

Master in Chemical Engineering

Study of Dip content in the tire textile reinforcements

A Master's dissertation

of

Maria Inês de Almeida Rocha

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Supervisor at FEUP: Prof. Joana Peres

Supervisor at Continental - ITA: Eng. Ana Martins

Dr. Thomas Kramer



Departamento de Engenharia Química

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Perdi a conta das vezes em que perdi o fio à meada.

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Abstract

Nowadays transports are considered essential to quotidian life. Consequently, tires have been getting more importance each day, since they are the most important element for the movement of vehicles. To assure the quality of the tire, as well as security and good performance, textile reinforcements are of major importance in this industry. Continental - Indústria Têxtil do Ave, S.A. is one of the top industries in this area and their main concern is the quality of its products.

One of the most significant aspects in building a tire is the cord-to-rubber adhesion. This step is accomplished by dipping the textile in a solution responsible for the bonding between the fiber and the rubber. In order to have a proper quality control of this process, it is necessary to quantify the amount of dip in each cord, which is called dip pick-up. To measure dip pick-up several methods can be used and this Master Thesis focus on the usage of Time Domain-Nuclear Magnetic Resonance method (TD-NMR).

The main goals of this project were to calibrate this device to new textiles, improve the samples preparation and compare data between different methods in order to verify the reliability of TD-NMR. A new calibration curve for Rayon textiles was developed and it has been proved that the dip pick-up of samples of Strong Hybrid can be measured with the curve already made for Standard Hybrid. Furthermore, a reduce of 25 minutes in the samples preparation was accomplished.

These studies will allow an improvement of the quality control system in this industry.

Keywords:

Tire, textile reinforcement, dip, dip pick-up, TD-NMR

Resumo

Hoje em dia os transportes são considerados um bem essencial na vida quotidiana. Por consequência, os pneus têm ganho mais importância a cada dia que passa, uma vez que são um elemento fundamental no movimento dos veículos. De forma a assegurar a qualidade do pneu, assim como a segurança e um bom desempenho, os reforços têxteis são uma parte de grande importância nesta indústria. A Continental - Indústria Têxtil do Ave, S.A. é uma das maiores indústrias nesta área, a sua maior preocupação é a qualidade dos seus produtos.

Um dos aspetos mais relevantes na construção de um pneu é a adesão da corda à borracha. Este passo é concretizado através da impregnação do têxtil numa solução responsável pela ligação entre a fibra e a borracha. No sentido de ter um controlo de qualidade apropriado neste processo é necessário quantificar a quantidade de solução de impregnação presente no têxtil, chamada *dip pick-up*. Para medir esta variável diferentes métodos podem ser utilizados, esta dissertação irá focar-se no uso da Ressonância Magnética Nuclear no Domínio do Tempo (TD-NMR).

Os principais objetivos desta tese foram calibrar este equipamento para novos têxteis, melhorar a preparação das amostras e comparar dados entre os diferentes métodos com o intuito de verificar a fiabilidade do TD-NMR. Uma curva de calibração para o Rayon foi desenvolvida e foi provado que a quantidade de solução de impregnação presente nas amostras de corda Híbrido Triplex pode ser medida com a curva de calibração criada para o Híbrido Padrão. Foi também alcançada uma diminuição de 25 minutos na preparação de amostras.

Estes estudos irão permitir uma melhoria no sistema de controlo de qualidade nesta indústria.

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

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, 11 of February of 2019

Maria Inês de Almeida Rocha

(Maria Inês de Almeida Rocha)

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Notation and Glossary

C_{mk}	Machine critical capability	
C_p	Process capability	
C_{pk}	Process critical capability	
Dtex	Decitex	g/ 10 000 m
D_{PU}	Dip Pick-up Percentage of solid dip impregnated	%
$D_{PU_{per\ dipped\ cord}}$	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
$m_{greige\ cord}$	Greige cord mass	g
P_{pk}	Process potential critical capability	
PPL	Measure of the overall capability of the process based on the lower specification limit	
PPU	Measure of the overall capability of the process based on the upper specification limit	
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
Greige Cord	Cord without any treatment
LDU	Lab Dipping Unit
LTL	Lower Target Limit
OPU	Oil pick up
PET	Polyethylene terephthalate fibers
PI	Product Industrialization
TD-NMR	Time Domain-Nuclear Magnetic Resonance
UTL	Upper Target Limit

1 Introduction

A tire is actually more than just a round piece of rubber. A lot of technology is involved in building one and assuring its security. This type of technology is developed every day at Continental all over the world. To build a tire, several techniques and materials are needed, such as the implementation of textiles, which will allow a higher complexity and a reinforcement of this quotidian object.

1.1 Framing and presentation of the work

Continental - Indústria Têxtil do Ave (C-ITA) has a department called PI (Product Industrialization) and R&D (Research and Development). PI works in the development of new materials and different techniques to improve and assure the quality of the products. To improve the process of verifying the quality of the cords, C-ITA required a new equipment based on TD-NMR (Time Domain Nuclear Magnetic Resonance). This equipment analysis the solid-to-liquid ratio of fat compositions, so that it is possible to calculate the percentage of D_{PU} (Dip Pick-Up) in the cord. D_{PU} is the percentage of impregnated solution in the cord. This solution is usually named dip and is used to improve the cord-rubber adhesion.

TD-NMR is a nondestructive method and a quicker one when compared with the Weighing or Chemical methods. However, to obtain quantitative results, a calibration of the device is needed. The results are obtained through the measurement of the energy released by the protons of a certain sample when excited by a magnetic field in a low frequency, transiting between energy levels and then returning to its initial state. The device reads the electrical signal emitted by the released energy of the protons, which is associated with the number of protons and consequently the sample's mass. A higher mass leads to a higher signal emission (Silva et al. 2016).

The calibration curves for PET (Polyethylene Terephthalate), Nylon and for one type of Hybrid (Aramid + Nylon) were already discovered and validated. Therefore, the production control is already using this equipment to test these products. The present project will allow C-ITA to use TD-NMR to analyze the D_{PU} (%) of other cords, such as Rayon and a new Hybrid (Aramid x 2 + Nylon), which is stronger and has a different dtex.

1.2 Presentation of Continental - Indústria Têxtil do Ave

Continental, founded in 1871 in Hannover - Germany, is one of the most prestigious tire companies in the world and has more than 550 units in 60 countries. 1 in each 3 cars in Europe is commercialized with Continental tires.

Indústria Têxtil do Ave, S.A was founded in 1950, in Lousado, to fulfill the need of Mabor to improve the tire resistance and the service time by adding textile reinforcements. In 1993 this plant became part of Continental Corporation; its name was changed to Continental - Indústria Têxtil do Ave (C-ITA) and it is the main producer of textile reinforcements for the rubber industry. At Continental, there are only two plants who manufacture this product: one in Portugal and other in the United States (Continental Corporation).

Since the tire is the only interface between the vehicle and the road, the main concern of Continental is and always will be the safety and the comfort that the tire provides to the passengers. The tire must be strong enough to resist different environments and temperatures, must support the weight of the vehicle and it has to have the right pressure so that its response is adapted accordingly to the conditions they have to handle, given the road friction and its irregularities can affect the vehicle's performance. The pneumatic tire has the ability to act like a damper system, absorbing the road impacts due to the air it has trapped inside. It responds really well to soil irregularities, providing the passengers an easier and comfortable drive (Lindenmuth 2006).

1.3 Contributions of the Work

The present Master Thesis was developed with the aim of continue the implementation of TD-NMR in dip pick-up measurement for new materials.

In the first part of this project it was possible to develop a new calibration curve for Rayon and to prove that Strong Hybrid can be measured with the calibration curve already made for Hybrid.

An optimization of the time was also possible to experiment, being able to reduce from 30 to 5 minutes in the heating support, used for conditioning the samples before being read in TD-NMR, saving 25 minutes to C-ITA in quality control.

A verification of the reliability of TD-NMR as a quality tool was also made, by comparing data from this method with the results from Wet Chemical method.

This work has helped C-ITA improving the quality control, allowing an improvement of productivity of this company.

1.4 Organization of the Thesis

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

Section 1: Introduction. This chapter summarizes the history of Continental corporation and the insertion of C-ITA as well as a brief contextualization of the problem and the main purposes of this work.

Section 2: Context and state-of-the-art. Description of the materials used and the importance of a tire.

Section 3: Materials and methods. Technical description of the methods and equipment used.

Section 4: Results and Discussion. Results and respective analysis.

Section 5: Conclusion. Main conclusions of this project

Section 6: Assessment of the work done. Global appreciation of the work done in this project.

Section 7: References. The bibliography used in this work can be checked in this section.

Appendix: Additional information, graphics and tables to allow better understanding of the work.

2 Context and State of the art

C-ITA is responsible for producing the textile part of Continental's products. In this plant, feedstock (in form of yarn) can be transformed into cord and fabric, after suffering an extensive process where all the little steps are monitored.

2.1 Tire and its composition

The only connection between the vehicle and the road is the tire, whose contact area is only a small part of the rubber, thus a lot of conditions have to be tightly controlled, such as the air pressure and the composition and quality of the material. Vehicle load causes tires to deflect until the average contact area pressure is balanced by the tires' internal air pressure. This piece of the vehicle 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. It must also have a good direction stability and ability to absorb road irregularities.

Due to the friction between the road and the tire, a vehicle has the ability to start, stop and turn corners. Therefore, the tire design is really important, not only to provide the vehicle's movement but also to deal with different weather conditions, such as dry, wet, snow-covered and icy surfaces. The tire tread designs enable water to escape from the tire-road contact area (named footprint), minimizing hydroplaning, while providing a reasonable balance between the conflicting requirements of good dry traction, low wear and low noise. This feature to absorb road irregularities is the key benefit of the pneumatic tire, since it acts as a spring and a damper system to absorb impacts and road surface irregularities (Lindenmuth 2006).

The tire has more on its constitution than just rubber. The textile reinforcements are a very important part of the tire and are produced in C-ITA, while the other compounds are produced in several other different Continental plants, each one of them responsible for one or more components. For a typical passenger car tire, the composition is described in Figure 1 (a) and the constitution in Figure 1 (b) representing the different types of materials used.

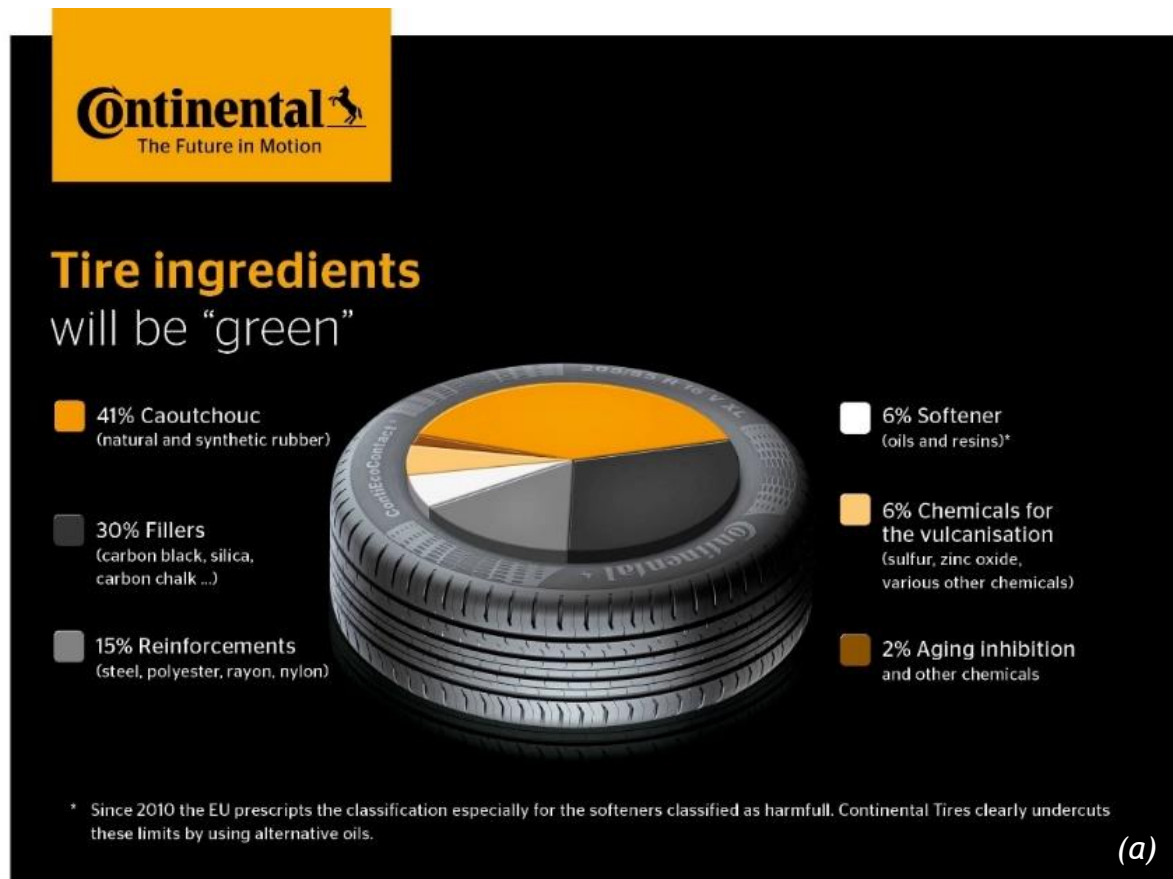


Figure 1 - Composition of the tire (a) and example of the tire constitution (b) (Continental, 2017).

Tires can be categorized by type depending on the carcass arrangements. There are three types: Diagonal Bias, Belted Bias and Radial. The first, Diagonal tires, are still used in some applications for trucks, trailers and farm implements, as well as in emerging markets. Bias tires have body ply cords that are laid at angles substantially smaller than 90° to the tread centerline, extending from bead to bead. This type of tire has a simple construction which make it easy to manufacture, however as the tire deflects shear occurs between body plies which generates heat. (Lindenmuth 2006).

Belted bias tires are bias tires with belts, or breaker plies, added in the tread region. Belts restrict expansion of the body carcass in the circumferential direction, strengthening and stabilizing the tread region. Since it has stiffness added in the tread area it improves wear and management. However, it has a higher cost associated due to its elevated complexity and the body ply shear during deflection generates heat.

Radial tires are the most used type of tires nowadays due to its ability to deflect more easily under load, thus generating less heat, giving lower rolling resistance and having a better high-speed performance. This type of tire presents body ply cords that are laid radially from bead to bead, nominally at 90° to the centerline of the tread and two or more belts that are laid diagonally in the tread region to add strength and stability. Increased tread stiffness from the belt significantly improves wear and handling which is one of the advantages of this tire, nevertheless, its complex construction increases material and manufacturing costs (Lindenmuth 2006).

2.2 Textile Reinforcements

Tire cords are the skeleton of the tire as they define the shape of the tire, support the loads, give strength and provide the ability to contain air pressure.

The reinforcement materials - tire cord - must provide the tire with axial and lateral rigidity for acceleration, braking and cornering and dimensional stability for uniformity, handling, and ride as well as resistance to collisions and fatigue.

To fulfill this job, cord should have good lateral flexibility and consequently, low bending stiffness. It must also be twisted to allow the filaments to exert axial strength in concert with other filaments in the structure and to prevent cord from operating in compression.

The textile reinforcements are used in different parts of the tire, according to its function, fabric is used in *carcass* (above *Inner liner*) and the cord at the *cap-ply*. These

compounds can be observed in Figure 1. These parts are both composites of rubber and cord, thus the cord must have properties to allow the incorporation of the textile in the rubber. Because the textile does not have the needed qualities naturally, since it is a non-reactive material, it has to suffer a process named dipping in which it is dipped in a solution that allows a better adhesion between the textile and the rubber, improving the cohesion. This step is one of the most important during the preparation of the textile. Not only it allows proper adhesion to rubber, but also will confer its final mechanical properties (Hearle 2015; Lindenmuth 2006; Louis et al. 2014).

2.3 Textile Terminology

To fully understand this work it is crucial to comprehend the terminology and the concepts involved. The concepts and the respective explanation are described in the following table.

Table 1 - Important concepts and respective information (Adapted from Lindenmuth et al., 2006).

Concept	Explanation
<i>Fiber</i>	Units of matter having length at least 100 times their diameter or width.
<i>Filament</i>	Smallest continuous element of a tire cord.
<i>Yarn</i>	Assembly of filaments.
<i>Cord</i>	Twisted structure composed of two or more yarns.
<i>Greige Cord</i>	Cord without chemical treatment.
<i>Decitex (dtex)</i>	Linear density in grams per 10 000 meters of fiber.
<i>Twist Level</i>	Number of turns per meter (tpm) of a twisted cord or yarn.
<i>Twist Direction</i>	Twist direction is termed “S” if the spiral turns clockwise from top to bottom for a vertically held cord and “Z” for a similar counter clockwise turning.
<i>Cord Construction</i>	Gives the information of how many yarns exists in the cord and how they are twisted.

<i>Tenacity</i>	Force at a specific strength, expressed in centinewtons per dtex.
<i>Load</i>	Force applied to cord expressed in newton.
<i>Elongation</i>	Percentage of elongated cord when subjected to a force.

The textile reinforcement can be structured in 4 levels of design and complexity: filament, yarn, cord and fabric, as exemplified in Figure 2. The filament is part of a structure of the spun fiber. A number of filaments laid together creates a yarn. One, two or more yarns twisted (S or Z direction) together constitute a cord. Finally, the cord can be weaved into a fabric or be used as a cord to reinforce the cap-ply (Lindenmuth 2006).



Figure 2 - Example of a yarn, cord and fabric, from greige to dipped form, named from left to right.

2.4 Fibers

In C-ITA different feedstock are used: E.g. Aramid, Nylon, Rayon and PET. These fibers have different properties which allow the tire to have a big range of characteristics:

- **Aramid:** Very strong polyamide, which can support a lot of force without great deformation. It is 2 to 3 times stronger than PET and Nylon. This kind of fiber has very high strength and stiffness and is heat-resistant. However, this material can be expensive to work with and it's very difficult to cut due to its physical properties.
- **Nylon:** This material is made of synthetic long chain polymers produced by continuous polymerization/spinning or melt spinning. It has a great elongation capability and low sensitivity to moisture though it supports less force, compared to the other materials.

- **Rayon:** Is made from cellulose and produced by wet spinning. Although it is very sensitive to moisture this compound has good resistance to heat and is easy to manage.
- **PET:** Synthetic long-chain polymer produced by continuous polymerization/spinning or melt spinning. This material has high strength with low shrinkage and low service growth, low heat set and low cost. However, it is not as resistant to heat as Nylon or Rayon (Raw Materials | MEHLER ; Whewell 2018).

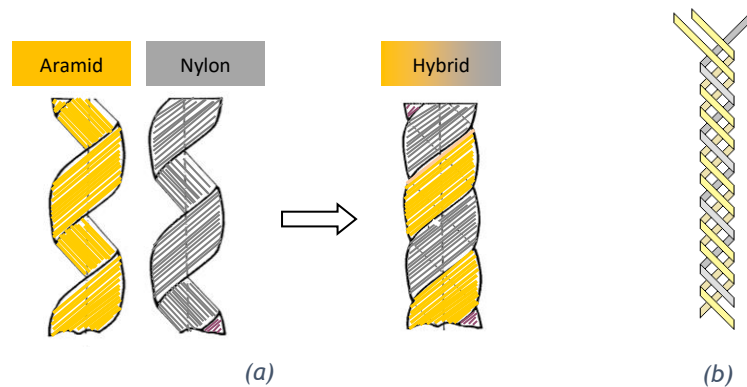


Figure 3 - Composition of a Hybrid with 2 cords (a) and with 3 cords (b) (adapted from Basics of reinforcements, Kramer).

To improve the cord and the resistance of the material, cords are made with different yarns. This material is called Hybrid and is constituted by aramid (1) and Nylon (1), as described in Figure 3. A new cord, called strong Hybrid has been developed and is composed of one yarn of aramid (1) and two of Nylon (2). This material combines the best characteristics of the two materials. The properties of the different materials used in C-ITA can be observed in Figure 4 according to Tenacity and Elongation (Kramer).

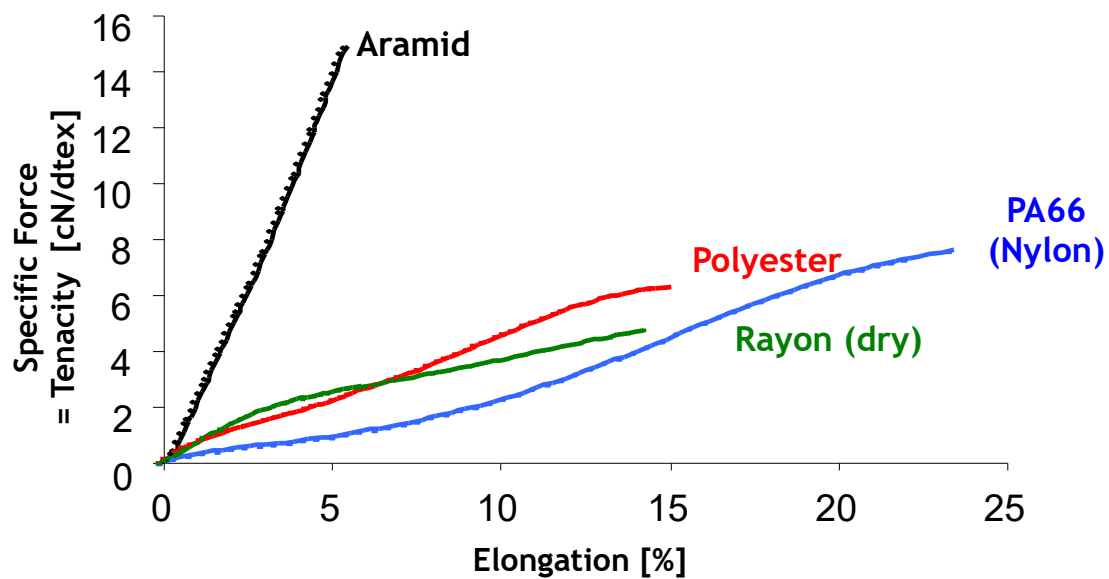


Figure 4 - Force Elongation Curve of Dipped Cord (adapted from Basics of reinforcements, Kramer).

To make a cord the yarn can be twisted in two different directions: S and Z. The twist direction is termed “S” if the spiral turns clockwise from top to bottom for a vertically held cord and “Z” for a similar counter clockwise turning. Usually, yarns are twisted in “Z” and afterwards when twisting the yarns together to form a cord, they are twisted in “S” as illustrated in Figure 5 (Lindenmuth 2006; Whewell 2018).

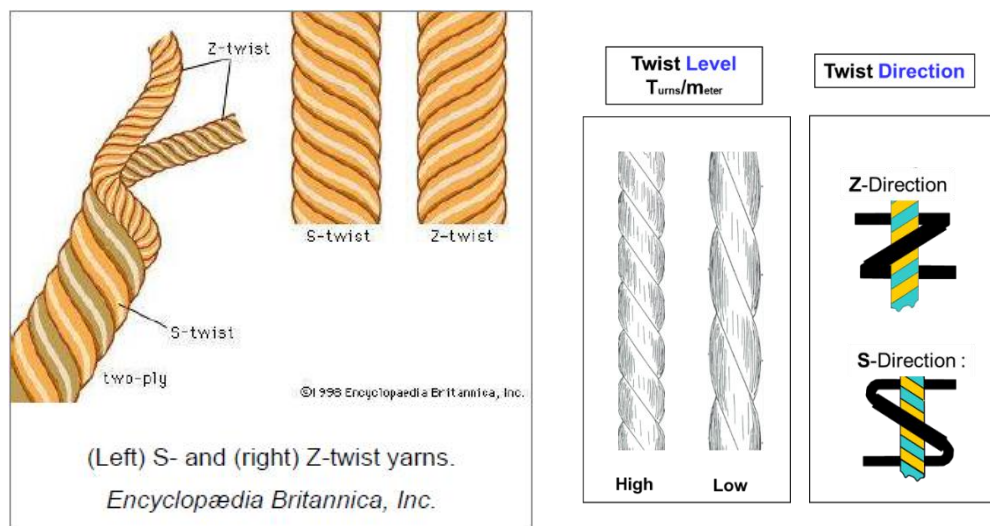


Figure 5 - Twisted cord: directions and level (adapted from Encyclopedia Britannica and Basics of reinforcements, Kramer).

2.5 Dip Solution and Dipping Process

To assure the quality of the tire comes the need to reinforce it with textile. Since we are talking about two very different materials, a highly elastic rubber, and a cord with high strength and low elongation properties, it is necessary to have a bridge agent between the two. This agent is called dip. The prime goal of the cord adhesive is to avoid separation at the cord-adhesive interface, at the rubber-adhesive interface, and within the adhesive itself. This objective is achieved by using proper dipping procedures.

In order to improve the cord-to-rubber adhesion the cords need to suffer a process named dipping. In this process, cords (or fabric) are dipped in a solution (latex adhesive) that will serve as an intermediary to enhance its bonding to rubber. To create a solid interface layer in the fibers' surface the cords need to suffer a high-tension heat treatment. A diagram of the process can be observed in Figure 6, in which is possible to perceive that the dip acts like a bridge between fiber and rubber (Lindenmuth 2006; Louis et al. 2014).

The dipping solution - Resorcinol-Formaldehyde-Latex (RFL) - is constituted by water, latex (stable emulsion of polymeric particles) and a resin which allows the adhesion between cord and rubber due to its ability to create mainly covalent bonds and forming a matrix. The resin which is formed by the resorcinol and formaldehyde provides bonding to the cord. The latex used is styrene-butadiene-2-vinyl pyridine (VP latex), this component bonds to the rubber compound due to co-vulcanization (Louis et al. 2014).

With the aim of minimizing environmental problems, since the residues from RFL dip processing still have to be handled as special waste, an alternative resin was studied in previous projects. This dip provides similar properties to the cord, is easier to use and to produce, plus it has the advantage of being more environmentally friendly.

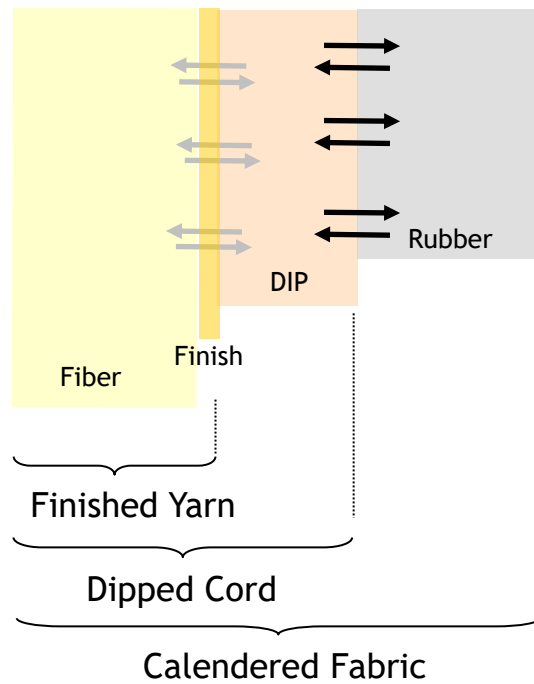


Figure 6 - Scheme representing dip as ligand (adapted from Kramer, 2013).

The RFL dipping covers a variety of treatments that vary according to the type of cord and rubber used. Each fiber needs a specific dip recipe with an established Solid Content Percentage (SC). For some materials, a primary dip is needed to allow the creation of the bonding matrix, due to its extremely non-reactive properties; it is called pre-dip and is a solution of epoxy resin and isocyanate, which is used for activation of the cord so it properly connects to the dip. In the case of Nylon or Rayon, a standard treatment with RFL dip is sufficient, as the reactivity of these cords is high enough (Louis et al. 2014).

Some of the suppliers already make this step by imbuing the fibers with an oil finish that will allow the functionalization of the cord.

In C-ITA, to provide the treatment of the cord a machine called *Single-end* is used. This machine contains four ovens. Initially, the greige cord is stretched in tensioning rollers. Before the first and the third ovens a bath where pre-dip and dip can be put, respectively. If it's not necessary to activate the cord with pre-dip, the third and the fourth oven are turned off. At the end of the treatment, the cord is rolled in bobbins and later shipped to the costumers.

To produce fabric, a different machine is used, called *Zell*. Its functioning is similar to *Single-end*, however in the Zell machine one roll of fabric is dipped at a time, while in the *Single-end* hundreds of cords can be dipped at the same time.

For investigation purposes PI has its own equipment, named *LDU - Lab Dipping Unit*, that allows the replication of these dipping units at a laboratory scale and to change conditions, such as temperature, speed, tension and stretching.

2.5.1 Dip measurement and quality control

With the purpose of monitoring the quantity and the quality of the dipping process, there are several trials that can be done. One example is the “peel adhesion test”, represented in Figure 7, which consists in separating the complex rubber plus cord in two parts with a tensile tester to evaluate the adhesion. To consider the results good, the cords cannot be visible to the naked eye.



Figure 7 - Example of a peel adhesion test results: showing a good result, on the left, and a bad one on the right.

For this project, the method used to quantify the amount of dip in each cord - the Dip Pick-up Percentage (D_{PU}) per greige cord - is being tested and optimized. It can be measured by one of the following methods:

Standard Methods:

1) Wet-Chemical Method

In this method the cord is dissolved and the remaining residue, which is the dip present in the cord, is weighed (m_3).

Initially the cord needs to be dried and weighed (m_1). The fibers are dissolved in acid and then through filtration the solvent is removed and the dip residue is

recovered. The dip is dried and the solid residue ($m_3 - m_2$) is weighed. Afterwards, Equation 1 is applied to calculate the D_{PU} ,

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

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

This method takes a lot of time to be completed and has a lot of associated errors.

2) Weighing Method

The weighing method can only be used with textiles with low hygroscopic nature. It presents a lot of errors associated, mainly due to the differences between the greige and the dipped cord. Therefore, the usage of this method is avoided as much as possible in C-ITA.

In this method, the dipped cord is compared to the greige cord through its weight. To minimize the associated errors, the greige cord is thermofixed within the same conditions as the dipped cord. This step will allow the greige cord to be as similar as possible to the dipped one, so the only variable will be the presence of dip. In this method it is necessary to prepare 10 samples per spool, from 30 spools from production, which are then folded in a lace form with 10 meters each. Afterwards they are dried and weighed and then compared with the greige cord in the same conditions. The percentage of Solid Content in the dipped cord is given by the equation below:

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

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

C-ITA recently acquired a new equipment based in the TD-NMR method (Time Domain-Nuclear Magnetic Resonance). This method provides benefits when compared to the standard methods. As an advantage, TD-NMR is more reliable, has a high quality, a low error occurrence associated, is non-destructive and is overall quicker. The usage of this equipment increases the productivity of C-ITA regarding to quality control.

TD-NMR can also be called low-field NMR and is a nondestructive, time-domain pulsed method. However, even though it shows several advantages the quantitative results can only be obtained with further calculation or calibration of this device.

The TD-NMR machine works based on the spin of protons (^1H), as it creates a magnetic field in the place where the sample will be analyzed to excite the protons and change their energy level. The proton spins align themselves with this induced magnetic field and will be submitted to two different types of magnetic pulses. This disturbance is known as the Hahn-echo sequence and is applied on the sample. The pulse sequence consists of two rf (radio frequency) pulses. The first pulse, at 90° , creates an FID (Free induction decay) signal. The second pulse, emitted at 180° has twice the duration of the leading pulse and the signal obtained is generated by the fiber's sample. 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. When the pulse is deactivated, the spins return to their equilibrium position, emitting the energy that they had to receive to be moved from that position. Thereby, it's possible to measure the amount of dip by doing the difference between the first and second signal, as it is shown in Figure 8 (Bruker; Dalitz et al. 2012; Devices and Magnetic Resonance Imaging Systems; Todt et al. 2001).

The equipment obtains the percentage of Solid Content by measuring the energy released by the protons of a certain sample when excited by a magnetic field in a low frequency. This energy emits an electrical signal that is read by the device which is associated with the number of protons and consequently the sample's mass; thus, a higher sample's mass leads to a higher signal emitted (Silva et al. 2016).

The determination of D_{PU} is based on different relaxation properties of the materials present in the sample, this is, the cord and the dip, both are solid components, however, the dip has a shorter relaxation time. Different types of protons and different dipoles' constitutions will have different relaxation times (Joseph P. Hornak, 1996).

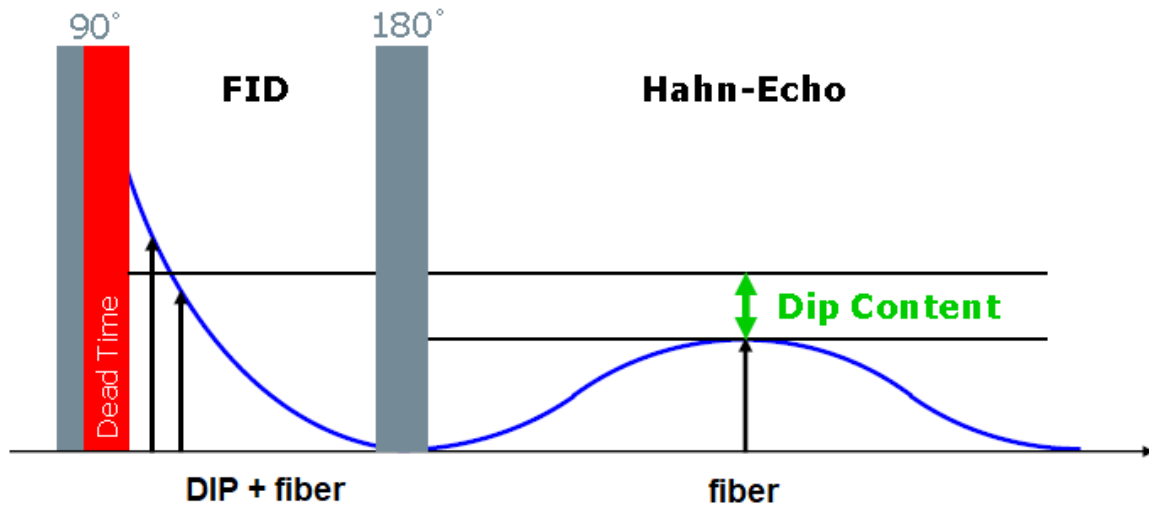


Figure 8 - Hahn echo sequence representation (Adapted from Bruker, 2016).

1) Method

TD-NMR spectrometers operate at warm temperatures in order to stabilize the magnetic field so, before the sample is measured, it is conditioned in a heating device at 40 °C to assure that it is at the right temperature. The samples need to be previously dried, since the echo signal from free water interferes with the one from dip, due to the relaxation times of free water and oil being rather similar.

2) Advantages / Disadvantages

It has been proven that this method varies mainly with the variation of dip content, this is, the complexity of the cord and the dtex doesn't influence the D_{PU} for the same material.

It is a very sensitive method allowing credible results. To handle the cord is necessary to use gloves, as it has been proved in previous Master Thesis that the particles present in hands can influence the results. Also, the tubes have to be clean so they will not influence the analysis of the signal, since it is a very sensitive device. This is a method that needs to be done with precision.

When compared to the other standard methods, the TD-NMR method is superior, since the sample preparation is reduced to a minimum and the analysis is complete within seconds. Moreover, chemical solvents are not required which makes it a more environmentally friendly method (Todt et al. 2001).

Nowadays, the concern to find better products keeps increasing, so the importance with quality control is an urge for the industry. The use of reliable processes and technology, such as TD-NMR, gives an advantage to C-ITA; when correctly calibrated not only does it save time, but also gives more credible results (Dalitz et al. 2012).

2.6 Statistical Analysis

To analyze the collected results and to gather conclusions from them, it is essential to an engineer the use of statistics. Statistics is considered the science of data that allows an engineer to collect, present, analyze, and use data in order to make decisions, solve problems, and design products and processes. Statistical techniques can be a powerful tool and can be used to make decisions and draw conclusions about populations, through parameter estimation and hypothesis testing (Montgomery and Runger 2003).

2.6.1 Hypothesis Testing

Hypothesis testing is a statistical method that is used in making statistical decisions using experimental data and it is basically an assumption that made about the population parameter. It enables the comparison between a population's parameter with a specified value, or to another parameter of a different population. In the present context, population means any finite or infinite collection of individual units or objects (Montgomery and Runger 2003).

In the hypothesis test, two statements are formulated: the null hypothesis (H_0) - considered true - and the alternative hypothesis (H_1).

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.

$$H_0: \mu_{\text{TD-NMR}} = \mu_{\text{Chem}} \quad (3)$$

$$H_1: \mu_{\text{TD-NMR}} \neq \mu_{\text{Chem}} \quad (4)$$

$\mu_{\text{TD-NMR}}$ and μ_{Chem} are both means of populations from TD-NMR method and from the Wet-Chemical method, respectively.

With two variables, the Wet-Chemical and TD-NMR methods, the hypothesis test will be based on the difference in the means $\mu_{\text{TD-NMR}} - \mu_{\text{Chem}}$ of two normal distributions where the variances can or not be known.

To report the results of a hypothesis test at a specified α -value or level of significance the p-value approach can be used. The p-value for a t-test is the smallest level of significance at which the null hypothesis (H_0) would be rejected. 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 and Runger 2003).

2.6.2 Confidence Interval

Although hypothesis testing is a useful procedure, sometimes it does not provide all the information needed. Therefore, the confidence interval is used, which consists of an interval that act as a good estimate of the unknown parameters. The confidence interval (CI) of a certain parameter θ is an interval with the form $l \leq \theta \leq u$ where the values l and u are endpoints called the lower- and upper-confidence limits, respectively, calculated from the given data based on the probability theory. The probability theory states that there is a probability of $1-\alpha$ of selecting a sample for which the true value of the parameter θ is contained by the confidence interval.

For a normal population with known variance, if $\bar{x}$ is the sample mean of a random sample of size n , a $100(1-\alpha) \%$ CI on μ is given by:

$$\bar{x} - z_{\alpha/2} \sigma/\sqrt{n} \leq \mu \leq \bar{x} + z_{\alpha/2} \sigma/\sqrt{n} \quad (5)$$

where $z_{\alpha/2}$ is the upper $100 \alpha/2$ percentage point of the standard normal distribution.

There is a close relationship between the test of a hypothesis about any parameter θ and the confidence interval for θ . If $[l, u]$ is the $100(1-\alpha) \%$ confidence interval for the parameter θ , the test of size α of the hypothesis

$$H_0: \theta = \theta_0 \quad (6)$$

$$H_1: \theta \neq \theta_0 \quad (7)$$

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

2.7 Assessment of previous work

C-ITA has been dedicated to improving the quality control of the products. The present dissertation is the fifth Master Thesis with this theme and the goal of using TD-NMR to measure the percentage of Solid Content in dipped cords. The device is already calibrated for several materials, such as Nylon, PET and Hybrid (with 2 yarns). However, for PET textiles the calibration curve was not approved for different suppliers and dtex.

This current dissertation focuses on the calibration to the remaining materials, Strong Hybrid and Rayon, so that TD-NMR can be used at its fullest, with all the advantages already indicated.

The previous Thesis also studied the influence of various factors on the D_{PU} results. For the dipping process, it was proved that the velocity, the temperature and the Solid Content of dip have a high influence on D_{PU} , and the optimal processing conditions were already discovered.

Regarding to the sample preparation of the TD-NMR method, it was proved that the usage of gloves in handling the sample is essential and also that samples can be cut instead of manufacturing laces, depending on the dtex of the cord and the preference of the user. The cord needs to be properly dried otherwise it will lead to an increased measured value of D_{PU} .

3 Materials and Methods

In this chapter, all the used methods and materials are presented. In the first part of this project, was proposed to check if the measurement of D_{PU} of the Strong Hybrid (1680+1680+470)x1x3 can be done with the calibration already made for the Hybrid (1680+1400)x1x2, see Figure 9. The difference between the Hybrids is that the standard one is composed by two yarns: one Nylon 6.6 and one Aramid, while the more recent cord has three yarns: two Aramids and one Nylon 6.6. The two cords have different dtexs and different constructions, however the dip is the same. It has been proved in previous dissertations that the only variables that could influence the signal of the TD-NMR are the composition of the dip and different suppliers. With this assumption, 30 samples from the production were tested with the calibration curve of Hybrid and to confirm the results the Weighing method was applied. Samples of Strong Hybrid were sent to the Central Laboratory in Germany to be tested by the Chemical method.

In the second part was suggested that a calibration of Rayon was made. Rayon is very sensitive to moisture, so all the steps had to be done very carefully to avoid the gain of moisture, since water molecules would affect the reading in TD-NMR. In C-ITA, in the future different dips can be applied, varying, as it was described in section 2, the resin and natural latex, so it becomes a more sustainable process. In order to increase the productivity, two calibration curves were made, one for each dip, however, only the one that is used nowadays was validated, since the production only uses the standard one.

In the third part of the project, since Nylon is already being tested with the TD-NMR for quality control, these results were compared with the previous ones measured with the chemical method. The main goal was to check the stability and reliability of this new device.

Besides the objectives proposed, an optimization of the time that the samples need to be in the heating device at 40 °C was made. 30 minutes is the time that is settled to all materials, however reducing that time can allow the all process to be more efficient. Since Rayon is a very conductive material, this variable was also tested to the material that has the worst conductivity, this is, the Hybrid due to aramid, to guarantee that the time can be used to the rest of the materials.

The software used to perform all the statistical evaluations was the Minitab 17, which is used by Continental for these types of evaluations and studies.

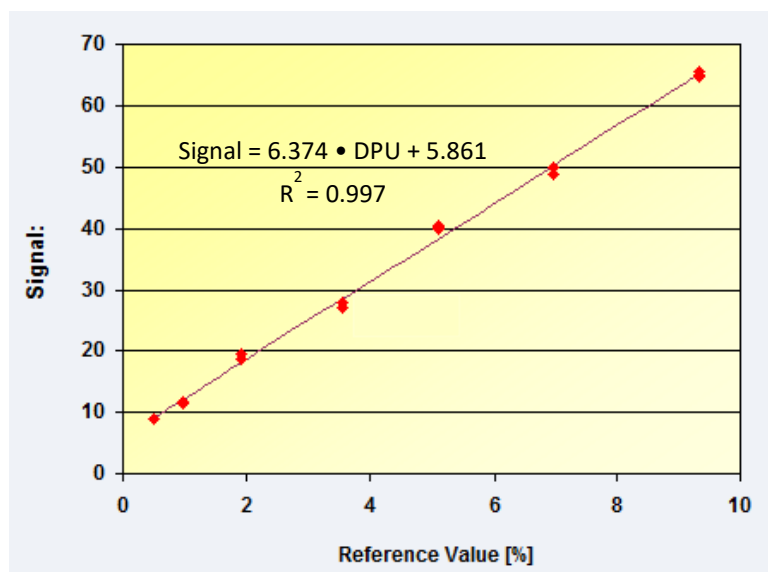


Figure 9 - Calibration curve for Standard Hybrid in the TD-NMR device software "minispec Plus 6.0.3".

3.1 Materials

In this Master Thesis the work was made mostly with Hybrid, and Rayon. Data from Nylon was also analyzed. Each cord has a different specification according to the yarns and the supplier, what matters the most to this work is the range of the values of Dip Pick-Up that are acceptable.

3.2 Dipping process

In order to reproduce and to be able to investigate and test different variables, C-ITA owns a machine called Lab Dipping Unit (LDU), as already explained in section 2. The LDU, shown in Figure 10, can replicate the dipping units, only on a laboratory scale.

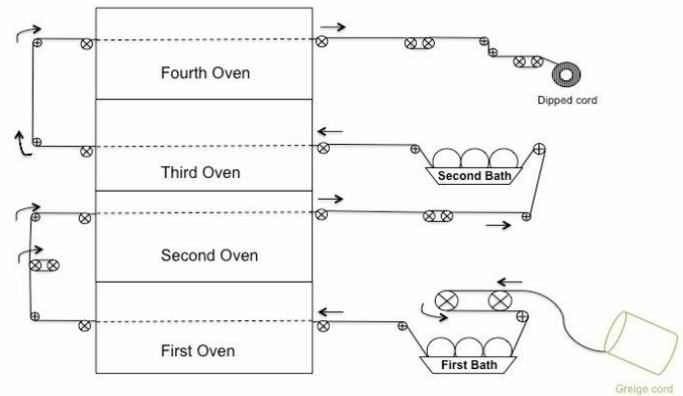


Figure 10 - LDU machine on the left and LDU scheme on the right (adapted from Martins, 2013).

In this project different materials were used: Strong Hybrid and Rayon. The conditions in the LDU machine such as velocity, stretch and oven temperature were used according to the textile used and adapted from the production settings. For Strong Hybrid textile - which Dip is the same as Nylon (with SC of 22 %) - no pre-dip was needed, so it was only used the first and second ovens. Similarly, for Rayon the third and the fourth ovens weren't necessary. To produce the calibration curve for Rayon different SC (%) were used, however the proportions of dip stay the same, as it will be explained in section 3.3.

3.3 D_{PU} measurement

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. The specifications for each material used are on Table 2. There are three different ways to measure: using the Wet-Chemical method, the Weighing method, or the more recent, Time-Domain Nuclear Magnetic Resonance method.

Table 2 - Materials D_{PU} specifications.

Textile	Lower Target Limit (%)	Target (%)	Upper Target Limit (%)
Rayon	2	4	6
Strong Hybrid	4.5	6.5	8.5

3.3.1 Wet-Chemical Method

The Wet-Chemical is the official method to measure the quantity of dip pick-up in Continental.

In this project, the Wet-Chemical method was used as a reference method to obtain the D_{PU} (%) in order to calibrate the TD-NMR for Rayon. For Hybrid this method is not yet available in C-ITA.

The amount of dip pick-up in textile fibers, yarns and fabrics is determined by dissolving the fiber in a suitable solvent and determine the remain dip gravimetrically. To measure 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 obtain a sample with at least a weight of 1 gram for Rayon cords. The sample needs to be dried in the oven at 105 °C for one hour and a half. The sample is weighed into an Erlenmeyer flask and the mass is registered, corresponding to m_1 of Equation 1.
2. Dissolve the sample with a suitable solvent for a defined amount of time. The solvents and time are established according to Table 3.
3. Filtrate the sample using a previous weighed crucible (m_2), a washing fluid and a pump system. The washing fluid is established in Table 3.
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. Weigh the crucible. The registered mass will correspond to m_3 of Equation 1.

The result is reported as % by weight, based on the greige material.

Table 3 - Textiles' solvents and washing fluids.

Textile	Solvent	Dissolution time (h)	Washing Fluid
<i>Rayon</i>	Formic acid - Zinc chloride solution - 50 mL	1	Formic acid 85 % - 50 mL + Water - 50 mL
<i>Hybrid</i>	1) Formic acid - 85% - 50 mL 2) Sulfuric acid conc. - 800 mL	1 + 72	1) Formic acid 85 % - 50 mL + Water - 50 mL 2) Sulfuric acid conc. - 50 mL + Sodium bicarbonate - 20 mL + Water - 500 mL + ethanol - 50 mL

In Figure 11 it is possible to see the procedure for this method.



Figure 11 - Wet-Chemical method procedure for Rayon.

3.3.2 Weighing Method

This method is only used when the Wet-Chemical can't be applied, this is, in materials where the chemical method is too time-consuming, which are PET and Hybrid. Due to its errors associated, for example, is the measurement that depends on the person operating and not on a calibrated device, the use of this method is avoided. Which can lead to be considered a not very reliable method, and also it is not compatible to a big scale production.

This method consists on comparing the weight of the cords before and after the dipping process. The greige cord, to be as similar as the dipped cord, has to be thermofixed in the LDU in the same conditions: velocity, temperature, tensions but no dip solution. Is necessary to prepare 10 replicas with 10 meters each for each one of the 30 spindles that is being tested, as shown in Figure 12. Afterward, the cords are dried in the oven for an hour at 105 °C and later weighed and compared with the greige cord in the same conditions. The percentage of Solid Content in the dipped cord is given by Equation 2.

This method was used in 30 samples of Strong Hybrid from the production to be compared with the results obtained with TD-NMR. In TD-NMR method the Strong Hybrid

was tested using the calibration curve made for the Standard Hybrid, represented in Figure 9.



Figure 12 - Representation of the samples for Weighing method: greige cord on the left and dipped on the right side.

3.3.3 TD-NMR Method

For the tested materials, different sample preparation methods were used in order to improve the simplicity and the productivity of the test. For Strong Hybrid the traditional sample method was used and can be observed in Figure 13, meanwhile for Rayon, the new method of cutting the sample was the chosen one.

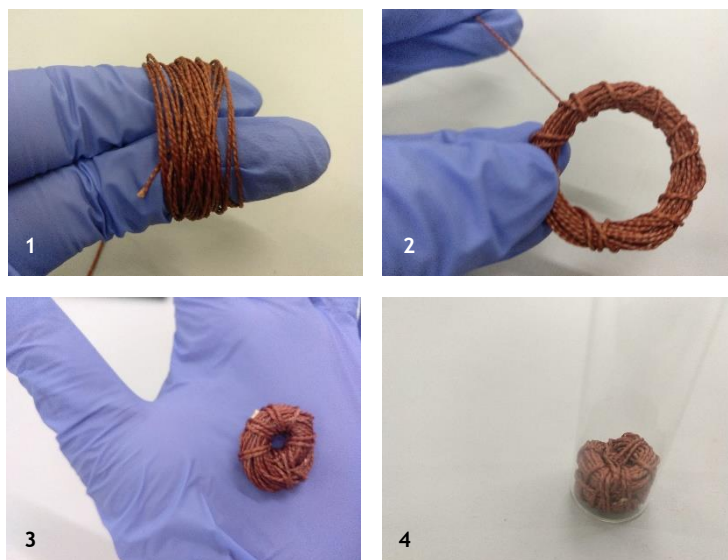


Figure 13 - Traditional sample method procedure.

To measure the amount of dip pick-up in the samples with TD-NMR device, the procedure was the following:

1. Identify the samples tubes and measure their weight with the lids on.

2. Cut a piece of cord with around 1 gram.
3. Prepare the sample and placing it in the tube according to Figure 13 to Hybrid and cutting the sample to Rayon.
4. Put the tubes, without lids, in the oven for at least one hour to Hybrid and one hour and a half to Rayon.
5. Put the lids inside the tubes and leave it to cool down at room temperature.
6. Weigh the samples again and then, heat them up to 40 °C in the heating device for at least 30 minutes.
7. Measure each sample with the TD-NMR device three times.

3.4 Time optimization

In TD-NMR method the samples need to be at the right temperature, which is 40 °C, to be as stable as possible. To reach this temperature according to the standard method the tubes need to be at least 30 minutes at the heating device.



Figure 14 - Procedure of the time optimization test. On the left the samples are represented, on the middle the heating support and on the right the TD-NMR equipment.

In order to predict the time impact in the heat support at 40 °C, several tests were done, using Rayon - a good thermal conductor, and Hybrid - which has Aramid, a bad thermal conductor. 5 and 30 minutes in the heating support were tested, and later analyzed the results, always comparing to the established time value - 30 minutes, with the help of *Minitab*, using a paired t-test via hypothesis test.

3.5 Calibration curves

First of all, to create a calibration curve is necessary to vary the percentage of Solid Content of the dip in 4 different concentrations to have 4 points with different D_{PU} (%),

this is a trial by error method. In Figure 15 is possible to observe the difference between the same greige cord after being dipped with different percentage of Solid Content. To do this step the percentage of Solid Content need to be monitored, using the equipment in Figure 16. Once the SC (%) is the required one, the cord can be dipped in LDU (Figure 10), the conditions stay the same to all the 4 different SC (%).



Figure 15 - Rayon cords with different percentages of Solid Content.

With the dipped cord, knowing the SC (%), the D_{PU} (%) is discovered through the Wet-Chemical method, where the results must have a standard deviation lower than 0.4 %. The next step consists in the calibration of the equipment, knowing the mass and the D_{PU} (%) is possible to calibrate the TD-NMR to that material.

To validate a curve 30 samples from the production are required. Then the results from TD-NMR are compared to the ones obtained with the Wet-Chemical method using *Minitab* to facilitate the calculations, via hypothesis test.



Figure 16 - Solid Content measurement device.

4 Results and discussion

The main work in this Master Thesis was done with the TD-NMR equipment with the aim of calibrate it and optimize the process of reading the amount of dip pick-up in a sample of dipped cord.

The TD-NMR gives the result in percentage of dip pick-up per dipped cord. D_{PU} is defined as the amount of dip pick-up per greige cord, being necessary to convert the obtained values.

$$D_{PU_{per\ greige\ cord}} = \frac{m_{DIP}}{m_{greige\ cord}} \times 100 \quad (8)$$

$$D_{PU_{per\ dipped\ cord}} = \frac{m_{DIP}}{m_{dipped\ cord}} \times 100 \quad (9)$$

$$m_{greige\ cord} = m_{dipped\ cord} - m_{DIP} \quad (10)$$

Combining the equations above:

$$m_{DIP} = \frac{D_{PU_{per\ dipped\ cord}}}{100} \times m_{dipped\ cord} \quad (11)$$

$$D_{PU_{per\ greige\ cord}} = \left(\frac{\frac{D_{PU_{per\ dipped\ cord}}}{100} \times m_{dipped\ cord}}{m_{dipped\ cord} \times (1 - \frac{D_{PU_{per\ dipped\ cord}}}{100})} \right) \times 100 \quad (12)$$

Simplifying the Equation 12:

$$D_{PU_{per\ greige\ cord}} = \frac{D_{PU_{per\ dipped\ cord}}}{100 - D_{PU_{per\ dipped\ cord}}} \quad (13)$$

Therefore, to obtain the TD-NMR results in D_{PU} ($D_{PU_{per\ greige\ cord}}$) is necessary to use Equation 13. 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 Strong Hybrid

In theory the TD-NMR should only be influenced by the Solid Content, the passing velocity in the LDU and the interaction between temperature and Solid Content as it was proved in previous Master Thesis. Consequently, since Standard Hybrid (1680+1400)x1x2 and Strong Hybrid (1680x2+470x1)x3 have the same dip and only differ in the construction (see Figure 17) the TD-NMR calibration curve of Standard Hybrid, represented in Figure 9 should fit the Strong Hybrid.

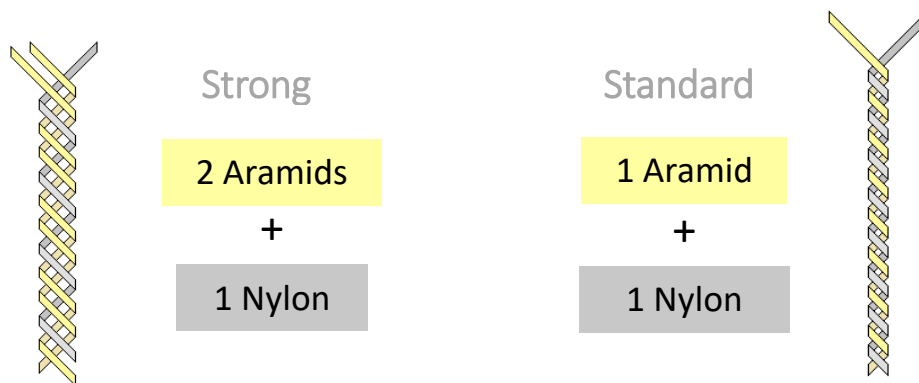


Figure 17 - Construction of Strong Hybrid at the left and Standard Hybrid at the right side.

In order to determine whether the curve already created to Standard Hybrid could possibly fit to measure the D_{PU} of Strong Hybrid, 30 samples from the production were tested. The results from the measurement are represented in Figure 18 with an average of $(10.5 \pm 0.6) \%$, the specification for D_{PU} is characterized as lines.

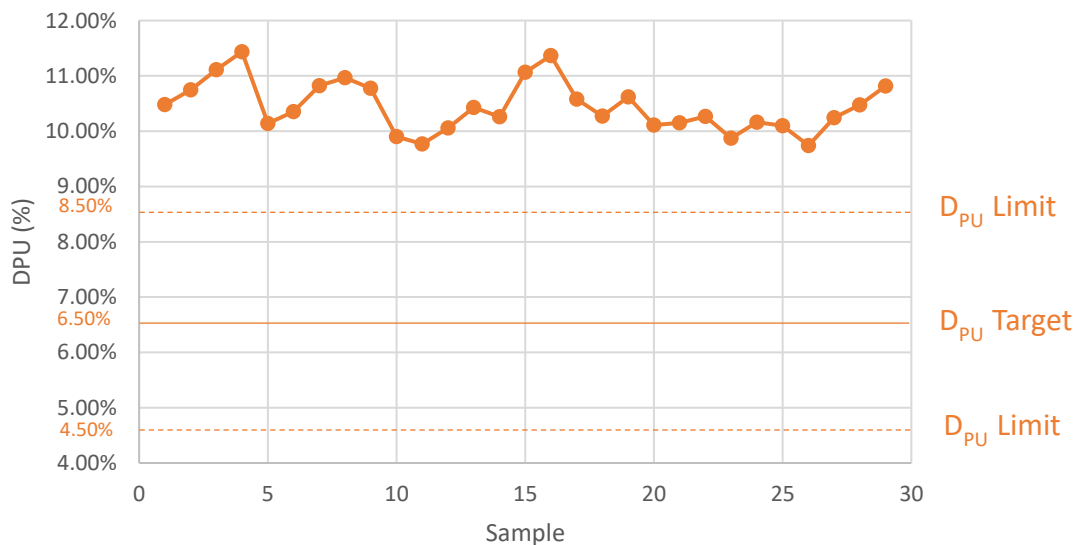


Figure 18 - TD-NMR results for Strong Hybrid.

Observing the graphic is possible to conclude that the measurements are outside the desired range. This fact can imply that the specification for Strong Hybrid may currently need some adjustments.

In order to verify the results obtained with TD-NMR a sample of Strong Hybrid was sent to the Central Laboratory in Hannover to be measured through the Wet-Chemical method. The results are shown in Table 4.

Table 4 - Comparison of TD-NMR and Wet-Chemical methods for one sample.

Method	D _{PU} average (%)	Measurements
<i>Wet-Chemical</i>	10.7 ± 0.150	3
<i>TD-NMR</i>	10.8 ± 0.039	3

Observing the comparison between the two methods is possible to check their similarity, verifying that, for the same sample, the results with the Standard Hybrid calibration curve and results via Wet Chemical method are similar and with a lower standard deviation by TD-NMR.

The Weighing method was also applied, giving an D_{PU} average of (12.3 ± 0.820) % which illustrate a higher standard deviation than TD-NMR. The higher value can be explained with the error associated with this method, listed in section 3.3.2.

With these results it is possible to affirm that the TD-NMR provides similar results to Wet-Chemical method and, due to its simplicity, it's a better way to measure the D_{PU} of Strong Hybrid samples using Standard Hybrid calibration curve.

The use of this method will allow Continental to save time in Strong Hybrid quality control.

4.2 Rayon

To create a new calibration curve in TD-NMR, 4 points with different D_{PU} are needed. The amount of dip pick-up can be changed by varying the Solid Content in dip solution. The reference range for the D_{PU} percentage of the points in a calibration curve are described in Table 5. It is possible to estimate the Solid Content maintaining the recipe proportions. Therefore, 4 different Solid Content cords were dipped in LDU, and to confirm the values the D_{PU} of the Wet-Chemical method was used.

Table 5 - Values for calibration of Rayon.

Samples	Limits	Calibration Values
A	Between LTL-1% and LTL	1 % - 2 %
B	Between LTL and target	2 % - 4 %
C	Between Target and UTL	4 % - 6 %
D	Between UTL and UTL+1%	6 % - 7 %
	LTL	2 % Lower Targeted Limit
	Target	4 %
	UTL	6 % Upper Targeted Limit

Three samples for each Solid Content needed to have a standard deviation lower than 0.4 %, according to Continental standards, for each sample, three measurements need to be tested with a standard deviation lower than 0.4 %. The results for the Wet-Chemical method can be observed in Table 6.

Table 6 - Dipping results via Wet-Chemical method for Rayon cords.

Sample	Solid Content (%)	D _{PU} (%)	Average (%)	Standard deviation (%)
A	5.09	1.70	1.67	0.04
		1.67		
		1.63		
B	9.87	3.39	3.17	0.25
		3.22		
		2.90		
C	17.74	5.30	5.10	0.19
		5.06		
		4.93		
D	22.38	6.58	6.37	0.37
		6.59		
		5.95		

Using the results obtained from Wet-Chemical method as a reference and by knowing the masses of the samples it is possible to calibrate the TD-NMR equipment, creating a calibration curve for Rayon, represented in Figure 19.

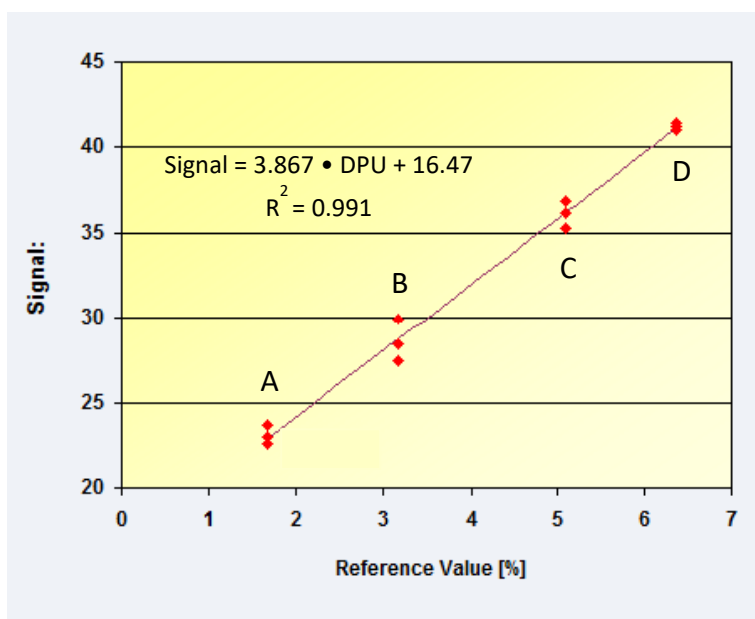


Figure 19 - Calibration curve for Rayon in the TD-NMR device software "minispec Plus 6.0.3".

With the aim of validating the calibration curve, 30 samples from the production were analyzed and the results obtained with the TD-NMR were compared with the ones from the production obtained using the Wet-Chemical method.

Observing the Figure 20 is possible to check that the results from TD-NMR are near the desired target. The results with Wet-Chemical method have a higher average, of $(4.94 \pm 0.55) \%$ while with TD-NMR the average of dip pick-up was $(3.99 \pm 0.60) \%$.

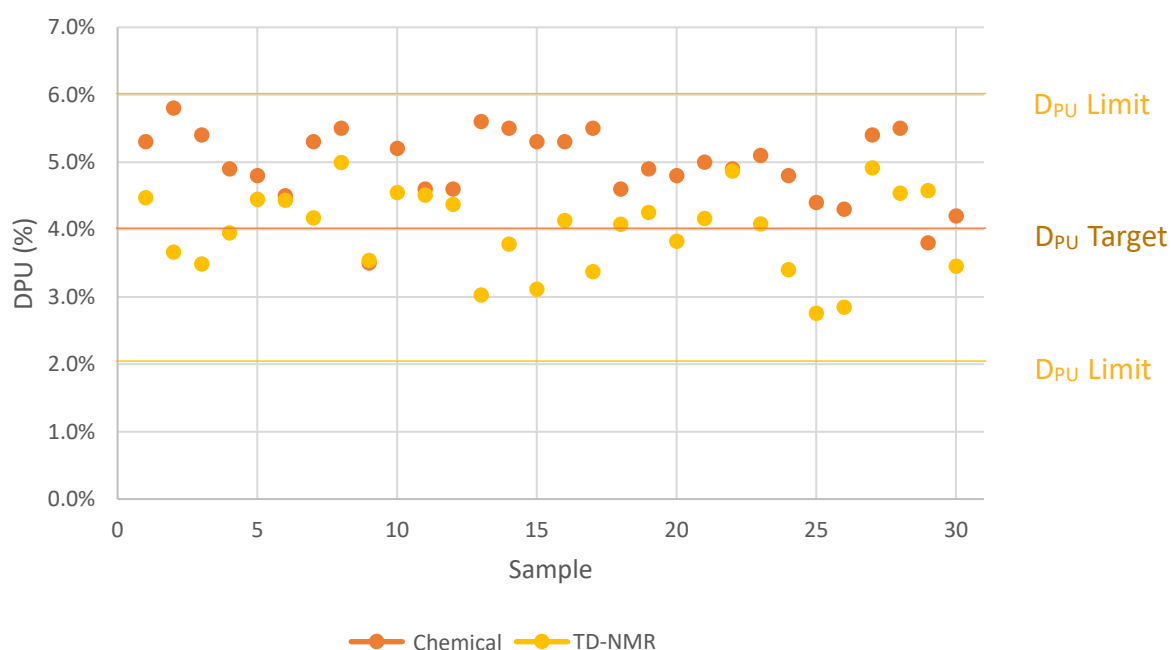


Figure 20 - Comparison of the results obtained by Wet-Chemical and TD-NMR of 30 samples from the production.

First, to check the normality of the samples for each method was performed a normality test, with the help of Minitab, the results can be observed in Appendix A.2 (Figure A.2.4 and Figure A.2.5). Both gave a result of p-value greater than 0.05, assuming a normal distribution, the forward tests were performed.

Afterwards a hypothesis test for verifying the equality of variances of both populations was made. The results can be analyzed in Figure A.2.3 (Appendix A.2). With a p-value greater than 0.05 in both tests perform by Minitab is possible to conclude that variances do not differ significantly.

Knowing that both populations are normal and have equal, yet unknown variances, a hypothesis test using a two-sample t-test was made in order to check whether the means differ significantly between the two populations. The test was made for a significance level of 5 % and the p-value obtained was lower than 0.0001. Since the p-value is lower than 0.05 the null hypothesis is rejected, which means that the means of the two methods are different.

However, and as noticed before, by comparing the two methods in Figure 20 is possible to conclude that the results from TD-NMR are nearest the D_{PU} target, which means that TD-NMR is more reliable than Wet Chemical Method. Also, as usually the Wet-Chemical Method has higher results due to external influences, such as: the crucible may not be well dried, different operators can execute the same measurement which leads to more errors, with so many steps is more likely to lose some weight of the sample. The production only makes one measurement, so it also increases the error associated.

Table 7 - Two sample t-test results for the comparison of Wet-Chemical and TD-NMR methods.

Difference of means	Confidence Interval	P-value	Margin of error
0.00952	(-0.01252; -0.00651)	<0.0001	0.00301

Through the analysis of Table 7, is possible to calculate the difference between the means of the results obtained by Wet-Chemical and TD-NMR. The means differ (0.952 ± 0.30) % which is less than 1 %, the standard limit in Continental. Assuming that TD-NMR presents better results and even though the 2-sample t-test rejected the null hypothesis, according to Continental standard value this calibration can be approved.

Another dip was tested in order to make a second calibration curve. This new dip, as already explained in Section 2.5, is made with a different resin.

Similar to when used the standard dip, a calibration curve with 4 different Solid Content was developed, the results for the dipping process are shown in Table 8.

Table 8 - Dipping results via Wet-Chemical method for rayon cords with the new dip.

Sample	Solid Content (%)	D _{PU} (%)	Average (%)	Standard deviation (%)
A	5.28	1.62	1.67	0.06
		1.55		
		1.66		
B	9.53	2.93	3.32	0.36
		3.37		
		3.66		
C	16.72	4.53	4.84	0.38
		4.72		
		5.27		
D	21.93	6.17	6.45	0.37
		6.31		
		5.87		

After that, the calibration curve was made, represented in Figure 21.

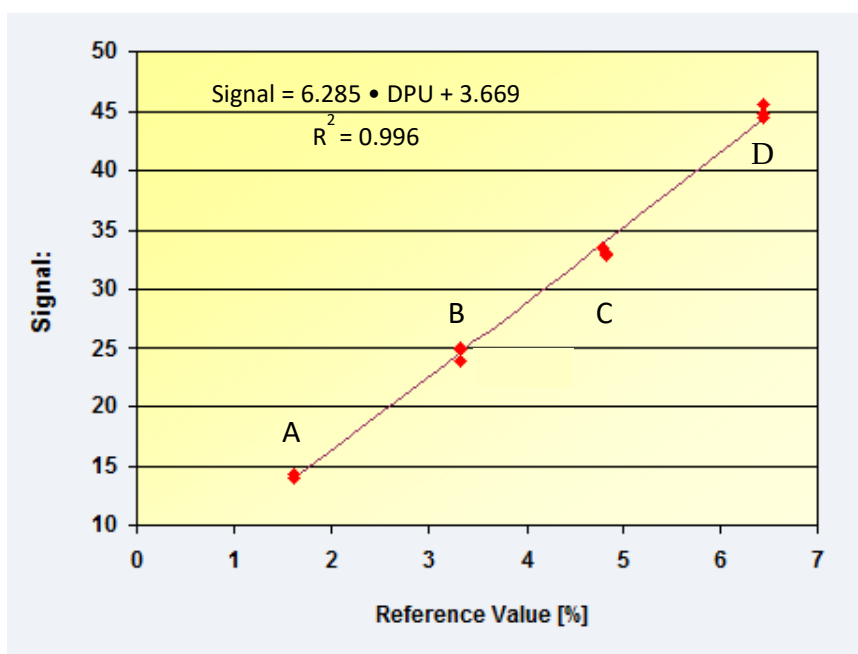


Figure 21 - Calibration curve for Rayon with the new dip in the TD-NMR device software "minispec Plus 6.0.3".

On the second part of the process the validation of the curve cannot be currently achieved, since this dip is not being use in the production.

Comparing the two calibration curves with different dips, in Figure 22, is possible to conclude that they are different, presenting different slopes, evidencing the influence of different dips in the dip pick-up measurements.

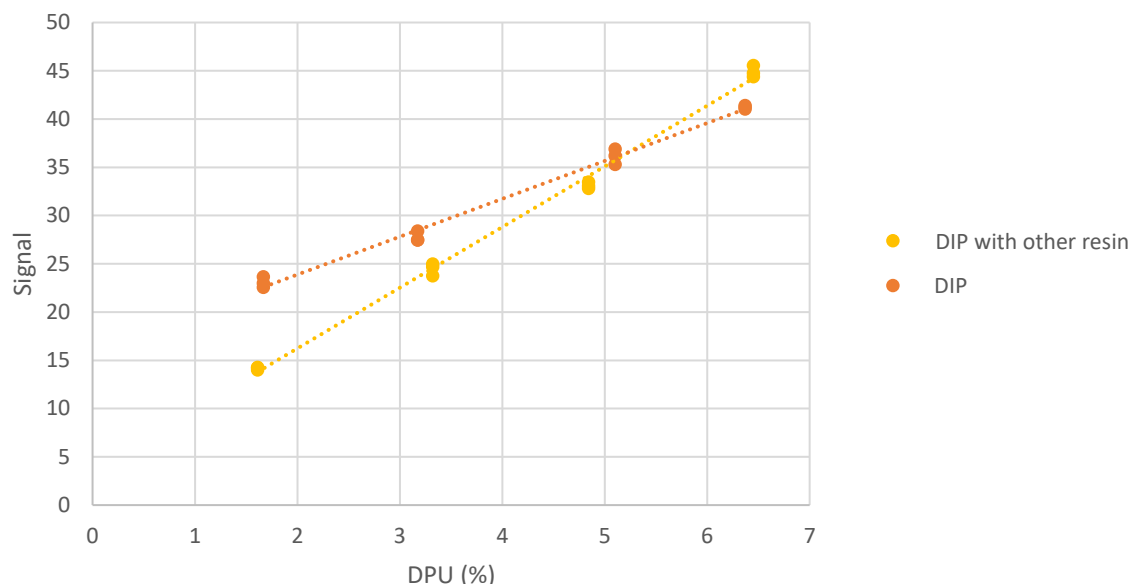


Figure 22 - Comparison of two Rayon calibration curves with different dips.

4.3 Data comparison

In this part of the work, data from the measuring with TD-NMR of Nylon were compared to the ones obtained through Wet-Chemical in the previous year.

In order to have a more visual evaluation, linear regressions of percentage of dip pick-up over the time were made to each sample for TD-NMR and Wet-Chemical methods.

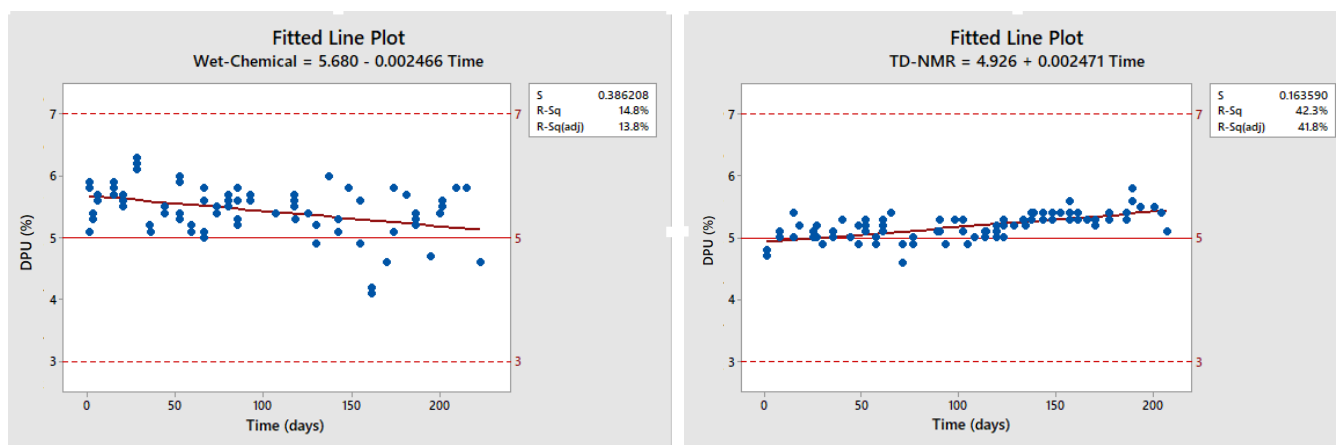


Figure 23 - Variation of dip pick-up over the time of Nylon A with a dtex of 470x1x2. Results from Chemical method at the left and TD-NMR at the right.

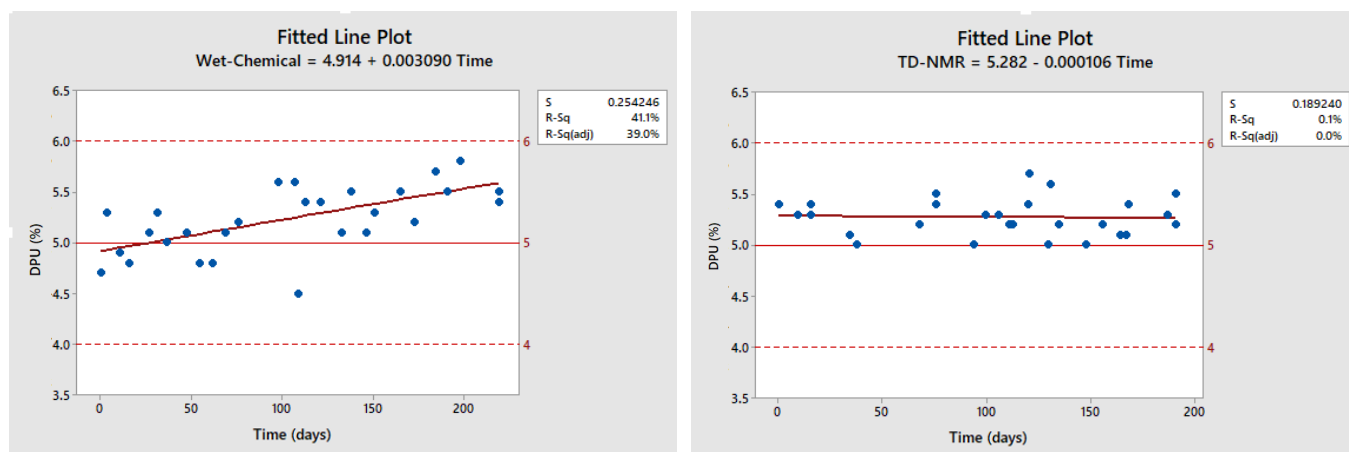


Figure 24 - Variation of dip pick-up over the time of Nylon B with a dtex of 1400x1x2. Results from Chemical method at the left and TD-NMR at the right.

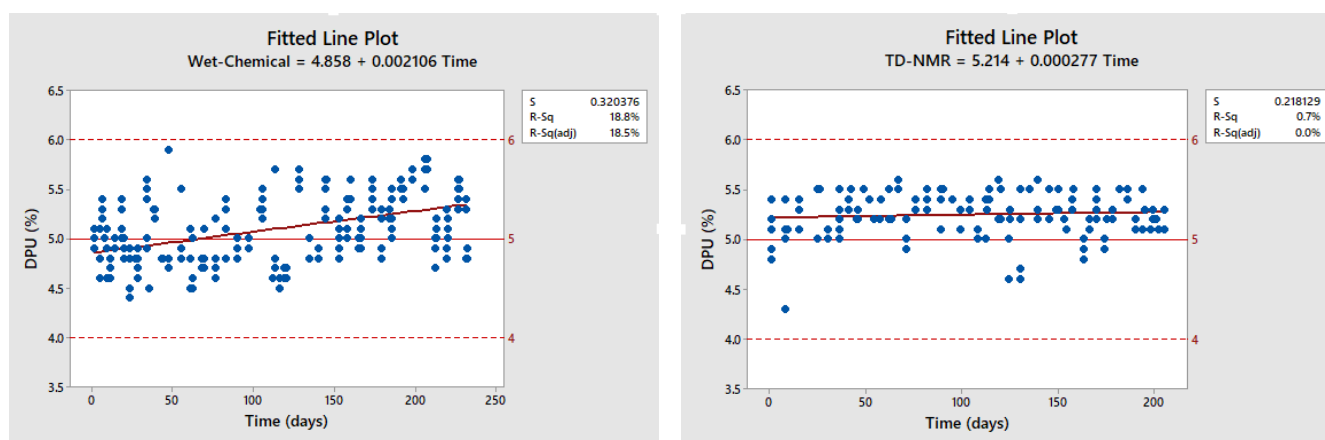


Figure 25 - Variation of dip pick-up over the time of Nylon C with a dtex of 1400x1x2. Results from Chemical method at the left and TD-NMR at the right.

Different Nylon textiles were analyzed to this study, they differ on dtex and supplier. The limits of the specification of dip pick-up are represented as dashed lines and the target as a continue line.

Through the analysis of Figure 23, Figure 24 and Figure 25 is possible to check the reliability of TD-NMR, once their graphics exhibits lower slopes and lower dispersion which indicates the stability of this method.

To make a more authentic statistical analyses the quality capability was tested. To each population the normality distribution was verified, the results can be observed in Figure 26 and from Figure A.3.1 to Figure A.3.5. Later, the graph for the capability analysis was constructed and can be seen in Figure 27 and from Figure A.3.6 to Figure A.3.10, the variables suffer a transformation in order to become a normal distribution, since some of the results didn't follow that distribution.

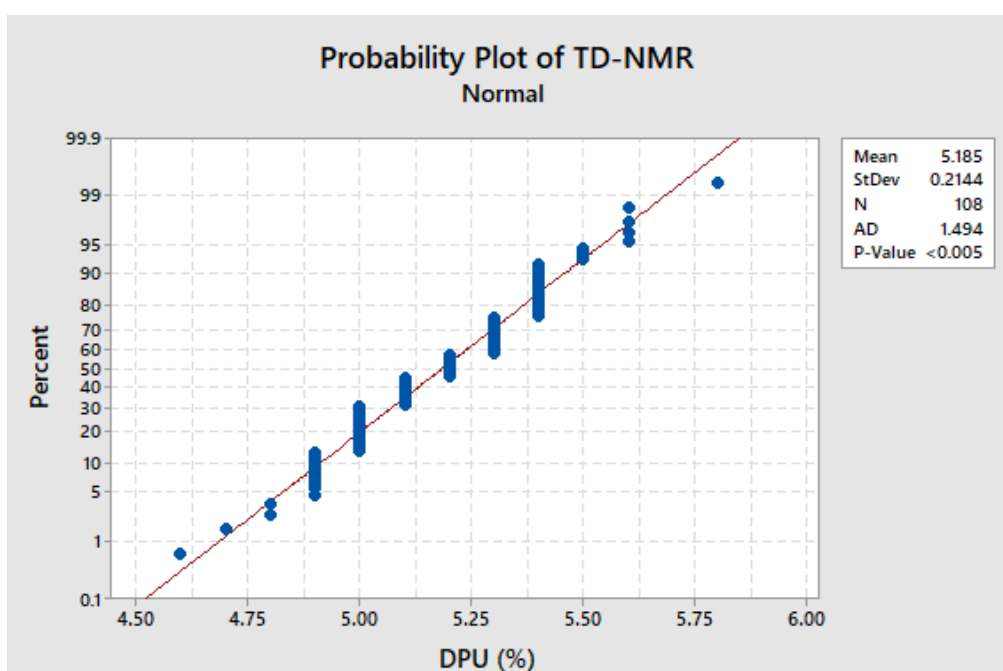


Figure 26 - Normality test for Nylon A TD-NMR results.

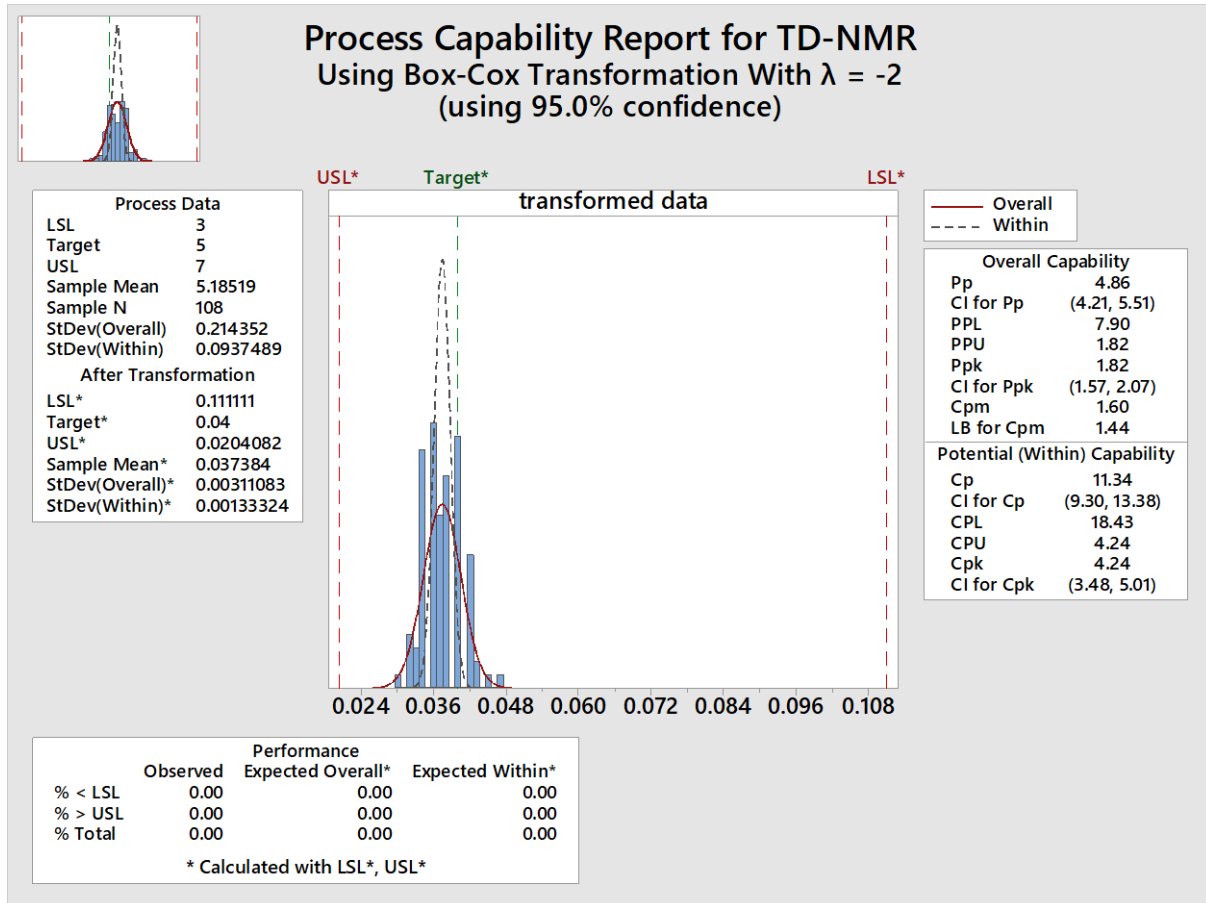


Figure 27 - Quality capability analysis of Nylon A TD-NMR results.

To analyze the results obtained with quality control charts, some standard values were followed and can be checked in Table 9.

C_p represents the process capability, is the ratio of the specification dispersion to the process spread, higher C_p values indicate a more capable process. C_{pk} is the process capability index and compares the distance from the process mean to the closest specification limit. If the two variables are equal the process results are centered (Isixsigma; Minitab Blog; Minitab Support; Statistical Process Control).

Table 9 - Capability indexes interpretation (Minitab Support).

Variable	Test	Conditions
C_{mk}	Machine critical capability	≥ 1.67 : the machine is capable and under control
		< 1.67 : the machine must be corrected
C_{pk}	Process critical capability	≥ 1.33 : the process is capable and under control
		$1.00 \leq C_{pk} < 1.33$: the process is conditionally capable
		< 1.00 : the process is not capable and must be corrected
P_{pk}	Process potential critical capability	≥ 1.67 : the new process is capable and under control

Observing the graphics of this experience (Appendix A.3) is possible to conclude that only the material B has a normal distribution, since p-value is greater than 0.05 (α imposed) in both methods. For the materials that does not follow a normal distribution a transformation of the variables was done in order to make them normal, allowing to reach more proper conclusions.

Analyzing the graphics is possible to assess that C_{pk} is lower than C_p , so to TD-NMR the process is not centered, neither is with the Wet-Chemical method. Since C_{pk} , in all the examples, is greater than 1.33 (benchmark value) the process is capable and under control. Higher C_p values indicate a more capable process, which can be observed in TD-NMR with material A when compared with the Wet-Chemical process. In the graphics of Nylon C the two curves of TD-NMR that represents the overall process and the subgroups (results within the same day) are nearest than the ones on Wet-Chemical capability chart.

P_{pk} , PPU and PPL are measures of overall process capability. They measure the distance between the process average and the specification limits, compared to the process spread. PPL measures how close the process mean is running to the lower specification limit, PPU measures how close the process mean is running to the upper specification limit and P_{pk} equals the lesser of PPU and PPL. If the three variables are equal, the process is centered at the exact midpoint of the specification limits.

When $PPL > PPU$ is more likely to produce defective units that violate the upper specification limit. If $PPL < PPU$ is more likely to produce defective units that violate the lower specification limit (Minitab Support).

Table 10 - Quality capability analysis TD-NMR results.

	Nylon	Variable		
		PPL	PPU	P _{pk}
Value	A	7.90	1.82	1.82
	B	2.28	1.31	1.31
	C	1.28	1.60	1.28

Table 11 - Quality capability analysis Wet-Chemical results.

	Nylon	Variable		
		PPL	PPU	P _{pk}
Value	A	2.79	0.96	0.96
	B	1.27	0.77	0.77
	C	1.47	0.70	0.70

The results of this test can be consulted in Table 10 and Table 11. Is possible to conclude that with TD-NMR for material C PPL is lower than PPU so is more likely to produce units with a dip pick up near the lower specification. For the materials A and B, PPU is lower than PPL so is more likely to produce units with a dip pick up near the upper specification limit. With the Wet-Chemical method for all the materials PPU is lower than PPL so is expected to produce units with a dip pick up near the upper specification limit.

Is also possible to conclude from the graphics that with TD-NMR the results have a better distribution, since in Wet-Chemical they are more scattered.

Overall, since the standard deviation in TD-NMR is lower than in Wet-Chemical, the variability of the data is inferior. However, although this method seems stable and reliable to use as a quality tool, to have a more consistent analysis, more data and time are needed.

4.4 Time optimization

According to the standard method the samples need to be at least 30 minutes in the heat support to reach the desire temperature. However, an improvement in this step could lead to a quicker process and consequently to a better productivity in quality control.

In order to predict the time impact in the heat support at 40 °C, several tests were made with two materials: Rayon and Hybrid. 30 samples from the production were

used in these tests, where was experienced how would the D_{PU} measurement react by staying only 5 minutes in the heating support.

4.4.1 Rayon

Rayon has a good thermal conductivity, so it was a good material to get started. To assure 30 samples were enough a Power Test was made with the help of Minitab, assuming a maximum acceptable difference between the samples of 0.2 %. Using the standard deviation of the 30 samples of 0.06 %, with a power of 1 we have confidence that 30 samples are enough to detect a difference of 0.2 %, the results can be observed in Figure 28.

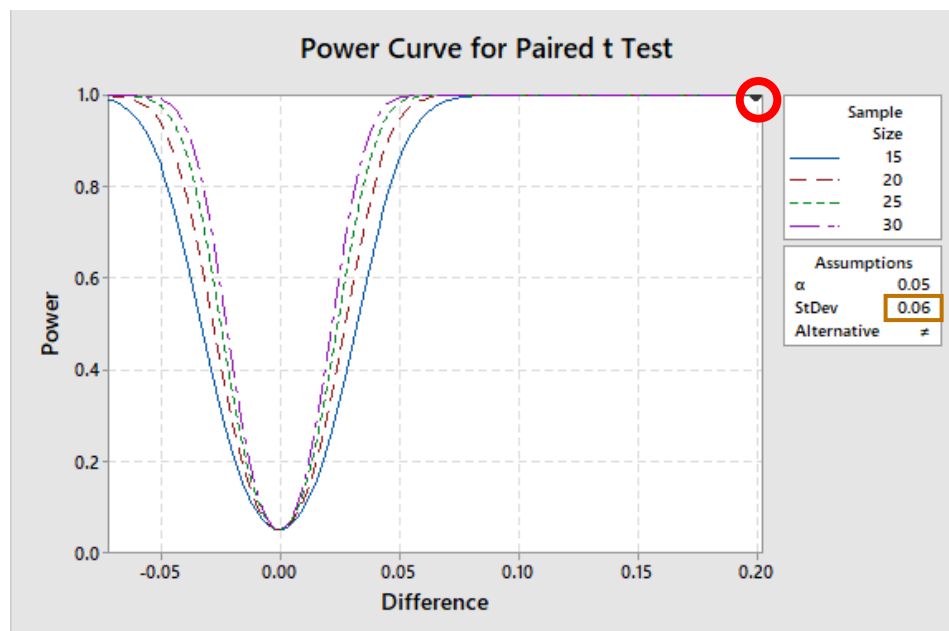


Figure 28 - Power Curve for Paired t-test for 15, 20, 25 and 30 samples of Rayon via Minitab.

The results from 5 and 30 minutes are compared in Figure 29, where the specifications of the material are represented as D_{PU} limits. A paired t-test was performed to check the similarity between the time results. 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 0.208. Since the p-value is higher than 0.05 the null hypothesis is not rejected, so the means do not differ significantly.

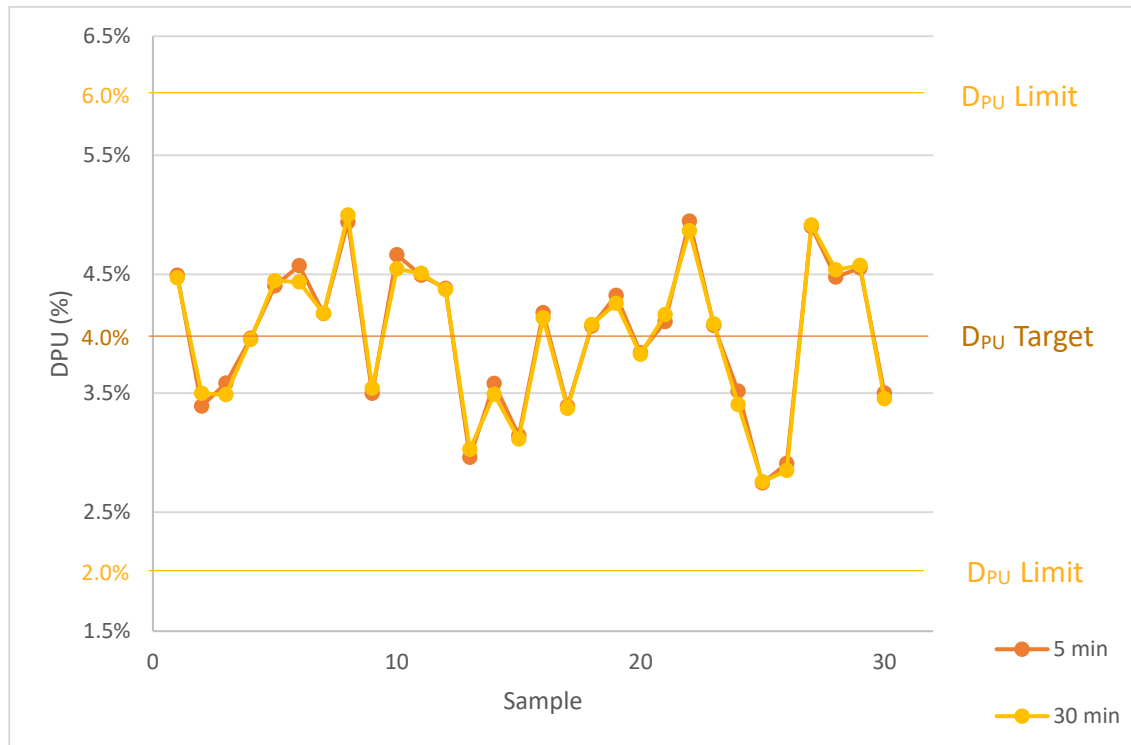


Figure 29 - Test results for 5 and 30 minutes for 30 samples of Rayon

In the boxplot representation, in Figure 30, it can be checked that the distribution is similar between the two times. The boxplot is a graphical summary of the distribution of a sample that shows its shape, central tendency, and variability. Comparing the two sets, it is possible to conclude they are similar in all the parameters.

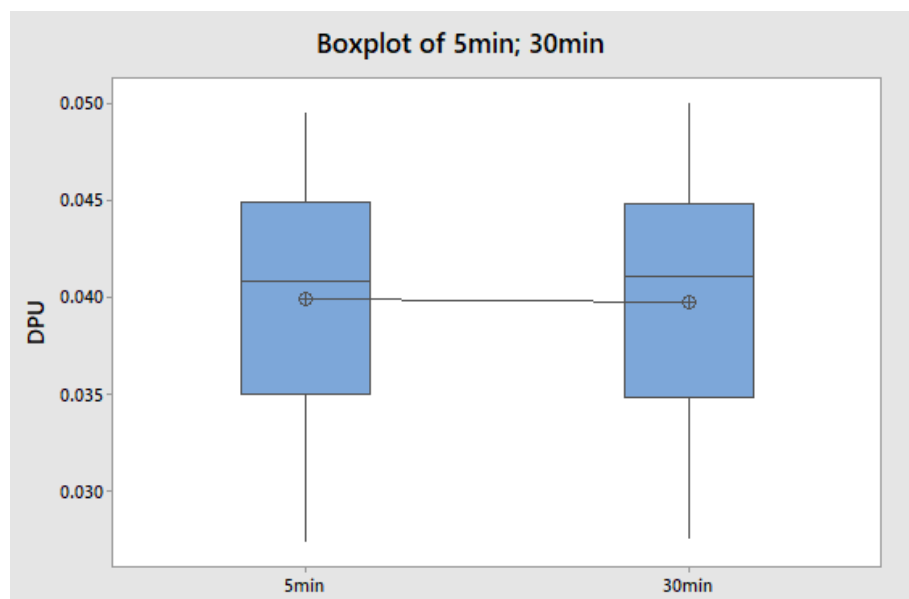


Figure 30 - Dip pick-up boxplot representation for 30 samples of Rayon after 5 minutes and 30 minutes in the heating support via Minitab.

4.4.2 Hybrid

With the aim of validating this optimization for all materials in C-ITA a material with worst thermal conductivity was also tested, Standard Hybrid which was the one available in production.

Similarly to Rayon, a Power Test was applied, using the standard deviation of the 30 samples of 0.037 %, the results were alike, proving that with 30 samples the confidence in the method was very high, which can be observe in Figure A.4.4.

The results for the test performed right after 5 and 30 minutes are compared in Figure 31. A paired t-test was also done for a significance level of 5 % and p-value obtained was 0.131. Since the p-value is higher than 0.05 the null hypothesis is not rejected, so the means do not differ significantly.

In the boxplot representation, in Figure 32, it can be observed that the distribution is very similar between the results for the two times. Three outliers can be detected, however they do not constitute a problem since they are within the specification, as it can be checked in Figure 31. Still, observing the graphic is possible to conclude that the measurements are nearest the bottom limit, which may imply that the specification for Hybrid may need some adjustments.

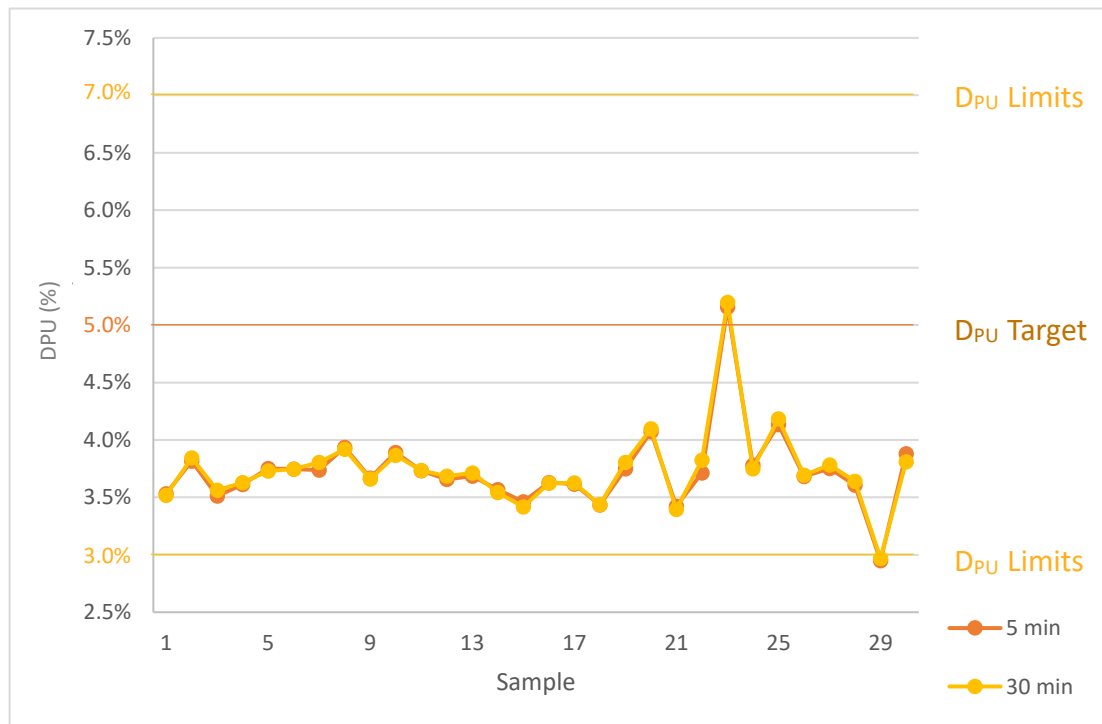


Figure 31 - Test results for 5 and 30 minutes for 30 samples of Hybrid.

As proved, 5 minutes is enough time in the heating support to the sample reach the temperature within TD-NMR, which is 40 °C. This experiment is valid to the materials with a better conductivity than Standard Hybrid, which, in C-ITA, are all except Strong Hybrid and Aramid (Alagirusamy and Das 2010).

Due to the lack of time and of production samples, since it's not usual the manufacture, it wasn't possible to prove the time optimization for these two materials.

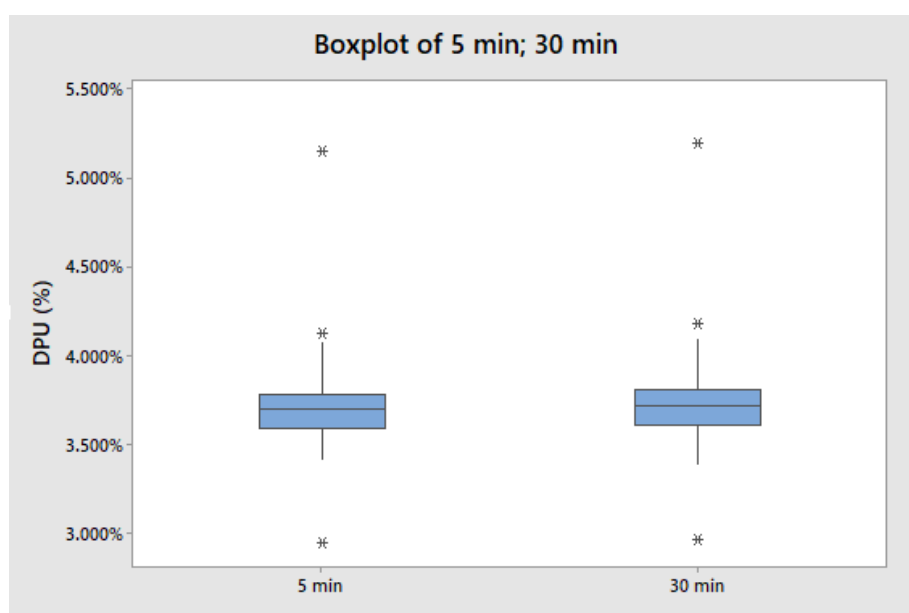


Figure 32 - Dip pick-up boxplot representation for 30 samples of Hybrid after 5 minutes and 30 minutes in the heating support via Minitab.

5 Conclusion

This project helps proving, once more, that TD-NMR presents a lot of advantages when compared with the traditional methods, since it is a faster, more reliable and environmentally friendly method. This master thesis also contributed to a better understanding and to the implementation of the TD-NMR method to measure D_{PU} for Hybrid and Rayon textiles in C-ITA, thus allowing an improvement in quality control.

All of the proposed goals were achieved with success. This work was able to prove that, as expected, the calibration curve already made for Standard Hybrid can fit Strong Hybrid allowing the measurement of the percentage of dip pick-up by TD-NMR, saving time and future work. The specifications for Hybrids may need some adjustments.

A calibration curve for Rayon was developed by calibrating the TD-NMR device for this material which allows a more reliable and faster quality control for Rayon textiles in C-ITA. Furthermore, with the approval of this calibration curve, C-ITA will no longer needs to make the quality control by the Wet-Chemical method, which means that there is no need to buy expensive chemicals and more security for the employees, since they will no longer work with dangerous chemicals. This, allying with the reduction of time spent in the quality control process, is a great improvement in this industry.

By comparing the results from Wet Chemical and TD-NMR methods, it was possible to prove that the last one is more stable and reliable than the traditional ones. However, to have a more consistent analysis more data and time are needed.

As an extra goal, it was proposed to optimize the TD-NMR samples preparation. This was also accomplished and a reduction of 25 minutes in the measurement process was achieved, resulting in an increment of productivity in quality control.

In conclusion, this project improved the measurement for this recent method and contributed to expanding the range of textiles that can be measured by the TD-NMR device in C-ITA.

6 Assessment of the work done

6.1 Objectives Achieved

The initial goal of this project was to calibrate the TD-NMR device to allow its use for Rayon and Strong Hybrid textiles. A calibration curve for Rayon was developed and it has been proved that the curve already made for Hybrid can also fit Strong Hybrid measurements, as expected.

6.2 Other Work Carried Out

As an extra goal, it was proposed to optimize the TD-NMR samples preparation. A reduction of 25 minutes in the preparation of the samples process was achieved.

6.3 Limitations and Future Work

Time was one of the biggest difficulties. To create a new calibration curve several trials are needed when using the Wet-Chemical method, which requires more time.

Additionally, the lab and all the equipment need to be shared with other co-workers and interns, which can delay the projects. Also, when making the dip for Rayon at higher percentages of Solid Content the solution started to coagulate very easily which affects the impregnation, so more than one trial was needed. To Strong Hybrid, the fact that C-ITA cannot use the Wet-Chemical method delayed this project, once we needed to wait for the results of Central Laboratory.

For future work, validation of the Rayon calibration curve for other suppliers and dtex will be necessary, since currently it is not a possible step due to the fact that C-ITA is not producing different Rayon materials. Additionally, it is missing validation for the 5 minutes time-test for Strong Hybrid and for Aramid so it can be implemented in all materials. In the data comparison part, 6 months is an insufficient time to compare data, this work should be repeated in the future, so more proper conclusions can be achieved. Approving the PET calibration curve for different suppliers and dtex and creating a calibration curve for Aramid should also be done.

6.4 Final Assessment

I am really proud of this Master Thesis and all the work I have done and I hope that all this work can help increasing the productivity of C-ITA. It has been a real pleasure to get the opportunity to work in this company and to meet such amazing people.

7 References

- Alagirusamy, R., and A. (Apurba) Das. 2010. *Technical Textile Yarns : Industrial and Medical Applications*. CRC Press.
- Bruker, 2016. “Domínio de Tempo (TD)-NMR.” 2016. <https://www.bruker.com/pt/products/mr/td-nmr.html> (January 4, 2019).
- “Continental Portugal.” <https://www.continental-corporation.com/pt-pt> (October 4, 2019).
- Dalitz, Franz, Markus Cudaj, Michael Maiwald, and Gisela Guthausen. 2012. “Progress in Nuclear Magnetic Resonance Spectroscopy Process and Reaction Monitoring by Low-Field NMR Spectroscopy.” 60: 52-70.
- “Devices and Magnetic Resonance Imaging Systems.” https://users.fmrib.ox.ac.uk/~peterj/safety_docs/fda_primer.html (February 8, 2019).
- Hearle, J W S. 2015. *Advances in Composites Manufacturing and Process Design 11 - Mechanical Properties of Textile Reinforcements for Composites*. Elsevier Ltd.
- “Isixsigma.” <https://www.isixsigma.com/tools-templates/capability-indices-process-capability/process-capability-cp-cpk-and-process-performance-pp-ppk-what-difference/> (February 8, 2019).
- Joseph P. Hornak. 1996. *The Basics of NMR*.
- Kramer, Thomas. “Basics of Reinforcements.”
- Lindenmuth, B. E.; McDonel. 2006. “An Overview of Tire Technology.” In *The Pneumatic Tire*, Nhtsa - Nacional Higway Traffic Safety Administration.
- Louis, A, J W M Noordermeer, W K Dierkes, and A Blume. 2014. *TECHNOLOGIES FOR POLYMERIC CORD / RUBBER ADHESION IN TIRE APPLICATIONS* *Elastomer Technology and Engineering Faculty of Engineering Technology Enschede , The Netherlands Presented at the Fall 186 Th Technical Meeting of Rubber Division , ACS Nashville , Te.*
- “Minitab Blog.” <https://blog.minitab.com/blog/statistics-and-quality-data-analysis/cp-and-cpk-two-process-perspectives-one-process-reality> (February 8, 2019).
- “Minitab Support.” [---

References](https://support.minitab.com/en-us/minitab/18/help-and-how-</p></div><div data-bbox=)

to/quality-and-process-improvement/capability-analysis/how-to/capability-analysis/normal-capability-analysis/interpret-the-results/key-results/ (January 4, 2019).

Montgomery, Douglas C, and George C Runger. 2003. *Applied Statistics and Probability for Engineers Third Edition*.

“Raw Materials | MEHLER.” <https://www.mehler-ep.com/en/produkte/technologies/raw-materials/> (September 24, 2018).

Silva, Lorena M A et al. 2016. “NMR Investigation of Commercial Carbon Black Filled Vulcanized Natural Rubber Exposed to Petrodiesel / Biodiesel Mixtures.” *Fuel* 186: 50-57.

“Statistical Process Control.” <http://www.statisticalprocesscontrol.info/glossary.html#Capability> (February 8, 2019).

Todt, Harald et al. 2001. “Quality Control with Time-Domain NMR.” 103: 835-40.

Whewell, Edward Noah Abrahart Charles S. 2018. “Development Of Textiles And The Textile Industry” ed. *Britannica Encyclopedia*. : 1-52. <https://www.britannica.com/topic/textile>.

Appendix A

A.1

Table A.1.1- Weighing method results for Strong Hybrid.

Sample bobbin	Weigh average of dried sample (g)	D _{PU} (%)
Greige cord	4.008	-----
1	2.545	12.95
2	2.230	13.71
4	3.276	12.18
5	3.211	12.56
6	3.548	12.77
7	3.889	13.21
8	4.270	11.79
9	4.555	13.19
12	5.542	12.41
57	14.102	11.48
58	14.278	10.49
59	17.012	11.47
80	22.241	10.50
82	22.769	12.03
89	31.204	12.13
92	21.132	12.53
93	32.543	12.48
94	32.873	12.30
96	26.263	11.56
97	33.899	13.85
99	27.042	12.81
101	22.908	11.72
102	23.090	11.15
103	28.044	13.02
104	23.499	11.41
105	36.543	12.45
106	23.920	12.27
107	20.871	13.05
108	24.313	11.91

Table A.1.2 - TD-NMR method Results for Strong Hybrid.

Sample	Tube + lid mass (g)	Tube + lid + dried sample mass (g)	Dried sample mass (g)	D _{PU} Average (%)
1	16.172	17.000	0.828	10.5
2	16.247	17.090	0.843	10.7
4	16.358	17.164	0.806	11.1
5	16.165	16.984	0.819	11.4
6	16.316	17.119	0.803	10.1
7	16.251	16.913	0.662	10.4
8	16.191	16.964	0.773	10.8
9	16.231	17.025	0.794	11.0
12	16.316	17.124	0.808	10.8
57	16.269	17.050	0.782	9.9
58	16.267	17.150	0.883	9.8
59	16.246	17.059	0.813	10.1
80	16.286	17.093	0.808	10.4
82	16.302	17.106	0.805	10.3
89	16.295	17.105	0.810	11.1
92	16.223	17.067	0.844	11.4
93	16.404	17.186	0.782	10.6
94	16.214	17.023	0.809	10.3
96	16.220	17.026	0.806	10.6
97	16.187	16.977	0.790	10.1
99	16.228	17.033	0.805	10.2
101	16.273	17.084	0.811	10.3
102	16.111	16.988	0.877	9.9
103	16.214	17.030	0.817	10.2
104	16.377	17.165	0.788	10.1
105	16.241	16.984	0.743	9.7
106	16.249	17.069	0.820	10.2
107	16.249	17.062	0.813	10.5
108	16.252	17.052	0.800	10.8

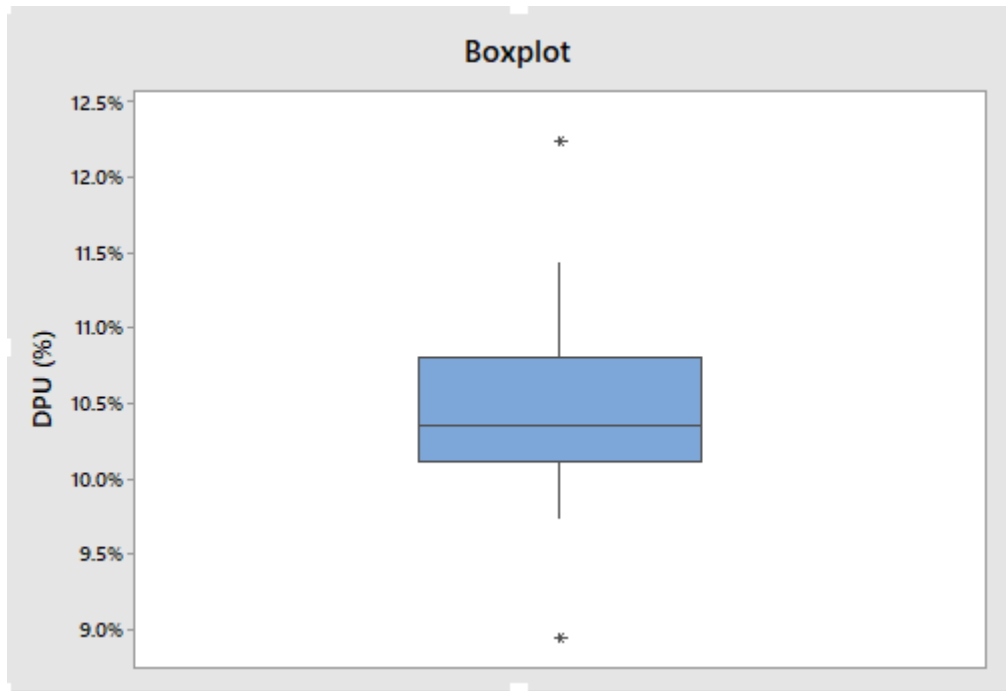


Figure A.1.1 Distribution of dip pick-up results of Strong Hybrid.

A.2

Table A.2.1 - Dipping results via Wet-Chemical method for Rayon cords.

Sample	Solid Content (%)	m ₁	m ₂	m ₃	D _{PU} (%)	D _{PU} Average (%)	Standard deviation (%)
A	5.09	1.039	30.242	30.260	1.70	1.67	0.04
		1.206	30.128	30.147	1.67		
		1.067	30.594	30.611	1.63		
		1.197	30.430	30.469	3.39		
B	9.87	1.041	30.483	30.515	3.22	3.17	0.25
		1.049	30.727	30.757	2.90		
		1.079	30.433	30.487	5.30		
		1.056	30.024	30.075	5.06		
C	17.74	1.015	30.419	30.467	4.93	5.10	0.19
		1.051	30.344	30.408	6.58		
		1.016	29.788	29.851	6.59		
		1.019	30.589	30.646	5.95		
D	22.38	1.016	29.788	29.851	6.59	6.37	0.37
		1.019	30.589	30.646	5.95		
		1.016	29.788	29.851	6.59		
		1.019	30.589	30.646	5.95		

Table A.2.2 - Rayon samples preparation values for TD-NMR.

D _{PU} (%)	Solid Content (%)	Sample	Tube + lid	Tube + lid + dried sample mass (g)	Dried sample mass (g)
1.667	5.09	A1	16.121	17.042	0.921
		A2	16.378	17.585	1.207
		A3	16.362	17.467	1.105
3.173	9.87	B1	16.241	17.684	1.443
		B2	16.317	17.940	1.623
		B3	16.404	17.893	1.489
5.099	17.74	C1	16.263	17.364	1.101
		C2	16.294	17.341	1.047
		C3	16.272	17.315	1.043
6.373	22.38	D1	16.196	17.705	1.510
		D2	16.214	17.708	1.494
		D3	16.287	17.640	1.354

Table A.2.3 - TD-NMR Rayon calibration curve results.

D _{PU} (%)	Signal	Standard deviation (%)
1.667	23.631	0.55
	22.536	
	22.976	
3.173	29.878	1.22
	27.468	
	28.396	
5.099	35.271	0.80
	36.181	
	36.865	
6.373	41.034	0.18
	41.389	
	41.223	

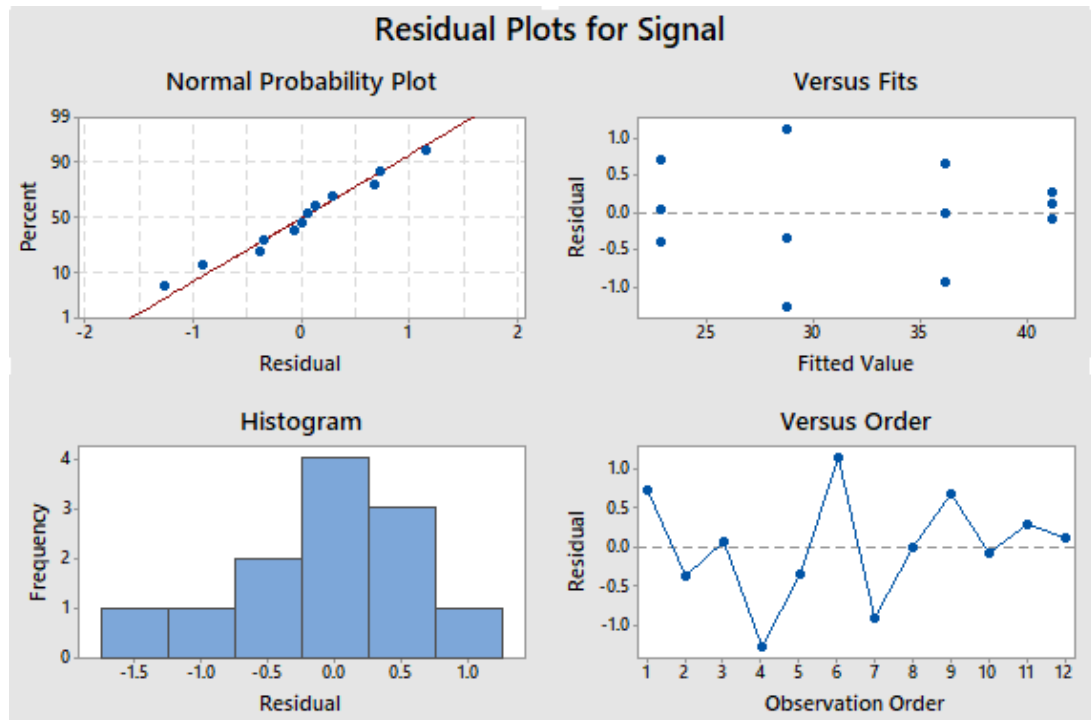


Figure A.2.1 - Statistical analysis for Rayon calibration curve.

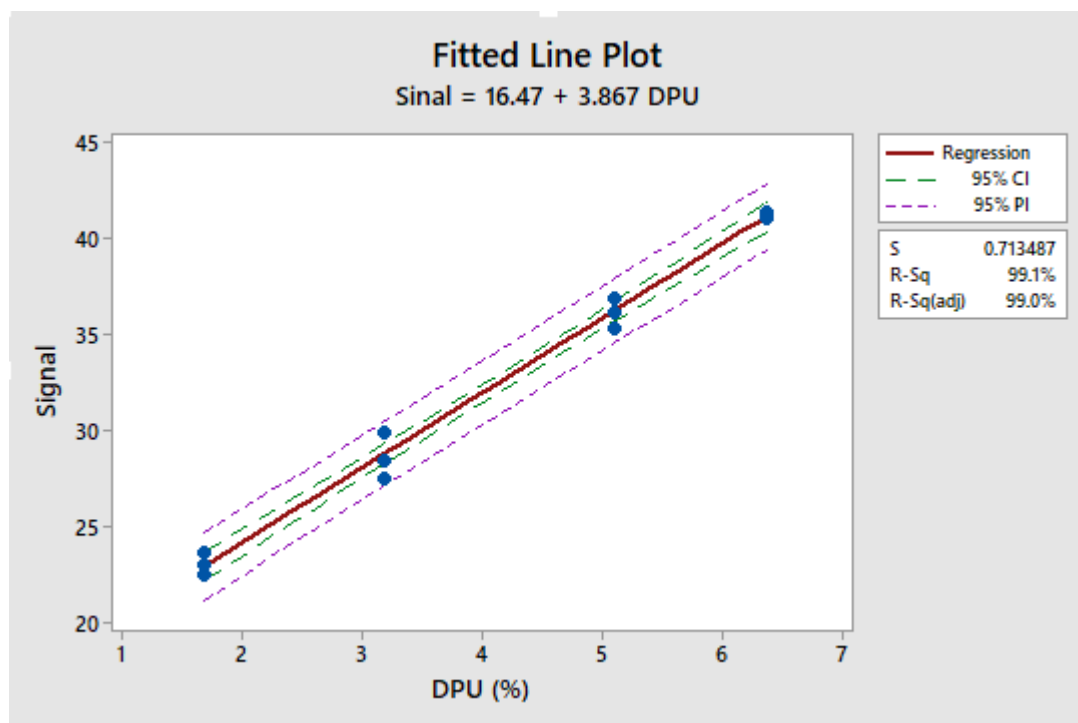


Figure A.2.2 - Linear Regression of the calibration curve for Rayon.

Table A.2.4 - Rayon samples preparation values to validate the calibration curve.

Sample	Tube + lid mass (g)	Tube + lid + dried sample mass (g)	Dried sample mass (g)	D _{PU} (%) (TD-NMR)	D _{PU} (%) (Wet-Chemical)
1	16.316	17.260	0.944	4.5	5.3
2	16.322	17.171	0.849	3.7	5.8
3	16.191	17.111	0.920	3.5	5.4
4	16.218	17.120	0.902	4.0	4.9
5	16.267	17.290	1.023	4.4	4.8
6	16.317	17.347	1.031	4.4	4.5
7	16.230	17.264	1.034	4.2	5.3
8	16.280	17.149	0.869	5.0	5.5
9	16.176	17.193	1.017	3.5	3.5
10	16.321	17.386	1.065	4.5	5.2
11	16.165	17.116	0.951	4.5	4.6
12	16.314	17.470	1.156	4.4	4.6
13	16.251	17.447	1.196	3.0	5.6
14	16.173	17.083	0.910	3.8	5.5
15	16.252	17.350	1.098	3.1	5.3
16	16.199	17.106	0.907	4.1	5.3
17	16.314	17.326	1.012	3.4	5.5
18	16.315	17.245	0.930	4.1	4.6
19	16.316	17.387	1.071	4.3	4.9
20	16.308	17.305	0.997	3.8	4.8
21	16.260	17.425	1.165	4.2	5.0
22	16.195	17.265	1.070	4.9	4.9
23	16.174	17.253	1.079	4.1	5.1
24	16.252	17.317	1.065	3.4	4.8
25	16.360	17.321	0.961	2.8	4.4
26	16.162	17.060	0.898	2.8	4.3
27	16.213	17.179	0.966	4.9	5.4
28	16.327	17.505	1.178	4.5	5.5
29	16.218	17.440	1.222	4.6	3.8
30	16.322	17.280	0.958	3.5	4.2

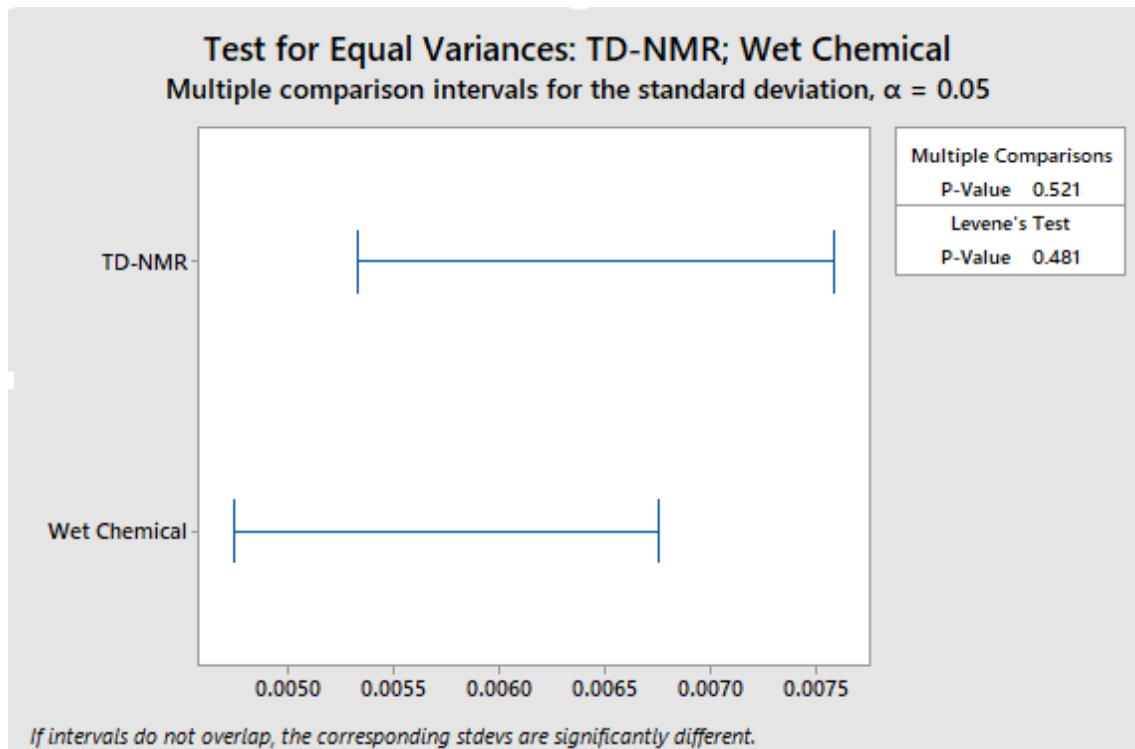


Figure A.2.3 - Equal variances test for TD-NMR and Wet-Chemical methods.

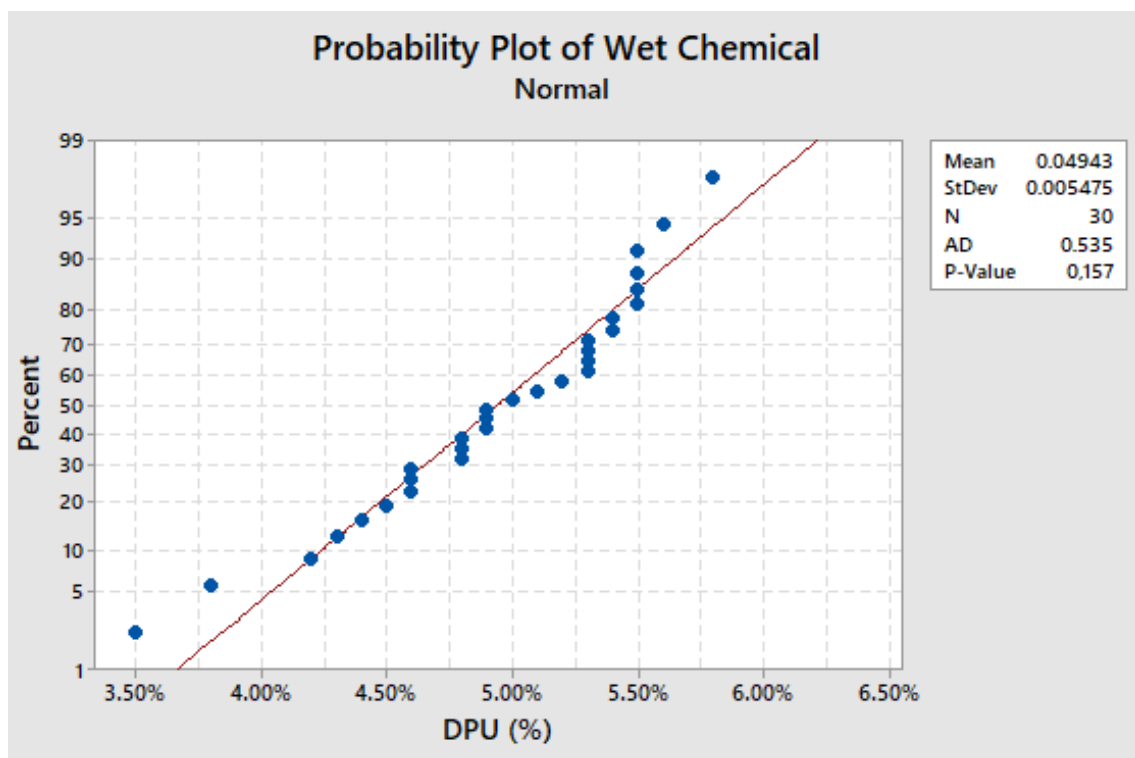


Figure A.2.4 - Normality test for Wet-Chemical method.

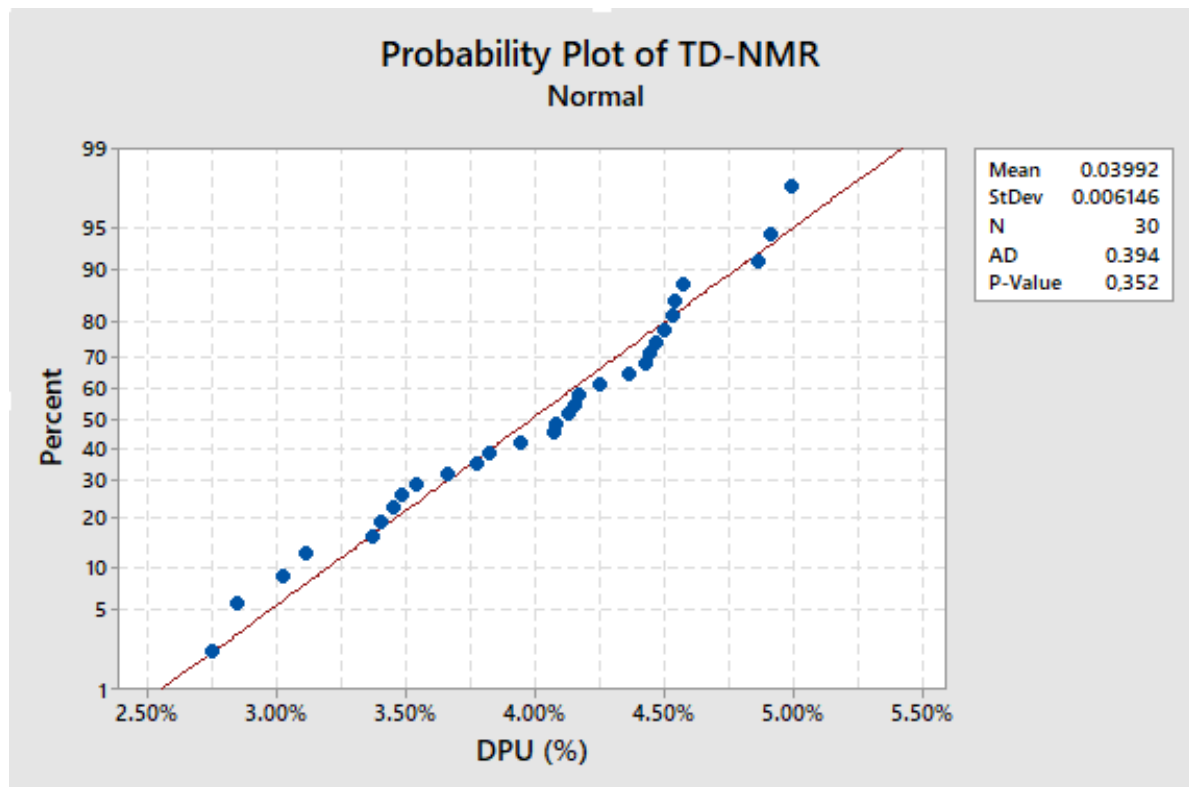


Figure A.2.5 - Normality test for TD-NMR method.

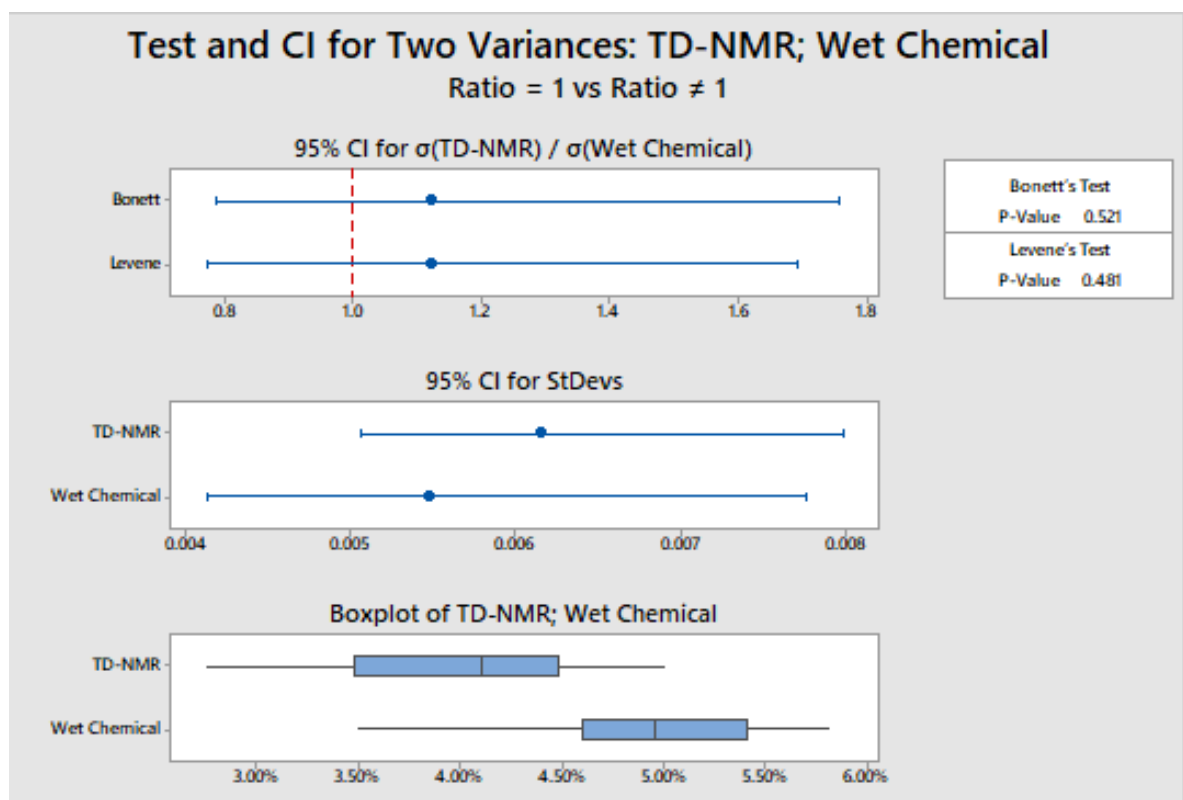


Figure A.2.6 - Statistical analysis and comparison of the two methods.

Table A.2.5 - TD-NMR Rayon calibration curve results with the new dip.

D _{PU} (%)	Signal	Standard deviation (%)
1.609	13.994	0.14
	14.216	
	14.247	
3.320	23.736	0.65
	24.971	
	24.688	
4.840	33.053	0.33
	32.814	
	33.463	
6.448	45.546	0.60
	44.73	
	44.381	

A.3

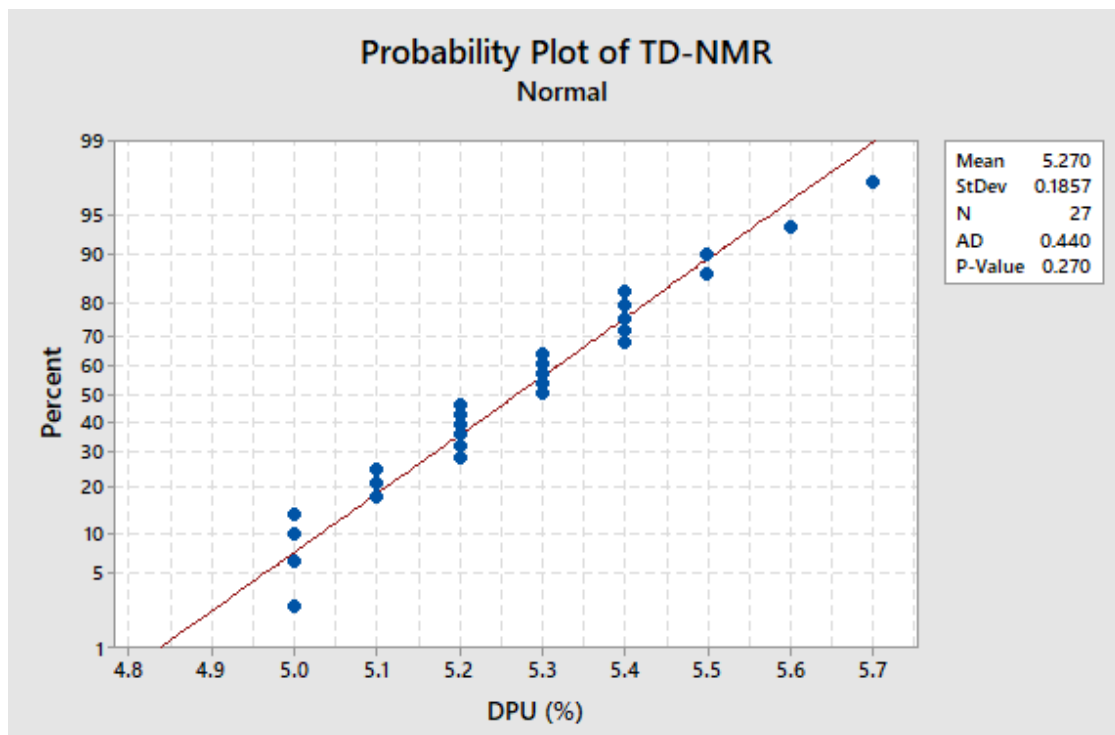


Figure A.3.1 - Normality test for Nylon B TD-NMR results.

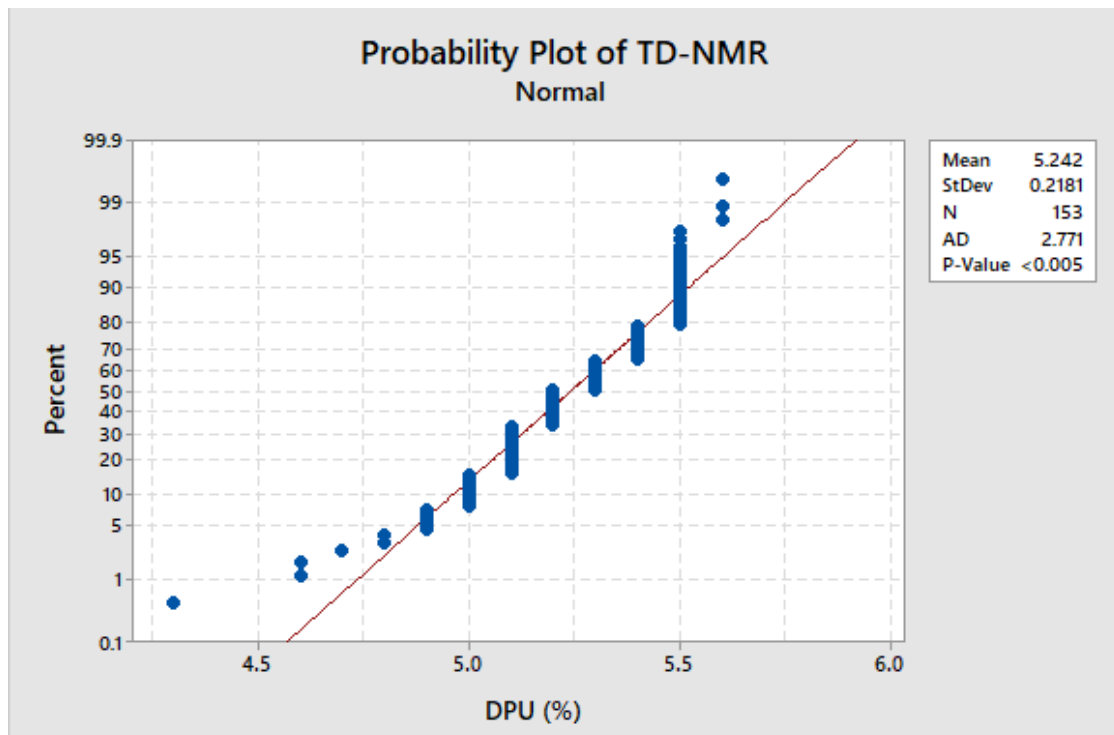


Figure A.3.2 - Normality test for Nylon C TD-NMR results.

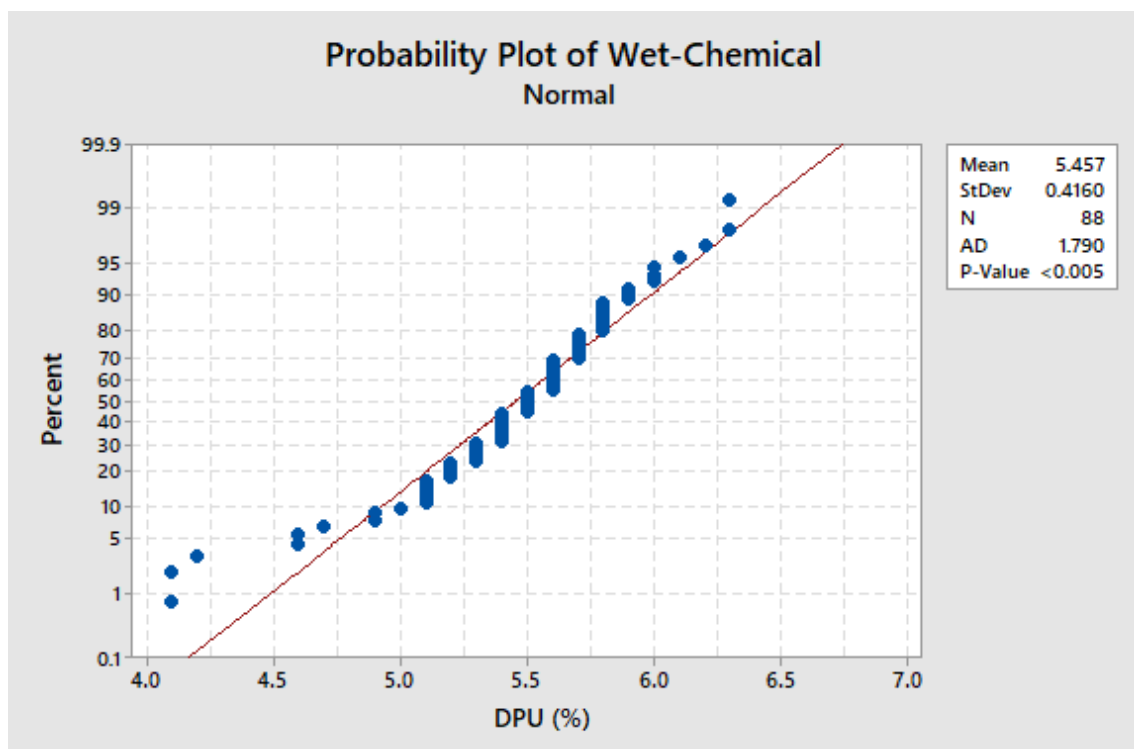


Figure A.3.3 - Normality test for Nylon A Wet-Chemical results.

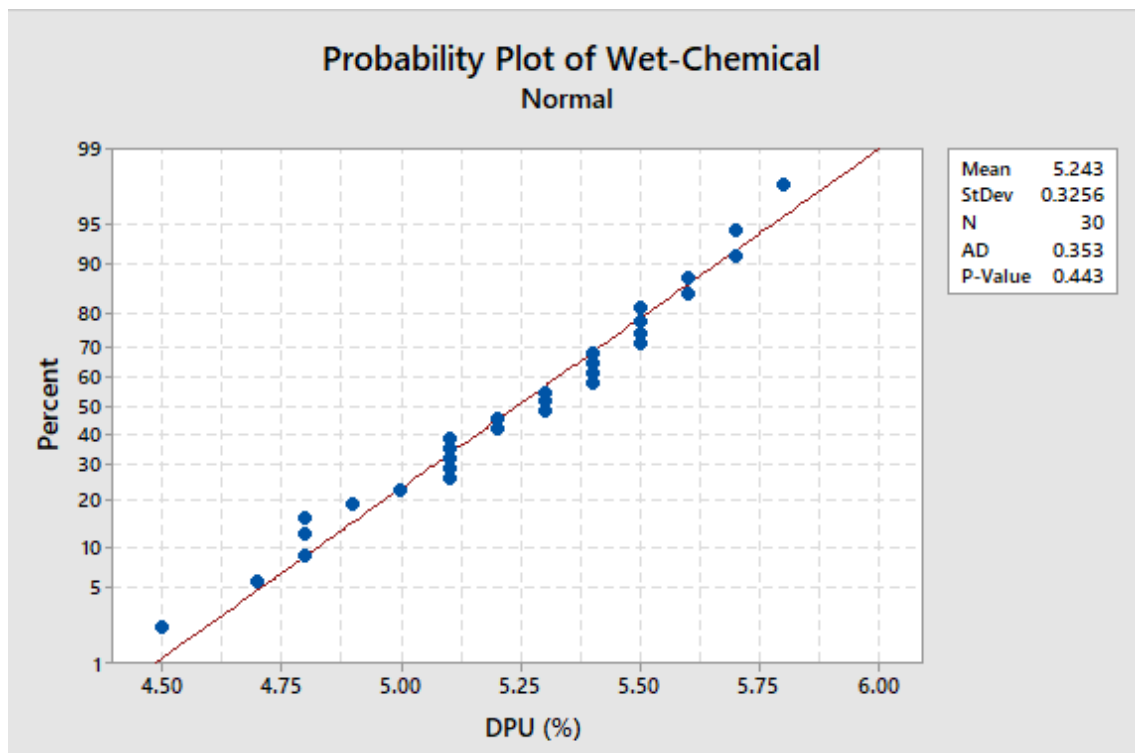


Figure A.3.4 - Normality test for Nylon B Wet-Chemical results.

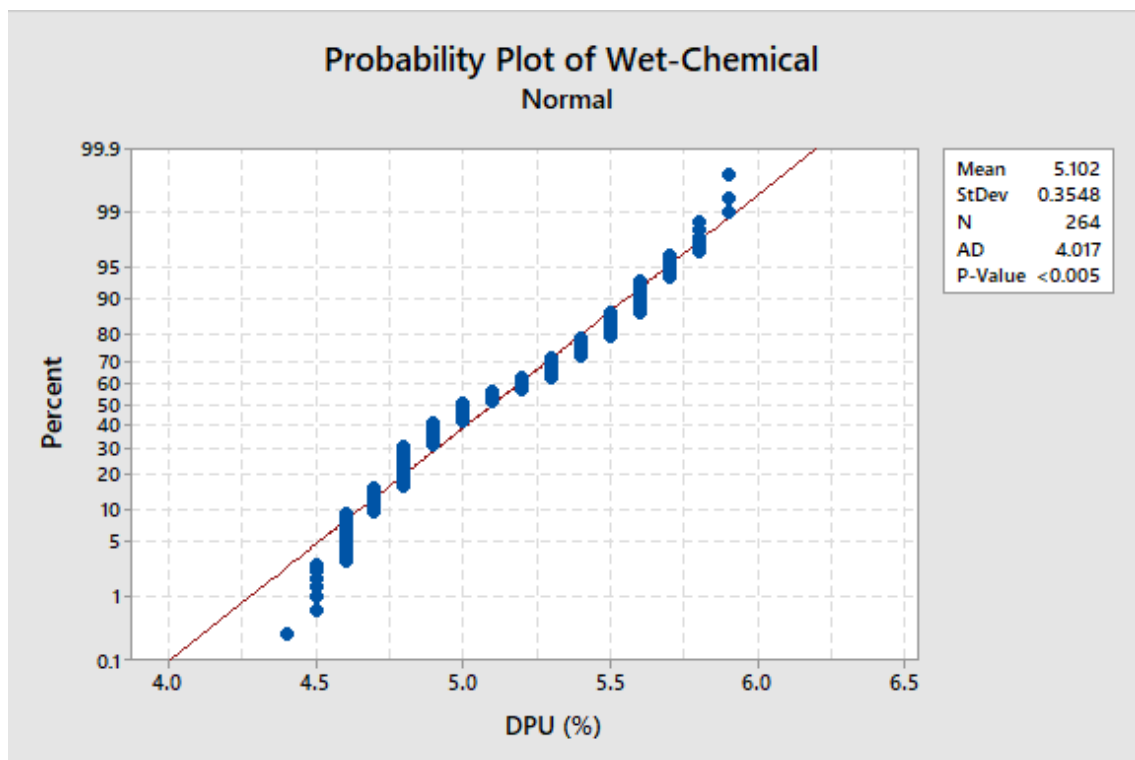


Figure A.3.5 - Normality test for Nylon C Wet-Chemical results.

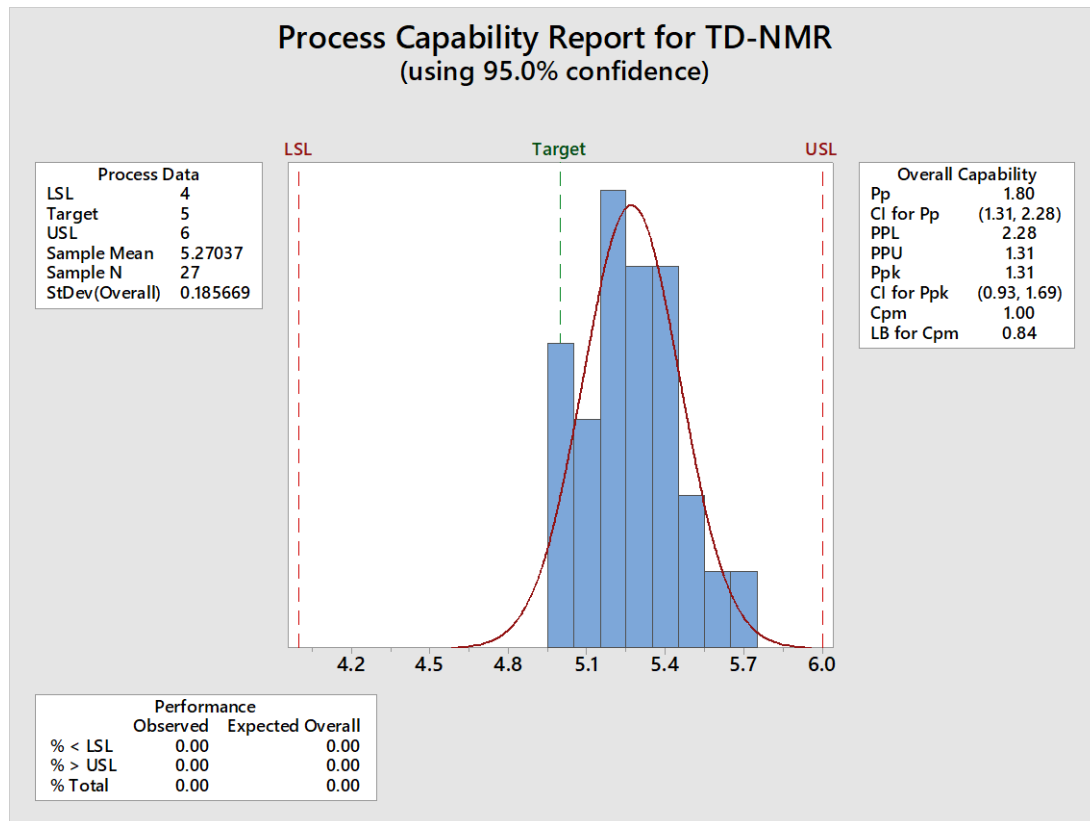


Figure A.3.6 - Quality capability analysis of Nylon B TD-NMR results.

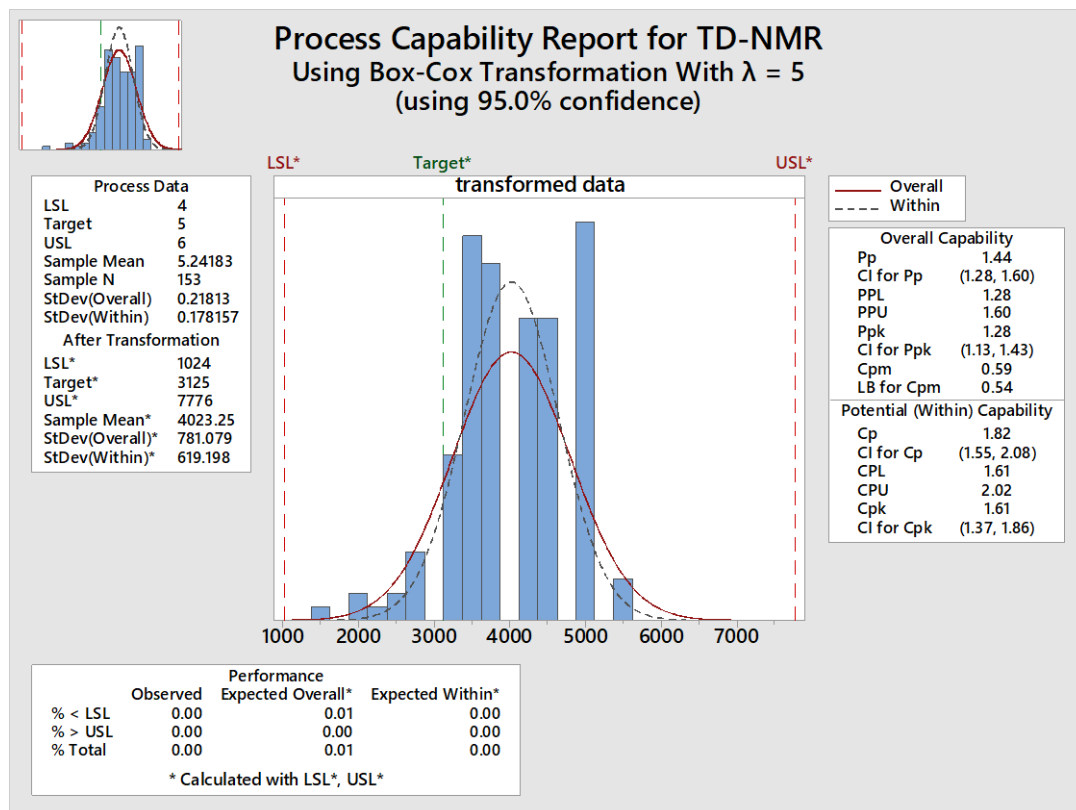


Figure A.3.7 - Quality capability analysis of Nylon C TD-NMR results.

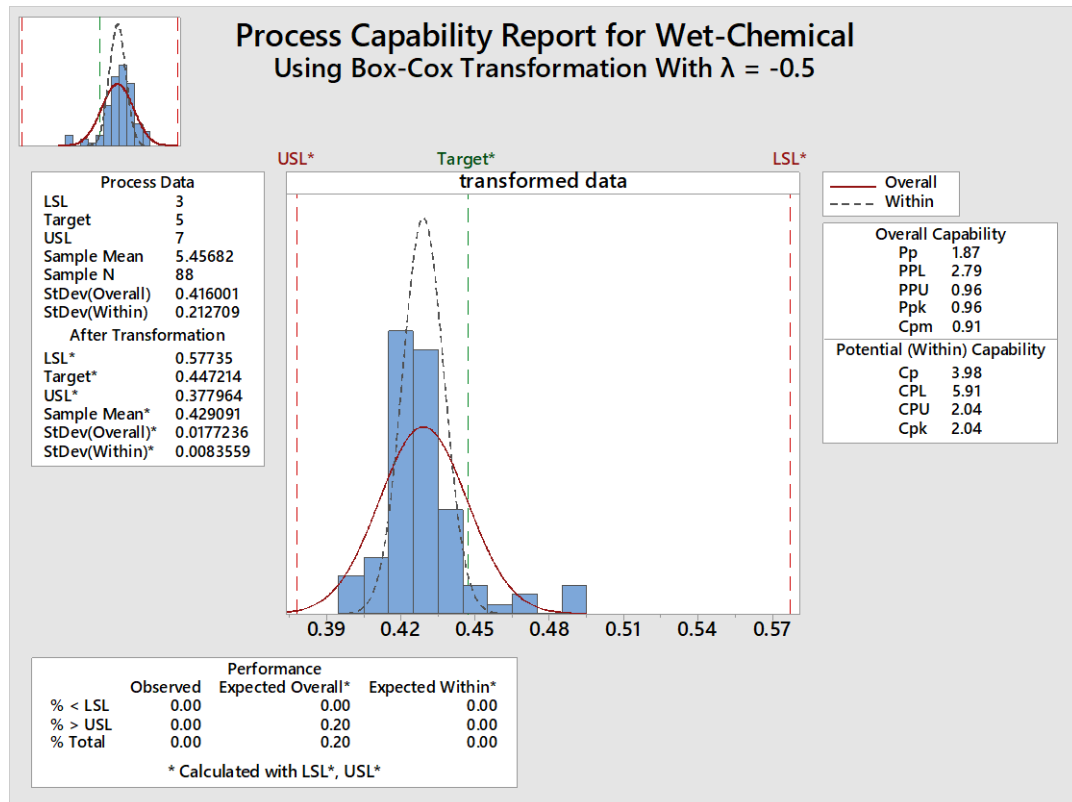


Figure A.3.8 - Quality capability analysis of Nylon A Wet-Chemical results.

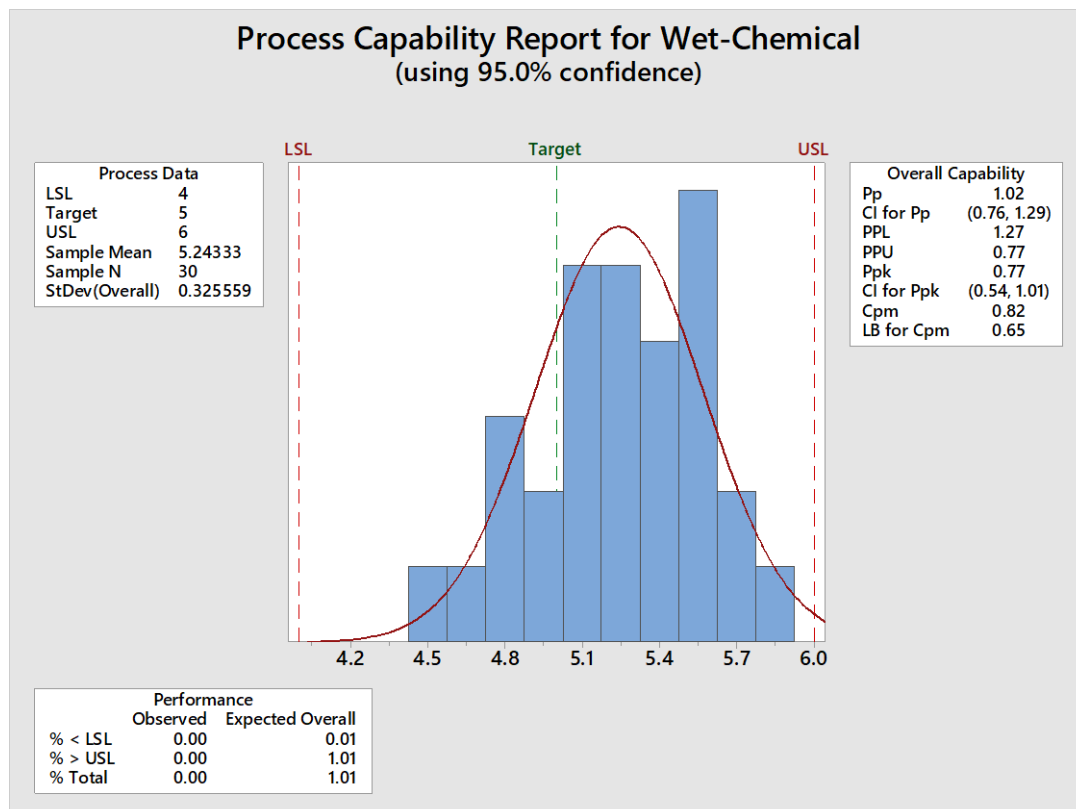


Figure A.3.9 - Quality capability analysis of Nylon B Wet-Chemical results.

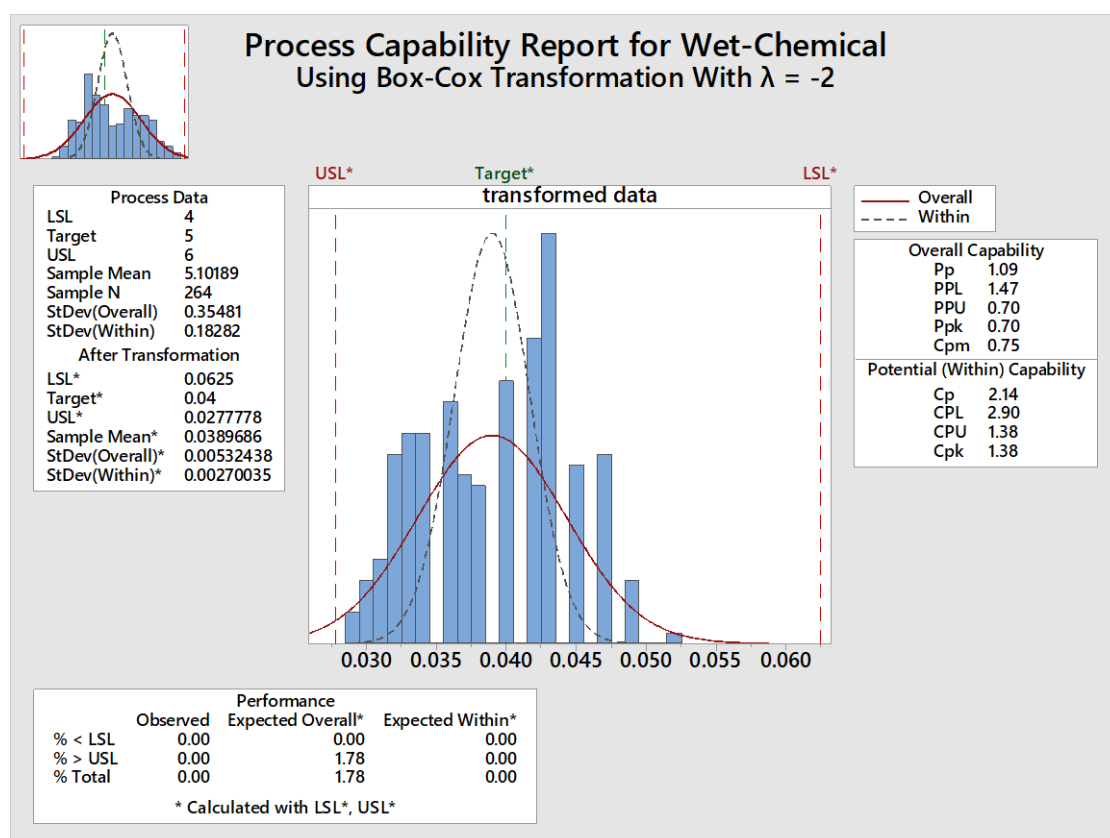


Figure A.3.10 - Quality capability analysis of Nylon C Wet-Chemical results.

A.4

Table A.4.1 - Time optimization test: Rayon samples preparation values for TD-NMR.

Sample	Tube + lid mass (g)	Tube + lid + dried sample mass (g)	Dried sample mass (g)
R1	16.316	17.260	0.944
R2	16.227	17.280	1.053
R3	16.191	17.111	0.920
R4	16.218	17.120	0.902
R5	16.267	17.290	1.023
R6	16.317	17.347	1.031
R7	16.230	17.264	1.034
R8	16.280	17.149	0.869
R9	16.176	17.193	1.017
R10	16.321	17.386	1.065
R11	16.165	17.116	0.951
R12	16.314	17.470	1.156

R13	16.251	17.447	1.196
R14	16.247	17.151	0.904
R15	16.252	17.350	1.098
R16	16.199	17.106	0.907
R17	16.314	17.326	1.012
R18	16.315	17.245	0.930
R19	16.316	17.387	1.071
R20	16.308	17.305	0.997
R21	16.260	17.425	1.165
R22	16.195	17.265	1.070
R23	16.174	17.253	1.079
R24	16.252	17.317	1.065
R25	16.360	17.321	0.961
R26	16.162	17.060	0.898
R27	16.213	17.179	0.966
R28	16.327	17.505	1.178
R29	16.218	17.440	1.222
R30	16.322	17.280	0.958

Table A.4.2 - Rayon time optimization test: Dip pick-up results for 5 and 30 minutes.

Sample	5 minutes		30 minutes		Standard deviation between the two times (%)
	D _{PU} (%)	Average (%)	D _{PU} (%)	Average (%)	
R1	4.475	4.491	4.469	4.469	0.015
	4.523		4.444		
	4.475		4.494		
R2	3.389	3.390	3.583	3.497	0.075
	3.391		3.443		
	3.390		3.465		
R3	3.579	3.585	3.482	3.488	0.068
	3.599		3.507		
	3.576		3.476		
R4	3.886	3.961	3.977	3.950	0.007
	4.023		3.940		
	3.974		3.934		
R5	4.365	4.403	4.480	4.445	0.029
	4.421		4.434		
	4.424		4.420		
R6	4.604	4.573	4.411	4.433	0.099
	4.533		4.444		
	4.582		4.444		

R7	4.136	4.167	4.179	4.170	0.002
	4.216		4.147		
	4.149		4.183		
R8	4.925	4.937	5.013	4.995	0.041
	4.920		4.948		
	4.966		5.024		
R9	3.463	3.499	3.542	3.540	0.029
	3.519		3.504		
	3.515		3.574		
R10	4.636	4.662	4.576	4.546	0.082
	4.698		4.617		
	4.652		4.444		
R11	4.480	4.490	4.528	4.508	0.012
	4.550		4.480		
	4.441		4.515		
R12	4.390	4.379	4.309	4.369	0.007
	4.373		4.448		
	4.375		4.349		
R13	2.963	2.960	3.050	3.028	0.048
	2.956		3.001		
	2.962		3.032		
R14	3.565	3.583	3.571	3.489	0.066
	3.585		3.379		
	3.598		3.518		
R15	3.162	3.144	3.141	3.113	0.022
	3.113		3.123		
	3.157		3.077		
R16	4.129	4.176	4.136	4.133	0.031
	4.207		4.138		
	4.193		4.123		
R17	3.328	3.392	3.315	3.372	0.014
	3.446		3.401		
	3.401		3.400		
R18	4.046	4.062	4.067	4.076	0.010
	4.046		4.082		
	4.093		4.080		
R19	4.288	4.322	4.251	4.253	0.048
	4.336		4.222		
	4.341		4.286		
R20	3.859	3.839	3.824	3.826	0.009
	3.782		3.778		
	3.876		3.878		
R21	4.131	4.101	4.153	4.160	0.042
	4.060		4.158		

	4.111		4.170		
R22	4.832	4.946	4.869	4.865	0.058
	5.006		4.857		
	5.001		4.868		
R23	4.080	4.069	4.116	4.082	0.009
	4.041		4.050		
	4.088		4.080		
R24	3.514	3.518	3.462	3.403	0.081
	3.505		3.402		
	3.535		3.345		
R25	2.792	2.744	2.697	2.757	0.009
	2.752		2.757		
	2.688		2.816		
R26	2.971	2.908	2.824	2.849	0.042
	2.871		2.910		
	2.882		2.812		
R27	4.924	4.899	4.942	4.913	0.010
	4.914		4.847		
	4.859		4.952		
R28	4.462	4.474	4.583	4.536	0.044
	4.469		4.524		
	4.491		4.502		
R29	4.561	4.553	4.607	4.574	0.015
	4.550		4.527		
	4.549		4.588		
R30	3.538	3.501	3.485	3.453	0.034
	3.463		3.451		
	3.504		3.422		

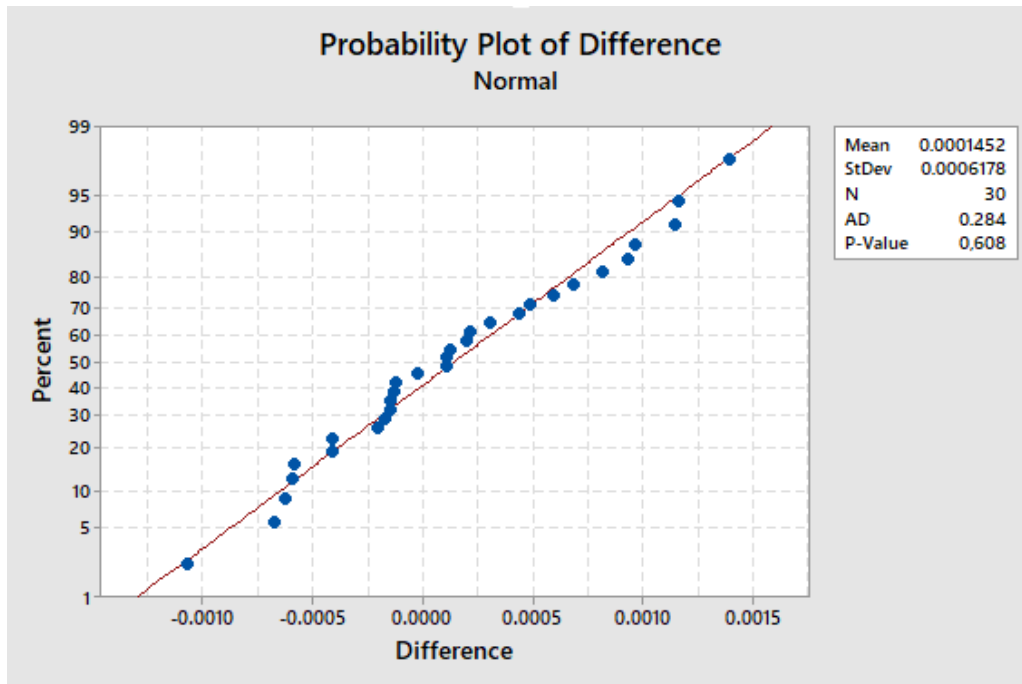


Figure A.4.1 - Rayon time optimization test: Normality test for the difference between 5 and 30 minutes test results.

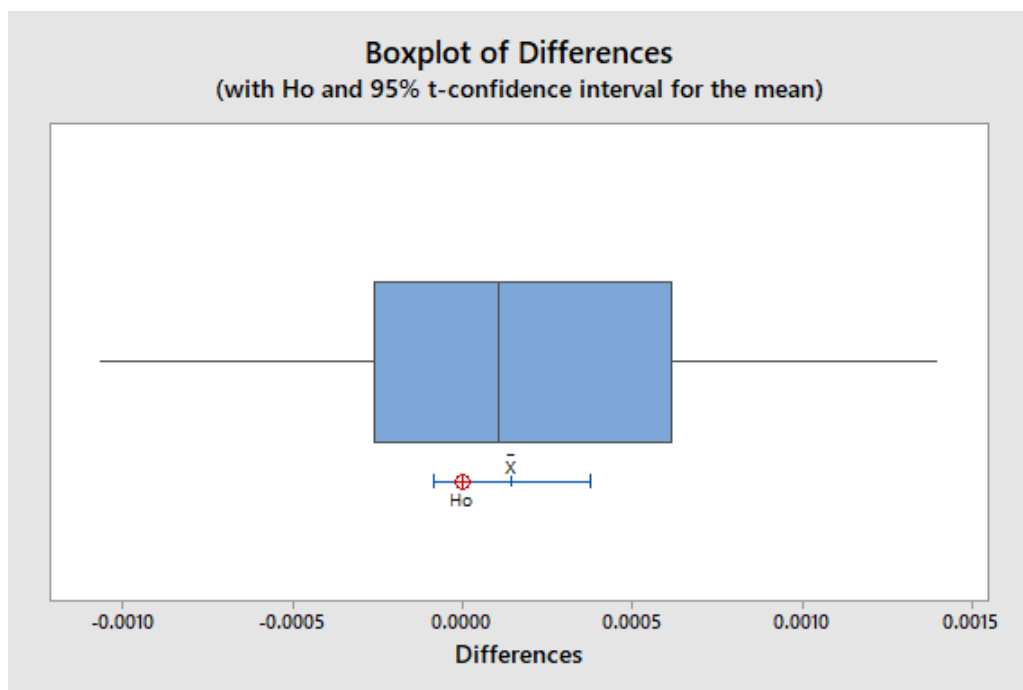


Figure A.4.2 - Rayon time optimization test: Boxplot for the difference between 5 and 30 minutes test results.

Paired T-Test and CI: 5min; 30min

Paired T for 5min - 30min

	N	Mean	StDev	SE Mean
5min	30	0.03991	0.00624	0.00114
30min	30	0.03976	0.00624	0.00114
Difference	30	0.000145	0.000618	0.000113

95% CI for mean difference: (-0.000086; 0.000376)

T-Test of mean difference = 0 (vs $\neq$ 0): T-Value = 1.29 P-Value = 0.208

Figure A.4.3 - Rayon time optimization test: Paired T-Test results in Minitab.

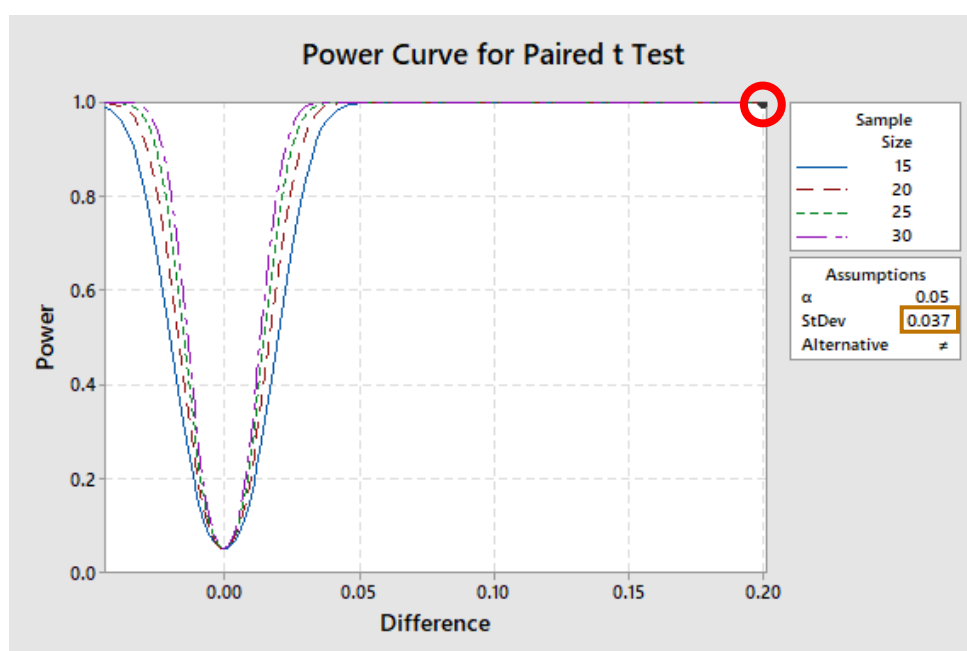


Figure A.4.4 - Power Curve for Paired t-test for 15, 20, 25 and 30 samples of Hybrid via Minitab.

Table A.4.3 - Time optimization test: Hybrid samples preparation values for TD-NMR.

Sample	Tube + lid mass (g)	Tube + lid + dried sample mass (g)	Dried sample mass (g)
H1	16.325	17.268	0.943
H2	16.219	17.269	1.050
H3	16.196	17.209	1.013
H4	16.162	17.163	1.001
H5	16.228	17.244	1.016
H6	16.330	17.335	1.005
H7	16.362	17.384	1.023
H8	16.263	17.274	1.011

H9	16.228	17.254	1.026
H10	16.177	17.201	1.024
H11	16.253	17.268	1.015
H12	16.316	17.339	1.023
H13	16.317	17.321	1.004
H14	16.314	17.341	1.027
H15	16.309	17.327	1.018
H16	16.197	17.201	1.004
H17	16.254	17.264	1.010
H18	16.256	17.269	1.013
H19	16.200	17.190	0.990
H20	16.317	17.335	1.018
H21	16.167	17.185	1.018
H22	16.269	17.257	0.988
H23	16.322	17.462	1.140
H24	16.231	17.266	1.035
H25	16.282	17.296	1.015
H26	16.278	17.312	1.034
H27	16.231	17.241	1.010
H28	16.176	17.185	1.009
H29	16.193	17.190	0.997
H30	16.221	17.229	1.008

Table A.4.4 - Hybrid time optimization test: Dip pick-up results for 5 and 30 minutes.

Sample	5 minutes		30 minutes		Standard deviation between the two times (%)
	D _{PU} (%)	Average (%)	D _{PU} (%)	Average (%)	
H1	3.498	3.531	3.491	3.516	0.010
	3.513		3.488		
	3.581		3.571		
H2	3.820	3.816	3.826	3.844	0.020
	3.803		3.851		
	3.824		3.855		
H3	3.506	3.511	3.574	3.564	0.037
	3.500		3.552		
	3.528		3.565		
H4	3.608	3.612	3.645	3.629	0.012
	3.618		3.624		
	3.609		3.618		
H5	3.797	3.752	3.790	3.728	0.016
	3.706		3.668		
	3.752		3.727		
H6	3.690	3.746	3.790	3.747	0.000

	3.774		3.720		
	3.774		3.729		
H7	3.701	3.739	3.814	3.805	0.047
	3.794		3.807		
	3.722		3.794		
H8	3.854	3.936	3.873	3.920	0.012
	3.974		3.916		
	3.981		3.971		
H9	3.643	3.667	3.695	3.658	0.006
	3.667		3.654		
	3.690		3.627		
H10	3.864	3.892	3.922	3.866	0.018
	3.890		3.842		
	3.922		3.834		
H11	3.703	3.733	3.751	3.736	0.002
	3.757		3.699		
	3.740		3.758		
H12	3.660	3.656	3.723	3.684	0.020
	3.621		3.685		
	3.686		3.643		
H13	3.649	3.685	3.747	3.712	0.020
	3.684		3.715		
	3.720		3.674		
H14	3.587	3.569	3.553	3.542	0.019
	3.521		3.516		
	3.598		3.556		
H15	3.423	3.461	3.418	3.417	0.031
	3.335		3.391		
	3.624		3.441		
H16	3.583	3.629	3.590	3.623	0.004
	3.624		3.647		
	3.681		3.631		
H17	3.632	3.615	3.592	3.628	0.009
	3.575		3.662		
	3.637		3.629		
H18	3.427	3.435	3.432	3.437	0.001
	3.450		3.449		
	3.429		3.430		
H19	3.796	3.750	3.812	3.806	0.039
	3.725		3.802		
	3.730		3.802		
H20	4.071	4.073	4.073	4.098	0.017
	4.107		4.073		
	4.041		4.146		

H21	3.386	3.423	3.373	3.396	0.019
	3.449		3.392		
	3.434		3.421		
H22	3.719	3.713	3.811	3.823	0.078
	3.759		3.854		
	3.659		3.804		
H23	5.196	5.157	5.158	5.199	0.030
	5.148		5.204		
	5.128		5.235		
H24	3.832	3.780	3.755	3.748	0.022
	3.744		3.743		
	3.762		3.747		
H25	4.101	4.132	4.145	4.183	0.036
	4.183		4.209		
	4.114		4.195		
H26	3.697	3.681	3.662	3.694	0.009
	3.655		3.692		
	3.691		3.728		
H27	3.731	3.753	3.795	3.782	0.021
	3.728		3.741		
	3.799		3.810		
H28	3.616	3.608	3.629	3.640	0.023
	3.590		3.649		
	3.617		3.641		
H29	2.936	2.949	2.991	2.968	0.014
	2.954		2.940		
	2.957		2.974		
H30	3.875	3.881	3.820	3.810	0.050
	3.889		3.825		
	3.879		3.785		

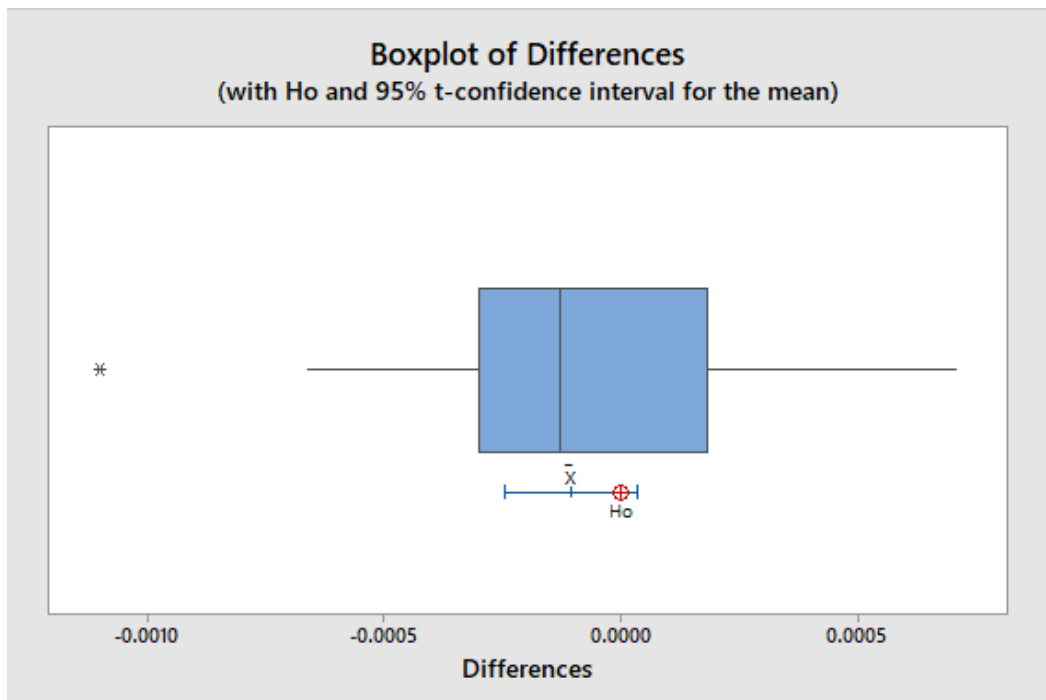


Figure A.4.5 - Hybrid time optimization test: Boxplot for difference between 5 and 30 minutes test results.

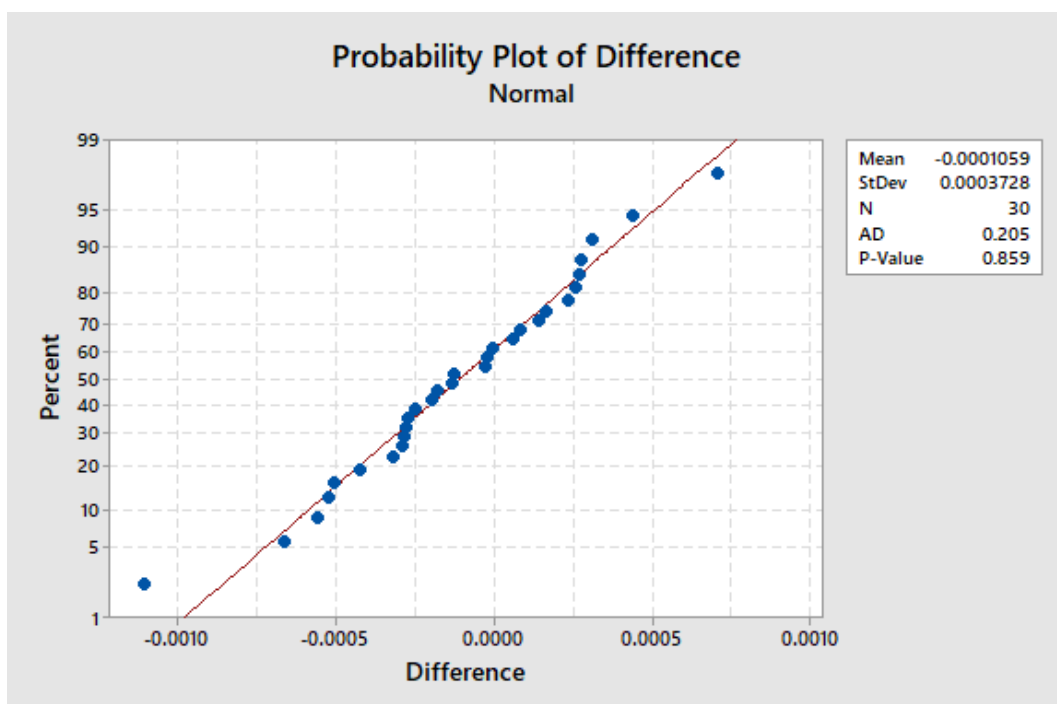


Figure A.4.6 - Hybrid time optimization test: Normality test for difference between 5 and 30 minutes test results.

Paired T-Test and CI: 5 min; 30 min

Paired T for 5 min - 30 min

	N	Mean	StDev	SE Mean
5 min	30	0.037295	0.003456	0.000631
30 min	30	0.037401	0.003537	0.000646
Difference	30	-0.000106	0.000373	0.000068

95% CI for mean difference: (-0.000245; 0.000033)

T-Test of mean difference = 0 (vs $\neq$ 0): T-Value = -1.56 P-Value = 0.131*Figure A.4.7 - Hybrid time optimization test: Paired T-Test results in Minitab.*

