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STUDY OF DIP CONTENT IN THE TIRE TEXTILE REINFORCEMENTS

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Abstract

Tires have a unique function in the automobile industry, being the most important element for the movement of the vehicle. To have a tire with quality, security and good performance, excellent textile reinforcements are some of the required components. A good adhesion of these reinforcements to the rubber matrix is the key aspect to build a good tire. For that matter, the textiles are coated with a dip solution responsible for the bonding between the fiber and the rubber. It is of an extreme importance to study the amount of solution in the cords for quality control, as a low amount of solution can lead to safety issues.

Continental – Indústria Têxtil do Ave, S.A., is one of the leaders in tire textile reinforcements, focusing on the quality of its products due to the use of analyses techniques that better evaluate and characterize them.

For a better measurement of the amount of solution in the textiles, a new technological device named Time Domain Nuclear Magnetic Resonance was been acquired and a new methodology was established and validated by previous authors. This method is much simpler, faster and reliable compared to the previous one, the wet chemical method.

This project aims to improve the sampling methodology associated to this new device, calibrate it for new textile materials and study the influence of cords' components on it, such as the cords' textile used and the constituents of the dip solution. A new sampling methodology was approved and a calibration curve for polyethylene terephthalate (PET) materials was created and validated. Additionally, it was also established that the solution used to coat the cords has a big influence on the results presented by the new device and the cords' textile does not appear to cause a variation in the results.

These studies will allow a better implementation of the new device in the production department, overall improving the quality control system for the products produced in this company.

Keywords: tire, textile reinforcements, PET, TD-NMR, quality control.

Resumo

Os pneus têm uma função única na indústria automóvel, sendo um dos elementos mais importantes para a circulação do veículo. Para se ter um pneu com qualidade, segurança e bom desempenho, uns dos componentes requeridos são excelentes reforços têxteis. Uma boa adesão destes reforços à matriz de borracha é um dos aspetos chave para construir um bom pneu. Para esse efeito, os têxteis são revestidos com uma solução de impregnação, responsável pela ligação entre a fibra e a borracha. É de extrema importância estudar a quantidade de solução nas cordas para controlo de qualidade, visto que uma pequena quantidade de solução pode levar a problemas de segurança.

Continental – Indústria Têxtil do Ave, S.A., é um dos líderes de reforços têxteis de pneus, focando-se na qualidade dos seus produtos devido ao uso de técnicas de análise que os avaliam e caracterizam melhor.

Para uma melhor medição da quantidade de solução nos têxteis, um novo dispositivo tecnológico chamado de ressonância magnética nuclear no domínio do tempo foi adquirido e uma nova metodologia foi estabelecida e validada por autores anteriores. Este método é muito mais simples, rápido e fiável em comparação ao anterior, o método químico.

Este projeto procura melhorar a metodologia de preparação de amostras associada a este dispositivo, calibrá-lo para um novo material e estudar a influência dos componentes das cordas neste, como o tipo de têxtil usado e os constituintes da solução de impregnação. Uma nova metodologia de preparação de amostras foi aprovada e uma curva de calibração para materiais de politereftalato de etileno (PET) foi efetuada e validada. Adicionalmente, também foi estabelecido que a solução usada para revestir as cordas tem uma maior influência nos resultados obtidos pelo novo equipamento enquanto que o tipo de têxtil das cordas não parece causar variação nos resultados.

Estes estudos permitirão uma melhor implementação do novo dispositivo no departamento da produção, melhorando, de uma forma geral, o sistema de controlo de qualidade para os produtos produzidos nesta empresa.

Palavras-chave: pneus, reforços têxteis, PET, TD-NMR, controlo de qualidade.

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, 26 of June of 2018

Ana Luís Carvalho Matos Bezerra

(Ana Luís Carvalho Matos Bezerra)

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Notation and Glossary

Dtex	Decitex	g/ 10 000 m
D_{PU}	Dip Pick-up Percentage	%
$D_{PU_{per\ dipped\ cord}}$	Dip Pick-up Percentage per dipped cord	%
$D_{PU_{per\ greige\ cord}}$	Dip Pick-up Percentage per greige cord	%
m_{DIP}	DIP mass	g
$m_{dipped\ cord}$	Dipped cord mass	g
$m_{greig\ cord}$	Greige cord mass	g
S_C	Solid Content Percentage	%

List of Acronyms

C-ITA	Continental – Indústria Têxtil do Ave, S.A.
CI	Confidence Interval
DIP	Dipping Solution
FID	Free Induction Decay
ITA	Indústria Têxtil do Ave S.A
LDU	Lab Dipping Unit
LTL	Low Target Limit
OPU	Oil pick up
PET	Polyethylene terephthalate fibers
TD-NMR	Time Domain Nuclear Magnetic Resonance
UTL	Upper Target Limit

1 Introduction

Tires perform an exclusive function in the automobile industry due to its characteristics that allow the vehicle mobility in all terrains and environments. The idea that a tire is a simple object with low technology is a misconception. Several techniques and materials, such as the implementation of fabrics in a tire, are responsible for the high complexity level associated to this object.

1.1 Framing and presentation of the work

Continental, founded in Hannover, Germany in 1871, is one of the top five suppliers in the automobile industry. It produces high-quality tires that improve both performance and safety of the driving experience. Continental started producing tires for bicycles, quickly expanding to the automobile industry, with tires that did not have tread patterns. Only in the twenty century, it started to implement tread patterns in tires, being the first world company to do so. Throughout the years Continental innovated and improved their products to establish a superior level, always with a concern for the passenger’s safety and comfort. The use and research for the most recent technology is also a factor that allows this company to compete in the automobile industry (Continental, 2010).

In 1950, *Indústria Têxtil do Ave, S.A* (ITA) was founded to fulfill *Mabor*’s textile necessities. Only in 1993, it was acquired by Continental along with Mabor, changing its name to *Continental - Indústria Têxtil do Ave* (C-ITA). In C-ITA textiles reinforcements, that is going to be applied in tires, are produced and later shipped to Continental tire plants in Europe. After the textiles reinforcements' production, is necessary to do a treatment so they adhere to tire's rubber part. This dip treatment is also performed in C-ITA with a dipping solution (DIP). The amount of DIP applied to a certain textile is a crucial factor in the cord to rubber adhesion, since a small amount leads to a weak adhesion and consequentially unsafe driving conditions. Prior to the textiles’ shipping, C-ITA needs to verify the amount of DIP to have a proper quality control. Thereby C-ITA invested in a time domain nuclear magnetic resonance (TD-NMR) device to measure the dip pick-up percentage (D_{PU}) in the final product (Continental, 2018).

In this context, the present project aims to improve the overall methodology to dip pick measurement, using the TD-NMR machine.

1.2 Contributions of the Work

This project continued the implementation of the TD-NMR in dip pick-up measurement for new materials.

On my project's first part, I proposed a new sampling methodology that will contribute to a better implementation of the TD-NMR device in the production department in C-ITA. In the project's second part a calibration curve was established for PET textiles and validated for different PET textiles (with different suppliers and linear density). Moreover, in the last part of my project, the textiles and the components of the solution used to coat them were studied to see if they had an influence in the TD-NMR device results.

In a general manner, my work improved the TD-NMR device implementation, allowing a better quality control at C-ITA.

1.3 Organization of the thesis

This project is divided in 8 chapters:

- Chapter 1: Introduction. Presentation of the industry and company and contextualization of the developed work.
- Chapter 2: Context and State of the art. Contextualization of the project describing the tire and textiles reinforcements industry and listing the methodology and equipment used.
- Chapter 3: Materials and methods. Descriptions of the used methods and equipment in the project.
- Chapter 4: Results and Discussion. Presentation and analyses of the results obtained during the course of this project.
- Chapter 5: Conclusion. Conclusions achieved by the results of this project.
- Chapter 6: Assessment of the work done. Global appreciation of the work done in this project.
- Chapter 7: References. List of the references utilized in this project.
- Appendix: Additional information of the developed work.

2 Context and State of the art

2.1 Tire

The tire is the only element that contacts the surface road, being an essential part in the vehicle and having to assure the demands and expectations of the passengers in a secure manner. Although it seems to be a simple object with a sole purpose - to move the vehicle - this piece of engineering has a complex structure and variety of functions not always perceptible to the common passenger (Continental, 2010).

Long before its invention, wheels were used since the ancient Egypt times being constantly reinvented and adapted according to the needs of the civilization throughout the years. Later, in 1888, the pneumatic tire was invented, first used for bicycles and afterwards in automobiles. Continental was a pioneer when it comes to the innovation of tires, starting to produce them in 1898. Tires not only allowed automobiles to travel at higher speeds but could also provide a more comfortable ride. In the 1950s the tubeless tires were invented, followed by belted bias tires in 1960s and radial tires in the 1970s, this evolution and improvement is still implemented in the current days in order to obtain a better product. Continental is an example in this area, producing only high-tech products, always with a concern in improving and pushing the quality even further (Brewer *et al*, 2006; Continental, 2010).

Currently the radial tire is the most common used one and must perform a variety of functions such as transmitting the forces which drive, brake, and guide the vehicles as well supporting vehicle load and providing long-term service. Good direction stability and the capacity to absorb road irregularities are other examples of tire’s requirements. It is important to enhance that these functions must be attained even in unfavorable conditions (Brewer *et al*, 2006).

As it can be seen in Figure 1, a tire is constituted by 9 components made by different materials in different amounts. The constituents of these components are mainly rubber (41 %), followed, in a decreasing order, by filers (30 %), reinforcing materials (15 %), plasticizers (6 %), chemicals for vulcanization (6 %) and anti-ageing agents and other chemicals (2 %) (Brewer *et al*, 2006).

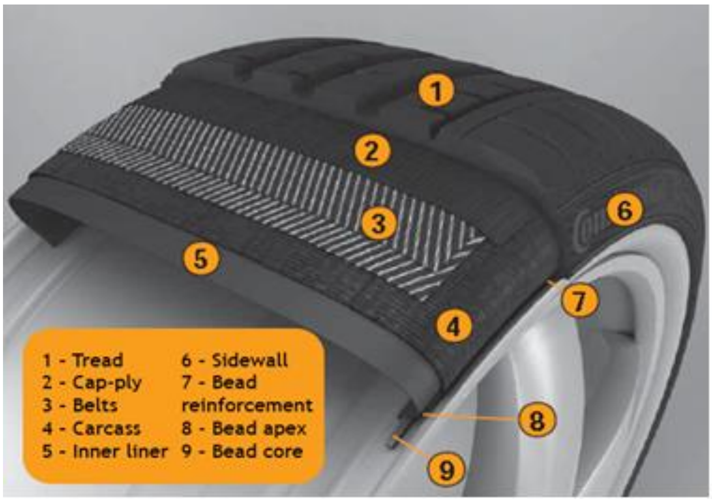

Figure 1 - Example of the tire constitution (adapted from Continental, 2013).

The outer layer of a tire, which contacts the surface road, is called tread. It is constituted by synthetic or natural rubber, and its main functions are deliver the required grip on the surface roads, wear-resistance and direction stability. The design pattern of this element has an extreme importance since it allows a better grip to the surface road in adverse conditions and avoids aquaplane. Nowadays, tread patterns are continuously enhanced and developed and smooth patterns are only found in motor racing vehicles. All these qualities must be incorporated so the passenger’s ride has an excellent quality (Brewer *et al*, 2006; Continental, 2010).

To achieve stability at higher speeds, the tire has a cap-ply which consists in nylon or hybrid strips embedded in rubber. These are wrapped in a circumferential geometry covering the belts edges to restrict expansion derived by the centrifugal forces that are amplified in high velocities (Brewer *et al*, 2006; Continental, 2010).

Under the cap-ply, two steel belts are applied in opposite directions to endure directional stability by restricting the cords expansion which are present in the carcass’s textile. This tire element is also capable of reducing the rolling resistance and expanding the tire’s mileage performance (Brewer *et al*, 2006; Continental, 2010).

The carcass, often designated as body ply, is constituted by rubberized rayon or polyester cords. The cords are laid radially around the tire thus controlling its internal pressure by providing the necessary strength to do so. The carcass is also accountable for maintaining the tire’s shape (Brewer *et al*, 2006; Continental, 2010).

The inner liner, located on the tire inner surface, acts as a tube sealing the air-filled inner chamber. This thin tube seals the chamber by lowering the permeation outwards through the tire and is made of butyl rubber (Brewer *et al*, 2006; Continental, 2010).

To endure external damage and unfavorable atmospheric conditions the tire has a sidewall of natural rubber. The rubber is formulated to resist cracking, therefore protecting the tire's carcass from damaging of external forces. Moreover, in this element the necessary information such as manufacture and size designation among others is written (Brewer *et al*, 2006; Continental, 2010).

The bead reinforcement, the bed apex and the bead core, shown in Figure 1 constitute the bead bundle. Both the first and second element provide direction stability and steering precision, the aped apex also improves comfort to the ride. The bead core is made of steel wires to ensure the tire's properly fit in the rim of the wheel, so does not slip out of position (Continental, 2010).

Tires can be categorized by type depending on the carcass arrangements, as is shown in Figure 2**Erro! A origem da referência não foi encontrada.**.

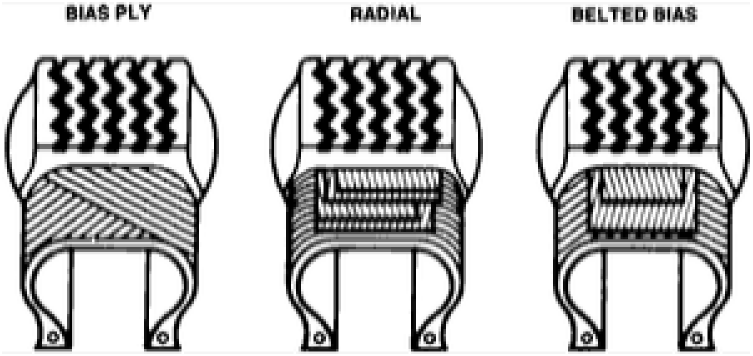

Figure 2 - Different types of arrangements (adapted from Nichols, 1998).

Nowadays the radial tire, is the most used assembly in which the cords are laid perpendicular to the direction of the traveling. Sideways, they seem to run radially, hence the radial tire name. Although this assembly provides support and stability, the cords are not capable of absorbing the lateral of circumferential forces by the acceleration of the vehicle, so is necessary to support them with other elements. Better high-speed performance and lower rolling resistance are other positive aspects regarding the radial tire, these advantages occur because the body cords can deflect under load easily, generating less heat. Additionally, the increase tread stiffness expands wear and handling (Brewer *et al*, 2006).

Diagonal tire, or bias tire, has body ply cords laid at angles lower than 90 ° to the tread centerline. The main advantage of this type comes from its easy construction and manufacture. The main problems concerning this arrangement are the generation of heat that occurs as the tire deflects originating shear between body plies. The poor wear characteristics resulting by the tread motion is another disadvantage to be taken into account. Diagonal tires are most used in trucks, trailers and farm implements (Brewer *et al*, 2006).

Belted bias tire has belts in the tread region in order to strengthen and stabilize this region by coffining the body carcass expansion in the circumferential direction. The belts provide a better wear and handle. However, generation of heat still occurs due to shear of the body ply. This type of tire also requires higher material and manufacturing cost (Brewer *et al*, 2006).

2.2 Textile Reinforcement

At the moment, billions of tires are used in a vast diversity of vehicles ranging between bicycles and tractors to space shuttle landing gear. Although the technical needs can variate according to the type of tire there are aspects that need to be conformed and maintain throughout its use such as quality, security and overall good performance. Thereby an excellent reinforcement (made of textiles) is one of the components that a tire needs to possess (Brewer *et al*, 2006).

The textile industry is responsible for the production of the textile reinforcement materials applied in the carcass and cap-ply of a tire. C-ITA is an example of a textile unit working as a supplier for Continental tires plants in Europe. The textiles produced in it are polyethylene terephthalate (PET), nylon, rayon and aramid. These are responsible for containing the air pressure and provide strength and stability to the sidewall, making a good driving experience to the passenger. Besides the four textiles mentioned above, C-ITA also uses nylon and aramid to produce hybrid cords with a different behavior and better properties (Brewer *et al*, 2006; Continental, 2018).

Regarding to fibers polyethylene terephthalate (PET) is the largest volume synthetic fiber produced worldwide, resulting of a polymerization reaction between dimethyl terephthalate and ethylene glycol. Moreover, it has high strength with low shrinkage, a low heat set and low service growth. Despite not being as heat resistant when compared to nylon or rayon, this is one of the cheapest fibers in the market (Brewer *et al*, 2006; Lewin, 2006).

Nylon fibers are the most communally used in radial tires as cap or overlay ply and its success led to the commercialization of other synthetic fibers as well as inorganic fibers. This synthetic long chain polymer is produce by a continued polymerization or melt spinning. It has a good heat resistance and strength, low modulus and glass transition temperature and a low sensitivity to moisture (Brewer *et al*, 2006; Lewin, 2006).

Rayon is used as belt reinforcement or a body ply cord. It is made by wet spinning and has cellulose as its primary source. Its main advantages are stable dimensions, heat resistance and good handling characteristics. Nevertheless, there are some problems associated to it such as the expensive cost, the sensitivity to moisture and the environmental issues associated to the manufacturing (Brewer *et al*, 2006).

Aramid is a synthetic, high tenacity organic fiber two to three times stronger than polyester and nylon. It is made by solvent spinning and acts as a substitute for the steel cord as stabilizer ply material or belt due to its light weight. In spite of having some issues such as the difficulty of cut and the elevated cost, it is very used since it has a good heat resistance and high strength and stiffness (Brewer *et al*, 2006).

Prior to its use as a textile reinforcement, fibers have to be submitted to chemical and physical modifications. Fibers can be categorized in four levels of complexity: filament is the simplest one, passing through yarn, cord and finally fabric. Yarns are continuous strand of fibers grouped or twisted together. When two or more yarns are twisted together, or even a single yarn is twisted, it forms a cord. Hybrid cords are made with different yarn materials, as it was mentioned before (Fidan *et al*, 2002; “Types of yarn”, 1998).

Cords can be twist in two opposite directions, clockwise (“Z”) or counter-clockwise (“S”). As it is shown in Figure 3, the yarns are most commonly twisted in a “Z” direction and later twisted in a “S” direction. This process is made in a twisting machine to produce greige cord. The greige cord manufactured in C-ITA is later combined and transformed into fabric that is going to be used in the carcass (“Types of yarn”, 1998; Wahl n.d.).

Cords can also be categorized by the primary material, number of yarns used to produce it and linear density, being the last one defined as decitex (dtex). Decitex is the weight in grams of a length of 10,000 meters (Brewer *et al*, 2006; Wahl n.d.).

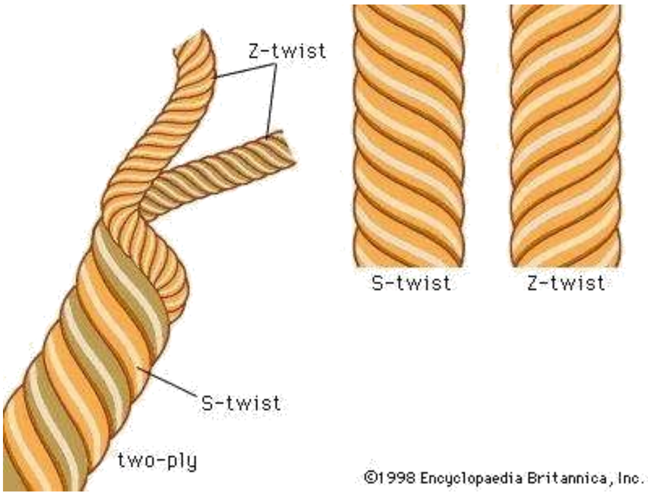

Figure 3 – Possible twist direction (“Types of yarn”, 1998).

2.2.1 Dipping process

When it comes to cord adhesion in the rubber, this is a difficult process to be accomplished only by a physical treatment. Due to difference of the polarity between these two components the lack of compatibility needs to be overcome, therefore it is necessary to do a treatment in the cords or fabric that are going to be used as textile reinforcement. In general, polymerics cords have a smooth and inert surface as well as a polar character, thereby the interactions between them and the non-polar rubber are very weak. The most common treatment made to the cords is the Resorcinol-formaldehyde-latex (RFL) technique in which a dipping solution (DIP) is used. The cords are dipped in the solution and later, to create a solid interface layer in the fibers' surface, they are stretched and dried in ovens (Brewer *et al*, 2006; Louis *et al*, 2014).

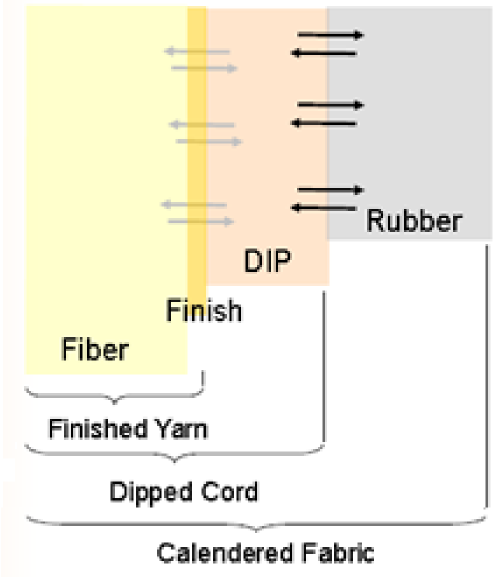

Figure 4 – Cord adhesion into rubber (adapted from Wahl, n.d.).

In Figure 4 it is possible to see that the DIP acts as a barrier between the fiber and the rubber. The dipping solution is constituted by water, a latex emulsion and a resin made of resorcinol and formaldehyde. C-ITA uses resole RF-resin type, heat cured and base catalyzed. The resin bonds with the fiber due to covalent chemical bonds formed in the interface fiber-DIP. Although physical bonds are later formed, the chemical bonds are the main contribution to adhesion as they are very strong and highly durable. The latex used is styrene-butadiene-2-vinyl pyridine (VP latex) that facilitates the adhesion of the DIP to the rubber due to vulcanization (Durairaj, 2005; Louis *et al*, 2004).

The RFL dipping covers a variety of treatments that varies according to the type of cord and rubber used, only the technique remains the same. Each fiber needs a specific DIP recipe with an established Solid Content (S_C). Furthermore, some PET and aramid fibers, which are much less reactive to the standard RLF treatment, need to be pretreated with a solution that acts as intermediate layer between the fiber and the DIP. The solution contains epoxides that form chemical bonds with both the fiber and DIP resin and later the resin reacts with the rubber compound (Louis *et al*, 2014).

To dip the cords C-ITA uses an equipment called Single-end shown in Figure 5. In this machine the greige cord (cord without any treatment) unwinds in the same place in which the dipped cord winds, hence the name “single-end”. First the greige cord is stretched in tensioning rollers and is forwarded to the first bath, afterwards the cord goes to the first oven to be dried. After the first oven the cord goes through the second oven in which it is hot stretched and acquires the final properties.

If the cord requires a pre-dip it is necessary to use the third and fourth oven, otherwise the ovens will be turn off and the cord won’t suffer any additional treatment. In the first case, the first bath contains the pre-dip and the second bath the dip solution; the first and second oven perform in the same way. The third oven acts as a second dry zone and the fourth as a normalizing oven. In the end of the process the cord is rolled in bobbins and later shipped to the costumers.

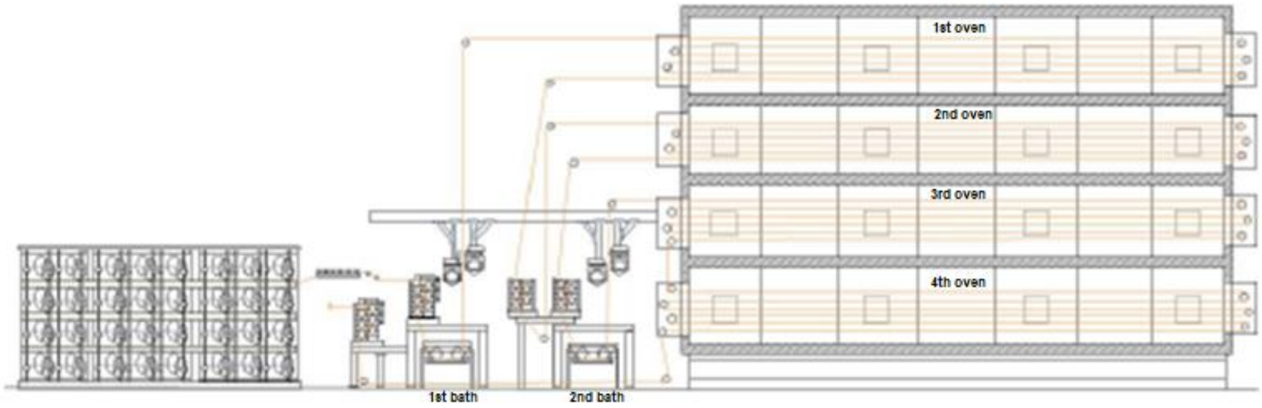

Figure 5 – Single-end scheme (adapted from Martins, 2013).

C-ITA also dips fabrics in a device named Zell, represented in Figure 6. Contrary to the Single-end, the greige fabric and the dipped fabric are not in the same side and Zell has more ovens. Additionally, in the Zell machine the fabric is dipped one at a time, while in the Single-end hundred cords can be impregnated at the same time.

Moreover, for investigation purposes, C-ITA has a machine called Lab Dipping Unite (LDU) to replicate these dipping units, only on a laboratory scale.

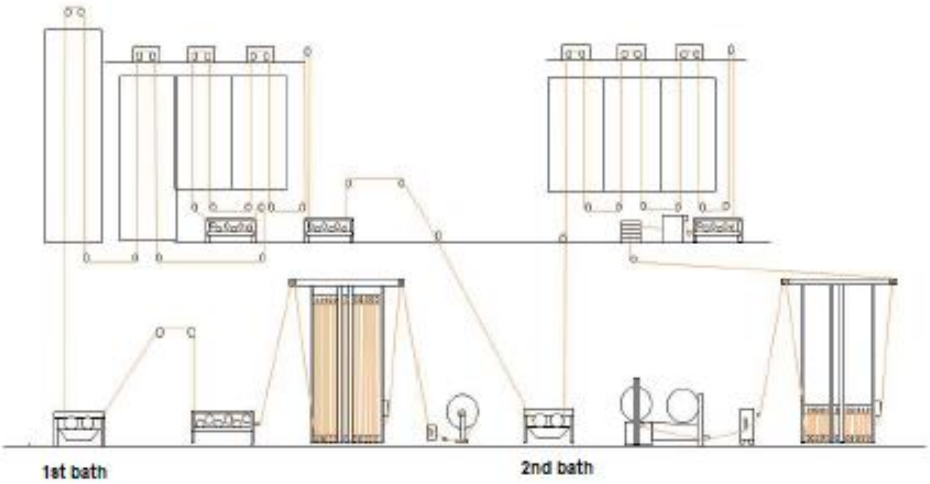

Figure 6 – Zell scheme (adapted from Martins, 2013).

C-ITA establishes all the variable conditions such as S_C, stretch, velocity and temperature. Additionally, studies are made to improve the dipping process and new materials are used so they can later introduce in the range of products.

In C-ITA the amount of DIP is quantified for safety and economic matters, as a higher amount leads to waste and environmental concerns. On the other hand, a lower quantity than the required leads to a poor adhesion that can cause safety problems in the tires and subsequently in the driving conditions. To verify the cords' adhesion to the rubber, C-ITA performs peel adhesion tests. If the adhesion is not good the cord will separate from the rubber, as it can be seen by the left sample in Figure 7. To consider the results good the cords have to be properly inserted in the rubber, so they cannot be visible to the naked eye, as it is shown by the right sample in Figure 7.

Figure 7 – Peel adhesion results

2.2.2 DIP measurement and quality control

As already stated, in C-ITA every type of textile requires a certain amount of DIP. Ergo, to quantify the amount of DIP in each cord the Dip Pick-up Percentage (D_{PU}) per greige cord is measured. The measurement is usually made by the wet chemical method or, more recently, by the Time Domain-Nuclear Magnetic Resonance (TD-NMR) method.

2.2.2.1 Wet Chemical Method and Weighing Method

In C-ITA, the wet chemical method is currently the official method to measure the amount of DIP in cords. In this method the fibers in the dipped cord are dissolved. Despite being the official method, it has many disadvantages such as the high amount of errors associated, and the environmental issues associated due to the use of dangerous chemicals. An equally important disadvantage is the long period of time required to perform this method, which makes it impracticable for quality control for some textiles like aramid and PET.

The wet chemical method requires the following steps: (i) dissolution of fibers, (ii) solvent removal by filtration and recovering of the dip residue, (iii) dry the dip, and (iv) weight the solid residue. Afterwards, Equation 1 is applied to calculate the D_{PU},

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

in which, m_3 is the solid residue weight in g plus the weight of the crucible, m_2 is the glass filter crucible weight in g and m_1 is the sample weight in g.

Owing to the hygroscopic nature of most cords the humidity present in the environment can affect the results, so they need to be dried at 105 ºC before the weight measurement. Nevertheless, few textiles, namely PET, have a low hygroscopic nature so the weight is not as affected by humidity. For these cases the D_{PU} is measured by a weighing method (Equation 2) that does not involve fibers dissolution, and the greige cord is thermofixated and used as reference value.

$$D_{PU} = \frac{m_{dipped\ cord} - m_{greig\ cord}}{m_{greig\ cord}} \times 100 \qquad (2)$$

2.2.2.2 TD-NMR method

Due to the impracticability of the wet chemical method, more methods are being used and studied to perform quality control, not only faster but also with a high quality and low error occurrence associated. In this matter, new developments in spectroscopic techniques for process control are being used and studied and Time Domain Nuclear Magnetic Resonance method is a recent one that serves as a replacement for the wet chemical method.

Although low field TD-NMR is a quick and nondestructive method, quantitative results can only be obtained with further calculation or calibration of the TD-NMR device. This method results by the measurement of the energy released by the protons of a certain sample when these are excited by a magnetic field in a low frequency. The energy release by the protons emits an electrical signal that is read by the device. The signal is associated with the number of protons and consequently the sample mass, so a higher sample's mass leads to a higher signal emitted (Silva *et al*, 2016).

Every atom has, in its nucleus, protons and neutrons that spin in an axis, this property is named spin angular momentum. Due to the electric charge of the protons, the spinning motion produces a magnetic moment along the spin axis, but most particles are paired so that the net magnetic properties are canceled. Only the particles that present an odd number of protons do not have a complete cancellation of the magnetic properties and, therefore, have a magnetic moment. The hydrogen (^{1}H) nucleus has the strongest moment and it is highly abundant, especially in biological systems (CDRH Magnetic Resonance Working Group, 1997).

The TD-NMR device emits magnetic pulses that excite the sample's protons to a higher energy state, afterward, when the pulse is deactivated, the protons will release the absorbed energy. Thereby, the signal captured from the TD-NMR results from the difference between the energy absorbed by the protons' spins and the energy emitted by it. The pulses can be emitted at 90 and 180 degrees, and each angle affects the protons' spinning in a different way. At the end of the pulse with 90° the signal emitted by the sample's protons is at the maximum intensity. However, the intensity diminishes rapidly to the protons' original energy state in an exponentially damped sine wave form being detected by a receiver coil. The sinusoidal wave is designated as free induction decay (FID), represented in Figure 8 (CDRH Magnetic Resonance Working Group, 1997).

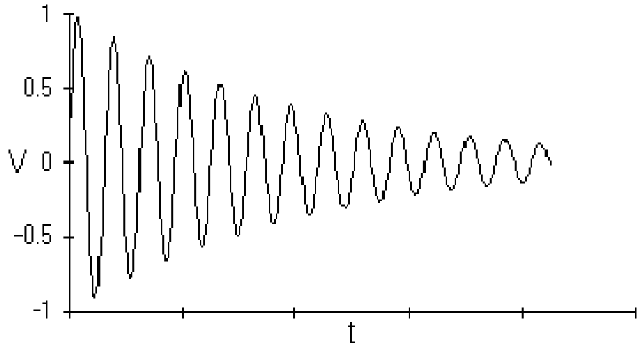

Figure 8 – Free induction decay wave (Adapted from CDRH Magnetic Resonance Working Group, 1997).

When the sample is first exposed to a magnetic pulse at 90º and subsequently at 180º the provoked disturbance is called a Hahn echo sequence. This sequence is used to determine the spin finish content, often named oil pick up (OPU), in yarns based on the components' different transverse relaxation properties. The yarn, being a solid, has a shorter relaxation time than the liquid OPU. When the first pulse (with a 90º angle) acts on the sample both OPU and yarn produce a signal. However, the same does not happen when the 180º pulse is emitted. In this case, the signal attributed to the ^{1}H spins of the yarn decayed already due to his shorter relaxation time, so the signal obtained will only be originated by the OPU (Dalitz *et al*, 2012).

In a similar way, C-ITA uses this method to measure the amount of DIP in the samples. The main difference relies on the fact that both the DIP and the fiber are solid. Since the DIP has a shorter relaxation time, the signal obtained after the 180º pulse will be generated by the fiber's sample. Thereby, it is possible to measure the amount of DIP through the difference between the first and second signal, as it is shown in Figure 9 (Bruker, 2016).

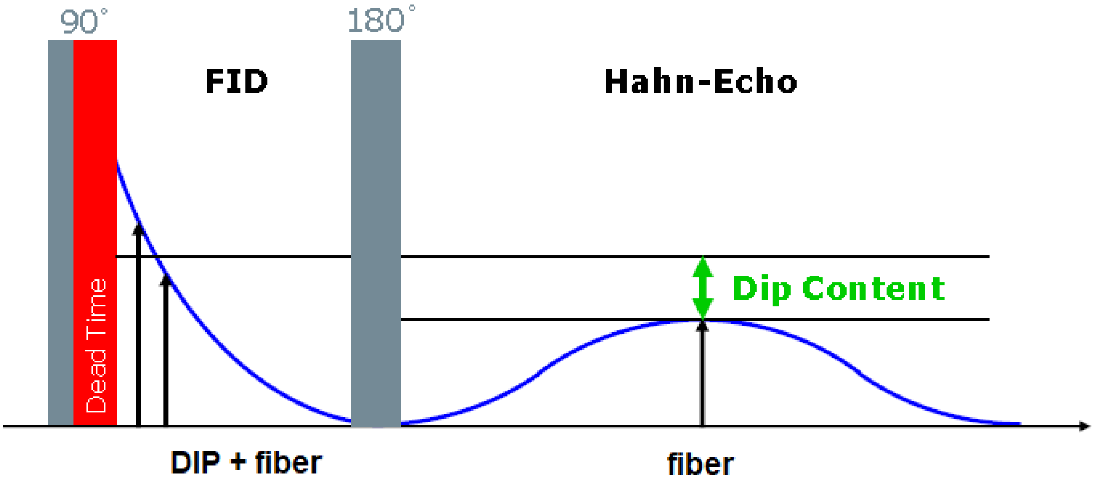

Figure 9 – Hahn echo sequence representation (Adapted from Bruker, 2016).

Nowadays the urge to a better product quality with an optimum use of equipment and energy keeps increasing. A reliable process analytical technology, like the TD-NMR method, to control and assure the product quality is an increasingly advantage to industries, such as C-ITA. Providing that the instrument has been correctly calibrated, the results are much reliable when compared to the traditional wet chemical method (Dalitz *et al*, 2012).

2.3 Statistical Analyses

Statistics is considered the science of data used in many fields such as engineering. It deals with the collection, presentation, analysis and use of data in order to make decisions to a variety of problems. It is also useful to design and apply new products and processes. The field in which the methods used to make decisions and draw conclusions about populations[1] is called statistical inference and can be dived in two areas: parameter estimation and hypothesis testing (Montgomery *et al*, 2003).

2.3.1 Hypothesis Testing

A statistical hypothesis test is often used in a data analyses stage of a comparative experiment. It is a statement about the one or more populations' parameters, as, for example, the mean or variance. It enables the comparison between a population's parameter to a specified value, or to another parameter of a different population (Montgomery *et al*, 2003).

In the hypothesis test, two statements are formulated: the null hypothesis (H_0) – considered true – and the alternative hypothesis (H_1). To test a hypothesis is devised a procedure for taking a random sample, computing an appropriate test statistic and then rejecting or falling to reject the null hypothesis based on the test's value. There are two types of error that may occur when testing hypotheses. If a null hypothesis is rejected when is true, it is called a type I error. If the null hypothesis is not rejected when it is false, a type II error has occurred. In hypothesis testing the procedure is to specify a value of the probability of type I error α, called significance level of the test (Montgomery, 2017).

To compare the variances of two populations, each following a normal distribution, the null hypothesis states that the two variances of each population are equal – Equation 3. The alternative hypothesis states that the variances are not equal – Equation 4.

$$H_o: \sigma_1^2 = \sigma_2^2 \tag{3}$$

$$H_1: \sigma_1^2 \neq \sigma_2^2 \tag{4}$$

In which σ_1^2 is the variance of a population with mean μ_1 and σ_2^2 is the variance of a second population with mean μ_2. Let $X_{11}, X_{12} \dots X_{1n_1}$ be a random sample from the population with the variance σ_1^2 and mean μ_1, and $X_{21}, X_{22} \dots X_{2n_2}$ be a random sample from the second population with variance σ_2^2 and mean μ_2. Knowing that S_1^2 and S_2^2 are the sample variances, the ratio

$$F_0 = \frac{S_1^2}{S_2^2} \tag{5}$$

---

[1] In the present context, population means any finite or infinite collection of individual units or objects.

has a Fisher-Snedecor distribution with $n_1 - 1$ and $n_2 - 1$ degrees of freedom. The null hypothesis would be rejected if $F_0 > F_{\frac{\alpha}{2}, n_1-1, n_2-1}$ or $F_0 < F_{1-\frac{\alpha}{2}, n_1-1, n_2-1}$, in which $F_0 > F_{\frac{\alpha}{2}, n_1-1, n_2-1}$ is the upper $\frac{\alpha}{2}$ percentage point and $1 - \frac{\alpha}{2}$ is the lower percentage point of the Fisher-Snedecor distribution with $n_1 - 1$ and $n_2 - 1$ degrees of freedom (Montgomery, 2017).

For the hypothesis test of the means of two populations, with equal variances, that follow a normal distribution, the null hypothesis states that the means are equal, while the alternative hypothesis states the contrary – the means are not equal.

$$H_o: \mu_1 = \mu_2 \tag{6}$$

$$H_1: \mu_1 \neq \mu_2 \tag{7}$$

μ_1 and μ_2 are both means of populations 1 and 2, respectively.

The appropriate statistical test to do in this situation is the two-sample test in which the result is given by the following equation,

$$T_0 = \frac{\overline{Y_1} - \overline{Y_2}}{S_P\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \tag{8}$$

$$S_P^2 = \frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2} \tag{9}$$

where $\overline{Y_1}$ and $\overline{Y_2}$ are the sample means, n_1 and n_2 are the sample sizes, S_1^2 and S_2^2 are two individual sample variances. The denominator in the Equation 8 is called standard error of the difference between the means in the numerator. To know the test results T_0 must be compared to the t-*Student* distribution with n_1 + n_2 – 2 degrees of freedom. To reject the null hypothesis, $|T_0| > T_{\frac{\alpha}{2}, n_1+n_2-2}$, where $T_{\frac{\alpha}{2}, n_1+n_2-2}$ is the upper $\frac{\alpha}{2}$ percentage point of the t distribution with n_1 + n_2 – 2 degrees of freedom (Montgomery, 2017).

A more practical way to report the results of a hypothesis test at a specified α-value or level of significance is through the p-value approach. In a formal definition, the p-value is the smallest level of significance that would lead to rejection of the null hypothesis (*H₀*) 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 (Montgomery et al., 2003).

2.3.2 Confidence Interval

To have a good estimation of the unknown parameters is necessary to use a confidence interval (CI). The confidence interval of a certain parameter θ is an interval with the form $l \leq \theta \leq u$. The values *l* and *u* are endpoints calculated from the given data based on the probability theory. The probability theory states that there is a probability of 1-α of selecting a sample for which the true value of the parameter θ is contained by the confidence interval. Thereby, if in repeated random samplings, a large number of such intervals are constructed, 100(1-α) % of them will contain the true value of θ. The margin of error of the interval estimate of θ equals half the confidence interval amplitude. The 100(1-α) % confidence interval for θ can be used as decision criteria to reject or not the null hypothesis on one hypothesis test. For the parameter θ, the test size α of the hypothesis

$$H_o: \theta = \theta_0 \tag{10}$$

$$H_1: \theta \neq \theta_0 \tag{11}$$

leads to the rejection of the null hypothesis if and only if θ_0 is not in the 100(1-α) % confidence interval (Montgomery *et al*, 2003).

2.4 Assessment of previous work

Even though the TD-NMR method is quite recent in C-ITA, work has already been made with this device. A calibration curve (Figure 10) was already been made and validated for the Nylon 940 textile, ergo the D_{PU} can be measured by the TD-NMR device.

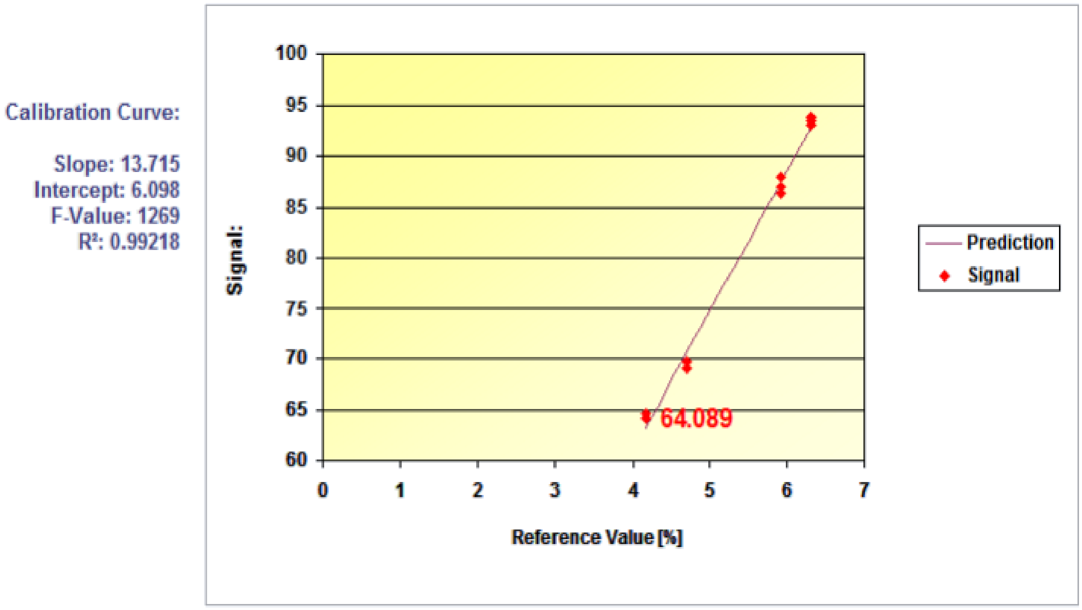

Figure 10 – Nylon 940 calibration curve.

A serial of other factors that may influence the D_{PU} results were also studied in previous works. Some of the factors regarding the sample preparation of the TD-NMR method (described in chapter 3), and others concerning the dipping process of the cords were studied. When it comes to the preparation of samples by the TD-NMR method the proper drying and handling of the samples was studied. Both showed influence on the TD-NMR results, as inappropriate drying leads to an increase of D_{PU} and the absence of gloves in the sample preparation also affects the D_{PU} results.

For the dipping process, the factors studied were the solid content of the dipping solution, passing velocity in the LDU, oven temperature and cord stretch. Due to experimental runs and statistical analyses, it was determined that the factors which showed a higher influence in the D_{PU} results were the S_C (which showed the highest effect), the velocity and the interaction between temperature and S_C.

3 Materials and Methods

In this chapter, the materials and methods used throughout this project are presented. The project is divided into three parts. In the first part, the only method applied was the dip pick-up measurement using the TD-NMR machine. Additionally, using statistical analyses, it was possible to achieve a new TD-NMR sampling method.

The second part consisted of calibrating the TD-NMR machine for PET textile, for that a calibration curve was computed using the wet chemical method and other using the weighing method. Furthermore, it was studied if the calibration curve could also be used to measure the D_{PU} in other PET textiles with different suppliers and dtex. Once again, it was necessary to use a series of statistical tests to see if it was possible to validate the calibration curve for all PET textiles.

In the third and last part of the project, the main goal was to study the textile and DIP constitution influence in the TD-NMR. It was made a calibration curve for nylon 940 with a different DIP. As it can be seen in Table 1, this curve was later compared to the curve shown in Figure 10 and the PET calibration curve, trough statistical analyses.

Table 1 – Calibration Curves schematization.

Calibration curves	Previous Work	Project’s Second Part	Project’s Third Part
Nylon 940	Created and validated		Comparison between all curves
PET		Created and validated	
Nylon with Rayon’s DIP			Created and studied

3.1 Dipping process

As already mentioned in chapter 2, C-ITA has a machine called Lab Dipping Unite (LDU), shown in Figure 11, to replicate the dipping units, only on a laboratory scale.

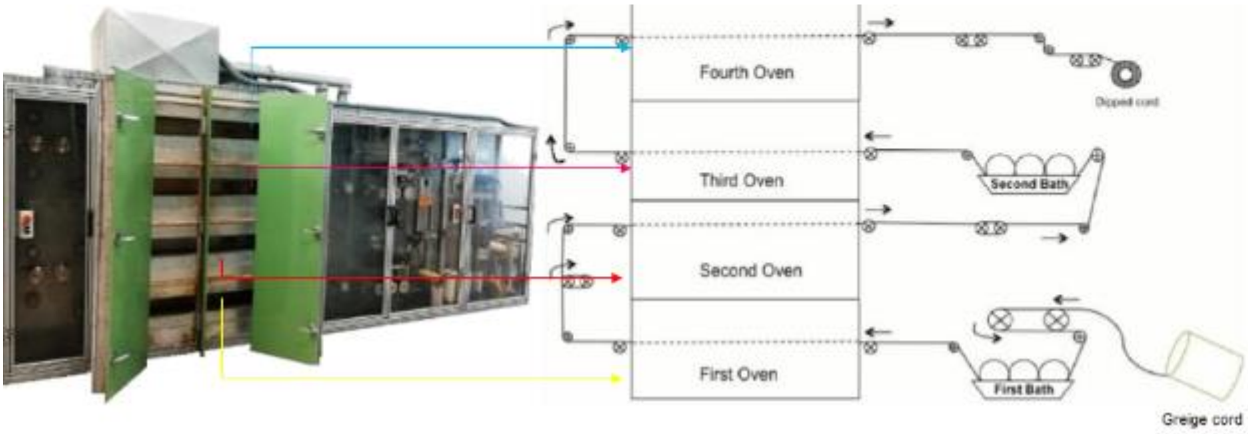

Figure 11 – LDU machine on the left and LDU scheme on the right (adapted from Martins, 2013).

In this project, two different textiles were used: nylon and non-activated PET. Conditions in the LDU machine such as velocity, stretch and oven temperature were used according to the textile used. For the nylon textile, it was only used the first bath and the first and second oven. In the second part of the project, the textile used was non-activated so the second bath and the third and fourth oven were only used when a pre-DIP was required. The DIP used in this project was also different for each textile.

3.2 DPU measurement

3.2.1 Weighing method

In C-ITA, the dipped cords and fabrics produced in the Single-End and Zell units, have a certain amount of D_{PU} that needs to be measured for quality control. For some textiles, such as PET, the wet chemical method requires a long amount of time to the fibers be dissolved. Thereby, since these have a low hygroscopic nature, the weighing method is applied to these types of textiles. To do so, it is important to have a dipped cord and a greige cord that has been thermofixed in the PET's dipping conditions.

The procedure consists in cutting ten samples with ten meters each, as it can be shown in Figure 12. Afterward, they are dried in the oven for an hour at 105ºC and later weighed.

Figure 12 – Samples used in the weighing method.

3.2.2 Wet chemical method

In this project, the wet chemical method was used for each textile, so the results could be used to calibrate the TD-NMR device.

To measure the amount of dip pick-up in textile fibers, via wet chemical method, it is necessary to proceed according to the following protocol.

1. Cut the dipped cord in small pieces, with a maximum length of 0.5 cm, until obtaining a sample with at least a weight of 1 gram for nylon and rayon cords, and 3 grams for PET cords. The sample mass is registered and corresponds to m1 of Equation 2.
2. Dissolve the sample with a suitable solvent for a defined amount of time. The solvents and time are established according to Table 2.
3. Filtrate the sample using a previous weighted crucible (m_2), a washing fluid and a pump system. The washing fluid is established in Table 2.
4. Dry the crucible containing the dip pick-up, in an oven for a minimum of two hours.
5. Cool down the crucible in a desiccator until room temperature.
6. Weight the crucible. The registered mass will correspond to m_3 of Equation 3.

In Figure 13 it is possible to see the protocol's steps.

Table 2 - Textiles' solvents and washing fluids

Textile	Solvent	Dissolution time (h)	Washing Fluid
Nylon	Formic acid 85 % - 50 mL	1	Formic acid 85 % - 50 mL + Water – 50 mL
PET	Potassium hydroxide solution 34 % – 100 mL	3	Water – 1000 mL

Figure 13 - DIP measurement via wet chemical method for nylon textiles.

3.2.3 Time Domain Nuclear Magnetic Resonance

3.2.3.1 Sample preparation

For measuring the amount of dip pick-up in the samples with the TD-NMR device the following procedure must be done:

1. Identify the samples tubes and measure its weight with the caps on.
2. Cut a piece of cord with a 3-meter length.
3. Prepare the sample and put in the tube according to Figure 14.
4. Put the tubes, without caps, in the oven for at least one hour.
5. After one hour take out the tubes and immediately put the caps on. Leave it to cool down for about 30 minutes.
6. Weight the samples again. Afterwards, heat them up to 40ºC in the heating device.
7. Measure each sample with the TD-NMR device.

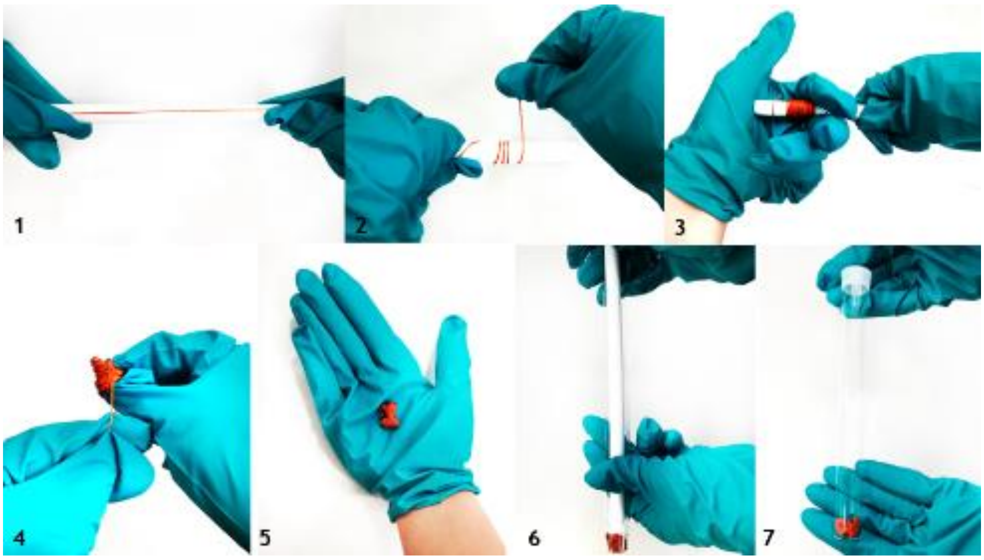

Figure 14 - Sample preparation for the TD-NMR method.

3.2.4 New method for TD-NMR sampling

Currently, to use the TD-NMR device, the samples must be tied up in a bow form and should not have more than 2 cm length. Since the samples are very small it can be quite difficult to make, which could consist in a problem when this device will be used on a current basis in the production section of C-ITA. An easier and faster alternative to prepare the samples is to cut the cord, as it is done in the wet chemical method.

In order to use the new method is necessary to do an analysis to see if the device results are not affected by the way the samples are prepared. To do so, 60 samples were prepared and measured with the same cord: nylon 470. Of the 60 samples, 30 were made by the traditional method – bows – and the other 30 were cut into small pieces, as it can be seen in Figure 15. It was made sure that the samples had a similar weight and the samples' height was also measured for the new method.

Figure 15 - Different sampling method.

3.3 Calibration curves

For both second and third part of the project, calibration curves were made for two types of textiles. A calibration curve for the PET textile was made in the second part of the project, it was also tested if this curve could be used in other PET textiles with different dtex and suppliers. In the project's third part a calibration curve was made for nylon 940 textile dipped with rayon's DIP.

To create a calibration curve is necessary to have four cords with a specified amount of D_{PU}. To do so is necessary to dip those cords with the amount of S_C necessary to obtain the required values of D_{PU}. Oftentimes, more than four cords are dipped until obtaining the desired ones. The D_{PU} values are measured by the wet chemical method, and later with those values and the values of S_C for each cord, the calibration curve is computed. According to the type of textiles D_{PU} values vary as it can be seen in Table 3.

Table 3 – D_{PU} necessary to each cord for each textile's type.

Type	Cord	D_{PU} value				
		-1 % LTL	LTL*	Target value	UTL**	+1 % UTL
PET	1	Between 0.5 % and 1.5 %.				
	2		Between 1.5 % and 2.5 %.			
	3			Between 2.5 % and 3.5 %.		
	4				Between 3.5 % and 4.5 %.	
Nylon	1	Between 3.5 % and 4.5 %.				
	2		Between 4.5 % and 5.5 %.			
	3			Between 5.5 % and 6.5 %.		
	4				Between 6.5 % and 7.5 %.	

*LTL – Low Target Limit; **UTL – Upper Target Limit

The target values are 2.5 % and 5.5 %, the LTL values are 1.5 % and 4.5 %, and the UTL are 3.5 % and 6.5 % for PET and nylon, respectively.

4 Results and discussion

It is important to enhance that the TD-NMR machine reads the amount of dip pick-up in the sample, being the sample dipped cord. Thereby, the result of the TD-NMR device is the percentage of dip pick-up per dipped cord (Equation 13). Since the D_{PU} is defined as the amount of dip pick up per greige cord (Equation 12), it is necessary to convert the values obtained by the device.

$$D_{PU_{per\ greige\ cord}} = \frac{m_{DIP}}{m_{greige\ cord}} \times 100 \tag{12}$$

$$D_{PU_{per\ dipped\ cord}} = \frac{m_{DIP}}{m_{dipped\ cord}} \times 100 \tag{13}$$

$$m_{greige\ cord} = m_{dipped\ cord} - m_{DIP} \tag{14}$$

Combining the equations above:

$$m_{DIP} = \frac{D_{PU_{per\ dipped\ cord}}}{100} \times m_{dipped\ cord} \tag{15}$$

$$D_{PU_{per\ greige\ cord}} = \left(\frac{\frac{D_{PU_{per\ dipped\ cord}}}{100}}{1 - \frac{D_{PU_{per\ dipped\ cord}}}{100}} \right) \times m_{dipped\ cord} \tag{16}$$

Dividing the Equation 15 for $m_{dipped\ cord}$ and multiplying by 100:

$$D_{PU_{per\ greige\ cord}} = \frac{D_{PU_{per\ dipped\ cord}}}{100 - D_{PU_{per\ dipped\ cord}}} \tag{17}$$

Therefore, is possible to convert the TD-NMR results in D_{PU} ($D_{PU_{per\ greige\ cord}}$) with Equation 17. All the values of the TD-NMR machine presented in this project are already converted in dip pick up percentage per greige cord.

Throughout this work the results were analyzed in the program Minitab that provides statistical guidance for interpreting statistical tables and graphs in a practical way.

4.1 New method for TD-NMR sampling

As already mentioned in section 3.2.4, 30 samples were made in a bow form and other 30 were made by cutting the cord in small pieces. The population that contains the 30 samples in a bow form was named “laces”, and the population with 30 samples that were cut was named “cuts”. The D_{PU} was measured for all the samples in the TD-NMR machine, and the results are presented in Table A.1.1.

First, it was made a hypothesis test for the variances of each population, where the null hypothesis states that the variances of each population are equal. For that, a variance test was done to determine whether the variances or the standard deviation of the two groups differ.

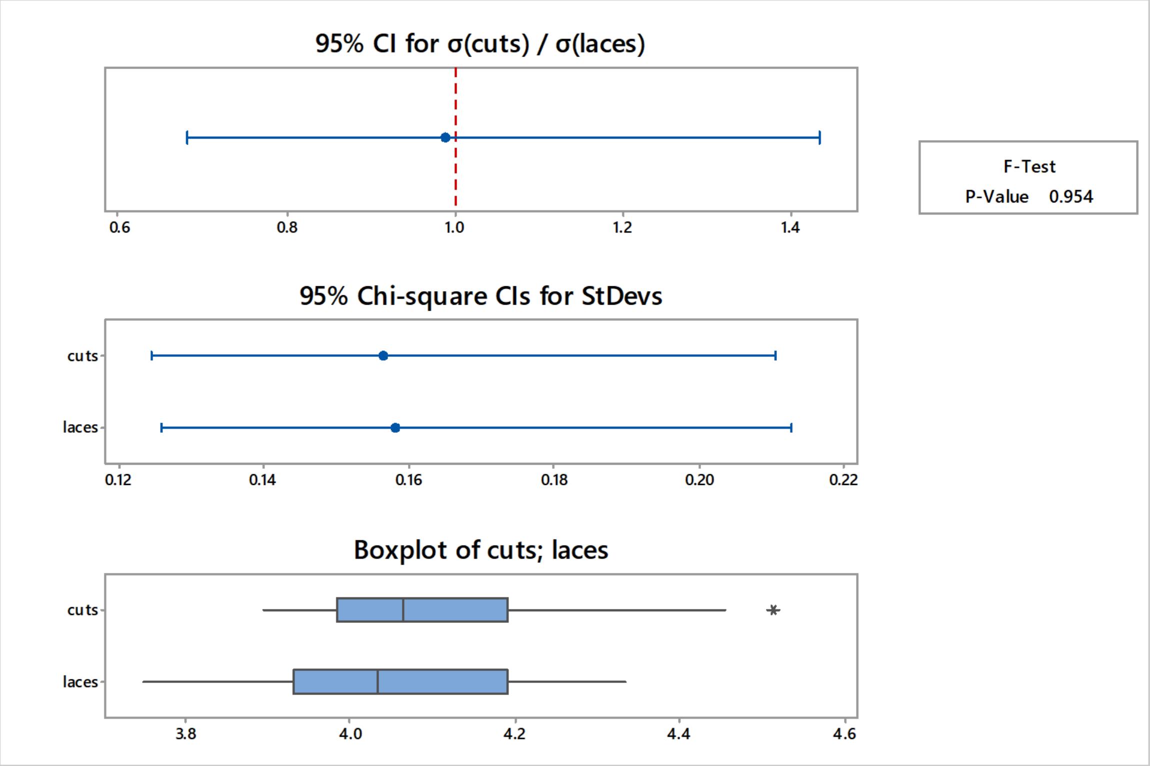

Figure 16 – Variance test results for laces and cuts samples.

From Figure 16, it is possible to verify that the null hypothesis is not rejected, for a significance level of 5 %, since the p-value is higher than 0.05 (0.955 and 0.679 for both Bonett's test and Levene's test, respectively). Hence, it is possible to affirm that both populations have equal variances.

Knowing that both populations have equal, but unknown, variances, a hypothesis test to the means of each population was made using 2-sample t test. This test determines whether the means differ significantly between two groups. The test was made for a significance level of 5 % and p-value obtained was 0.094. Since the p-value is higher than 0.05 the null hypothesis is not rejected, so the means do not differ significantly.

Figure 16 also shows a deviated value for the *cuts* results in the boxplot section. To see if the largest or smallest value of the population is an outlier, an outlier test was run in the Minitab program. In this test, the null hypothesis states that all values in the sample are from the same normally distributed population. The results are shown in Figure 17.

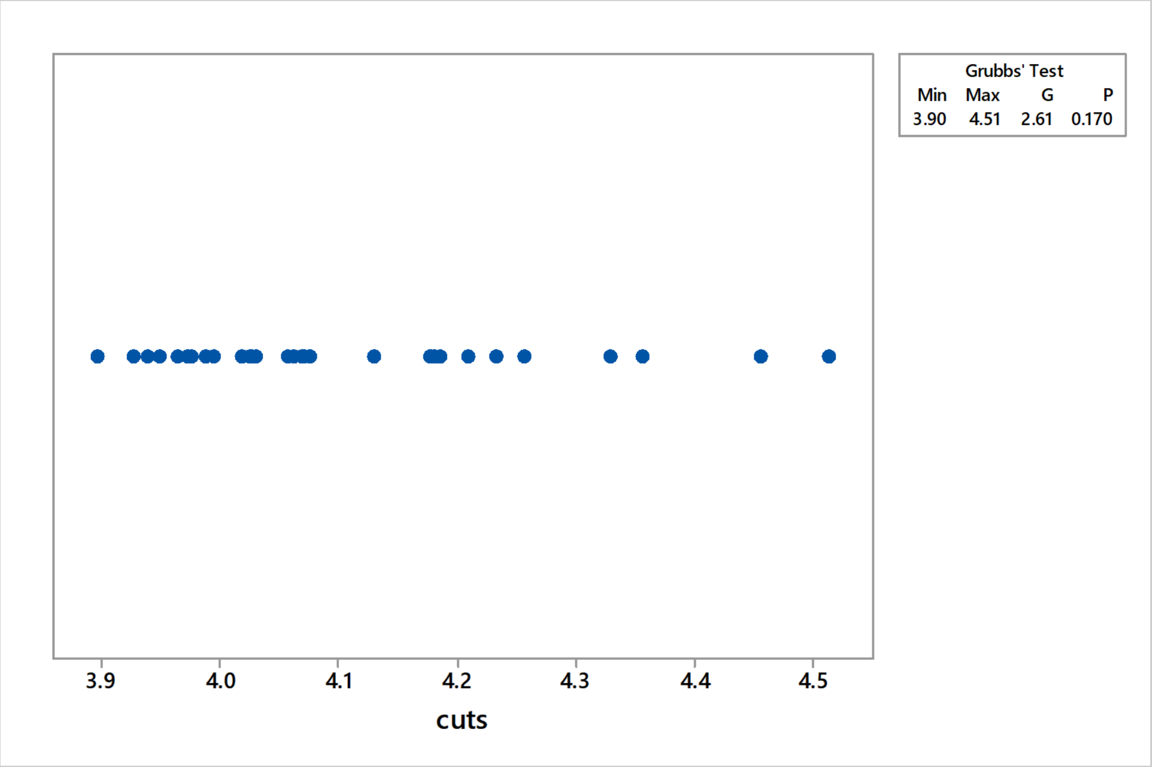

Figure 17 – Outlier plot and test results for cuts samples.

The p-value obtained in the test (0.170) is far superior to 0.05, so the null hypothesis is not rejected, so, it can be said that all the samples belong to the same normally distributed population.

For TD-NMR sampling, it was advised to use samples with a height inferior to 2 cm, which consists in a problem for the new method. Because the cut cord tends to be less compact, when compared to the samples in a bow form, it occupies more space inside the test tube increasing the sample's height. Thereby, as it was mentioned in 3.2.4 section, the height of each sample from the *cut* population was measured by a ruler to verify its influence on the TD-NMR result. The height of each sample is also attached in Table A.1.1.

A correlation test was performed in the program Minitab. The methods used in this test are the Pearson correlation, that calculates the linear correlation coefficient for each pair of variables, and the Spearman rank-order correlation, that calculates the rank-order correlation coefficient for each pair of variables. For both tests the p-value obtained was higher than 0.05, 0.055 for Pearson correlation and 0.275 for Spearmen correlation. Since the null hypothesis was not rejected, it appears that, for the range of heights measured, the height of the sample does not influence the TD-NMR result, despite some samples having a height equal to 2.5 cm.

In regard to TD-NMR sampling, taken into consideration the tests performed for both *laces* and *cuts* populations, the new methodology can be used to prepare the samples.

4.2 PET calibration curve

To investigate the difference between the wet chemical method and the weighing method, two calibration curves were made. Thereby, after obtaining the four cords necessary to do the calibration curve by the wet chemical method, the D_{PU} of each cord was also measured by the weighing method. The cords were made of a PET textile with a 2200 dtex and a certain supplier, this PET textile will be named *PET_{2200}*.

To obtain the correct value of D_{PU} is necessary to perform wet chemical method multiple times until obtaining three values in which the standard deviation is lower than 0.4 %. The final D_{PU} value is the average of those three values. The values of each trial for the wet chemical and the weighing method are attached in Table A.2.1 and Table A.2.2, respectively. The final D_{PU} result for each method is shown in Table 4.

Table 4 – D_{PU} measurements by wet chemical and weighing methods.

Cord	$D_{PU\ wet\ chemical}$ (%)	$D_{PU\ weighing}$ (%)	Difference (%)
1	1.47	2.77	1.30
2	1.89	3.40	1.51
3	3.36	4.40	1.04
4	3.80	4.52	0.72

For the same cord the results obtained by both methods are quite different, in most cases higher than 1 %. It appears that the weighing method is not the most appropriated for measure the D_{PU}, so a further analysis of this process should be done in the future.

Figure 18 and Figure 19 shows the calibration curves for the wet chemical and the weighing method, respectively.

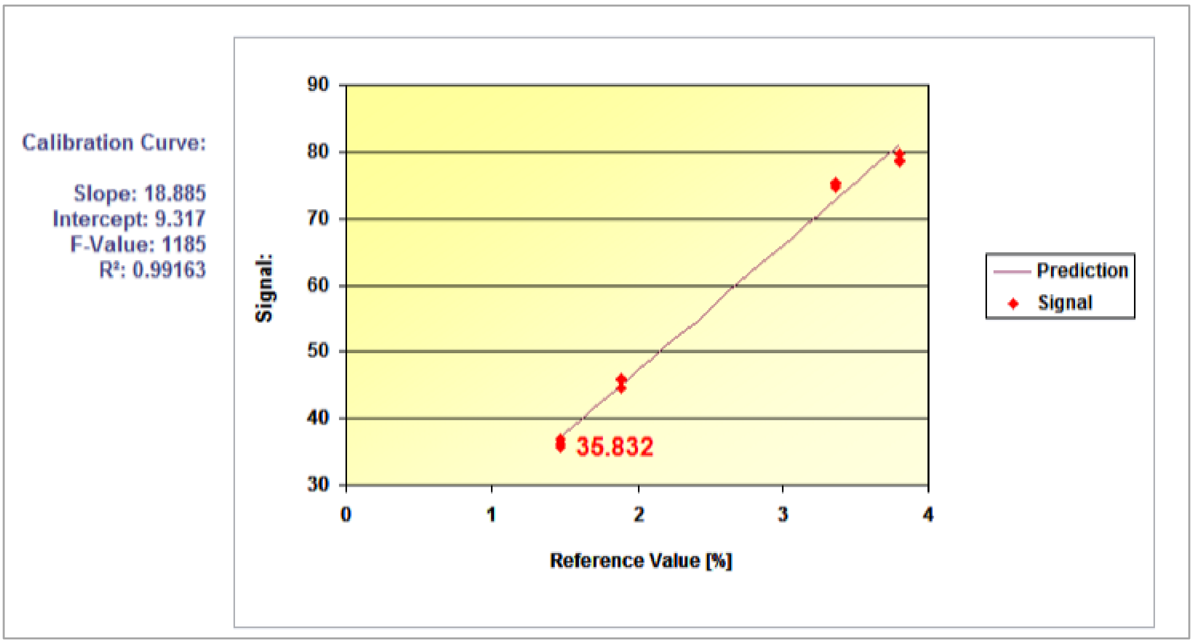

Figure 18 – PET_{2200}'s calibration curve with D_{PU} results obtained by the wet chemical method.

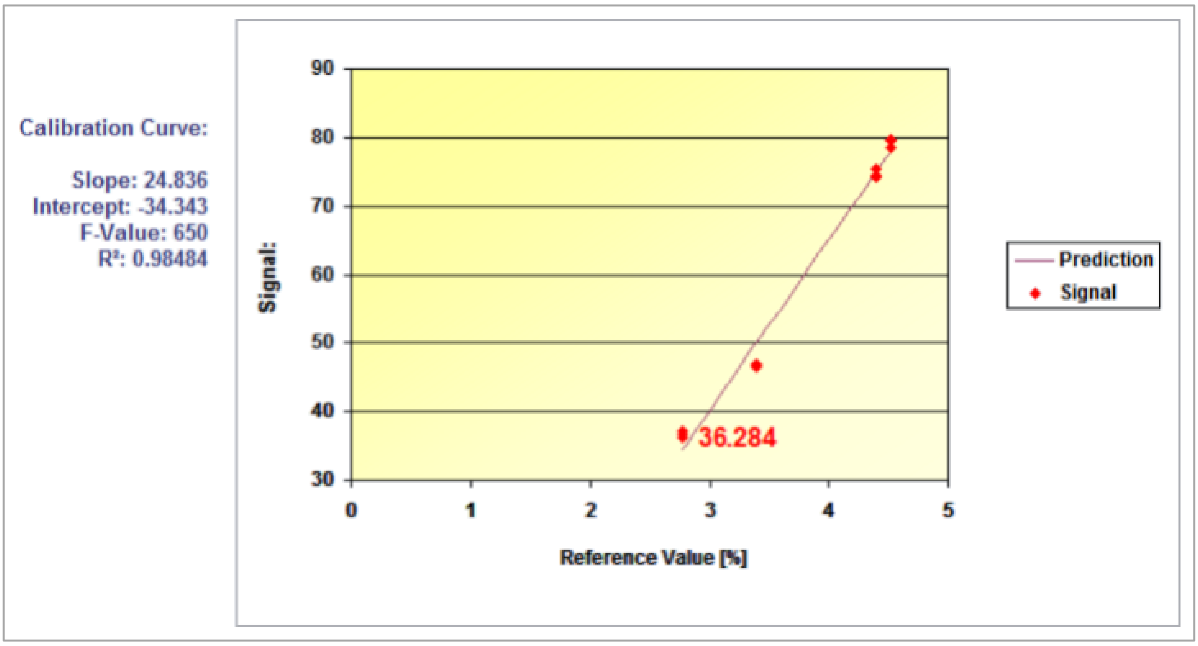

Figure 19 - PET_{2200}'s calibration curve with D_{PU} results obtained by the weighing method.

The curve obtained by the wet chemical method will be named wet_{curve}, the one obtained by the weighing method will be wei_{curve}. Despite the significant difference of D_{PU} values shown in Table 4, in a first analysis, both wet_{curve} and wei_{curve} seem suitable since the coefficient of determination (R^2) is higher than 0.900, 0.992 for wet_{curve} and 0.985 for wei_{curve}. Even though both curves seem to be acceptable, it is necessary to verify if both can be used to measure the amount of DIP. To do so, 30 samples from the production, of the same type of textile (same supplier, dtex and dipping conditions) used to compute the calibration curve were measured for both curves. The samples were obtained from the Zell machine.

The 30 samples obtained by the production were collected throughout a certain period, this means that the day in which these were produced differs, some can be produced on the same day as others could be produced in the month before. Even though the samples are from the same type of PET textile, and the conditions and DIP recipes applied to the dipping production are stablished, in an industrial level, it is difficult to obtain the same exact conditions in different time frames.

4.2.1 Zell results

The samples were measured in the TD-NMR machine using the *Wet curve* and *Wei curve*. Each sample was measured three times, so for each curve, 90 measures were made. To verify the curves accuracy, the results obtained by each curve were compared among themselves and with the values obtained by the production department. In Table A.2.3 (attached) is possible to see the average of D_{PU} for each sample according to the curve used to do the measurement and the values of D_{PU} obtained by the production department for each sample. The D_{PU} values of the TD-NMR obtained using the wet_{curve} will be named *Wet*, the ones obtained by the wei_{curve} will be named *Wei* and the production values will be named *Production*.

First, it was made a scatterplot (Figure 20) to see if the results for the curves and the production laid in the same range of values. The x-axis is the sample number and the y-axis the D_{PU} value. In a first approach, it is noticeable that *Wei* values are higher compared to the rest.

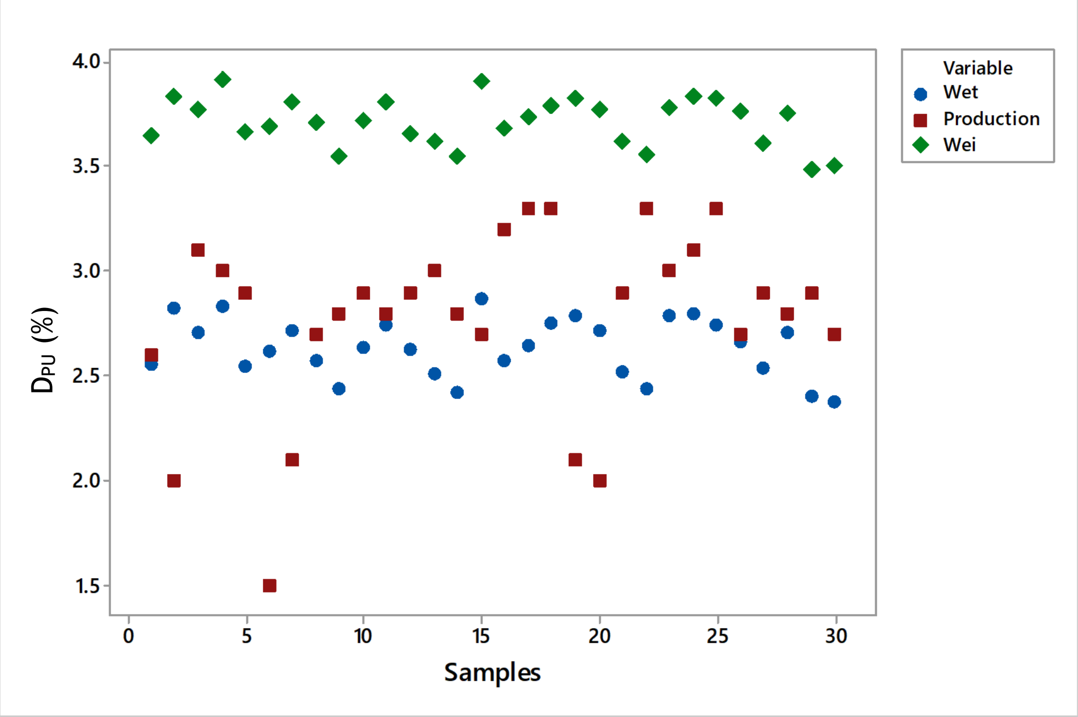

Figure 20 – Scatterplot for Wet, Wei and Production samples.

A one-way ANOVA test was made, with the null hypothesis stating that all means are equal. Equal variances were assumed for analyses. The results showed a null p-value, meaning that at least one mean is different from the others. Additionally, a Tukey pairwise comparison among means was done to identify the different ones. This test creates confidence intervals (CIs) for all pairwise differences between the means of populations (*Wet*, *Wei*, and *Production*). The results are shown in Figure 21 and Table 5.

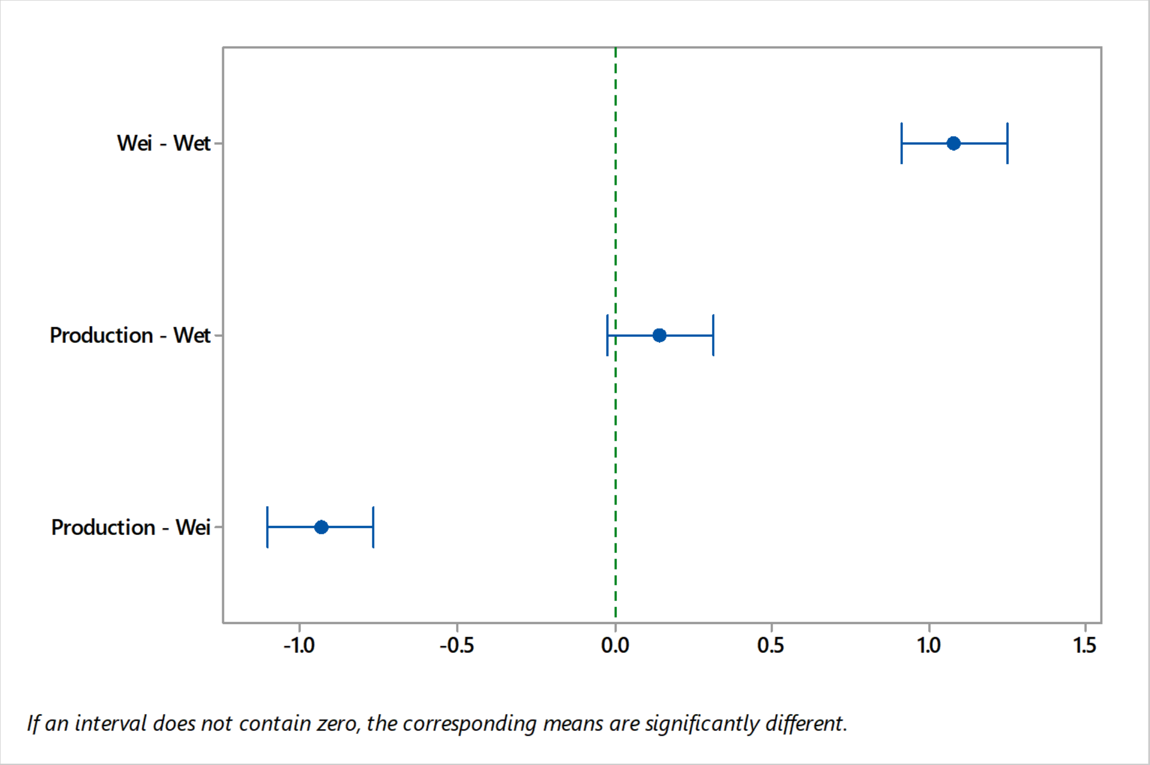

Figure 21 – Tukey CIs for differences of means for Wet, Wei and Production populations.

In Figure 21, only the *Wet-Production* pair has a confidence interval that contains the zero, meaning that the means of these two populations are not significantly different. Additionally, in Table 5 the p-value obtained for this comparison is higher than 0.05, thus the null hypothesis is not rejected. Therefore, it is possible to conclude that the wet_{curve} can be used to measure the amount of D_{PU} as the results demonstrated that the means of both populations are equal.

Table 5 – Tukey pairwise comparison results for Wet, Wei and Production populations.

Difference of Levels	Difference of means	Confidence Interval	p-value	Margin of error
Wei - Wet	0.0108	(0.00911; 0.0125)	0.000	0.00168
Production - Wet	0.00141	(-0.000268; 0.00309)	0.117	0.00168
Production - Wei	0.00937	(-0.0111; -0.00769)	0.000	0.00168

For the *Wei* population, the results demonstrate that this is statistically different when compared to the *Production* population since in both cases the p-value is inferior to 0.05 and the confidence interval does not contain zero. Furthermore, between the *Wet* and *Wei* results and the *Production* and *Wei* results, the means differ more than 1 % (1.07 % ± 0.17 % for *Wei-Wet* and 0.94 % ± 0.17 % for *Production-Wei*), the standard limit in C-ITA, so the wei_{curve} cannot be used to measure the D_{PU} results. This is contradicting to what is expected because in the production department the D_{PU} is measured by the weighing method. One explanation to the difference between the *Wei* and *Production* may due to the fact that, even though the production section uses the weighing method, the methodology applied is a little different because the greige cord is not thermofixated.

A further analysis of the residuals of the D_{PU} values was made and the residual plots are shown in Figure 22. The residuals are the difference between the observed valued and the fitted response value. In the normal probability plot, on the left side, is possible to see a point further than the others indicating a presence of an outlier. Despite that, the residual graph does not indicate the existence of large deviations for the assumption of normality of random errors as the values appear to follow a linear shape. The residual versus fits plot shows that the assumption of equal variances to perform the ANOVA test does not appear to have severe problems. In addition, the residuals versus order plot shows that the residuals fluctuate in a random pattern around the center line, thus the values appear to be independent.

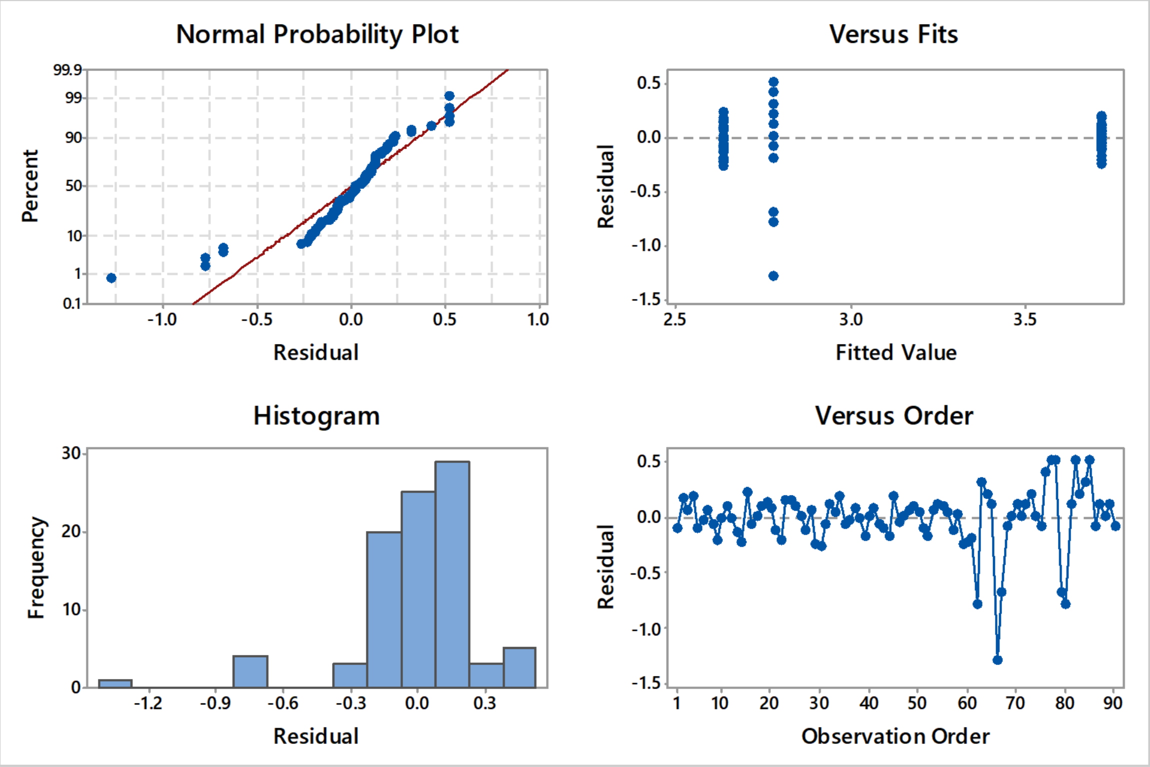

Figure 22 - Residual Plots for the D_{PU} values of Wet, Wei and Production.

4.2.2 Different dtex and supplier

To see if the calibration curve (wet_{curve}) can be used with all types of textile, it should be measured the D_{PU} of three other types of PET: one with the same dtex and different supplier than PET_{2200}, other with same supplier and different dtex, and other with a different supplier and dtex. To measure a different type of PET it is necessary to collect 30 samples of it. In this project, only the PET textiles presented in Table 6 were measured because C-ITA does not produce a PET textile with the same dtex of PET_{2200} and different supplier in the amount necessary. Thereby, for PET_{1440} and PET_{dif} 30 samples of each were collected from the production department and measured with the *wet curve*.

Table 6 – Characteristics of the different PET textiles

Dtex	Supplier	
	A	B
2200	✓ PET_{2200}	✗ Not measured
1440	✓ PET_{1440}	✓ PET_{dif}

4.2.2.1 Dtex

For PET_{1440}, the DPU results obtained by the TD-NMR device will be named Wet_{1440} and the production department will be named $Production_{1440}$, both are attached in Table A.2.4. A normality test was made to both populations' samples to verify if they followed a normal distribution, the results (attached in Figure A.2.1) for population $Production_{1440}$ presented a p-value inferior to 0.05, thereby this population does not follow a normal distribution. Even though, with a further analysis to the graph it does not appear to have a severe deviation from the normality assumption. Therefore, a variance test was done, assuming that both populations followed a normal distribution.

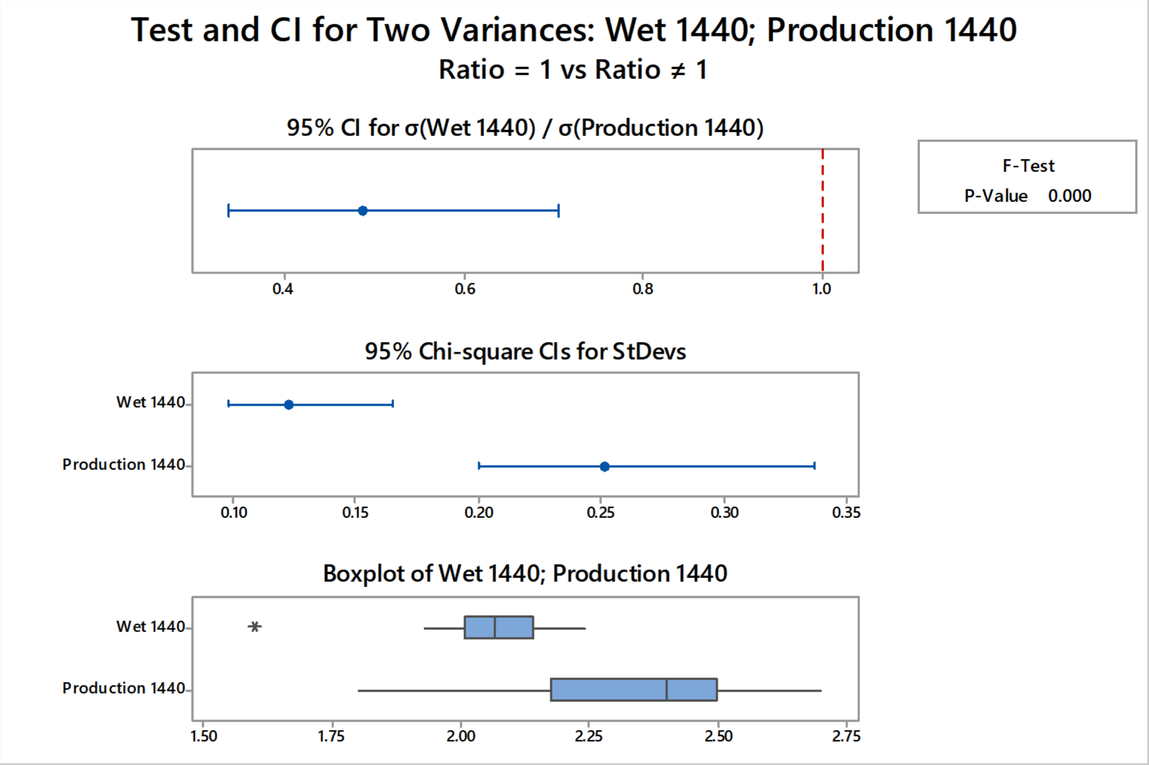

Figure 23 – Variance test results for Wet$_{1440}$ and Production$_{1440}$ populations.

In the variance test, the null hypothesis states that the ratio between the variances of each population is equal to 1, meaning they are identical. As it can be seen in Figure 23, the confidence interval does not contain the value 1, and the p-value is less than 0.001, thereby these populations do not have equal variances.

Since the variances of each population are not equivalent, a 2-sample t test was performed but without the assumption of equal variances. The results showed that the null hypothesis was rejected, as the confidence interval did not contain the value 0 and the p-value is null.

Table 7 – 2-sample t test results for Wet$_{1440}$ and Production$_{1440}$ populations.

p-value	Confidence Interval	Estimate for Difference of means	Margin of error
0.000	(-0.00365; -0.00159)	-0.00262	0.00103

Even though from a statistical manner the means are significantly different, it has to be taken into account a practical view. As it can be seen from Table 7, the means differ in 0.26 % ± 0.1 %, this difference is far inferior to 1 %, which, from a practical and industrial point of view, is not significant. Henceforth, the D_{PU} values of *PET*$_{1440}$ can be measured by the TD-NMR device.

4.2.2.2 Different dtex and supplier

For PET_{dif}, the results obtained by the TD-NMR device will be named *Wet_dif* and the production department will be named *Production_dif* and are also attached in Table A.2.5.

Similarly, to approach made for PET_{1440}, a normality test was made to both populations' samples and the results showed that the population *Wet_dif* does not follow a normal distribution since the p-value is below 0.05, as it is shown in Figure 24. This because the first two samples had a high D_{PU} value, this could happen if the dipping conditions for this samples were slightly different in the day these were made.

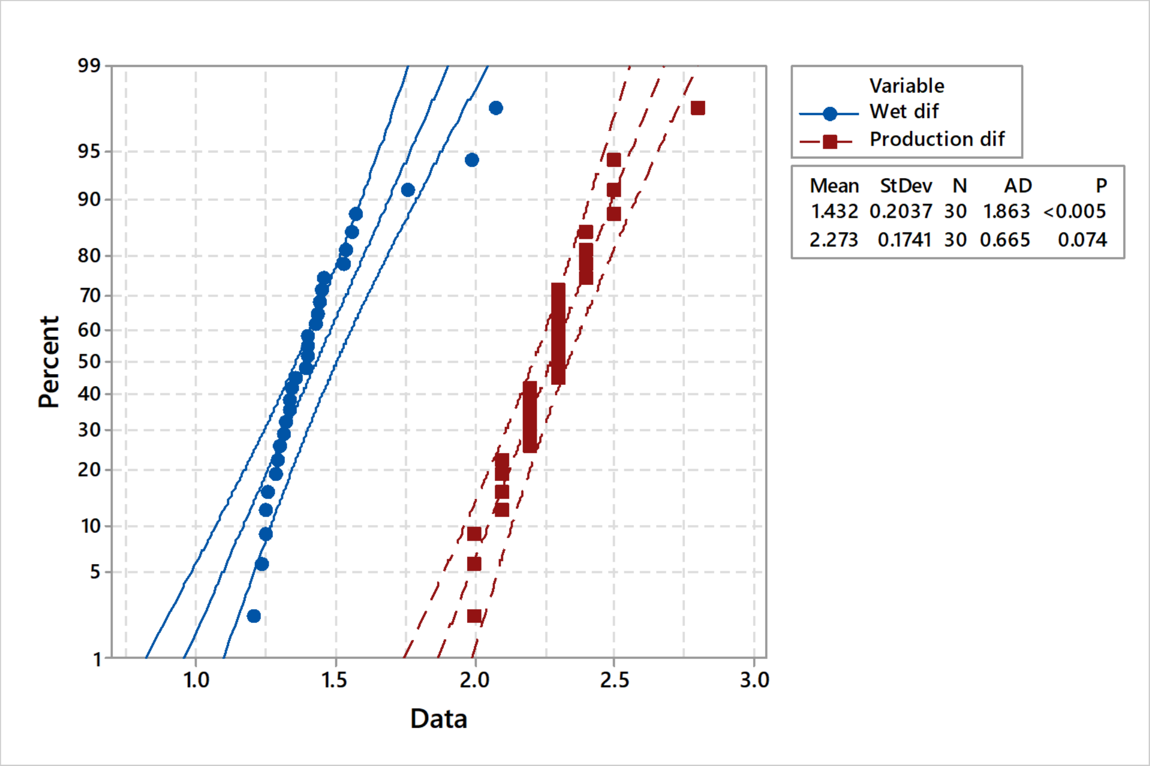

Figure 24 – Probability Plots for Wet_dif and Production_dif populations.

An outlier test was made to *Wet_dif* samples to identify if those two values were outliers. The results are presented in Figure A.2 2 (attached), since the p-value is inferior to 0.05 it appears that those values are outliers. Knowing that, a normality test was made to *Wet_dif* samples without the first two values of the 30 samples and the p-value was 0.231, much higher than 0.05. Therefore, without the first two samples, the *Wet_dif* population appears to follow a normal distribution.

A variance test (Figure 25) was made to both populations without the first two samples of each, assuming that both populations followed a normal distribution. The confidence level included the value 1 and the p-value is higher than 0.05, thus the null hypothesis is not rejected and the ratio between the variances is equivalent to one.

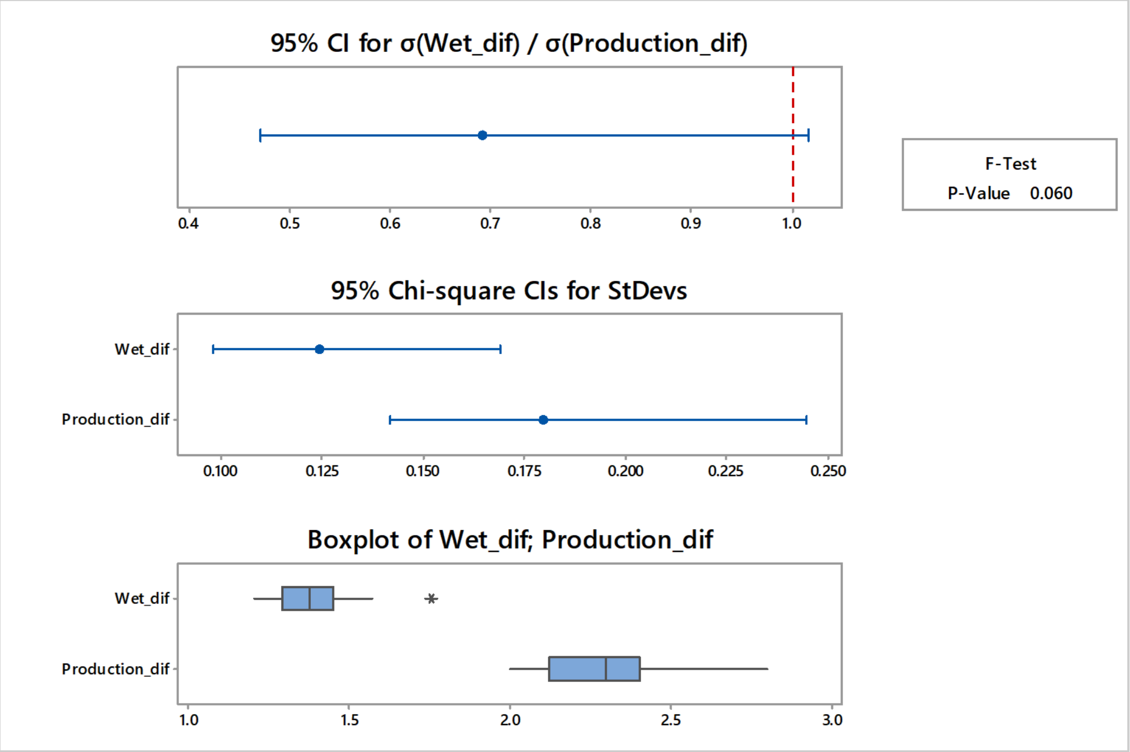

Figure 25 – Variance test results for Wet_diff and Production_diff populations.

Afterwards, it was made a 2-sample t test to the same samples assuming equal variances. The results presented in Table 8 show a p-value inferior to 0.05 and the confidence interval did not include value 0. Again, from a statistical point of view the means do differ, but in a practical manner the difference is inferior to 1 % (0.89 % ± 0.08 %) thus the TD-NMR device can be used to measure the D_{PU} for PET_{dif}.

Table 8 – Two sample t-test results for Wet_dif and Production_dif populations.

p-value	Confidence Interval	Estimate for Difference of means	Margin of error
0.000	(-0.00939; -0.00744)	0.00887	0.000830

So, for both PET_{1440} and PET_{dif}, the *wet curve* can be used to measure the D_{PU}. But to prove, with certainty, that all the other PET textiles can be measured by this curve they would have to be measured with the TD-NMR device, 30 samples at a time, an impractical conception for industries like C-ITA that have a large number of different PET textiles. In previous works, it was proven that the TD-NMR device could be used to measure all nylon fabrics with different dtex and supplier. So, in a practical view, this information combined with the fact that PET_{1440} and PET_{dif} can be measured by the TD-NMR device may infer that PET textiles, regardless the dtex and supplier, could be also measured by this device.

4.3 Textile and DIP constituent influence

The following section of the work is divided into two parts: the first regarding the study of the textile's influence in the D_{PU} measurements by the TD-NMR device, and the second concerning the study of the DIP constituents' influence in the D_{PU} measurements.

4.3.1 Textile's influence

It was decided to compare PET and Nylon textiles since their DIPs have the same constituents, only in different amounts. If the signal emitted is different it will be probably due to the difference between the textiles, on the contrary, if the signal is equal it will mean that the results present by the machine are not influenced by the sample's textile.

In that way, in this section, the samples of PET_{2200} used in section 4.2.1 were also measured using the nylon 940 calibration curve (obtained in previous work). The group of D_{PU} values obtained by this curve will be named *Ncurve* and are attached in Table A.3.1.

Even though the main goal of this study is to compare the values of each calibration curve for the different textiles, the values will also be compared to the production values to see if it is possible to validate nylon calibration curve to measure the D_{PU} in *PET_{2200}* samples.

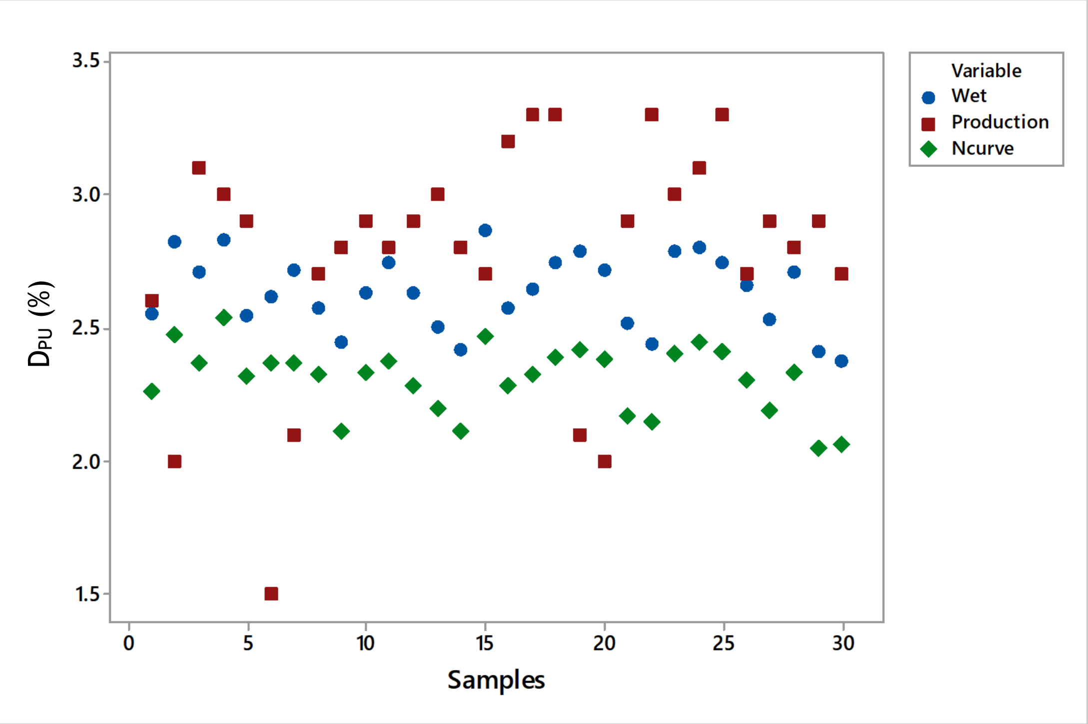

Figure 26 – Scatterplot for Wet, Ncurve and Production samples.

By the scatterplot (Figure 26) is possible to see that the *Ncurve* values seem to be lower when compared to the *Wet* values and *Production* values. But, contrary to the *Wei* values (shown in Figure 20), the *Ncurve* values seems much less deviated from the *Wet* and *Production* values.

A one-Way ANOVA was done for all populations, assuming equal variances, and, again, the p-value obtained was null, so there is at least one mean that differs from the other. For a better understanding of the means, a Tukey pairwise comparison was also made, and the results are showed in Figure 27 and Table 9. In Figure 27, is possible to see the confidence intervals for the difference of means between each population, once again only the pair *Wet-Production* contains the value zero. For the other two comparisons, in none of them, the difference between means seems to be null.

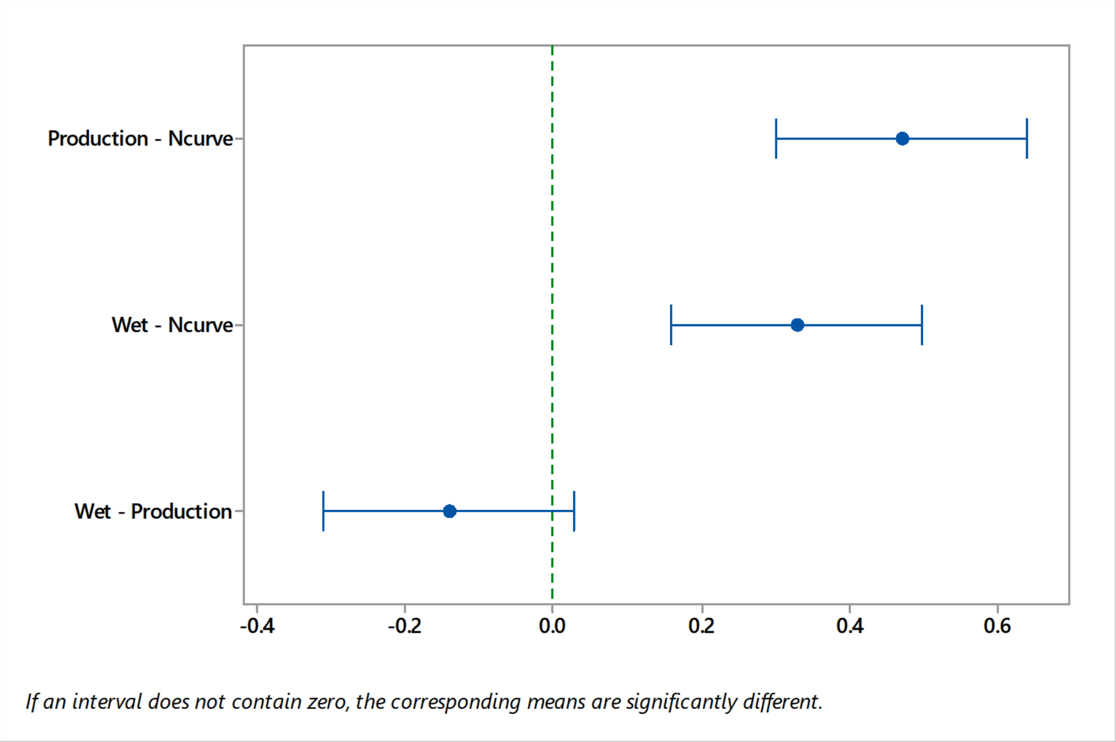

Figure 27 – Tukey CIs for differences of means for Wet, Ncurve and Production populations.

In Table 9 is possible to see the estimated difference of means of each pair of populations, to the pair *Production-Ncurve* and *Wet-Ncurve* the difference in means does not appear to be significant in practical point a view. Again, the confidence intervals for each pair of populations do not have the highest value superior to 1 %, as the difference between the means of the pair *Production-Ncurve* lays between the 0.30 % and 0.64 %, and between the pair *Wet-Ncurve* lays between 0.16 % and 0.28 % with a confidence of 95 % Thereby, in a practical way, the nylon calibration curve could also be used to measure PET_{2200}.

Table 9 – Tukey Pairwise Comparison results for Wet, Ncurve and Production populations.

Difference of Levels	Difference of means	Confidence Interval	p-value	Margin of error
Production - Ncurve	0.00470	(0.00301; 0.00639)	0.000	0.00169
Wet - Ncurve	0.00329	(0.00159; 0.000279)	0.000	0.00169
Wet - Production	0.00141	(-0.00311; 0.00498)	0.121	0.00169

An analysis of the residuals was made, the normal probability plot, in Figure 28, does not seem to show severe deviates from a normal distribution. The assumption of equal variances did not appear to cause problems as the fits plot does not show notable irregularities. Again, the values seem to be independent as they fluctuate around zero in the order plot.

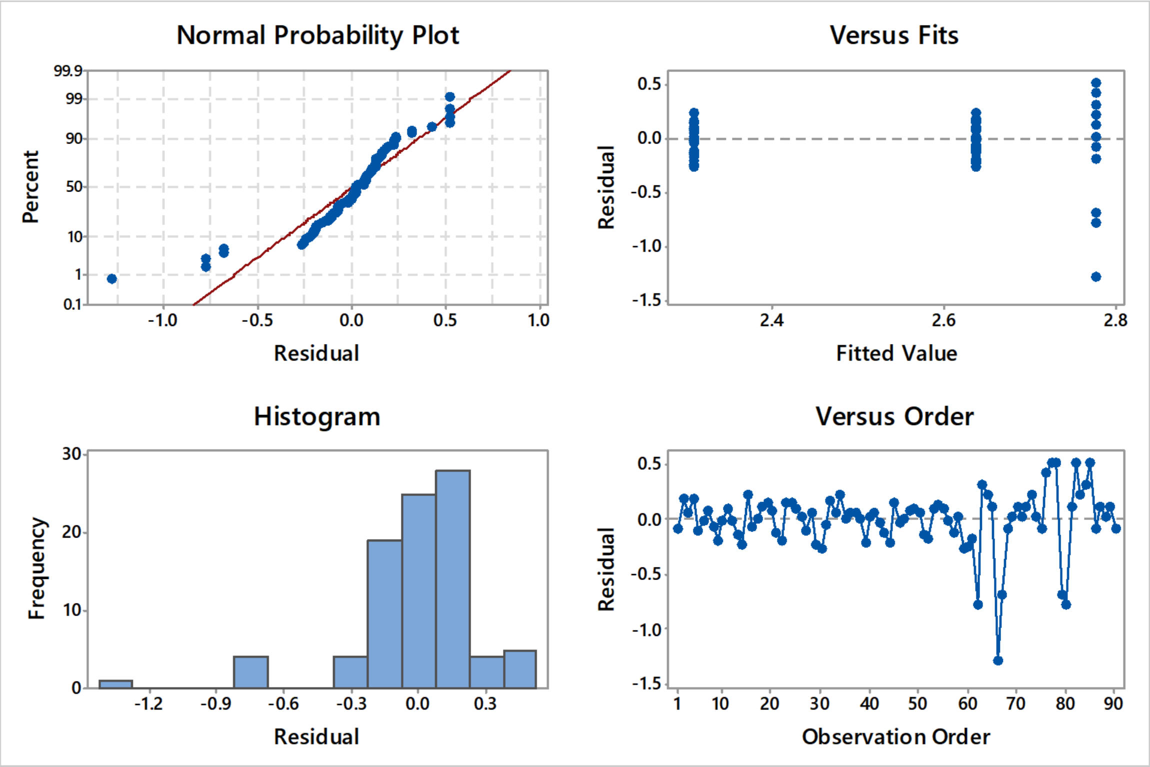

Figure 28 – Residual Plots for the D_{PU} values of Wet, Ncurve and Production samples.

Since statically there is a difference between the *Wet* and *Ncurve* results, in a first analysis, it appears that the TD-NMR has the sensibility to detect the differences between *PET_{2200}* and nylon textiles. This is contradictory to what is expected since the resultant signal in the device should only be originated by the DIP, because it relies on the difference between the signal of the cord plus the DIP and the cord without the DIP, as it is shown in Figure 9 in chapter 2.

Early it was explained that PET textiles need to be coated with a pre-solution to a proper adhesion to the rubber occur. The pre-DIP solution has a very low S_C, usually around the 2.3 %, but, as it was observed in previous works, the solid content has the highest effect on D_{PU}, so even a small percentage can influence the measurements. By Figure 29 is possible to see the relationship between the D_{PU} and S_C values for *PET*$_{2200}$.

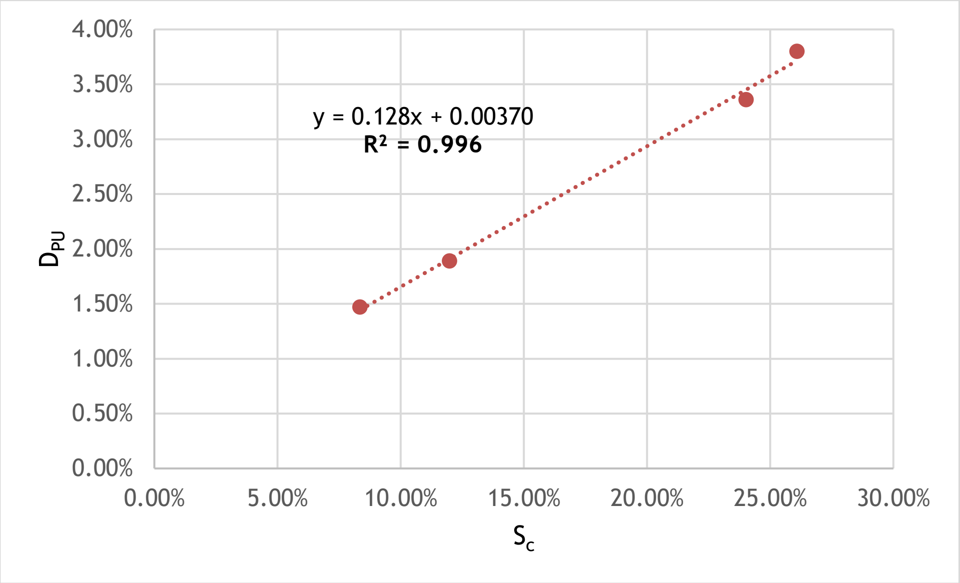

Figure 29 – Relationship between D_{PU} and S_C values for PET2200.

$$D_{PU} = 0.128S_C + 0.0037 \qquad (18)$$

The *PET*$_{2200}$ calibration curve was computing with a cord that was also dipped with the pre-DIP. Knowing that the average value of S_C for the pre-DIP is 2.3 %, using Equation 18, this corresponds to a D_{PU} of 0.66 %. Even though this is a small difference it can have an influence on the results as the estimated difference in means between the *Wet* and *Ncurve* populations is 0.33 % and 0.47 % between the *Ncurve* and *Production* populations. Thus, the difference between results appears to be due to the S_C present in the pre-DIP.

Concluding, the D_{PU} values obtained by the device appear to be indeed only affected by the DIP and not by the type of textile used.

4.3.2 DIP composition influence

For the second part, the DIP composition influence in the TD-NMR was studied, to do so it is important to study a dipping solution with different constituents. Subsequently, it was decided to do a calibration curve with nylon 940 textile dipped in rayon's DIP, which has two different components than the nylon's DIP. The curve was made according to the nylon's conditions, in both the impregnation and D_{PU} values necessary to the curve. The curve is shown in Figure 30 and will be named *Nrayon*.

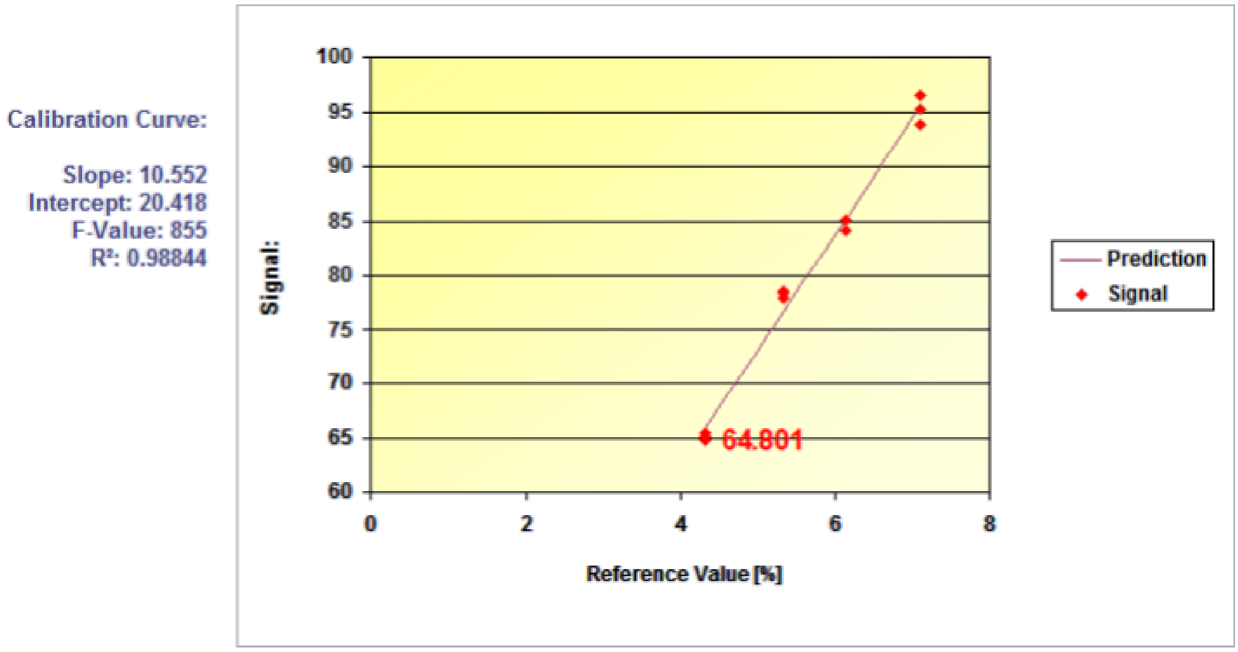

Figure 30 – Calibration curve of nylon 940 with rayon's DIP.

In Table 10 is possible to see the DPU measurements by the wet chemical method used to compute the calibration curve.

Table 10 - D_{PU} measurements by wet chemical method.

Cord	$D_{PU\ wet\ chemical}$ (%)	S_C (%)
1	4.31	11.34
2	5.33	13.91
3	5.98	15.07
4	7.10	17.53

After obtaining the calibration curve it was measured 30 samples of nylon 940 with the nylon calibration curve and *Nrayon*, the results are attached in Table A.3.2. It was not necessary to do a validation for this curve with samples from the production since it will not be used to measure D_{PU} of nylon textiles in C-ITA. Thus, similarly to the approach used in section 4.1 of this chapter, it was only necessary to compare 30 samples of a nylon textile to see if the results are equal or not. It is expected for the results to be different since the device reads the signal emitted by the DIP's components, therefore a different constitution of it will emit a different signal.

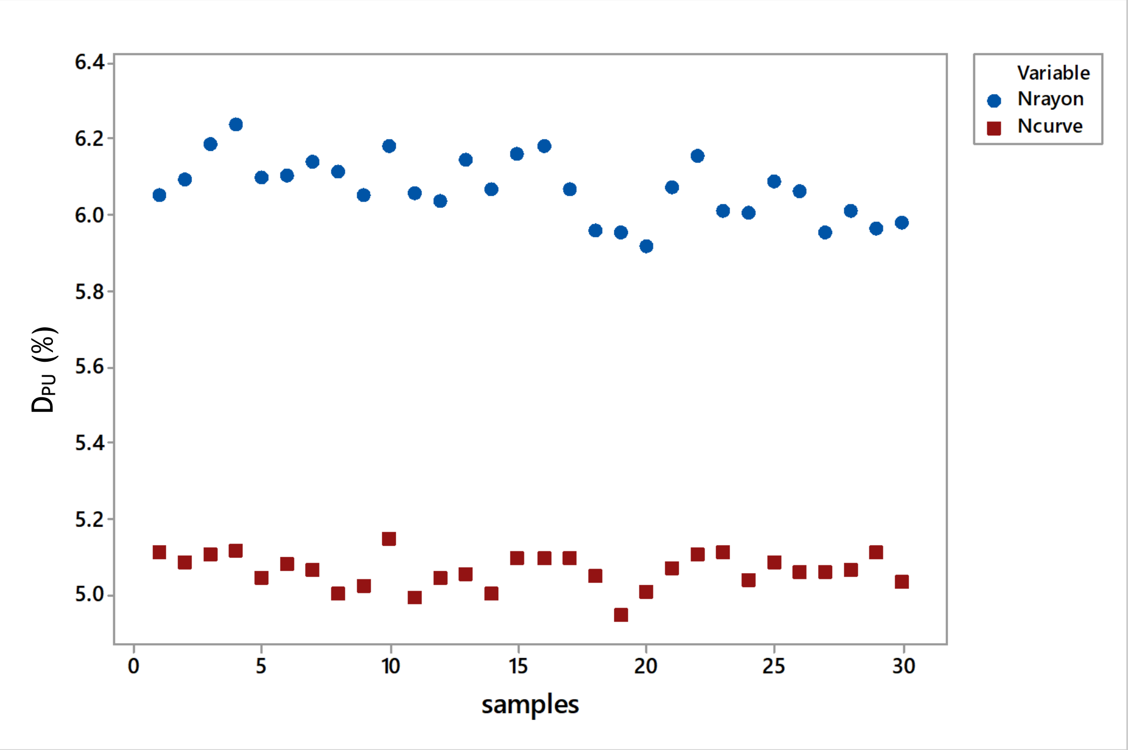

Figure 31 – Scatterplot for Nrayon and Ncurve samples.

Figure 31 shows a big difference between the results obtained by both curves, as the *Nrayon* samples have the highest values. Even though the difference appears to be significant by the graph, by the y-axis is possible to see that it can be around 1 %, or inferior to it.

Before doing a 2-sample t test to compare the means of each population, the variances of each population were analyzed, and the results are shown in Figure 32. The variance test showed that the confidence interval does not contain the value 1 and the p-value (0.002) is inferior to 0.05, so the null hypothesis is rejected, and the variances do not seem to be identical.

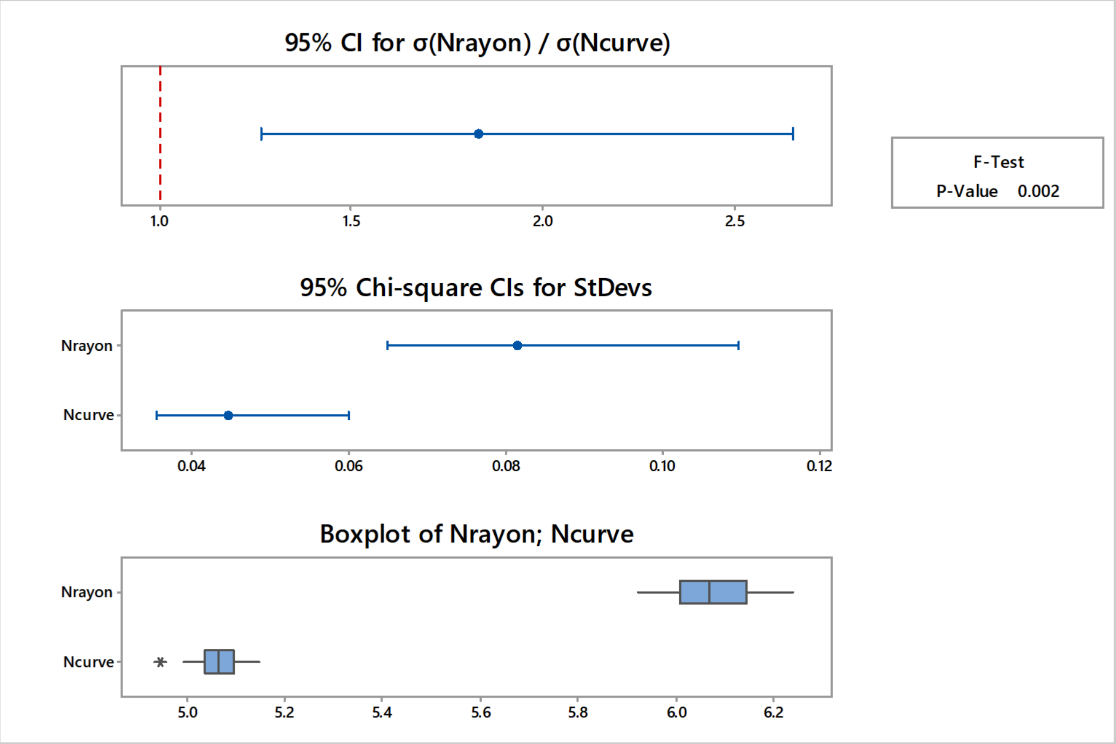

Figure 32 – Variance test results for Nrayon and Ncurve populations.

Afterwards, the 2-sample t test was done to both populations and the results are shown in Table 11. The estimated difference of means as a value of 1 % and the difference between values can go up as to 1.04 %. So, there is a significant difference between the means of both populations, which means that both curves are different, as it was expected.

Table 11 – Two sample t-test results for Nrayon and Ncurve populations.

p-value	Confidence Interval	Estimate for Difference of means	Margin of error
0.000	(0.00974; 0.0104)	0.0101	0.000342

The difference between nylon calibration curve and *Nrayon*, is most likely due to the DIP used for each curve, as the textiles used for them were alike. This goes according to what is expected, as the TD-NMR device reads the signal emitted by the DIP, so, if this is altered, the signal emitted will be different, resulting in a different D_{PU} value.

5 Conclusion

The presented project contributed to a better understanding and implementation of the TD-NMR method to measure D_{PU} for PET textiles in C-ITA, thus allowing an improvement in quality control.

In the first part of the project, the new method for TD-NMR sampling was studied and approved as both methods showed similar results for D_{PU} measurement. The main advantaged of cutting the cord, instead of doing small bows, relies on its facility to do so which is a key point to the production section in C-ITA.

A calibration curve for PET textiles was made in the project's second part. This curve was created using D_{PU} values obtained by the wet chemical method. Later, PET samples, from the Zell unit, were measured by this curve and compared to the values obtained by the production. The test results for the means of the attained values showed a p-value of 0.117, so it appears that they don't differ, thereby this curve was validated for PET_{2200}. Additionally, another curve computed by the weighing method was also studied and compared to the production values. Since the difference between the measured values was superior to 1 %, the standard limit in C-ITA, this curve was not approved. Furthermore, the PET calibration curve was also validated to measure PET textiles with different dtex and suppliers, as the results obtained for two PET textiles, one with different dtex and other with different dtex and supplier, did not show a significant difference by the C-ITA standards.

Lastly, the influence of the textile and DIP used on the TD-NMR device measurements was studied. To study the textile's influence, the PET calibration curve was compared to the nylon calibration curve since PET and nylon textiles are dipped with a solution that has the same constituents but in different amounts. It was found that both curves can be used to measure the D_{PU} of both textiles, in C-ITA standards, thus the textile does not appear to influence the results obtained by the TD-NMR device. To study the DIP constitution influence, a calibration curve was made for nylon textile dipped in rayon's DIP, which has two more components, and compared to nylon calibration curved used in C-ITA. The results showed a significant difference (about 1.01 %), thereby the results attained by TD-NMR device appear to be indeed affected by the solution used to dip the textiles.

This project contributed to expand the range of textiles that can be measured by the TD-NMR device in C-ITA. It also improved the sampling methodology for this new method and helped to better understand the device used in it.

6 Assessment of the work done

6.1 Objectives Achieved

The initial goal of this project was to calibrate the TD-NMR device to the PET textiles and better understand how the cord's components (DIP and fiber) influence the device's signal. A calibration curve was made and validated for all PET textiles and it was verified that the DIP amount and constitution is responsible for the results presented by the machine. Moreover, during the development of the work a new sampling method was proposed and approved.

6.2 Limitations and Future Work

The time was one of the biggest limitations imposed during the developed work. To obtain the calibration curve for PET textiles it was necessary to do several trials through the wet chemical method, which takes at least seven hours for PET textile. Additionally, the lab was shared with other co-workers that also need to do wet chemical trials for nylon and PET textiles, this combined to the low supply of material resulted in other limitation.

Moreover, C-ITA the TD-NMR device started to be used by other co-workers from other departments. In this method, a heating device is used to heat the samples to 40ºC. Part of the device, that contains the slots for the samples' tubes, is also used for the drying process (that lasts an hour) and cooling process (that requires at least 15 minutes). To study or validate each textile it was necessary to do 30 samples but only 15 were measured at a time because the heating device only has 2 parts with 16 slots each and other co-workers need to use it. A solution to this problem could be the acquirement of another support to use in the oven and in the cooling process of the samples.

For future work other materials produce in C-ITA, such as rayon, should also be calibrated for the TD-NMR device. Likewise, the nylon calibration curve should also be studied to measure the D_{PU} in other materials, besides PET textiles, that require a similar dipping solution to nylon's DIP.

6.3 Final Assessment

This project and consequent internship was an accomplished personal goal. The co-workers encountered during this phase were always helpful and contributed for the fluency of the developed work. It was a rewarding sensation being able to further implement the TD-NMR device in C-ITA and also acquire more information for the D_{PU} measurement.

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Appendix A

A.1

Table A.1.1 - Dip pick up and height measurements for laces and cuts populations.

Sample	D_{PU} laces (%)	D_{PU} cuts (%)	h (cm)
1	4.23	4.23	2.5
2	4.33	4.18	2.0
3	4.29	4.07	2.5
4	4.07	4.21	2.5
5	4.19	4.06	2.0
6	4.26	4.26	2.0
7	4.19	4.18	2.0
8	4.05	4.02	2.5
9	4.05	4.07	2.0
10	4.13	4.08	2.5
11	3.98	4.08	2.5
12	4.03	4.03	2.5
13	4.07	3.94	2.0
14	4.04	4.02	2.1
15	3.88	3.95	1.9
16	3.98	3.89	2.3
17	3.94	3.97	1.9
18	3.98	3.97	2.2
19	4.06	3.93	2.3
20	3.96	4.03	1.8
21	4.20	4.32	1.5
22	3.75	4.13	2.0
23	3.94	3.99	1.9
24	3.81	4.51	1.8
25	3.81	4.19	1.8
26	3.79	3.97	1.6
27	3.95	4.06	1.9
28	3.92	4.36	1.5
29	4.26	4.46	1.5
30	3.92	3.99	1.7

A.2

Table A.2.1- Results of the wet chemical method for each cord.

Cord	S_C (%)	Sample	D_{PU} (%)	Average (%)	Standard deviation (%)
1	8.35	1	1.48	1.47	0.05
		2	1.41		
		3	1.50		
2	11.99	4	1.83	1.89	0.06
		5	1.89		
		6	1.96		
3	24.03	7	3.40	3.36	0.07
		8	3.27		
		8	3.40		
4	26.09	10	3.70	3.80	0.10
		11	3.90		
		12	3.79		

Table A.2.2 – Results of the weighing method for each cord.

Cord	1	2	3	4
Sample	D_{PU} (%)			
1	2.82	4.02	4.23	4.70
2	3.25	3.77	4.37	4.31
3	2.45	2.20	4.50	4.37
4	3.15	3.48	4.21	4.74
5	2.94	3.71	4.31	4.86
6	2.10	2.96	4.39	5.03
7	3.19	3.54	4.25	3.98
8	3.60	2.72	4.00	4.95
9	1.66	3.46	5.30	4.09
10	2.55	4.20	4.41	4.19

Table A.2.3 – DPU values of populations Wet, Wei and Production for PET$_{2200}$ textile.

Sample	***Wet*** **(%)**	***Wei*** **(%)**	***Production*** **(%)**
1	2.55	3.65	2.60
2	2.82	3.84	2.00
3	2.71	3.77	3.10
4	2.83	3.91	3.00
5	2.54	3.66	2.90
6	2.62	3.70	1.50
7	2.71	3.81	2.10
8	2.57	3.71	2.70
9	2.44	3.55	2.80
10	2.63	3.72	2.90
11	2.74	3.81	2.80
12	2.63	3.66	2.90
13	2.51	3.62	3.00
14	2.42	3.55	2.80
15	2.87	3.90	2.70
16	2.57	3.68	3.20
17	2.64	3.74	3.30
18	2.75	3.79	3.30
19	2.79	3.82	2.10
20	2.72	3.77	2.00
21	2.52	3.62	2.90
22	2.44	3.55	3.30
23	2.79	3.79	3.00
24	2.80	3.84	3.10
25	2.75	3.82	3.30
26	2.66	3.77	2.70
27	2.53	3.61	2.90
28	2.71	3.76	2.80
29	2.41	3.48	2.90
30	2.37	3.50	2.70

Table A.2.4 - DPU values of populations Wet_{1440} and $Production_{1440}$ for PET_{1440} textile.

Sample	Wet_{1440} (%)	$Production_{1440}$ (%)
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

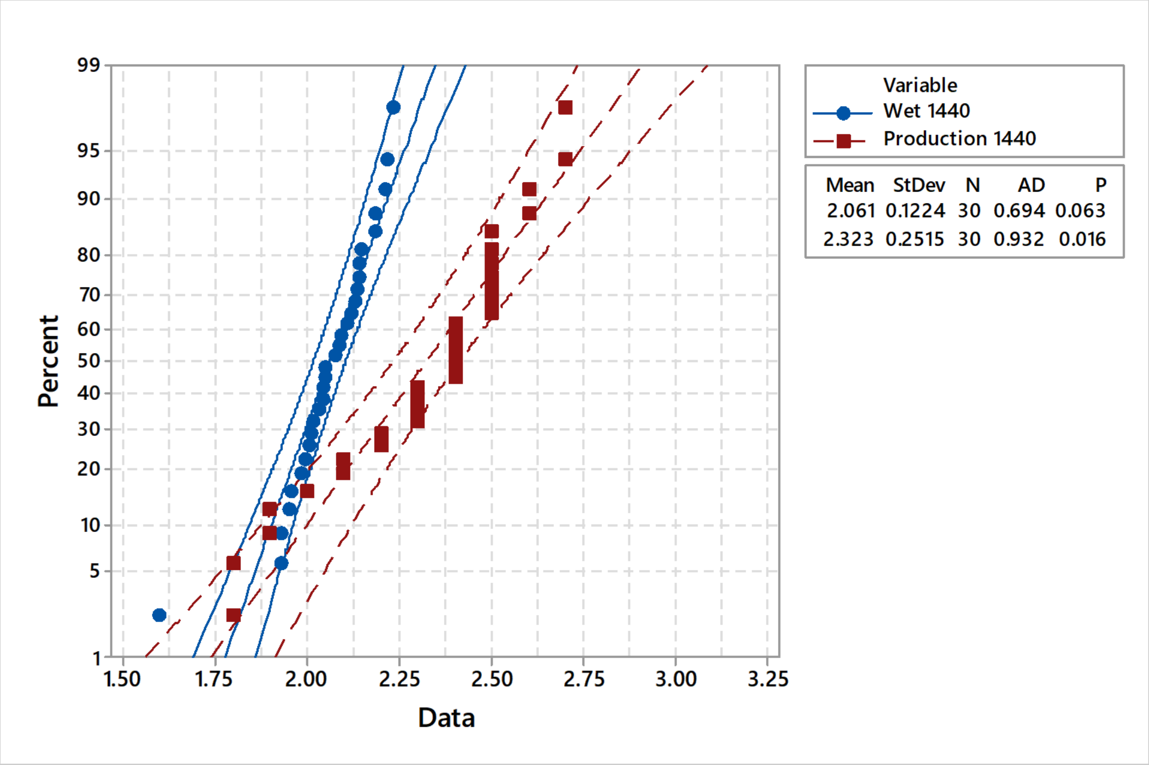

Figure A.2.1 - Probability Plot for Wet$_{1440}$ and Production$_{1440}$ populations.

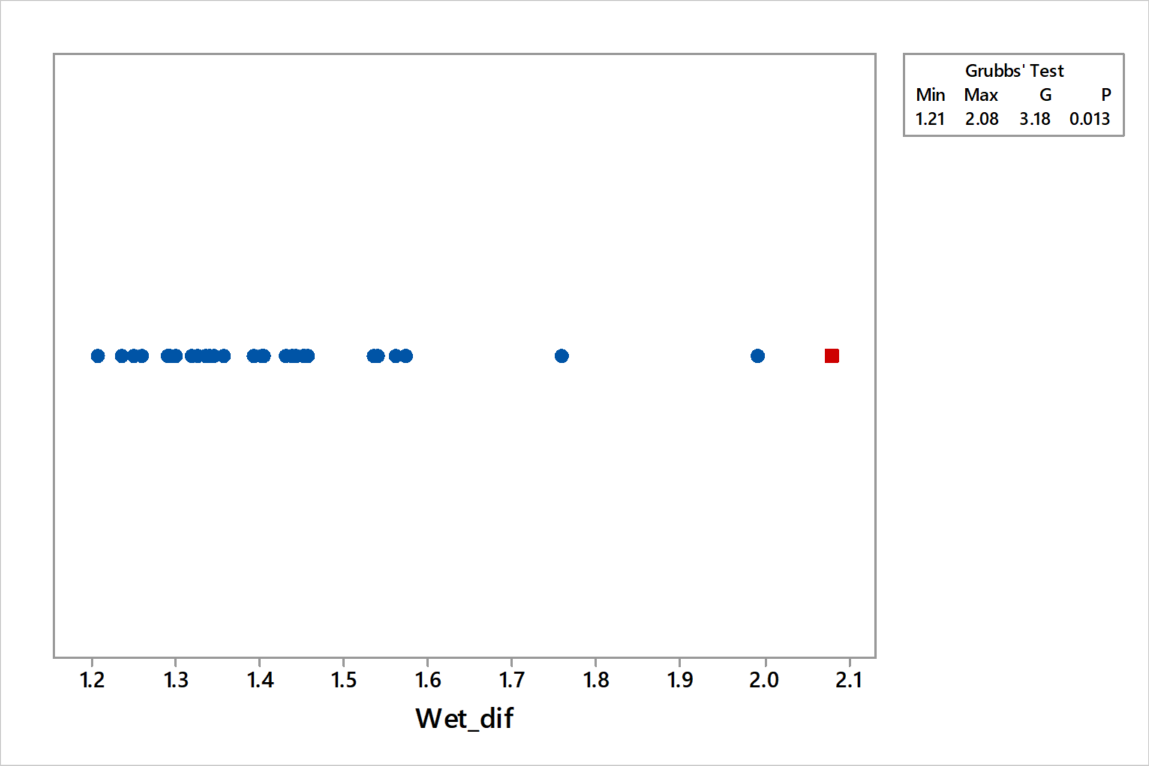

Figure A.2 2 - Outlier test and results for Wet_dif samples.

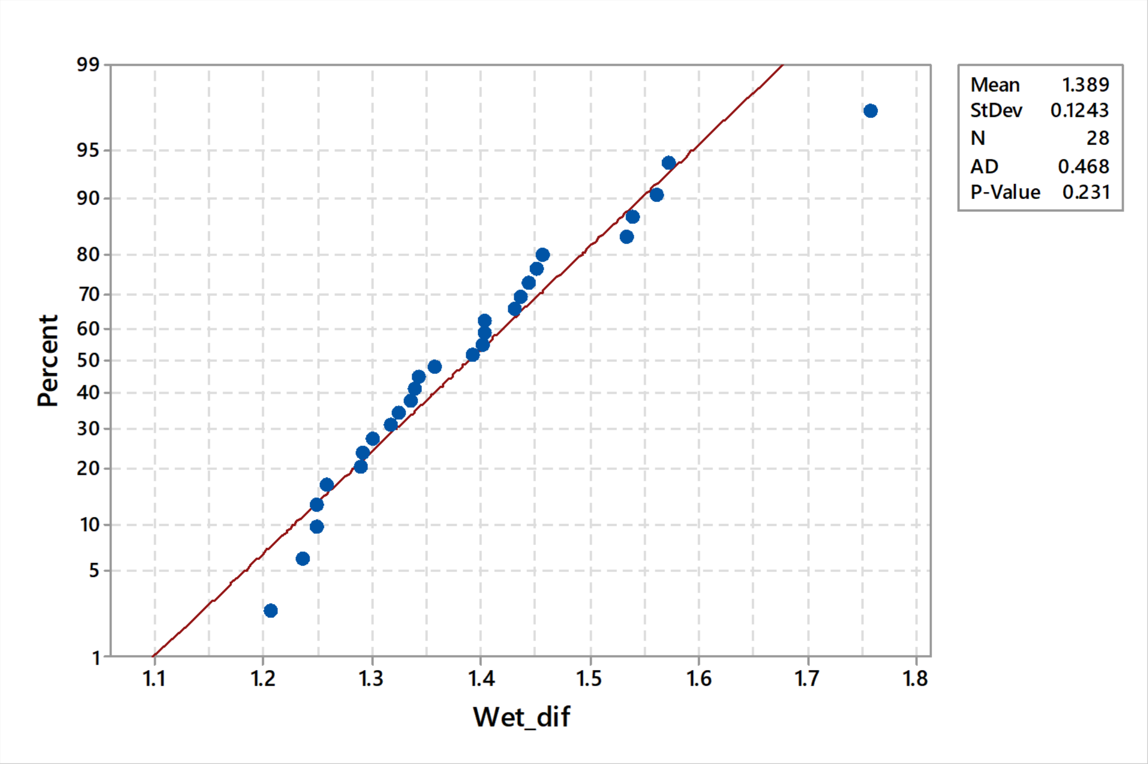

Figure A.2.3 – Normality test for Wet_dif population.

Table A.2.5 -DPU values of populations Wet_dif and Production_dif for PET$_{dif}$ textile.

Sample	*Wet_dif* (%)	*Production_dif* (%)
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

A.3

Table A.3.1 – DPU values of populations Wet, Ncurve and Production for PET$_{2200}$.

Sample	***Wet*** (%)	***Wei*** (%)	***Production*** (%)
1	2.55	2.26	2.60
2	2.82	2.48	2.00
3	2.71	2.37	3.10
4	2.83	2.54	3.00
5	2.54	2.32	2.90
6	2.62	2.37	1.50
7	2.71	2.37	2.10
8	2.57	2.32	2.70
9	2.44	2.11	2.80
10	2.63	2.34	2.90
11	2.74	2.37	2.80
12	2.63	2.28	2.90
13	2.51	2.20	3.00
14	2.42	2.11	2.80
15	2.87	2.47	2.70
16	2.57	2.28	3.20
17	2.64	2.33	3.30
18	2.75	2.39	3.30
19	2.79	2.42	2.10
20	2.72	2.38	2.00
21	2.52	2.17	2.90
22	2.44	2.14	3.30
23	2.79	2.40	3.00
24	2.80	2.45	3.10
25	2.75	2.41	3.30
26	2.66	2.31	2.70
27	2.53	2.19	2.90
28	2.71	2.33	2.80
29	2.41	2.05	2.90
30	2.37	2.06	2.70

Table A.3.2 - DPU values of populations Nrayon and Ncurve for nylon 940 textile.

Sample	*Nrayon* (%)	*Ncurve* (%)
1	6.06	5.11
2	6.09	5.08
3	6.19	5.10
4	6.24	5.11
5	6.10	5.04
6	6.11	5.08
7	6.14	5.07
8	6.12	5.00
9	6.05	5.03
10	6.18	5.15
11	6.06	4.99
12	6.04	5.05
13	6.14	5.05
14	6.07	5.00
15	6.16	5.09
16	6.18	5.10
17	6.07	5.09
18	5.96	5.05
19	5.96	4.95
20	5.92	5.01
21	6.08	5.07
22	6.16	5.10
23	6.01	5.11
24	6.01	5.04
25	6.09	5.08
26	6.06	5.06
27	5.96	5.06
28	6.01	5.07
29	5.96	5.11
30	5.98	5.03