Master in Chemical Engineering

Study of Dip content in the tire textile reinforcements

A Master's dissertation

of

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Abstract

Tires are one of the most important components of motor vehicles since they allow car movement and provide the only interface between the vehicle and road surface. To increase tire performance, the industry started to introduce textile reinforcements in tire construction. Textile reinforcements are responsible for helping to maintain the air pressure, stability and strength of tires. *Continental – Indústria Têxtil do Ave, S.A.* is one of the main producers worldwide of textile reinforcements.

In order to guarantee a successful reinforcement effect and consequently, a safety performance from tires, it is essential to have good adhesion between cords and rubber compounds. These fibers need to receive physical and chemical treatment before being applied in tires. One of the most important factors when it comes to cord and rubber adhesion is the quantity of coating applied. The coating is called the dip solution and its function is to generate bonding between fibers and rubber. It is necessary to do strict quality control to the amount of coating applied, which is called dip pick-up. To measure the amount of dip pick-up present in cords, different methods can be used, such as the Wet-Chemical method, the Weighing method and a Time Domain-Nuclear Magnetic Resonance method (TD-NMR).

The main purpose of this project is to calibrate the TD-NMR device for a new textile and to better understand the fiber influence in TD-NMR measurement. A new calibration curve was done for an activated polyethylene terephthalate (PET) textile. Also, it was proved that it is possible to measure the amount of dip of three more non-activated PET textiles with a calibration curve already made in previous Master Thesis for a non-activated PET textile.

This project will allow the extent of TD-NMR implementation to measure the dip content of all type of textiles, which will contribute to a more accurate and faster quality control in the company.

Keywords: Tire, textile reinforcement, dip, dip pick-up, TD-NMR, PET

Resumo

Os pneus são dos componentes mais importantes dos veículos automóveis. Uma vez que, eles permitem a sua movimentação e fornecem a única interface entre o veículo e a estrada. Com o intuito de melhorar o desempenho do pneu, a indústria automóvel começou a incorporar têxteis de reforço na construção de pneus. Os têxteis de reforço são responsáveis por manter a pressão do ar, a estabilidade e a força do pneu. A *Continental - Indústria Têxtil do Ave, S.A.* é uma das principais produtoras mundiais de têxteis de reforço.

Para garantir um reforço bem sucedido e, consequentemente, um desempenho seguro por parte dos pneus, é essencial garantir uma boa adesão entre as cordas e os componentes de borracha. Para as cordas poderem ser incorporadas no pneu, têm de ser submetidas previamente a um tratamento químico e físico. Um dos fatores mais importantes para assegurar a adesão entre as cordas e a borracha é a quantidade de revestimento aplicado. O revestimento aplicado é denominado por solução de impregnação e a sua função é criar uma ligação entre a fibra e a borracha. É necessário efetuar um controlo de qualidade rigoroso à quantidade de revestimento aplicado, o que é denominado por *dip pick-up*. Para medir a quantidade de *dip pick-up* presente em cada corda, existem diversos métodos, tais como, o método químico, o método de pesagem e o método Ressonância Magnética Nuclear no Domínio do Tempo (TD-NMR).

O propósito principal deste projeto é calibrar o método do TD-NMR para um novo têxtil e entender melhor a influência da fibra na medida efetuada pelo equipamento de TD-NMR. Uma nova curva de calibração para um têxtil ativado de polietileno tereftalato (PET) foi efetuado. Foi também provado que é possível medir a quantidade de solução de impregnação de mais três têxteis de PET não ativados numa curva de calibração criada anteriormente numa Tese de Mestrado para um têxtil não ativado de PET.

Este projeto permitirá expandir a implementação do TD-NMR para efetuar medições à quantidade de solução de impregnação para todos os tipos de têxtil, contribuindo assim para um controlo de qualidade da empresa mais preciso e rápido.

Palavras-chave: Pneu, reforços têxteis, solução de impregnação, *dip pick-up*, TD-NMR, PET

Declaration

I hereby declare, on my word of honour, that this work is original and that all non-original contributions were properly referenced with source identification.

Porto, 1 of July of 2019

Joana Isabel Azevedo dos Santos

(Joana Isabel Azevedo dos Santos)

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Notation and Glossary

C_p	Specific heat capacity	$J \cdot kg^{-1} \cdot K^{-1}$
Dtex	Decitex	g/ 10 000 m
D_{PU}	Dip Pick-up Percentage of solid dip impregnated	%
$D_{\mathrm{PU\ per\ dipped\ cord}}$	Dip Pick-up Percentage per dipped cord	%
$D_{\mathrm{PU\ per\ greige\ cord}}$	Dip Pick-up Percentage per greige cord	%
F_0	Ratio of Samples' Variance	
m	Mass	g
m_{DIP}	Dip mass	g
$m_{\mathrm{dipped\ cord}}$	Dipped cord mass	g
$m_{\mathrm{greige\ cord}}$	Greige cord mass	g
R^2	Coefficient of Determination	
S^2	Samples' Variance	
S_C	Solid Content Percentage	%
StDev	Samples' Standard Deviation	
T_g	Glass transition temperature	ºC
T_m	Melting temperature	ºC

Greek letters

α	Significance Level
$\Delta H_{100\ \%\ \mathrm{crystalline}}$	Enthalpy of fusion of 100 % crystalline form
ΔH_m	Enthalpy of fusion
μ	Populations' Mean
σ	Populations' Standard Deviation
σ^2	Populations' Variance

List of Acronyms

AA	Activated
C-ITA	Continental – Indústria Têxtil do Ave, S.A.
CI	Confidence Interval
DSC	Differential Scanning Calorimetry
FID	Free Induction Decay
LDU	Lab Dipping Unit
LTL	Lower Target Limit
nAA	Non-activated
PET	Polyethylene terephthalate
RFL	Resorcinol-Formaldehyde-Latex
TD-NMR	Time Domain-Nuclear Magnetic Resonance
UTL	Upper Target Limit

1 Introduction

Tires are highly engineered structural composites of today's motor vehicles and must perform a variety of functions even in the most extreme conditions, such as dampen, assure good directional stability, and provide long-term service. In order to accomplish that, multiple levels of techniques and materials are required. For instance, the incorporation of textile reinforcements in a tire, which contributes to the improvement of the tire performance.

1.1 Framing and presentation of the work

A pneumatic tire is reinforced by textiles that provide strength, stability and hold the air pressure. *Continental - Indústria Têxtil do Ave, S.A.* (C-ITA) is responsible for the production of the textile reinforcements used in Continental's tires.

An important step to utilize textile fibers in tires is the dip treatment, where textile fibers are coated with a special dipping solution to allow proper bonding between the fiber and the surrounding rubber matrix in the tire. One of the key influencing factors in the cord to rubber adhesion is the quantity of coating that is applied to the fiber.

In order to improve the quality control, C-ITA recently bought a time domain nuclear magnetic resonance (TD-NMR) equipment to measure the amount of dip pick-up (D_{PU}) that is present on the cord. D_{PU} is the percentual amount of the dipped solution in the cord.

Previous work has already been developed about this Master Thesis theme. The calibration curve for nylon, hybrid (a combination of one yarn of nylon and one yarn of aramid), rayon and polyethylene terephthalate (PET) have already been discovered and validated. However, the PET calibration curve has not been validated for different suppliers. The present Master Thesis focuses on the validation of PET calibration curve of three more non-activated PET textiles, and the development of a new calibration curve for an activated PET textile in order to allow C-ITA to adopt TD-NMR method to measure the amount of D_{PU} in a faster and more practical way for the different PET materials.

1.2 Presentation of Continental – Indústria Têxtil do Ave

Continental AG, founded in 1871 in Hannover - Germany, is one of the leading automotive companies in the world as a supplier of tires, brake systems, systems and components for powertrains and chassis, instrumentation, infotainment solutions, vehicle electronics and technical elastomers. Continental operates in 53 countries and has over 200,000 employees producing innovative solutions, as well as operating and delivering high quality products (Continental 2019).

Indústria Têxtil do Ave, S.A., was founded in 1950, in Lousado, to produce the needed textiles for the Mabor tires. The company became, alongside Mabor, part of Continental in 1993, and its name changed to Continental - Indústria Têxtil do Ave (C-ITA). C-ITA mainly produces textile reinforcements, which in their majority are exported to Continental plants in Europe. Besides producing reinforcement textiles for tires, C-ITA is also a research and development facility for the textiles of the future.

1.3 Contributions of the Work

This Master Thesis continues the implementation of TD-NMR device in dip pick-up measurement of C-ITA fibers.

In the first part of my project, I studied three non-activated PET materials using a calibration curve already done in a previous Master Thesis. I proved that the amount of D_{PU} in these cords can be measured with confidence in TD-NMR device. I validated the calibration curve for three additional PET materials.

In the second part of the project, I did a calibration curve for an activated PET material.

In the last part of the project, I performed differential scanning calorimetry (DSC) tests with the intent to understand better the reason why hybrid cords cannot be measured by nylon's calibration curve. Additionally, I performed a DSC test to study non-activated PET and activated PET to confirm that these materials do not have different thermal properties.

1.4 Organization of the Thesis

This thesis is divided in 8 chapters, which are organized in the following way:

Chapter 1: Introduction. Brief presentation of Continental corporation and C-ITA, contextualization of the problem, as well as the work objectives.

Chapter 2: Context and state-of-the-art. The chapter where the tire and the production process of textile reinforcements are explained.

Chapter 3: Materials and methods. Description of all the materials, procedures and techniques used.

Chapter 4: Results and Discussion. In this chapter, the results obtained are analyzed and discussed.

Chapter 5: Conclusion. Main conclusions achieved out of the obtained results.

Chapter 6: Assessment of the work done. Overall judgment about the work developed.

Chapter 7: References. A list of all the references used throughout the thesis.

Appendix: Complementary information required to follow the development of the project.

2 Context and State of the art

2.1 Tire

The pneumatic tire was invented in 1888 by Dunlop, firstly for bicycles and afterward for automobiles. In 1898, Continental started producing tires with the purpose of offering a safe ride and enabling automobiles to travel at higher speeds. In 1904, Continental developed the first automobile tire with a tread pattern and started the addition of carbon black that made tires tougher and more durable. Four years later, Continental launched another innovative product – the removable wheel rim, which made it easier to change a tire. Nowadays, tires manufactured by Continental are extremely high-tech products and their maximum speed has risen from 210 $km \cdot h^{-1}$ to 350 $km \cdot h^{-1}$, at the same time the weight of the tire has been reduced significantly (Continental, 2013).

Since tires provide the interface between the vehicle and the road, safety is a major priority in tire development at Continental. A tire must support the weight of the car, it must be capable of transmitting strong longitudinal and lateral forces (during braking, accelerating and cornering maneuvers) in order to ensure road holding safety. It should offer optimal adhesion to road surfaces even in the most extreme weather conditions. Regarding longevity and durability, a tire should be robust and highly resistant against external influences, it should maintain its specified dimensions over its lifecycle and be able to provide a long-term service (Continental, 2013; Leister, 2018).

A tire is constituted by 20 or more components, with 15 or more being rubber compounds. Tire ingredients are mainly natural and synthetic rubber (41 %), fillers (30 %), reinforcement materials such as steel, polyester, rayon, nylon and aramid (15 %), plasticizers (6 %), chemicals for vulcanization (6 %) and anti-ageing agents and other chemicals (2 %). The components of a radial tire, which is the typical tire used in passenger vehicles, are represented in **Figure 1** (Continental, 2019).

Figure 1 - Example of tire constitution (Continental, 2019).

Tread is the tire component in contact with the road. The tread is made of blends of natural and synthetic rubber. It must provide the necessary grip on all road surfaces, wear-resistance, good cornering characteristics with minimum noise generation and directional stability. The primary purposes of the tread pattern are to improve road adhesion and to expel water that can affect the tire's contact with the road surface (Continental, 2013; Mark et al., 2005).

Cap ply is made of nylon or hybrid cords embedded in the rubber. It allows automobiles to achieve higher speed rates. The cap ply is wrapped circumferentially on top of the belts and its goal is to restrict expansion of the tire from centrifugal forces during high speed (Lindenmuth, 2006).

Belts are layers of high-strength steel or textile cords, which are located under the tread, that serve to stiffen the casing. Belts protect the ply cords from road hazards, enhances shape retention and directional stability, thereby improving the overall tire resistance and performance (Mark et al., 2005).

The **carcass**, also named body ply, is constituted by cord and rubber. The cords are laid radially across the tire, providing strength, containing air pressure and helping to maintain the tire's shape. In **Figure 1**, it is possible to see a tire with a regular size

that has one body ply. Regarding tires with larger sizes, two body plies are often used (Lindenmuth, 2006).

The **inner liner** is a thin component of the tire made with butyl rubber. It helps to retain the compressed air inside the tire by lowering permeation outwards through the tire (Lindenmuth, 2006).

The **side wall** is made of natural rubber and it serves to protect the body plies from external damage, such as abrasion, impact and flex fatigue. It also protects the casing from atmospheric conditions, for example, ozone, UV radiation and heat (Lindenmuth, 2006).

Bead area components include the apex and the bead reinforcement, which enhance directional stability, steering precision and improve comfort (Continental, 2013).

There are three types of tires depending on the carcass arrangement: the diagonal tires, the belted bias tires and radial tires. According to Lindenmuth (2006), "the **diagonal, or bias, tires** are still used today in some applications for trucks, trailers and farm implements, bias tires have body ply cords that are laid at angles substantially less than 90º to the tread centerline, extending from bead to bead. These tires have a simple construction and ease of manufacture, however, as the tire deflects, shear occurs between body plies which generate heat".

According to Lindenmuth (2006), "the **belted bias tires**, as the name implies, are bias tires with belts added in the tread region. Belts restrict expansion of the body carcass in the circumferential direction, strengthening and stabilizing the tread region. These tires have improved wear and handling due to added stiffness in the tread area, although, body ply shear during deflection generates heat and the manufacturing cost is higher".

According to Lindenmuth (2006), "**radial tires** have body ply cords that are laid radially from bead to bead, nominally at 90º to the centerline of the tread. Two or more belts are laid diagonally in the tread region to add strength and stability. Their radial body cords deflect more easily under load, thus they generate less heat, give lower rolling resistance and better high-speed performance. Increased tread stiffness from the belt significantly improves wear and handling. However, these tires have complex construction which increases material and manufacturing costs".

2.2 Textile Reinforcement

Reinforcement materials can be divided into textile, metal and rubber compounds. Metal reinforcements are made of steel cords embedded in the rubber. Textile reinforcements used in C-ITA are nylon, polyethylene terephthalate (PET), rayon and aramid fibers. C-ITA also produces hybrid cords made with nylon and aramid, which have better properties. Textile reinforcements can be used in different parts of the tire. Fabric is used in the carcass and the cords in the cap-ply. Fibers must be submitted to a chemical and physical process before being able to be used as a reinforcement.

Tire cord fabrics are the strength elements of a tire, define the tire shape, give stability, support the load and help to maintain the air pressure. Cords provide the axial and lateral rigidity for acceleration, braking and cornering, provide fatigue and bruise resistance for durability (Continental, 2013).

2.2.1 Fibers

Nylon fibers are synthetic long chain polyamides. There are two main methods to produce these fibers, either by continuous polymerization or melt spinning. The most common use is in radial tires as the cap-ply or overlay ply. They have good heat resistance, strength and low sensitivity to moisture (Lindenmuth, 2006).

Polyethylene terephthalate (PET) fibers are synthetic long chain polymers produced by continuous polymerization/spinning or melt spinning. These fibers are typically used in radial body plies and the carcass. They have high strength with low shrinkage, low heat set, and they are water resistant and affordable when compared to other reinforcement fibers. However, they are not as heat resistant as nylon or rayon fibers (Lindenmuth, 2006).

Rayon fibers are made from cellulose produced by wet spinning. The most common usage is in the carcass and belt reinforcement. They have good heat resistance and handling characteristics. However, they are expensive, sensitive to moisture and have environmental manufacturing issues (Lindenmuth, 2006).

Aramid fibers are an aromatic polyamide and high tenacity organic fibers produced by solvent spinning. These fibers are stronger and more heat resistant than PET and nylon fibers. They can be used in the carcass, in bead reinforcement, and for belt or stabilizer ply material as a lightweight alternative to steel cord. They have very high strength, stiffness and heat resistant. However, they are expensive (Lindenmuth, 2006).

2.2.2 Cord Design

Fibers can be divided into four levels of design: filament, yarn, cord and fabric. The filament is the smallest continuous component in a textile. Yarn is the assembly of filaments. A cord is formed when two or more yarns are twisted, then the cord can be weaved into a fabric or be used as a reinforcement cord (Lindenmuth, 2006).

Cords are defined by the material they are made of, cord construction, the linear density and twist level. **Linear density** is the weight per length of the fiber, and it is defined as decitex (*dtex*), which refers to the weight in grams of a length of 10,000 meters. **Twist level** is the number of turns per meter of the cord (BISFA, 2009).

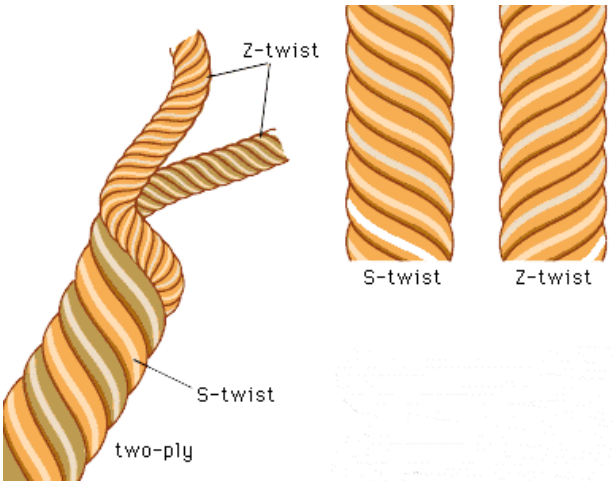

Figure 2 - Directions of twisted cord (adapted from Encyclopedia Britannic, 1998).

The **cord construction** begins with the spinning process, where the yarns are formed. Then the yarns are twisted, producing a greige cord (cord without physical and chemical treatment). Twisting can be applied in two distinct directions, "Z" (counter-clockwise) or "S" (clockwise). Usually, yarns are twisted individually in the "Z" direction followed by the twisting of multiple yarns in the "S" direction, as seen in **Figure 2**. Weaving is the next process, where cords are woven and the greige fabric is produced. After this, it is necessary to apply a physical and chemical treatment to the fabric (dipping process), which will provide the effective adhesion between the fiber and the rubber.

C-ITA receives the raw material from several suppliers already in the form of yarns. Therefore, the first step is the twisting process. If the objective is to produce fabric, then a weaving process is needed to transform the greige cord into fabric, however, if the purpose is to produce a single cord, the greige cord can pass directly to the final stage of dipping. Fabric produced by the weaving machines is used for the

carcass, the reinforcement cords are applied in the cap-ply of the tire and as a bead reinforcement. The twisting and weaving machines at C-ITA can be seen in **Figure 3**.

Figure 3 - Twisting machines on the left and Weaving machines on the right at C-ITA.

2.3 Dip solution and Dipping Process

In order to assure a safety performance from tires, it is essential to have a good adhesion when fibers are used in combination with rubber. A low adhesion is verified between fibers without treatment and the rubber matrix, due to a significant difference in modulus and polarity. A reinforcing effect is only successful if the load forces can efficiently be transferred from the rubber to the cord. If lack of adhesion is verified, the fiber will easily slip into the rubber matrix and the composite will not have the desired performance (Wennekes, 2008; Louis et al., 2014).

The prime goal of the cord adhesive is to avoid separation at the cord-adhesive interface, at the rubber-adhesive interface, or within the adhesive itself. In order to achieve cord-to-rubber adhesion, the cords must be submitted to treatment. In this treatment, greige cords, or fabric, are dipped in a solution that will provide an interface that allows the bonding between the cord and the rubber. At C-ITA, the dip used is a resorcinol-formaldehyde-latex (RFL)-based solution. In **Figure 4,** it is possible to observe that the dip acts as a bridging agent between the fiber and the rubber.

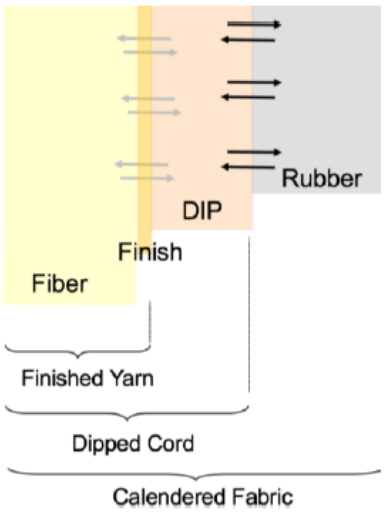

Figure 4 - Fiber-rubber adhesion (Wahl, 2003).

The RFL-dip is an emulsion of rubber latex in a solution constituted by resorcinol and formaldehyde in water. The latex emulsion itself is not enough for the cord to develop an interaction with the rubber matrix of the compound and with the fiber, so it is necessary to add resorcinol and formaldehyde. Thereby the dip increases its polarity and mechanical properties. An RFL-dip solution can be prepared in two stages. In the first stage, an aqueous solution of resorcinol and formaldehyde is matured for several hours at room temperature. In the second stage, the resin solution is added to a mixture of water and latex. Then the resin forms a bond with the fiber due to covalent chemical bonds formed in the interface fiber-dip. The latex used is a synthetic styrene-butadiene-2-vinyl pyridine (VP latex). The latex component bonds to the rubber compound due to co-vulcanization, which is a process that improves rubber elasticity and strength. Each fiber has its specific dip recipe with an established Solid Content Percentage (S_C) (Wennekes, 2008; Lindenmuth, 2006).

While working with nylon or rayon, a standard treatment with RFL-dip is sufficient, since the reactivity of these fibers is high enough. In contrast, non-activated PET and non-activated aramid fibers feature a highly inert surface, which makes them unreactive towards rubber to RFL coating. In these cases, adhesion is not verified, so it is necessary to submit the fibers to a pre-treatment. A pre-dip is used to activate the fibers to allow the bonding to the dip. The pre-dip is a solution of epoxy resin and isocyanate. Some suppliers of C-ITA already provide this pre-treatment to the fibers, in this case only the standard treatment with RFL-dip is needed. (Louis et al., 2014).

Nowadays, the industry is making efforts to replace the RFL-dip systems for other dip alternatives more environmentally friendly. Despite that, the RFL-dip

systems still deliver the best results when it comes to adhesion between rubber and fibers. This is the main advantage of this treatment, but the residues of RFL-dip still need to be treated as a special waste (Louis et al., 2014).

Reinforcement textiles are subjected to high temperatures (thermo-fixation), to tension over a specific amount of time and to chemical treatment (dipping process). At C-ITA, there are two dipping machines that provide the required treatment to textile reinforcements, Single-end (**Figure 5**) and Zell machine (**Figure 6**).

The **single-end** machine is used to dip cords. This machine has four ovens. In the beginning, the greige cord (cord without treatment) is stretched in tensioning rollers and is dipped in the first bath (located before the first oven), which contains the dipping solution. Then, the cord enters the first oven, which works as a dry zone, and after that, the cord is forwarded to the second oven, which works as a hot stretch zone. If the cord needs to be activated, in the case of non-activated PET and non-activated aramid, it is necessary to use the third and fourth oven. In this case, the first bath contains the pre-dip and the second bath, the dip. The first and second oven act as a dry zone and as a hot stretch zone, respectively. The third oven acts as a second dry zone and the fourth zone as a normalizing zone. At the end of the treatment, the cord is rolled into a bobbin and the product is ready to be shipped.

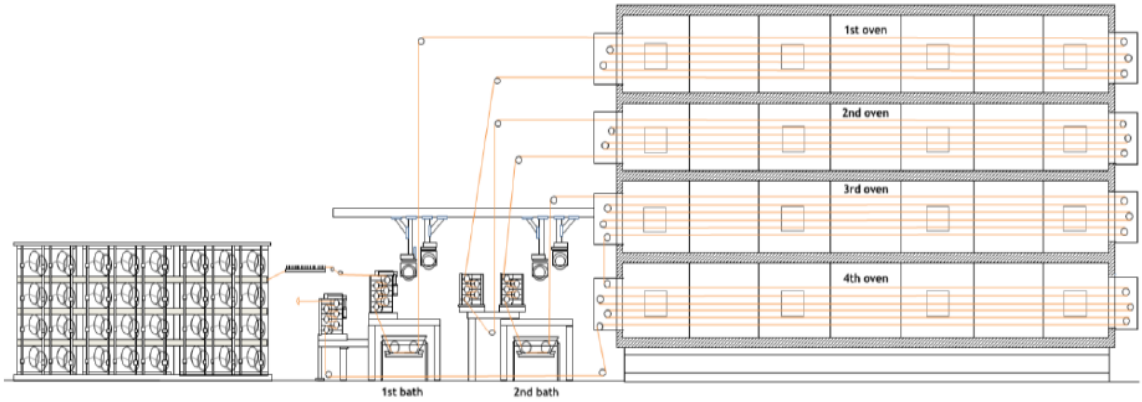

Figure 5 - Scheme of the Single-end machine (adapted from Martins, 2013).

The **Zell** machine is used to dip fabric. This machine has a similar way to function to the single-end machine. However, there are some differences. Zell has more ovens than Single-end machine, greige fabric and dipped fabric are not wound up in the same side and in the Zell machine rolls of fabric are dipped one at a time, while in Single-end several cords can be dipped at the same time.

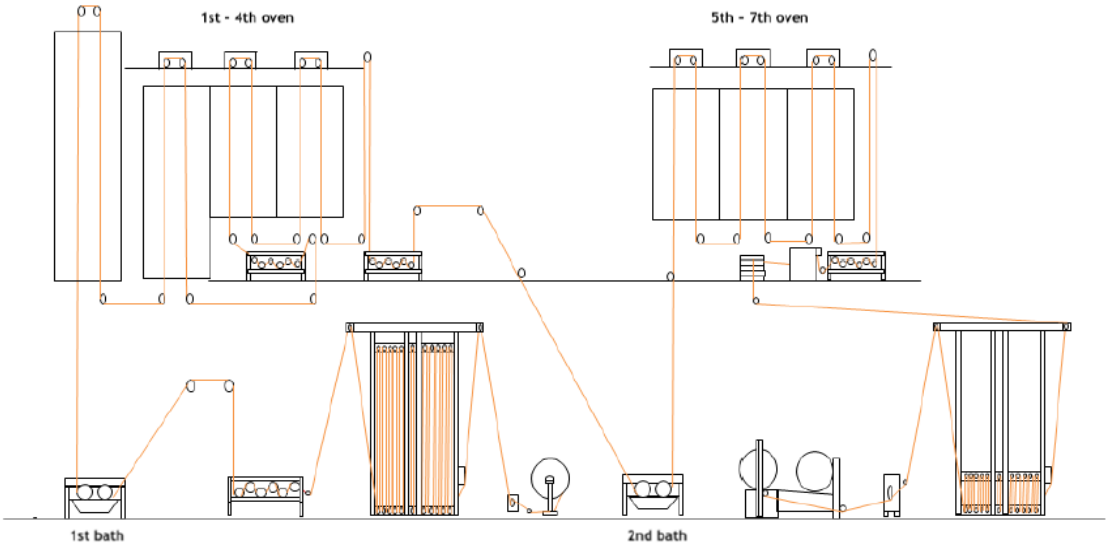

Figure 6 - Scheme of the Zell machine (adapted from Martins, 2013).

C-ITA has an equipment for investigation purposes called Lab Dipping Unit (LDU), which replicates at a laboratory scale these dipping units. It is possible to study different parameters, such as S_c, temperature, velocity, tension and stretching. In this equipment, it is possible to improve dip recipes to implement later in production.

2.4 Dip measurement and quality control

Before shipping its final products, C-ITA performs several tests to verify the quality and safety of the products. One of the tests performed to check the cords' adhesion to the rubber is the "peel adhesion test", represented in **Figure 7**. If a good adhesion is not verified cords easily get separated from rubber, showing a weak rubber-to-cord adhesion. To consider the test successful, the cords cannot be visible to the naked eye.

Figure 7 - Peel adhesion test result: bad result (at left) and a good one (at right).

As already mentioned, cord performance is directly related to the amount of dip. Therefore, it is necessary to guarantee an ideal amount of dip, since a low quantity of dip leads to bad adhesion, while an excess quantity leads to resources waste and is not environmentally friendly. Thus, the determination of the amount of dip is crucial. To quantify the amount of dip in the cord, C-ITA measures the Dip Pick-up Percentage per greige cord. The following methods are used:

Standard Methods:

1) Wet-Chemical Method

In this method, the D_{PU} is determined by differences in mass (gravimetric method). Initially, the cord needs to be dried and weighed (m_1). This method consists in the dissolution of the cord in a suitable solvent, filtration of the solution through a crucible to recover the dip residue, and then the dip is dried and weighed ($m_3 - m_2$). Afterwards, Equation 1 is used to determinate the D_{PU}.

$$D_{\mathrm{PU}} = \frac{m_3 - m_2}{m_1 - (m_3 - m_2)} \times 100 \quad (1)$$

where m_1 is the sample weight in grams (g), m_2 is the glass filter crucible weight in g and m_3 is the solid residue plus the crucible weight in g.

This method has some disadvantages, as it requires a long time to be completed, has a significant amount of errors associated and it uses harmful chemicals to the environment, which are needed to dissolve the fiber.

2) Weighing Method

Cords have a high affinity to water, so it is necessary to dry them before weighing them. However, the weight of some materials is not affected by humidity, such as PET. In this case, the D_{PU} can be measured by this method.

In this method, the D_{PU} is determined by comparing the weight of the dipped cord and the greige cord. The greige cord is thermofixed within the same conditions as the dipped cord and is used as a reference value. The amount of D_{PU} in the dipped cord is obtained by Equation 2.

$$D_{\mathrm{PU}} = \frac{m_{\text{dipped cord}} - m_{\text{greige cord}}}{m_{\text{greige cord}}} \times 100 \quad (2)$$

This method is not as accurate as the other methods since it has many errors associated. Therefore, this method is avoided at C-ITA.

Time Domain-Nuclear Magnetic Resonance Method (TD-NMR):

Time-domain nuclear magnetic resonance (TD-NMR), or also named low-resolution method, is based on small and permanent low-field magnets. TD-NMR method has distinctive characteristics, such as low error associated, rapidity, convenience, preservation of sample integrity, high correlation and reproducibility, which makes it an excellent alternative to traditional methods (da Rocha et al., 2017).

Since NMR is a resonance method, a resonance condition must be fulfilled to allow energy level transitions within the atom. TD-NMR method produces a magnetic field with low frequency around the sample, causing each atom to align its spin in the same direction as the magnetic field. Then, the device measures the energy re-emitted by the excited protons. From this energy, it results in an electrical signal that is read in the domain of time (Todt et al., 2006).

TD-NMR is a pulse method and the pulse sequence generated is called spin-echo or *Hahn*-echo sequence, which affects the behavior of the protons' spins. The pulse sequence consists of two radiofrequency pulses with different angles (90º and 180º). The first pulse creates a Free Induction Decay (FID) signal, which will influence the equilibrium of the protons and they will transit to an excited state. After the pulse is deactivated, the protons return to their equilibrium state, releasing the energy absorbed. The signal captured by the TD-NMR results of the difference between the energy absorbed and released by the protons' spins. Then the second pulse is applied, which has twice the duration of the leading pulse. The purpose of the second pulse is to generate an echo signal of the FID signal due to the time-reversal of the decay of the FID signal. Moreover, the FID amplitude is governed by the sum of components A and B, in this case, the dip and the fiber. In this way, with one pulse sequence, components can easily be separated and analyzed quantitatively (Todt et al., 2006; Hornak, 1996; CDRH Magnetic Resonance Working Group, 1997).

C-ITA resorts to this method to measure the amount of dip in the cord samples. Both the dip and the fiber are solid, but since the dip has a shorter relaxation time than the fiber it is possible to measure the amount of dip through the difference between the first and second signal, as it can be seen in **Figure 8**. The higher the signal obtained, the higher the dip concentration (Bruker, 2016).

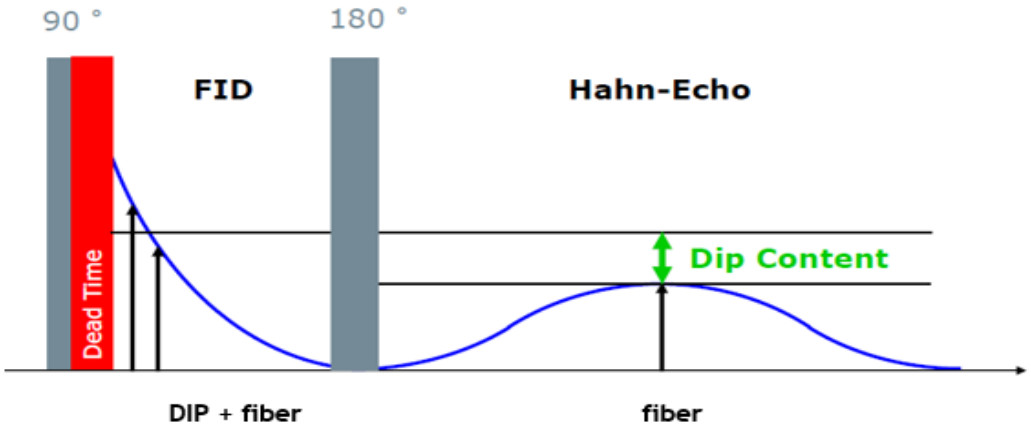

Figure 8 - Hahn echo sequence representation (Adapted from Bruker, 2016).

When compared to the other methods, TD-NMR method is far superior, and with proper calibration previously done, it allows to obtain faster and more accurate results. Sample preparation and the analysis are faster, and it is a more environmentally friendly method since it does not require chemical solvents. Additionally, TD-NMR is a nondestructive method, making it possible the preservation of samples (Todt et al., 2006).

There are some concerns to consider, TD-NMR is a very sensitive device that requires precision. TD-NMR spectrometers (magnet and probe) operates at a warm and stable temperature in order to stabilize the magnetic field. Therefore, the samples need to be dried previously and they must be at the same temperature as the device. It has been proved before in Master Theses done at C-ITA that is necessary to use gloves to prepare the samples in order to not disturb the NMR signals.

2.5 Statistical Analysis

Statistical methods are an important tool in many fields, such as engineering. Statistic allows engineers to collect, analyze and interpret the data, in order to make the best decisions, to solve problems, and design products and processes. Statistics provide descriptive and analytical methods to understand and deal with variability that occurs in data. The main methods used at data analysis of a comparative experiment are statistical hypothesis testing and confidence interval estimation of parameters (Montgomery et al., 2003).

2.5.1 Hypothesis Testing

While solving problems sometimes is necessary to decide whether to accept or reject a statement about a parameter under study, which is called a hypothesis testing. According to Montgomery (2003), “a statistical hypothesis is usually a statement about

a set of parameters of population distribution. It allows the comparison between a population's parameter to a specific value, or to another parameter of a different population".

According to Devore (2011), "the hypothesis testing has two contradictory hypotheses under consideration, the null hypothesis (H_0) and the alternative hypothesis (H_1). The null hypothesis will be rejected in favor of the alternative hypothesis only if sample evidence suggests that H_0 is false. The two possible conclusions from a hypothesis-testing analysis are then rejected H_0 or fail to reject H_0".

For the hypothesis test of the variances of two populations, each one following a normal distribution, the null hypothesis states that the two variances are equal, while the alternative hypothesis states the opposite.

$$H_o: \sigma_1^2 = \sigma_2^2 \quad (3)$$

$$H_1: \sigma_1^2 \neq \sigma_2^2 \quad (4)$$

where σ_1^2 and σ_2^2 are the variances of population 1 and 2, respectively (Montgomery et al. 2003).

Knowing that S_1^2 and S_2^2 are the samples variances, the following ratio F_0

$$F_0 = \frac{S_1^2}{S_2^2} \quad (5)$$

has a Fisher-Snedecor distribution with $n_1 - 1$ and $n_2 - 1$ degrees of freedom. The null hypothesis is rejected when $F_0 > F_{\frac{\alpha}{2}, n_1-1, n_2-1}$ or $F_0 < F_{1-\frac{\alpha}{2}, n_1-1, n_2-1}$, in which $F_{\frac{\alpha}{2}, n_1-1, n_2-1}$ is the upper $\frac{\alpha}{2}$ percentage point and $F_{1-\frac{\alpha}{2}, n_1-1, n_2-1}$ is the lower percentage point of the Fisher-Snedecor distribution. (Montgomery et al. 2003).

For the hypothesis test of the means of two populations, with equal variances, that follow a normal distribution, two statements are formulated, the null hypothesis states that the means are equal, and the alternative hypothesis states the opposite.

$$H_o: \mu_1 = \mu_2 \quad (6)$$

$$H_1: \mu_1 \neq \mu_2 \quad (7)$$

where μ_1 and μ_2 are the means of population 1 and 2, respectively (Montgomery et al. 2003).

To report the results of a hypothesis test, usually, a p-value approach is used, where the null hypothesis is accepted or rejected at a specified α-value or level of significance. According to Montgomery (2003), "the p-value is the smallest level of significance that would lead to rejection of the null hypothesis H_0 with the given data.

When the null hypothesis is true, the p-value is the probability that the test statistic will take on a value that is at least as extreme as the observed value of the statistic".

2.5.2 Confidence Interval

According to Montgomery (2003), "a confidence interval (CI) of a certain parameter θ is an interval of the form l ≤ θ ≤ u where the values l and u are endpoints called the lower - and upper - confidence limits, respectively. According to the probability theory, there is a probability of $1-\alpha$ of selecting a sample for which the CI will contain the true value of the parameter θ". A CI helps to estimate unknown parameters (Montgomery et al., 2003).

Hypothesis test about a parameter θ and the confidence interval for the same parameter are correlated. If [l, u] is the $100 \cdot (1-\alpha)\,\%$ CI for the parameter θ, the test of size α of the hypothesis

$$H_0: \theta = \theta_0 \tag{8}$$

$$H_1: \theta \neq \theta_0 \tag{9}$$

will lead to rejection of H_0 if and only if θ is **not** in the $100 \cdot (1-\alpha)\,\%$ CI [l, u] (Montgomery et al., 2003).

2.6 Characterization of Polymers using Differential Scanning Calorimetry (DSC)

In order to try to understand why the amount of D_{PU} in hybrid cords cannot be measured by nylon's calibration curve, hybrid and nylon materials were studied using the DSC method. Additionally, PET textiles were also tested to see if there were thermal properties differences between the nAA PET textiles and the AA PET textiles.

Differential Scanning Calorimetry (DSC) provides important techniques to study and characterize polymers thermal properties. DSC thermal analysis allows, for instance, identifying unknown polymers, determining best processing temperatures, qualitative comparison of materials, estimating percent crystallinity, measuring heat capacity, estimating the degree of cure, estimating upper use temperature from glass transition temperature (T_g) and melting temperature (T_m) (EAG LABORATORIES).

A heat flux DSC containing a thermal cell with a sensor registers over time the temperature difference between a crucible that contains the sample and a reference crucible, which is empty (containing only air). An exothermic step (for example, "cold" crystallization) can occur if the sample emits more energy than the reference does,

the temperature of the sample is higher than the temperature of the reference crucible. In this case, in the DSC plot, it is possible to see an increase in heat flow. If the temperature of the sample is smaller than the temperature of the reference crucible, an endothermic step occurs (for example, glass transition and melting) (EAG LABORATORIES).

When fusion happens, an endothermic peak occurs, whose area is proportional to the enthalpy of fusion of the material crystalline fraction. The percentual amount of crystallinity is obtained by Equation 10.

$$crystallinity\ (\%) = \frac{\Delta H_m}{\Delta H_{\,100\ \%\ \text{crystalline}}} \times 100 \qquad (10)$$

2.7 Assessment of previous work

C-ITA purchased a time domain nuclear magnetic resonance (TD-NMR) equipment to improve the quality control of products. TD-NMR is used to measure the amount of D_{PU} that is present on dipped cords. Previously work has been developed with TD-NMR device in Master Thesis. TD-NMR is already calibrated for nylon, hybrid (2 yarns from different materials combined), rayon and PET (**Figure 9**). However, for PET textiles, the calibration curve is not validated for different suppliers.

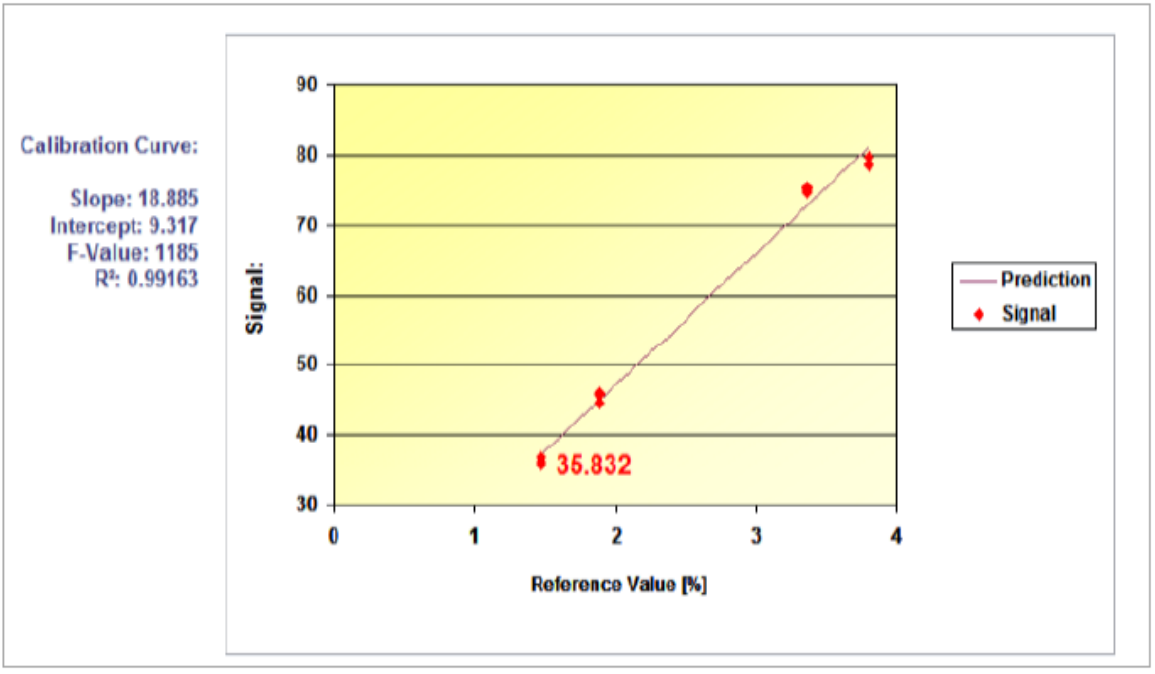

Figure 9 - PET calibration curve (Bezerra, 2018).

In previous Master Theses, it was also studied the influence of different parameters on D_{PU} results, such as temperature, velocity and Solid Content. Regarding the TD-NMR method, an additional method to prepare samples has been developed. Additionally, it was proved that it is necessary to dry the samples properly and to handle samples gloves are required since it can affect the D_{PU} results. Also, optimization of time in one of the steps of TD-NMR procedure has been accomplished.

This current Master Thesis focuses on the development of a new calibration curve for an AA PET textile and the validation of nAA PET calibration curve for different suppliers so that C-ITA can implement the TD-NMR method for all the different suppliers used in production and improve their quality control.

3 Materials and Methods

In this chapter, all the materials and methods used throughout the work are presented. The project focusses mainly in the continuation of the implementation of PET dip pick-up measurement in the TD-NMR device. The PET calibration curve already created was done for supplier A and *dtex* of 2200x2, and it was validated for non-activated (nAA) materials of the same supplier. However, this calibration curve was not validated for different suppliers and for activated (AA) PET materials. nAA PET materials and AA PET materials have a similar construction, however, the composition of the dips used are different. It has been proved in previous Master Theses that the composition of the dip and suppliers can affect the TD-NMR signal. Data from previous Master Theses were used in the studies carried out. In **Table 1**, it is possible to see what was studied in the past Master Thesis and what is going to be studied.

The first part of the project focusses on the study of nAA PET materials. A calibration curve was done in previous Master Thesis. Since only two of the four suppliers of nAA PET were measured in this calibration curve, the two remaining suppliers of nAA PET materials were studied, with the intent to verify if the calibration curve is suitable to measure the amount of D_{PU} in the cords. Thus, samples from production were collected and measured in the TD-NMR device. Furthermore, it was necessary to use statistical analyses to study the reliability and confidence of the results obtained. The statistical software used was *Minitab 18*.

In the second part of the project was proposed to do a calibration curve of AA PET material of supplier B and with a *dtex* of 3340x2. It was necessary to collect 30 samples from production in order to validate the calibration curve. It was also necessary to use statistical analyses to study the reliability and confidence of the results obtained.

The third part of the project focusses on the DSC tests of nylon and hybrid materials. It has been proved before in past Master Theses, that D_{PU} values obtained by the TD-NMR device seem to be more significantly affected by the dip used and not by the type of textile. DSC tests were performed with the aim to understand why the amount of D_{PU} in hybrid materials cannot be measured in nylon's calibration curve since these two materials have the same dip recipe. Additionally, DSC tests for nAA PET and AA PET materials were also performed in order to evaluate if there are significant thermal differences between these materials.

Table 1 - Work Plan Schematization.

Textile	*Dtex*	Supplier	Previous Work	Project's First Part	Project's Second Part
nAA PET	2200x2	A	Calibration Curve created and approved		
nAA PET	1440x2	A	Validated		
nAA PET	1440x2	B	Not validated		
nAA PET	1440x2	C		Validated	
nAA PET	1840x2	D		Validated	
nAA PET	3340x2	D		Validated	
AA PET	3340x2	B			Calibration Curve created and approved

3.1 Materials

In this Master Thesis, the materials used throughout the work were mainly PET materials, non-activated and activated.

Nylon and hybrid cords were also studied using DSC tests.

3.2 Dipping process

C-ITA has an equipment called Lab Dipping Unit (LDU), as it can be seen in **Figure 10**, that replicates at a laboratory scale these dipping units, as already mentioned in Chapter 2. In this equipment, only one cord can be dipped at the same time. Each textile has its dipping solution and specifications, such as Solid Content, temperature, velocity, tension and stretching.

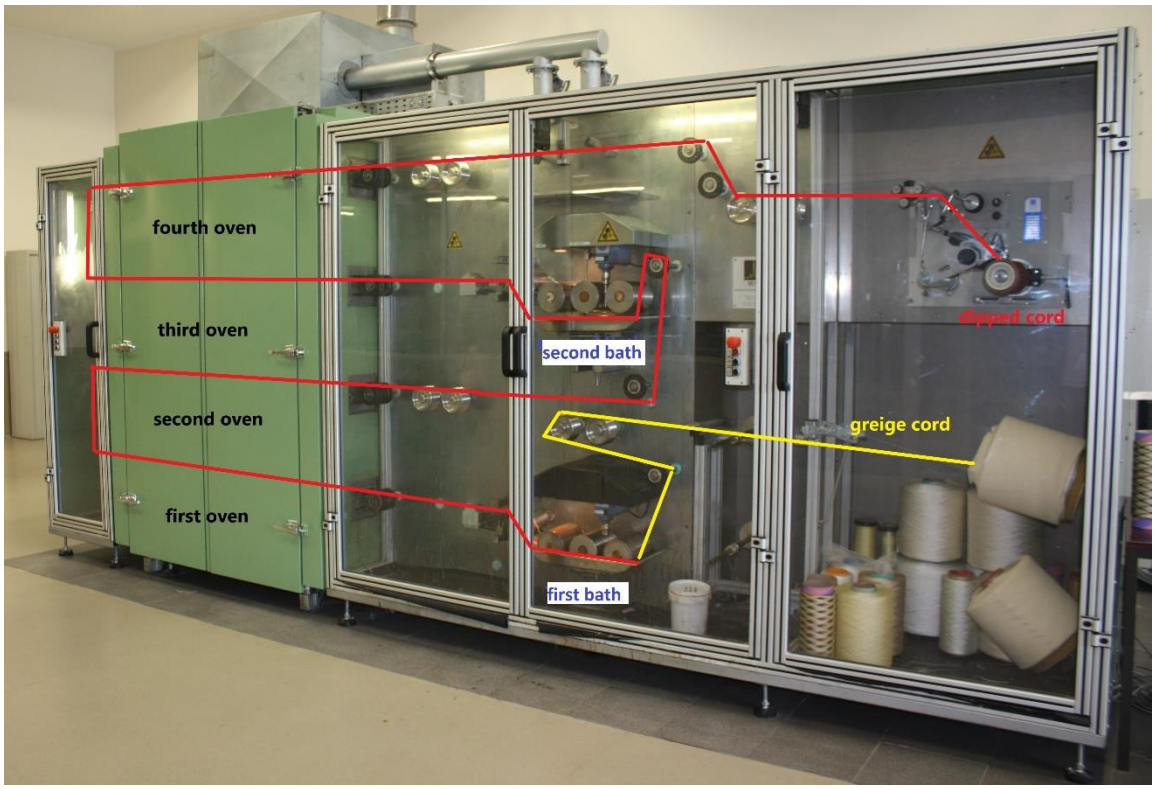

Figure 10 - LDU machine scheme.

In this project, the materials studied were mainly non-activated and activated PET textile. AA PET was dipped in LDU machine. While working with AA PET, it is necessary to use two different dips, therefore the first and second baths and all ovens are needed.

3.3 D_{PU} measurement

At C-ITA, dipped cords and fabrics are submitted to strict quality control before being shipped to customers. One of the tests performed is the D_{PU} measurement, where each material has its specifications. The specifications for each PET material are present in **Table 2**. There are three methods to perform this test: the Wet-Chemical method, the Weighing method and the TD-NMR method. Throughout the Master Thesis, due to the high amount of errors associated with the Weighing method, only the Wet-Chemical method and TD-NMR were used.

Table 2 - D_{PU} textile specifications.

Textile	*Dtex*	Supplier	Lower Target Limit (%)	Target (%)	Upper Target Limit (%)
nAA PET	2200x2	A	1.5	2.5	3.5
nAA PET	1440x2	A	1.5	2.5	3.5
nAA PET	1440x2	B	1.5	2.5	3.5
nAA PET	1440x2	C	1.5	2.5	3.5
nAA PET	1840x2	D	1.0	2.0	3.0
nAA PET	3340x2	D	1.3	2.3	3.3
AA PET	3340x2	B	4.0	5.0	6.0

3.3.1 Wet-Chemical Method

The Wet-Chemical method is the official method to measure the dip pick-up content. The amount of D_{PU} on textile fibers, yarns and fabrics are determined by dissolving the textile fiber in a suitable solvent. The remaining dip is determined gravimetrically and is reported as % per weight, based on the greige fiber. To use this method, it is necessary to perform three main steps: sample preparation, dissolution of fiber and sample filtration. The steps of the Wet-Chemical method procedure can be seen in **Figure 11**. The following procedure is applied:

1. Cut the dipped material into pieces of a maximum of 5 mm length until the sample weight has 1 g, in the case of PET is necessary to cut pieces until 3 g is collected. Dry the sample for 1 h at 105 ºC in a drying oven, cool down the sample until room temperature in a desiccator. Weigh the sample into an Erlenmeyer flask, m_1 of Equation 1 is obtained.
2. Dissolve the sample with a suitable solvent for a defined amount of time, the solution with the fiber needs to be heated and is necessary to add a stirrer bar. In the case of working with PET textiles, it is necessary to connect the flask to a condenser. The solvent and time required to dissolve a PET fiber are shown in **Table 3**.
3. Weigh a dried crucible that is going to be needed in filtration, m_2 of Equation 1.
4. Filtrate the sample using a previously weighed crucible, a specific washing fluid and a pump system.
5. Dry the crucible in a drying oven for at least 2 hours at 105 ºC.

6. Cool down the crucible in a desiccator to room temperature. After that, weigh the crucible, corresponding to m_3 of Equation 1. The amount of D_{PU} is obtained by Equation 1.

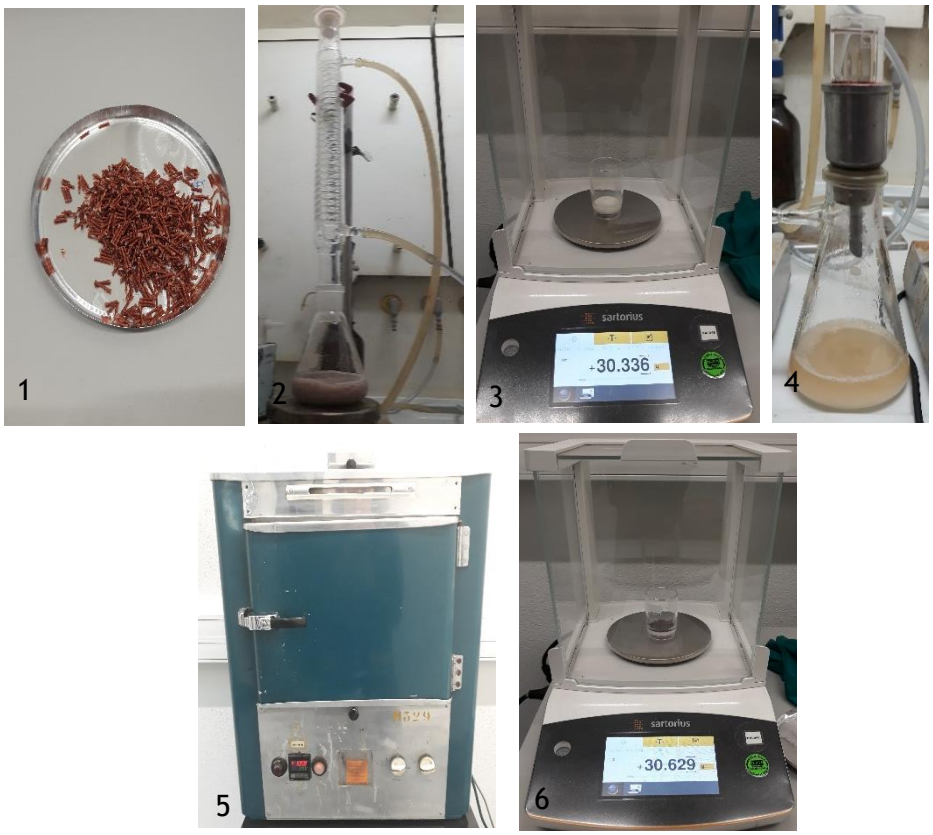

Figure 11 - Wet-Chemical method procedure.

Table 3 - Textile solvent and washing fluid.

Textile	Solvent	Dissolution time (h)	Washing Fluid
$PET_{3340,\ B}$	Potassium hydroxide solution 34 %	5	Deionized water

3.3.2 TD-NMR Method

TD-NMR is the method that provides better and faster results. However, it is necessary a previous calibration for each material. Currently, there are two methods to prepare samples, the traditional one and the new method of cutting. In the traditional method, the samples must be tied up in a bow form and should have no more than 2 cm of height. In the new method of cutting, the samples are cut in small pieces. While working with PET textiles, the new method of cutting samples was chosen due to its simplicity and practicability. The steps of the TD-NMR method procedure can be seen in **Figure 12**. The following procedure is applied:

1. Identify the samples tubes and weigh them with the lids on. Then, cut small pieces of the dipped cord until the samples obtained weight has 1 g each. Afterwards, introduce the samples in tubes and put the tubes, without the lids, in the drying oven for at least 1 hour at 105 ºC.
2. Put the lids in the tubes and cool down the tubes at room temperature. After, weigh the samples tubes again.
3. Put the samples tubes in a heating device support for at least 30 minutes at 40 ºC.
4. Measure the samples with the TD-NMR device three times each. The amount of D_{PU} is obtained by Equation 16.

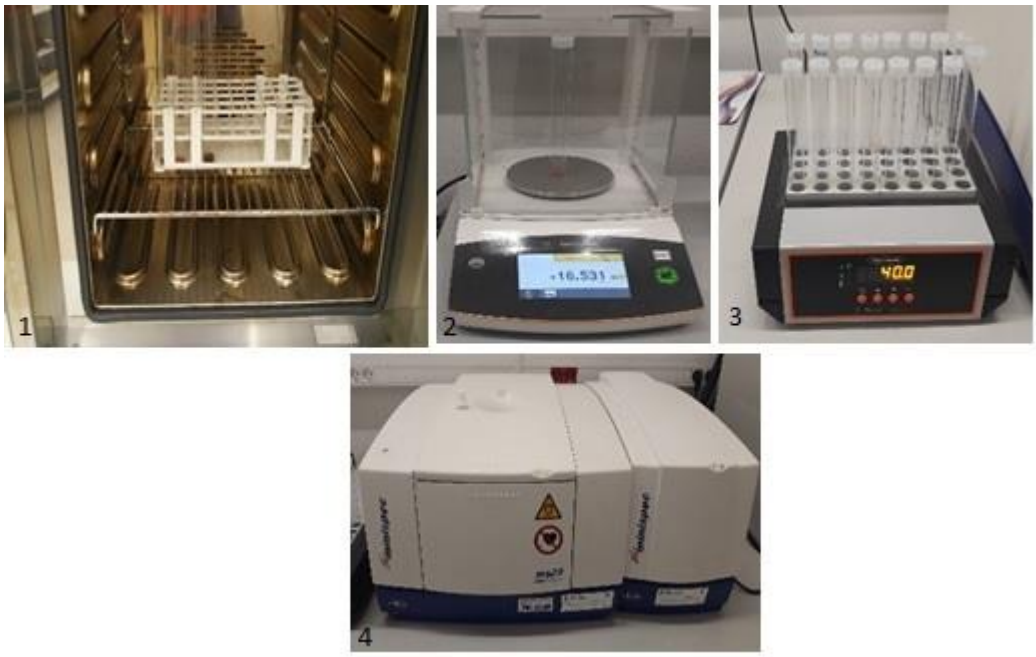

Figure 12 - TD-NMR method procedure.

3.4 Calibration Curve

To create a calibration curve for the TD-NMR equipment, it is necessary to have four cords with different amounts of D_{PU} (%). In order to have these different amounts of D_{PU}, the cords need to be dipped with a specific percentual amount of Solid Content. This process is a trial by error method until the required values of D_{PU} are achieved, which can be quite time-consuming.

The value of S_c (%) of the dip is monitored by the equipment present in **Figure 13**. Afterwards, the cords are dipped using the LDU machine. The D_{PU} values are measured by the Wet-Chemical method. At least three D_{PU} values with a standard deviation lower than 0.4 % are needed.

Figure 13 - Sc (%) measurement equipment.

According to Continental standards, the values of D_{PU} (%) used to create a calibration curve of PET textile should be distributed and within the following pre-established range:

Table 4 - Range of D_{PU} values for AA-PET textile.

Cord	D_{PU} value (%)				
	- 1 % LTL	LTL[1]	Target	UTL[2]	+ 1 % UTL
1	3.0 – 4.0				
2		4.0 – 5.0			
3			5.0 – 6.0		
4				6.0 - 7.0	

[1] LTL - Low Target Limit; [2] UTL- Upper Target Limit; LTL = 4.0 %; Target = 5.0 %; UTL = 6.0 %

With the values of D_{PU} present in the cords and knowing the mass of the sample, the calibration curve of TD-NMR equipment can be computed for the material under study. To validate a calibration curve, 30 samples from the production are required. The D_{PU} values obtained by the TD-NMR method are compared to the values obtained by Wet-Chemical method using *Minitab 18* software.

3.5 Differential Scanning Calorimetry (DSC)

At C-ITA, there are calibration curves for nylon and hybrid (made with one yarn of nylon and one yarn of aramid) materials. The dip recipe used to obtain dipped hybrid cords is the same as nylon. Despite that, it is not possible to measure the amount of D_{PU} present in hybrid using nylon's calibration curve. It has been proved before in past

Master Theses, that D_{PU} values obtained by the TD-NMR equipment seem to be only affected by the dip used and not by the type of textile.

In order to understand why the D_{PU} present in hybrid cords cannot be measured by nylon's calibration curve, DSC tests were conducted. Furthermore, to evaluate if there are thermal properties differences between the nAA PET and the AA PET textiles, DSC tests were also performed. The DSC tests were performed in the equipment DSC 214 Polyma (**Figure 14**). To do a DSC test, the following procedure is applied:

1. Before starting the analysis, the DSC equipment needs to stabilize for 30 minutes.
2. The initial conditions, such as temperature, desired gases and purge flow, are defined by the user.
3. While the DSC equipment stabilizes, an "empty" crucible is prepared and weighed, which is going to be the reference crucible. The sample is cut into little pieces to fit the crucible, the desired weight is between 5 and 10 mg. Then, the crucibles can be placed inside the DSC equipment.
4. A "Temperature Program" needs to establish. This program defines the temperatures, flows, desired gases, purge gases and heating rate (10 $K{\cdot}min^{-1}$) that we want to expose the sample. Usually, a fast pre-heat is done to remove humidity and contaminations that can be present in the sample. This pre-heat is followed by a cooling step. Then, the sample is heated until the desired temperature, followed by a cooling step and by an "isothermal" step to guarantee that the equipment and sample reach the desired temperature of cooling. Another heat step is prepared, with the intent to reach the initial point of decomposition of the material.
5. The analysis begins, and it is necessary to wait for about 2 hours to get the results. Then, to perform another test is necessary to wait for the equipment to cool down.

Figure 14 - DSC 214 Polyma device.

4 Results and discussion

The TD-NMR device measures the amount of dip pick-up per dipped cord, while the Wet-Chemical and Weighing method measure the amount of dip pick-up per greige cord. The D_{PU} is defined as the amount of dip pick-up per greige cord. Thereby, when the TD-NMR method is used, it is necessary to convert the value of D_{PU} from dipped cord to greige cord.

$$D_{\mathrm{PU\ per\ greige\ cord}} = \frac{m_{\mathrm{DIP}}}{m_{\mathrm{greige\ cord}}} \times 100 \tag{11}$$

$$D_{\mathrm{PU\ per\ dipped\ cord}} = \frac{m_{\mathrm{DIP}}}{m_{\mathrm{dipped\ cord}}} \times 100 \tag{12}$$

$$m_{\mathrm{greige\ cord}} = m_{\mathrm{dipped\ cord}} - m_{\mathrm{DIP}} \tag{13}$$

Combining the equations above:

$$m_{\mathrm{DIP}} = \frac{D_{\mathrm{PU\ per\ dipped\ cord}}}{100} \times m_{\mathrm{dipped\ cord}} \tag{14}$$

$$D_{\mathrm{PU\ per\ greige\ cord}} = \left(\frac{\frac{D_{\mathrm{PU\ per\ dipped\ cord}}}{100} \times m_{\mathrm{dipped\ cord}}}{m_{\mathrm{dipped\ cord}} \times (1 - \frac{D_{\mathrm{PU\ per\ dipped\ cord}}}{100})} \right) \times 100 \tag{15}$$

Simplifying Equation 15:

$$D_{\mathrm{PU\ per\ greige\ cord}} = \frac{D_{\mathrm{PU\ per\ dipped\ cord}}}{100 - D_{\mathrm{PU\ per\ dipped\ cord}}} \text{ x } 100 \tag{16}$$

Therefore, using Equation 16, it is possible to convert the TD-NMR results in D_{PU} per greige cord. All the values present in this project are already converted to the corrected values of dip pick-up per greige cord.

Throughout this Master Thesis, the results were analyzed and compared with the help of Minitab program, that provides statistical guidance to interpret and understand statistical tables and graphs in a practical way.

To simplify the terminology of the textiles studied in the Master Thesis, PET textiles will be named with the following abbreviation $\mathrm{PET}_{\mathrm{dtex,\ supplier}}$. The abbreviations used throughout the work are presented in **Table 5**.

Table 5 - Materials, *dtex*, supplier and respective abbreviation used throughout the writing.

Textile	*Dtex*	Supplier	Abbreviation
nAA PET	2200x2	A	$PET_{2200,\ A}$
nAA PET	1440x2	A	$PET_{1440,\ A}$
nAA PET	1440x2	B	$PET_{1440,\ B}$
nAA PET	1440x2	C	$PET_{1440,\ C}$
nAA PET	1840x2	D	$PET_{1840,\ D}$
nAA PET	3340x2	D	$PET_{3340,\ D}$
AA PET	3340x2	B	$PET_{3340,\ B}$

4.1 Non-activated PET (nAA PET)

In the past Master Thesis, a nAA PET calibration curve was created and validated. The PET textile used was $PET_{2200,\ A}$. Furthermore, the calibration curve was approved to measure the D_{PU} of $PET_{1440,\ A}$. The D_{PU} values for $PET_{2200,\ A}$ and $PET_{1440,\ A}$ are attached in **Table A.1** and **Table A.2**.

Additionally, in previous Master Thesis, a nAA PET textile with the same *dtex* of the textile used in the calibration curve but from a different supplier was tested ($PET_{1440,\ B}$). It was concluded that there was a statistically significant difference between the TD-NMR method and the Weighing method used in production. Therefore, the calibration curve was not validated to measure the D_{PU} amount of $PET_{1440,\ B}$. The D_{PU} values for $PET_{1440,\ B}$ are attached in **Table A.3.**

Only two of the four suppliers of nAA PET textiles were studied. In order to determine whether the calibration curve already created is suitable to measure the amount of D_{PU} for the suppliers that were not studied, samples from production were collected and tested in the TD-NMR device. The samples cannot have more than six months to be still valid. These samples were collected from Zell machine.

4.1.1 PET with *dtex* of 1440x2 of supplier C

To study $PET_{1440,\ C}$, 30 samples were collected from production and were measured in the TD-NMR equipment using the calibration curve already made for PET textiles. Each sample was measured in the TD-NMR method three times, in total, 90 measures were done. To verify the accuracy and viability of the results obtained by TD-NMR device, a comparison with production department values was made. The values of the production department are obtained by the Weighing method.

Throughout the thesis, the values obtained by the TD-NMR method will be named *TD-NMR* and the values obtained by the production department will be named *Production*.

In **Figure 15**, the x-axis corresponds to the sample number and y-axis is the D_{PU} value. The D_{PU} textile specifications are represented as lines. Through **Figure 15** is possible to see that the results from TD-NMR are close to the D_{PU} target and within the limits of the specification. The D_{PU} results obtained by the Weighing method have a slightly higher average, of 2.44 ± 0.27 %, while the average of D_{PU} results from TD-NMR is 2.40 ± 0.16 %. The D_{PU} values for $\mathrm{PET}_{1440,\,\mathrm{C}}$ measured by the Weighing method and TD-NMR are attached in **Table A.1.1**.

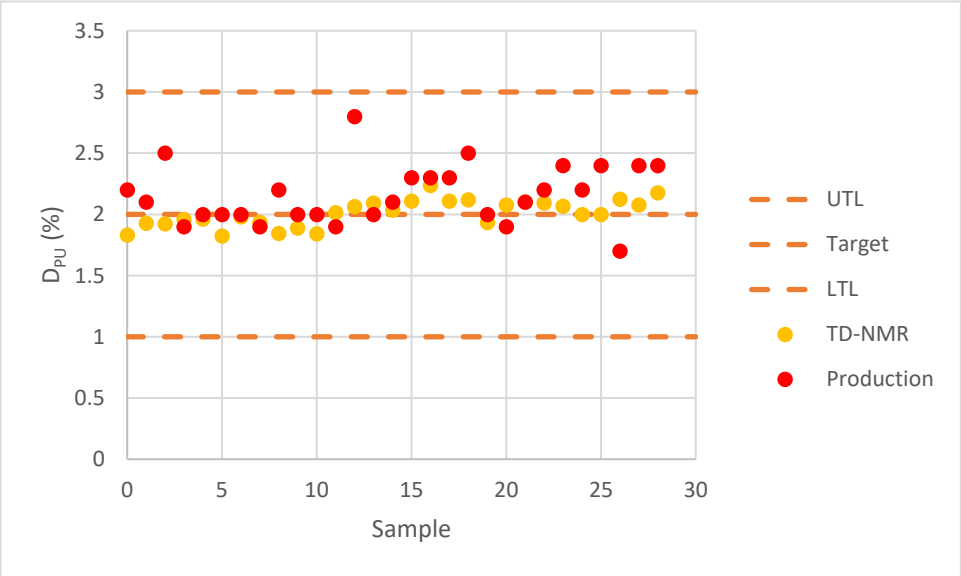

Figure 15 - Results obtained by the Weighing method and the TD-NMR method for $\mathrm{PET}_{1440,\,\mathrm{C}}$.

It is necessary to use statistical analyses to study the reliability and confidence of the results obtained. To check if the samples for each method follow a normal distribution, a normality test was made for each method. The result of the normality test indicates whether the null hypothesis should be rejected or accepted. In this case, the null hypothesis states that the population samples follow a normal distribution, the alternative hypothesis states the opposite. Both normality tests gave a result with a p-value higher than 0.05. Therefore, the null hypothesis is not rejected, and it can be concluded that both populations follow a normal distribution. The results of the normality test are attached in **Figure A.1.1** and **Figure A.1.2.**

Afterwards, a variance test was done, assuming that both populations follow a normal distribution. The two variances analysis test determines whether the variances or the standard deviations of two populations differ from each other. It also calculates a 95 % CI for the standard deviation of the populations. Additionally, this test calculates

a range of values that is likely to include the ratio of the populations' standard deviations. The values of the standard deviation and variance of the samples are represented in **Table 6**. In **Figure A.1.3**, it is possible to see the outcome of the variance test obtained by Minitab program. It is possible to affirm that the values measured by the TD-NMR method have a lower standard deviation and variance than the values measured by the Weighing method (Production). These results were expected since TD-NMR is a more accurate method.

Table 6 - Variance test results for populations of $PET_{1440,\,C}$.

Variable	*StDev* (%)	Variance	95 % CI for σ	Estimated Ratio of StDev	95 % CI for Ratio using F
TD-NMR	0.162	0.0260	(0.129; 0.217)	0.594	(0.410; 0.861)
Production	0.272	0.0740	(0.217; 0.366)		

In a variance test, the null hypothesis states that the ratio between the standard deviations of the populations is equal to 1, the alternative hypothesis states that this ratio is different from 1. As can be seen in **Table 6,** the CI of the standard deviation ratio does not include the value 1, and the p-value is 0.006. Since the p-value is less than 0.05, the null hypothesis is rejected, which means that these populations do not have equal variances.

Assuming different population variances, a 2-sample t-test was made. The 2-sample t-test evaluates if the populations' means are significantly different. In **Figure A.1.4,** it is possible to see boxplot representation of the D_{PU} values with the samples mean for both samples. The null hypothesis states that the means do not differ from each other. The results of this test can be seen in **Table 7**. The test was made with a significance level of 5 % and the p-value obtained is 0.499. Therefore, the null hypothesis is not rejected. The means of the two methods are not different. Therefore, the amount of D_{PU} of $PET_{1440,\,C}$ can be measured by the TD-NMR method.

Table 7 - Results of 2-sample t-test for $PET_{1440,\,C}$.

Variable	Mean (%)	Difference (%)	95 % CI for Difference	p-value
TD-NMR	2.401	-0.03950	(-0.1558; 0.07690)	0.499
Production	2.440			

4.1.2 PET with *dtex* 1840x2 of supplier D

To study $PET_{1840,\ D}$, 29 samples were collected from production and were measured in the TD-NMR equipment using the calibration curve already made for PET textiles ($PET_{2200,\ A}$).

The D_{PU} values are represented in **Figure 16.** The results from TD-NMR are close to the desired target. The D_{PU} results obtained by the Weighing method have a higher average, of 2.16 ± 0.24 %, than the values obtained by the TD-NMR method, which are 2.01 ± 0.11 %. The D_{PU} values for $PET_{1840,\ D}$ measured by TD-NMR and by the production department, are attached in **Table A.1.2.**

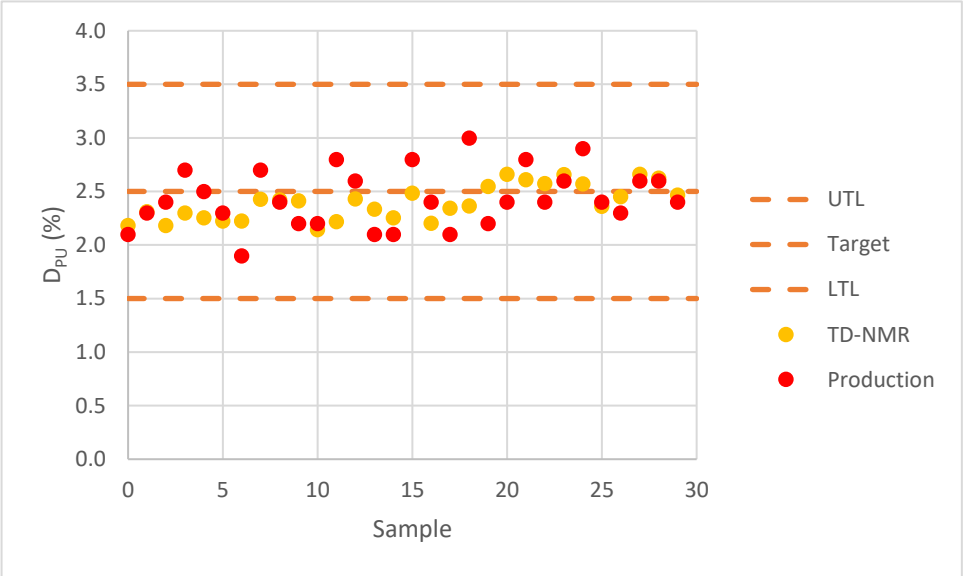

Figure 16 - Results obtained by the Weighing method and the TD-NMR method for $PET_{1840,\ D}$.

Using the same approach made for $PET_{1440,\ C}$, a normality test was done for both populations. The results show that the D_{PU} values of Production and TD-NMR follow a normal distribution since the p-value for both populations is higher than 0.05. The results of the normality test are attached in **Figure A.1.5** and **Figure A.1.6.**

Assuming a normal distribution for both populations, a variance test was made. The values of the standard deviation, variance and ratio of the standard deviations of the samples are represented in **Table 8**. The TD-NMR results have a lower standard deviation and variance than the Production results. In **Figure A.1.7**, it is possible to see the outcome of the variance test obtained by Minitab program. The variance test shows that the CI for the ratio of the standard deviations does not include the value 1. Additionally, the p-value of the test is less than 0.05. In this case, the null hypothesis is rejected. Therefore, the populations do not have equal variances.

Table 8 - Variance test results for populations of $PET_{1840,\ D}$.

Variable	StDev (%)	Variance	95 % CI for σ	Estimated Ratio of StDev	95 % CI for Ratio using F
TD-NMR	0.108	0.0120	(0.086; 0.146)	0.452	(0.310; 0.659)
Production	0.240	0.0570	(0.190; 0.324)		

Afterwards, a 2-sample t-test was made, assuming a different variance for the populations. The p-value obtained was 0.004. Therefore, the means of the two methods are different. Boxplot representation of the D_{PU} values with the samples mean for both methods can be seen in **Figure A.1.8.** The results are presented in **Table 9**. The means of the populations have an approximate difference of 0.15 ± 0.10 %. The means differ in a statistical point of view, but practically the difference is at most of 0.25 % which is less than 1 %, the Continental standard. Thus, the D_{PU} present in $PET_{1840,\ D}$ textile can be measured by the TD-NMR method.

Table 9 - Results of 2-sample t-test for $PET_{1840,\ D}$.

Variable	Mean (%)	Difference (%)	95 % CI for Difference	Margin of error (%)	p-value
TD-NMR	2.012	-0.1497	(-0.2485; -0.05080)	0.09885	0.004
Production	2.162				

4.1.3 PET with *dtex* 3340x2 of supplier D

To check if the calibration curve already made for PET textile ($PET_{2200,\ A}$) is suitable to measure the D_{PU} of the $PET_{3340,\ D}$ textile, 16 samples were collected and tested in TD-NMR device. It was only possible to collect 16 samples since this material is not produced often at C-ITA.

The TD-NMR and production results are represented in **Figure 17.** The D_{PU} values measured by the D-NMR method are close to the target and within the specifications for this textile. The TD-NMR results, 2.21 ± 0.15 %, are closer to the desired target, than the production results, 2.03 ± 0.15 %. The D_{PU} results measured by both methods are attached in **Table A.1.3.**

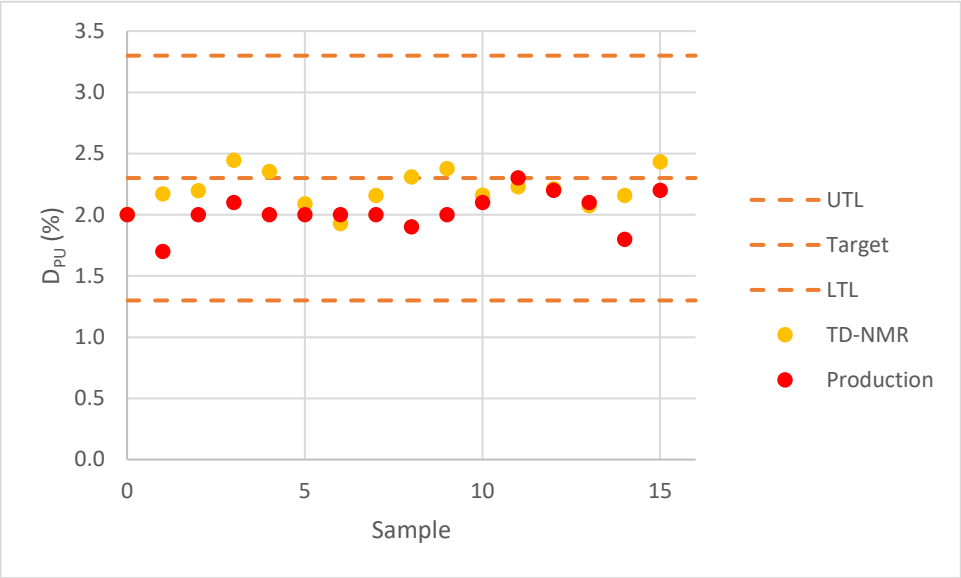

Figure 17 - Results obtained by the Weighing method and the TD-NMR method for $PET_{3340,\ D}$.

Applying the same approach made for $PET_{1440,\ C}$ and $PET_{1840,\ D}$ textiles, a normality test was made for both populations. The results of the statistical test are attached in **Figure A.1.9** and **Figure A.1.10.** The results show that for both populations, the D_{PU} values follow a normal distribution since the p-value for both populations is greater than 0.05.

Assuming for both populations a normal distribution, a variance test was made. In **Table 10**, it is possible to see the values of the standard deviation, variance and ratio of the standard deviations of the samples. In **Figure A.1.11**, it is possible to see the outcome of the variance test obtained by Minitab program. The variance test shows that the CI for the ratio of the standard deviations includes value 1. Moreover, the p-value obtained is 0.992, which is higher than the significance level of 0.05. The null hypothesis is not rejected, and it is possible to conclude that the variances of the populations do not differ significantly.

Table 10 - Variance test results for populations of $PET_{3340,\ D}$.

Variable	StDev (%)	Variance	95 % CI for σ	Estimated Ratio of StDev	95 % CI for Ratio using F
TD-NMR	0.148	0.0220	(0.109; 0.229)	0.997	(0.590; 1.687)
Production	0.148	0.0220	(0.110; 0.230)		

Assuming an equal variance for the populations, 2-sample t-test was made. Boxplot representation of the D_{PU} values with the samples mean for both samples can be seen in **Figure A.1.12**. The results of the 2-sample t-test are represented in **Table**

11. The p-value is less than 0.05 and the means have a difference of 0.18 ± 0.11 %. In a statistical point of view, the means are different. However, in a practical way, this difference is not significant. Additionally, the difference is lower than 1 %, which is the Continental standard. Therefore, the amount of D_{PU} in $PET_{3340,\ D}$ textile can be measured by the TD-NMR method.

Table 11 - Results of 2-sample t-test for $PET_{3340,\ D}$.

Variable	Mean (%)	Difference (%)	95 % CI for Difference	Margin of error (%)	p-value
TD-NMR	2.206	0.181	(0.074; 0.288)	0.107	0.002
Production	2.025				

Since, it was only possible to collect 16 samples for $PET_{3340,\ D}$ textile, a power curve test was made using Minitab software, with the intent to check if sample size would be able to guarantee a trustworthy result. A power curve test ensures if a 2-sample t-test has an adequate sample size to achieve acceptable power. The test was made assuming a maximum difference of 0.005 (0.5 %) between the population's means and a maximum standard deviation of 0.004 (0.4 %). A power value of 0.9 is, most of the times, an adequate result. The results can be seen in **Figure 18Erro! A origem da referência não foi encontrada.** and **Table 12**. When the sample size has 16 observations the power obtained is 0.928, i.e., in 92.8 % of the time the test can detect

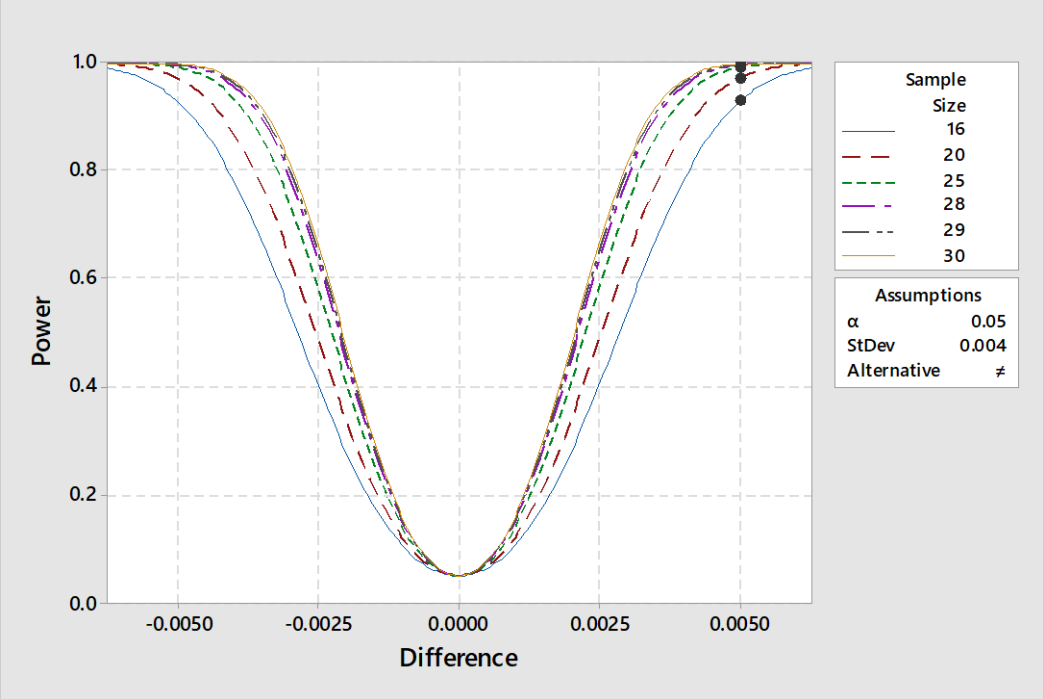

Figure 18 - Power curve test.

a true difference of 0.5 % between D_{PU} means (Minitab support), which provides high confidence in the results obtained for $PET_{3340,\ D}$ textile.

Table 12 - Power curve test results.

Sample Size	Power
16	0.928
20	0.971
25	0.991
28	0.996
29	0.997
30	0.997

4.2 Activated PET Calibration Curve (AA PET)

The cords used for the calibration curve, were of an AA PET textile with a *dtex* of 3340x2 and a supplier B. This textile will be named $PET_{3340,\ B}$. To do a calibration curve by the Wet-Chemical method, four cords with different amounts of D_{PU} are necessary. It was proved before in Master Theses, that the calibration curve done using the Wet-Chemical method is more accurate and has a better coefficient of determination (R^2), than the calibration curve obtained by the Weighing method. Thus, the Wet-Chemical method was chosen to measure the amount of D_{PU} present in each cord. The reference range for the D_{PU} values necessary for each point of the calibration curve for $PET_{3340,\ B}$ is presented in **Table 4**. A different amount of D_{PU} is obtained varying the amount of Solid Content present in the dip recipe. The cords were dipped in LDU machine.

Each point of the calibration curve needs three D_{PU} values with a standard deviation of less than 0.4 %, which is a Continental standard. Therefore, it is necessary to perform multiple attempts until the *StDev* is lower than 0.4 %. The final D_{PU} value of each point is the average of the three values obtained. The results of the D_{PU} measurement using the Wet-Chemical method are represented in **Table 13**.

Table 13 - D_{PU} results via Wet-Chemical method for PET cords.

Cord	Solid Content (%)	D_{PU} (%)	Average D_{PU} (%)	StDev (%)
1	10.11	3.63 3.23 3.68	3.51	0.25
2	12.20	4.13 3.88 3.98	4.00	0.13
3	13.42	4.93 5.06 5.13	5.04	0.10
4	17.51	5.71 5.97 6.39	6.02	0.34

Afterwards, with the D_{PU} values of each point and with the mass of each sample, the calibration curve can be computed for the TD-NMR device, as it can be seen in **Figure 19.**

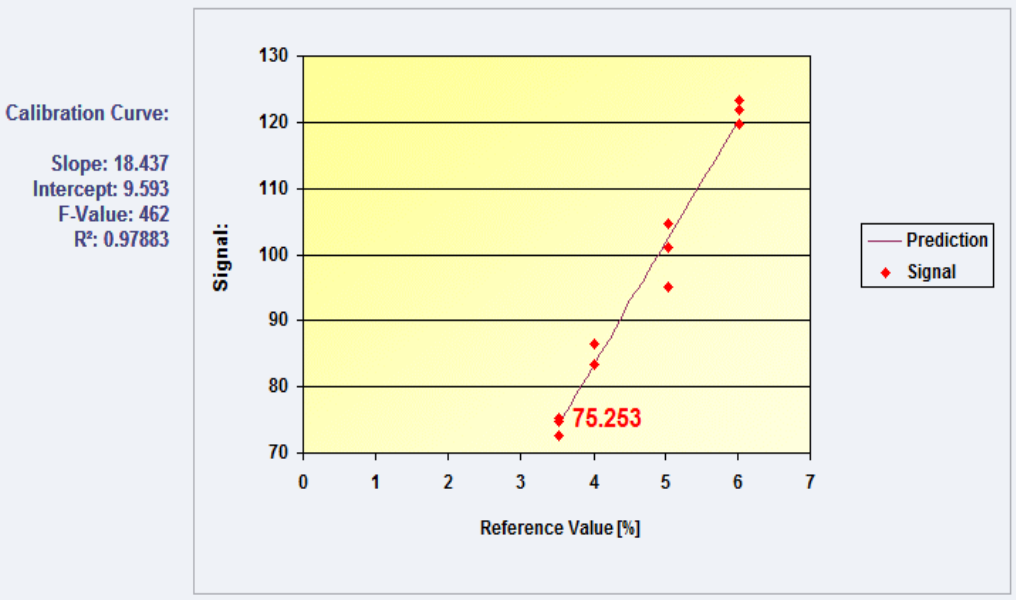

Figure 19 - Calibration curve for $PET_{3340,\ B}$ in the TD NMR device software "minispec Plus 6.0.3".

A further analysis of the residual values of the calibration curve created was done and it can be seen in **Figure 20.** The residuals are the difference between the observed values and the fitted response values. A residual plot helps to determinate whether the model is adequate and meets the assumptions of the analysis. The model assumptions made were normality data, equal variance and independence of the random errors. If these assumptions are satisfied in the statistical analysis, then it is possible to conclude that the ordinary least squares regression will produce unbiased estimations with minimum variance. In the normality plot, the residual plot does not indicate significant deviations for the normality assumption, as the residuals appear to form a straight line. The residual versus fitted value shows a random pattern of residuals on both sides of 0, it appears to be in accordance with the equal variance assumption. Moreover, the residual versus order plot shows that the residuals fluctuate in a random pattern around the center line, therefore, it can be concluded that the values appear to be independent.

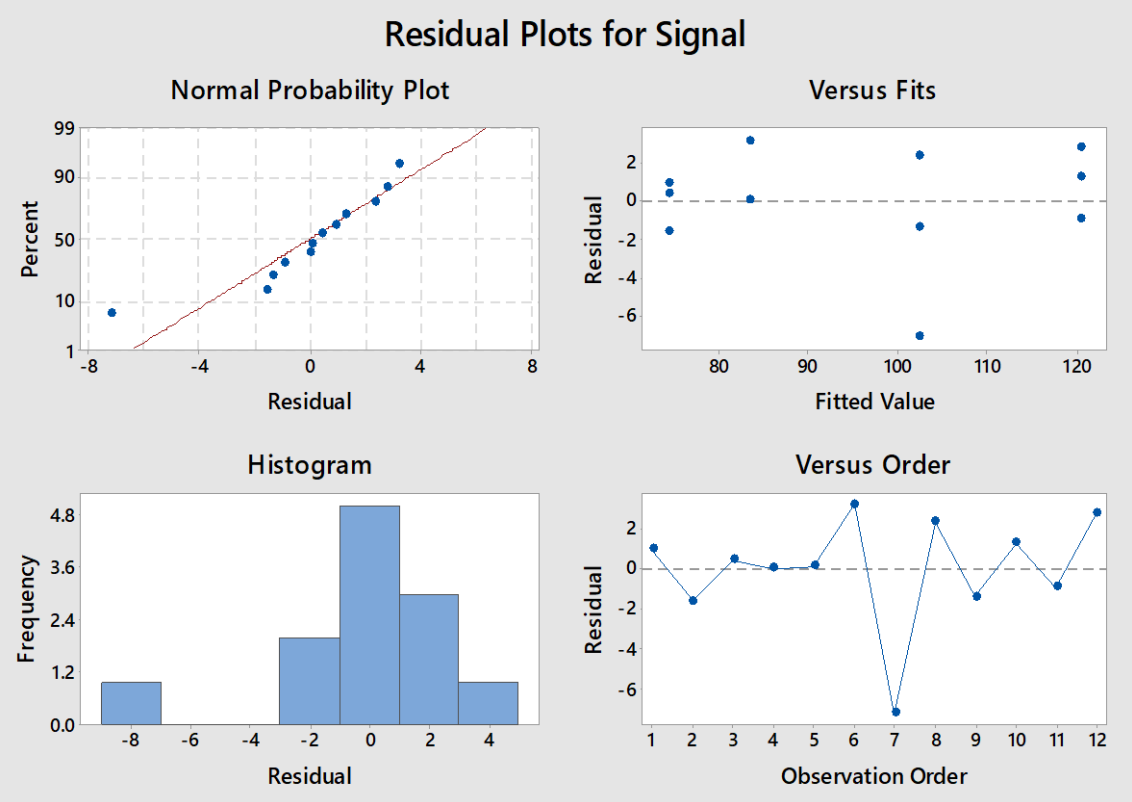

Figure 20 - Residual Plots for calibration curve created.

To check if the linear regression model is a good fit for the data of the calibration curve (**Figure A.2.1**), further analysis was done. The value S obtained, 2.88, is a measured in the units of the response variable (in this case, the signal measured by TD-NMR device) and represents how far the data values fall from the

fitted values. The lower the value of S, the better the model describes the response. Additionally, both R-squared, 97.9 %, and adjusted R-squared, 97.7 %, have close values. It can be said that 97.9 % of the variation verified of the D_{PU} values can be explained through the model. Therefore, the linear regression model appears to provide a good fit.

The calibration curve seems to be suitable since the coefficient of determination (R^2) is higher than 0.900, which is the Continental standard. Although, it is necessary to verify if the calibration curve can measure the amount of D_{PU} of production samples. To do so, 30 samples from production were collected and measured using the new calibration curve. The results obtained by TD-NMR method were compared to the values obtained by the production department, which are measured by the Weighing method.

Seeing the **Figure 21**, it is possible to see that the TD-NMR results are within the specification, with the exception of two values. Thus, for the statistical analyzes, these two points were not considered. With a sample size of 28, the power of the t-test is 0.996 (**Table 12**), which assures high confidence in the results obtained for $PET_{3340,\,B}$ textile. The results obtained by the TD-NMR have a lower average, of 5.42 ± 0.29 %, while the results obtained by the production department have an average of 5.48 ± 0.25 %. The D_{PU} results measured by both methods are attached in **Table A.2.1.**

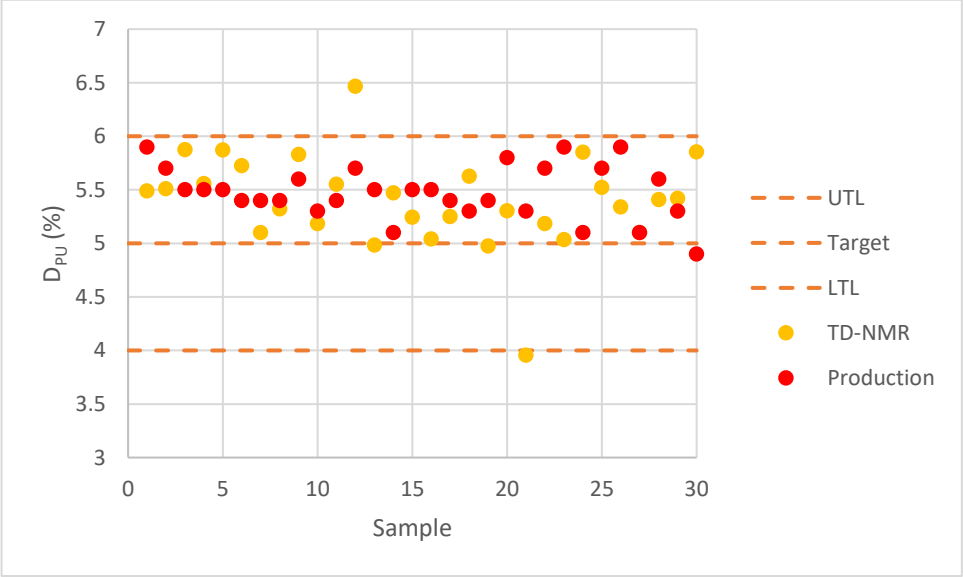

Figure 21 - Results obtained by the Weighing method and the TD-NMR method for $PET_{3340,\,B}$.

Initially, to verify if the samples for each method follow a normal distribution, a normality test was done, the results can be observed in **Figure A.2.2** and **Figure A.2.3.** The results for both methods have a p-value greater than 0.05, which means that the samples for each method follow a normal distribution.

Assuming a normal distribution for each method, a variance test was done. The results can be seen in **Table 14** and **Figure A.2.4**. It is possible to conclude that the variances of the populations do not differ significantly since the p-value obtained is 0.490.

Table 14 - Variance test results for populations of $PET_{3340,\,B}$.

Variable	StDev (%)	Variance	95 % CI for σ	Estimated Ratio of StDev	95 % CI for Ratio using F
TD-NMR	0.288	0.0830	(0.228; 0.392)	1.144	(0.778; 1.681)
Production	0.252	0.0630	(0.199; 0.343)		

Afterwards, assuming equal variance for both populations and with the intent to verify if the means of the methods differ from each other, a two-sample t-test was performed (**Table 15**). The test was done with a significance level of 5 %, the p-value obtained was 0.413. Since the p-value is greater than 0.05, the null hypothesis is not rejected, and it is possible to conclude that the means of the methods are not different. Therefore, the amount of D_{PU} in $PET_{3340,\,B}$ textile can be measured using the new calibration curve.

Table 15 - Results of 2-sample t-test for $PET_{3440,\,B}$.

Variable	Mean (%)	Difference (%)	95 % CI for Difference	p-value
TD-NMR	5.415	-0.0596	(-0.2046; 0.0853)	0.413
Production	5.475			

4.3 DSC tests

The operation conditions of the DSC tests are an initial temperature of 20.0 ºC, a heating rate of 10 $K{\cdot}min^{-1}$ and the purge gas is nitrogen with a flow of 40 $ml{\cdot}min^{-1}$. The sample was heated until the desired temperature, followed by a cooling step and by an "isothermal" step. Additionally, another heat step was done to reach the initial point of decomposition of the material.

4.3.1 Hybrid and Nylon

To verify the different thermal properties between hybrid and nylon materials and to better understand why the D_{PU} present in hybrid cords cannot be measured by nylon's calibration curve, DSC tests were performed. The sample weight used was 6.9 mg for hybrid and 7.7 mg for nylon. The maximum temperature reached was 480 ºC for hybrid and 350 ºC for nylon. The results obtained can be seen in **Figure 22.**

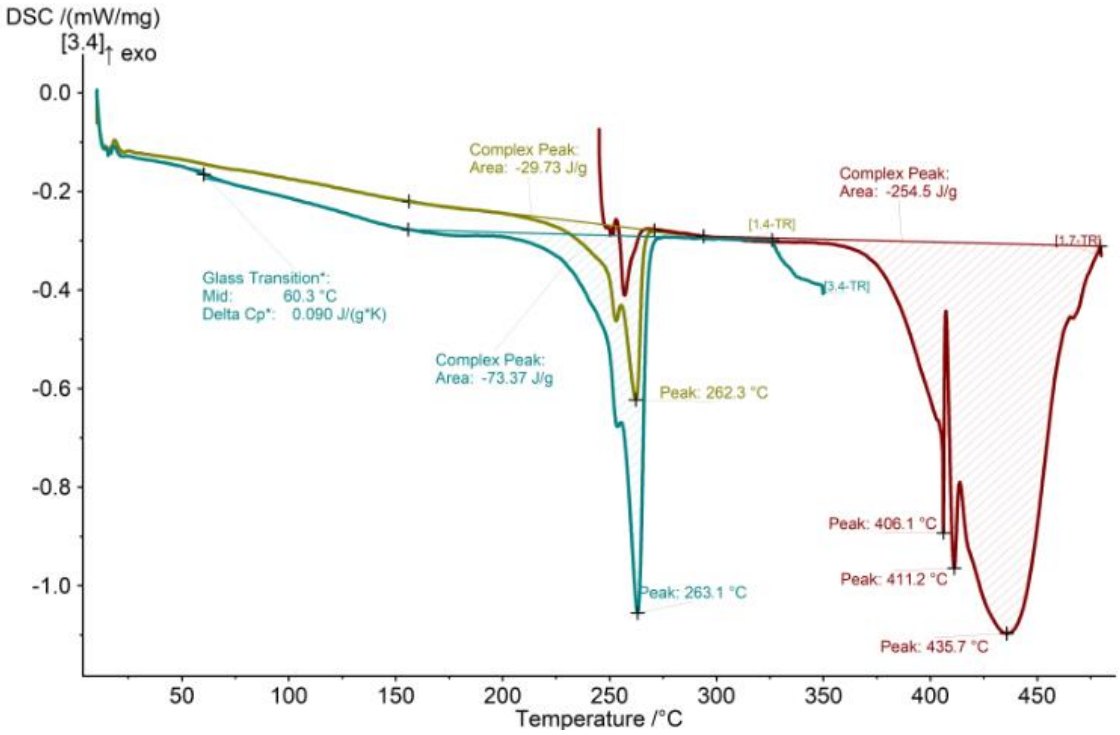

Figure 22 - DSC scan of Hybrid and Nylon.

For nylon textile (represented in blue in **Figure 22**), the glass transition occurs around 60.3 ºC, this transition is followed by an endothermic peak due to melting, which occurs around 263.1 ºC. Around 325 ºC, the heat flow begins to decrease, which means that the decomposition of nylon started. Hybrid textile (represented in green and red in **Figure 22**), is a combination of one yarn of nylon and one yarn of aramid. There is an endothermic peak at 262.3 ºC due to the melting of nylon. As seen in **Figure 22**, hybrid textile preserves the thermal properties of nylon, since the melting temperature (T_m) does not have significant differences when compared to the melting temperature of nylon's data. The peak area of melting transition is different because the nylon sample has more content of nylon than the sample of hybrid. In nylon's sample, the nylon crystallinity obtained using Equation 10 is 40 %, and in hybrid's sample, it was 16 %. It is possible, to conclude that the fibers have significantly different crystallinity, therefore fibers present different thermal properties.

After 325 ºC, the data is not conclusive (represented in red in **Figure 22**). The decomposition of nylon begins at 325 ºC, thus the peak around 325 ºC can be due to the decomposition of nylon and not because of the glass transition of the aramid. After this temperature is difficult to see the thermal transitions of aramid since there are too many phenomena happening simultaneously. To correctly visualize the thermal transitions of aramid, only the aramid should be tested and not the hybrid material. Also, it would be necessary to reach a higher temperature to see the beginning of aramid decomposition.

As mentioned before, the TD-NMR method measures the amount of dip through the difference between the signal of the fiber and the dip (**Figure 8**). The dip recipe used to impregnate hybrid textile is the same as nylon. Therefore, the dip signal obtained by TD-NMR device is the same for both textiles. If the fiber signal is significantly different, then the difference between the fiber and dip signals is also going to be significantly different. As seen is DSC test, hybrid and nylon fibers appear to have different thermal properties since the crystallinities obtained for nylon are significantly different. These differences seem to be significant while measuring the amount of D_{PU} by the TD-NMR method. This explains why it is not possible to perform a correct measure of the amount of D_{PU} in hybrid textile using nylon's calibration curve. The calibration curves of hybrid and nylon are presented in **Figure A.3.1** and **Figure A.3.2.**, respectively. In this case, the TD-NMR method is affected significantly by the dip used and by the fiber itself. In this case, the type of textile appears to affect the measure by the TD-NMR device.

4.3.2 PET

To verify if non-activated and activated PET have different thermal properties, a DSC was done. The sample weight used was 10.0 mg for nAA PET and 9.0 mg for AA PET. The samples used are from the same supplier (supplier B). The maximum temperature reached was 350 ºC. The results obtained can be seen in **Figure 23.**

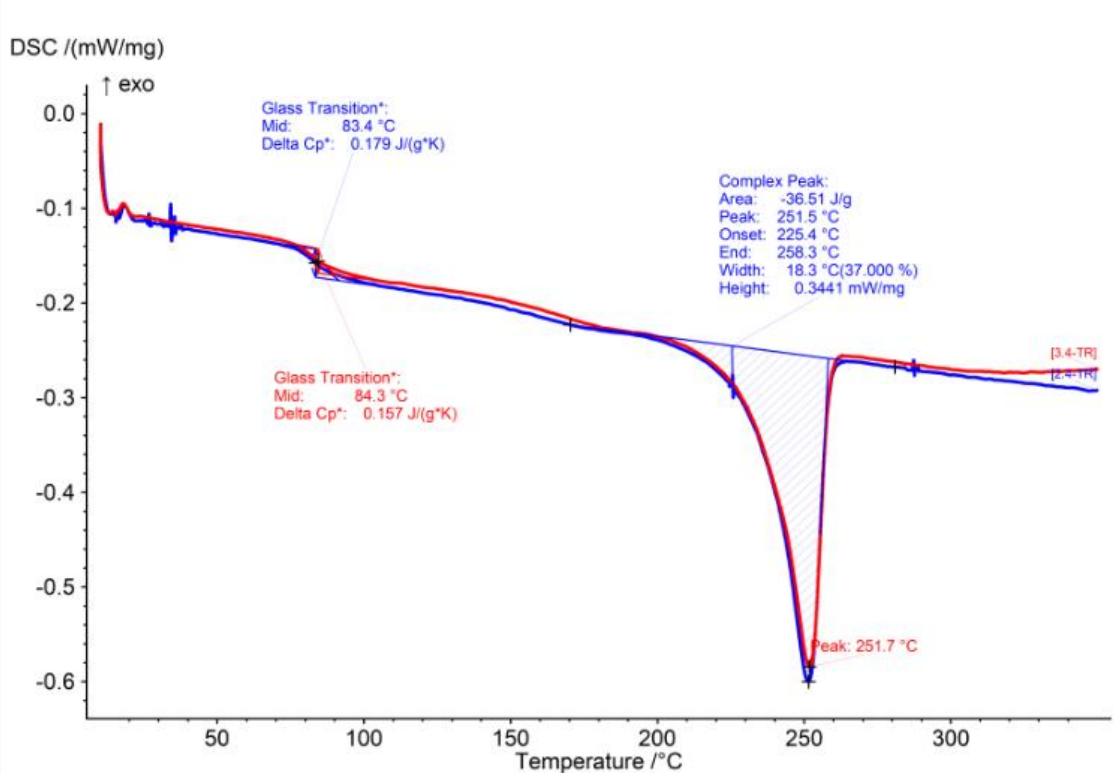

Figure 23 - DSC scan of non-activated and activated PET.

For the nAA PET textile (represented in blue on **Figure 23**), the glass transition occurs around 83.4 ºC, this transition is followed by an endothermic peak due to melting, which occurs around 251.5 ºC. For the AA PET textile (represented in red in **Figure 23**), the glass transition happens at 84.3 ºC and the endothermic melting event happens at 251.7 ºC.

The delta C_p of both materials is low, probably this happens because the interval temperatures of glass transition are too wide, which complicates the delta C_p estimation. It is possible to conclude that both PET materials do not seem to have different thermal properties. So, the different treatments that the fibers suffer (being non-activated and activated) do not affect the transition temperatures. Regarding thermal properties, the fibers do not appear to have differences between them, which, is also reflected in the calibration curve of nAA PET (**Figure 9**) and AA PET (**Figure 19**) since the curves have a similar slope and intercept, despite the calibration curves having a different range of D_{PU} values.

5. Conclusion

The purpose of this Master Thesis is to continue the implementation of TD-NMR method quality control, in order to measure the amount of dip pick-up of PET textiles at C-ITA.

In the first part of the project, three nAA PET textiles were studied. It was proved that the means of the two methods, the TD-NMR method and the Weighing method, are not significantly different and the difference of the means meets the Continental standard limit of 1 %. Therefore, the calibration curve already done in previous Master Thesis was validated to measure more three nAA PET textiles, for different suppliers and *dtex*.

For the second part of the project, a calibration curve was done for an AA PET textile with *dtex* of 3340x2 of supplier B. In order to obtain the D_{PU} values of each cord, the Wet-Chemical was the method used. Afterwards, to validate the calibration curve, 30 samples from production, were collected and measured by the calibration curve created in the TD-NMR device. Then, the measurements obtained by the TD-NMR method were compared to the measurements obtained by the production department, that uses the Weighing method. It was not verified significant differences between the two methods and the values obtained by the TD-NMR meet Continental requirements of 1 %. A calibration curve for AA PET textile was made and validated for this textile.

Lastly, to better understand why the amount of D_{PU} in hybrid cords cannot be measured by nylon's calibration curve, DSC tests were done. It is possible to conclude that hybrid and nylon fibers have significantly different thermal characteristics. In the TD-NMR method, the amount of D_{PU} is obtained by the difference of the dip signal and the fiber signal. The dip used is the same so the dip signal is equal in both materials. Despite that, it is not possible to measure the D_{PU} present in hybrid cords using nylon's calibration curve. In this case, the signal of the fiber itself appears to affect the measure done by TD-NMR method. Additionally, nAA PET and AA PET textiles were also studied by DSC test. Regarding thermal properties, these textiles do not appear to have differences between them.

This project allows C-ITA to have one calibration curve for nAA PET and one for AA PET textiles. This way, the TD-NMR method implementation is expanded, and consequently, quality control is improved.

6. Assessment of the work done

6.1 Objectives Achieved

Since there is already a calibration curve for non-activated PET textiles, the main goal was to calibrate the TD-NMR device for an activated PET material. This is going to allow C-ITA to measure the amount of $\mathrm{D_{PU}}$ of almost all the PET textiles in a faster and more accurate manner using the TD-NMR method. Additionally, one of the aims was also to understand better why the amount of D_{PU} in hybrid cords cannot be measured by nylon's calibration curve.

The previous calibration curve done for nAA PET textile was validated to measure more three nAA PET textiles. A calibration curve for AA PET textile was made and validated. Also, it was verified that the signal of the fiber itself in TD-NMR method appears to affect the D_{PU} measure when it comes to hybrid and nylon fibers.

6.2 Limitations and Future Work

Regarding limitations, the main difficulty was, without a doubt, the time available. To do a calibration curve, it is necessary to use the Wet-Chemical method. This method is a method by trial and error approach, which requires weeks to accomplish and several attempts are needed to have a standard deviation lower than 0.4 % for each point of the curve. Also, the activated PET used to do the calibration curve was difficult to dissolve and each attempt took much time due to the high *dtex* of the textile. Additionally, while working with PET using the Wet-Chemical method, it was only possible to perform one essay a day.

Moreover, the lab and all the equipment need to be shared with all the co-workers and interns, which can delay the work. Additionally, a new chemical lab is being built, which made it impossible to perform chemical tests for a week.

For future work, validation of the new PET calibration curve for other suppliers and *dtex* will be necessary. However, currently, it is not possible, since C-ITA is not producing other activated PET textiles. C-ITA is developing dip recipes, for them to become more environmentally friendly. If it is proved that these new dip recipes show good adhesion properties, new calibration curves are going to be needed to measure the amount of D_{PU} . Furthermore, C-ITA has now a new chemical laboratory. For future work, C-ITA is going to try to get approval to do dip pick-up measurement by Wet-

Chemical method for standard hybrid and for aramid materials. Moreover, further DSC tests should be done to study the behavior and effect of fibers in TD-NMR measurement.

6.3 Final Assessment

I am forever grateful to C-ITA for this incredible and learning experience. I am proud of the work that I developed. It was not always straightforward, however, with the help and good ambiance provided by my co-workers, everything became easier to overcome. I hope that the work developed can contribute to improve C-ITA quality control.

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Annex A

Table A.1 - D_{PU} results for $PET_{2200,\ A}$ textile (Bezerra, 2018).

Sample	D_{PU} (%) TD-NMR	D_{PU} (%) Production
1	2.55	2.60
2	2.82	2.00
3	2.71	3.10
4	2.83	3.00
5	2.54	2.90
6	2.62	1.50
7	2.71	2.10
8	2.57	2.70
9	2.44	2.80
10	2.63	2.90
11	2.74	2.80
12	2.63	2.90
13	2.51	3.00
14	2.42	2.80
15	2.87	2.70
16	2.57	3.20
17	2.64	3.30
18	2.75	3.30
19	2.79	2.10
20	2.72	2.00
21	2.52	2.90
22	2.44	3.30
23	2.79	3.00
24	2.80	3.10
25	2.75	3.30
26	2.66	2.70
27	2.53	2.90
28	2.71	2.80
29	2.41	2.90
30	2.37	2.70

Table A.2 - D_{PU} results measured by TD-NMR and Production values for $PET_{1440, A}$ textile (Bezerra, 2018).

Sample	D_{PU} (%) TD-NMR	D_{PU} (%) Production
1	2.22	2.50
2	2.04	2.10
3	1.60	2.60
4	2.14	2.40
5	2.11	2.30
6	1.98	2.70
7	2.19	2.50
8	2.01	2.30
9	2.12	2.30
10	2.13	2.50
11	1.96	2.70
12	2.09	2.50
13	2.05	2.20
14	2.03	2.10
15	2.21	2.50
16	2.00	2.20
17	1.93	1.80
18	1.95	2.00
19	2.05	1.90
20	2.14	1.80
21	2.18	1.90
22	1.93	2.50
23	2.14	2.40
24	2.24	2.40
25	2.04	2.40
26	2.08	2.40
27	2.02	2.50
28	2.09	2.40
29	2.01	2.60
30	2.14	2.30

Table A.3 - D_{PU} results measured by TD-NMR and Production values for $PET_{1440, B}$ textile (Bezerra, 2018).

Sample	D_{PU} (%) TD-NMR	D_{PU} (%) Production
1	1.99	2.30
2	2.08	2.20
3	1.44	2.30
4	1.53	2.40
5	1.33	2.50
6	1.40	2.50
7	1.25	2.10
8	1.34	2.20
9	1.26	2.00
10	1.30	2.20
11	1.32	2.40
12	1.44	2.80
13	1.54	2.30
14	1.40	2.30
15	1.21	2.10
16	1.29	2.00
17	1.25	2.40
18	1.36	2.20
19	1.76	2.30
20	1.45	2.00
21	1.39	2.10
22	1.29	2.10
23	1.46	2.30
24	1.24	2.30
25	1.57	2.30
26	1.43	2.30
27	1.34	2.50
28	1.40	2.20
29	1.56	2.20
30	1.33	2.40

Appendix A

A.1

Table A.1.1 - D_{PU} results measured by TD-NMR and Production values for $PET_{1440, c}$ textile.

Sample	D_{PU} (%) TD-NMR	D_{PU} (%) Production
1	2.18	2.10
2	2.31	2.30
3	2.18	2.40
4	2.30	2.70
5	2.26	2.50
6	2.23	2.30
7	2.23	1.90
8	2.43	2.70
9	2.42	2.40
10	2.41	2.20
11	2.14	2.20
12	2.22	2.80
13	2.43	2.60
14	2.34	2.10
15	2.26	2.10
16	2.48	2.80
17	2.20	2.40
18	2.35	2.10
19	2.37	3.00
20	2.55	2.20
21	2.66	2.40
22	2.61	2.80
23	2.58	2.40
24	2.66	2.60
25	2.57	2.90
26	2.36	2.40
27	2.45	2.30
28	2.66	2.60
29	2.63	2.60
30	2.47	2.40

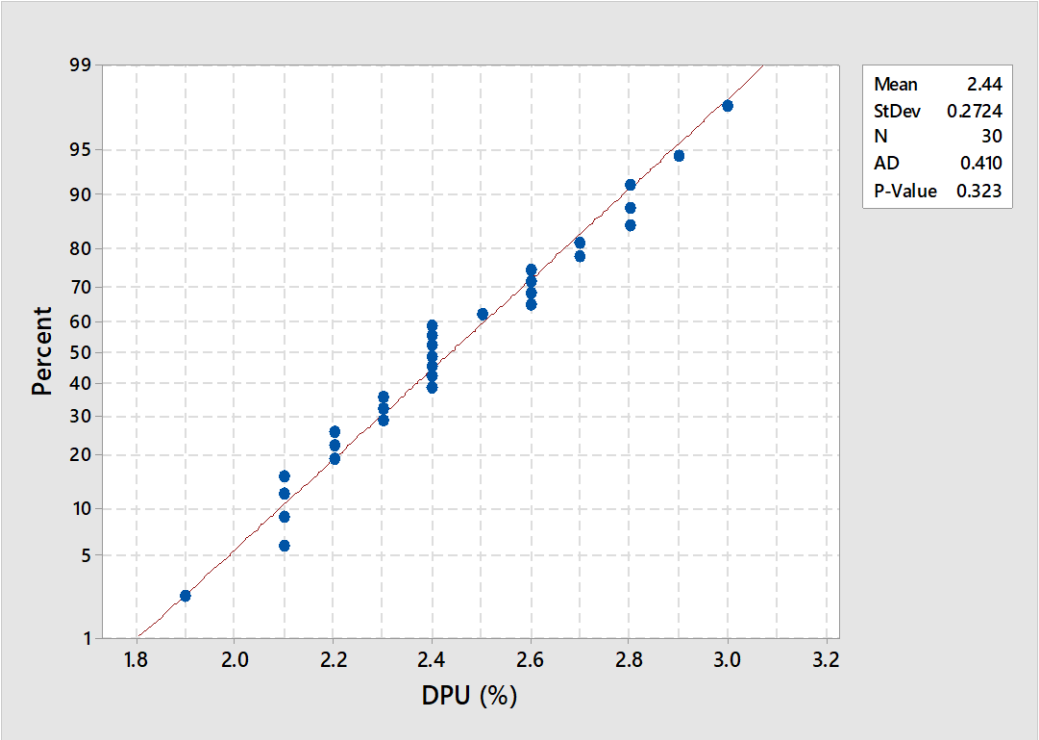

Figure A.1.1 - Normality test for Production population for $PET_{1440, C}$.

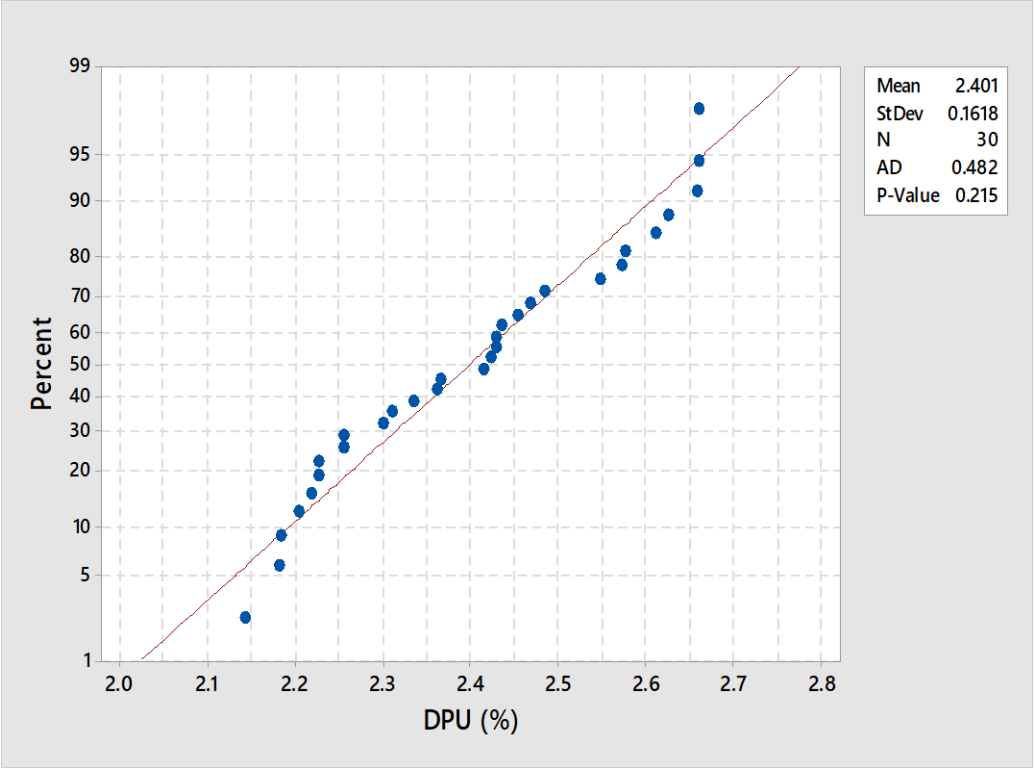

Figure A.1.2 - Normality test for TD-NMR population for $PET_{1440, C}$.

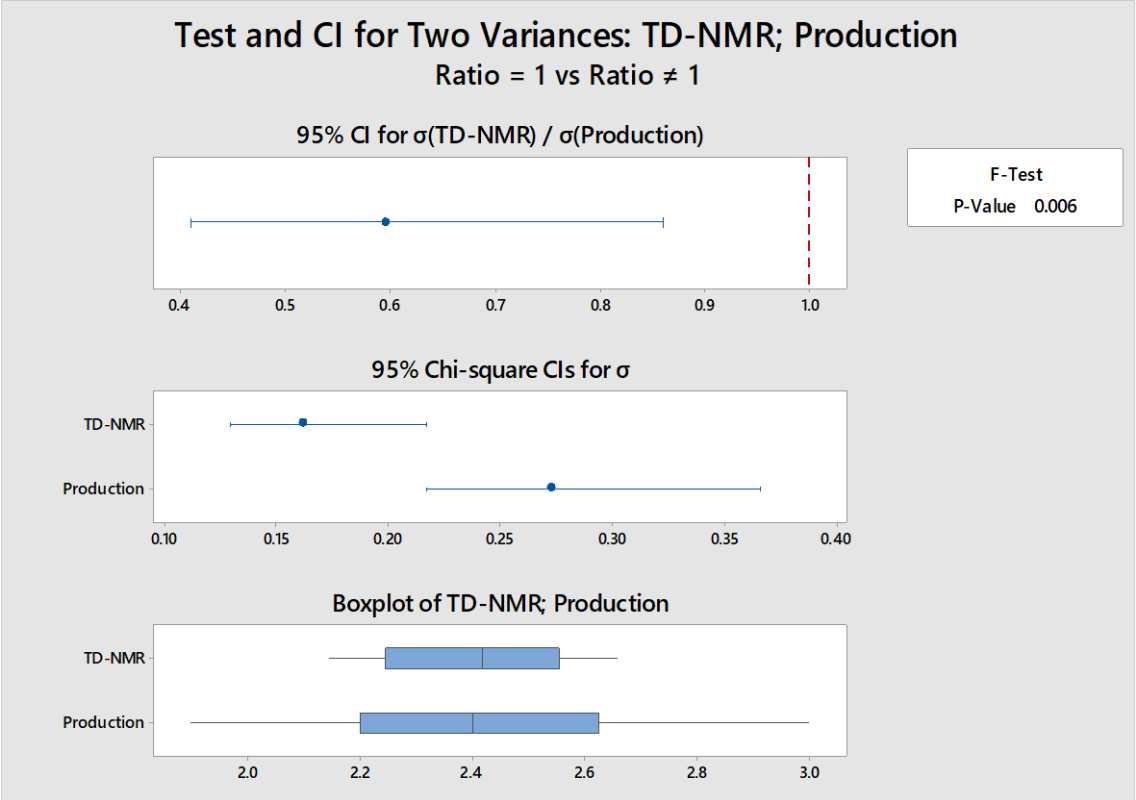

Figure A.1.3 - Variance test results for TD-NMR and Production populations for $PET_{1440, C}$.

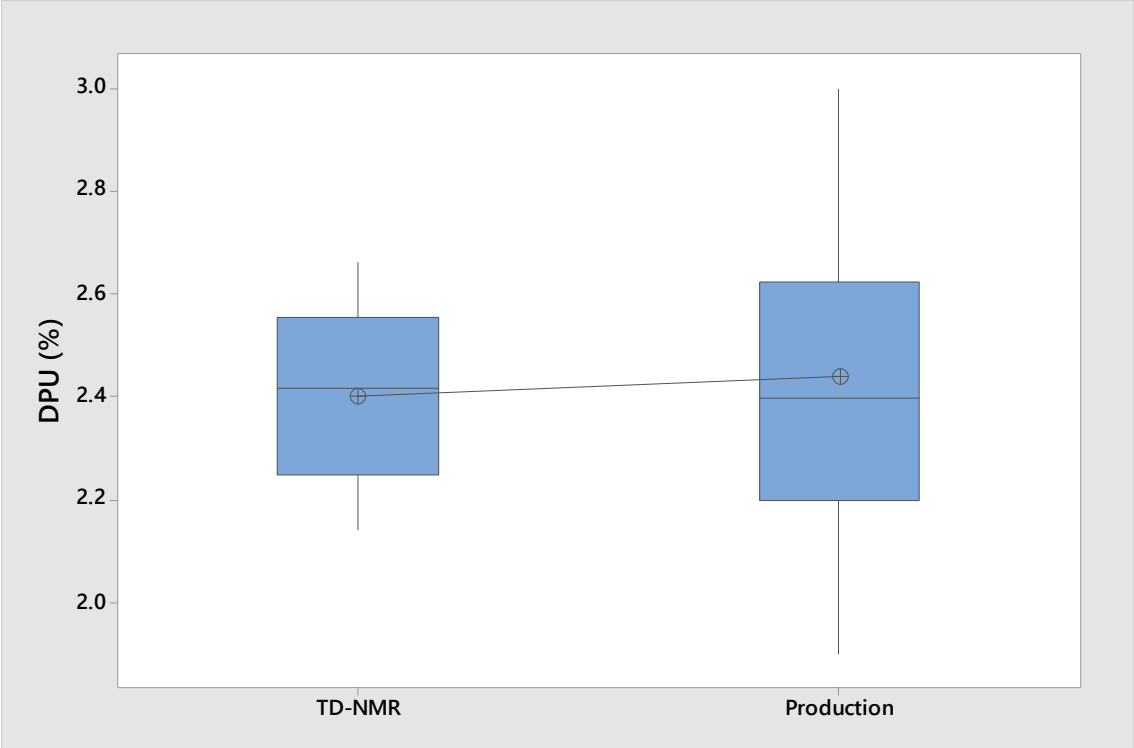

Figure A.1.4 - Distribution of D_{PU} values and samples' means for $PET_{1440, C}$ textile.

Table A.1.2 - D_{PU} results measured by TD-NMR and Production values for $PET_{1840, D}$ textile.

Sample	D_{PU} (%) TD-NMR	D_{PU} (%) Production
1	1.83	2.20
2	1.93	2.10
3	1.92	2.50
4	1.96	1.90
5	1.96	2.00
6	1.83	2.00
7	1.98	2.00
8	1.94	1.90
9	1.85	2.20
10	1.89	2.00
11	1.84	2.00
12	2.02	1.90
13	2.07	2.80
14	2.09	2.00
15	2.04	2.10
16	2.11	2.30
17	2.24	2.30
18	2.11	2.30
19	2.12	2.50
20	1.93	2.00
21	2.08	1.90
22	2.10	2.10
23	2.09	2.20
24	2.07	2.40
25	2.00	2.20
26	2.00	2.40
27	2.13	1.70
28	2.08	2.40
29	2.18	2.40

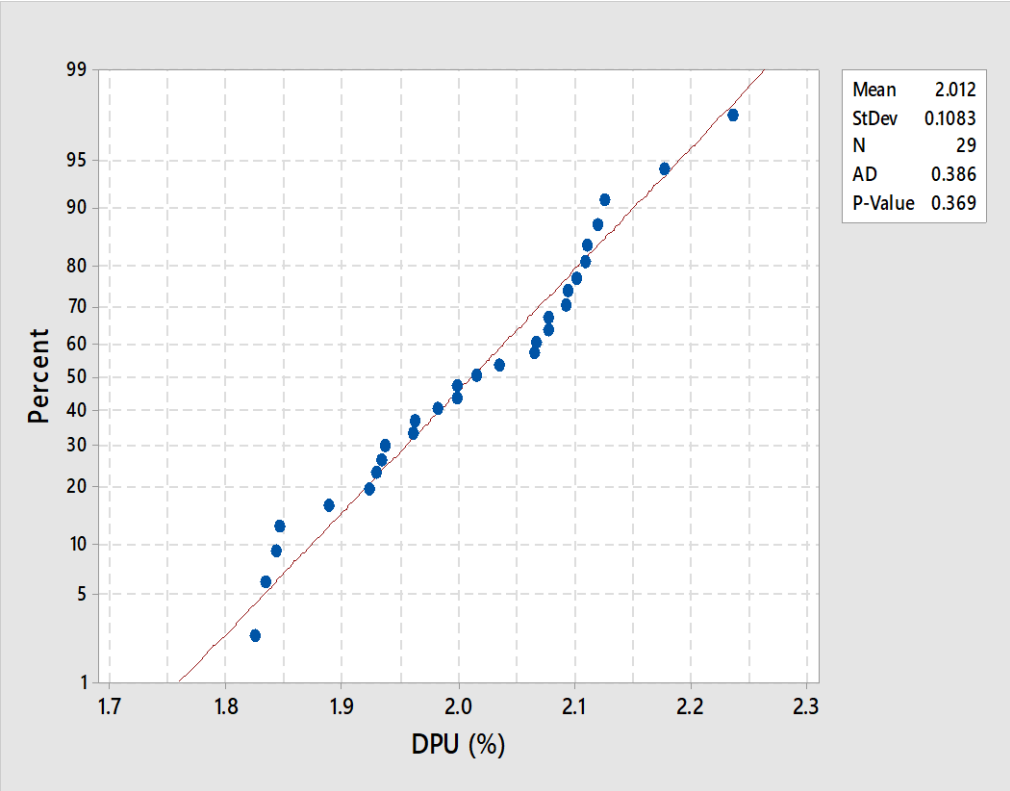

Figure A.1.5 - Normality test for TD-NMR population for $PET_{1840,\ D}$.

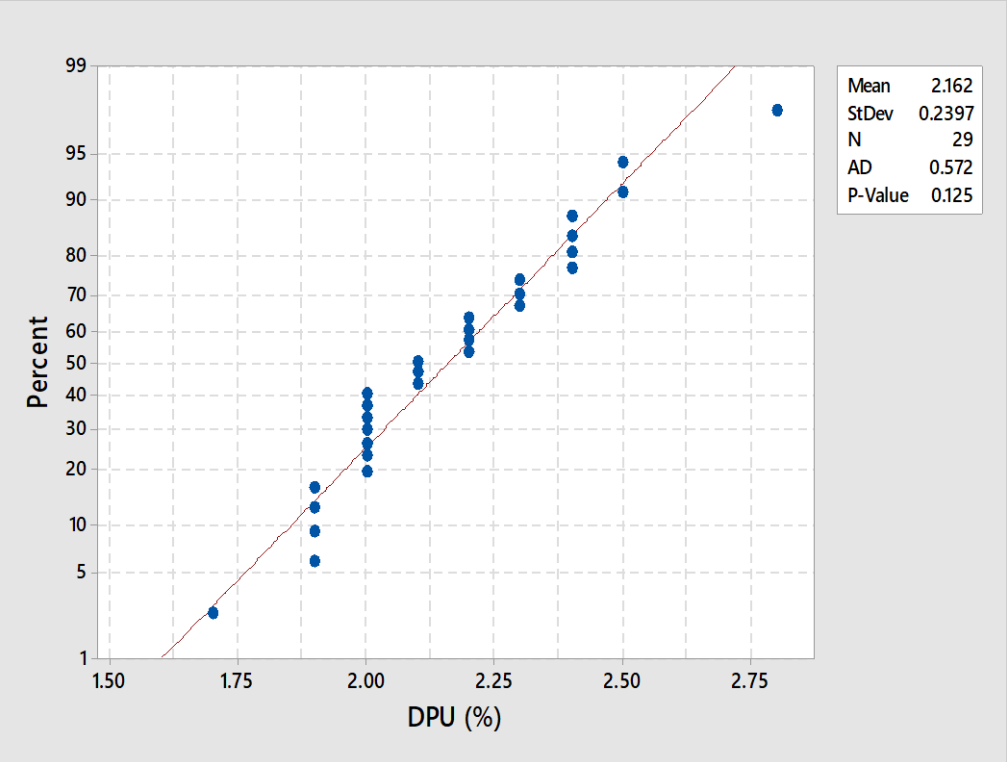

Figure A.1.6 - Normality test for Production population for $PET_{1840,\ D}$.

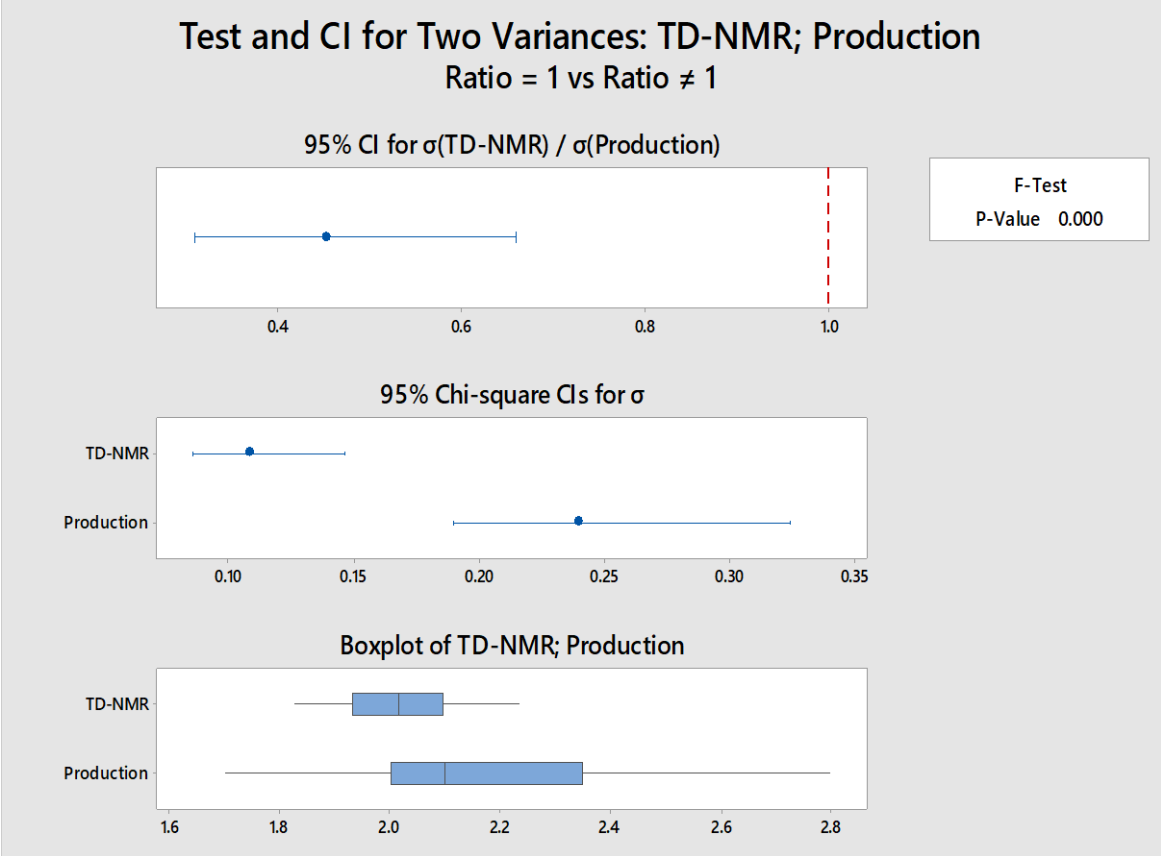

Figure A.1.7 - Variance test results for TD-NMR and Production populations for $PET_{1840,\ D}$.

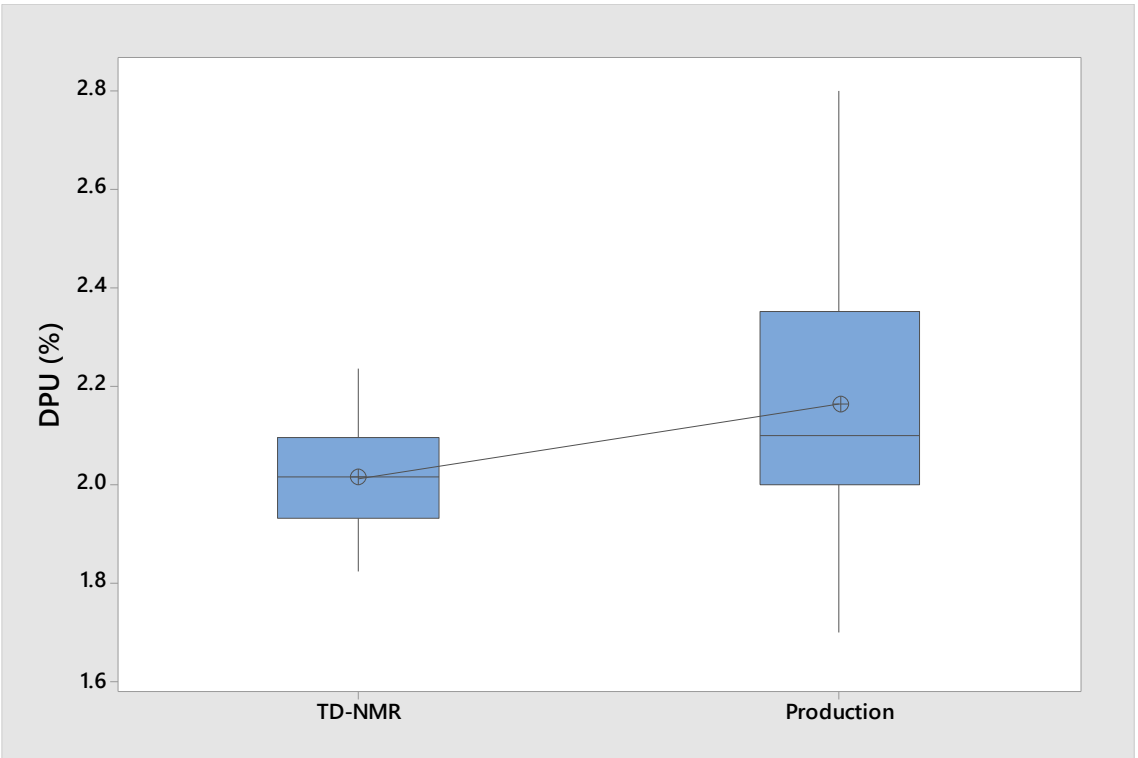

Figure A.1.8 - Distribution of D_{PU} values and samples' means for $PET_{1840,\ D}$ textile.

Table A.1.3 - D_{PU} results measured by TD-NMR and Production values for $PET_{3340,\ D}$ textile.

Sample	D_{PU} (%) TD-NMR	D_{PU} (%) Production
1	2.00	2.00
2	2.17	1.70
3	2.20	2.00
4	2.45	2.10
5	2.35	2.00
6	2.09	2.00
7	1.93	2.00
8	2.16	2.00
9	2.31	1.90
10	2.38	2.00
11	2.16	2.10
12	2.23	2.30
13	2.21	2.20
14	2.07	2.10
15	2.16	1.80
16	2.43	2.20

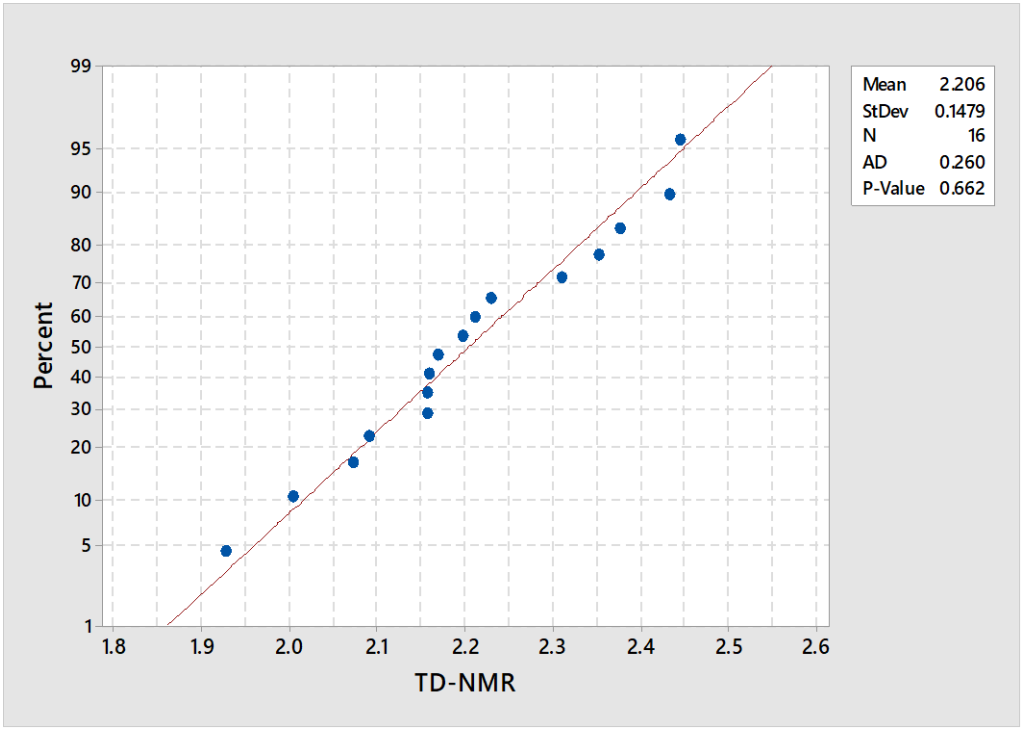

Figure A.1.9 - Normality test for TD-NMR population for $PET_{3340,\ D}$.

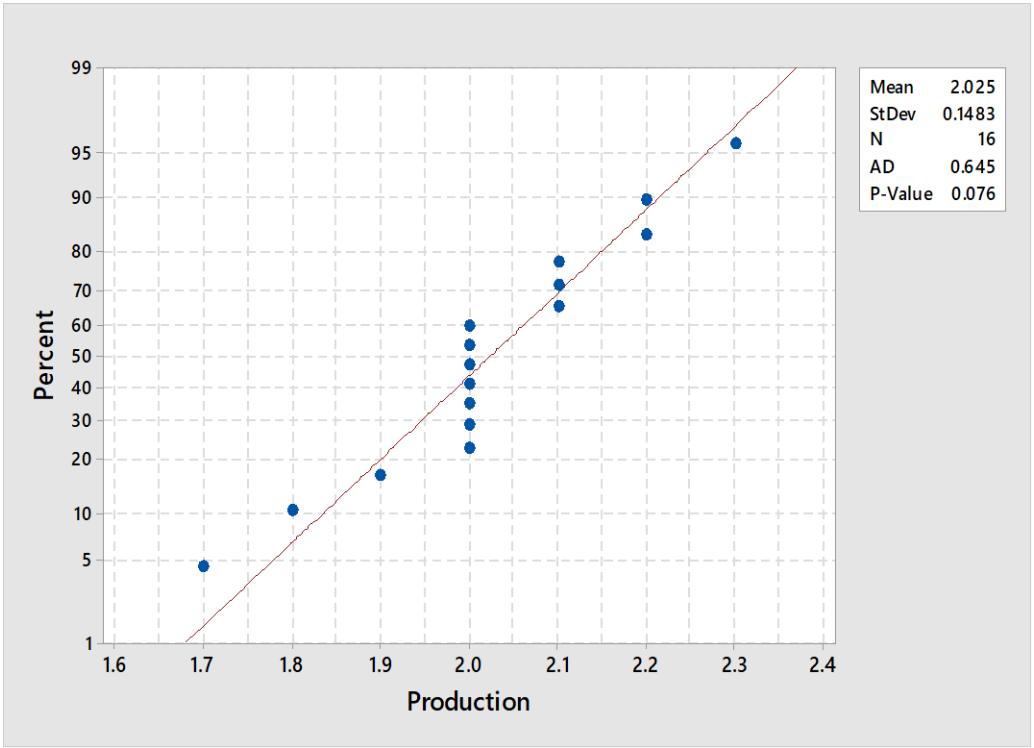

Figure A.1.10 - Normality test for Production population for $PET_{3340,\ D}$.

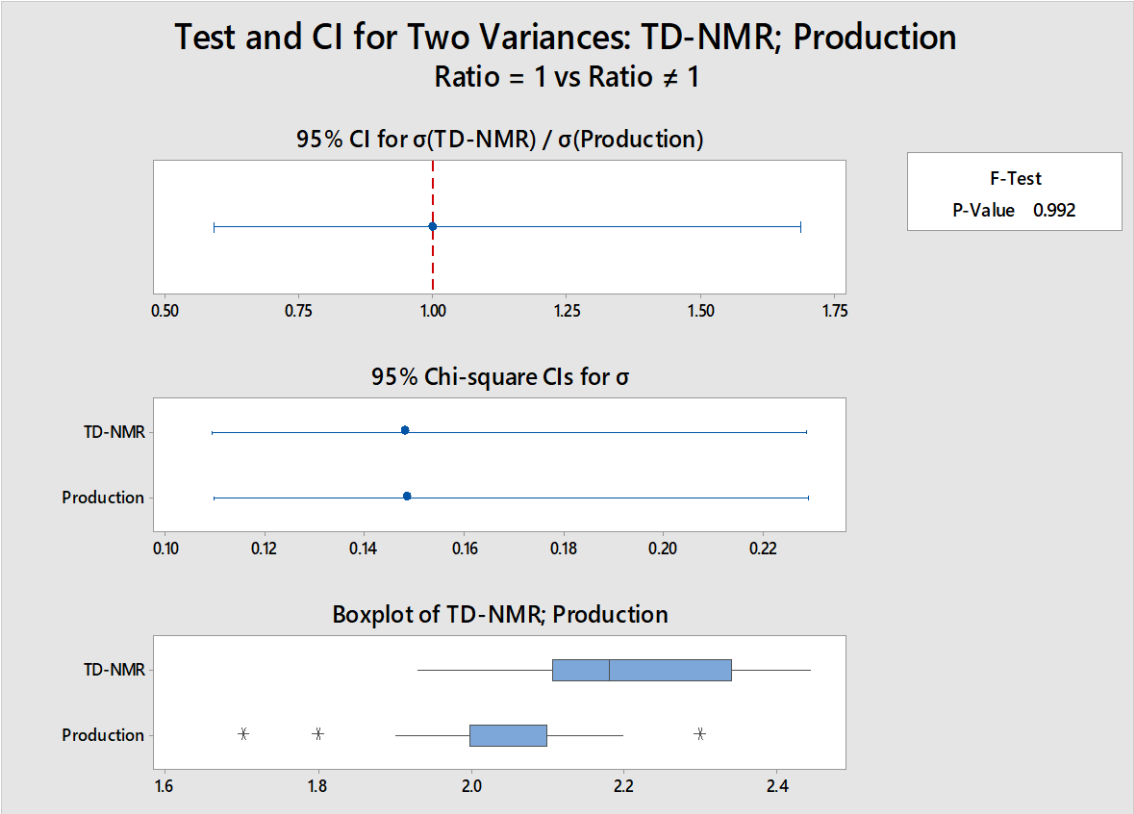

Figure A.1.11 - Variance test results for TD-NMR and Production populations for $PET_{3340,\ D}$.

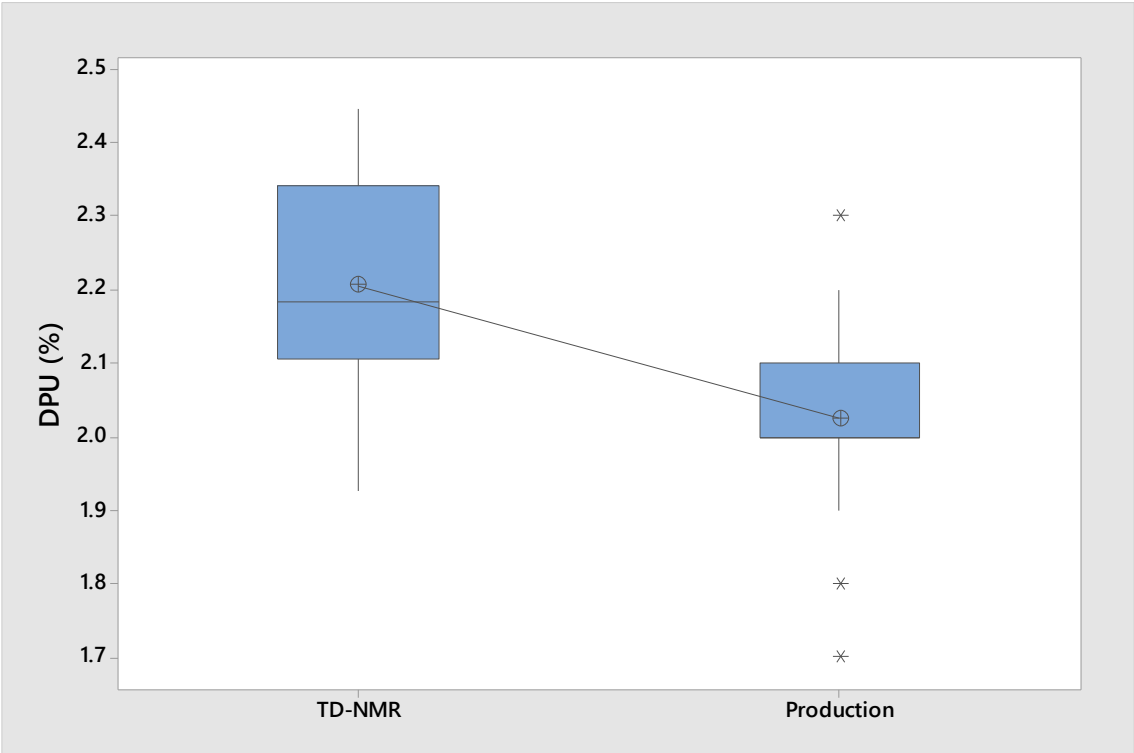

Figure A.1.12- Distribution of D_{PU} values and samples' means for $PET_{3340,\ D}$ textile.

A.2

Table A.2.1 - D_{PU} results measured by TD-NMR and Production values for $PET_{3340, B}$ textile.

Sample	D_{PU} (%) TD-NMR	D_{PU} (%) Production
1	5.49	5.90
2	5.51	5.70
3	5.88	5.50
4	5.56	5.50
5	5.87	5.50
6	5.72	5.40
7	5.10	5.40
8	5.32	5.40
9	5.83	5.60
10	5.19	5.30
11	5.55	5.40
12	6.47	5.70
13	4.98	5.50
14	5.47	5.10
15	5.24	5.50
16	5.04	5.50
17	5.25	5.40
18	5.63	5.30
19	4.98	5.40
20	5.30	5.80
21	3.96	5.30
22	5.18	5.70
23	5.04	5.90
24	5.85	5.10
25	5.52	5.70
26	5.34	5.90
27	5.10	5.10
28	5.41	5.60
29	5.42	5.30
30	5.86	4.90

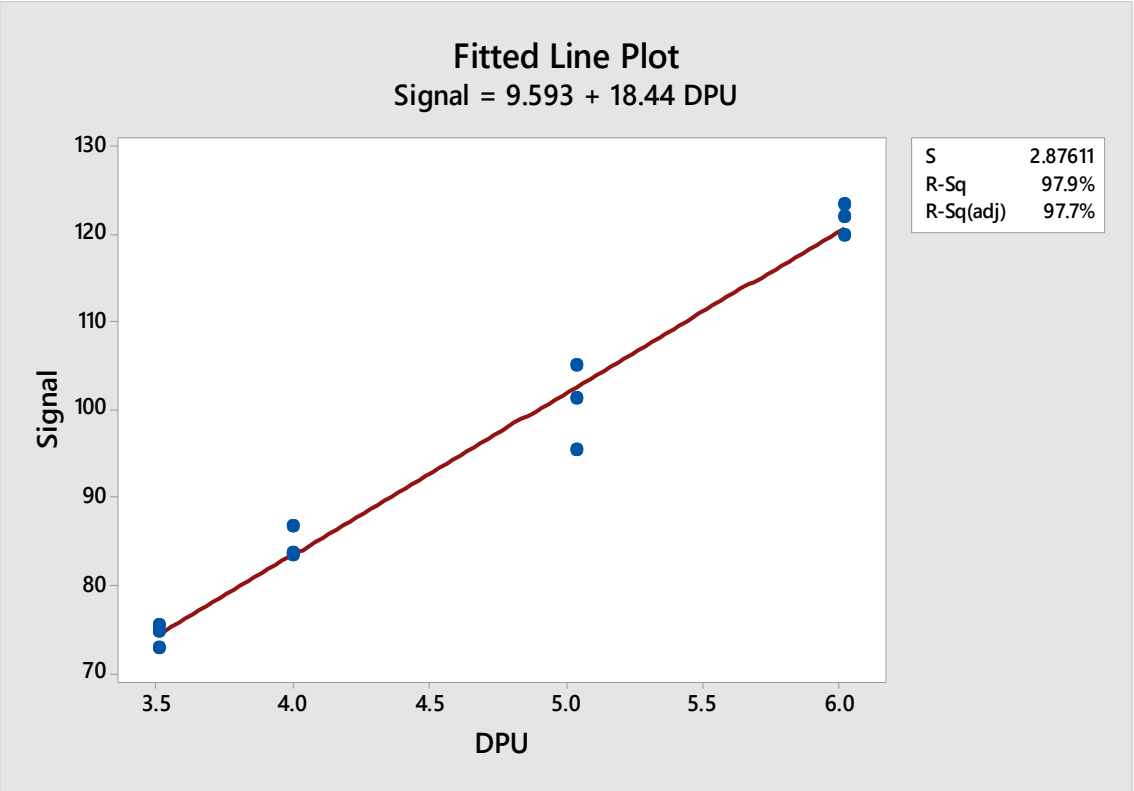

Figure A.2.1 - Linear Regression of PET calibration curve.

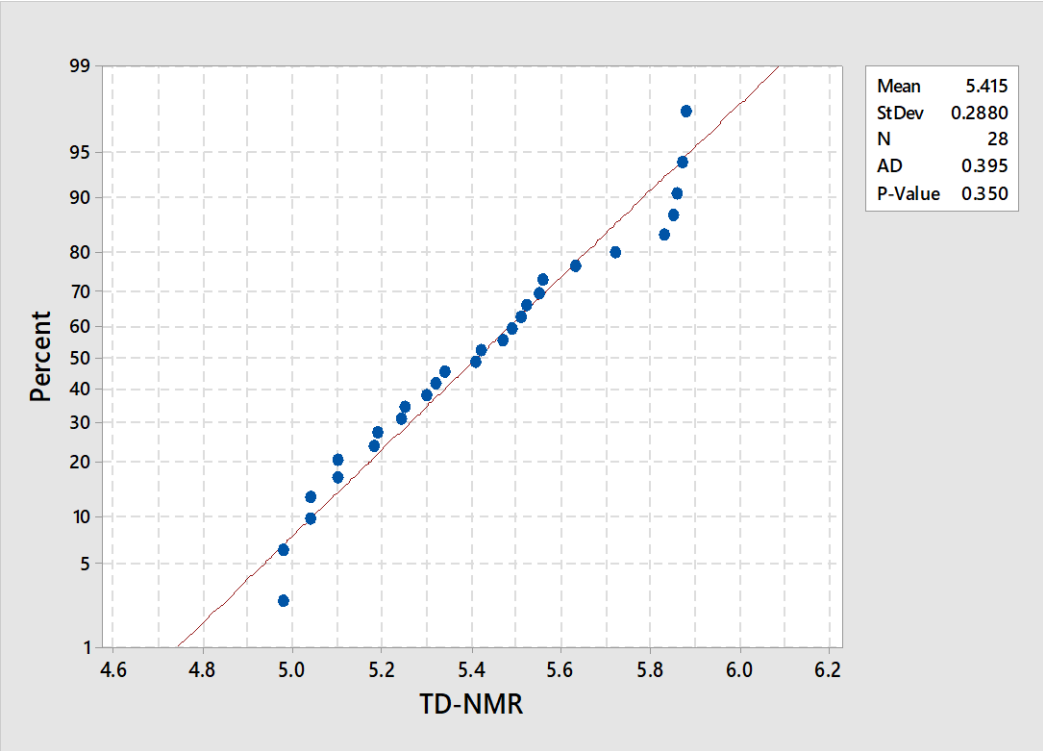

Figure A.2.2 - Normality test for TD-NMR population for $PET_{3440,\ B}$.

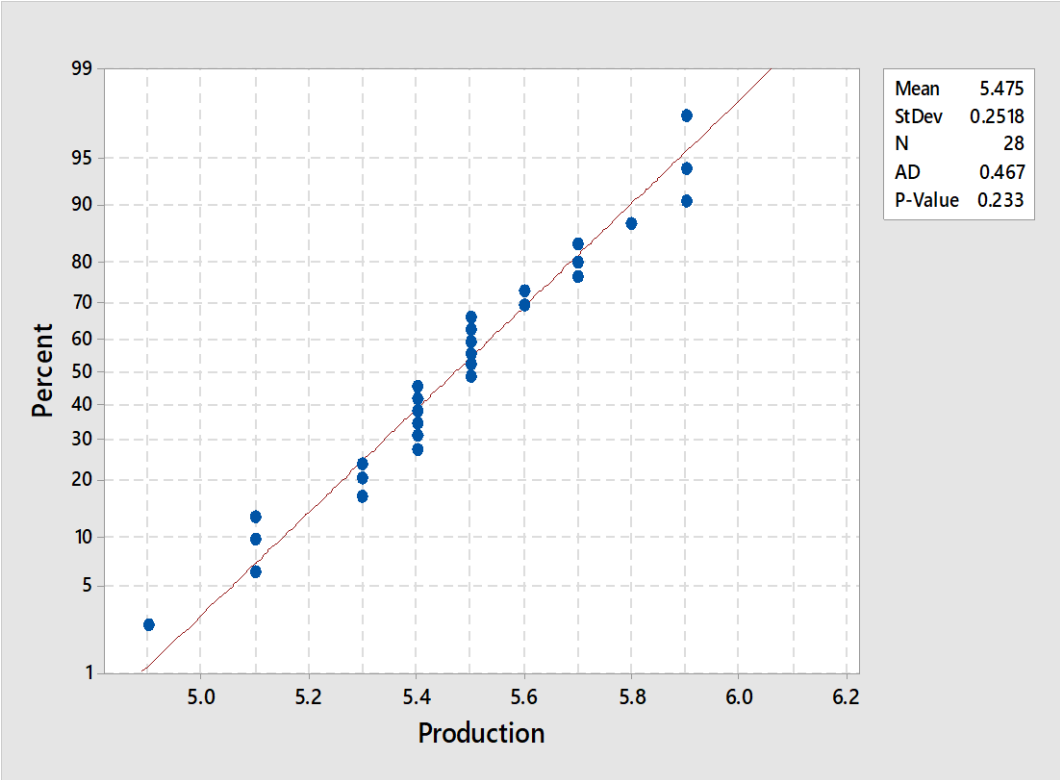

Figure A.2.3 - Normality test for Production population for $PET_{3440,\ B}$.

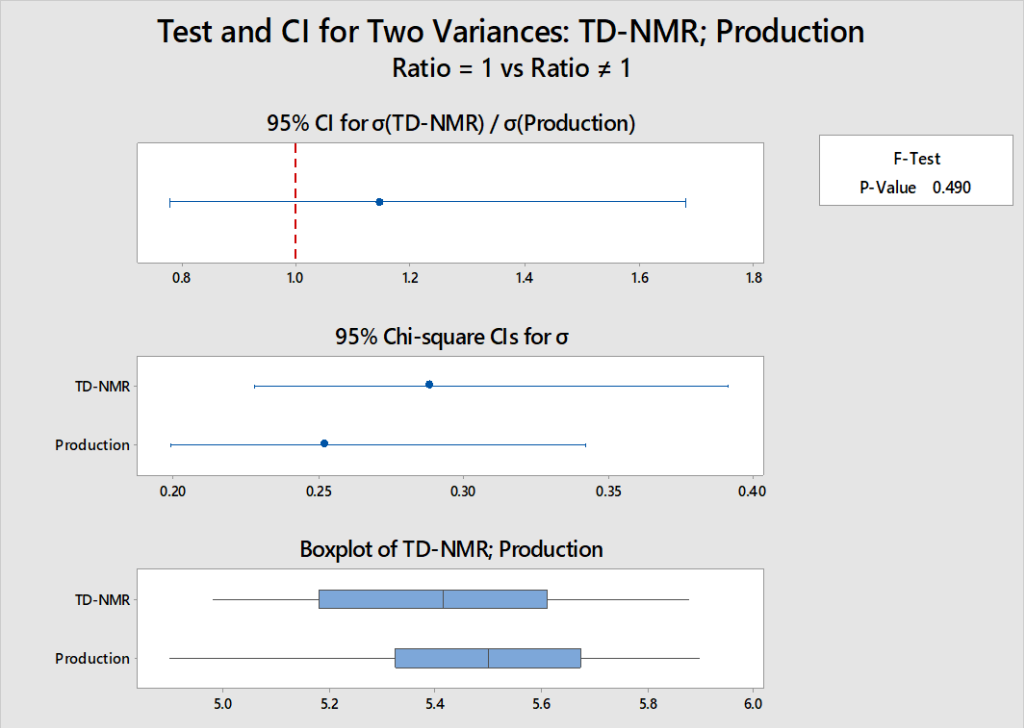

Figure A.2.4 -Variance test results for TD-NMR and Production populations for $PET_{3340,\ B}$.

A.3

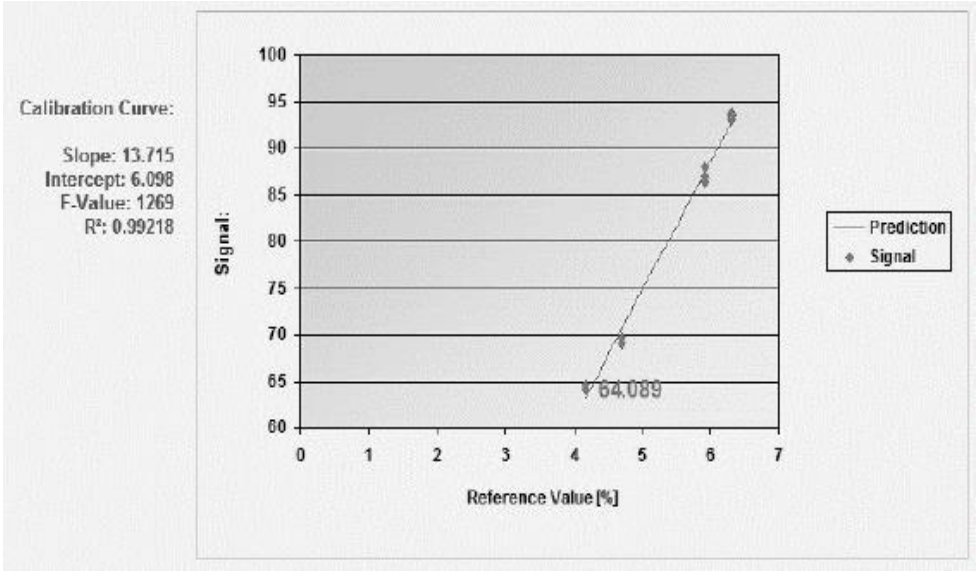

Figure A.3.1 - Nylon calibration curve in the TD-NMR device software "minispec Plus 6.0.3" (Pratapsi, 2018).

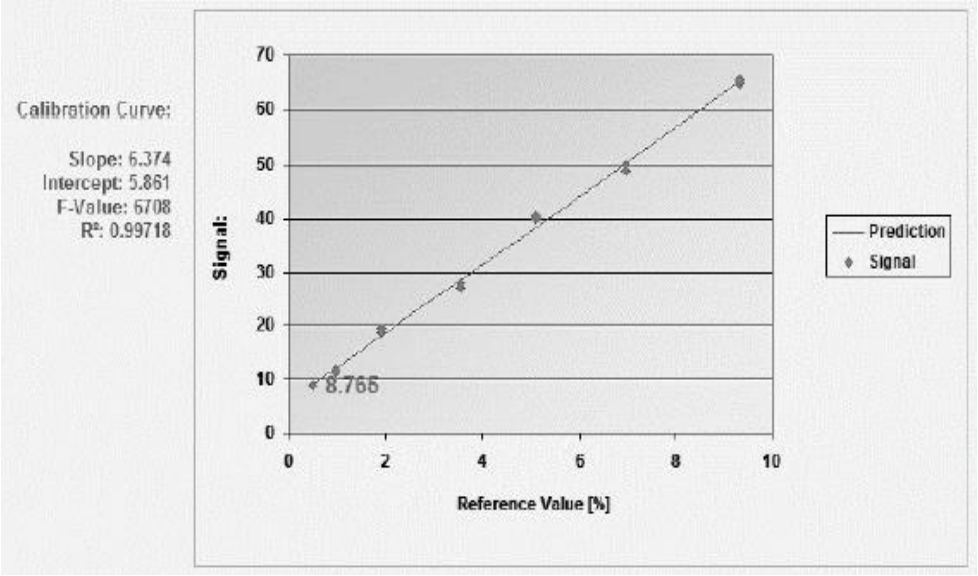

Figure A.3.2 - Hybrid calibration curve in the TD-NMR device software "minispec Plus 6.0.3" (Pratapsi, 2018).