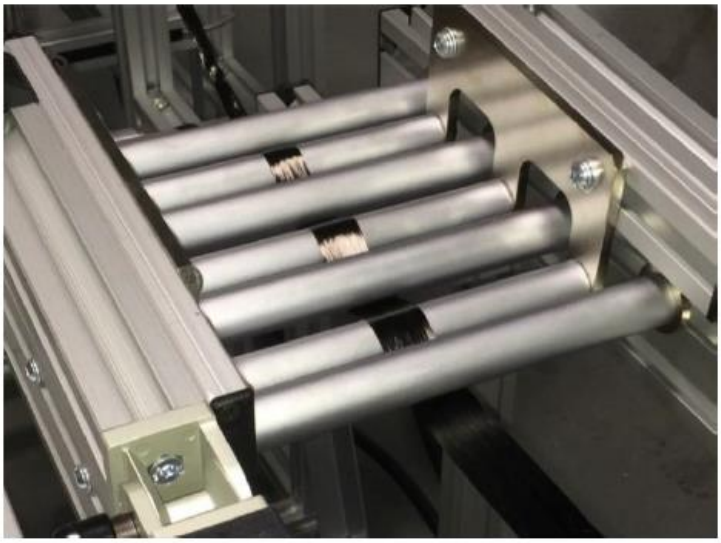

Figure 14 – Izumi International Inc mechanical fibre spreader [48]

This solution is regarded as a low cost and easy to install. It allows to adjust the angle on the spreading bars in order to obtain different spreading widths. Furthermore, the bars are stationary and coated with chrome to minimise filament breakage [48].

In addition, there are some optional specifications like a fibre heating system to assist loosen the fibres prior to spreading, tension control, a width monitor system, and a fibre filament breakage detector [48].

It is noteworthy that this solution can be combined with other technologies such as a pneumatic system. An air-assisted fibre tow spreading technology has reportedly achieved approximately three times the width of the initial received fibre tow [49].

Regardless of the chosen method for fibre spread technology, there are several parameters to consider. The space available to install the system is one of them. It could be desirable to retrofit the spreading method to an existing composite manufacture process or simply have some restrictions of space available. Then, there are the external requirements for the spreading system, like an external power source or pneumatic equipment. Finally, there is the cost associated with the system development and implementation. This parameter will be heavily influenced not only by the components necessary as well as the external ones like the previously mentioned ones.

2.4 Thermoplastic Matrix Prepregs Processing

The prepregs explained previously are used for processing the final composites, which can be made by continuous processes or for single part production. Currently, there is a

wide application to composite materials that reflects the various existing processes to transform the composite prepreg. Each application requires different requirements so there is a constant search and development of new processes to satisfy the needs of the industry. In this respect, some of these processes will be introduced.

2.4.1 Pultrusion

Pultrusion is a continuous manufacturing technique for processing composite profiles with constant cross section. This process is gaining a particular interest nowadays as pultrusion profiles offer good mechanical performances combined with high-cost efficiency in applications with long length composite materials [50]–[52].

There are different types of pultrusion based on the type of polymer. The first, is used with thermoset polymers and the second for thermoplastic polymers which is the aim of the study presented.

In the thermoset pultrusion method, the fibre from the roving is pulled through a resin bath or an injection box. After impregnation, the fibres are heated in a die to cure the resin. After leaving the die the tape is completely consolidated and has the desired shape, which is defined by the shape and measure of the die. The final bar is rigid and can be cut to the desired size. This mechanism can be seen below in Figure 15. Since the curing stage is the most important for this type of composite, it is necessary to ensure that the curing process is well controlled to make sure that no product degradation occurs that compromises the quality of the final product [51], [53], [54].

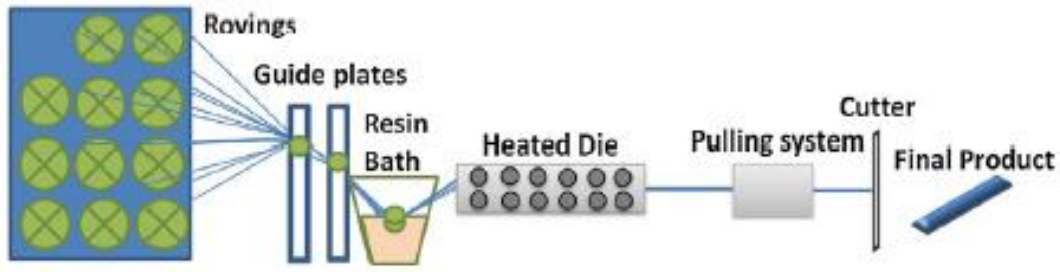

Figure 15 – Thermosetting pultrusion [51]

Thermoplastic pultrusion has been studied and improved based on thermoset pultrusion which is easier, as thermosets have low viscosity and therefore this type of pultrusion is better understood.

In thermoset pultrusion the fibres converge into a resin bath containing polymer, which is not the case with thermoplastics. Here, the yarn precursors that contain the thermoplastic prepreg are unwound from the spools. Next the prepregs tape are pulled into a preheating chamber, where the material reaches the required processing

temperature. The prepreg is then passed through a die which is heated to melt the polymer that was already impregnated into the fibres and with this the impregnation is easier in the heating die. The die applies pressure, thermoforms, and compacts the composite. The cooling system presented in the die lowers the temperature until the glass temperature of the polymer is reached. The pulling system makes the necessary force to oppose the viscous reaction and the friction between the die and the composite. Finally, it is possible to cut this composite to the desired length. This process is schematised in Figure 16 [55]–[57].

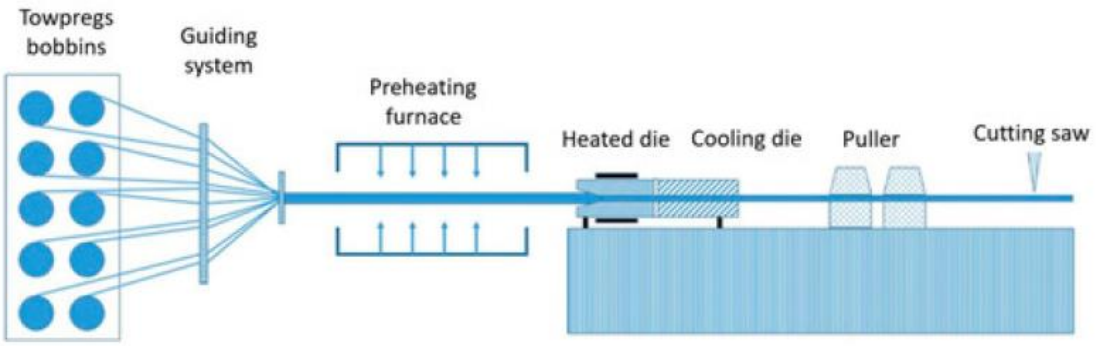

Figure 16 – Thermoplastic pultrusion [57]

Pultrusion is a closed-mould process, which makes it difficult to controlling the process by human means such as visual inspections and dimensional measurements. Consequently, it is necessary to have a strict control on some variables that directly affect the quality of the final product. It is necessary to control the thermal effects, more specifically to control excess temperature to ensure that there is no degradation of materials and flow effects, controlling the generation of voids and dry spots that make the final product weak as result of poor impregnation [52].

Note that pultruded profiles are applied in structures where longitudinal stiffness and strength are desired in a unidirectional orientation. This lies in the fact that the fibres reinforcements are oriented in a single direction and give the composite excellent properties in the longitudinal direction and poor properties in the transverse direction. In simple terms it can be stated that pultruded profiles are anisotropic [50].

2.4.2 Heated Compression Moulding

Compression moulding of thermoplastic composites has been studied since the 1990s when the principal thermoplastic polymers, especially polypropylene, together with glass fibres started to be used in the automotive industry. Prior to this, thermosetting based in sheet moulding compounds (SMC) were the most used material in compression moulding. Currently thermoplastic bulk moulding compounds (BMC), which can be cut into flakes, chips or prepregs, are gaining ground against thermoset SMC/BMCs as they offer better durability, their smoke has low toxicity, and fast production times can be achieved [58].

This process uses a heated plate press and a mould, divided into an upper and lower mould, to obtain as a result, the desired piece. By using a prepreg sheet, a thin plate of composite material or even powder it is possible to reach good results. First, the substrate is fixed in the lower mould, where it remains until it reaches the temperature that has been previously set for the heated plate. After the temperature is reached, the lower mould is moved vertically upwards, or vice versa, until it meets the upper mould. When the moulds are together, the pressure and temperature mould the material into the desired shape and form. At the end, the moulds separate, and the part is removed from the lower mould. Figure 17 below shows the mechanism [59]–[61].

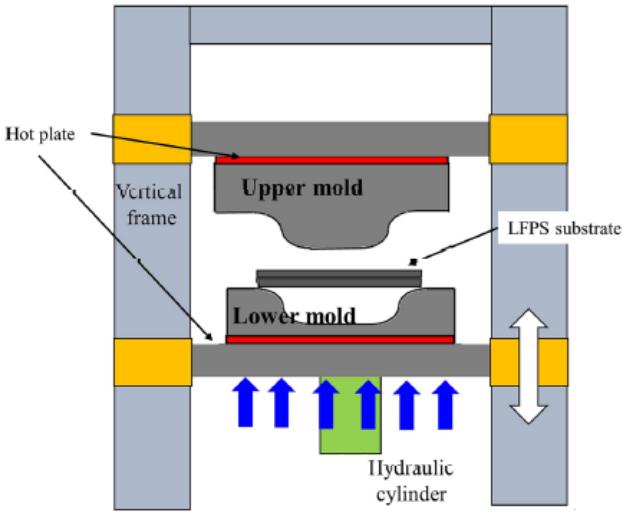

Figure 17 – Compression moulding (adapted from [59])

There are significant advantages to compression moulding. With this method it is possible to manufacture complex shaped parts with high mechanical strength when compared to parts made by injection moulding or using an autoclave. In addition, by using compression moulding it is possible to reduce production time. A great advantage of this method is that is has a very strict control of pressure and temperature due to the heated plate press, which makes the process very well controlled [58], [59].

EXPERIMENTAL

3 EXPERIMENTAL

This chapter will describe the practical and experimental component presented in this work.

3.1 Raw Materials

3.1.1 Reinforcement fibres

As it is known, there are several reinforcement fibres available in the market with different applications in the industry. For the present study it was defined as reinforcement material the carbon fibre, since it is one of the best engineering materials when it comes to strength and low density. The carbon fibre used is the PAN type from the manufacturer *SIGRAFIL*, reference C T50-4,0/240, with a linear weight of TEX. In Table 3 it is possible to observe some properties of the used carbon fibre.

Table 3 – Properties of the carbon fibre used, provided by the manufacturer

Properties	Units	Values
Tensile Strength	MPa	4000
Tensile Modulus	GPa	240
Linear Weight	TEX	3280
Elongation at Break	%	1.70
Density	g/cm^3	1.80
Filament Diameter	µm	7.00
Poisson Ratio	-	0.27

3.1.2 Thermoplastic Matrices

As explained in the theoretical part of this dissertation it is important to choose a thermoplastic considering its mechanical performance allied with cost. Thus, three different thermoplastics were used as polymeric material, polyamide (PA), polycarbonate (PC) and polyethylene terephthalate (PET). These thermoplastics have different applications in the industry, and so it is of interest to test these materials allied with carbon fibre and compare the properties obtained. In the Table 4 it is possible to find the properties of the thermoplastics used according to the manufacturer.

Table 4 – Properties of the thermoplastics used

Properties	Unit	PET	PA6	PC
Tensile Strength	MPa	40	78	64
Tensile Modulus	GPa	2.00	3.00	2.30
Density	g/cm^3	1.25	1.14	1.20
Processing Temperature	°C	250	230	300
Poisson Ratio	-	0.43	0.39	0.36

3.2 Production of Pre-impregnated Thermoplastic Tapes

The main objective of this work was to produce thermoplastic prepregs with carbon fibre being the reinforcement material. Thus, the production method used to obtain such prepregs was melt impregnation.

Furthermore, one of the proposed objectives for this dissertation was to obtain a great degree of impregnation in the carbon fibres, which is a big challenge.

The prototype used to produce the pre-impregnated was developed and produced at ISEP in the Composite Materials laboratory. This prototype used melt impregnation based on continuous pultrusion, which is described in 2.3.2.1.

The production process was divided in four stations, being as follows:

1. Fibre tow holder, device that allocates the carbon fibre tow and allow and easy unwinding. In addition, there is a small piece that helps the guide of the fibre.
2. Fibre spreader, which is responsible for separating the filaments thus increasing the contact area between the carbon fibres and the polymer that will be in contact in the impregnation bath.
3. Impregnation machine, which is divided between polymer pool and die. The polymer pool where the melting of the polymer takes place and subsequently the impregnation of the fibres which pass through the melted polymer. The die is responsible for consolidating the material, moulding it into the desired shape and size.
4. Winding system, responsible for pulling the fibre, winding, and storing the produced material.

Each station will be described and explained in more detail in the following pages.

Fibre Tow Holder

The carbon fibre is placed on a metal rod which is supported laterally in a way that no translation occurs. After proper storage of the fibre tow, it is unwound, and then guided through the small hole in the guiding piece. This mechanism can be seen in Figure 18.

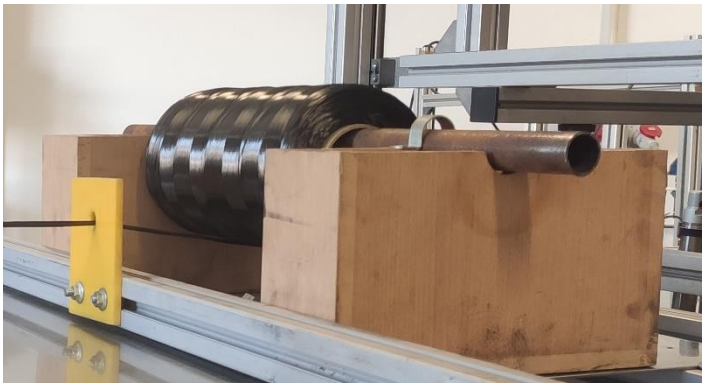

Figure 18 – Fibre tow holder

It is important to note that the filament must be tensioned before advance on the next stage to obtain the best possible results. If the fibre is not tensioned, the spreading system is not efficient since tension is required for the filaments to separate. Moreover, there is the possibility of the fibre breaking.

Fibre Spread

An important component of the setup is the spreader system demonstrated in Figure 19 and Figure 20.The spreader consists of two polycarbonate sheets and PLA rollers. The main objective of this mechanism is to force the fibre filaments to separate. Thus, the fibre must enter the mechanism tensioned, and passe through the rollers. The rollers

force the fibre along the path chosen, putting stress on the fibre, opening the filaments. This mechanism is important for the process as it increases the contact area of the fibres. The increased area leads to higher contact area between the fibres and the molten polymer increasing the degree of impregnation in the fibres.

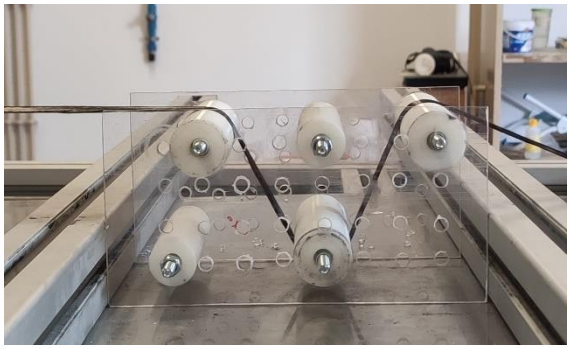

Figure 19 – Lateral view of the fibre spread

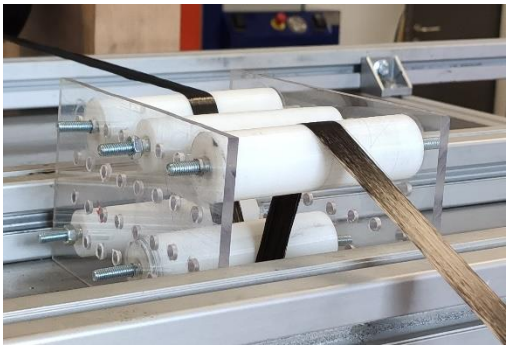

Figure 20 – Isometric view of the fibre spread

Impregnation Equipment

The impregnation equipment is divided into two different components as shown below in Figure 21. The first is called the polymer pool and is demonstrated at Figure 22, which is a container that is heated to the desired temperature, melting the polymer. Once the polymer is melted, the fibres are pulled and passed through impregnation pins, facilitating the impregnation of the fibres.

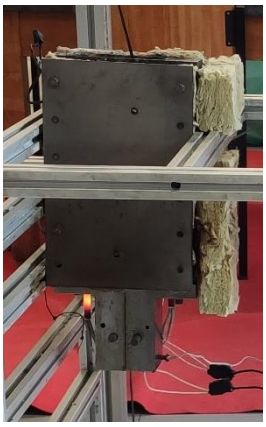

Figure 21 – Impregnation machine

Figure 22 – Molten polymer inside the polymer pool

The die is fixed to the bottom of the polymer pool. It is heated to a temperature slightly higher than the temperature used in the polymer pool, to ensure that the die can mould the tape to the desired shape and size.

Winding System

The last station of the process is the winding system in Figure 23. It is responsible for pulling and storage the material produced. Two rollers are used to pull the fibres, which are set in motion by and electric engine. This engine can be set at the desired speed. To store the fibre there is a reel which has the necessary torque to wind and help pull the fibre. The final tape is stored in reels with a capacity of 30 to 40 metres as shown in Figure 24.

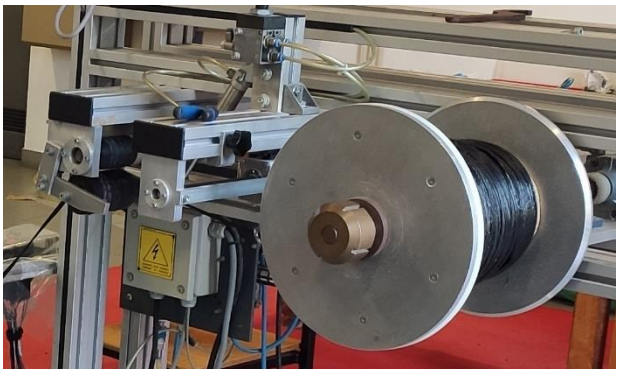

Figure 23 – Winding system

Figure 24 – Tape stored

3.3 Processing of Pre-impregnated Thermoplastic Tapes

This sub-chapter describes the equipments used for processing the pre-impregnated Tapes, by pultrusion and heated compression moulding.

3.3.1 Pultrusion

Pultrusion is a continuous processing technique which is described in 2.4.1. The Tapes were processed in the prototype pultrusion equipment installed in the Composite Materials Laboratory of ISEP. As described in the theorical part of this dissertation, the pultrusion equipment consists of four stations, which will be described below.

Unwinding and guidance system

The first station of the pultrusion machine consists of the unwinding and guiding system. It is a system consisting of metal rods arranged horizontally that serve as a support for the reels of material produced. This system has the capacity to support up to 32 reels simultaneously. Immediately afterwards, there is a sheet with an opening in the middle to make sure that all the Tapes enter correctly into the preheating oven. This system can be observed below in Figure 25 and Figure 26.

Figure 25 – Unwinding system

Figure 26 – Guidance system

Preheating oven

The main purpose of this oven is to start the heating of the tapes before they enter the heating die. This preheating will heat the polymer present in the prepreg tape which will facilitate the further process.

Figure 27 – Preheating oven

Heating and cooling die

The pultrusion head consists in the two dies, the heating and colling die. The heating die is responsible for heating the polymer, with the current set-up allowing to reach temperatures up to 350°C. The polymer contained in the tapes reaches processing temperatures, and the combination of prepregs in the die are consolidated through cycles of pressure and temperature. At the end, the die has a defined geometry which will mould the tapes to acquire the final shape of the pultruded material.

Figure 28 – Heating and cooling die

When the consolidated material leaves the heating die, it is at processing temperature. For this reason, it is necessary to pass the processed bar through another die with the same dimensions, that is called cooling die. The cooling die uses a water circulation system, which lower the temperature of the bar. Thus, this system ensures that the pultrusion bar is consolidated and with the desired dimension, before being pulled and cut.

Pulling system

The pulling system consists of two trolleys that use pneumatic actuators to pull the pultrusion profiles as can be seen in Figure 29. These trolleys are moved longitudinally with constant speed. When the profile reaches the desired length, it is cut. Pulling speeds with the prototype equipment starts at 0.2 meters per minute and can reach up to 1 meter per minute.

Figure 29 – Pulling system

3.3.2 Heated Compression Moulding

Heated compression moulding, described in 2.4.3 was used to transform the thermoplastic tapes into a composite laminate. The machine used for this process was a heated plate press which is installed in the Composite Materials Laboratory of ISEP, which can be seen below in Figure 30.

Figure 30 – Heated plate press

To manufacture the laminates, it was necessary to make composite fabrics from the thermoplastic tapes that were previously produced. Such fabrics were manufactured using plain weaving. Each laminate was produced stacking four fabrics. As the fabrics are not symmetrical, presenting the double of the tapes in one direction it is necessary to balance the stacking according to the direction of the tapes. Thus, the two inner layers of the stacking must present the same tape direction as well as the two outer layers. This stacking ensures that the manufactured laminate is symmetrical. In Figure 31 it is possible to see the four fabrics stacked.

Figure 31 – Fabrics stacked

When stacking the fabrics, it is necessary to place release film between the sample, to make sure that the material will not stick to the plates when the equipment start the cycle of heating and compression in the press. This can be seen below in Figure 32.

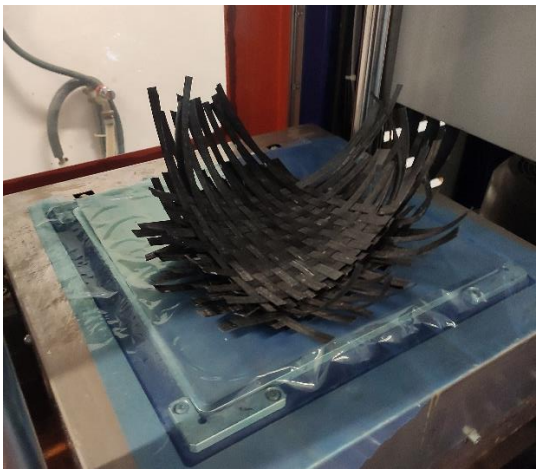

Figure 32 – Fabrics stacked inside the heated plate press

After the end of the processing cycle of the laminate, the composite is consolidated and ready for being cut in the desired shape. In Figure 33 and Figure 34 it is possible to observe the laminate inside the heated plate press after the end of the processing and the laminate properly cut.

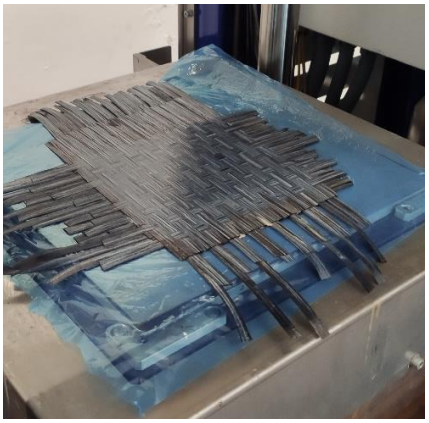

Figure 33 – Laminate after the cycle

Figure 34 – Cut laminate

3.4 Mechanical Characterisation of the Composites

To evaluate the quality of the composites obtained through pultrusion and heated compression moulding it was necessary to perform mechanical tests to evaluate the behaviour of the material produced, thus being possible to compare the different processing conditions. Calcinations were carried out, to understand the fibre content in

each condition. Bending tests were carried out to evaluate the strength of the material and the level of consolidation.

3.4.1 Calcination Tests

Calcinations tests were carried out to measure the level of polymer that the pultrusion profiles presented and samples from the laminate. With these tests it is possible to know the percentage of fibre and polymer that each condition presents, thus obtaining a qualitative evaluation of each process condition.

As it is being using carbon fibres as reinforcement it is not possible to use the standard ISO 1172 since it is only applicable for matrix with glass fibres as reinforcement. With that it was necessary to use a different method based on TGA (Thermogravimetry) to know the temperature that each polymer and carbon fibre start incinerating. When the exact temperature of each component was known, a muffle furnace was used to confirm the values obtained by TGA method. At the end the calcination of the pultrusion samples and the laminate were carried out in the muffle furnace. The methodology used will be described below.

First it is necessary to preheat the muffle furnace, which is demonstrated in Figure 35, to the required temperature. The muffle used is in the Composite Materials Laboratory of ISEP and is designated *NABERTHERM LHT08/16.*

Figure 35 – Muffle furnace

Then, using a precision balance shown in Figure 36, the crucibles must be weighted empty and after with the samples to be tested. It is important to highlight that it is necessary to use at least 2 grams of material to be tested, according to the standard. Two crucibles are also used for each condition to ensure better accuracy in the results.

Figure 36 – Precision balance

Finally, the crucibles are placed in the muffle furnace for 15 minutes. At the end of the cycle, the crucibles are reweighted to evaluate the percentage of mass that was lost by incineration. Below in Figure 37 and Figure 38 it is possible to observe the crucible with the sample before incineration and after, respectively.

Figure 37 – Crucible with sample before incineration

Figure 38 – Crucible with sample after incineration

To obtain results of the procedure performed it was necessary to apply two equations, according to the type of incineration. When there is a total incineration of the polymer at the testing temperature, the Equation 3.1 will be applied after the incineration of the composite, obtaining the respective mass fraction of the fibres for the composite. On the other hand, if there is no total incineration of the polymer, the remaining polymer must be considered for the calculation of the mass fraction of fibres and Equation 3.2 is applied. By solving the equation, the mass fraction of fibres in the composite can be obtained.

Mass fraction of fibres and polymers

As explained previously, this equation is applied to find out the respectively mass fraction of fibres (w_{ff}) and polymer (w_{fp}). If there is total incineration of the polymer only the mass fraction of fibres is calculated being that the final result.

$$w_{f\ (f,p)} = \frac{m_3 - m_1}{m_2 - m_1} \times 100 \tag{3.1}$$

Where:

$w_{f(f,p)}$– Mass fraction of fibres (w_{ff}) and polymer (w_{fp})

m_1 – Crucible mass [g]

m_2 – Crucible mass with sample [g]

m_3 – Crucible mass after incineration [g]

After determination of the mass fractions of the fibres, w_{ff}, and polymer, w_{fp}, it is possible to obtain the mass content of fibres of the composite applying the equation presented below. This equation is used when there is no total incineration of the polymer at the calcination temperature, so it is necessary to consider the mass of polymer left unburned in the sample after incineration.

Mass content of fibres of the composite

$$w_f = 1 - \frac{m_{final} - w_{ff} \times m_{comp}}{(w_{fp} - w_{ff}) \times m_{comp}} \tag{3.2}$$

Where:

m_{final} – Mass after incineration

m_{comp} – Mass of the sample

w_f – Mass content of fibres of the composite

w_{fp} – Mass fraction of polymer

w_{ff} – Mass fraction of fibres

3.4.2 Three-Point Bending Tests

The three-point bending tests were performed in the Composite Materials Laboratory of ISEP, using a universal testing machine from *Shimadzu* with a 100 kN load cell as can be seen in Figure 39. In this test, the specimen is supported between two supports with a distance that was defined by the standard ISO 14125. Subsequently, a force is applied using a punch, in the centre of the specimen. With this experiment it is possible to

characterise several properties of the material such as modulus of elasticity, tensile strength, and maximum deflection.

Figure 39 – Universal testing machine

Before performing the tests, it was necessary to cut all the specimens, using an electric saw, to the desired length. As the electric saw uses water to assist the cut operation, it is necessary to dry all the specimens before performing the tests, to guarantee that there is no negative influence. Thus, the specimens were placed inside a small oven at 60°C for one hour.

After drying the specimens, it is necessary to measure them. The samples had a standard length of 100mm and were measured in width and thickness in three different positions of the sample. Thereafter an average was made to ensure greater accuracy in the measurement of the width and thickness. After all this procedure, the specimens were tested, as can be seen in Figure 40.

To ensure that the results are trustworthy, six tests were performed for each condition for the pultrusion profiles and four for the heated compression moulding samples. All the test specimens were tested at a speed of 2mm/min and a distance between supports of 80mm, which is recommended for continuous fibre reinforced composites, as noted in ISO 14125.

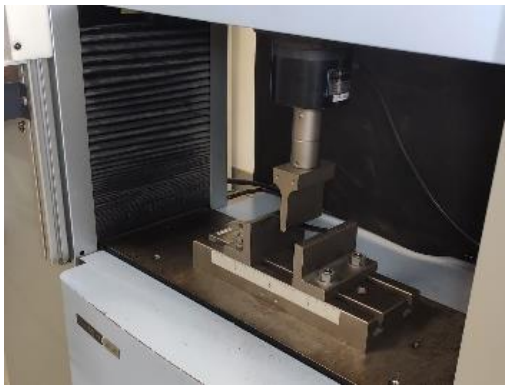

Figure 40 – Three-point bending test in progress

After all the tests performed, all the data and graphs were analysed and with that the principal properties of the material were found. In addition, it was necessary to employ some equations, which are presented below.

Flexural Strength

$$\sigma_f = \frac{3FL}{2bh^2} \tag{3.3}$$

Where:

σ_f – Flexural strength [MPa]

F – Load [N]

L – Distance between ties [mm]

b – Width of the specimen [mm]

h – Thickness of the specimen [mm]

Flexural Modulus

According to the standard, it is possible to obtain the flexural modulus through Equation 3.4 or through computational graphic analysis. In this dissertation the computational graphic analysis was used. To find the flexural modulus, a linear regression of the Stress-Strain graph was made for strain values between 0.0005 and 0.0025. After performing the linear regression, the flexural modulus is the slope of the straight line obtained.

$$E_f = \frac{L^3}{4bh^3}\left(\frac{\Delta F}{\Delta s}\right) \tag{3.4}$$

Where:

E_f – Flexural modulus of elasticity [MPa]

$\left(\frac{\Delta F}{\Delta s}\right)$ – Linear slope between strain values of 0.0005 and 0.0025 in the load-displacement graph [N/mm]

Strain

$$\varepsilon = \frac{6sh}{L^2} \tag{3.5}$$

Where:

ε – Strain in the outer surface of the specimen [-]

s – Maximum displacement [mm]

DISCUSSION OF RESULTS

4 DISCUSSION OF RESULTS

4.1 Calcination of Raw Materials

The raw materials used in this study were submitted to thermal testing to evaluate the behaviour at different temperatures. To this end, thermogravimetrical analysis (TGA) testing was carried out to assess the temperature at which the materials start to degrade and, in addition, to find out what the indicated processing window is.

The thermogravimetrical testing was carried out at the same conditions as those existing in a muffle furnace, as the calcination of the composites will be performed in this kind of furnace. For this reason, in the TGA test the airflow was removed and air was chosen as the atmosphere present. The heating rate was at 10°C per minute, as standard TGA tests are. For this test, the moment where degradation started is considered to start is at the moment where 2% of material has been lost due to thermal degradation.

After knowing the results of the TGA testing, it was necessary to corroborate the results obtained. In this way, burning tests were performed for each component separately in the muffle furnace and the results compared. To perform the burning tests, 4 specimens of each condition were subjected to temperature for 15 minutes.

In the following pages will be exposed the results obtained for the carbon fibre and for the 3 polymers used.

4.1.1 Thermal Analysis of Carbon Fibres

This test was performed to understand the behaviour of the reinforcement fibres at different temperatures. Contrary to glass fibres, which can sustain temperatures up to 1400°C without mass degradation, carbon fibres suffer loss of mass when subjected to higher temperatures. The results of the test are shown in Figure 41.

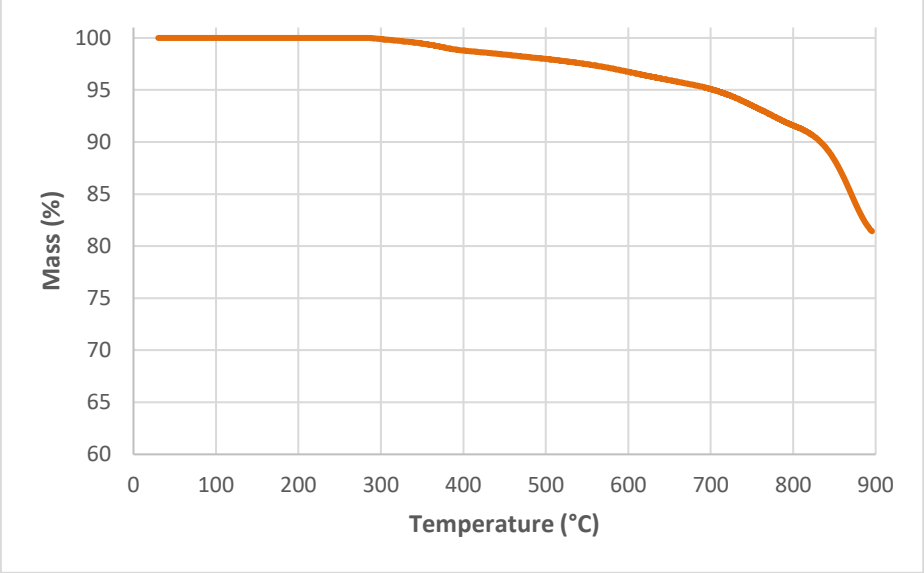

Figure 41 – Degradation of the carbon fibre

Analysing the figure above it is possible to verify that the moment where the carbon fibres start to lose mass after 500°C. To validate this result, 4 crucibles with a minimum of 2 grams of fibres were placed in the muffle furnace at 500°C for 15 minutes. After this, new weighing was done to evaluate the amount of fibre lost by incineration. These values are show in the Table 5.

Table 5 – Calcination of carbon fibres at 500°C

Carbon Fibres	Sample 1	Sample 2	Sample 3	Sample 4	Average
Remaining mass (%)	97.91	98.09	98.25	98.37	98.16 ± 0.17

Observing the Table 5, it is possible to conclude that the results obtained by the TGA test are reliable, since the values obtained for the calcination tests performed in the muffle furnace are the same with a value of 98%.

4.1.2 Thermal Analysis of PET

4.1.2.1 Degradation Temperature and Processing Window

A thermal analysis of PET was performed, and it was possible to conclude that the temperature at which this polymer initiates degradation is around 385°C. This can be seen below in Figure 42.

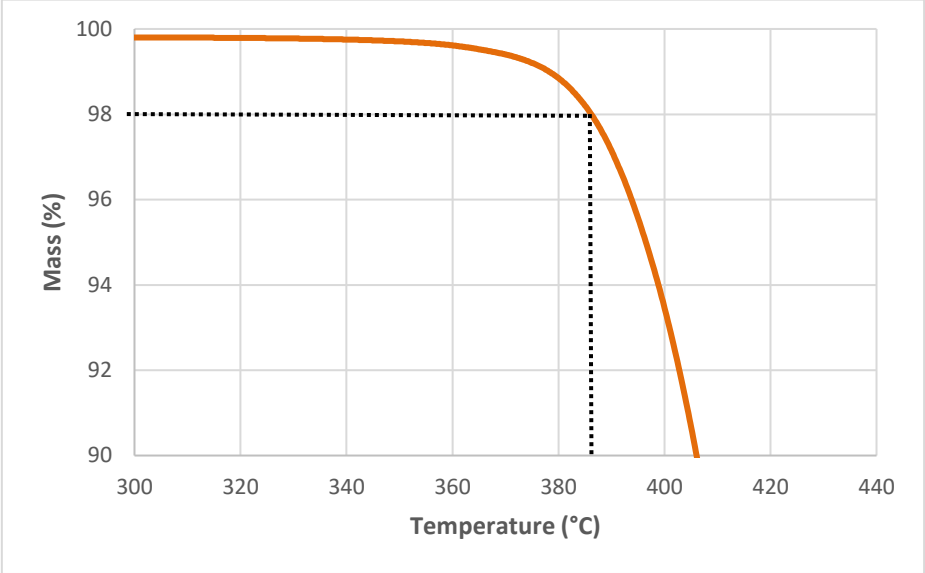

Figure 42 – Degradation of PET

With the degradation temperature of this polymer, it is possible to know the maximum temperature to which this polymer can be subjected without properties degradation. Furthermore, it is provided by the manufacturer that the melting temperature of this polymer is 250°C, which makes the processing window of this polymer very comfortable to produce tapes and its processing.

4.1.2.2 Calcination Temperature

To carry out the calcination tests it is necessary to know the right temperature for there is a total or almost total burning of the polymer. The selected temperature will be used in the calcination tests to have a reliable comparison. Figure 43 shows the TGA graph obtained.

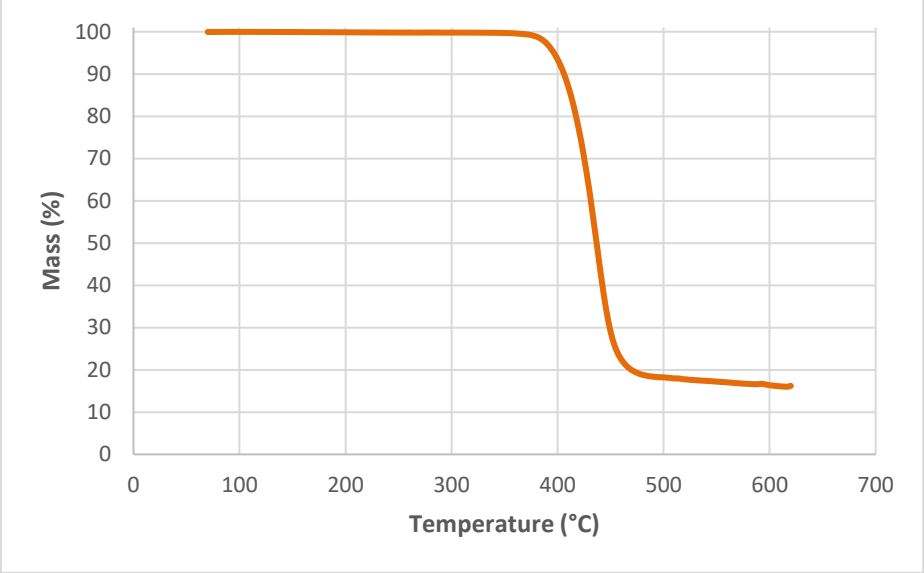

Figure 43 – TGA analysis of PET

Analysing the complete curve of the TGA graph obtained, it can be seen that there is no total incineration of this polymer at high temperatures. The values between 450°C and 600°C show a higher stabilization, being the value of 500°C more suitable to perform the calcination. At a temperature of 500°C, the remaining mass of polymer was about 18% and subsequently calcination tests were performed to corroborate the results obtained in the TGA test. The results of the calcination tests are presented in Table 6.

Table 6 – Calcination of PET at 500°C

PET	Sample 1	Sample 2	Sample 3	Sample 4	Average
Remaining mass (%)	13.48	13.61	14.26	13.71	13.76 ± 0.30

The values of the remaining mass of PET obtained through calcination tests were about 14%, which is a little lower than expected. The average difference is 4%, which is not such an unreasonable value considering that calcination in the muffle furnace is a sensitive process. For this reason, these values can be compared with the values obtained through TGA test, confirming the results.

4.1.3 Thermal Analysis of PA6

4.1.3.1 Degradation Temperature and Processing Window

The approach adopted to find the degradation temperature of polyamide was different, since this polymer is hygroscopic, which means that it absorbs the humidity present in the air. For this fact, by observation the curve it is possible to see that there is a small mass loss of 1% at 250°C which is associated with this property. For this reason, the degradation temperature will only be obtained when there is a total mass loss of 3%.

By direct observation of the Figure 44 it is possible to verify that the degradation temperature of polyamide starts at 350°C.

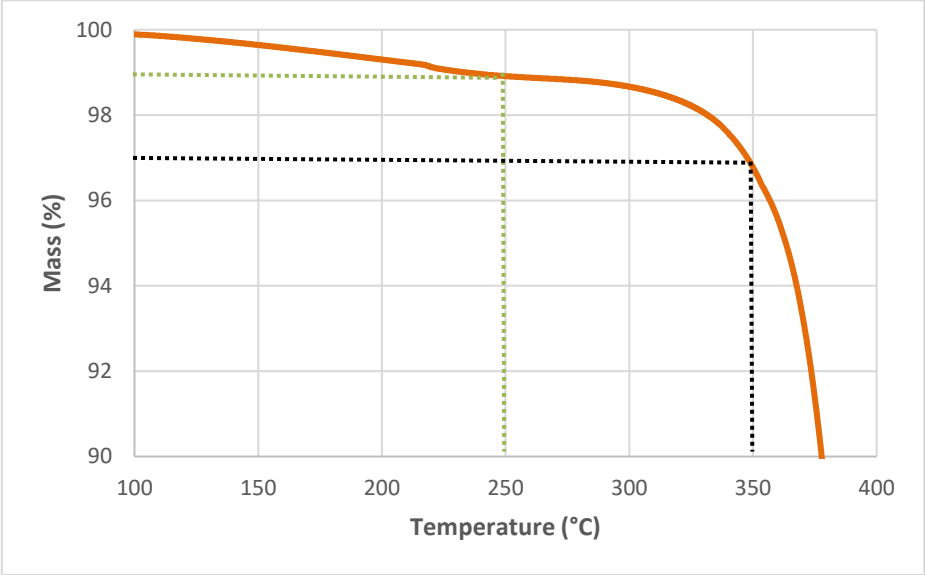

Figure 44 – Degradation of PA6

With the degradation temperature being 350°C it is possible to trace the processing window of this polymer. With a melt temperature of 230°C, the processing window of 120°C is large enough to ensure that there is no degradation of PA6 properties during the production and processing of the tapes.

4.1.3.2 Calcination Temperature

Similarly, to what was done with PET, the TGA test was performed to analyse at what temperature there is a total or partial loss of mass of the polymer. Figure 45 shows the curve obtained for PA6 during the TGA test.

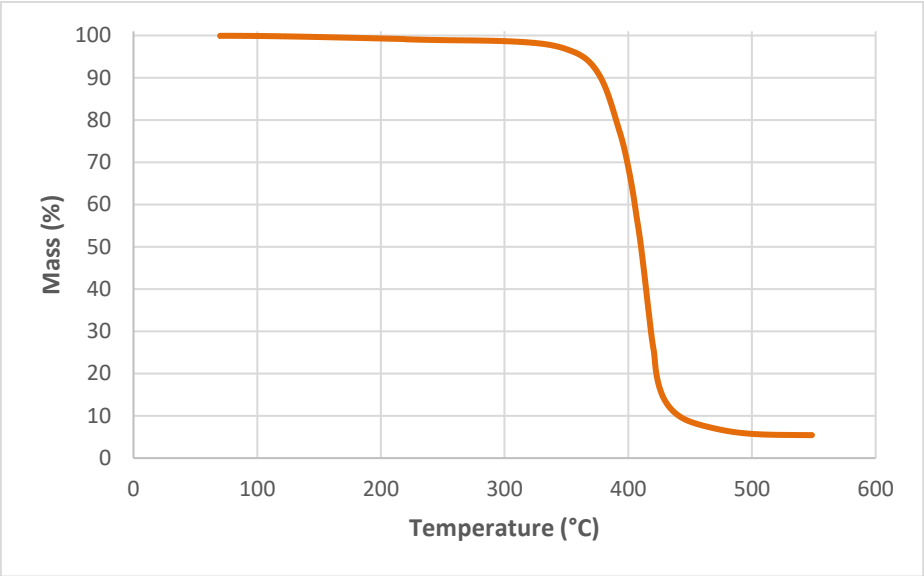

Figure 45 – TGA analysis of PA6

Analysing the TGA test curve it is possible to conclude that, for this polymer, the incineration at 500°C is practically total, obtaining only 2% of residual mass after burning. To confirm these values, the same procedure as for PET was performed using a muffle furnace. In Table 7 it is possible to observe the values obtained.

Table 7 – Calcination of PA6 at 500°C

PA6	Sample 1	Sample 2	Sample 3	Sample 4	Average
Remaining mass (%)	1.06	1.35	1.40	2.00	1.45 ± 0.34

The values of the remaining polymer at 500°C were about 2% which corresponds to the values obtained through the TGA test, showing reliability in the values obtained.

This value can be neglected, because it was verified the existence of residues inside the crucible after incineration, otherwise the value obtained would be even closer to 0. Thus, it is concluded that at 500°C the whole mass of polyamide incinerates.

4.1.4 Thermal Analysis of PC

4.1.4.1 Degradation Temperature and Processing Window

The polycarbonate TGA test was carried out to understand at what temperature the degradation of the material starts.

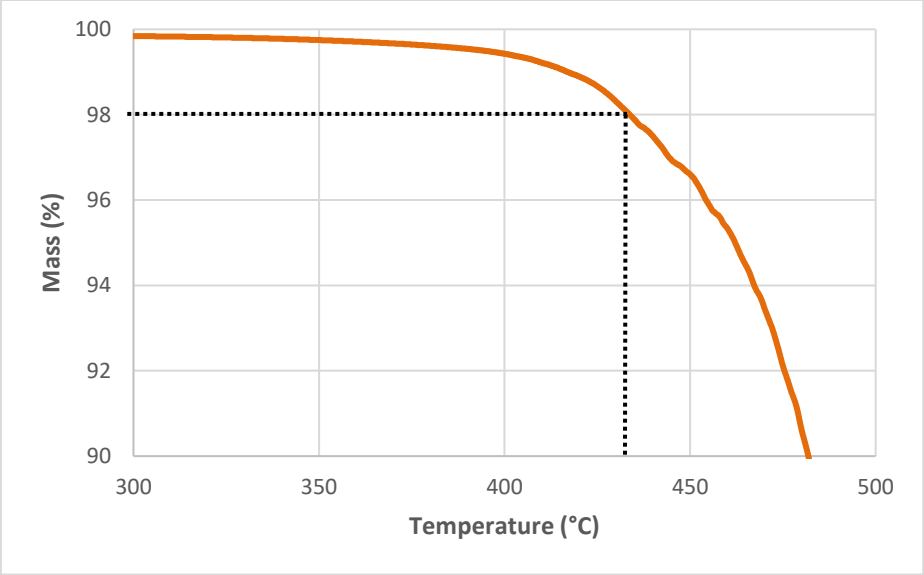

Figure 46 – Degradation of PC

Observing Figure 46, the temperature value at which the degradation of the material starts is around 435°C. This polymer has a melting temperature of 300°C, according to the manufacturer. This material can be processed with a range of 130°C without impoverishing the properties of the polymer.

4.1.4.2 Calcination Temperature

Similarly, to what was done with the polymers described above, it was necessary to study the TGA curve obtained for polycarbonate. It is interesting to note that this polymer is the most difficult to burn, so it is expected that it will be necessary to perform calcination test at higher temperatures. In Figure 47 it is possible to observe the TGA test of the polycarbonate.

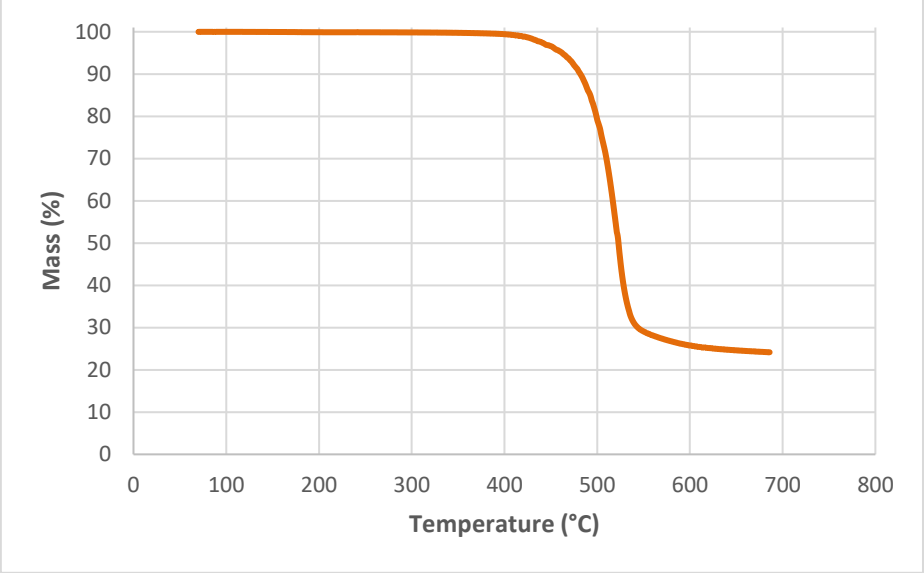

Figure 47 – TGA analysis of PC

As expected, the thermogravimetric curve of polycarbonate only starts to stabilise at higher temperatures, namely at 550°C. At this temperature, the burning is quite inefficient, with 30% of the sample mass remaining. To validate these values, calcination tests were carried out once again. The results of these tests are presented in Table 8.

Table 8 – Calcination of PC at 550°C

PC	Sample 1	Sample 2	Sample 3	Sample 4	Average
Remaining mass (%)	25.95	25.38	25.89	26.29	25.88 ± 0.33

According to the values in the table above, the values of the remaining mass of PC obtained via calcination tests were about 26%, which is in agreement with the values obtained by GA test.

As a higher temperature will be used for the PC calcination tests, it will be necessary to perform the verification for the carbon fibre using a temperature of 550°C. The values of this verification can be seen in Table 9.

Table 9 – Calcination of carbon fibre at 550°C

Carbon Fibres	Sample 1	Sample 2	Sample 3	Sample 4	Average
Remaining mass (%)	95.48	95.80	96.31	96.09	95.92 ± 0.31

With the results presented in the table above, it is possible to conclude that the results obtained by the TGA test agree with the values obtained for the calcination tests carried out in the muffle furnace. Thus, the remaining carbon fibre at 550°C is about 96%, which agrees with the values obtained from the TGA test.

4.2 Production of Carbon Fibres Reinforced Tapes

The production of the thermoplastic tapes was explained in detail in the previous chapter of this dissertation. The tapes were produced using three different thermoplastics with the carbon fibres, to understand the differences in their behaviour. The thermoplastics used have different thermal properties which led to differences in their processing. These processing parameters are in accordance with the thermal analysis that was evaluated in the chapter 4.1. Thus, in Table 10 it is possible to observe the melt impregnation parameters used in the manufacture of the different tapes.

Table 10 – Melt impregnation parameters

Parameter	Units	CF/PET	CF/PA6	CF/PC
Recipient Temperature	°C	250	230	270
Die Temperature	°C	240	220	260
Pulling Speed	m/min		4.0	

With the above mentioned parameters, it was possible to obtain stability in the process. The recipient temperature were obtained, based on the thermal properties of the material, and furthermore, several attempts were made so that all the polymer was in a state of low viscosity, being easier, the impregnation of the carbon fibre. It is important

to point out that the temperature used for processing the polycarbonate was not the same as that provided by the supplier, being used a lower temperature. This temperature was readjusted to lower temperatures, as it was found that at a lower temperature it was already possible to obtain a complete fusion of the polymer. At 270°C stability was achieved in the process when compared to the temperature value provided by the manufacturer. Regarding the die temperature, it was defined that a reduction of 10°C would be sufficient and acceptable to ensure the tape shape.

The value used for pulling speed is the one that gives the best impregnation level. When the pulling speed was increased, the impregnation level in the tape was reduced and the risk of breakage increased. On the other hand, reducing the speed did not affect the impregnation level, so any lower speed that would make the process long was discarded.

After all the tapes were produced, it was necessary to evaluate the amount of polymer in each roving of tape. To perform this first measurement, one metre of tape from each roving was weighed and compared with one metre of carbon fibre. It is important to note that this procedure is not accurate, which makes it necessary to perform calcination tests on the material transformed by pultrusion and heated compression moulding. The results obtained for the tape weights are shown in Table 11.

Table 11 – Amount of polymer in the tapes

Parameters	Units	CF/PET	CF/PA6	CF/PC
Average Fibre Mass Fraction	%	51.5	57.3	56.8
Standard Deviation	%	3.0	3.1	1.4
Average Fibre Volume Fraction	%	43.4	45.1	45.7
Standard Deviation	%	2.9	3.2	1.5

As shown in the table above, PET tapes obtained the best results in terms of impregnation with an average of 51.5% of fibre mass fraction. PET tapes were the easiest to produce, since this polymer offered good melting temperature stability and low viscosity, which facilitated the process.

PA and PC tapes obtained similar results, with results of about 57%. The PA tapes were the most difficult to produce by the described method, due to the high viscosity presented at the melting temperature, which made the process difficult. The production of PC tapes also offered some problems, but at higher speeds it was possible to counteract fibre breakage due to the high viscosity of the polymer. It should also be noted that the quality of the rovings remained practically unchanged as can be seen by the low standard deviation obtained.

The main problems with the tapes production method are the high force to which the fibre is subjected when the polymer is melted, leading to fibre breakage. This breakage leads to the need to stop the process, disassemble the equipment, reassemble it, and start the production again. In addition, the low heating optimisation of the process made it difficult to stabilise, which may have compromised the results.

4.3 Pultrusion

The next step after the producing the tapes was to transform them by pultrusion. This processing process required a careful selection of parameters, considering the properties of each polymer. These parameters will be demonstrated below.

First it is necessary to know how many rovings will be required for each polymer. To estimate the number, an expression relating the density, mass fraction of the fibre and the cross-sectional area of the profile to the linear weight of the fibre was used. The number of rovings was calculated using Equation 4.1.

$$Nr = \frac{\rho_{comp} \times w_f \times A}{m_{linear}} \tag{4.1}$$

Where:

Nr – Number of rovings

ρ_{comp} – Density of the composite [g/cm^3]

w_f – Mass content of fibres

A – Cross-section area [cm^2]

m_{linear} – Linear weight of the fibre [g/cm]

The density of the composite was calculated using the Rule of Mixtures, which is shown below in Equation 4.2.

$$\rho_{comp} = \rho_f \times v_f + \rho_p \times (1 - v_f) \tag{4.2}$$

Where:

ρ_f – Density of the fibre [g/cm^3]

ρ_p – Density of the polymer [g/cm^3]

v_f – Fibre volume fraction

By applying Equation 4.1 to the three types of polymers used, it was possible to conclude the number of rovings to use for each thermoplastic matrix.

4.3.1 Processing Parameters

After finding the number of rovings to be used and completing the study on the thermal properties of the carbon fibre and the polymers, it was possible to select the temperature values to be used, considering the processing window of each material.

The aim of this dissertation is to understand the impact on temperature variation between the same polymers. Besides, to identify which polymer presents the best mechanical properties when transformed by pultrusion. For this reason, two different conditions were tested for the same polymer, varying only the temperature.

In Table 12 are defined all the parameters that were used to produce the pultrusion profiles with stability in the process.

Table 12 – Pultrusion parameters

Parameters	Units	CF – PET		CF – PA6		CF – PC	
Condition	-	1	2	1	2	1	2
Number of Rovings	-	10					
Preheating Oven Temperature	°C	135		125		200	
Heating Die Temperature	°C	265	280	205	220	300	330
Cooling Die Temperature	°C	25					
Pulling Speed	m/min	0.2					

The minimum pulling speed of the available equipment for pultrusion of thermoplastic composites was 0.2 m/min. This speed was used for the processing of all profiles, since the pulling speed is a parameter that influences the process and will not be studied in this dissertation. Moreover, this speed is the one that provided the best stability to the process.

Regarding the temperature used in the heating die, the temperature values defined for the different conditions considered the process window of each polymer. These values ensured that there was no degradation of the material. The temperature of the cooling die was selected at the lowest possible value, 25°C, to ensure a higher geometric accuracy during the consolidation of the pultrusion profile.

The temperature of the preheating oven was initially set 120°C below the processing temperature to ensure some stabilisation in the process. However, this temperature is critical and had to be adjusted several times while the production was running. This adjustment had to be made due to a phenomenon that occurred at the entrance of the heating die called reflux. This phenomenon occurs when the temperature at the entrance of the heating die is too high, leading to polymer accumulation at the entrance. This accumulation leads to increased tape resistance, resulting in poor quality of the pultrusion profile due to low polymer content. In addition, it can cause the tape to break, making it necessary to stop the process and open the dies to solve the problem. To overcome this problem, it was necessary to reduce the temperature of the preheating oven to stabilise the process.

The pultrusion of PET tapes was the most challenging to perform and, therefore, the one that was subject to the largest number of adjustments during the processing of these tapes. During the processing of the tapes, it was noticed that the reflux phenomenon occurred frequently, so it was necessary to make several adjustments in the preheating temperature until stability was obtained at a temperature of 135°C. The processing of the tapes may have been the most difficult because the large amount of polymer that was in the tapes.

Pultrusion of PA tapes was slightly easier compared to PET ones due to less frequent reflux, even with the high viscosity of the polyamide. The temperature values in the heating die between 205°C and 220°C were stable and presented no problems during the processing of the tapes. The preheating oven had to be adjusted and the process started at a temperature of 100°C, which was inefficient until 125°C was set.

The PC pultrusion was exceptionally good, with no problems to mention. Process stability was achieved by using higher temperature in the preheating furnace, namely 200°C which helped the fusion of the polycarbonate in the tapes. Regarding the temperatures used in the heating die, the temperature between 300°C and 330°C proved to be suitable for this polymer processing. This concludes that PC is the best

polymer used to be transformed by pultrusion obtaining a high-quality finish and good geometric shape.

All pultrusion profiles need to be tested to assess their mechanical properties and understand the level of impregnation with the different parameters used. It is important to remember that the quality of the finish does not affect the properties of the material.

4.4 Heated Compression Moulding

For the manufacture of the laminates, it was necessary to define parameters to ensure that all the laminates were well consolidated. These parameters are critical because if the temperature and the pressure are too high, there will be material degradation and consequently low mechanical properties. To define the parameters, the material properties were used to ensure the preservation of the thermoplastic matrix and carbon fibre properties.

The three kinds of thermoplastic tapes have different curing cycles. These cycles are divided between heating, compression, and cooling. The three laminates were inserted in the heated plate press after performing the procedure explained in 3.3.2.

The parameters used for each thermoplastic polymer will be presented and explained in the following pages. All processed laminates were properly consolidated, presenting a good quality.

4.4.1 Process Parameters for Polyethylene Terephthalate

The parameters used for the consolidation of PET tapes into a laminate are shown in Table 13.

Table 13 – PET cycle

Parameter	Temperature (°C)	Pressure (MPa)	Time (min)
Heating	250	0	5
Compression	250	2.5	30
Cooling	20	2.5	120

The heating temperature should be rigorously chosen considering the thermogravimetric analysis previously performed for polyethylene terephthalate. This

heating is important to start the melting of the polymer before applying pressure to the material, in order to obtain a better homogenisation of the polymer between the contact area. The heating temperature of 250°C was selected according to the manufacturer's information and since it was found during the production of the tape that the polymer is completely melted at this temperature. Furthermore, 5 minutes for this process was considered enough to start the melting of the polymer.

During the compression stage, the temperature selected was the same as the heating temperature, changing only the pressure and time applied. Thus, a pressure of 2.5 MPa was used to consolidate the tapes into a laminate for a period of 30 minutes.

After the end of compression, the laminate is cooled down to room temperature for 2 hours. During the cooling period, the press continues to apply a pressure of 2.5 MPa to ensure that there is no warping of the laminate due to the drastic temperature variation.

4.4.2 Process Parameters for Polyamide

Table 14 shows the parameters used to consolidate the polyamide tapes in a composite plate.

Table 14 – PA6 cycle

Parameter	Temperature (°C)	Pressure (MPa)	Time (min)
Heating	230	0	5
Compression	230	2.5	30
Cooling	20	2.5	120

Similarly, to what was done for PET, for PA tapes the selection of parameters followed the same principle. The choice of heating temperature was again based on the temperature used to melt the polymer during the production of polyamide tapes. The heating time used was 5 minutes and proved to be sufficient to ensure the start of polymer melting with a temperature of 230°C.

The temperature during compression was kept the same as during the heating stage, and a pressure of 2.5 MPa was simultaneously applied for 30 minutes.

Finally, during the cooling step to room temperature, a constant pressure of 2.5 MPa was maintained for 120 minutes.

The PA laminate was the most difficult to produce, mainly because of the high stiffness of the PA tapes, which made the weaving phase difficult. Moreover, given the great difficult in performing this process manually, there were some ruptures of the tapes during the process, which may affect the mechanical properties of the laminate.

4.4.3 Process Parameters for Polycarbonate

For polycarbonate, the same selection principle was used as for PET and PA. Table 15 presents the parameters used for the heated compression moulding of the polycarbonate tapes.

Table 15 – PC cycle

Parameter	Temperature (°C)	Pressure (MPa)	Time (min)
Heating	300	0	5
Compression	300	2.5	30
Cooling	20	2.5	120

Like the parameters of the other polymers, with polycarbonate the same dwell time was used at each stage, as well as the pressure applied at each moment.

Unlike the other polymers, the polycarbonate has a higher melting temperature. For this reason, it can be seen that the temperature used in the heating and compression was 300°C. This temperature was based on the thermal properties of this material.

This laminate was the easiest to manufacture, since polycarbonate tapes had moderate stiffness, and because of this it was relatively easy to weave these tapes by hand. In addition, polycarbonate tapes were the most homogeneous in geometry. For this reason, no breaks occurred during the manufacture of the weaving composed of these tapes.

4.5 Mechanical Tests of Pultruded Profiles

This sub-chapter will present the results obtained for the mechanical tests of the pultrusion profiles. The mechanical tests that will be analysed are the 3 point bending tests and the calcination tests.

4.5.1 Fibre Content

To evaluate the fibre content of each pultrusion profile, calcination tests were performed to find out the percentage of carbon fibre in each one, being possible to evaluate its impregnation level. The fibre mass fraction of each condition will be found out, as well as the fibre volume fraction. The fibre volume fraction is the property that best characterises the fibre impregnation. A high percentage of fibre volume reports the existence of low impregnation while a low percentage shows polymer excess. Typical values for processes using unidirectional fibres, namely pultrusion, is around 60%.

To find out the mass of fibres in the PET and PC profiles, Equation 3.2 was used, since these polymers do not undergo total incineration at the conditions used. Regarding the PA specimens, Equation 3.1 was used, because the total incineration of the polymer occurs under the conditions in which the test was performed. The results can be seen below in Table 16.

Table 16 – Calcination tests of pultruded profiles

Tape	Testing Temperature (°C)	Condition	Average Fibre Mass Fraction (%)	Average Fibre Volume Fraction (%)
CF/PET	500	0.2 – 265°C	55.68	46.59
		0.2 – 280°C	53.61	44.52
CF/PA	500	0.2 – 205°C	56.33	44.96
		0.2 – 220°C	56.95	45.59
CF/PC	550	0.2 – 300°C	55.04	44.94
		0.2 – 330°C	55.57	45.47

As it is possible to observe in the table, there is such a great proximity of values, being the average of fibre volume fraction about 45%. These results are below the expected values for unidirectional fibre composites, demonstrating the existence excess polymer, which can drastically affect the specific properties of the material.

4.5.2 Flexural Testing

Bending tests were carried out to understand the behaviour of the material transformed by pultrusion. The results are going to be compared and presented in this chapter. It is important to note that all the graphs developed to analyse the results of the flexural tests can be found in appendix B.

The results of the flexural tests on the pultrusion profiles will be presented. It will be possible to observe the flexural strength that the specimens resisted, the flexural modulus and the strain at break.

4.5.2.1 Flexural Tests for CF/PET Composites

Table 17 – Results of bending tests for CF/PET composites

	Condition	Flexural Strength (MPa)	Flexural Modulus (GPa)	Strain at Break (%)
CF/PET	0.2 – 265°C	619.14 ± 93.12	45.80 ± 8.30	1.53 ± 0.14
	0.2 – 280°C	409.16 ± 32.49	35.69 ± 5.68	1.58 ± 0.19

The results for PET showed that there is a large difference in properties when the heating temperature of the die was changed. It can be observed that a temperature increases of 15°C made the mechanical properties of the material weaker.

Using a temperature of 265°C, a flexural strength of 600 MPa and a flexural modulus of 45 MPa were obtained. When increasing the temperature to 280°C, the material properties degraded, obtaining a flexural strength of 400 MPa and a flexural modulus of 35 MPa. Regarding the strain at break, the results remained the same with values around 1.50%.

The results obtained showed that at 280°C the processing for this type of tapes is not indicated, which negatively influence the material resulting in weaker mechanical properties.

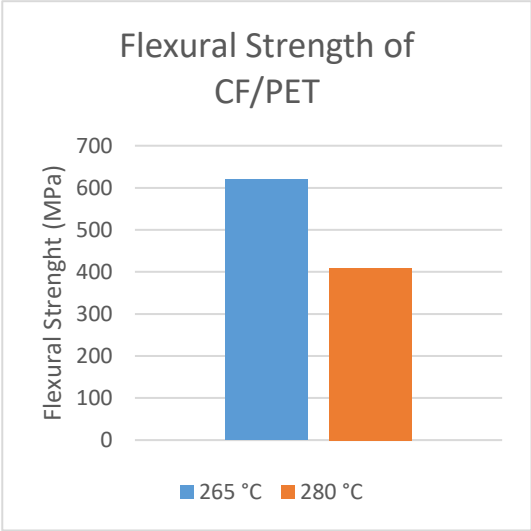

Figure 48 -CF/PET flexural strength evolution

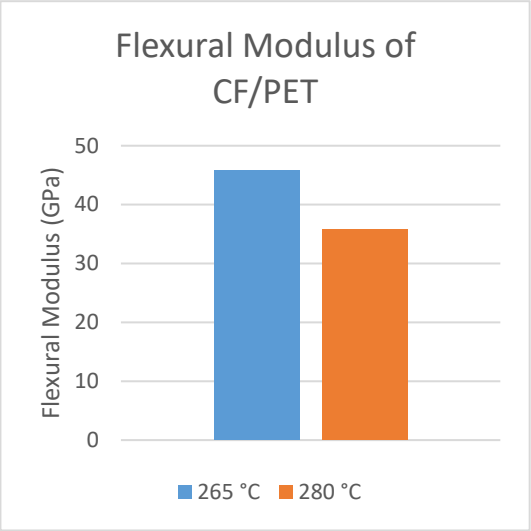

Figure 49 – CF/PET flexural modulus evolution

4.5.2.2 Flexural Tests for CF/PA6 Composites

Table 18 – Results of bending tests for CF/PA composites

	Condition	Flexural Strength (MPa)	Flexural Modulus (GPa)	Strain at Break (%)
CF/PA6	0.2 – 205°C	211.03 ± 24.26	33.83 ± 4.95	0.87 ± 0.12
	0.2 – 220°C	432.18 ± 43.34	41.22 ± 3.42	1.26 ± 0.05

In Flexural Tests for CF/PA6 Composites

Table 18 it can be seen between the two conditions analysed, there was an abysmal difference between the flexural strength obtained. The flexural strength for the 205°C condition was around 200 MPa while the condition with an increment of 15°C the value was about 400 MPa. The value of flexural modulus was similar with values of 34 GPa for the first condition and with 41 GPa for the condition with higher temperature as expected. The strain at break varied between 0.87% and 1.26%, not being a significant difference.

These results confirmed the fact that the use of lower temperatures is not indicated for polyamide, as this polymer presents a high viscosity at lower temperatures. With this high viscosity it is difficult to get a good impregnation of the fibres, which results in poor cohesion between the fibres. This poor impregnation leads to weaker mechanical properties.

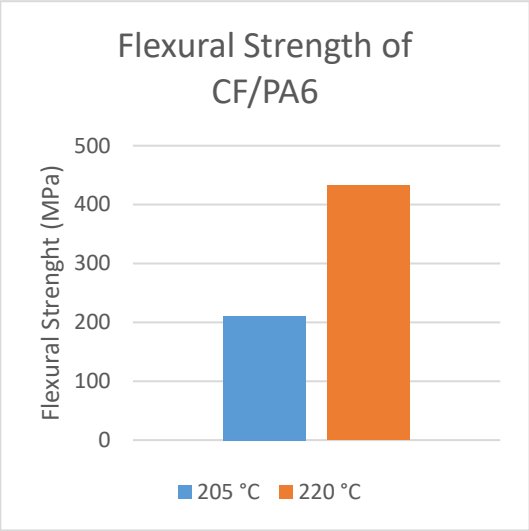

Figure 50 – CF/PA6 flexural strength evolution

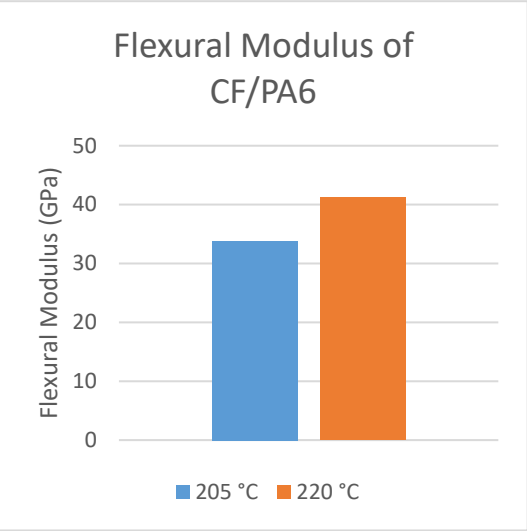

Figure 51 – CF/PA6 flexural modulus evolution

4.5.2.3 Flexural Tests for CF/PC Composites

Table 19 – Results of bending tests for CF/PC composites

	Condition	Flexural Strength (MPa)	Flexural Modulus (GPa)	Strain at Break (%)
CF/PC	0.2 – 300°C	753.90 ± 25.73	71.57 ± 1.21	1.20 ± 0.02
	0.2 – 330°C	823.21 ± 21.62	73.35 ± 1.55	1.22 ± 0.05

Polycarbonate specimens obtained better results than polyethylene terephthalate and polyamide specimens. The flexural modulus showed little difference, with values of 754 MPa for the condition at 300°C and 823 MPa for the 330°C condition. The flexural modulus obtained for the two conditions was practically the same, with values between 71 GPa and 73 GPa. The strain at break also remained unchanged, with values of 1.20%.

This polymer presents a great potential to be transformed by pultrusion, as can be seen by the results for both conditions. Furthermore, with this polymer it was possible to increase the speed of the process, obtaining good quality without production problems.

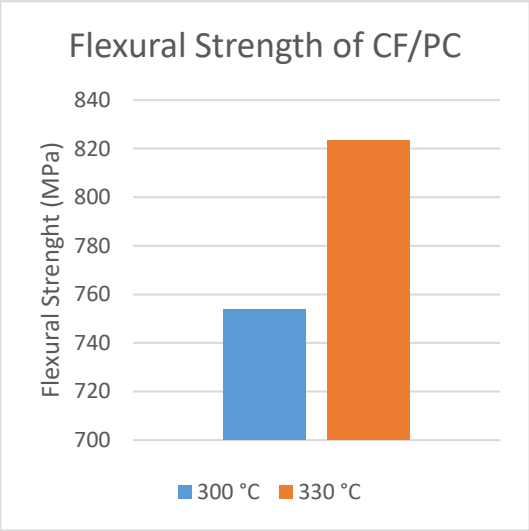

Figure 52 – CF/PC flexural strength evolution

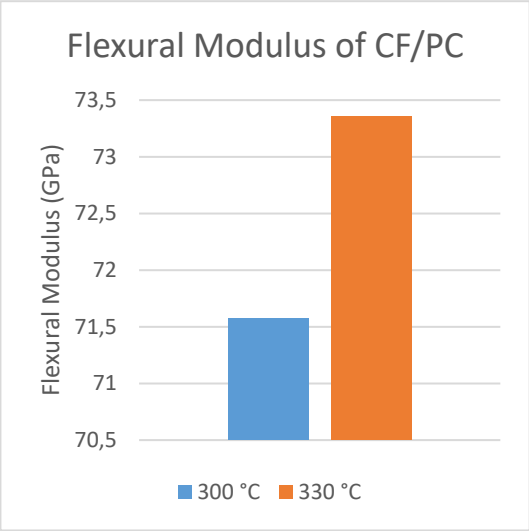

Figure 53 – CF/PC flexural modulus evolution

4.5.2.4 Overall Conclusions

Some conclusions based on the tests performed on the pultrusion profiles will be presented below. It is important to highlight that the condition with the best mechanical properties of each polymer will be compared between the different polymers.

- The material that presented the best flexural properties was the polycarbonate. Although it was the polymer that required the most temperature, it was quite easy to transform by pultrusion, achieving a great stability in the process.
- As for the temperature, it is possible to state that a small variation in the temperature is capable to improve the properties of the composite. It is possible to observe this effect more clearly in the profiles composed of PET and PA., where a variation of 15°C substantially improved the mechanical properties.
- The values of the flexural modulus of the PA and PET profiles were very close, with values in the range of 40 GPa. The flexural strength of PET is much higher than that obtained for PA.
- The strain at break of all materials was quite similar, with values around 1.2%.

To make a more effective comparison, the relative values of flexural strength and flexural modulus will be presented next. This comparison will be performed to evaluate the properties of the materials transformed without the influence of the fibre volume fraction of each tape. In Table 20 it is possible to observe the values obtained for the relative flexural strength and for the relative flexural modulus of the conditions that presented the best mechanical properties.

Table 20 – Relative results of the bending tests

Tape	Condition	Relative Flexural Strength (MPa/vf)	Relative Flexural Modulus (GPa/vf)
CF/PET	0.2 – 265°C	1328.91	98.31
CF/PA6	0.2 – 220°C	947.97	90.41
CF/PC	0.2 – 330°C	1810.45	161.33

By analysing Table 20, the following conclusion were reached:

- The values obtained for the relative properties are in accordance with the results of the flexural strength and flexural modulus of the pultrusion profiles.
- The composites transformed using PC tapes have the highest relative flexural strength, as well as the highest value of relative flexural modulus.
- The pultrusion profiles that used PA6 in their matrix are the ones with the worst relative properties. The relative flexural modulus of this polymer is close to the value of the profiles using PET as the matrix.

Table 21 shows the values of the flexural modulus calculated theoretically using the law of mixtures and the values obtained experimentally. The relative error is calculated in order to compare the values obtained experimentally with the values theoretically expected.

Table 21 – Comparison of the flexural modulus

Tape	Condition	Experimental Flexural Modulus (GPa)	Theoretical Flexural Modulus (GPa)	Relative Error (%)
CF/PET	0.2 – 265°C	45.80	112.88	-146%
	0.2 – 280°C	35.69	107.96	-202%
CF/PA6	0.2 – 205°C	33.83	109.56	-224%
	0.2 – 220°C	41.22	111.05	-169%
CF/PC	0.2 – 300°C	71.57	109.12	-52%
	0.2 – 330°C	73.35	110.38	-50%

Analysing Table 21, it is possible to state some conclusions, that are presented below:

- The expected flexural modulus values for pultrusion profiles are around 110 GPa, regardless of the type of polymer used.
- The pultrusion profiles that obtained values closer to the theoretical ones were the profiles that had PC in their constitution, with differences around 50%.
- The experimental results for the PET and PA6 pultrusion profiles show differences greater than 150%. These values may indicate that the properties provided by the manufacturers are exaggerated, influencing the theoretical values or that the transformation process by pultrusion was not so well achieved for these polymers.

4.6 Mechanical Tests of Heated Compression Moulding Specimens

This subchapter will present the results obtained for the mechanical tests of the heated compression moulding samples. The mechanical tests that will be analysed will be the 3-point bending tests and the calcination tests.

4.6.1 Fibre Content

The calcination tests for the laminates processed by heated compression moulding were carried out following the same procedure as for the pultrusion profiles.

Table 22 – Calcination tests of heated compression moulding specimens

Tape	Condition	Testing Temperature (°C)	Fibre Mass Fraction (%)	Fibre Volume Fraction (%)
CF/PET	2.5 MPa	500	57.36	48.30
CF/PA6		500	63.49	52.41
CF/PC		550	70.20	61.10

Observing Table 22 it is possible to see that the number of fibres in the polycarbonate laminate has the highest values of fibre volume fraction, with values around 61%. This value shows the existence of a lower percentage of polymer than the one desired for this procedure. This result may indicate that there was little polymer in the internal areas of the laminate, causing a weak bond between the different layers, which may lead to decreases in mechanical properties.

Regarding the polyethylene terephthalate and polyamide laminates, the results of the fibre volume fraction are very close to 50%. These results indicate that the curing cycle was correctly chosen, since fibre volume is equal to the amount of polymer. This is an excellent result which confirms that a good impregnation has been obtained.

4.6.2 Flexural Testing

The heated compression moulding specimens were tested to evaluate the mechanical properties of the laminate. All specimens were cut in the direction of the fibres to obtain a more reliable and rigorous comparison between the three laminates produced. It is important to note that all the graphs developed to analyse the results of the flexural tests can be found in appendix C.

Table 23 – Results of bending tests for heated compression moulding specimens

Tape	Flexural Strength (MPa)	Flexural Modulus (GPa)	Strain at Break (%)
CF/PET	192.22 ± 27.14	48.18 ± 3.12	0.47 ± 0.04
CF/PA	333.13 ± 52.07	40.86 ± 11.93	1.06 ± 0.29
CF/PC	314.82 ± 17.07	57.11 ± 23.29	0.80 ± 0.10

In Table 23 it is possible to observe the main properties obtained through the bending tests performed.

Observing the table, it is possible to understand that the polyamide and the polycarbonate laminates presented a very close flexural strength with values around 300 MPa. In relation to the polyethylene terephthalate laminate, the value obtained was 192 MPa.

As for the flexural modulus, the maximum value obtained was 57 GPa and, as expected, it was obtained for the polycarbonate tapes. The laminate manufactured with polyamide tapes obtained a modulus of 40 GPa, being the lowest value obtained for the laminates produced. For the polyethylene terephthalate a modulus of 48 GPa was achieved.

The strain at break presented values about 1% for the PA and PC laminates and values of 0.5% for PET laminate, with a low standard deviation.

CONCLUSIONS

5 Conclusions

With this work it was possible to evaluate the production of unidirectional tapes composed of carbon fibres and thermoplastic polymers and their processing by pultrusion and heated compression moulding.

The tapes were produced in a prototype designed, assembled and manufactured in the facilities of ISEP, with the purpose of making a machine able to produce carbon fibre reinforced thermoplastic tapes at relatively low cost. The pultrusion was performed through an existing prototype in the Composite Materials Laboratory of ISEP and for the heated compression moulding a standard heated plate press was used.

Finally, a tuning of parameters was carried out during the processing of the tapes obtained, with the aim of obtaining the best possible properties in the final material.

The main conclusions resulting from the study are as follows:

1. Melt impregnation is a technology that enables the production of a continuous pre-impregnated thermoplastic material, at an acceptable rate. Furthermore, the production of the equipment is relatively simple, allowing the production of a prepreg tape.
2. As expected, during the manufacturing of the tapes, difficulties are noted in reducing properly the viscosity of the polymer to impregnate the carbon fibres. The higher viscosity of the thermoplastics was counterbalanced with the development of pressure in the die.
3. Regarding the pultrusion process, the use of thermoplastic tapes proved to be efficient for set-up and for being capable of obtaining processing speeds of 0.2 m/min with ease. The produced composites revealed properties compatible with structural applications.
4. During pultrusion processing, temperature is a critical parameter, and with a small variation in the temperature it is possible to increase or decrease the properties of the pultruded composites.
5. Regarding the heated compression moulding, it was found that the parameters used performed a good consolidation of the tapes. The versatility of the prepreg tapes allows the production of more complex shaped parts.

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APPENDIX

7 APPENDIX

7.1 Appendix A – Technical Datasheets

7.1.1 Carbon Fibre – C T50 – 4,0/240

Material data of our SIGRAFIL® continuous carbon fiber tows

Typical properties	Units	C T50-4.0/240	C T50-4.6/260	C T50-4.8/280
Number of filaments		50k	50k	50k
Fineness of yarn dry	tex [g/1000 m]	3420	3420	3070
Density	g/cm³	1.80	1.80	1.78
Single filament diameter	µm	7.0	7.0	6.6
Tensile strength	GPa	4.0	4.6	4.8
Tensile modulus	GPa	240	260	280
Elongation at break	%	1.70	1.70	1.65
Single filament resistivity	µΩm	15	17	16

Compatible matrix systems for our SIGRAFIL® continuous carbon fiber tows

Matrix compatibility
Epoxy, polyurethane, phenol
Vinyl ester (and all radical-based curing systems), unsaturated polyester
Polyurethane, polycarbonate, polyester, polysulfone, cyanate ester, polyamide, BMI, PESU, PEEK, PEKK, PVC, polyimide
Polypropylene
Polyamide
PA-RIM process (in-situ polymerization of caprolactam, e.g. reactive PA processing)

Enhanced performance by sizing

By applying different types of sizing, the carbon fibers can be optimally matched to different matrix systems. In this way, it is possible to produce application-tailored versions as well as the standard materials. So, together with our customers, we find optimized solutions for their challenges.

Nomenclature

SIGRAFIL C T50-4.0/240-E100

1 | 2 | 3 | 4 | 5 | 6

1	Brand name	SIGRAFIL
2	Material	C = carbon
3	Type	T = Continuous tow
4	Number of filaments	50 = 50 000
5	Mechanical properties	Tensile strength/elastic modulus in GPa
6	Sizing type	e.g. E100 = epoxy

7.1.2 Polyamide granules

PERFORMANCE PLASTICS

PRODUCT INFORMATION

RADILON S HS 305 M BK

Material code *Colour code*

DESCRIPTION

PA6 injection moulding grade. Nucleated, fast cycling. Black colour.

General purpose grade, suitable for parts requiring high productivity.

ISO 1043 : PA6

MATERIAL HANDLING AND PROCESSING

The material is delivered in moisture-proof packaging ready for processing. Maximum recommended water content for best processing is 0.15%. Typical conditions with a desiccant drier: temperature 80 ° C, dew point -20 ° C or below, time 2-4 h or more.

Special care must be taken to avoid moisture absorption and contamination with other polymers when adding regrind material. Colour variation and mechanical properties reduction may occur and should always be carefully monitored.

Processing Parameters

Melt Temperature:	Mold Temperature:	Injection Speed:
250 ÷ 280 °C	70 ÷ 80 °C	Medium

PRODUCT SAFETY AND APPROVALS

For safety instruction please refer to Material Safety Data Sheet

Underwriters Laboratories Inc. certified material. File number: E116324 www.ul.com

RoHS compliant 2011/65/UE and following amendments

PERFORMANCE PLASTICS

TECHNICAL DATA SHEET

RADILON S HS 305 M BK

Material code *Colour code*

PROPERTY		STANDARD	UNIT	VALUE DAM*	VALUE Cond**
Physical Properties					
Density		ISO 1183	Kg/m³	1140	
Moulding shrinkage – Parallel / Normal	270/60/30***	ISO 294-4	%	0,9 / 1	
Moisture absorption 23°C – 50%RH	2mm thk	ISO 62	%	2.7	
Water absorption, immersion at 23°C	2mm thk	ISO 62	%	9,5	
Viscosity Index (Sulfuric Acid)		ISO 307	ml/g	146	
Mechanical Properties					
Tensile Modulus	1mm/min	ISO 527-2/1A	MPa	3000	1200
Stress at Yield	50mm/min	ISO 527-2/1A	MPa	78	40
Yield Strain	50mm/min	ISO 527-2/1A	%	4,2	30
Nominal Strain at Break	50mm/min	ISO 527-2/1A	%	30	>50
Flexural Modulus	2mm/min	ISO 178	MPa	2800	
Flexural Strength	2mm/min	ISO 178	MPa	105	
Charpy Notched Impact Strength	+23°C	ISO 179/1 eA	KJ/m²	6	11
Charpy Notched Impact Strength	-30°C	ISO 179/1 eA	KJ/m²	4	
Thermal Properties					
Melting Temperature	10°C/min	ISO 11357-1-3	°C	220	
Heat Deflection Temperature	1.8 MPa	ISO 75/2Af	°C	55	
Heat Deflection Temperature	0.45 MPa	ISO 75/2 B f	°C	170	
Vicat Softening Temperature	50°C/h	ISO 306/B50 50N	°C	190	
Flammability Properties					
Flammability	0.8mm	UL 94	class	V2	
Glow Wire Flammability Index	2mm	IEC 60695-2-12	°C	750	
Automotive interior flammability	3mm thk	ISO 3795	mm/min	0	
Electrical Properties					
Volume resistivity	500V	IEC 60093	ohm - m	1 E+13	1 E+11
Surface resistivity	500V	IEC 60093	ohm	1 E+12	1 E+10
Comparative Tracking Index	Sol.A	IEC 60112	-	500	

*DAM = Dry As Moulded state **Cond = Conditioned state similar to ISO 1110 ***Melt Temp [°C] / Mold Temp [°C] / Cavity press [MPa]

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7.1.3 Polycarbonate granules

LOTTE ADVANCED MATERIALS

ASTM Property

INFINO		
	Grade	SC-1220UR
	Resin Type	PC

E&E, Consumer Product

Item	Measuring Method	Condition	Unit	Value
Physical				
Specific Gravity	ASTM D792	Natural or representative color	-	1.2
Melt Flow Index	ASTM D1238	300℃, 1.2kg	g/10min	22
Mold Shrinkage(MD)	ASTM D955	Flow at 3.2mm(MD)	%	0.5~0.7
Mold Shrinkage(TD)	ASTM D955	X-Flow at 3.2mm(TD)	%	0.5~0.7
Mechanical				
Tensile Strength at Yield	ASTM D638	50mm/min	kgf/cm2	640
Tensile Strain at break	ASTM D638	50mm/min	%	110
Tensile Modulus	ASTM D638	50mm/min	kgf/cm2	23000
Tensile Strength at break	ASTM D638	50mm/min	kgf/cm2	640
Flexural Strength	ASTM D790	2.8mm/min	kgf/cm2	920
Flexural Modulus	ASTM D790	2.8mm/min	kgf/cm2	23000
Izod Impact Strength(notched)	ASTM D256	1/4 inch at 23°C	kgf·cm/cm	10
Izod Impact Strength(notched)	ASTM D256	1/8 inch at 23°C	kgf·cm/cm	75
Rockwell Hardness	ASTM D785	R-Scale	-	120
Thermal				
Heat Deflection Temperature	ASTM D648	18.56kgf/cm2, 6.4mm	°C	125
Heat Deflection Temperature	ASTM D648	4.6kgf/cm2, 6.4mm	°C	136
VICAT Softening Temperature	ISO 306	B/50	°C	145
Flammability				
Flammability	UL94	V-2	mm	0.75~3.2

1. The value above is the representative value of the NP or representative color and may have deviation. It can only be used for selecting materials.
2. The value above shall not be regarded as a material specification and cannot be used for molding designs.

7.1.4 Polyethylene Terephthalate granules

越南百宏实业有限公司
BILLION INDUSTRIAL (VIET NAM) CO.,LTD
LOT 43-16, ROAD N14, PHUOC DONG INDUSTRIAL PARK, PHUOC DONG COMMUNE,
GO DAU DISTRICT, TAY NINH PROVINCE, VIET NAM

PET RESIN CHIPS SPECIFICATION

CODE NO. : 31W56/W **WATER BOTTLE GRADE (AA GRADE)**

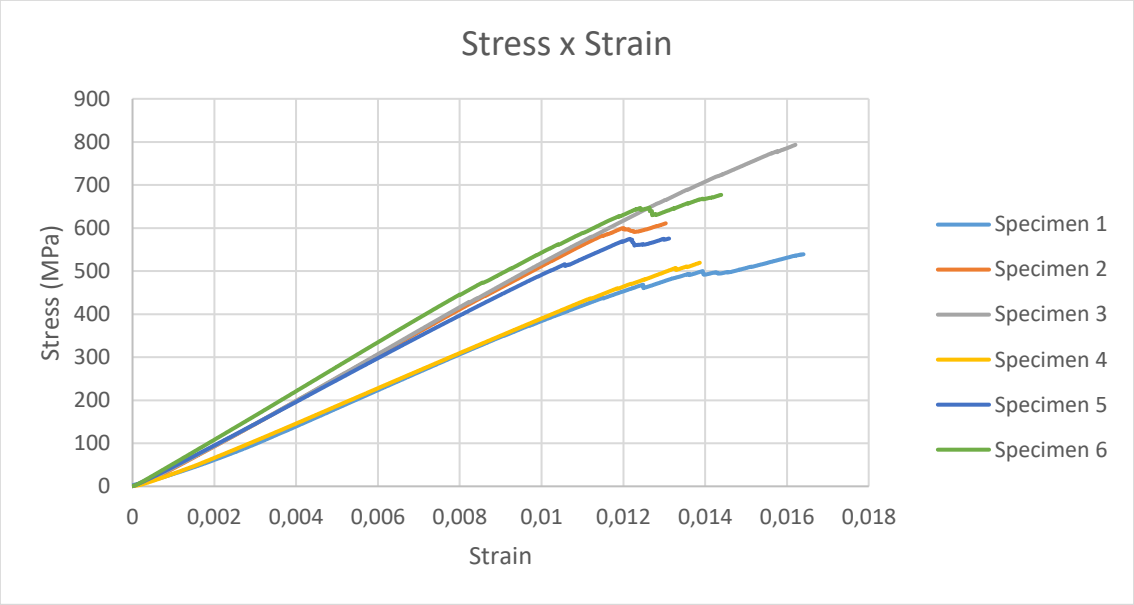
ITEM	UNIT	INDEX	TEST METHOD
IV	dl/g	0.80±0.02	ASTM D4603-03
AA	ppm	≤1.0	GC
DEG	%	1.25±0.2	GC
Melting Point	℃	249±2	DSC
COOH	mmol/kg	≤35	Titration
L Value	-	≥80	GS
B Value	-	≤0	GS
Crystall-zation	%	≥45	DSC
Humidity	%	≤0.4	IR
Impurities	granula/500g	NULL	GS
ASH	%	≤0.08	GS
DUST	mg/kg	≤100	GS

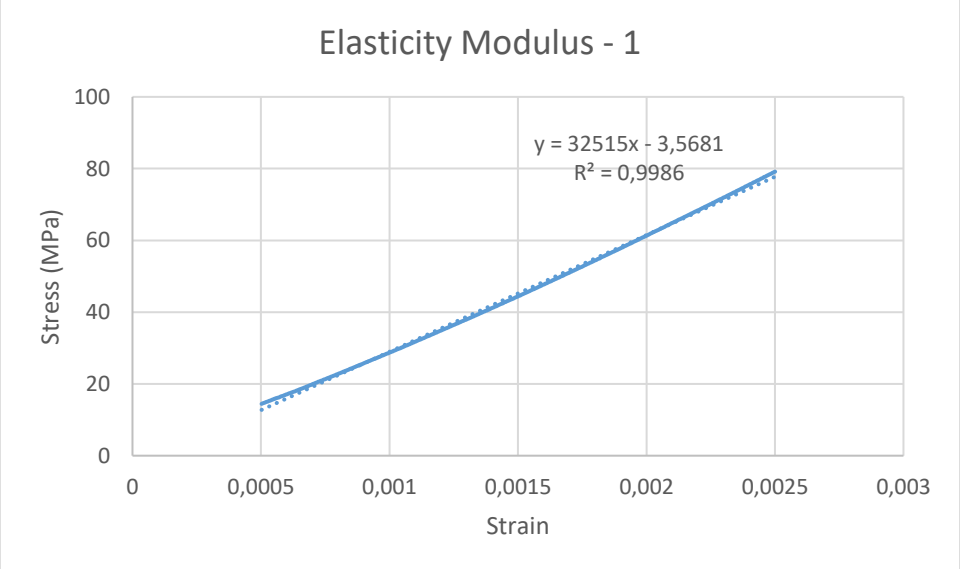
BILLION Q.C. DEPT.
MAY 13, 2020

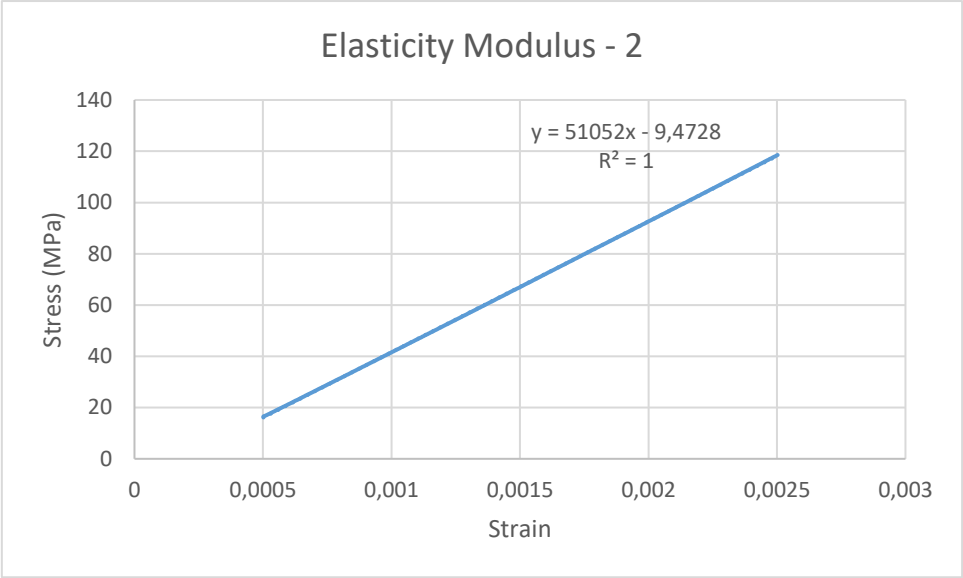
7.2 Appendix B – Graphs Obtained from the Bending Tests of Pultrusion Profiles

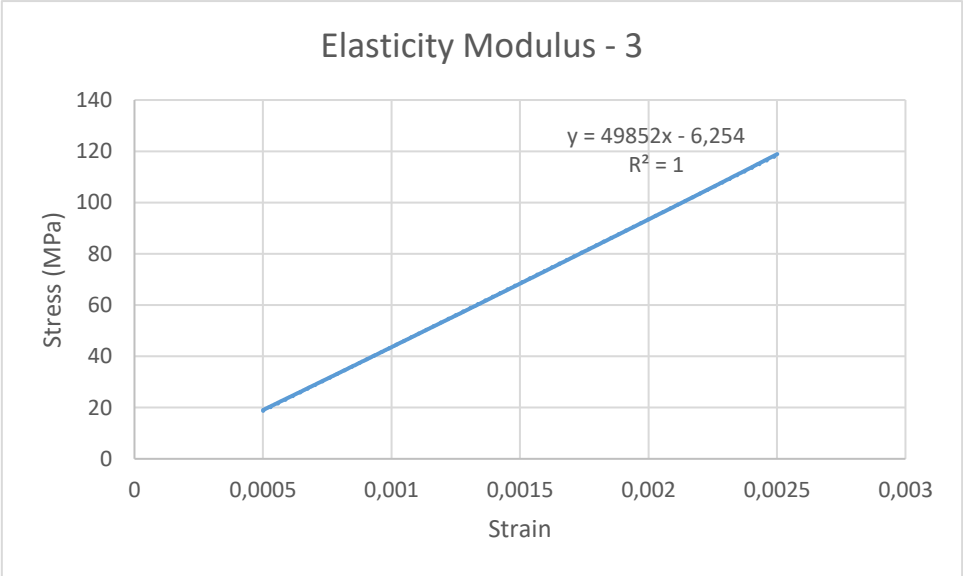
7.2.1 PET

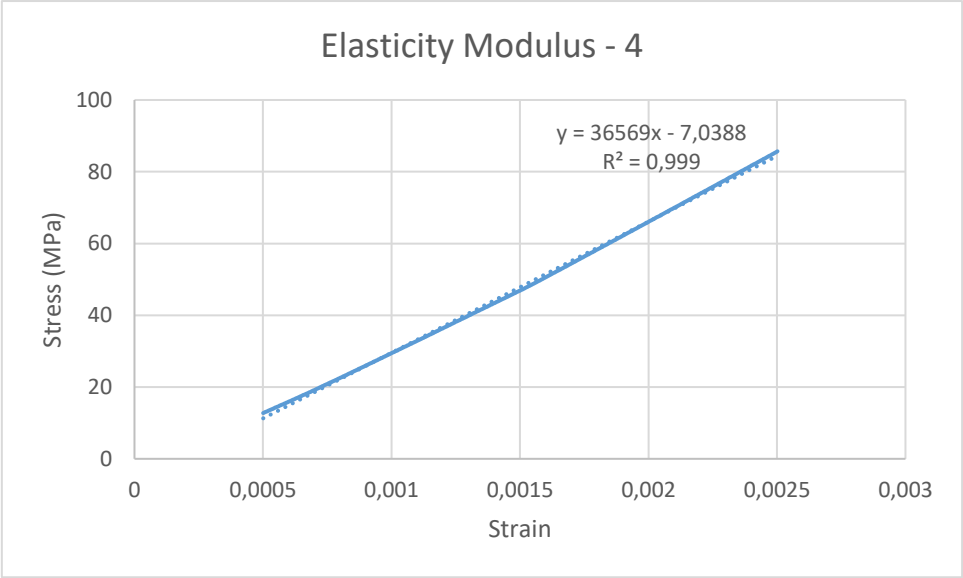
7.2.1.1 0,2 – 265°C Condition

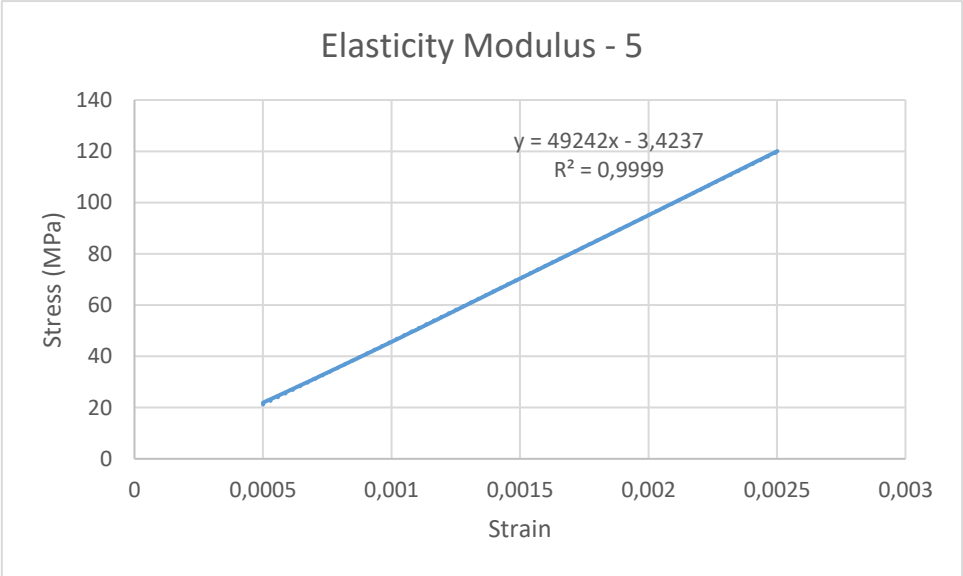


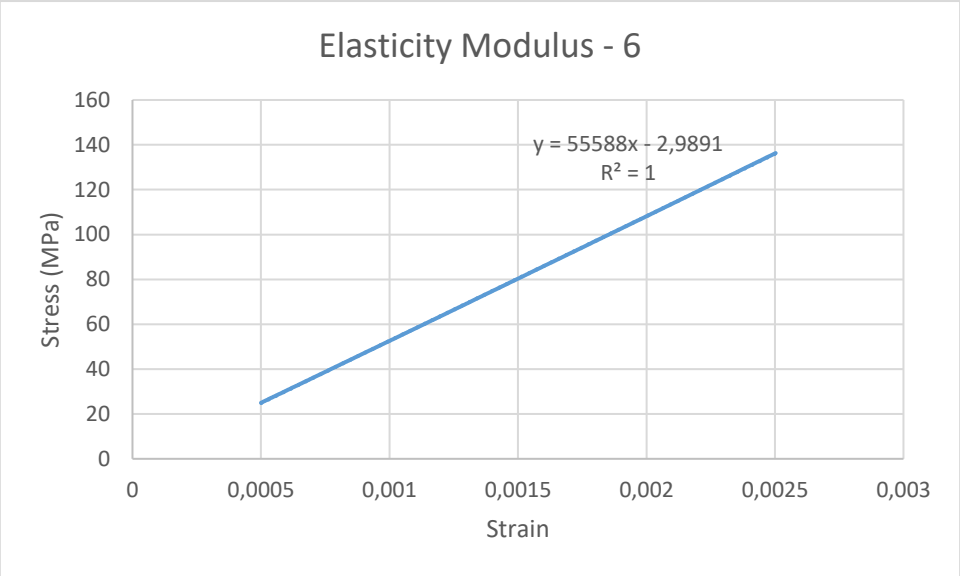



Elasticity Modulus - 2
y = 51052x - 9,4728
R² = 1
Stress (MPa)
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

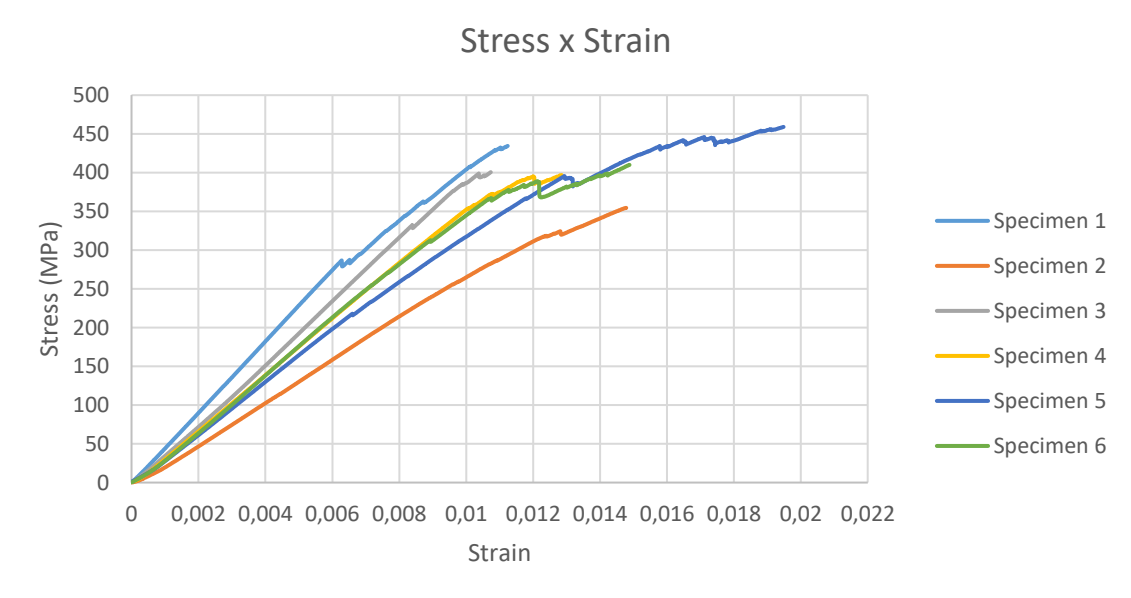

Elasticity Modulus - 3
y = 49852x - 6,254
R² = 1
Stress (MPa)
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

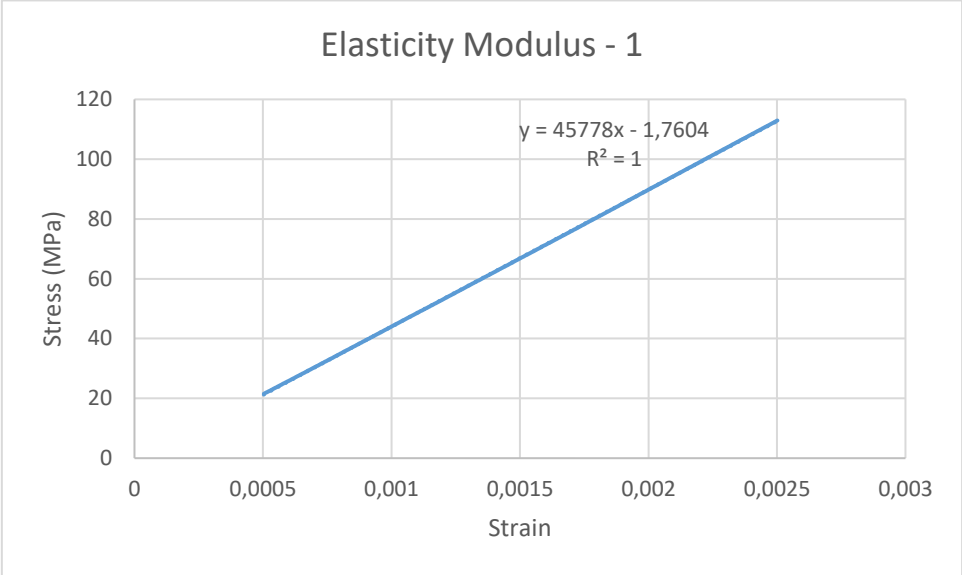

Elasticity Modulus - 4
y = 36569x - 7,0388
R² = 0,999
Stress (MPa)
Strain
0
20
40
60
80
100
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

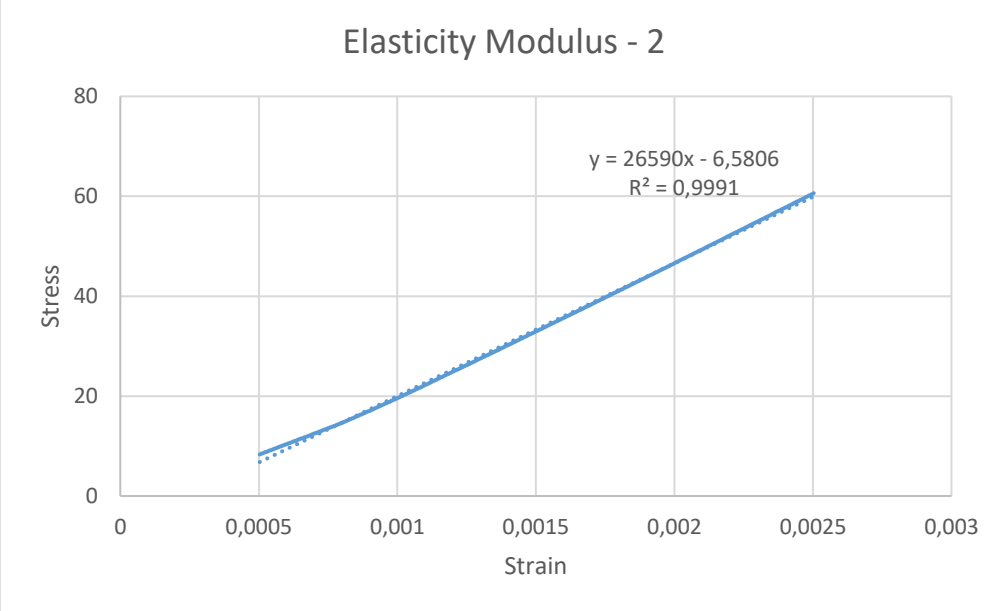

Elasticity Modulus - 5
y = 49242x - 3,4237
R² = 0,9999
Stress (MPa)
Strain
0
20
40
60
80
100
120
140
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

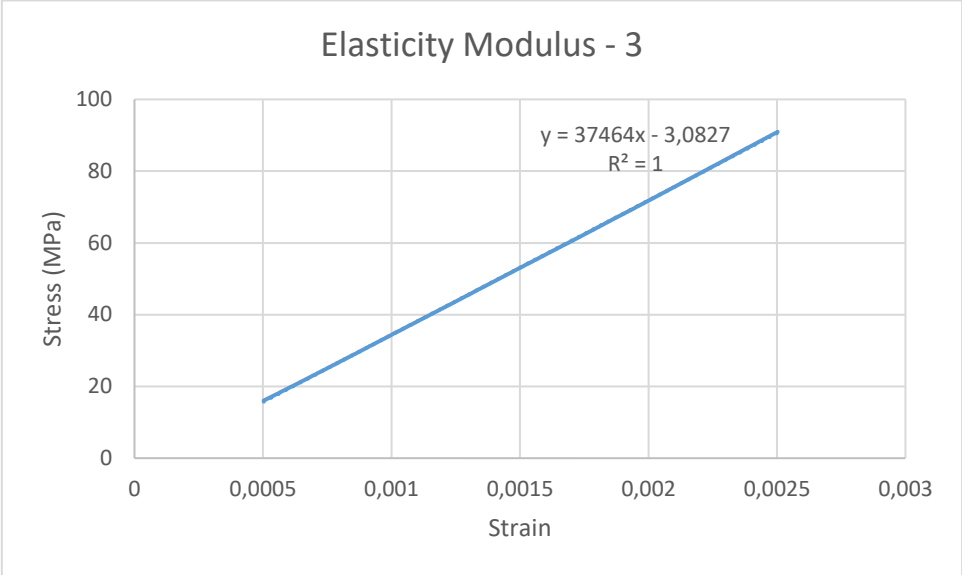


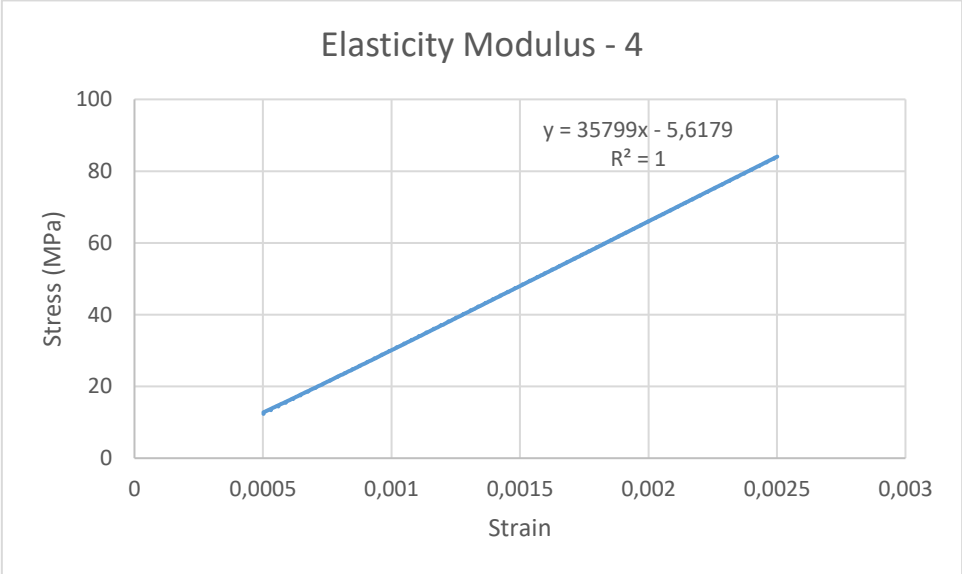
7.2.1.2 0,2 - 280°C Condition

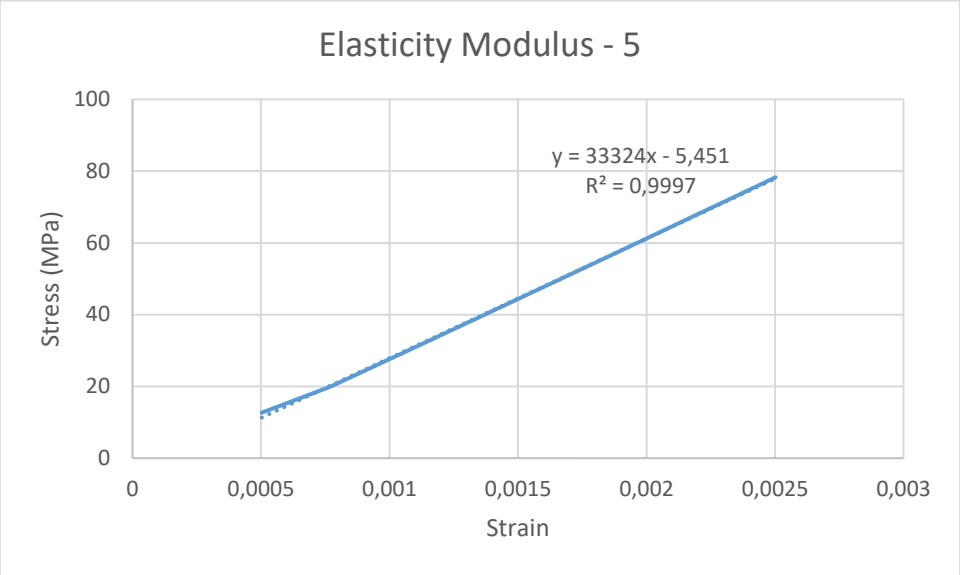


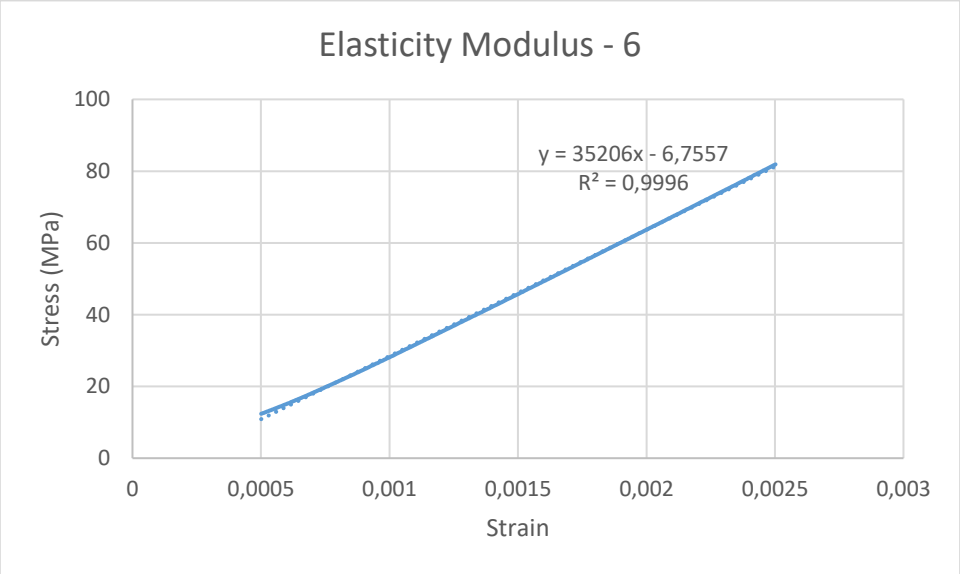

Elasticity Modulus - 1
y = 45778x - 1,7604
R² = 1
Stress (MPa)
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain


Elasticity Modulus - 2
y = 26590x - 6,5806
R² = 0,9991
Stress
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain


Elasticity Modulus - 3
y = 37464x - 3,0827
R² = 1
Stress (MPa)
Strain
0
20
40
60
80
100
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

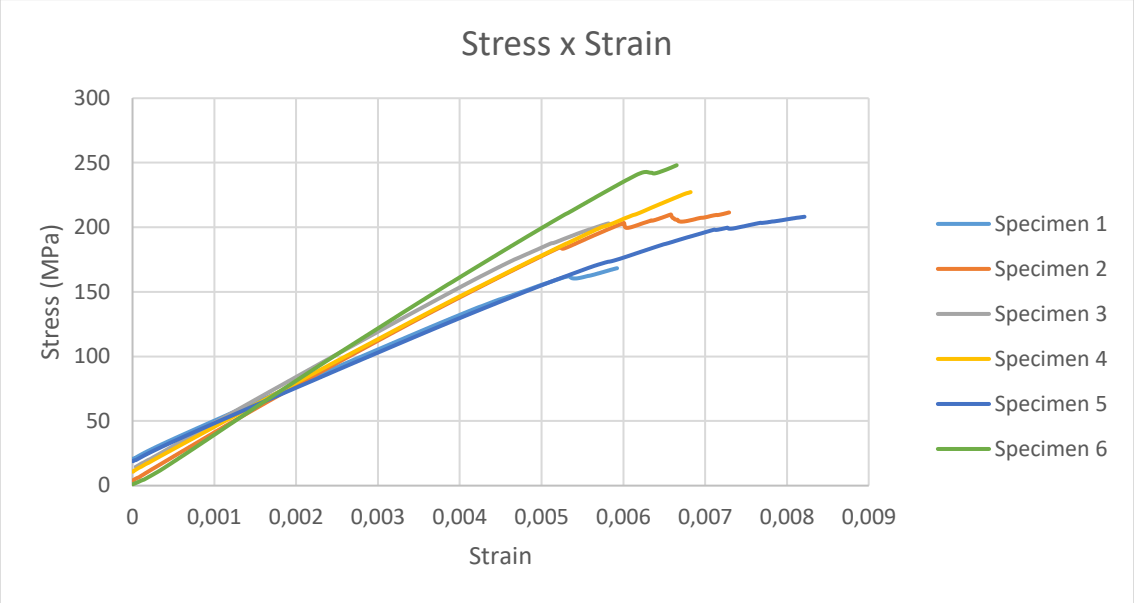

Elasticity Modulus - 4
y = 35799x - 5,6179
R² = 1
Stress (MPa)
Strain
0
20
40
60
80
100
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

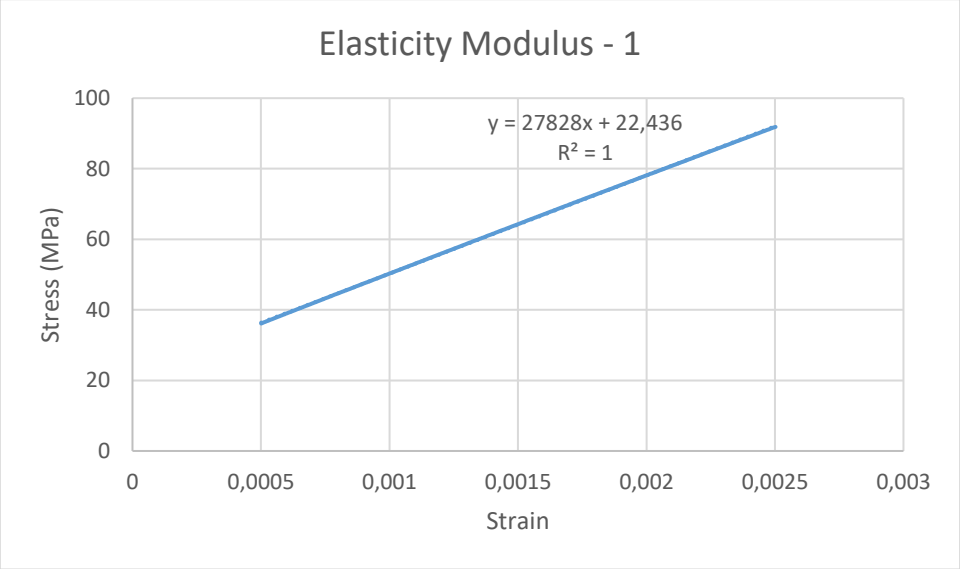

Elasticity Modulus - 5
y = 33324x - 5,451
R² = 0,9997
Stress (MPa)
Strain
0
20
40
60
80
100
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

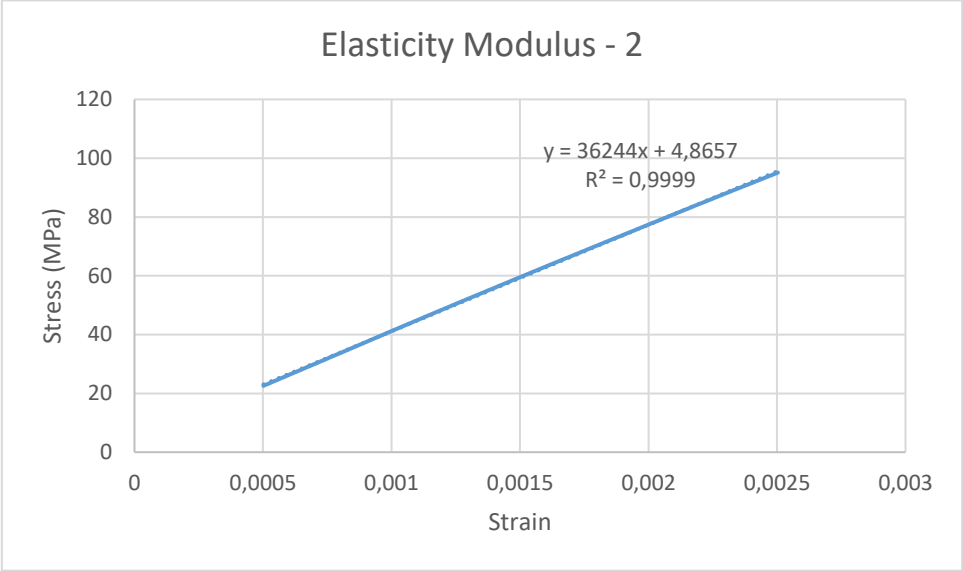

Elasticity Modulus - 6
y = 35206x - 6,7557
R² = 0,9996
Stress (MPa)
Strain
0
20
40
60
80
100
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

7.2.2 PA6

7.2.2.1 0,2 - 205°C Condition






Elasticity Modulus - 2
y = 36244x + 4,8657
R² = 0,9999
Stress (MPa)
Strain
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40
60
80
100
120
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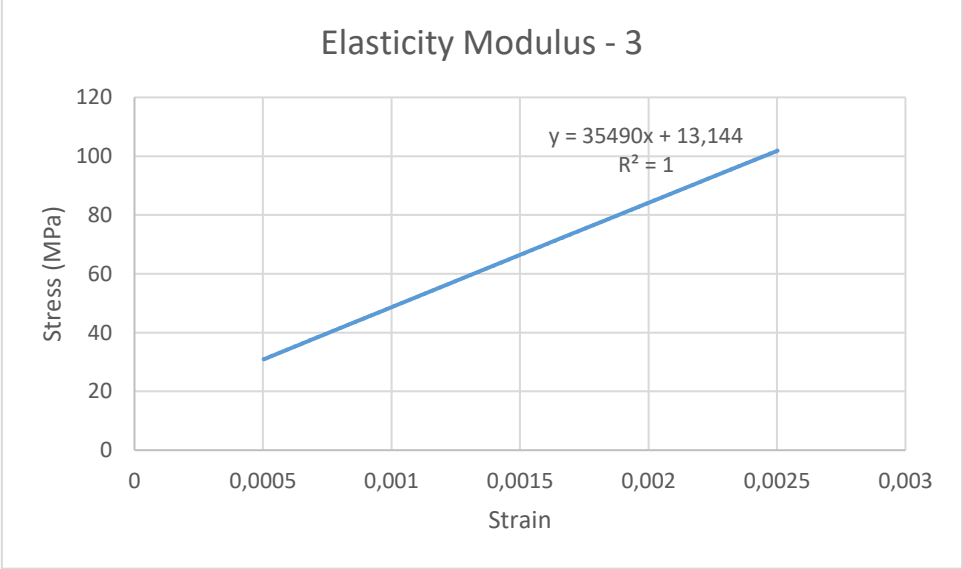
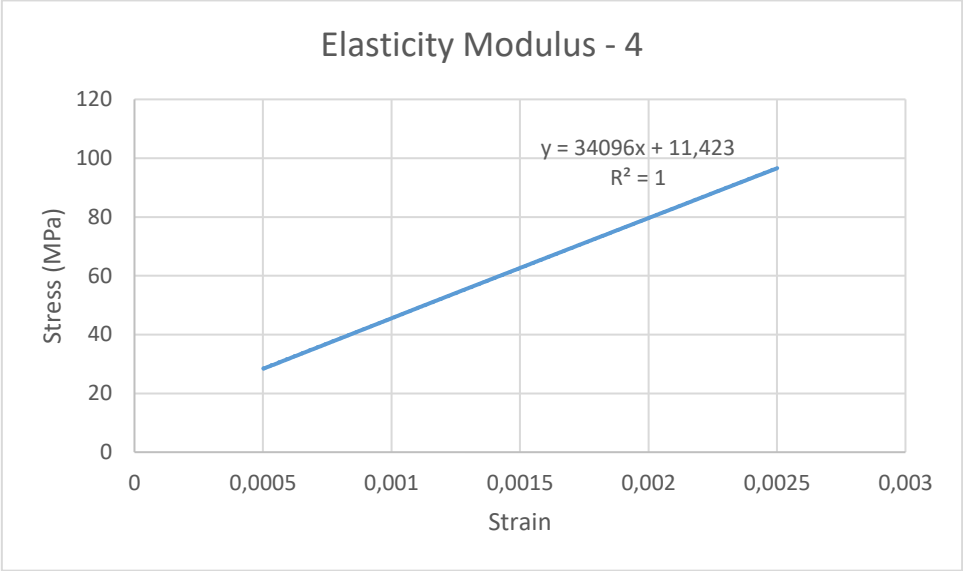
0,0005
0,001
0,0015
0,002
0,0025
0,003


Elasticity Modulus - 3
y = 35490x + 13,144
R² = 1
Stress (MPa)
Strain
0
20
40
60
80
100
120
0
0,0005
0,001
0,0015
0,002
0,0025
0,003


Elasticity Modulus - 4
y = 34096x + 11,423
R² = 1
Stress (MPa)
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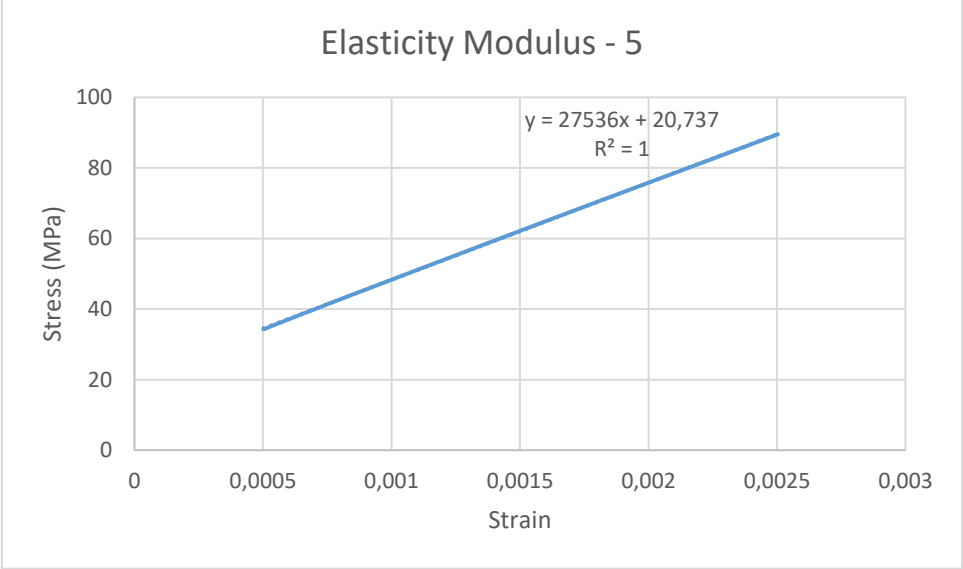
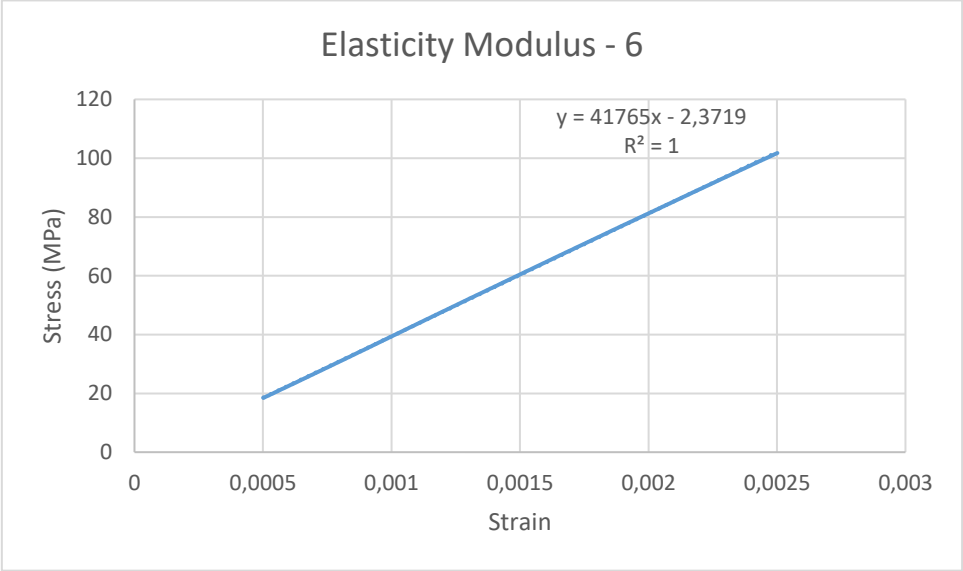
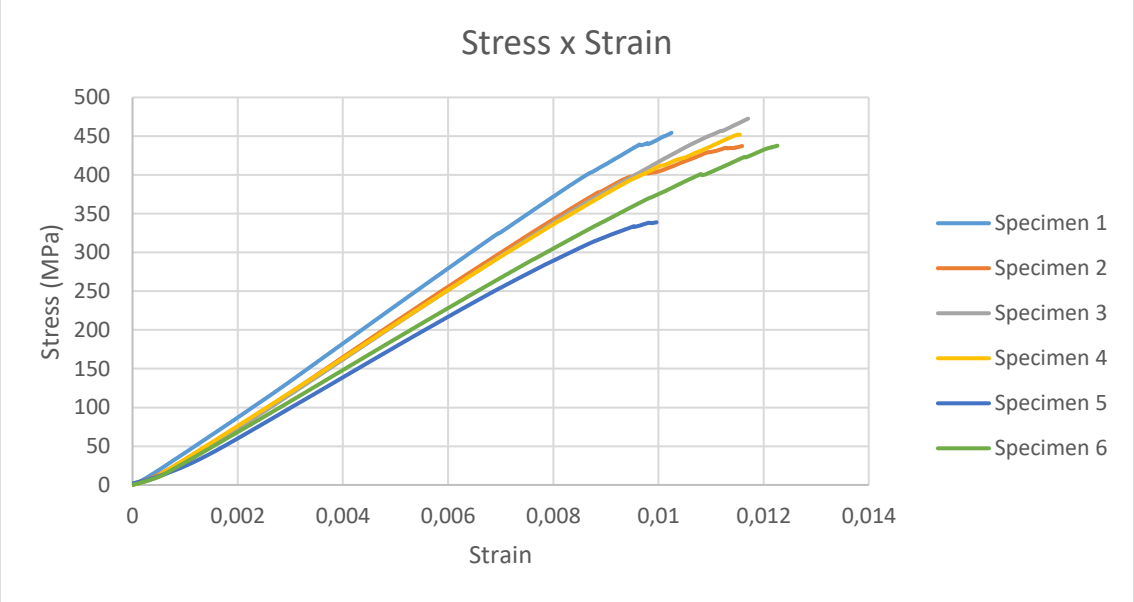
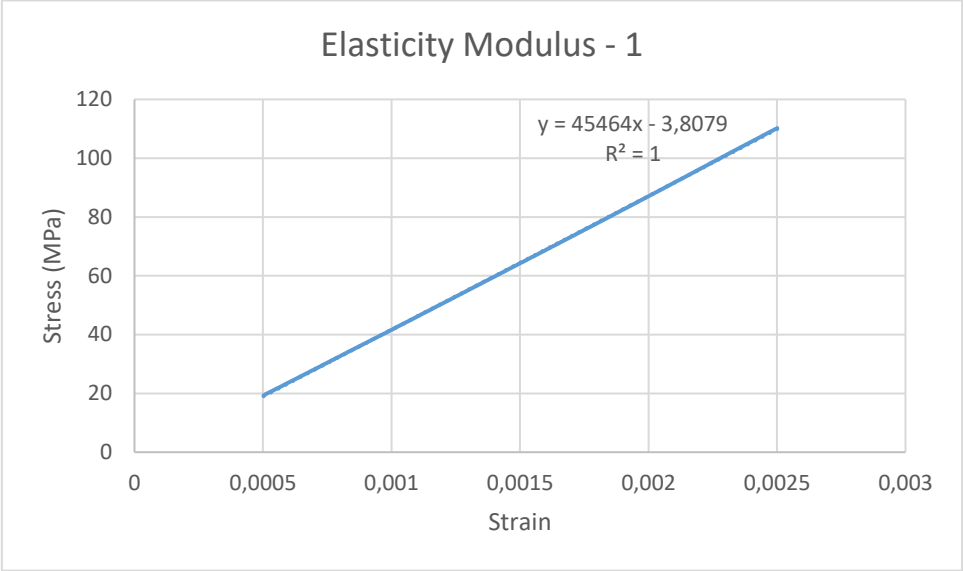
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

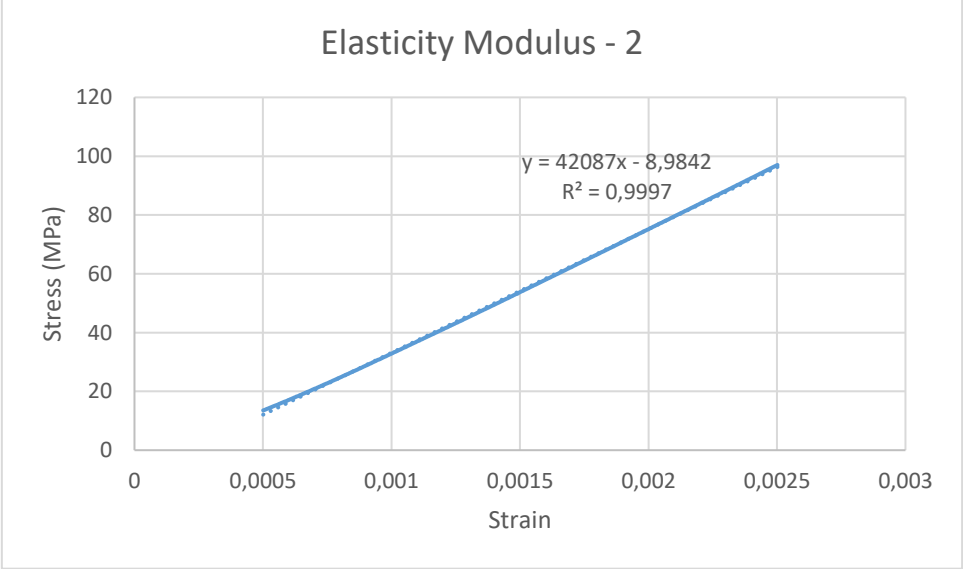

Elasticity Modulus - 5
y = 27536x + 20,737
R² = 1
Stress (MPa)
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

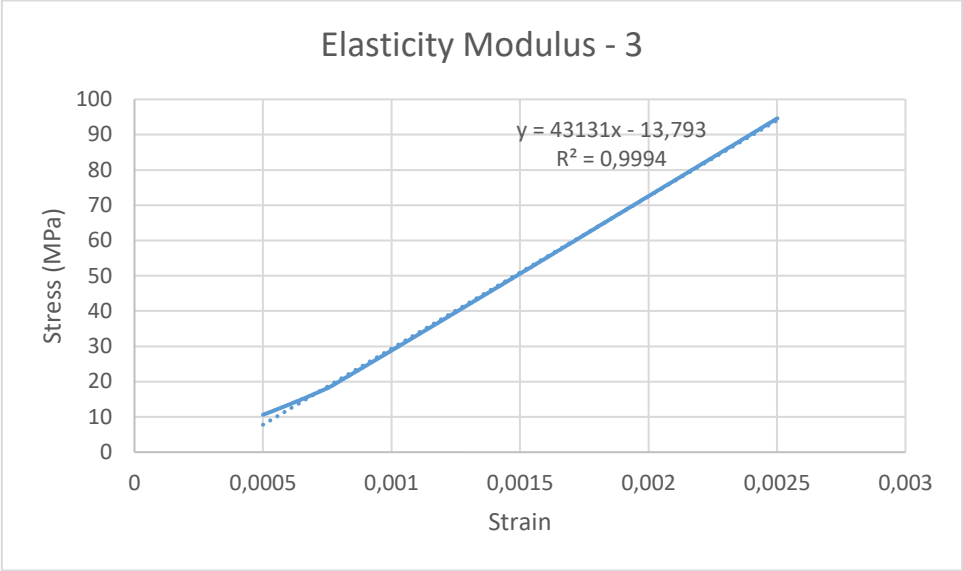


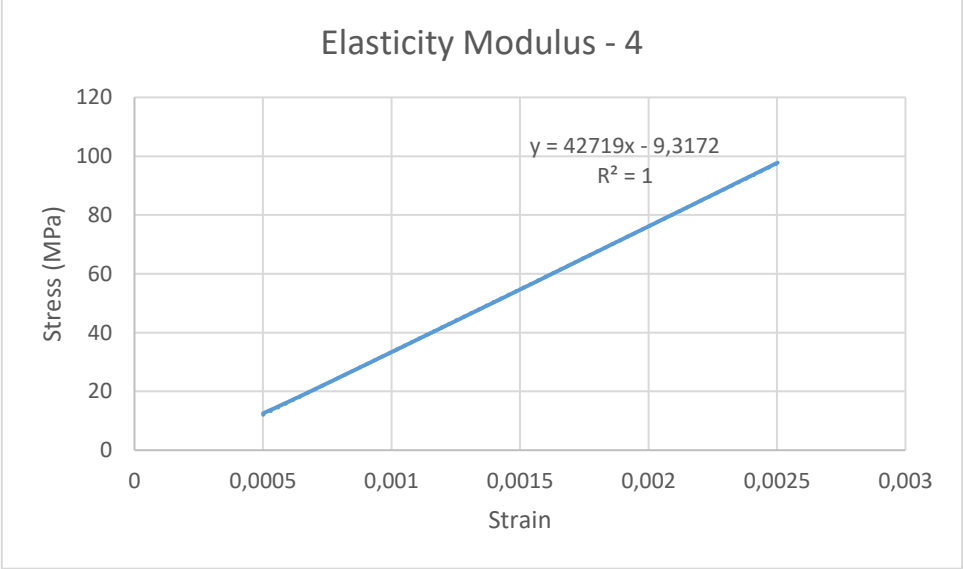
7.2.2.2 0,2 - 220°C Condition

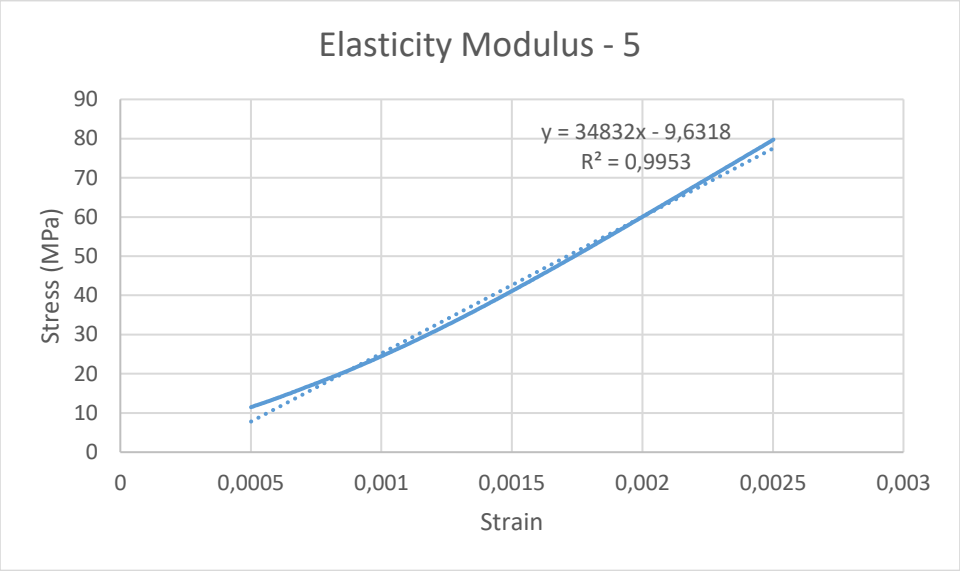


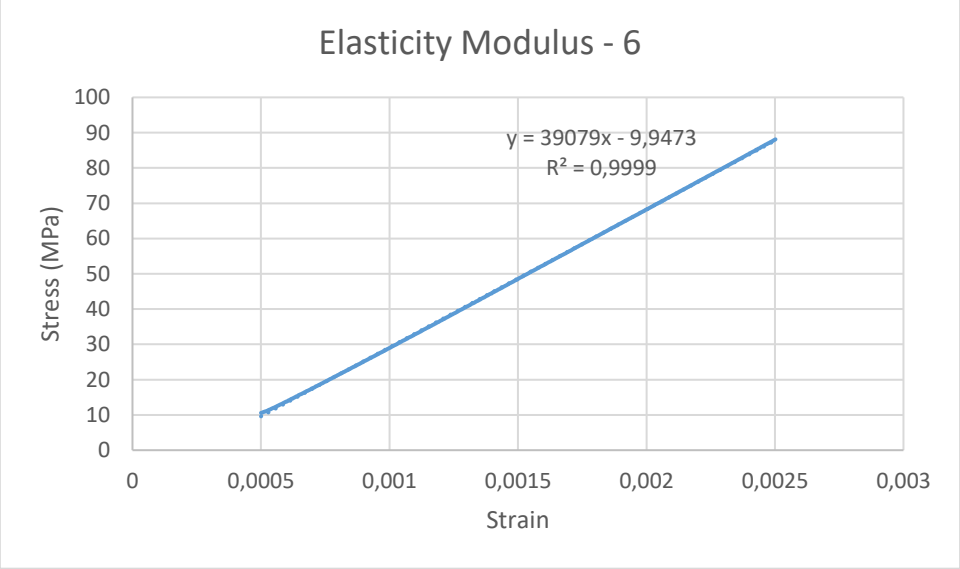

Elasticity Modulus - 1
y = 45464x - 3,8079
R² = 1
Stress (MPa)
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain


Elasticity Modulus - 2
y = 42087x - 8,9842
R² = 0,9997
Stress (MPa)
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain


Elasticity Modulus - 3
y = 43131x - 13,793
R² = 0,9994
Stress (MPa)
Strain
0
10
20
30
40
50
60
70
80
90
100
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

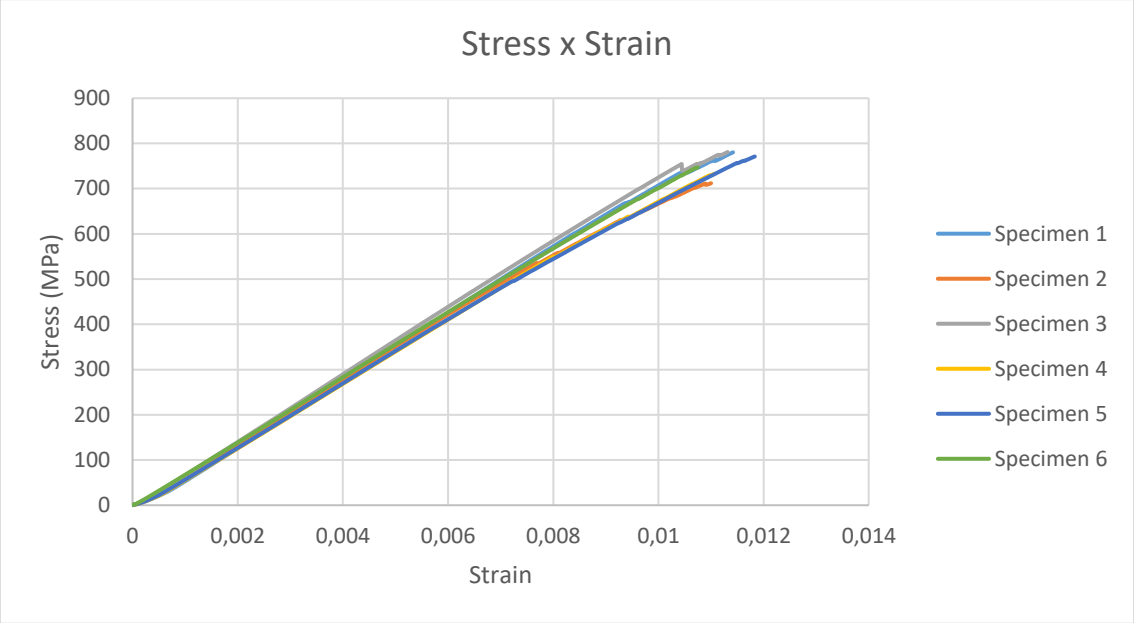

Elasticity Modulus - 4
y = 42719x - 9,3172
R² = 1
Stress (MPa)
Strain
0
20
40
60
80
100
120
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

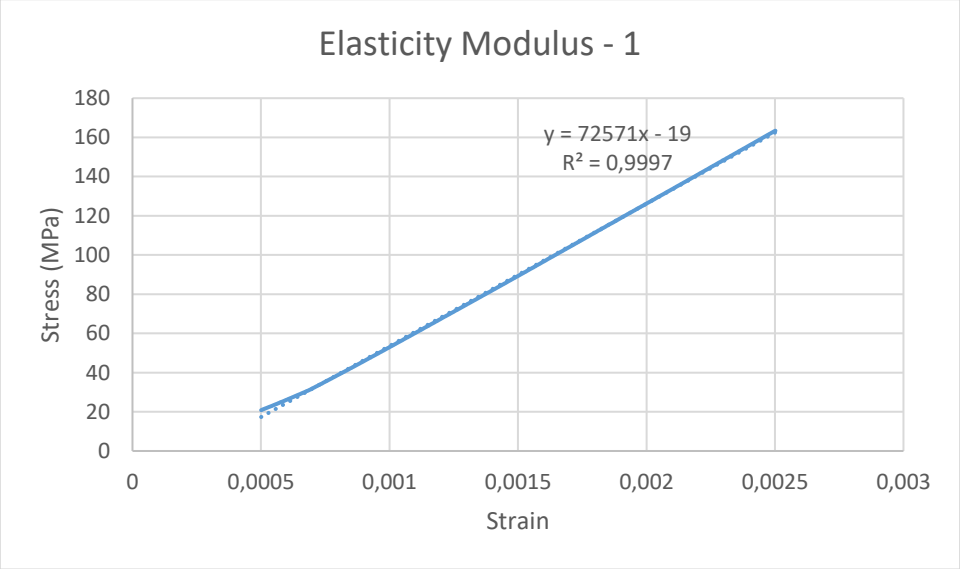

Elasticity Modulus - 5
y = 34832x - 9,6318
R² = 0,9953
Stress (MPa)
Strain
0
10
20
30
40
50
60
70
80
90
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

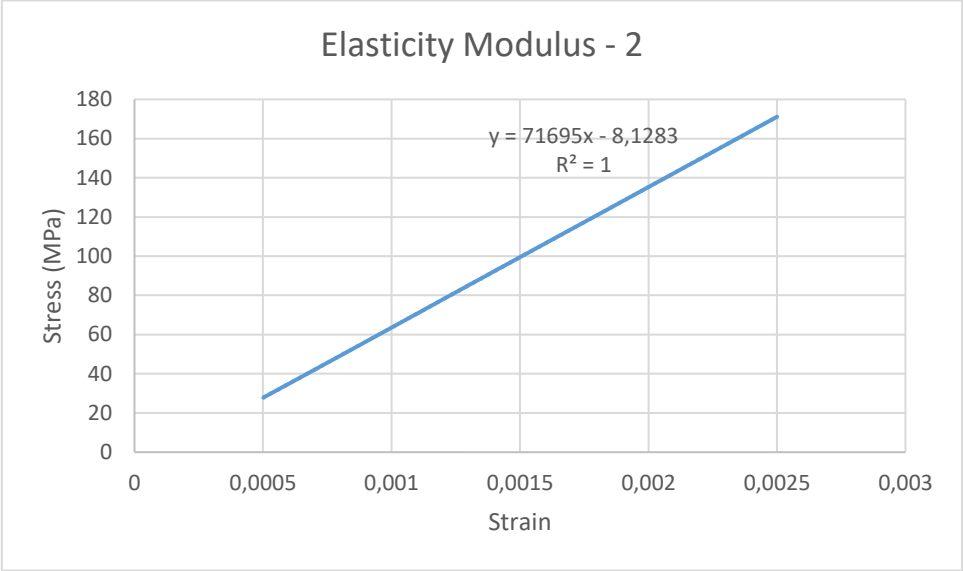

Elasticity Modulus - 6
y = 39079x - 9,9473
R² = 0,9999
Stress (MPa)
Strain
0
10
20
30
40
50
60
70
80
90
100
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

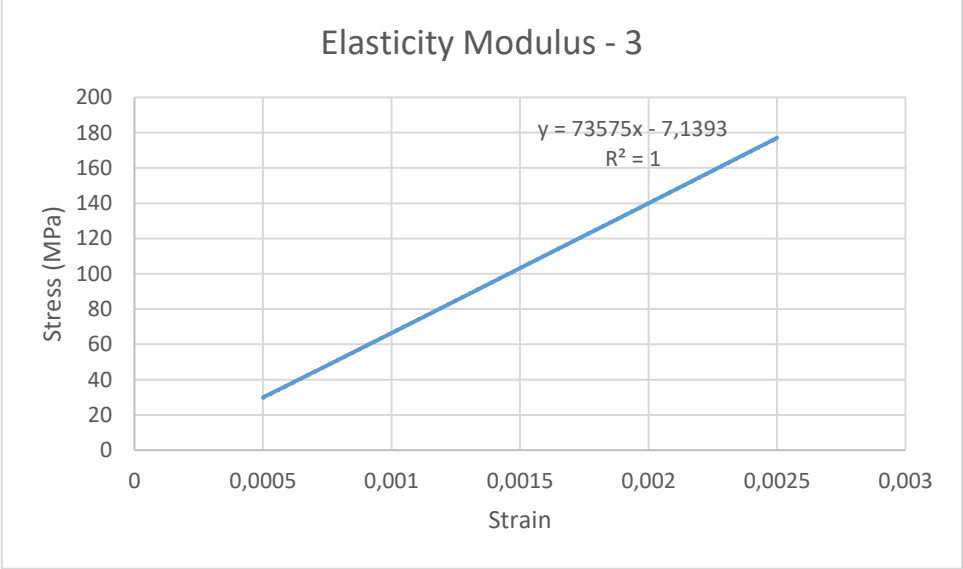
7.2.3 PC

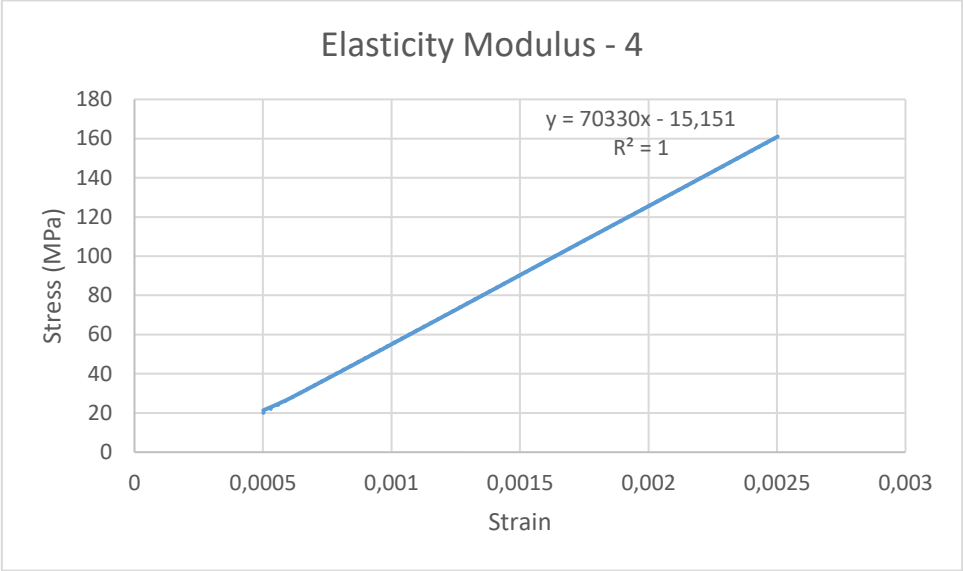
7.2.3.1 0,2 - 300°C Condition

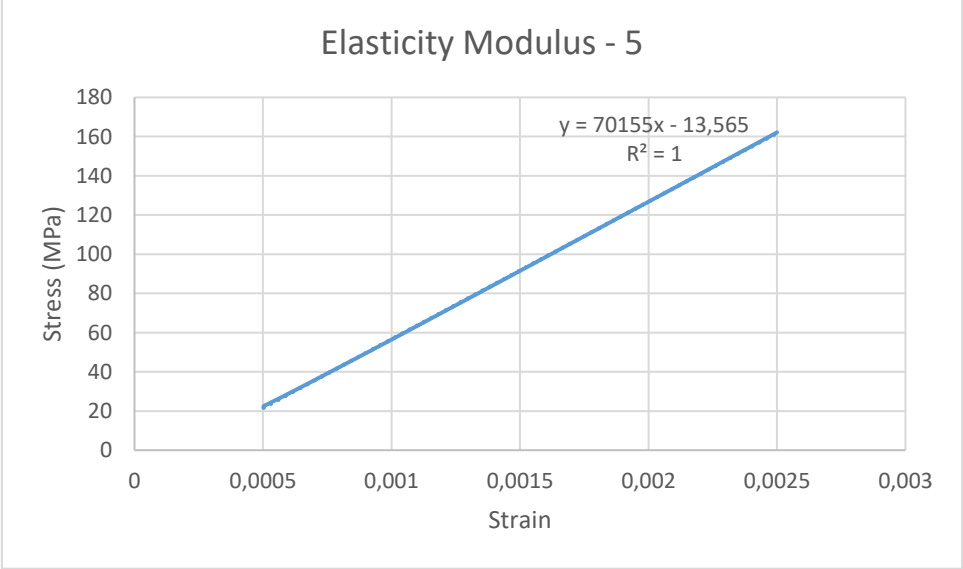


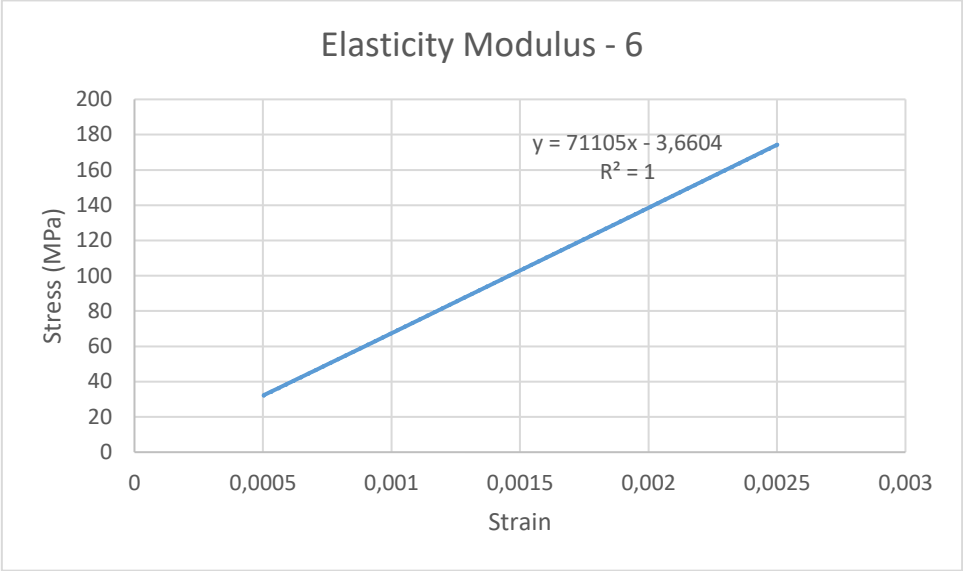



Elasticity Modulus - 2
y = 71695x - 8,1283
R² = 1
Stress (MPa)
180
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

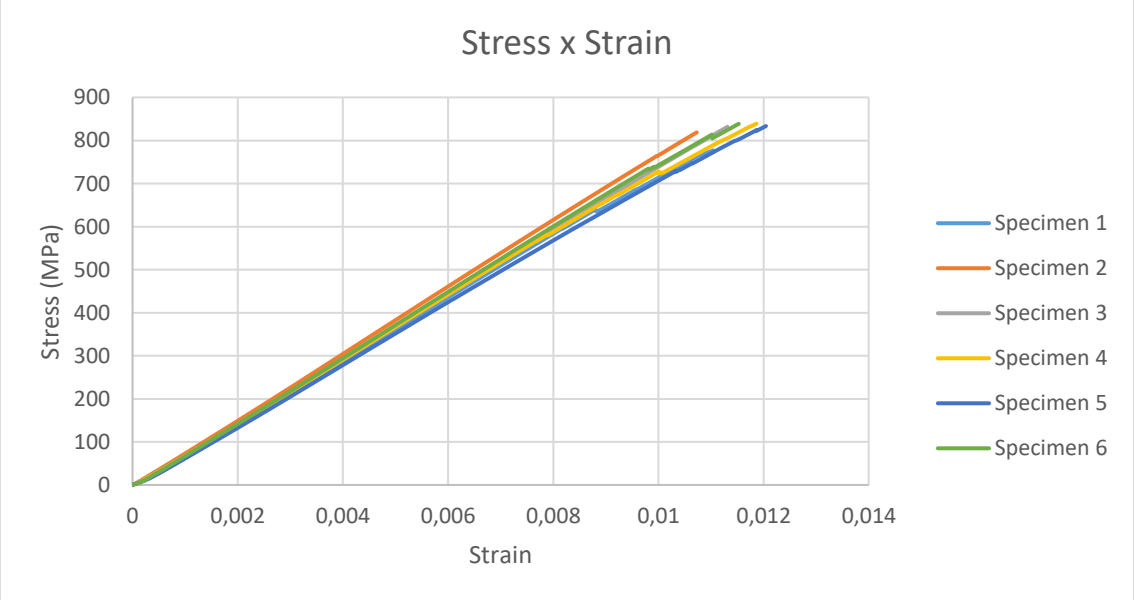

Elasticity Modulus - 3
y = 73575x - 7,1393
R² = 1
Stress (MPa)
200
180
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

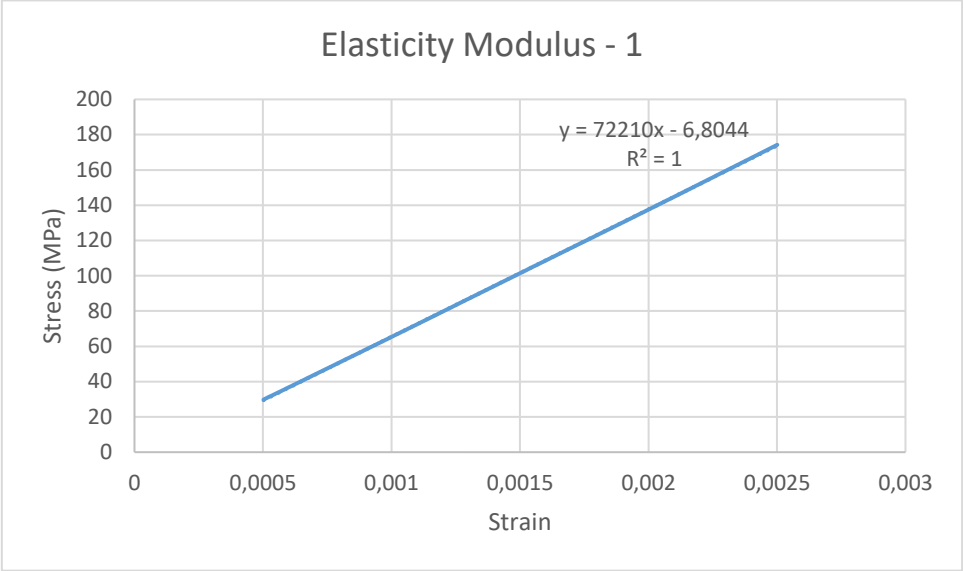

Elasticity Modulus - 4
y = 70330x - 15,151
R² = 1
Stress (MPa)
180
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

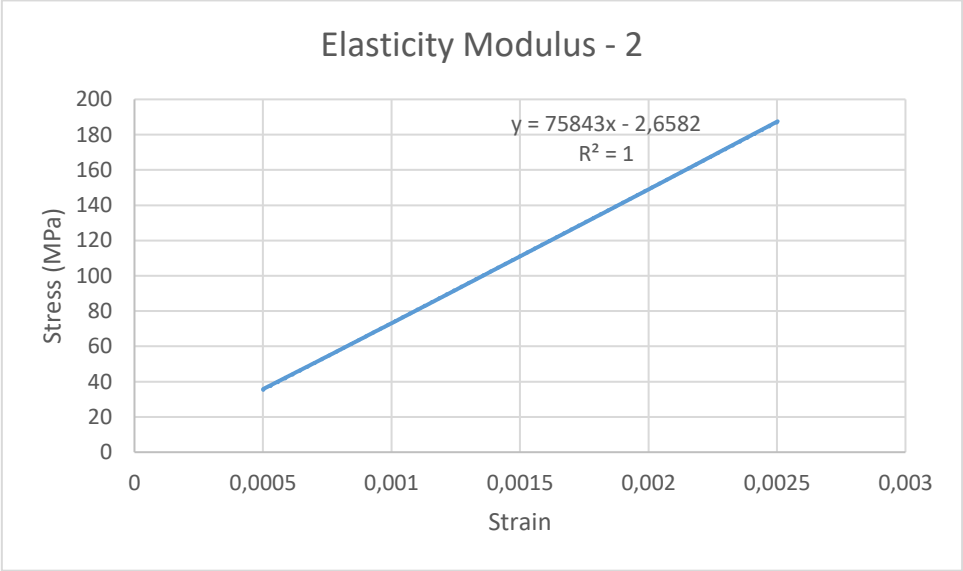

Elasticity Modulus - 5
y = 70155x - 13,565
R² = 1
Stress (MPa)
180
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

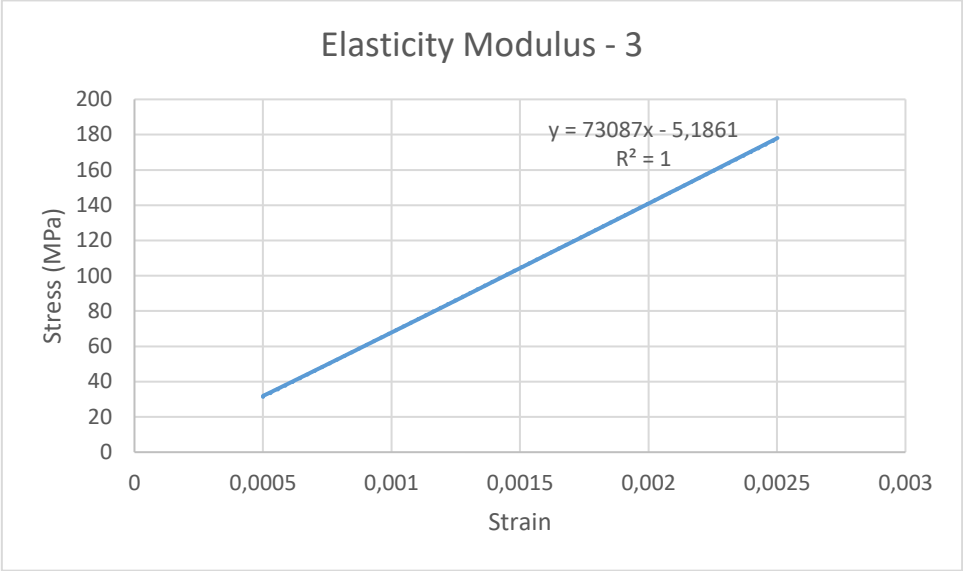


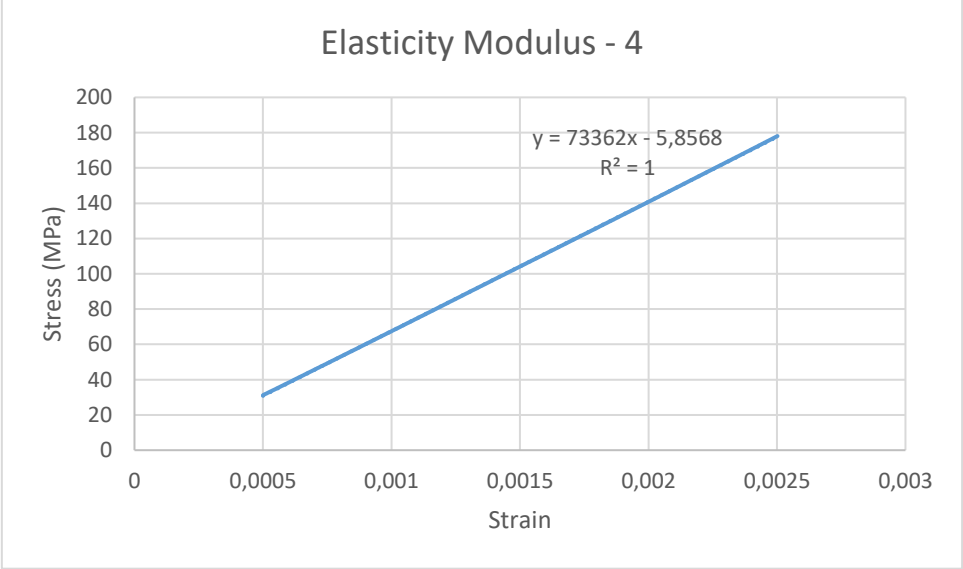
7.2.3.2 0,2 - 330°C Condition

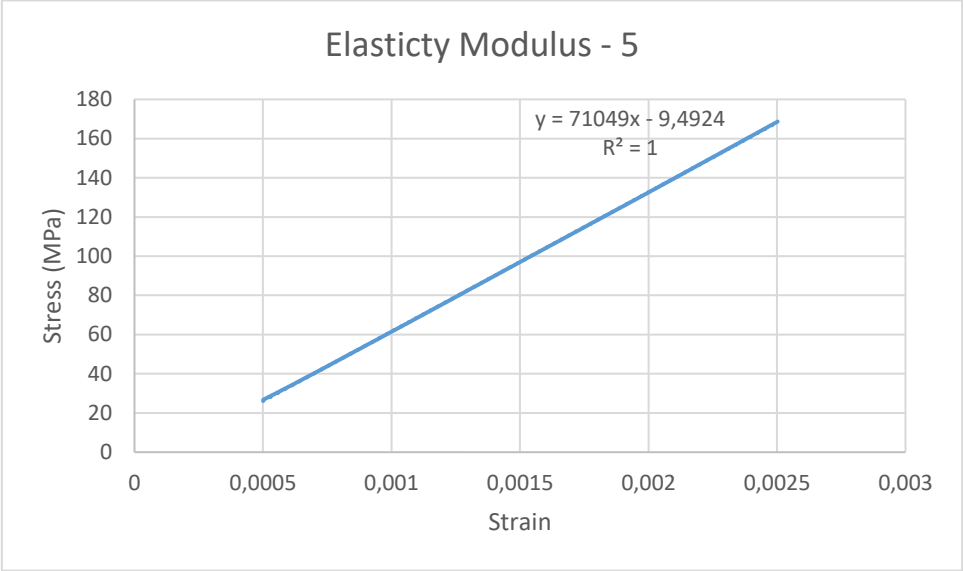


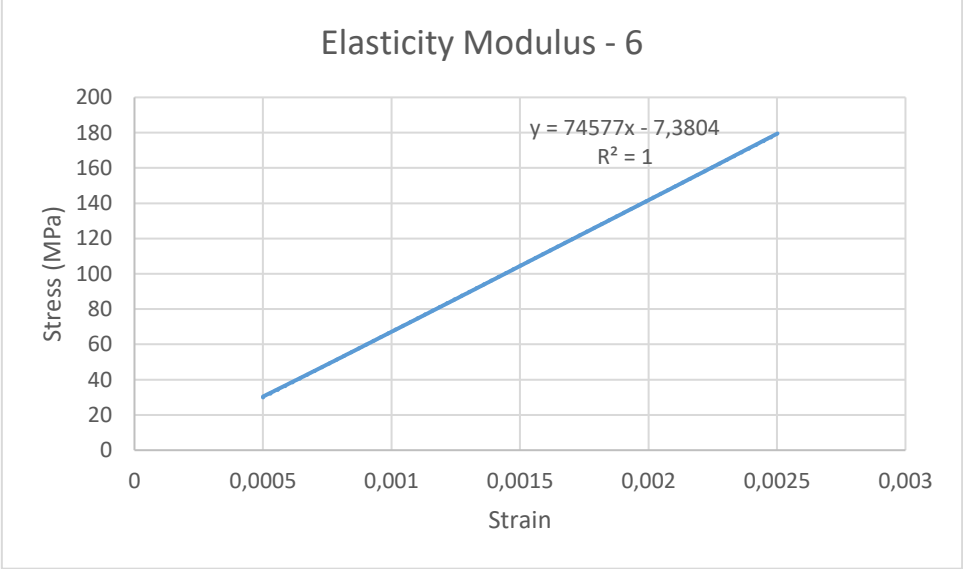

Elasticity Modulus - 1
y = 72210x - 6,8044
R² = 1
Stress (MPa)
200
180
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain


Elasticity Modulus - 2
y = 75843x - 2,6582
R² = 1
Stress (MPa)
200
180
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain


Elasticity Modulus - 3
y = 73087x - 5,1861
R² = 1
Stress (MPa)
200
180
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

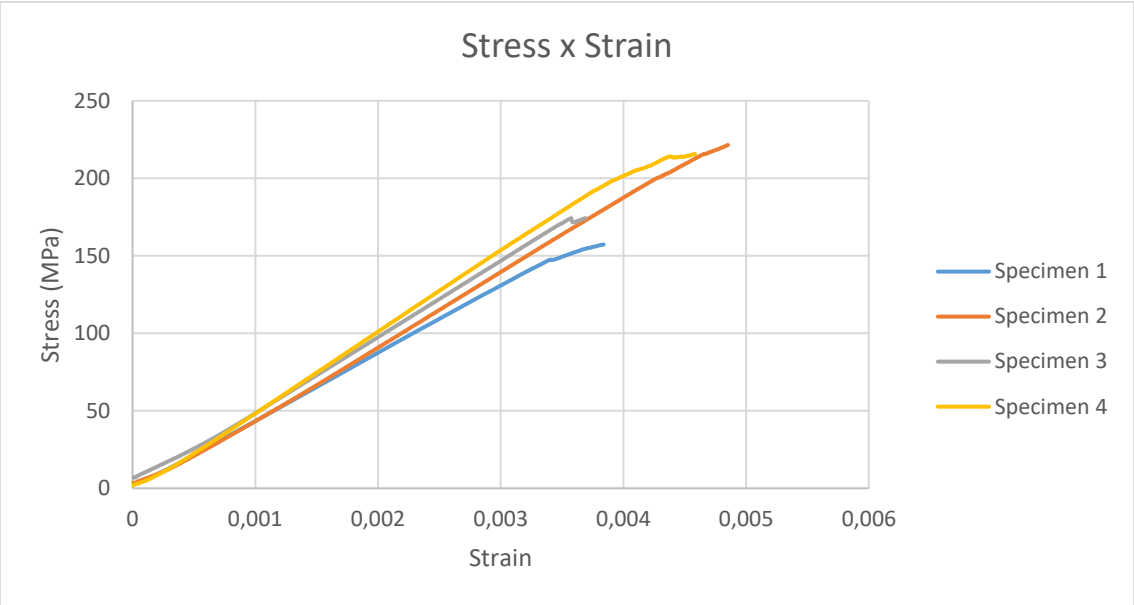

Elasticity Modulus - 4
y = 73362x - 5,8568
R² = 1
Stress (MPa)
200
180
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

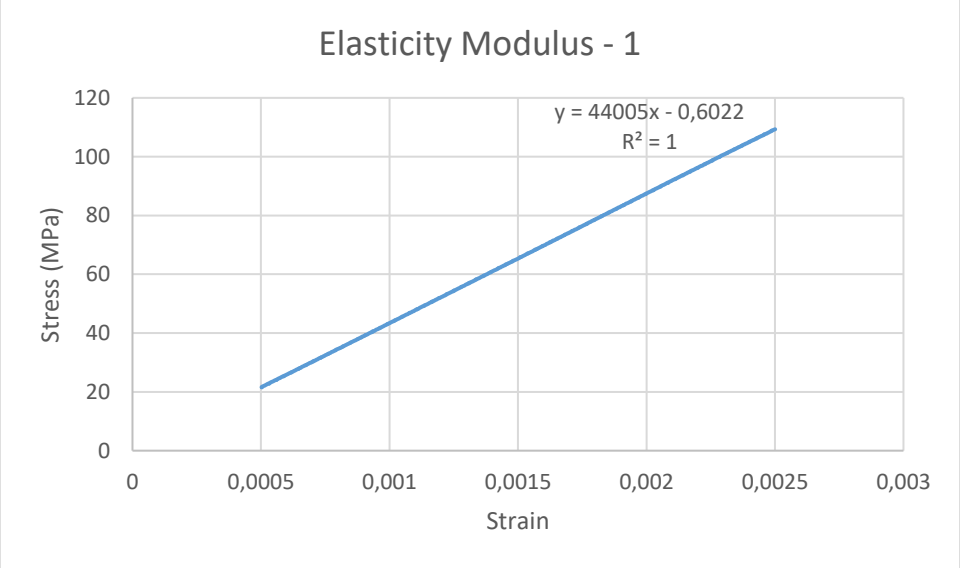

Elasticty Modulus - 5
y = 71049x - 9,4924
R² = 1
Stress (MPa)
180
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

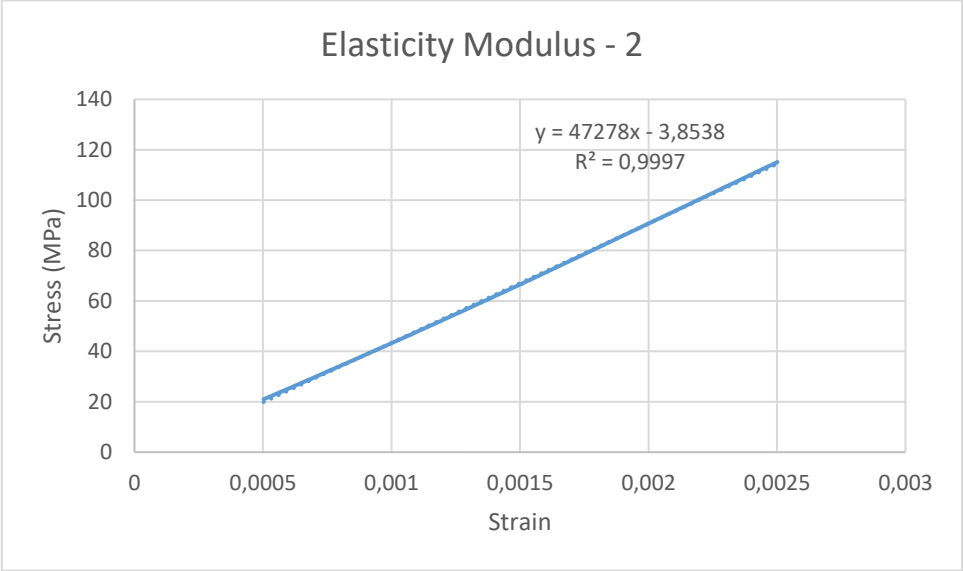

Elasticity Modulus - 6
y = 74577x - 7,3804
R² = 1
Stress (MPa)
200
180
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain

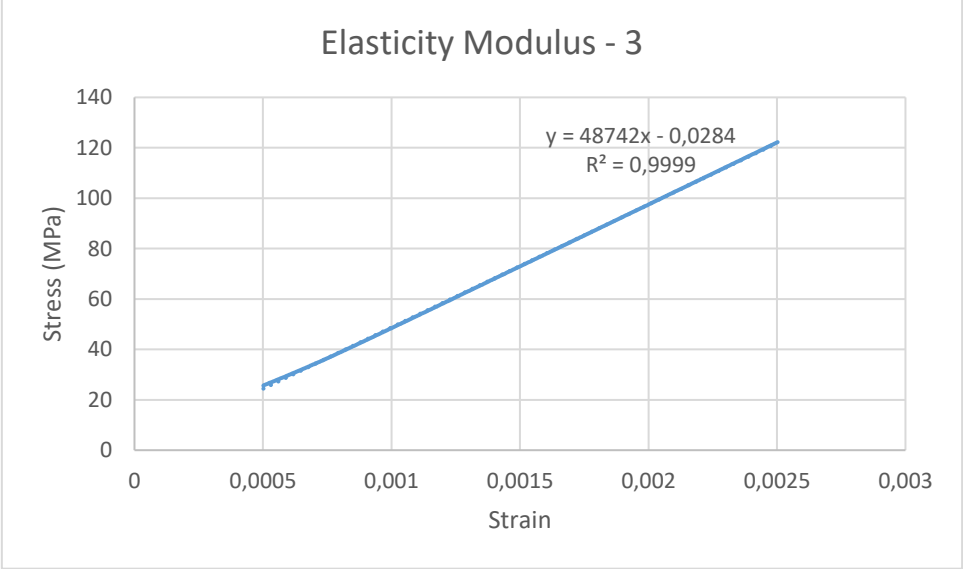
7.3 Appendix C - Graphs Obtained from the Bending Tests of Heated Compression Moulding Laminates

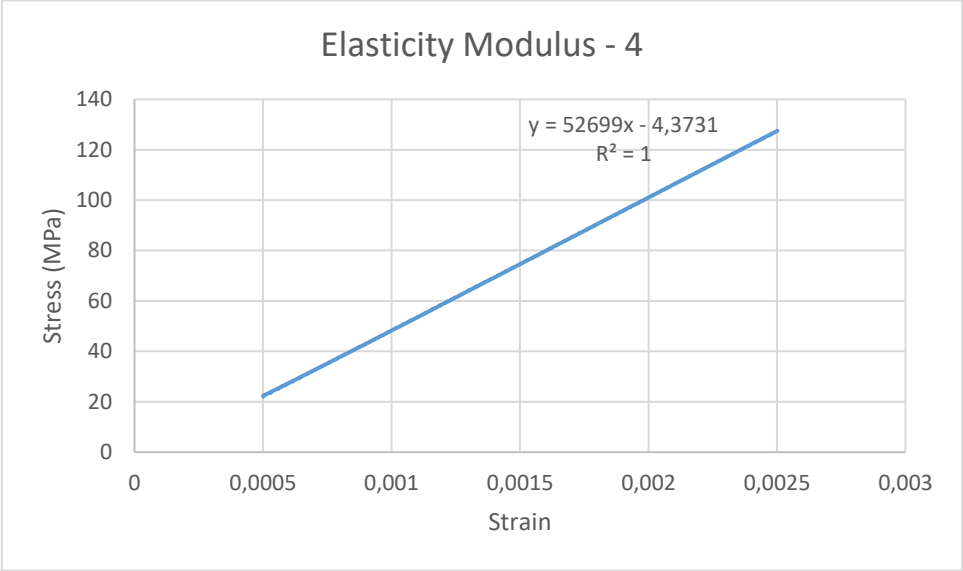
7.3.1 PET Laminate



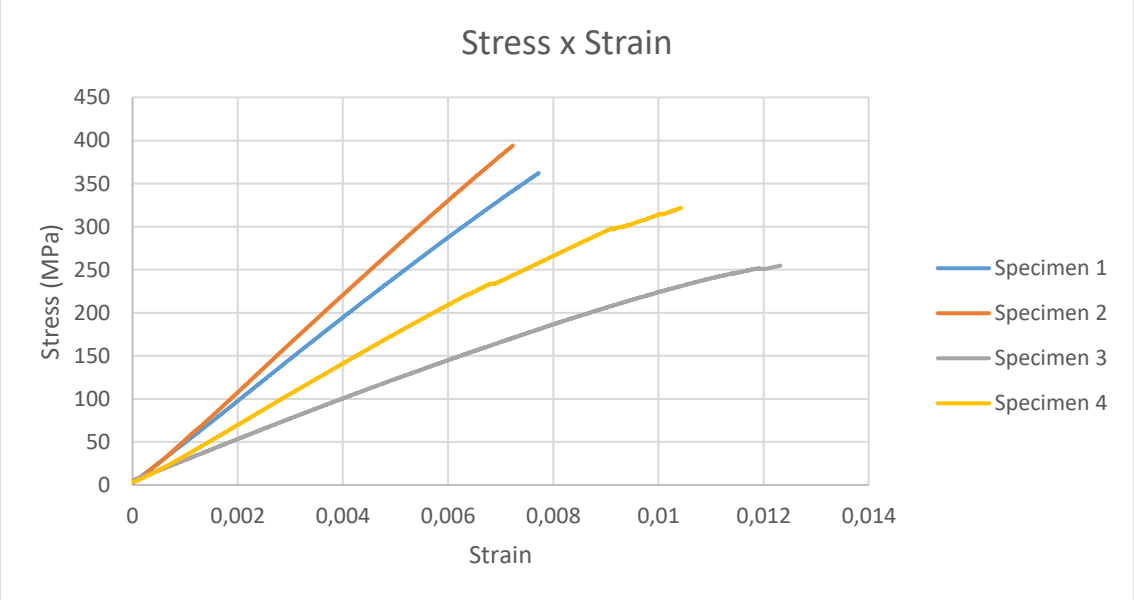


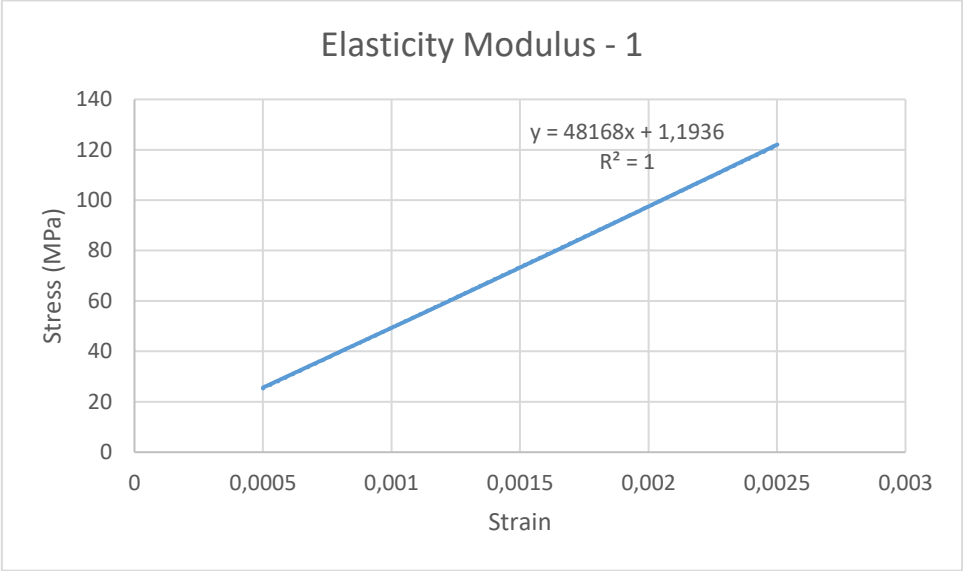

Elasticity Modulus - 2
y = 47278x - 3,8538
R² = 0,9997
Stress (MPa)
Strain
0
20
40
60
80
100
120
140
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

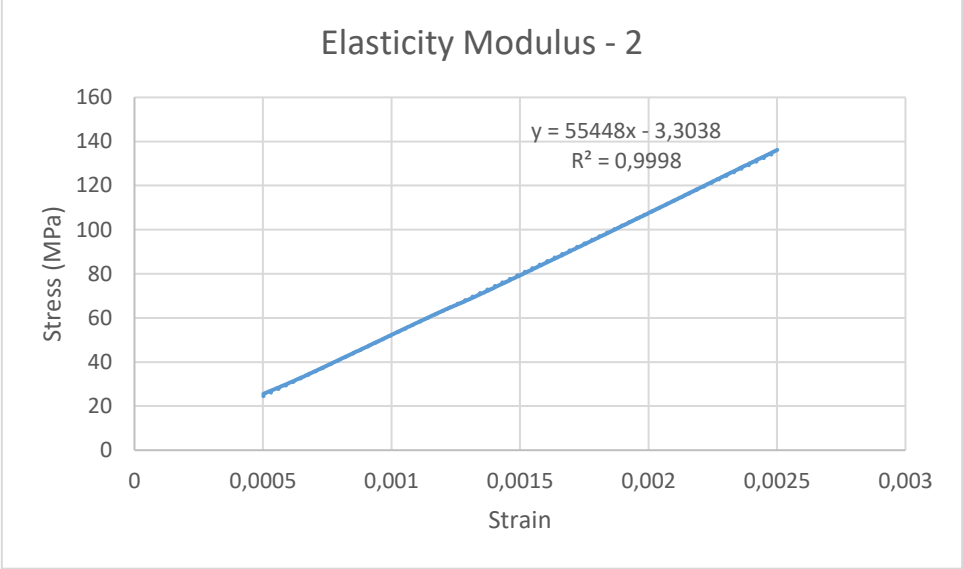

Elasticity Modulus - 3
y = 48742x - 0,0284
R² = 0,9999
Stress (MPa)
Strain
0
20
40
60
80
100
120
140
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

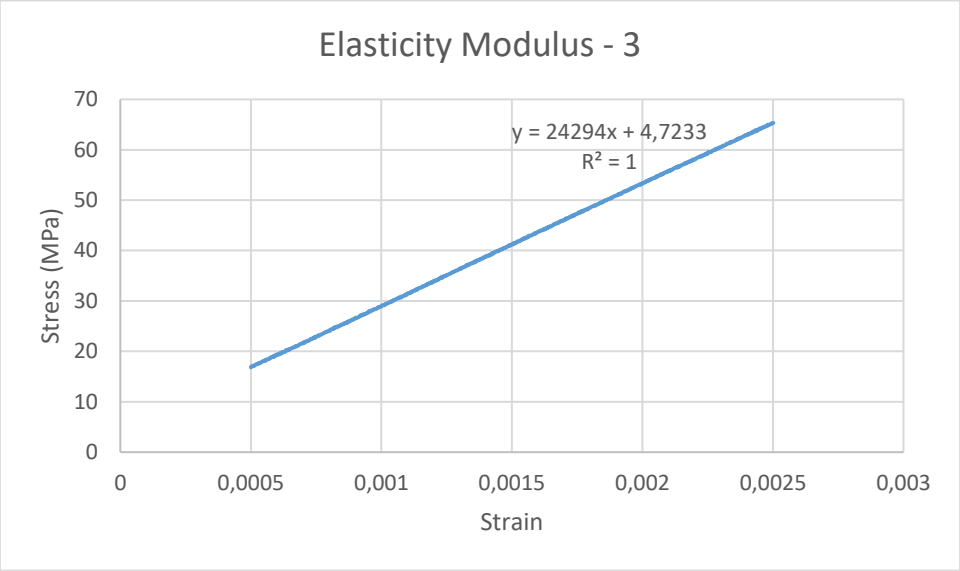


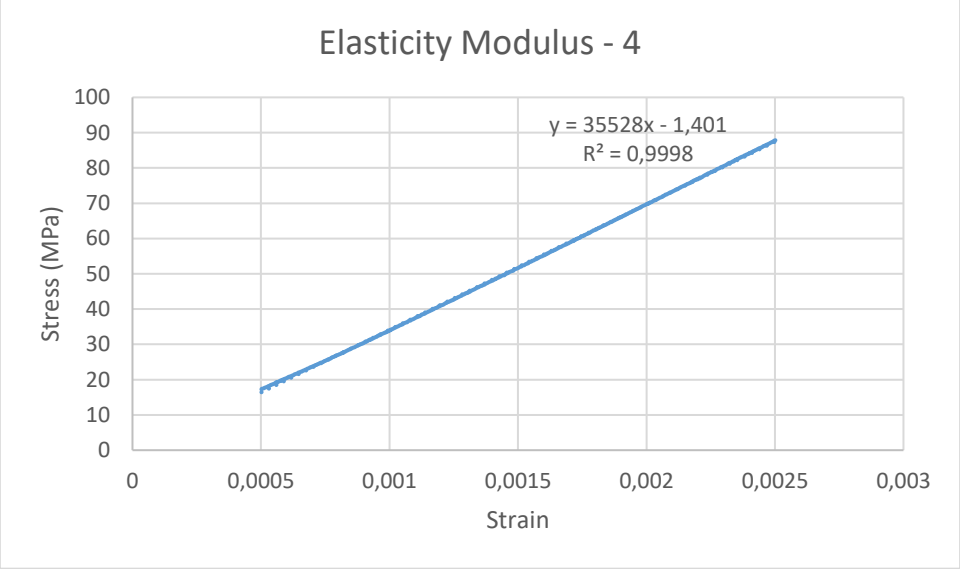
7.3.2 PA6 Laminate



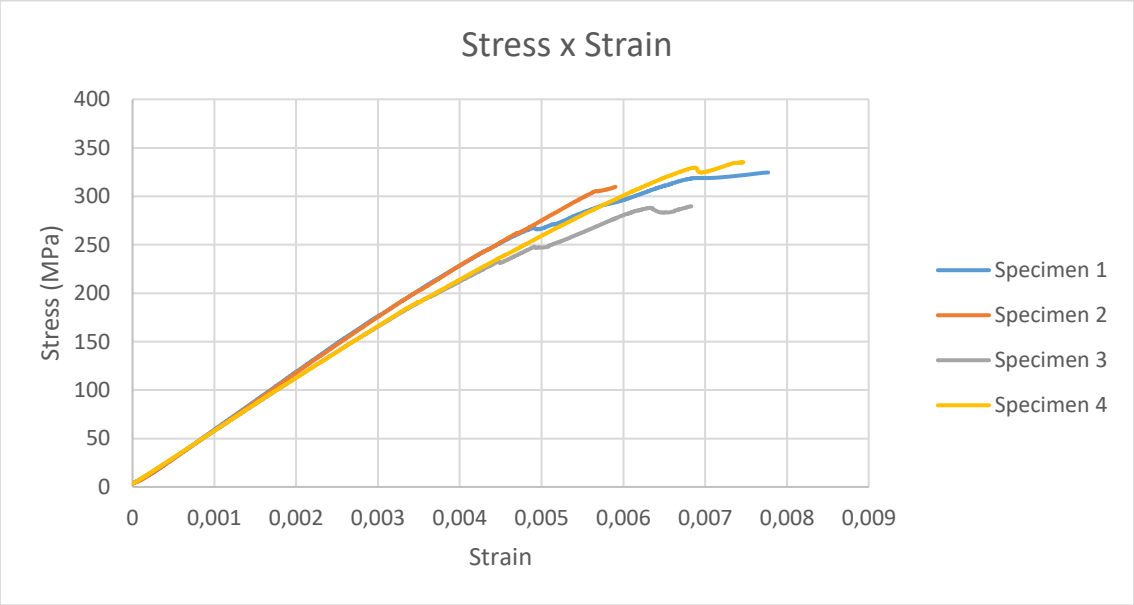

Elasticity Modulus - 1
y = 48168x + 1,1936
R² = 1
Stress (MPa)
Strain
0
20
40
60
80
100
120
140
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

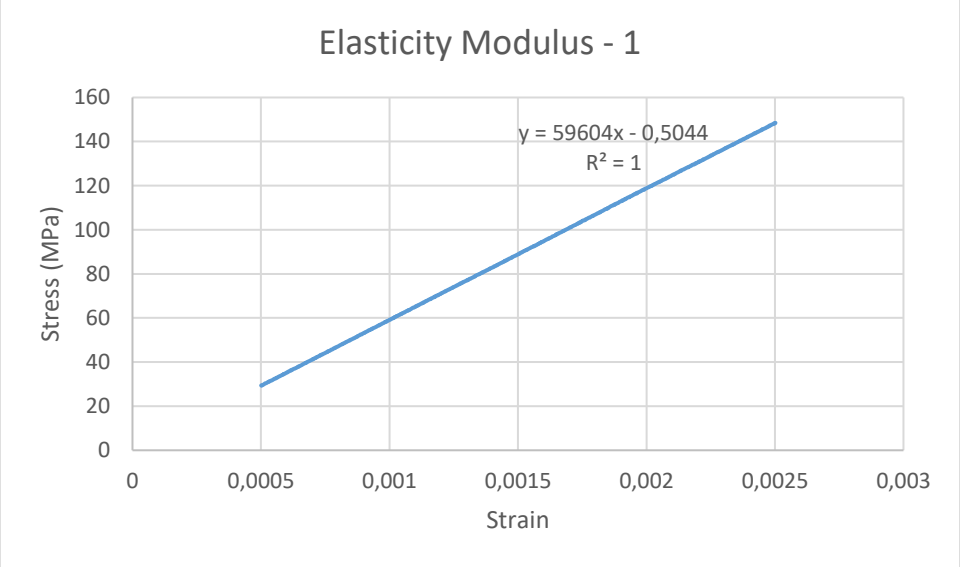

Elasticity Modulus - 2
y = 55448x - 3,3038
R² = 0,9998
Stress (MPa)
Strain
0
20
40
60
80
100
120
140
160
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

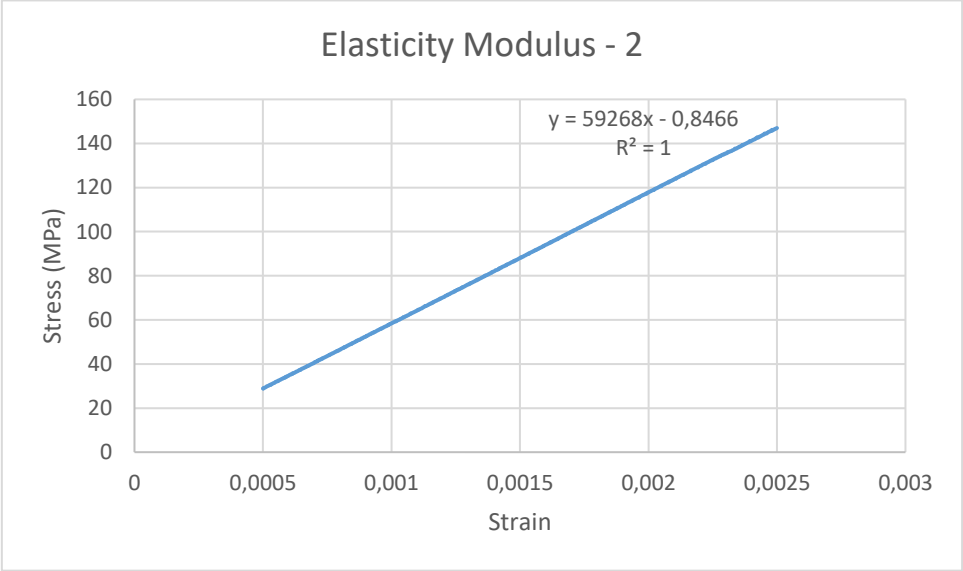

Elasticity Modulus - 3
y = 24294x + 4,7233
R² = 1
Stress (MPa)
Strain
0
10
20
30
40
50
60
70
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

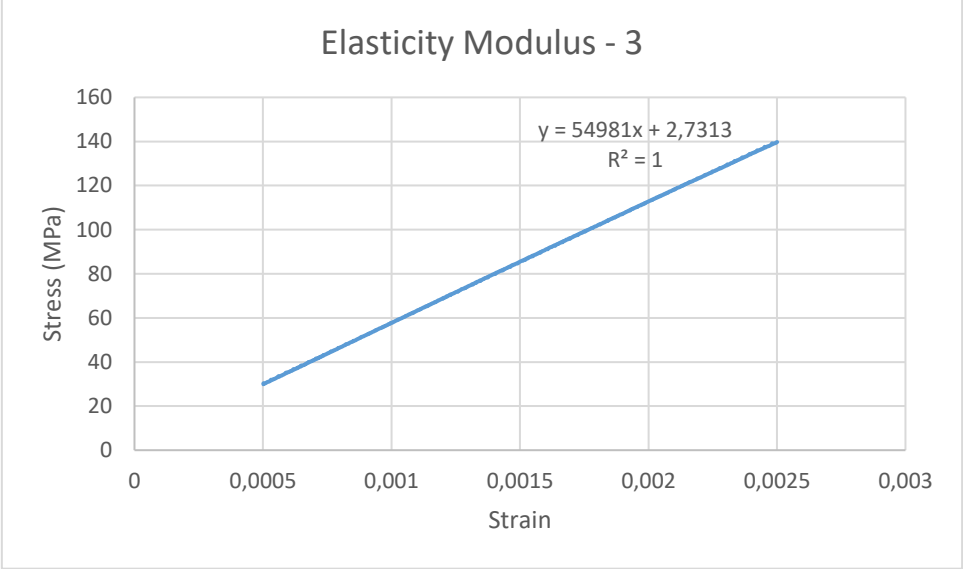

Elasticity Modulus - 4
y = 35528x - 1,401
R² = 0,9998
Stress (MPa)
Strain
0
10
20
30
40
50
60
70
80
90
100
0
0,0005
0,001
0,0015
0,002
0,0025
0,003

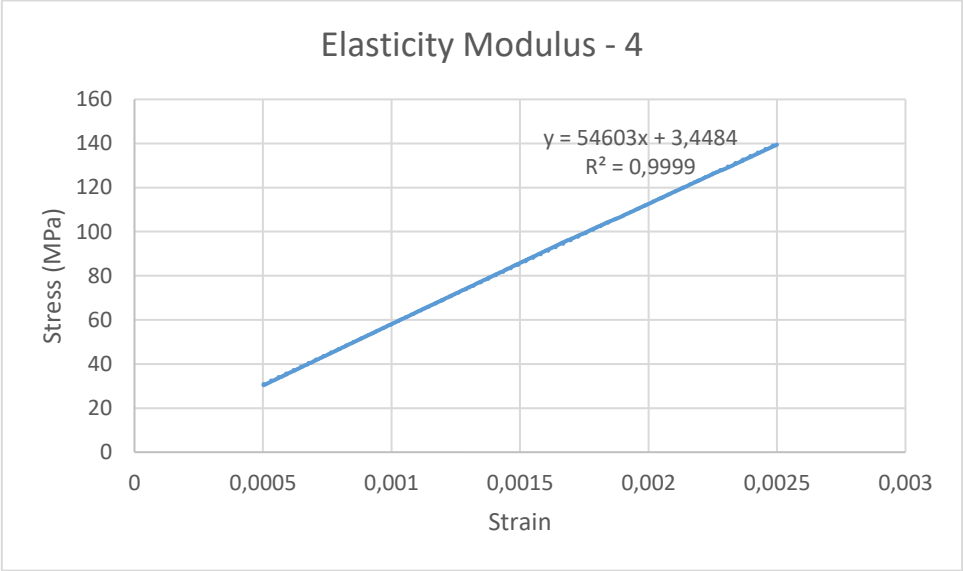
7.3.3 PC Laminate






Elasticity Modulus - 2
y = 59268x - 0,8466
R² = 1
Stress (MPa)
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain


Elasticity Modulus - 3
y = 54981x + 2,7313
R² = 1
Stress (MPa)
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain


Elasticity Modulus - 4
y = 54603x + 3,4484
R² = 0,9999
Stress (MPa)
160
140
120
100
80
60
40
20
0
0
0,0005
0,001
0,0015
0,002
0,0025
0,003
Strain