

DIP CONTENT IN THE TIRE TEXTILE REINFORCEMENTS: A COMPARISON OF METHODS

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Reinforcements: A Comparison of Methods***

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Abstract

The tire is a product in constant evolution and development as it is one of the most important components in all types of vehicles. As the only connecting element between the car and the road it is crucial that this product provides passenger safety in all types of weather conditions. In order to achieve good results, different materials and techniques are used when manufacturing a tire. One example of this is the use of textile reinforcements.

These reinforcements are formed using fibers that do not have rubber bonding properties by nature, so they need to undergo a process called dipping. In this operation the material receives a treatment with the help of a dip solution that will later give it the ability to efficiently bond with the rubber. During the dipping process, the amount of dip solution that gets applied to the fiber is essential to ensure proper adhesion results between the fiber and the rubber.

Continental - Indústria Têxtil do Ave (C-ITA), specializes in the manufacturing of textile reinforcements used in Continental tires and also technical fabric for vehicle interiors. To do the quality control of the dipped materials, a diversity of tests is conducted by the company, being one of them the percentual quantification of dipping solution present in the fiber (*DPU*). To perform this test, three methods can be used: Wet-Chemical, Weighing and Time Domain Nuclear Magnetic Resonance (TD-NMR). The use of this last method allowed C-ITA to perform faster and more precise *DPU* analysis when compared to the other two. Since C-ITA uses different types of fibers for its textile reinforcements, the TD-NMR equipment must be calibrated for each material in order to perform the *DPU* analysis. The device was already calibrated for every material besides aramid, and so, one of this dissertation's main purposes was to do that last calibration. The TD-NMR was successfully calibrated for aramid, although validation of the curve is still needed.

C-ITA has also a certified laboratory that is responsible for testing and analyzing textile samples sent from other Continental plants around the world. The objective of this countercheck process is to verify whether the samples meet the quality requirements set by the company. Another main objective of this work was to analyze an existing countercheck database containing the test results for all of the received samples and compare them regarding the *DPU* results obtained by the TD-NMR and Wet-Chemical methods. The result of that analysis was that the two methods are not significantly different. Infrared spectroscopy has also been proved helpful to better understand the results given by the TD-NMR equipment.

Keywords: Tire, textile reinforcements, DIP, TD-NMR, countercheck

Resumo

O pneu é um produto em constante evolução e desenvolvimento uma vez que é um dos constituintes mais importantes em todo o tipo de veículos. Sendo o único elemento de ligação entre o carro e a estrada, é crucial que este produto proporcione segurança aos passageiros em todo o tipo de condições meteorológicas. Para atingir bons resultados, diferentes materiais e técnicas são utilizados aquando da manufatura do pneu. Um exemplo disso são os reforços têxteis.

Estes reforços são criados utilizando fibras que por natureza não têm propriedades adesivas para com a borracha, o que significa que as mesmas necessitam de ser submetidas a um processo chamado impregnação. Nesta operação o material é tratado com uma solução de impregnação que mais tarde lhe irá conferir tais propriedades adesivas. Durante o processo de impregnação, a quantidade de solução utilizada é muito importante para garantir bons resultados de adesão.

A empresa Continental-Indústria Têxtil do Ave (C-ITA) é especializada na manufatura de reforços têxteis para os pneus Continental e também na produção de tecidos técnicos para interiores automóveis. Para fazer o controlo de qualidade dos materiais impregnados a empresa efetua vários testes, sendo um deles a quantificação percentual da quantidade de solução de impregnação presente na fibra. Para realizar este teste três métodos podem ser utilizados: químico, pesagem e Ressonância Magnética Nuclear no Domínio do Tempo (TD-NMR). O uso deste último permitiu à empresa realizar os testes de quantificação de solução de impregnação na fibra de uma forma mais rápida e precisa do que os outros dois. Para se poder realizar essa análise o equipamento TD-NMR tem de estar calibrado para cada material. Um dos principais objetivos desta dissertação foi calibrar o equipamento para o único material em falta, a aramida. Essa calibração foi feita com sucesso, no entanto a reta necessita de ser validada.

A Continental-ITA tem também um laboratório certificado que é especializado no controlo de qualidade de amostras têxteis enviadas por outras fábricas do grupo Continental, tendo em conta as exigências da empresa. Este processo tem o nome de contra-prova. Outro dos objetivos deste trabalho foi analisar uma base de dados criada com os resultados dos testes efetuados nessas análises, comparando os resultados obtidos com o TD-NMR e o método químico. O estudo foi feito e foi demonstrado que os dois métodos não são significativamente diferentes. A espectroscopia de infravermelho surgiu também como uma ajuda para compreender os resultados obtidos pelo TD-NMR.

Palavras-chave: Pneu, reforços têxteis, solução de impregnação, TD-NMR, contra-prova

Declaration

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

Porto, February 10th of 2020

Inês Peixoto da Silva

(Inês Peixoto da Silva)

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Notation and Glossary

dtex	Decitex	g/ 10 000 m
<i>DPU</i>	Dip Pick-up	%
<i>DPU_{per dipped cord}</i>	Dip Pick-up per dipped cord	%
<i>DPU_{per greige cord}</i>	Dip Pick-up per greige cord	%
m_{DIP}	DIP mass	g
$m_{dipped\ cord}$	Dipped cord mass	g
$m_{greige\ cord}$	Greige cord mass	g
SC	Solid Content	%
StDev	Sample's Standard Deviation	

Greek Letters

α	Significance Level
μ	Populations' Mean

List of Acronyms

AA	Adhesion Activated
C-ITA	Continental - Indústria Têxtil do Ave, S.A.
CI	Confident Interval
DIP	Dipping Solution
DOE	Design of Experiment
FID	Free Induction Decay
FTIR	Fourier Transformed Infrared Spectroscopy
LDU	Lab Dipping Unit
LTL	Low Target Limit
nAA	Non-Adhesion Activated
OPU	Oil pick up
PET	Polyethylene terephthalate fibers
TD-NMR	Time Domain Nuclear Magnetic Resonance
UTL	Upper Target Limit

1 Introduction

1.1 Framing and presentation of the work

Modern tires are highly complex engineered products used in all types of vehicles that must perform a variety of functions without compromising roadholding quality, passenger and cargo safety. In order to achieve such characteristics, different materials and techniques are used when manufacturing a tire. One example of this is the use of textile reinforcements, which are mainly responsible for keeping internal pressure and the tire's shape.

The fibers used in these reinforcements do not have rubber bonding properties by nature, so they need to undergo a process called dipping. In this operation the fibers receive a treatment with the help of a dip solution that will later give them the ability to efficiently creating bonds with the tire rubber in the fibers' surroundings. During this process, the amount of dip solution that gets applied to the fiber is crucial to ensure proper adhesion results between the fiber and the rubber.

Continental - Indústria Têxtil do Ave (C-ITA), specializes in the manufacturing and testing of textile reinforcements used in Continental tires. One of the equipments used for fiber quality control is the time domain nuclear magnetic resonance (TD-NMR). This device has the ability to quantify the percentual amount of dip solution present in the fiber (*DPU*) and ultimately control whether that value is acceptable, considering Continental's *DPU* specification targets for each fiber. The use of this equipment allowed C-ITA to perform faster and more precise *DPU* analysis when compared to the standard methods also used by the company to quantify the amount of dip present in the fiber.

Since C-ITA uses different types of fibers for its textile reinforcements, the TD-NMR equipment must be calibrated for each material in order to perform the *DPU* analysis. In previous Master Theses the TD-NMR device has been already calibrated and validated for nylon (Pratapsi, 2017), rayon (Rocha, 2019), polyethylene terephthalate (PET) (Bezerra, 2018) and hybrid (a combination of aramid and nylon fibers) (Pratapsi, 2017). In this Master Thesis the equipment was calibrated for another material used in C-ITA: the aramid.

Besides producing and testing its own reinforcement textiles, C-ITA has also a certified laboratory that is responsible for testing and analyzing textile samples sent from all other Continental plants around the world. This process is called countercheck and its objective is to verify whether the samples meet the quality requirements set by the company or not, since they have different material suppliers and recipes for every plant. Keeping this in mind, an annual database is created every year containing all the

counterchecks made and the results of each one of them. In this Master Thesis that database was analyzed for the years of 2018 and 2019 in order to find some correlations amongst the data.

1.2 Presentation of Continental - Indústria Têxtil do Ave

Continental is a multinational company that was first established in 1871 in Hannover, Germany. As one of the leaders in the automotive industry, Continental offers a broad supply of solutions for various types of vehicles and industries, from tires to components of powertrains and chassis, electronics, interior safety systems and technical textiles. Present in 53 countries, the company employs over 200 000 staff members all over the world (Continental, 2019).

Founded in 1950 in Lousado, Portugal, Indústria Têxtil do Ave, S.A. was created to supply the pneumatic company Mabor with textile reinforcements for tires, in order to improve their quality and performance. In 1993 Continental acquired both Indústria Têxtil do Ave S. A. and Mabor, changing their names to Continental - Indústria Têxtil do Ave S. A. (C-ITA) and Continental Mabor. Currently, Continental owns two textile industries, being one of them C-ITA and the other one located in the USA. Both specialize in textile reinforcements for tires, however, C-ITA also specializes in the production of technical fabric for vehicle interiors. The majority of the material produced by C-ITA is exported to other Continental plants in Europe.

1.3 Contributions of the work

This Master Thesis continues the work developed in preceding Master Theses of calibrating the TD-NMR equipment for the different material fibers used in C-ITA.

In the first part, the countercheck database was analyzed in order to find some correlations amongst the data. The focus of the study was to compare the *DPU* results obtained by the TD-NMR method and the standard method used by Continental, the Wet-Chemical.

The results obtained in the first part of the project led to a second one, where Fourier Transformed Infrared Spectroscopy (FTIR) was used to analyze some fiber samples in order to study which dip solution component has a higher impact on the results given by the TD-NMR device.

In the third part of this work the TD-NMR was calibrated and tested for another material used by C-ITA, aramid.

Finally, in the fourth and last part of this Thesis, all of the existing calibration curves for the TD-NMR, for each material, were compared in order to analyze if it was possible to create a single calibration curve for all materials.

1.4 Organization of the Thesis

This thesis is composed of 8 chapters, which are organized the following way:

Chapter 1: Introduction. Brief presentation of the company Continental and C-ITA. Overview of the project and summarized description of the work objectives.

Chapter 2: Context and state of the art. Contextualization of the importance of a tire and the materials used by C-ITA for textile reinforcement. Explanation of the production processes and methods used for quality control.

Chapter 3: Materials and methods. Technical description of the procedures and methods used.

Chapter 4: Results and discussion. Presentation of the results obtained followed by its discussion.

Chapter 5: Conclusion. Achieved conclusions about the obtained results.

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

Chapter 7: References. Listing of all the bibliographic references used throughout the thesis.

Chapter 8: Annex and Appendix. Additional information used during the project to allow a better understanding of the details of the work done.

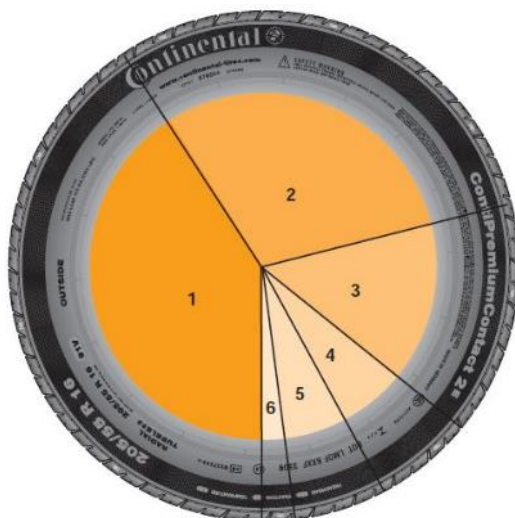
2 Context and State of the Art

2.1 Tire

When designing a car, the safety of the passengers is one of the major features that needs to be taken into consideration. Therefore, tires play a very important role in this aspect since they're the only connecting element between the road and the vehicle. Besides helping with speed and fuel consumption, the tire must be able to support the weight of the car and its load, it must have the ability to start, stop and turn corners safely and it must keep up with the road adversities even in the most extreme weather conditions. Tires have been in development for over a century, making them highly complex engineered products (Continental, 2019; Brewer et al., 2006).

Pneumatic tires appeared in the late 1800s as a development from solid rubber tires, primarily for bicycles and later on for automobiles. This progress in the tire structure enabled vehicles to travel at higher speeds and also provided a more comfortable ride. In the 1950s the tubeless tires were introduced, followed by belted bias tires in the 1960s and radial tires in the 1970s. Currently, radial tires are the most used construction in passenger car tires and can be separated into different layers, each with different functionalities, properties and materials (Brewer et al., 2006)

As it can be seen in **Figures 1 and 2**, a tire is composed of different materials and its structure can be divided into 9 sections.



1. Rubber
2. Fillers (carbon black, silica, carbon, others)
3. Reinforcing materials (textile cords, steel cords)
4. Plasticizers
5. Chemicals for vulcanization (sulphur, zinc oxide and others)
6. Anti-aging agents

Figure 1 - Materials present in the tire composition (adapted from Continental, 2013).



Figure 2 -Example of tire constitution (adapted from Continental, 2019).

The outer layer of a tire, which contacts the road surface, is called **tread**. It's composed of blends of synthetic and natural rubber, and its main purposes are to deliver the required grip to the surface, wear-resistance and direction stability. The design pattern of this element has an extreme importance in order to allow a better tire's grip on the road in the most adverse conditions (Brewer et al., 2006; Continental 2013).

To achieve stability at higher speeds, the tire has a **cap-ply** which consists of nylon or hybrid strips embedded in rubber. These are wrapped in a circumferential geometry covering the belts edges to restrict expansion derived by the centrifugal forces that are amplified in high velocities (Brewer et al., 2006; Continental 2013).

Under the cap-ply, the **steel-cord belts** are high-strength steel or textile cords applied in opposite directions to endure directional stability by restricting the ply cords expansion. This tire element is also capable of reducing the rolling resistance (Brewer et al., 2006; Continental 2013).

The **carcass**, often designated as body ply, is constituted by cord and rubber. The cords are laid radially around the tire in order to control its internal pressure by providing

the necessary strength to do so. The carcass is also responsible for maintaining the tire's shape (Brewer et al., 2006; Continental 2013).

The **inner liner**, located on the tire inner surface, acts as a tube sealing the air-filled inner chamber. This thin tube seals the chamber by lowering the permeation outwards through the tire and is made of butyl rubber (Brewer et al., 2006; Continental 2013).

To endure external damage and unfavorable atmospheric conditions the tire has a **sidewall** of natural rubber. The rubber is formulated to resist cracking, therefore it protects the tire's carcass from external forces damages such as abrasion or impact (Brewer et al., 2006).

The **bead reinforcement**, the **bed apex** and the **bead core**, shown in **Figure 2** constitute the bead bundle. Both the first and second element provide direction stability and steering precision, the bed apex also improves comfort to the ride. The bead core is made of steel wires to ensure that the tire properly fits in the rim of the wheel and does not slip out of position (Brewer et al., 2006; Continental 2013).

Tires can be categorized into three types depending on the carcass arrangements. The radial tire is the most used assembly in which the cords are laid perpendicularly to the direction of the traveling. When sideways, they seem to run radially, which explains the radial tire name. Although this assembly provides support and stability, the cords are not capable of absorbing the lateral or circumferential forces by the acceleration of the vehicle, so it is necessary to support them with other elements. Better high-speed performance and lower rolling resistance are other positive aspects regarding the radial tire, and these advantages occur because the body cords can deflect under load easily, generating less heat. Additionally, the increase in tread stiffness expands wear and handling (Brewer et al., 2006).

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

Belted bias tire has belts in the tread region in order to strengthen and stabilize this region by confining the body carcass expansion in the circumferential direction. The belts provide a better wear and handle. However, generation of heat still occurs due to shear of

the body ply. This type of tire also requires higher material and manufacturing cost (Brewer et al., 2006).

2.2 Textile Reinforcement

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

Nylon fibers are the most commonly used in radial tires as cap or overlay ply and its success led to the commercialization of other synthetic fibers as well as inorganic fibers. This synthetic long chain polymer is produced by a continued polymerization or melt spinning. It has a good heat resistance and strength, low modulus and glass transition temperature and a low sensitivity to moisture. The most common nylon fibers used in the textile reinforcement industry are nylon 6.0 and nylon 6.6. Nylon 6.0 is made from one monomer which has 6 carbon atoms whilst nylon 6.6 is made from 2 monomers with each one having 6 carbon atoms. (Brewer et al., 2006).

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

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

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

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

Cords can be twisted in two opposite directions, clockwise (“Z”) or counter-clockwise (“S”). As it is shown in **Figure 3**, the yarns are most commonly twisted in a “Z” direction and later twisted in an “S” direction. This process is made by a twisting machine to produce greige cord. The greige cord (cord without any treatment) manufactured in C-ITA can be later combined and transformed into fabric to be used in the carcass (“Types of yarn”, 1998; Wahl, 2003).

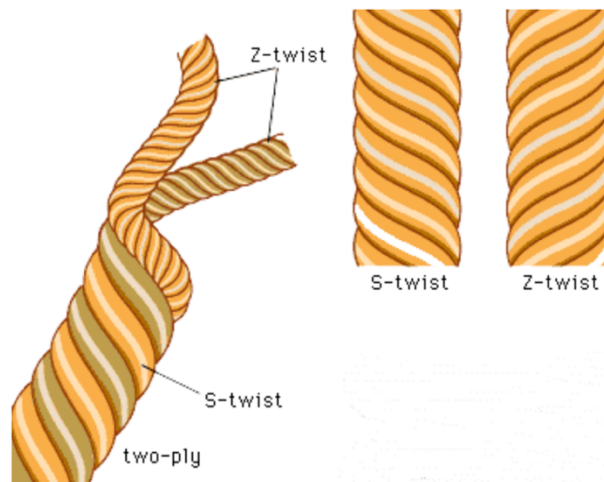


Figure 3 - Examples of twist direction (adapted from “Types of yarn”, 1998).

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

2.3 Dip Solution and Dipping Process

When it comes to cord adhesion in the rubber, this is a difficult process to be accomplished only by a physical treatment. Due to the difference of the polarity between these two components the lack of compatibility needs to be overcome. Therefore it is necessary to do a treatment in the cords or fabric that are going to be used as textile reinforcement. In general, polymeric cords have a smooth and inert surface as well as a polar character, thereby the interactions between them and the non-polar rubber are very weak. The most common treatment made to the cords is the Resorcinol-formaldehyde-latex

(RFL) technique in which a dipping solution (DIP) is used. The cords are dipped in the solution and later, to create a solid interface layer in the fibers' surface, they are stretched and dried in ovens (Brewer *et al.*, 2006; Louis *et al.*, 2014).

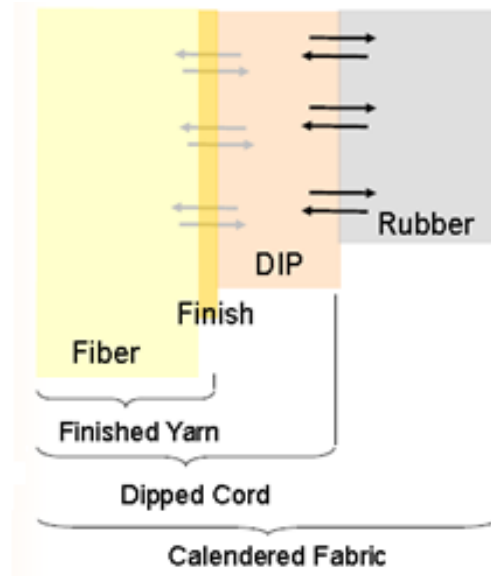


Figure 4 - Cord adhesion into rubber (adapted from Wahl, 2003).

In **Figure 4** it is possible to see that the DIP acts as a barrier between the fiber and the rubber. The dipping solution is constituted mostly by water, a latex emulsion and a resin made of resorcinol and formaldehyde. If latex alone was to be applied to the cords, it would provide an interaction with the rubber matrix of the compound but not with the fiber itself, resulting in weak mechanical properties for the latex layer. By adding resorcinol and formaldehyde, the dip layer increases in polarity and mechanical properties. The resin bonds with the fiber due to covalent chemical bonds formed in the interface fiber-DIP, as can be seen in **Figure 5**. Although physical bonds are later formed, the chemical bonds are the main contribution to adhesion as they are very strong and highly durable (Vollaro P., 2011).

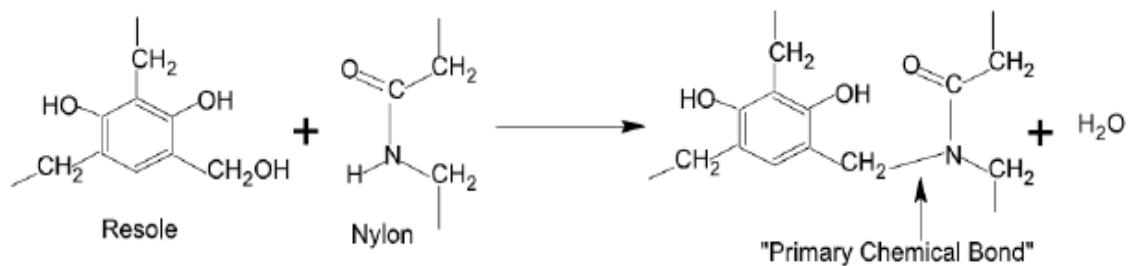


Figure 5 - Reaction scheme of a resole and nylon molecule forming a covalent bond (Adapted from Louis A. *et al.*, 2016).

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

To dip the cords C-ITA uses a production machine called Single-end shown in **Figure 6**. In this machine the greige cord unwinds in the same place in which the dipped cord winds, explaining the name “single-end”. First the greige cord is stretched in tensioning rollers and is forwarded to the first bath, which contains the dip solution, afterwards the cord goes to the first oven to be dried. After the first oven the cord goes through the second oven in which it is hot stretched and acquires the final properties.

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

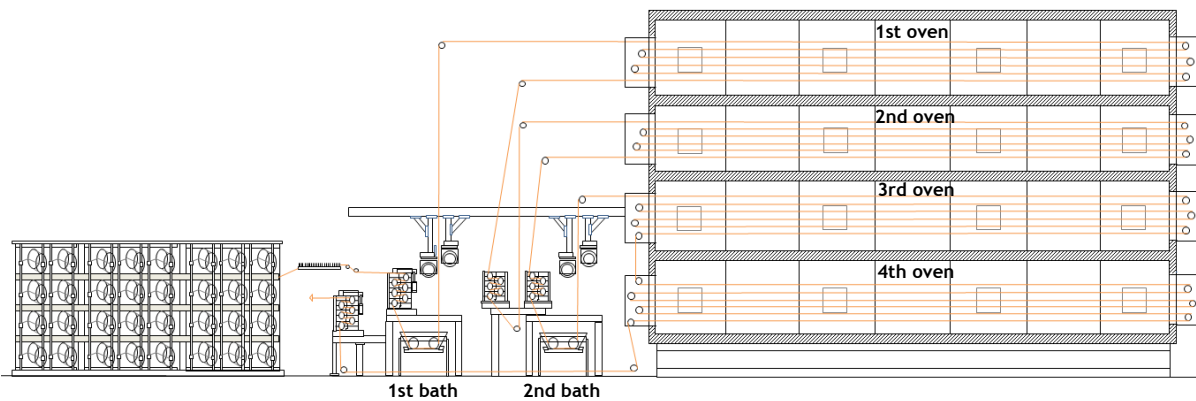


Figure 6 - Single-end scheme (adapted from Martins, 2013).

C-ITA also dips fabrics in a machine named Zell, represented in **Figure 7**. Contrary to the Single-end, the greige fabric and the dipped fabric do not unwind and wind on the same side. Another difference is that the Zell machine has seven ovens, instead of four. Additionally, the fabric is dipped one at a time, while in the Single-end 108 cords can be dipped at the same time.

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

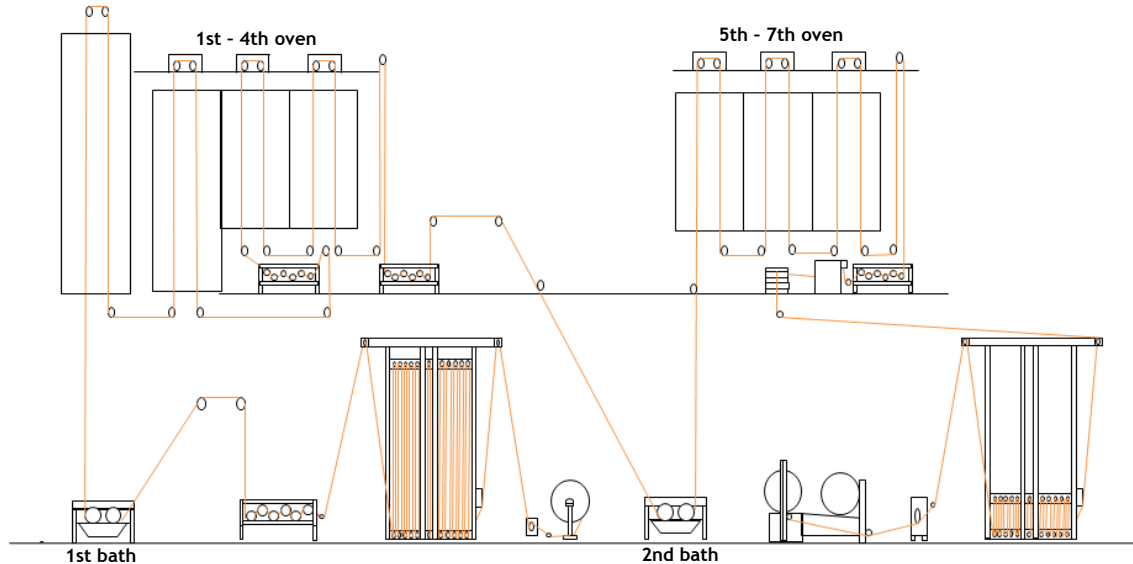


Figure 7 - Zell scheme (adapted from Martins, 2013).

C-ITA establishes all the variable conditions such as Solid Content (SC), stretch, velocity and temperature for the textiles to get dipped.

In C-ITA the amount of DIP is quantified for quality and economic matters, as a higher amount leads to waste and environmental concerns. On the other hand, a lower quantity than what's required leads to poor adhesion and low-quality reinforcement textiles. To verify the cords' adhesion to the rubber, C-ITA performs peel adhesion tests. If the adhesion is not good the cord will separate from the rubber, as it can be seen in the left samples in **Figure 8**. To be considered a good result, the cords have to be properly inserted in the rubber, so they cannot be visible to the naked eye, as it is shown in the right samples in **Figure 8**.



Figure 8 - Peel test results.

2.4 Quality control

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

2.4.1 Wet-Chemical and Weighing Methods

In C-ITA, the **Wet-Chemical** is one of the used methods to measure the amount of DIP in cords. In this method the fibers in the dipped cord are dissolved. The Wet-Chemical has many disadvantages such as the high amount of errors associated and the environmental issues related to the use of dangerous chemicals. An equally important disadvantage is the fact that this method is time consuming, making it impracticable for quality control for some textiles like aramid and PET.

The Wet-Chemical method requires the following steps: (i) dissolution of fibers, (ii) solvent removal by filtration and recovery of the dip residue, (iii) drying of the dip, and (iv) weighing the solid residue. Afterwards, Equation 1 is applied to calculate the *DPU*,

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

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

Another of the methods used by Continental to measure the *DPU* is called **Weighing Method**. Because of the hygroscopic nature of most cords, the humidity present in the environment can affect the results, so the samples need to be cut into laces and dried at 105 °C before the weight measurement. For these cases the *DPU* is measured using Equation 2, where the greige cord is thermofixated and used as reference value. Although this method does not require fiber dissolution, it has been proven to have even more errors associated than the Wet-Chemical.

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

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

Due to the impracticability of the wet chemical and weighing methods, the Time Domain Nuclear Magnetic Resonance method was chosen amongst other studied possibilities, as an alternative, due to its faster results and also high quality and low error occurrence associated.

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

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

The TD-NMR device emits magnetic pulses that excite the sample's protons to a higher energy state, afterward, when the pulse is deactivated, the protons will release the absorbed energy. Thereby, the signal captured from the TD-NMR results from the difference between the energy absorbed by the protons' spins and the energy emitted by it. The pulses can be emitted at 90 and 180 degrees, and each angle affects the protons' spinning in a different way. At the end of the pulse with 90° the signal emitted by the sample's protons is at the maximum intensity. However, the intensity diminishes rapidly to the protons' original energy state in an exponentially damped sine wave form being detected by a receiver coil. The sinusoidal wave is designated as free induction decay (FID), represented in **Figure 9** (CDRH Magnetic Resonance Working Group, 1997).

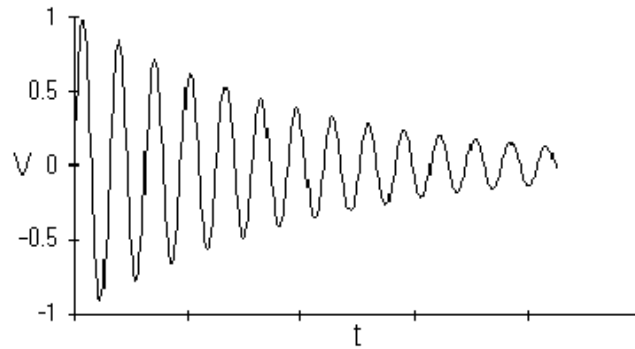


Figure 9 - Free induction decay wave (Adapted from CDRH Magnetic Resonance Working Group, 1997).

When the sample is first exposed to a magnetic pulse at 90° and subsequently at 180° the provoked disturbance is called a Hahn echo sequence. This sequence is used to determine the spin finish content, often named oil pick up (OPU), in yarns basing on the components' different transverse relaxation properties. The yarn, being a solid, has a shorter relaxation time than the liquid OPU. When the first pulse (with a 90° angle) acts on the sample both OPU and yarn produce a signal. However, the same does not happen when the 180° pulse is emitted. In this case, the signal attributed to the ^1H spins of the yarn decayed already due to his shorter relaxation time, so the signal obtained will only be originated by the OPU (Bruker, 2016).

In a similar way, C-ITA uses this method to measure the amount of DIP in the samples. The main difference relies on the fact that both the DIP and the fiber are solid. Since the DIP has a shorter relaxation time, the signal obtained after the 180° pulse will be generated by the fiber's sample. Thereby, it is possible to measure the amount of DIP through the difference between the first and second signals, as it is shown in Figure 10 (Bruker, 2016).

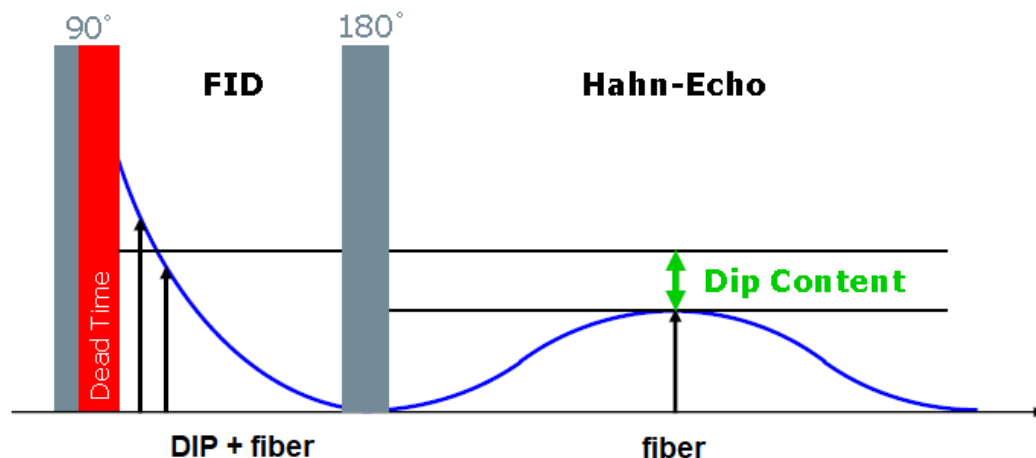


Figure 10 - Hahn echo sequence representation (Adapted from Bruker, 2016).

Nowadays, the urge to improve product quality with an optimum use of equipment and energy keeps increasing. A reliable process analytical technology, like the TD-NMR method, to control and assure the product quality is an increasing advantage to industries, such as C-ITA. Providing that the instrument has been correctly calibrated, the results are much reliable when compared to the traditional Wet-Chemical and weighing methods (Todt et al., 2006).

2.5 Statistical Analysis

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

2.5.1 Paired *t*-test

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

In the hypothesis test, two statements are formulated: the null hypothesis (H_0) - considered true - and the alternative hypothesis (H_1). The null hypothesis gets rejected in favor of the alternative hypothesis only if sample evidence suggests that H_0 is false. The two possible conclusions from a hypothesis-testing analysis are either to reject H_0 or fail to reject H_0 (Devore et al., 2011). There are also two types of errors that may occur when testing hypotheses. If a null hypothesis is rejected when it is true, it is called a type I error. If the null hypothesis is not rejected when it is false, a type II error occurs. In hypothesis testing the procedure is to specify a value of the probability of type I error α , called significance level of the test (Montgomery et al., 2003).

For the hypothesis test of the means of two populations, where the variances of both populations are unknown it is assumed that they follow a normal distribution and, the hypothesis tests and confidence intervals are based on the *t* distribution (Montgomery et al., 2003). When the samples of the two populations are collected in pairs under similar conditions, but these conditions may change from one sample to another, the hypothesis testing should be made using a paired *t*-test. This test is based on the difference in values for each pair of samples. If the two populations appear to be similar, then the mean of the

differences of values should be zero. Considering populations X_{1j} and X_{2j} the differences between each pair of samples are defined by $D_j = X_{1j} - X_{2j}, j = 1, 2, \dots, n$. The D_j 's are assumed to be normally distributed with mean μ_D and so, the hypothesis test for the paired t -test is made using the following hypothesis:

$$H_0: \mu_1 - \mu_2 = \mu_D = 0 \quad (3)$$

$$H_1: \mu_D \neq 0 \quad (4)$$

μ_1 and μ_2 are both means of populations 1 and 2, respectively (Montgomery et al., 2003).

The result given by the paired t -test is calculated using the following equation,

$$T_0 = \frac{\bar{D}}{S_D \sqrt{n}} \quad (5)$$

where \bar{D} is the sample average of the n differences D_1, D_2, \dots, D_n , n is the sample size, and S_D is the sample standard deviation of these differences. To know the test results, T_0 must be compared to the t -Student distribution with $n - 1$ degrees of freedom. To reject the null hypothesis, $|T_0| > T_{\frac{\alpha}{2}, n-1}$, where $T_{\frac{\alpha}{2}, n-1}$ is the upper $\frac{\alpha}{2}$ percentage point of the t distribution with $n - 1$ degrees of freedom (Montgomery et al., 2003).

A more practical way to report the results of a hypothesis test at a specified α -value or level of significance is through the p-value approach. In a formal definition, the p-value is the smallest level of significance that would lead to rejection of the null hypothesis (H_0) with the given data. When the null hypothesis is true, the p-value is the probability that the test statistic will take on a value that is at least as extreme as the observed value of the statistic (Montgomery et al., 2003).

2.5.2 Confidence Interval

To have a good estimation of the unknown parameters is necessary to use a confidence interval. The confidence interval of a certain parameter θ is an interval with the form $l \leq \theta \leq u$. The values l and u are endpoints calculated from the given data based on the probability theory. The probability theory states that there is a probability of $1-\alpha$ of selecting a sample for which the true value of the parameter θ is contained by the confidence interval. Thereby, if in repeated random samplings, a large number of such intervals are constructed, $100(1-\alpha)$ % of them will contain the true value of θ . The margin

of error of the interval estimate of θ equals half the confidence interval amplitude. The $100(1-\alpha)$ % confidence interval for θ can be used as decision criteria to reject or not the null hypothesis on one hypothesis test. For the parameter θ , the test size α of the hypothesis

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

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

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

2.6 Fourier Transformed - Infrared Spectroscopy (FTIR)

Most molecules will absorb light in the infrared region of the electromagnetic spectrum converting it into molecular vibration. Due to this, in the mid-infrared region, the absorption corresponds specifically to the bonds present in each molecule's functional groups. Using a spectrometer, the absorption of infrared radiation by the sample material versus the wavenumber (usually from 4000 to 600 cm^{-1}) is measured. In result, a distinctive spectrum for each molecular sample is obtained which can be used to identify organic and inorganic samples (Ganzoury et al., 2015; Bruker, 2020).

By using just Infrared Spectroscopy, the sample is irradiated with varying single wavelengths which provides dispersive results. By switching to the FTIR, all the spectral data can be collected in one single test. To achieve this solution, a continuum source of light is needed to produce light through a large range of infrared wavelengths. This infrared light is then directed through an interferometer and afterwards aimed at the sample (Bruker, 2020).

The outcome is an interferogram, a moderately raw signal that represents the intensity of light as a function of the position of a mirror. This signal is required to be Fourier-Transformed to allow obtaining a more standard infrared plot of intensity vs. wavenumber - therefore, we obtain the name FTIR (Bruker, 2020).

With FTIR analysis the identification of unknown materials is possible. It is also possible to test the quality and consistency of a sample or also quantify the amount of components in a mixture. (Ganzoury et al., 2015)

In infrared spectroscopy a variety of measurement techniques is necessary due to the wide range of samples that are usually investigated. When selecting the appropriate technique, the need for elaborate sample preparations is minimized, which simplifies data

analyses. Attenuated Total Reflection (ATR) has become the standard technique used for the measurement of FTIR spectra. The sample is pressed onto a crystal of a certain material (diamond, zinc selenide (ZnSe) or germanium), then the infrared light passes through this crystal and interacts with the sample. A spectrum that shows all the characteristics specific to the substance is obtained (Milosevic, 2004; Bruker, 2020).

2.7 Assessment of previous work

The TD-NMR equipment was acquired by C-ITA to improve product quality control and it has been proven to be a reliable, faster and accurate method when it comes to measuring the DIP content present in the fibers. In previous Master Theses a lot of work and study has been developed around this device and method. It has already been calibrated and validated for nylon, rayon, PET and hybrid. In this Master Thesis the TD-NMR was calibrated for aramid, another of the main fibers used in C-ITA.

Besides calibration, it has also been studied and proved that in the dipping process, the velocity, temperature and Solid Content have a strong influence on the results obtained for the *DPU* (Santos, 2018; Bezerra, 2018).

Regarding sample preparation, it has also been proven that the use of gloves throughout the whole process is essential to achieve accurate and reliable results. Apart from that, when cutting the samples, a new method was introduced, the cutting method. This method came in handy as it is a much simpler alternative than the standard lace tie up method. Finally, it was also proved that proper sample drying is needed to obtain accurate dip content results (Cardoso, 2017; Bezerra, 2018).

3 Materials and Methods

3.1 Materials

In the more practical part of the project, the TD-NMR calibration, the only material used was activated aramid with a cord construction of 1680 dtex x 2.

For the FTIR analysis Nylon 6.6 with a cord construction of 940 dtex x 2 was the used material.

3.2 Dipping Process

In order to replicate the dipping production process C-ITA has a lab scaled equipment called Lab Dipping Unit (LDU), so that it is possible to test different materials, dips and variables, as previously mentioned in chapter 2. For every material in study the dipping solutions and conditions of operation such as velocity, oven temperature, tension and stretching, vary. **Figure 11** represents the operating scheme of the LDU.

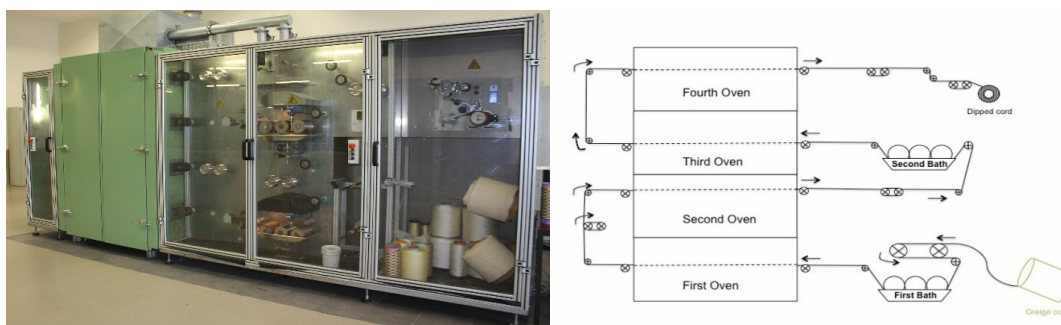


Figure 11 - LDU machine on the left and LDU operating scheme on the right (adapted from Martins, 2013).

In this case, aramid was the only used material, so the conditions of operation were adapted from the ones used in production. The aramid is dipped in the Zell machine as fabric and knowing that the LDU only dips one cord at the same time, that was taken into consideration when adapting the production settings into the LDU. Since the aramid was already activated, only one dip bath was needed, therefore only the first, second and third ovens were used.

3.3 Dip Pick-Up measurement

3.3.1 Wet-Chemical Method

One of the official methods used in Continental to measure the dip pick up content is the Wet-Chemical. Briefly, the Wet-Chemical method obtains the amount of *DPU* in textile cords or fabric by dissolving the fibers in a suitable solvent. The remaining dip gets filtered and dried to be weighed and reported as % per weight of greige fiber. In this thesis the method was used to calibrate the TD-NMR device for aramid using the different values of

DPU obtained. A more detailed description of the method is presented in the following procedure:

1. The dipped cord was cut into pieces with a maximum length of 5 mm until they weighed around 0.8 to 1 g. Next, the sample was dried for 1 hour in a drying oven at 105 °C and then moved from the oven into the desiccator to cool down until room temperature. The sample was weighed into an Erlenmeyer flask to obtain the parameter m_1 of **Equation 1**.
2. The cord was dissolved with a suitable solvent for a specific period of time. The mixture cord + solvent was at room temperature and a stirrer bar was added during the dissolving period. Regarding the aramid, the information about the solvent used and time for dissolution is shown in **Table 1**.
3. A crucible was dried in a drying oven for 4 hours at 105 °C. It was then moved from the drying oven into the desiccator to cool down until room temperature. The dried crucible was weighed to obtain parameter m_2 of **Equation 1**.
4. The sample was filtrated using the dried crucible, a proper washing fluid and a pump system. The washing fluid used to wash the aramid sample is referenced in **Table 1**.
5. The crucible containing the retained dip pick-up was dried in a drying oven for 2 hours at 105 °C. It was then left to cool down until room temperature in a desiccator.
6. The dried crucible was weighed to obtain parameter m_3 of **Equation 1**.

Table 1 - Textile solvent and washing fluids.

Textile	Solvent	Dissolution time (h)	Washing Fluid
Aramid	Sulfuric acid conc. - 800 mL	At least 72	Sulfuric acid conc - 50 mL + Sodium bicarbonate - 20 mL + Water - 500 mL

3.3.2 Weighing Method

The Weighing Method, as previously stated, is another of the used methods by C-ITA to measure the DIP content, though its accuracy cannot be the most reliable. To perform this method a greige thermofixated and a dipped cord are needed. The procedure is explained in the following steps:

1. 10 samples from the greige cord and the dipped cord were cut with 10 meters each;
2. The samples were tied up in the form of laces and put in a drying oven for 1 hour at 105 °C;
3. The samples were removed from the drying oven and weighed one at a time;
4. The average weight of the 10 samples for each cord was calculated and then **Equation 2** was used to obtain the *DPU*.

Regarding the Aramid, since the Wet-Chemical method is very time consuming, C-ITA uses a particular weighing method, different from the one explained above. This material is only produced and dipped in the form of fabric, therefore, only the Zell machine is used to dip the Aramid. In this case the *DPU* is also obtained by **Equation 2** but by merely weighing the non thermofixated greige fabric roll and after the dipped fabric roll.

3.3.3 TD-NMR Method

The TD-NMR has been proven so far as the method that provides the most accurate and fastest results regarding the measure of the dip pick-up content. It has been already calibrated for most of the textiles used in C-ITA. For the sample preparation two techniques can be used: the traditional and the cutting method. In the traditional method the cord is tied up into a bow form and it must not have more than 2 cm of height. In the cutting method the sample just needs to be cut into small pieces. For the aramid the cutting method was used. Keeping in mind that to conduct this analysis the use of gloves is obligatory, the procedure for the TD-NMR method is described in the following steps:

1. The sample tubes and lids were properly identified and then the tubes were weighed with the lids on.
2. A piece of dipped cord that weighed around 0.5 g was cut into pieces with a maximum length of 5 mm.
3. The samples were placed into the tubes and put in the drying oven without the lids for at least 1 hour at 105 °C.

4. The lids were placed on the tubes while still in the drying oven and then left to cool down until room temperature.
5. The sample tubes were weighed and put in a heating device at 40 °C for at least 5 minutes.
6. The dip pick-up content of the samples was measured in the TD-NMR device, three times each.

3.4 Calibration Curve

To create a calibration curve it's necessary to have four cords with a specified amount of *DPU* that is related to the material's *DPU* target range. To achieve those values it's necessary to dip those cords in the LDU with a specific amount of S_c . This is a trial by error process which leads, most of the time, to the dipping of more than four cords until the desired ones are obtained. The *DPU* values are measured by the Wet Chemical method, and at least three of those values for each cord need to have a standard deviation lower than 0.4 %. All of these steps become very time consuming when achieving the desired values, especially for aramid, since each Wet-Chemical trial lasts 3 days. Later, with the *DPU* values from the Wet-Chemical method used as a reference, the calibration curve is computed. According to Continental standards, the *DPU* values used to create the aramid calibration curve were determined and organized using the pre-established range present in **Table 2**:

Table 2 - *DPU* necessary for each cord of the calibration curve.

Type	Cord	<i>DPU</i>				
		LTL -1 %	LTL*	Target value	UTL**	UTL +1 %
Aramid	1	2.6 % - 3.6 %				
	2	3.6 % - 5.1 %				
	3	5.1 % - 6.6 %				
	4					6.6 % - 7.6 %

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

After the calibration is made, the curve needs to be validated. This validation consists of using 30 samples from production and comparing the results from the TD-NMR with the ones previously obtained by production quality control using the weighing method. For the curve to be validated, the values obtained by the two methods must not be significantly different.

3.5 Countercheck Database

Since Continental has plants and textile suppliers all over the world, it is important to check the quality and performance of these reinforcement materials to confirm if they meet the company's requirements. To do so, C-ITA has a certified laboratory that is responsible for receiving and analyzing textile samples sent from other plants around the world. They perform a variety of physical and chemical tests that determine whether the samples meet the quality standards or not, hence the term countercheck. One of the cord's features to be tested is the *DPU*, using both the TD-NMR and Wet-Chemical Methods. Regarding the TD-NMR analysis, it is executed using the calibration curves created for C-ITA's materials and dip solutions. It is important to keep in mind that dip solution recipes used by plants and suppliers other than C-ITA may differ.

For every sample received for countercheck, C-ITA created a database where they compiled the results obtained in every quality control test performed.

This Master Thesis focuses on the analysis and comparison of the *DPU* results obtained by the TD-NMR and Wet-Chemical methods. The majority of the study was made using the software Minitab 18.

3.6 FTIR

C-ITA, as it was previously referenced, receives cord samples from plants all over the world to be tested in terms of quality and performance. Since those cords come from different suppliers, they are dipped using different dip solution recipes and dip solution components, meaning, the latex used in C-ITA's DIP recipe probably isn't the exact same latex used in other suppliers' recipes. Since it has been already proved in previous Master Thesis that the DIP content has a significant effect on the TD-NMR signal results, the FTIR analysis appeared as method to understand better the molecular bonds formed during the dipping process and which DIP component is most responsible for the signal variations in the TD-NMR device.

To perform the FTIR analysis samples of nylon cord and dried DIP were collected. Regarding the nylon, greige and dipped cords with two different solid content values were used. A sample of each cord was cut and then, in the FTIR equipment, they were pressed

onto the crystal cell to be analyzed. The same happened with the solid DIP sample. Once the FTIR analysis starts, a beam of infrared light passes through the crystal and interacts with the sample. Some of the light reflects back but most of it gets absorbed by the sample and gets detected by the equipment. After this process a spectrum of Transmittance (%) vs. Wavenumber (cm^{-1}) is obtained and the base line of the spectrum is adjusted. This spectrum shows the molecular bonds existing in the sample, each with different intensities. To quantify those intensities, the transmittance values are converted into absorbance values which are then used to calculate the second derivatives of the spectrum. These derivatives are calculated using the means for every 17 points of the spectrum, a smoothing filter and a second order polynomial. These values are represented in the form of a plot.

The FTIR equipment used to perform these tests was a Vertex 70 spectrometer by the company Bruker, equipped with an ATR cell containing a diamond crystal with single reflection accessory. To obtain each spectrum, an average of 64 scans were taken with 4 cm^{-1} resolution in the $4000\text{-}500 \text{ cm}^{-1}$ range. In every sample, measurements were performed in triplicate and background was executed in between every analysis.

4 Results and Discussion

The values of DPU given by the TD-NMR device are the percentage of dip content per dipped cord (Equation 13). On the other hand, the Wet-Chemical and Weighing methods present the results in percentage of dip content per greige cord (Equation 12). Keeping this in mind it's necessary to convert the values obtained by the TD-NMR method from dipped cord into greige cord.

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

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

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

Combining the equations above:

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

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

Dividing Equation 11 for $m_{dipped\ cord}$ and multiplying by 100:

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

Therefore, is possible to convert the TD-NMR results in $DPU_{per\ greige\ cord}$ with Equation 13. All the values of the TD-NMR machine present 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 18 that provides statistical guidance for interpreting statistical tables and graphs in a practical way.

4.1 Countercheck Database Analysis

To begin with the countercheck database analysis, all the existing data from the years 2018 and 2019 were collected, organized and divided into several categories. **Figure 12** shows an overview of the database content.

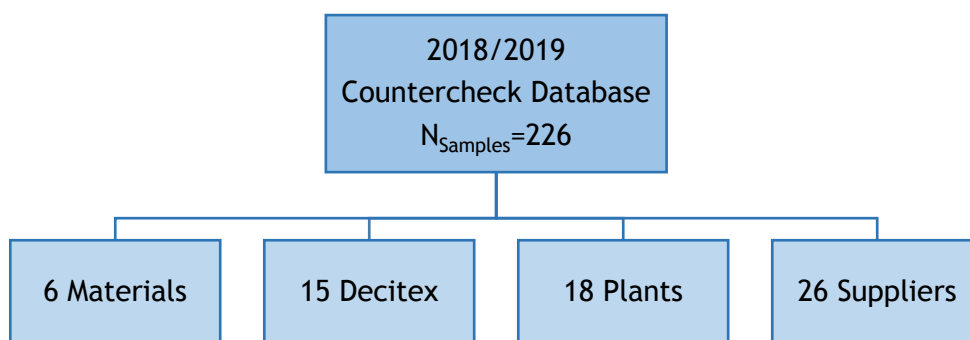


Figure 12 - Overview of the database content.

As it was previously referenced, the focus for the analysis of the database was to compare both of *DPU* values obtained with the Wet-Chemical and TD-NMR methods, for each sample received by C-ITA and see if the two methods were similar. Since the database contained over 200 samples, the first step was to see whether these values would fit in a linear regression model. The fitted line plot is represented in the following **Figure**:

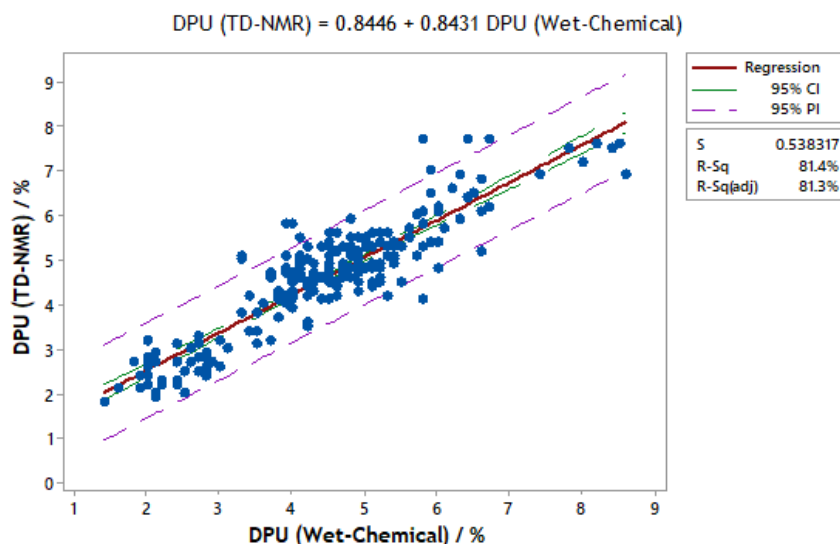


Figure 13 - Fitted line plot for global data with outliers.

The values appear to follow a linear regression, although further testing is needed to prove if they follow such model. The slope obtained for the regression line has a value of 0.8431 and the R-squared has a value of 81.4 %.

In an ideal situation of similarity between the two methods, the slope should take values closer to 1, as so should the R-squared. Another important fact to point out regarding **Figure 13** is the existence of some outlier points where the values for *DPU* have a significant difference between the two methods, which could go up to 2 %. To continue this study for the database, those points were not considered in the analysis, however they will be referenced later in the FTIR analysis.

Removing the outlier points, the number of samples passed from 226 to 215, so a new fitted regression line was created and it's shown in **Figure 14**.

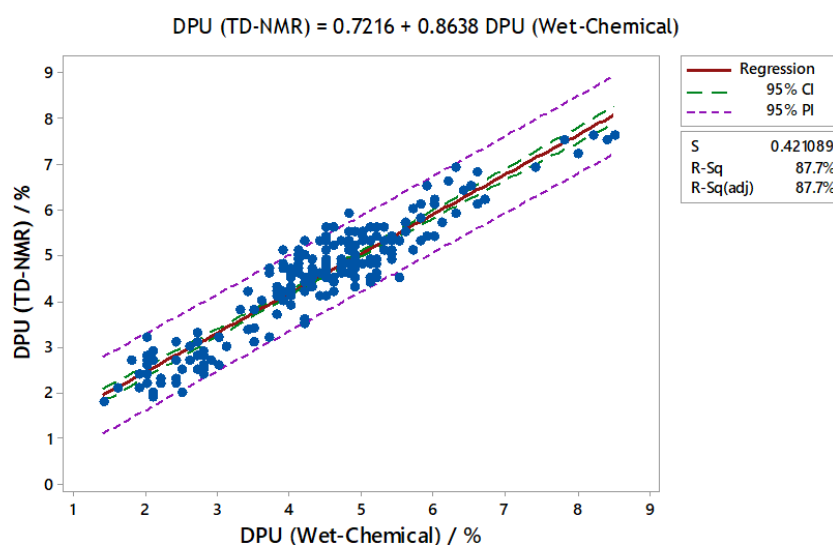


Figure 14 - Fitted line plot for global data.

Even though the outlier points were removed, this didn't result in significant improvements for the slope and R-squared values. The slope value passed from 0.8431 to 0.8638 and the R-squared value passed from 81.4 % to 87.7 %. This might mean that the similarity between the two methods is somewhat far from the ideal situation, from a first point of view. The next step was to verify if the data followed the assumptions of the regression line model, being these: a linear relation between the predictor and the response variable with a random variability around it represented by normal independent random errors with zero mean and equal variance. To check that, the residual plots were created and are presented in **Figure 15**.

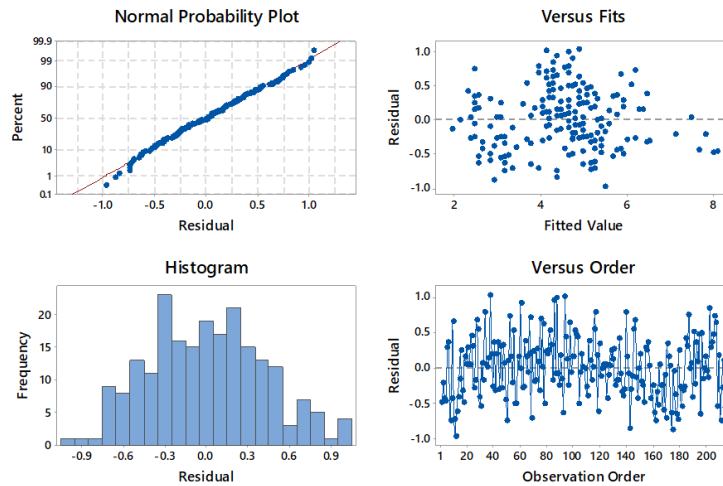


Figure 15 - Residual plots for DPU (TD-NMR) for global data.

First, it is important to know that the residuals are the difference between the observed and the fitted response values. Analyzing the residual plots, in the normality plot the residuals appear to follow an approximate normal distribution, as the values seem to follow a linear shape. In the residuals vs. fits, plot the data is randomly distributed without a pattern on both sides of 0, which appears to indicate that the linearity between variables with random errors with zero mean and equal variance assumption is followed. Furthermore, in the residuals vs. order plot, the values seem to follow a random pattern around the centerline, demonstrating that the random errors seem to be independent. Considering these results, it's possible to say that the values in study fit the regression line model.

After the study of the residual plots, it was time to test if the two *DPU* measuring methods were statistically different regarding the countercheck analysis, since it has been proved in previous Master Theses that for materials dipped and tested in C-ITA the two methods are similar. To test this possible similarity a paired *t*-test was performed. The null hypothesis states that the difference of the population means of the two *DPU* methods must be zero, meaning, the means must be equal. A significance level of 5 % was considered to perform this test. The results can be seen in **Table 3**.

Table 3 - Paired *t*-test results for global data.

Means difference (%)	Means difference standard error (%)	95 % CI for means difference	p-value
0.1223	0.0311	(0.0610; 0.1836)	< 0.001

The p-value obtained was less than 0.001. Therefore, there is statistical evidence that the means of the two methods are different and the null hypothesis is rejected. The means of the populations have an estimated difference of 0.12 ± 0.03 %. This indicates that the means differ from a statistical point of view, but in a more practical way the difference is at most of 0.15 % which is less than 1 %, the Continental standard. With this, it is possible to conclude that the two methods are not significantly different. The boxplot of the differences between the two methods is shown in the following **Figure 16**.

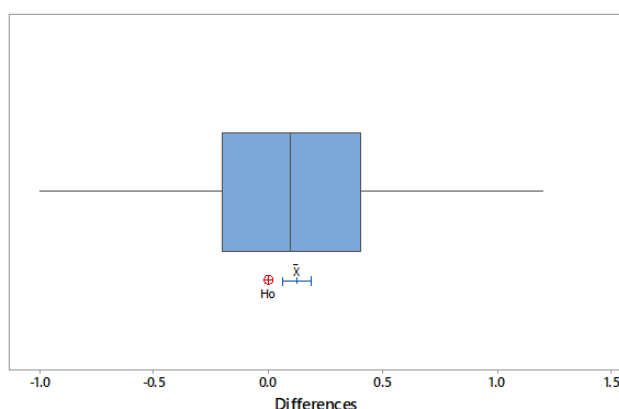


Figure 16 - Boxplot of the differences of the two methods for global data.

From the boxplot analysis, the values appear to be symmetrically distributed, which may suggest that the difference between samples follows a normal distribution.

Finished the global analysis of the values, it was time to make a more detailed study of the database. The next focus was to analyze the data for each material. An overview of the content for each material and a visual perception of where their *DPU* values are located in the global data points are presented in the following **Figure 17** and **Table 4**.

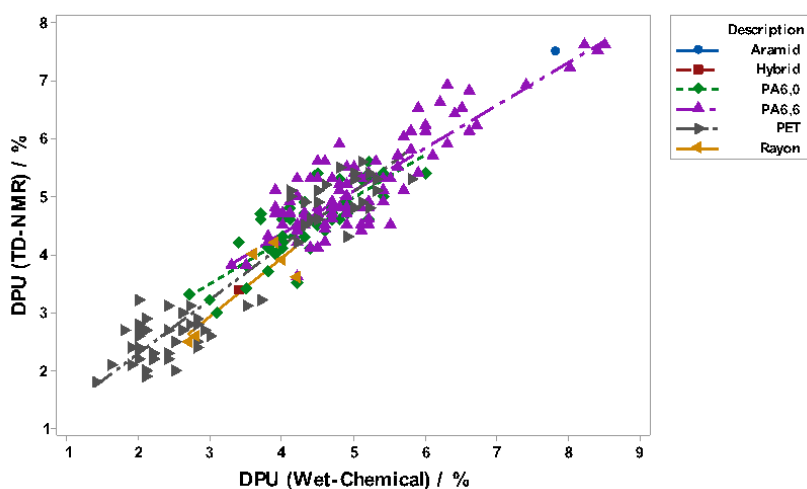


Figure 17 - Scatterplot of global values grouped by material.

Table 4 - Data overview for each material.

Material	Nylon 6.6		Nylon 6.0		PET	
N _{Samples}	101		46		60	
DPU Method	TD-NMR	Wet-Chemical	TD-NMR	Wet-Chemical	TD-NMR	Wet-Chemical
Mean	5.17	5.10	4.48	4.33	3.54	3.33
Median	5.00	4.90	4.60	4.30	2.95	2.80
STDev	0.86	1.02	0.63	0.70	1.27	1.29
95 % CI for μ	(4.99; 5.36)	(4.90; 5.30)	(4.21; 4.76)	(4.03; 4.63)	(3.29; 3.78)	(3.06; 3.59)

From the analysis of **Figure 17**, it's possible to see that nylon 6.6 and PET are the two materials that show a wider range of *DPU* values. It was only possible to do a more detailed study for both nylons and PET. The remaining materials didn't have enough samples to do a proper analysis. There was only one sample for hybrid and aramid, and six for rayon. From **Table 4** is possible to see that the means and medians of both methods for each material are very similar, which is a good start point to analyze the similarity between methods.

It is also possible to observe that the TD-NMR method has lower standard deviation values for all three materials and also a lower error associated to the confidence intervals for means. This might suggest that for the countercheck analysis the TD-NMR method gives more consistent and precise results than the Wet-Chemical. Nonetheless, further testing was conducted for each material individually, just like in the global data, to compare both the Wet-Chemical and the TD-NMR methods.

4.1.1 Nylon 6.6 and Nylon 6.0

Starting with the study for both nylon 6.6 and nylon 6.0, a fitted line plot was created to see if the data follows a linear regression model. The results can be seen in the following **Figure 18**.

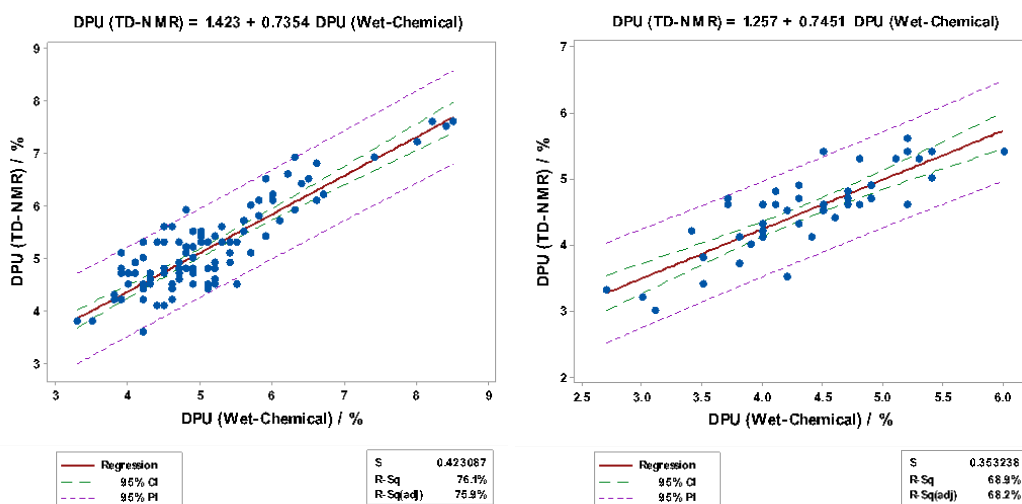


Figure 18 - Fitted Line Plot for nylon 6.6 (Left) and nylon 6.0 (Right).

Just like in the global data case, for both materials the values appear to follow a linear regression but when it comes to the similarity between the two methods it is somewhat far from the ideal situation. To confirm the linear regression model, residual plots were created and can be found in the appendix section (Figure A.1.1 and Figure A.1.2). Through the analysis of those plots it's possible to verify that the data checks out all the linear regression model assumptions, and so, it is considered that the values for both nylon 6.6 and nylon 6.0 follow that model.

Next, the paired t -test was conducted to analyze the similarity of DPU values for both the TD-NMR and the Wet-Chemical methods. The null hypothesis states that the difference of the means must be zero, meaning the means must be equal. A significance level of 5% was considered to perform this test. The results can be seen in Table 5.

Table 5 - Paired t -test results for nylon 6.6 and nylon 6.0.

Material	Means difference (%)	Means difference standard error (%)	95 % CI for means difference	p-value
Nylon 6.6	0.0744	0.0498	(-0.0243; 0.1732)	0.138
Nylon 6.0	0.1522	0.0578	(0.0358; 0.2686)	0.012

The p-value obtained for nylon 6.6 was 0.138. Therefore, there is no statistical evidence that the DPU means of the two methods are equal and the null hypothesis is not rejected. The two methods are not significantly different for nylon 6.6. In the case of nylon 6.0, the p-value obtained was 0.012, which is inferior to the significance level. Therefore,

there is statistical evidence that the *DPU* means of the two methods are different and the null hypothesis is rejected. The means of the populations have an estimated difference of 0.15 ± 0.06 %. This indicates that the means differ from a statistical point of view, but in a more practical way the difference is at most of 0.21 % which is less than 1 %, the Continental standard. This means that the two methods are also not significantly different for nylon 6.0. The boxplot of the *DPU* differences between the two methods for both materials was created and is located in the appendix files in **Figure A.1.3** and **Figure A.1.4**. The results of the boxplot show that the values are symmetrical and so it might suggest that the *DPU* difference between samples follows a normal distribution.

4.1.2 PET

Finally, the last material to be studied was PET and just like for the two other materials a fitted line plot was created to see if the data follows a linear regression model. The results are shown in **Figure 19**.

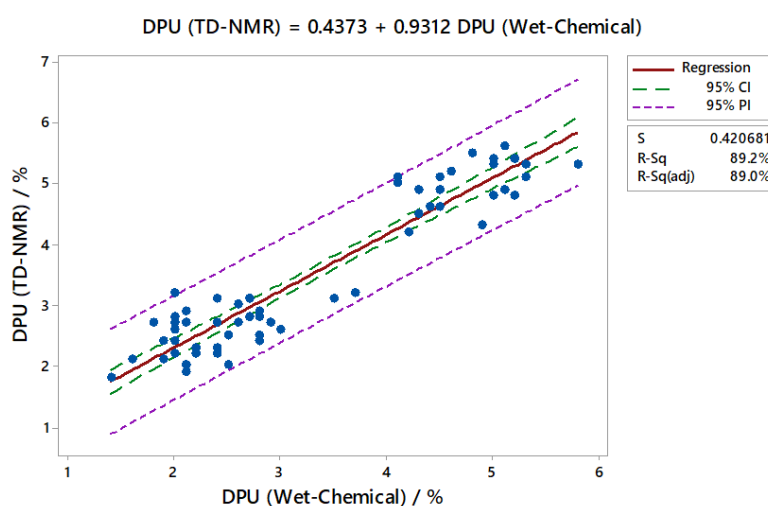


Figure 19 - Fitted line plot for PET.

The fitted line plot for PET shows interesting results, as it appears to exist two different populations. That might be explained by the fact that two types of PET exist: the non-adhesion activated (nAA) and the adhesion activated (AA). Further research was done by checking if each sample of PET was AA or nAA. In fact, the assumptions were somewhat correct. The nAA PET tended to have lower *DPU* values and the AA PET higher *DPU* values. However, there was one sample of non-adhesion activated PET that had low *DPU* values. Due to the existence of this case it is not possible to say with certainty that these two populations correspond each to nAA PET and AA PET. Considering this situation, the next step was to verify if the data followed the assumptions of the regression line model by checking the residual plots created for PET (**Figure 20**). Ideally, each population should be

analyzed individually, however, there were not enough samples available to do such testing and draw proper conclusions. Being this said, both populations were considered when conducting the following tests.

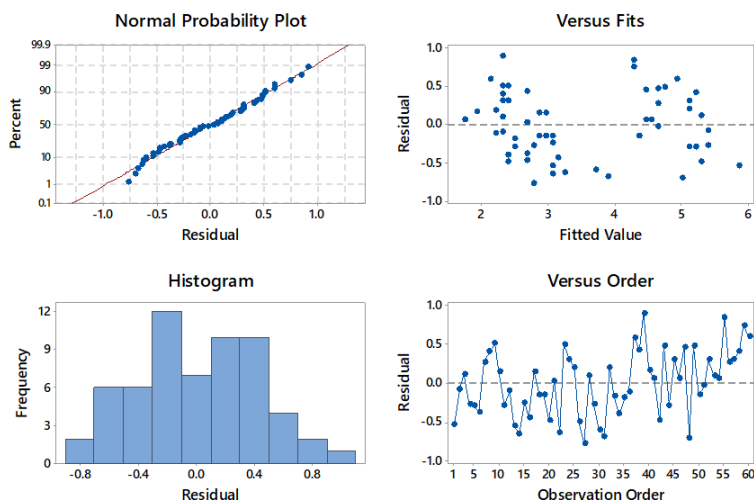


Figure 20 - Residual plots of DPU (TD-NMR) for PET.

Analyzing the residual plots, it's easy to notice in the residuals vs. fits plot that just like in the fitted regression line, the data appears to be distributed into two different groups. However, in an overall analysis everything indicates that the values fit the linear regression model. It is even possible to say that the same TD-NMR calibration curve could be used for both AA PET and nAA PET.

Regarding the paired t -test for PET, just like for other materials, the objective was to analyze the similarity of the DPU values for both the TD-NMR and the Wet-Chemical methods. The null hypothesis states that the difference of the population means must be zero, meaning, the means must be equal. A significance level of 5 % was considered to perform this test. The results can be seen in Table 6.

Table 6 - Paired t -test results for PET.

Means difference (%)	Means difference standard error (%)	95 % CI for means difference	p-value
0.2083	0.0550	(0.0982; 0.3185)	< 0.001

The p-value obtained was lower than 0.001, which is inferior to the significance level. Therefore, there is statistical evidence that the means of the two methods are different and the null hypothesis is rejected.

The means of the population have an estimated difference of 0.21 ± 0.06 %. This indicates that the means differ from a statistical point of view, but in a more practical way the difference is at most of 0.27 % which is less than 1 %, the Continental standard. This suggests that the two methods are also not significantly different for PET. The boxplot of the differences of the two methods was created and is located in the appendix files in **Figure A.1.5**. The results of the boxplot show that the values are symmetrical and so it might suggest that the difference between samples follows a normal distribution.

4.1.3 Decitex Study

Since it has been proved that for the countercheck analysis the TD-NMR and the Wet-Chemical methods do not show significant differences from each other when giving the *DPU* values of the samples, the next step was to study whether the decitex of the fiber has some correlation with the *DPU*.

Since every material has its range of decitex values, a boxplot containing the *DPU* value intervals, mean and median for every dtex, was created for each material. The boxplots for nylon 6.6 and nylon 6.0 are shown in the following **Figures 21 and 22**, respectively.

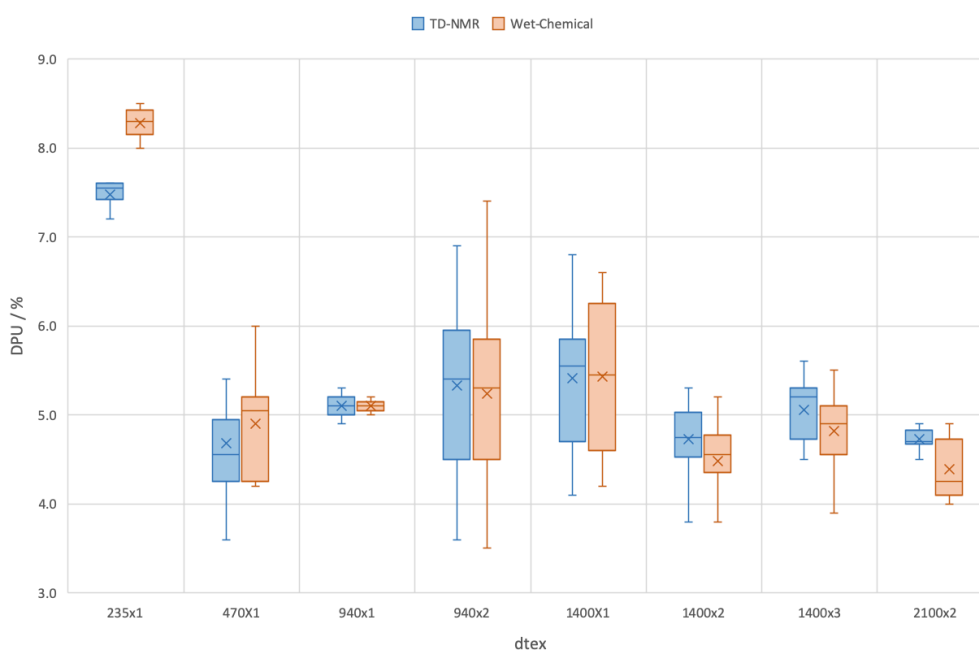


Figure 21 - Boxplot representation of dtex dip pick-up ranges for nylon 6.6.

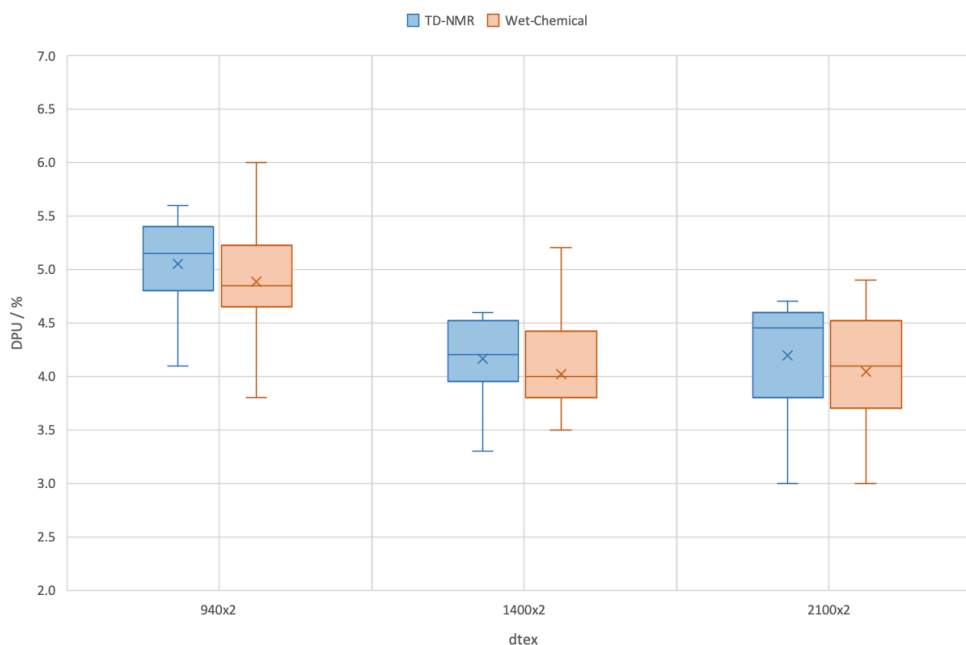


Figure 22 - Boxplot representation of dtex dip pick-up ranges for nylon 6.0.

From the analysis of **Figures 21 and 22**, it is possible to see a slight pattern of higher values of *DPU* for lower values of dtex and lower values of *DPU* for higher values of dtex. This pattern is more visible in the nylon 6.0 plot (**Figure 22**) since the number of samples for each decitex was very similar, unlike the plot for nylon 6.6, in which the number of samples for each decitex was not evenly distributed. Nonetheless, in this last case it is clear that the decitex that showed higher values of *DPU* was the 235 x 2. This correlation between the *DPU* and decitex is somewhat logical since the superficial area of the cord exposed to the dip solution during the dipping process is higher for lower values of dtex. It is also important to remember that this data comes from various types of plants and suppliers, and so, the dip solutions used by each one of them may differ. Keeping that in mind, to be sure of this correlation it would be interesting to conduct an experimental study in which cords from the same material but different dtex are dipped with the same DIP and see if the results correspond to the tendency observed in the countercheck samples. The same plot was made for PET samples (**Figure A.1.6**) but it was inconclusive when compared to the nylon ones. This might be explained by the fact of the existence of two populations, and in each of them the same values of dtex exist, which leads to bigger ranges of *DPU* for each one of them. To do a proper study, the populations would need to be analyzed individually, but unfortunately, the number of samples available for each population is not sufficient to do so.

4.2 FTIR Spectrum Analysis

Returning to the beginning of **section 4.1**, when the first fitted line plot containing the globality of samples from the countercheck database was showed (**Figure 13**), some outlier points were very noticeable, since the difference between the *DPU* values of the Wet-Chemical and TD-NMR methods was very clear. In some cases that difference would go up to 2 %. Since it has already been proved that the two methods are not significantly different, even in the countercheck analysis if those outliers are removed, such discrepancies should not exist and so, there would have to be an explanation for this to happen.

It was considered that the Wet-Chemical *DPU* results were the real ones and the TD-NMR results were incorrect. Such consideration was made because it has already been proved in previous Master Thesis that the TD-NMR signal can be affected by several factors during the dipping process. Some examples are the cord passing velocity during the dipping process, the interaction between the temperature and solid content of the DIP and most importantly, the solid content of the dipping solution itself. It is also known that the fiber doesn't affect the equipment's signal.

Keeping this in mind, the TD-NMR is calibrated for cords dipped using only C-ITA's dipping solutions, where the exact recipes and components of the DIP are known. However, the countercheck samples come already dipped from various suppliers where the recipe and exact components used are unknown. Probably, the discrepancies seen in the *DPU* values for the TD-NMR are explained by the fact that the recipes used by other suppliers are different from C-ITA's and the TD-NMR calibration curves do not fit the dip content from those suppliers.

The next step was to think which DIP component affects more the TD-NMR signal, and to test this, ideally, a design of experiment (DOE) would need to be created in which the concentration of every component of the DIP is varied individually and in combination with each other. After, using always the same material, the cords would be dipped in these different DIP combinations and tested using both the TD-NMR and the Wet-Chemical method. The comparison of these results would be conclusive to which DIP component most affects the TD-NMR signal. However, this DOE would require a considerable amount of time that did not exist during the course of this dissertation. With this being said, an alternative test would have to be found, and what came up as a suggestion was the use of FTIR analysis.

The RFL dipping solution is composed mostly of Resorcinol Formaldehyde Resin and VP Latex, a polymer of Vinyl Pyridine, Styrene and Butadiene. Also, these two components are the ones that contribute most with solid content to the DIP, so, from a logical point of view, the resin and the latex must be the ones that most affect the TD-NMR signal. Knowing their general molecular structure and also the structure of the fiber, using the FTIR analysis it's possible to see which molecular bonds are formed during the dipping process and which are more noticeable in the spectrum. For example, the ratio of Vinyl Pyridine, Styrene and Butadiene from the latex is not always the same, therefore if the VP Latex used by other suppliers is different from the one used by C-ITA, the FTIR spectrum will show that difference.

Ideally, to test this hypothesis, two cords with the same value of *DPU* obtained by the Wet-Chemical method should be compared: a countercheck outlier cord sample and a cord from the same material but dipped with C-ITA's dipping solution. However, when C-ITA does the countercheck analysis only keeps the samples for three months, and so, none of the outlier samples were still in C-ITA's possession because most of them were from 2018. Again, an alternative had to arise and what came up was to study cords from C-ITA dipped with different solid content dipping solutions, the greige cord itself and the dried DIP.

To perform this test it was used nylon 6.6 with a cord construction of 940 x 2 and two dipping solutions, one with SC=14.91 % and other with SC=21.23 %. **Figure 23** shows the comparison between the spectrums of the greige cord, dipped cord, and dried DIP.

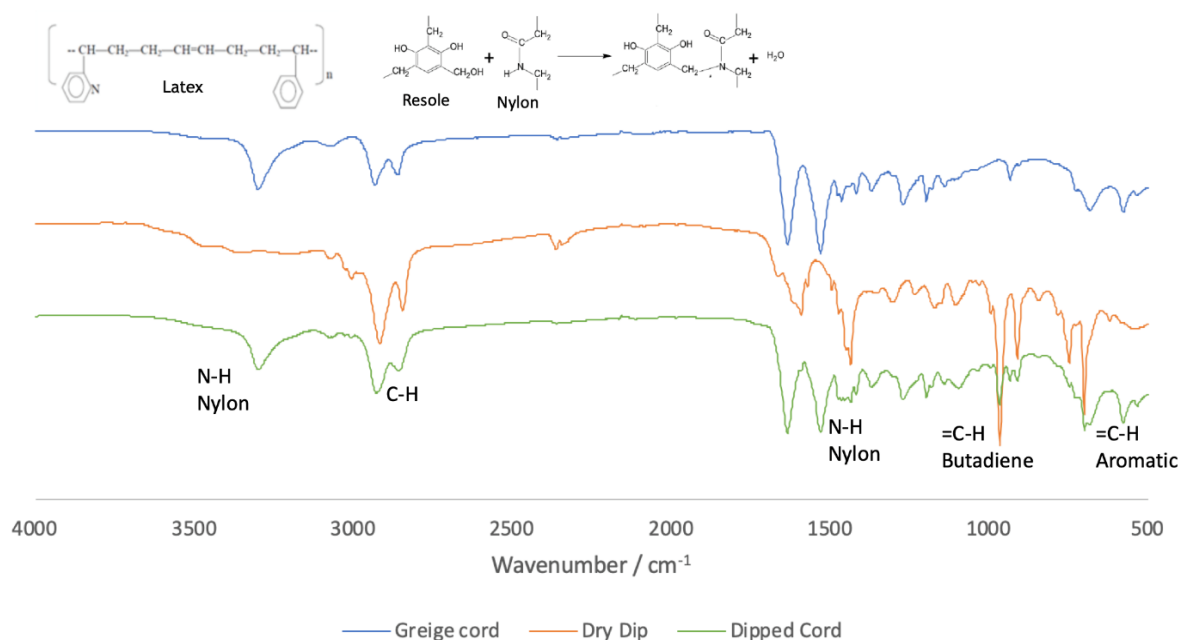


Figure 23 - FTIR spectrum of comparison between greige cord, dipped cord and dry DIP.

Through the analysis of the spectrums, it is clear to see which bonds from both the greige cord and dried DIP contribute most to the bonds shown in the dipped cord spectrum. The greige cord contributes mostly with two spectral bands: one on the range of the 3300 cm^{-1} that corresponds to molecular stretching vibration and another around 1530 cm^{-1} that corresponds to molecular bending vibration. Both of these bands come from the same bond in the amide functional group from the fiber's structure, the N-H bond. In the case of the DIP, the two most noticeable spectral bands that affect most the dipped cord spectrum are the following: around 964 cm^{-1} , corresponding to molecular bending vibration from the latex's butadiene alkene group ($=\text{C}-\text{H}$) and around 699 cm^{-1} , corresponding also to molecular bending but from the double bond of the aromatic groups ($=\text{C}-\text{H}$) from the latex.

Next, it was time to test the influence of the solid content of the DIP in the dipping process and how it affects the fiber-DIP bonds. **Figure 24** shows both spectrums of the dipped cords with different SC and also the spectrum of the greige cord.

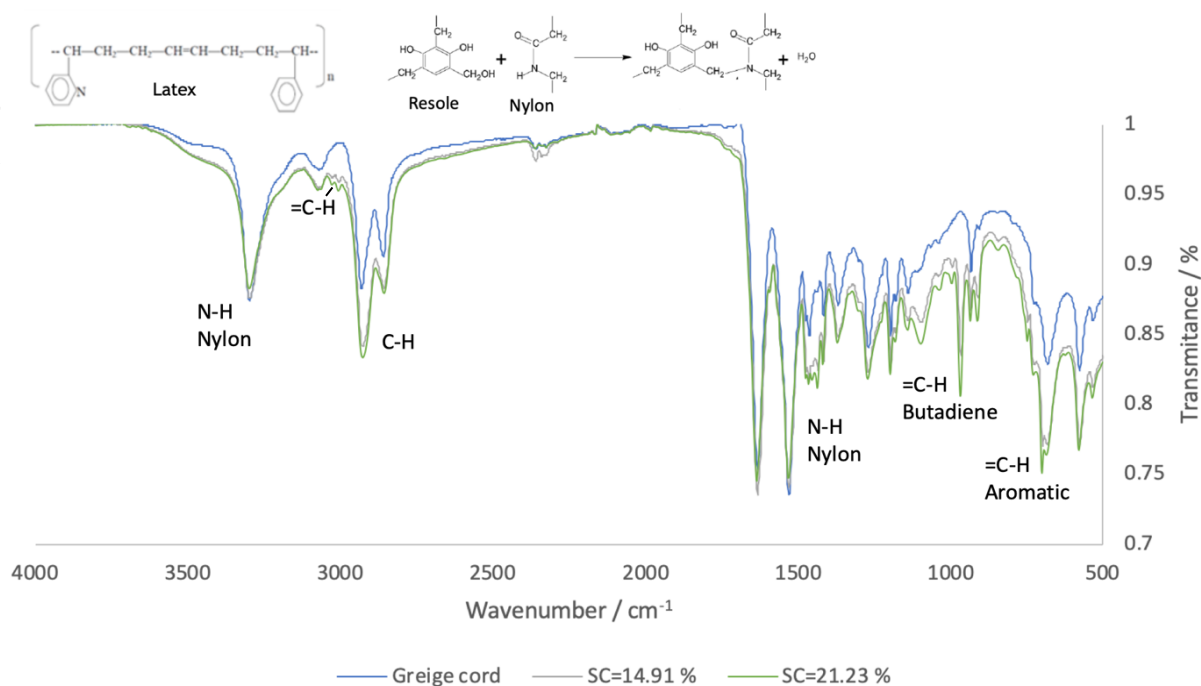


Figure 24 - FTIR spectrum for diferent solid content samples.

It is possible to see that both spectrums for SC=14.91 % and SC=21.23 % overlap, and it is difficult to interpret with clarity if there's any changes in between the spectral bands. To conduct that kind of analysis a second derivative plot of the spectrum absorbance vs. wavenumber was created. That plot allows to see the different peak intensities very clearly as it quantifies them. **Figures 25 and 26** show the zoomed in second derivative plot for both spectrums referred above.

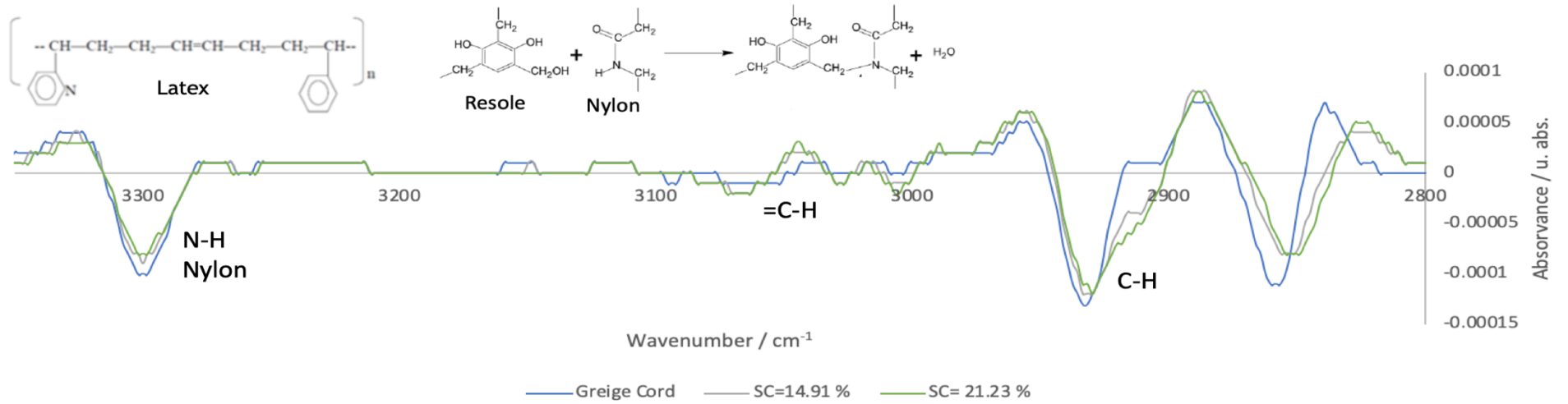


Figure 25 - FTIR second derivative plot for different solid content samples (3350 - 2800 cm^{-1}).

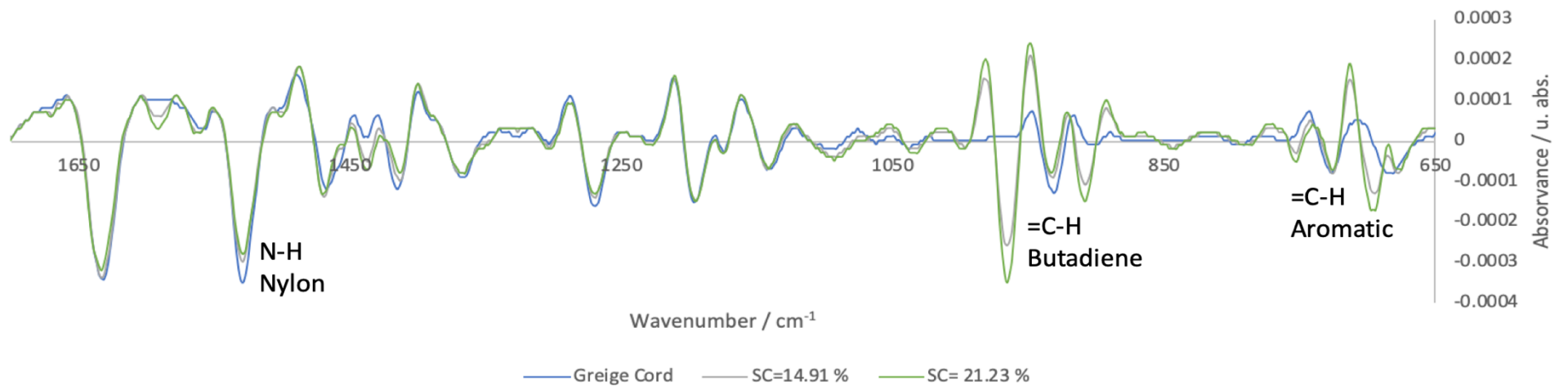


Figure 26 - FTIR second derivative plot for different solid content samples (1700 - 650 cm^{-1}).

These regions (3350 - 2800 cm^{-1} and 1700 - 650 cm^{-1}) were explicitly selected because they represent the areas where the most important peaks for this analysis are located. The complete plot can be found in the appendix section (**Figure A.2.1**).

To start the analysis of both figures, it is important to know that in these second derivative plots, more negative values of the peaks mean more intense spectral bands. Keeping this in mind, it's time to proceed to the analysis itself. Beginning with the peaks that correspond to the fiber (3300 cm^{-1} and 1530 cm^{-1}) it is possible to see that the intensity of the bands diminishes as the value of SC rises. This means that the fiber has reacted with the resin and created DIP-fiber bonds, as expected. For lower values of SC, the amount of N-H bonds that react with the DIP is also lower and so, the intensity of the band is bigger. Next, for the latex related peaks (964 cm^{-1} and 699 cm^{-1}) the opposite of the fiber peaks occurs. For higher values of SC the intensity of the bands is also bigger, which means that the latex molecules did not react with the fiber and so, for higher concentrations of latex, the bands will also be more intense. This is also an expected result because the latex is only supposed to react later, in the vulcanization process, when it will be responsible for providing linkage between the cord and the rubber. A third peak that helps to corroborate this analysis for the latex related bonds is located in the 3070 cm^{-1} region and it's better visualized in **Figure 24**. This peak corresponds to molecular stretching vibration coming from both double bonds (=C-H) present in the butadiene and the aromatic groups of the latex. Last but not least, for future analysis, it is important to keep track of proportion between the butadiene and aromatic groups bands, 964 cm^{-1} and 699 cm^{-1} respectively, because it might tell if the latex used in the dip is richer in one of the two groups and know the styrene, butadiene and vinyl pyridine ratio.

To conclude this section, in consideration of the results obtained, it's possible to say that the FTIR analysis is beneficial in studying the DIP-fiber bonds and the composition of the DIP itself. It is a good test to perform when a new outlier sample for the countercheck appears.

4.3 Aramid Calibration Curve

In order to calibrate the TD-NMR for aramid four cords with different amounts of *DPU* are needed. To obtain these samples, the cords need to be dipped in the LDU using dip solutions with different solid contents. Later, the cords are tested using the Wet-Chemical method, since it is the most precise to obtain reference *DPU* values for the calibration, even though it is time consuming especially for aramid.

For each cord, there has to exist at least three consistent *DPU* values with a standard deviation lower than 0.4 %, according to Continental's requirements. As previously referenced, this is a trial by error process and to obtain four valid cords for calibration, a total of nine cords were dipped and twenty-four Wet-Chemical tests were performed. The reference *DPU* values used for the calibration are presented in the following **Table 7**:

Table 7 -Reference dip pick-up values for aramid's calibration curve.

Cord	<i>DPU</i>				
	LTL -1 %	LTL	Target value	UTL	UTL +1 %
	2.6 %	3.6 %	5.1 %	6.6 %	7.6 %
1	2.64 %				
2	4.56 %				
3	6.51 %				
4					7.00 %

Using the reference *DPU* values mentioned above and the mass of each sample, the calibration was computed in the TD-NMR equipment as it can be seen in **Figure 27**:

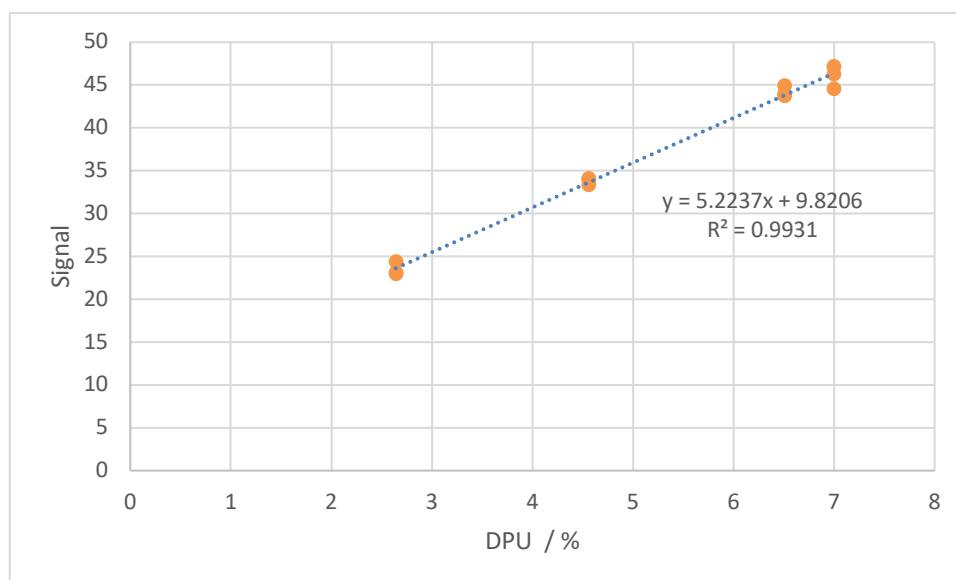


Figure 27 - Aramid's TD-NMR calibration curve.

The standard error (S) obtained has a value of 0.822, being the unit of this error the same as the response variable (signal measured by the TD-NMR).

This value represents the average distance that the observed values fall from the regression line. The lower the value of S , the closer the observed values are to the fitted line. Two other values obtained were the R-squared and the adjusted R-squared, being these 99.3 % and 99.2 %, respectively.

Since these values are almost identical, it means that 99.3 % of the variation verified in the values of the TD-NMR signal is attributed to the values of the DPU . Another important information regarding the value of the coefficient of determination (R^2) is that by Continental standards, a calibration is suitable if the R^2 is higher than 90 %, which in this case is verified.

To study if the calibration curve fits the linear regression model, the residual plots of the curve were analyzed and can be found in **Figure 28**. As it was previously referenced in the countercheck database section, the residuals are the difference between the observed and the fitted response values. Also, to fit the linear regression model, the data must meet the assumptions of the model, being these: a linear relation between the predictor and the response variable with a random variability around it represented by normal independent random errors with zero mean and equal variance.

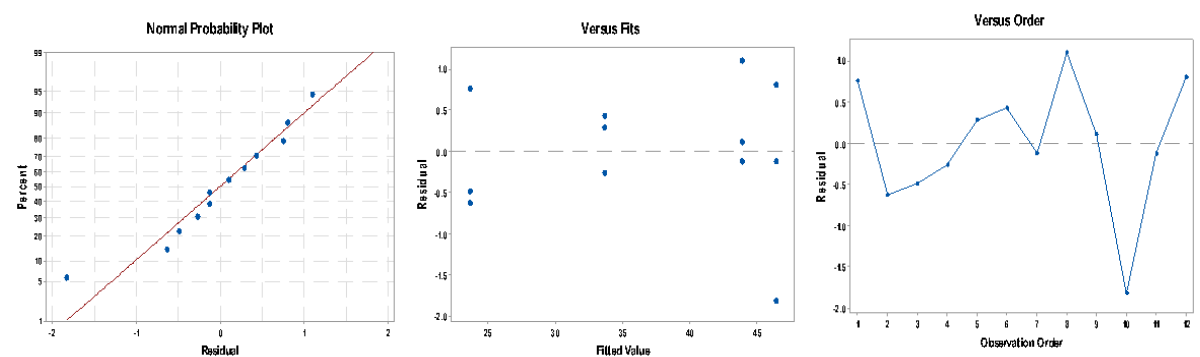


Figure 28 - Residual plots for signal.

Analyzing the residual plots, in the normality plot, the residuals appear to follow a normal distribution, as the values seem to follow a linear shape. In the residuals vs. fits plot the data is randomly distributed on both sides of 0, which appears to indicate that the equal variance assumption is followed. Furthermore, in the residuals vs. order plot, the values seem to follow a random pattern around the centerline, demonstrating that the values seem to be independent. Considering these results, it can be concluded that the calibration curve fits the linear regression model.

The next step was the validation of the curve, using 30 samples of aramid from production. However, since aramid is only dipped in the Zell machine and this also happens very sporadically, it was only possible to collect nine samples.

Although this amount of samples is not sufficient to make a validation of the curve, each one of them was still tested to see if the *DPU* values obtained in the TD-NMR match the *DPU* values from production. The results are shown in **Figure 29**:

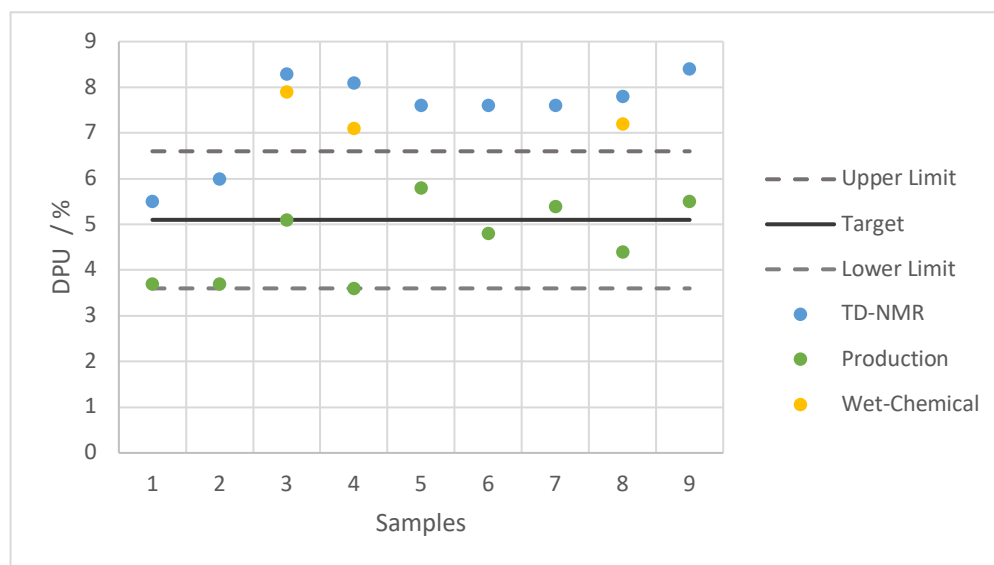


Figure 29 - Dip pick-up values for production samples.

As it can be seen, the *DPU* values obtained by the calibration curve in the TD-NMR are significantly different from the production ones. To check which values were more accurate, the three samples that presented greater differences between the *DPU* values were tested using the Wet-Chemical method and the results are also shown in **Figure 29**. It is possible to see that the Wet-Chemical values tend to be closer to the TD-NMR ones. This might mean that the dip pick-up method used by production does not give realistic *DPU* values. Such observation can be expected, considering that merely calculating the weight difference between the non thermofixed greige fabric roll and the dipped fabric roll has many errors associated. Nonetheless, further testing is needed to confirm if these differences in the *DPU* values from the two methods, TD-NMR and production's Weighing, are constant and systematic.

Another important observation can be made regarding **Figure 29**. Besides the first two samples, the *DPU* values of the remaining 7 appear to be above the upper target limits specified for the fiber, both on the TD-NMR and Wet-Chemical methods. This situation might suggest that the aramid's *DPU* specifications are not well adjusted.

Again, just like the previous observation, further testing is needed to verify if this pattern of out of range dip pick-up values is maintained.

4.4 One Curve Fits All

Since the TD-NMR calibration curves for all five materials used in C-ITA have been created, it was time to compare them and see whether they can be joined into a single curve to be used for all materials, hence the term “One Curve Fits All”. **Figure 30** shows the five existing calibration curves.

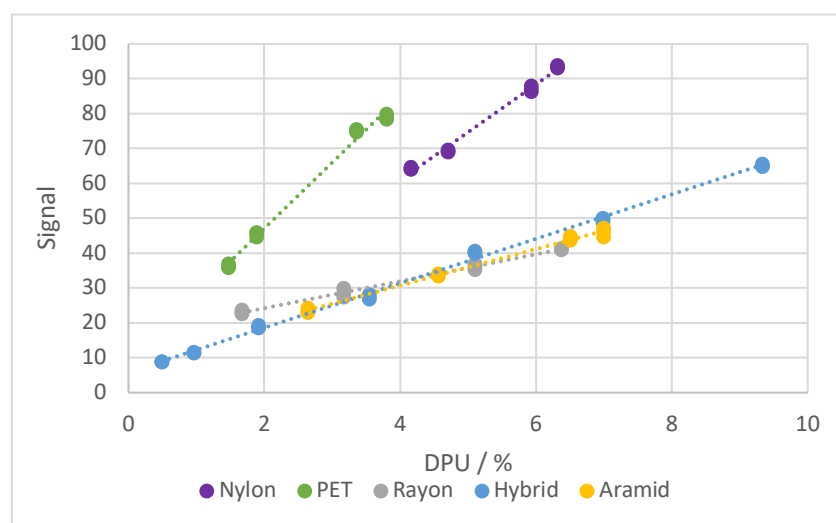


Figure 30 - Existing TD-NMR calibration curves.

From a first analysis the nylon and PET curves seem to be quite different from the remaining three. However, the rayon, hybrid and aramid curves appear to look very similar, although rayon’s curve slope is slightly smaller than the other two. To test the similarity of the curves, a study of the confidence interval at 95 % for each curve’s slope was made and the results are presented in **Figures 31**.

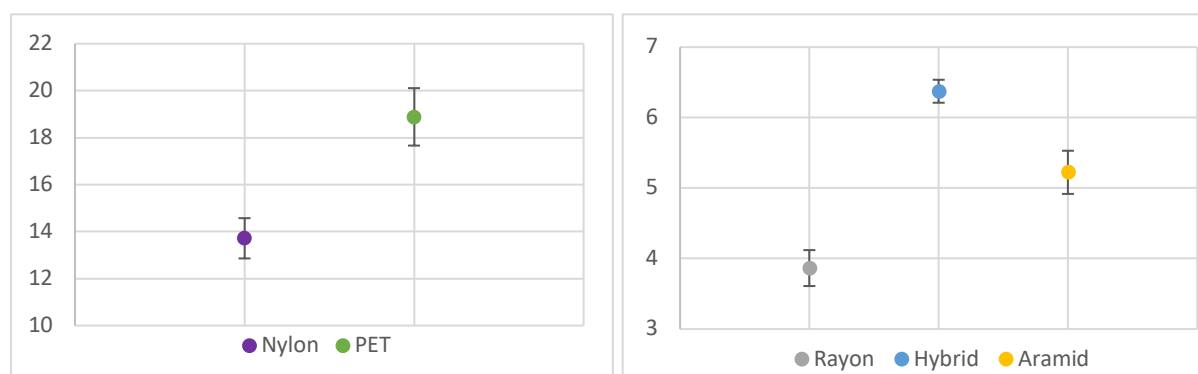


Figure 31 - CI for slopes representation.

From the analysis of the confidence intervals for the slopes, it's possible to observe that the nylon and PET (on the left) ones are in a completely different range than the slopes for rayon, hybrid and aramid (on the right). It is also possible to conclude that statistically all of the curve's slopes are considered different since their CI ranges don't overlap with each other. Due to this fact, the CI analysis for the intercept values of each curve was not conducted. Such analysis would have to be made if the slopes were not statistically different.

Even though the results for the confidence intervals of the calibration slopes were not satisfactory, a single calibration curve containing the data from hybrid and aramid's curves was created either way, since the two calibrations seem very similar to the naked eye. This combined curve is shown in **Figure 32**.

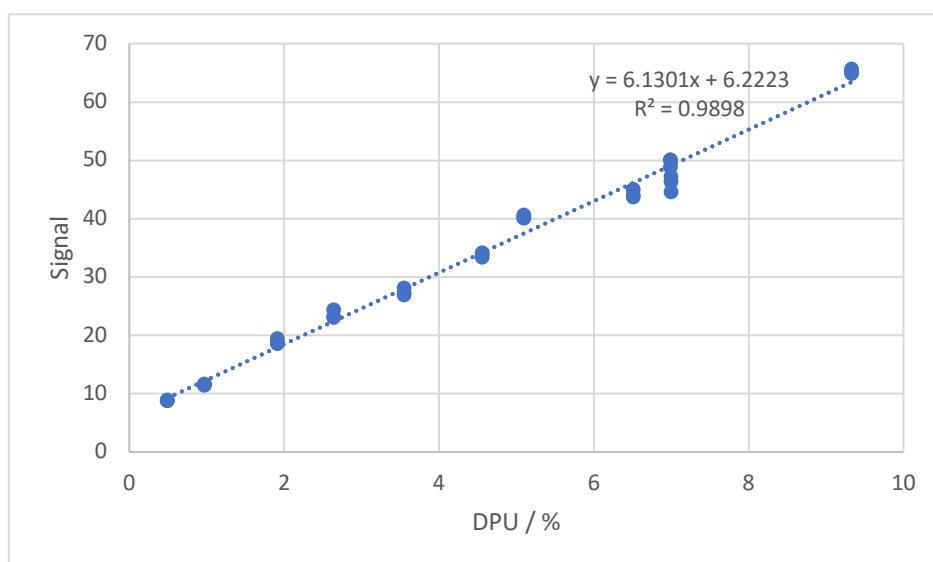


Figure 32 - Combined calibration curve of Hybrid and Aramid.

It is possible to observe that this combination of curves resulted in one with a quite positive outcome. The R-squared obtained was 98.98 % which is above the Continental standard, 90 %. From the residual plots analysis (**Figure A.4.1**), it was also possible to confirm that this curve fits in the linear regression model since all model assumptions were followed. Unfortunately, there was no time left to validate this curve because to do so, 30 samples of both aramid and hybrid need to be collected. After this, the *DPU* must be measured using the Wet-Chemical method for all 60 samples. Finally, the *DPU* values need to be tested for each material using the TD-NMR and both calibration curves for aramid and hybrid. Comparing the results obtained for each material, being these: *DPU* from the Wet-Chemical, *DPU* from the TD-NMR using hybrid curve and *DPU* from the TD-NMR using aramid curve, it is then possible to say with certainty if both curves can be joined into one.

5 Conclusion

The primary purposes of this dissertation were to finalize the TD-NMR equipment calibration for all C-ITA's materials, being aramid the remaining one, and help the company to better understand the existing countercheck database regarding the results for the TD-NMR and Wet-Chemical methods.

In the first part of this project, the database was analyzed and the *DPU* values for both the TD-NMR and Wet-Chemical methods were compared from a global point of view and then in a more detailed study for the three materials that had enough sample values for proper testing: nylon 6.6, nylon 6.0 and PET. In the case of PET it appeared to exist two different populations of values that would be explained by the existence of nAA and AA PET. This could not be proved because there was a sample of activated PET that was located within the population supposedly corresponding to non-activated PET. Nonetheless, regarding the TD-NMR and Wet-Chemical results comparison, for the global and individual material tests, the outcome was positive as it was proved that there is no significant difference between the two methods. All of the differences of means were below 1 % which is the Continental standard. Even though the results were positive it is still recommended for the company to use both methods when performing countercheck analysis. A comparison between the fiber's decitex and the *DPU* values was also made, using the countercheck samples and it showed a tendency of higher *DPU* values for lower decitex, which can be explained by the higher superficial areas exposed to the DIP during the dipping process.

During the countercheck database analysis some outliers were noticeable as the *DPU* values for both methods showed very different results, probably explained by the fact that the different cord suppliers use different DIP recipes and components than C-ITA. To better understand such difference, in the second part of this dissertation some FTIR analysis were performed in order to study the DIP-fiber interaction and the composition of the DIP itself since it has been proved in previous Master Thesis that the solid content of the DIP has a big influence on the TD-NMR signal. It was proved that the FTIR analysis is a worthy method to study such DIP-fiber interactions and DIP composition and can be used to analyze future countercheck outliers that may appear.

In the third part of this project, the TD-NMR device was successfully calibrated for aramid with a dtex of 1680 x 2, although validation was not possible due to a lack of production samples. It was also observed that the *DPU* measuring method used by production might not give realistic values. Finally, regarding the material's *DPU* specifications, it was suggested that these might need to be adjusted.

In the fourth and final part of this dissertation, all of the existing calibration curves were put together to make a comparison and see if they could be fitted into one single curve for all materials. The results showed that the majority of the curves are very different, although the hybrid and aramid curves seemed to fit into one single curve with an R-squared of 98.98 % which is higher than the required continental standard 90 %. However, validation of the curve is needed.

This project allowed C-ITA to have the TD-NMR device calibrated for most materials used in production. It also helped the company understand better the results obtained in the countercheck analysis, regarding the TD-NMR and Wet-Chemical methods. Both of these achievements help C-ITA's quality control to improve.

6 Assessment of the work done

6.1 Objectives Achieved

One of the main objectives of this project was to analyze the countercheck database to help C-ITA better understand the results obtained by comparing the *DPU* values for both TD-NMR and Wet-Chemical methods. It was proved that the methods are not significantly different and that FTIR analysis can be used to better understand the results for possible outliers.

The other main objective was to calibrate the TD-NMR for aramid, which was achieved, however validation of the curve was not possible due to lack of samples. It was also found that that production's *DPU* measuring method might not be the best and also that the *DPU* specifications for the material might need to be adjusted. As an extra objective the existing calibration curves for all of C-ITA's materials were compared to see if they would fit into a single curve, although, only the hybrid and aramid seem to fit into a single curve, but further validation is necessary.

6.2 Limitations and Future Work

Regarding limitations, the biggest one was definitely the time available. For the calibration curve the Wet-Chemical method is used and it is a trial by error process, considering that for aramid three days are needed to get results for each sample, it took more than three months to get the final calibration results. Moreover, the lab and all the equipment need to be shared with co-workers which led also to some delays in the calibration process.

For future work, validation of the aramid calibration curve is needed as well as for the hybrid and aramid combined calibration curve. It is also suggested making a DOE to study which dip solution component or components have a bigger influence on the TD-NMR signal to understand some existing discrepancies especially in the countercheck analysis. Finally, it would be interesting to confirm with certainty if it does in fact exist a correlation between the dtex and the *DPU* values.

6.3 Final Assessment

It was an honor being able to have this opportunity and to accomplish goals that sometimes seemed very far from reachable. Although the path was not always obvious and some difficulties appeared during the extent of this project, the help of my co-workers was crucial in the process of overcoming them. I am proud of helping the company's quality control improve and for being part of the C-ITA's team during the course of this dissertation.

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Annex A - TD-NMR Calibration

This annex contains previous dissertations' data regarding the existing TD-NMR calibration curves.

Table A.1 - Nylon calibration data (adapted from Pratapsi, 2017).

Sample	Mass (g)	SC (%)	Wet - Chemical Reference Value DPU (%)	TD-NMR Signal	TD-NMR Calculated Value DPU (%)
1	0.822	15.24	4.159	64.089	4.228
	0.792	15.24	4.159	64.103	4.229
	0.789	15.24	4.159	64.612	4.266
2	1.009	16.90	4.709	69.034	4.589
	0.957	16.90	4.709	69.100	4.594
	0.881	16.90	4.709	69.634	4.633
3	0.82	18.96	5.933	86.317	5.849
	0.821	18.96	5.933	86.999	5.899
	0.819	18.96	5.933	87.987	5.971
4	0.866	20.74	6.320	93.074	6.342
	0.814	20.74	6.320	93.444	6.369
	0.785	20.74	6.320	93.810	6.395

Table A.2 - Hybrid calibration data (adapted from Pratapsi, 2017).

Sample	Mass (g)	SC (%)	Wet - Chemical Reference Value DPU (%)	TD-NMR Signal	TD-NMR Calculated Value DPU (%)
1	0.875	28.33	9.329	65.57	9.367
	0.862	28.33	9.329	65.11	9.295
	1.022	28.33	9.329	64.82	9.251
2	0.952	22.53	6.989	50.03	6.929
	1.000	22.53	6.989	50.03	6.930
	0.907	22.53	6.989	48.85	6.744
3	1.011	16.75	5.097	40.00	5.356
	0.991	16.75	5.097	40.63	5.455
	1.129	16.75	5.097	40.18	5.384
4	1.100	10.75	3.548	28.08	3.486
	0.991	10.75	3.548	27.24	3.354
	1.061	10.75	3.548	26.82	3.288
5	1.119	6.97	1.912	19.39	2.123
	0.946	6.97	1.912	18.52	1.986
	1.001	6.97	1.912	18.74	2.020
6	1.184	3.67	0.966	11.56	0.894
	0.973	3.67	0.966	11.49	0.884
	0.907	3.67	0.966	11.40	0.868
7	1.095	3.13	0.491	8.77	0.456
	1.136	3.13	0.491	8.84	0.468
	0.927	3.13	0.491	8.79	0.459

Table A.3 - PET calibration data (adapted from Bezerra, 2018).

Sample	Mass (g)	SC (%)	Wet - Chemical Reference Value DPU (%)	TD-NMR Signal	TD-NMR Calculated Value DPU (%)
1	0.856	11.99	1.89	45.706	1.927
	0.897	11.99	1.89	44.567	1.867
	0.849	11.99	1.89	46.000	1.942
2	0.860	8.35	1.47	36.857	1.458
	0.742	8.35	1.47	35.832	1.404
	0.823	8.35	1.47	36.178	1.422
3	0.813	24.03	3.36	74.783	3.467
	0.933	24.03	3.36	75.221	3.490
	0.843	24.03	3.36	75.445	3.502
4	0.854	26.09	3.80	78.887	3.684
	0.989	26.09	3.80	79.839	3.734
	0.820	26.09	3.80	78.502	3.663

Table A.4 - Rayon calibration data (adapted from Rocha, 2018).

Sample	Mass (g)	SC (%)	Wet - Chemical Reference Value DPU (%)	TD-NMR Signal	TD-NMR Calculated Value DPU (%)
1	0.921	5.09	1.667	23.631	1.852
	1.207	5.09	1.667	22.976	1.682
	1.105	5.09	1.667	22.536	1.569
2	1.443	9.87	3.173	28.396	3.084
	1.623	9.87	3.173	29.878	3.467
	1.489	9.87	3.173	27.468	2.844
3	1.101	17.74	5.099	36.181	5.097
	1.047	17.74	5.099	35.271	4.862
	1.043	17.74	5.099	36.865	5.274
4	1.510	22.38	6.373	41.034	6.352
	1.494	22.38	6.373	41.223	6.401
	1.354	22.38	6.373	41.389	6.444

Appendix - Dip Pick-Up

A.1 - Countercheck Database

This section contains extra results obtained regarding the countercheck database analysis.

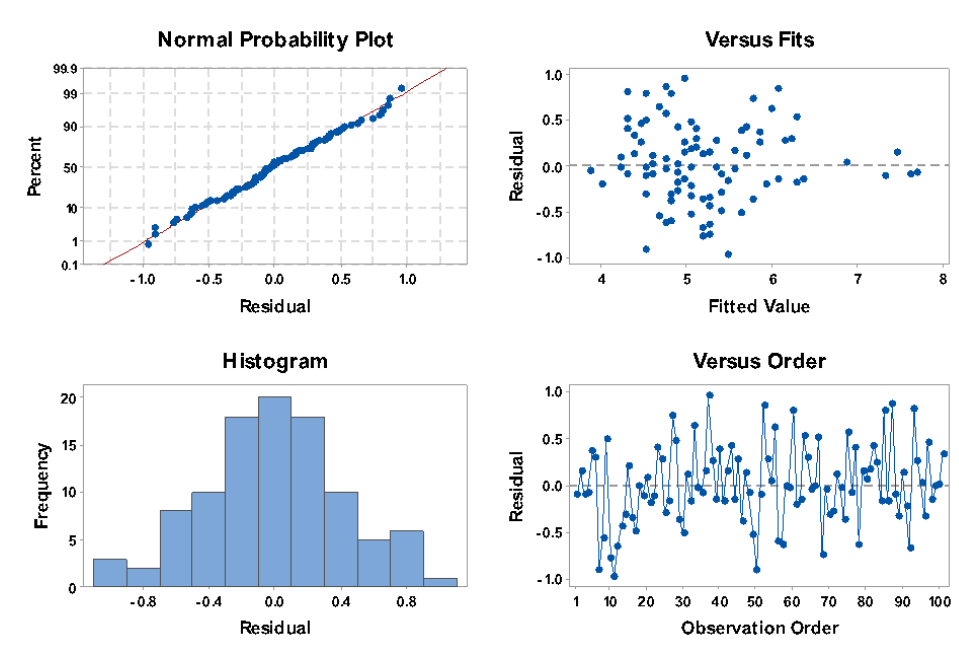


Figure A.1.1 - Residual plots for DPU (TD-NMR) for nylon 6.6.

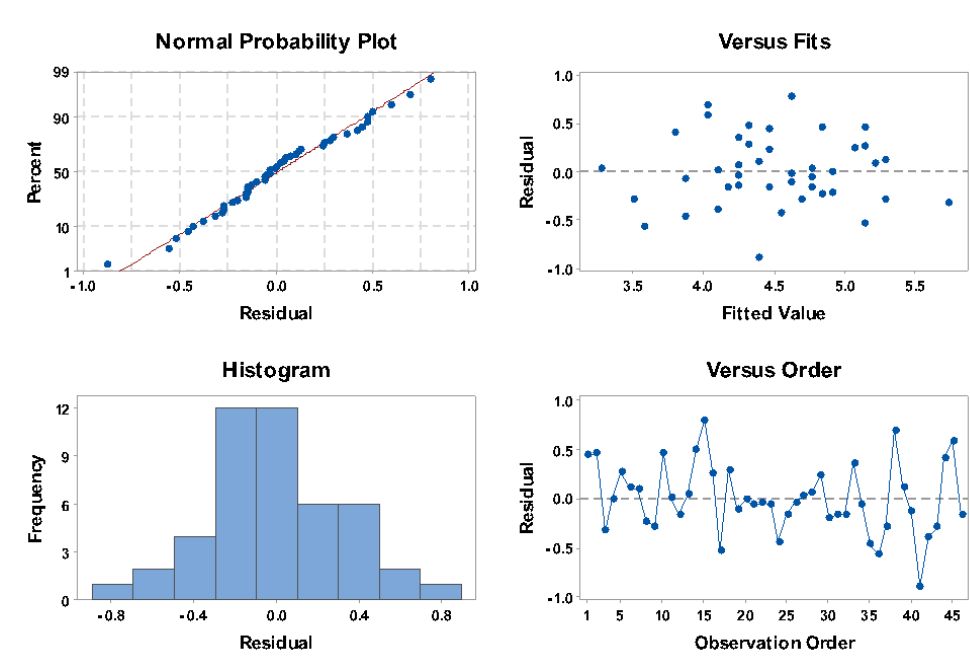


Figure A.1.2 - Residual plots for DPU (TD-NMR) for nylon 6.0.

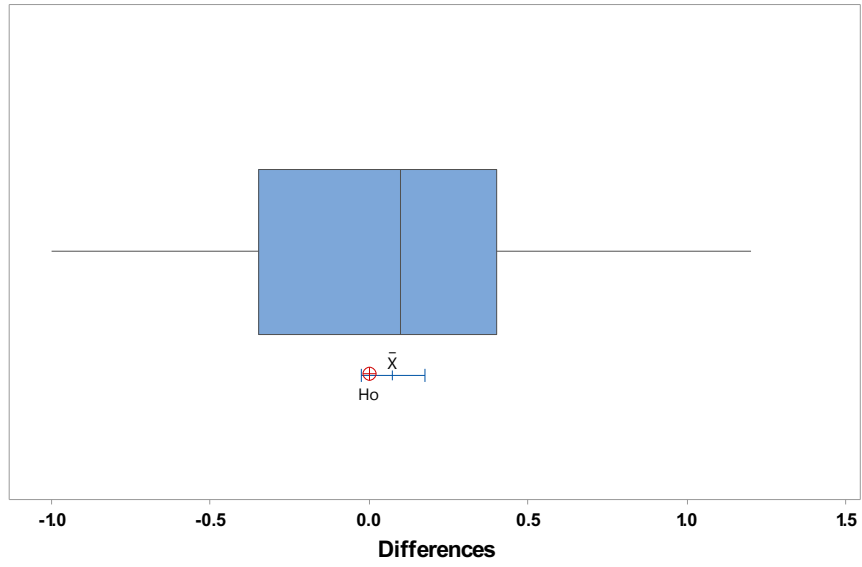


Figure A.1.3 - Boxplot of the differences of the two methods for nylon 6.6.

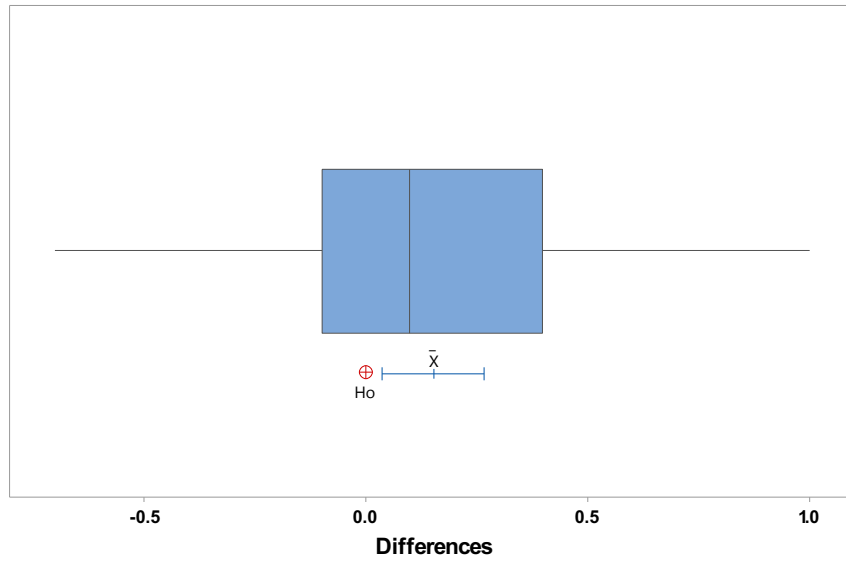


Figure A.1.4 - Boxplot of the differences of the two methods for nylon 6.0.

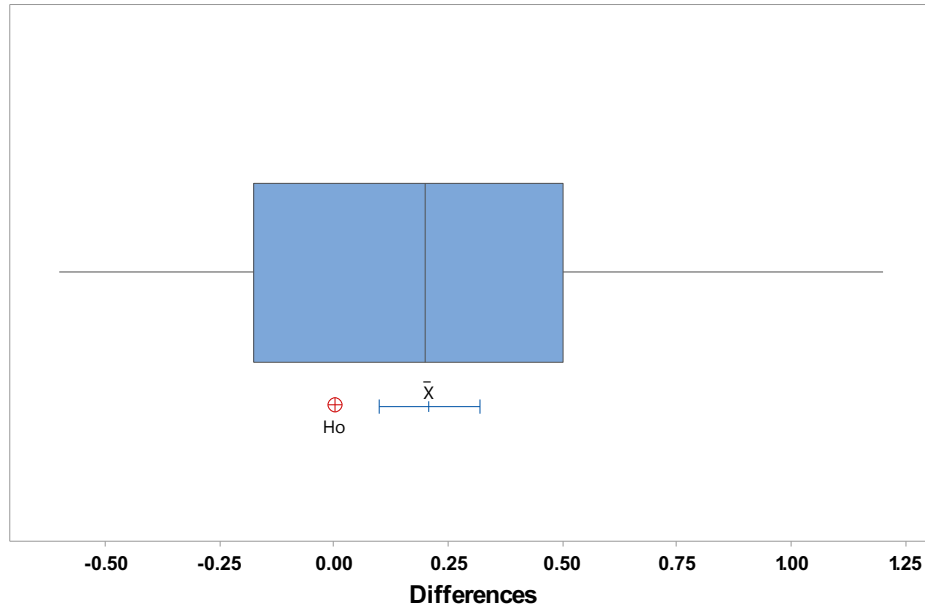


Figure A.1.5 - Boxplot of the differences of the two methods for PET.

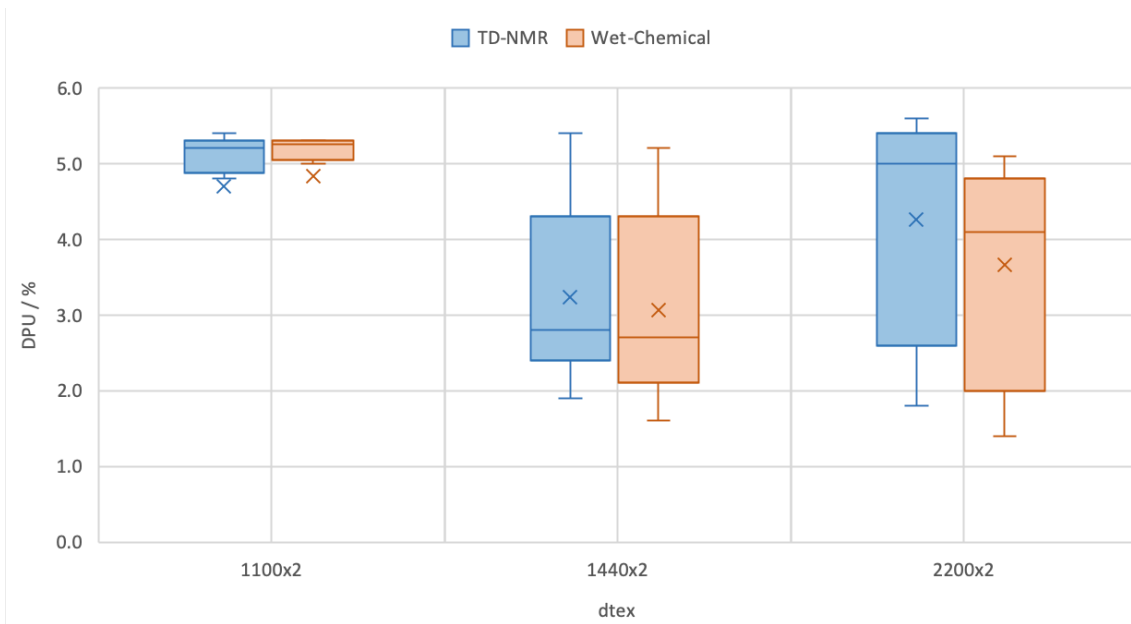


Figure A.1.6 - Boxplot representation of dtex dip pick-up ranges for PET.

A.2 - FTIR

This section contains extra information regarding the FTIR analysis.

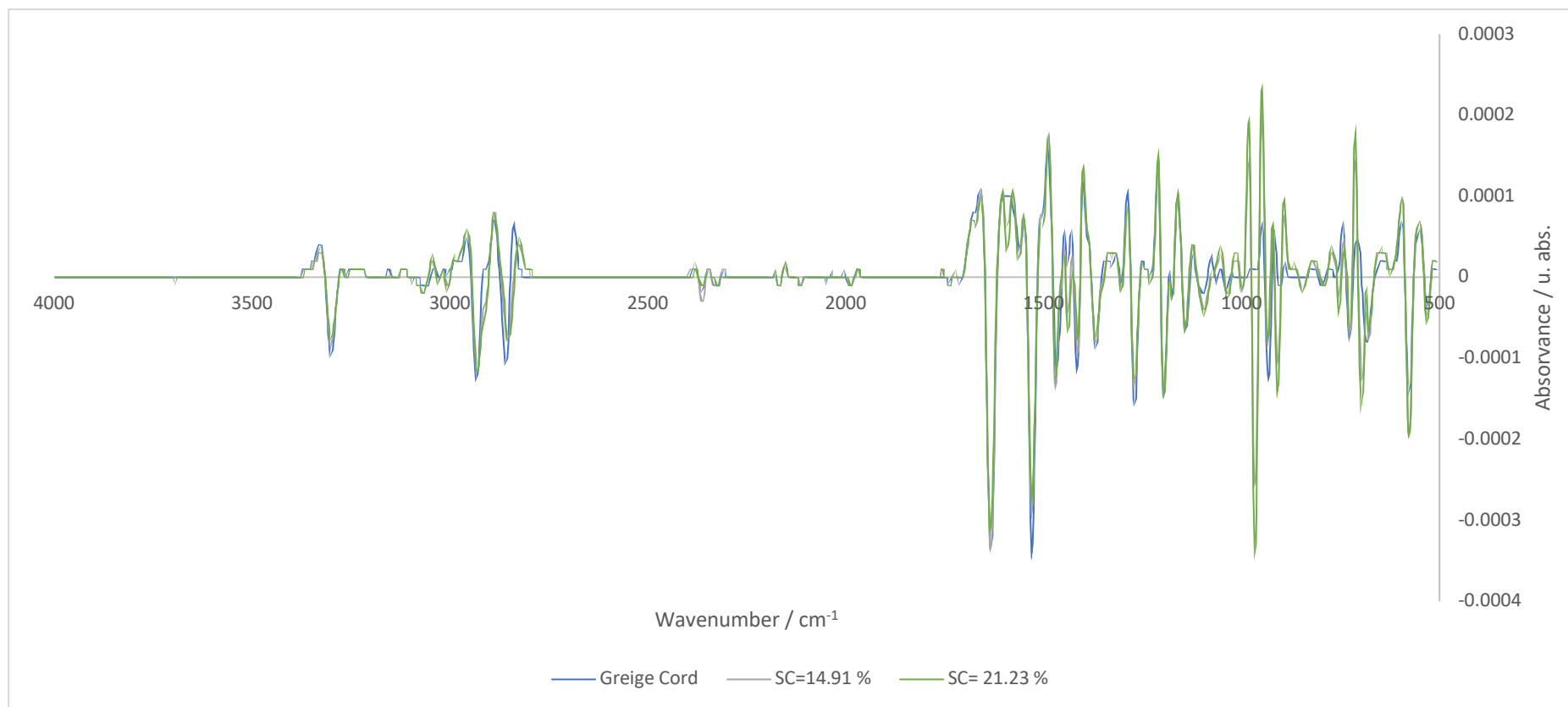


Figure A.2.1 - Complete FTIR second derivative plot for different solid content samples.

A.3 - Aramid Calibration Curve

This section contains extra information regarding aramid's calibration curve.

Table A.3.1 - Wet-Chemical DPU values from the aramid's calibration.

Sample	Trial	DPU (%)	Valid	Mean (%)	STDev (%)
1	1	12.78	No		
2	1	6.70	Yes	6.51	0.18
	2	6.49	Yes		
	3	6.34	Yes		
3	1	2.57	No		
	2	2.17	No		
	3	2.21	No		
	4	3.53	No		
	5	2.03	No		
4	1	4.76	Yes	4.56	0.17
	2	4.46	Yes		
	3	4.46	Yes		
	4	3.19	No		
	5	5.57	No		
	6	5.40	No		
5	1	7.09	Yes	7.00	0.25
	2	6.72	Yes		
	3	7.19	Yes		
	4	3.78	No		
	5	1.98	No		
6	1	2.54	Yes	2.64	0.10
	2	2.74	Yes		
	3	2.63	Yes		
	4	3.21	No		

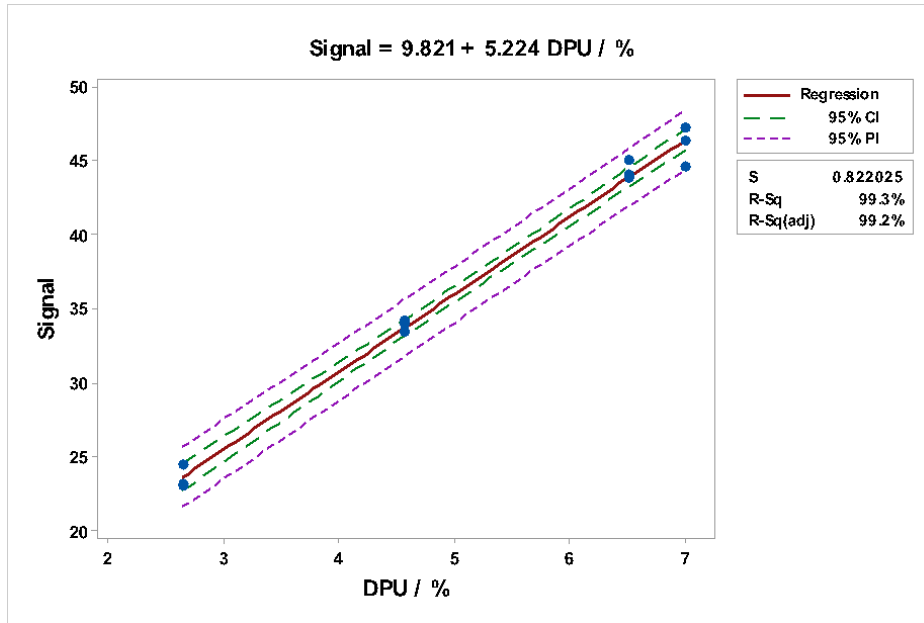


Figure A.3.3 - Fitted line plot for aramid's calibration curve.

A.4 - One Curve Fits All

This section contains extra information regarding the study of all calibration curves.

Table A.4.1 - Confidence intervals for each material's calibration curve element.

Material	Estimated slope	95 % CI for slope	Slope's Standard error	Estimated intercept	95 % CI for intercept	Intercept standard error
Nylon	13.715	(12.857; 14.573)	0.858	6.098	(1.506; 10.689)	4.591
PET	18.885	(17.663; 20.108)	1.223	9.317	(5.888; 12.746)	3.429
Rayon	3.865	(3.610; 4.120)	0.255	16.476	(15.339; 17.612)	1.136
Hybrid	6.374	(6.211; 6.537)	0.163	5.861	(5.037; 6.685)	0.824
Aramid	5.224	(4.917; 5.530)	0.306	9.821	(8.149; 11.492)	1.672

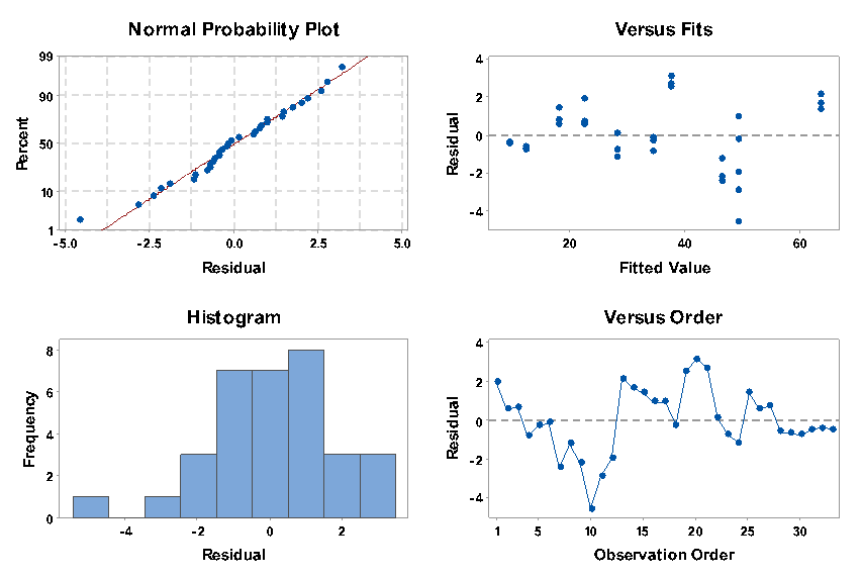


Figure A.4.1 - Residual plots for signal in the combined calibration curve of hybrid and aramid.

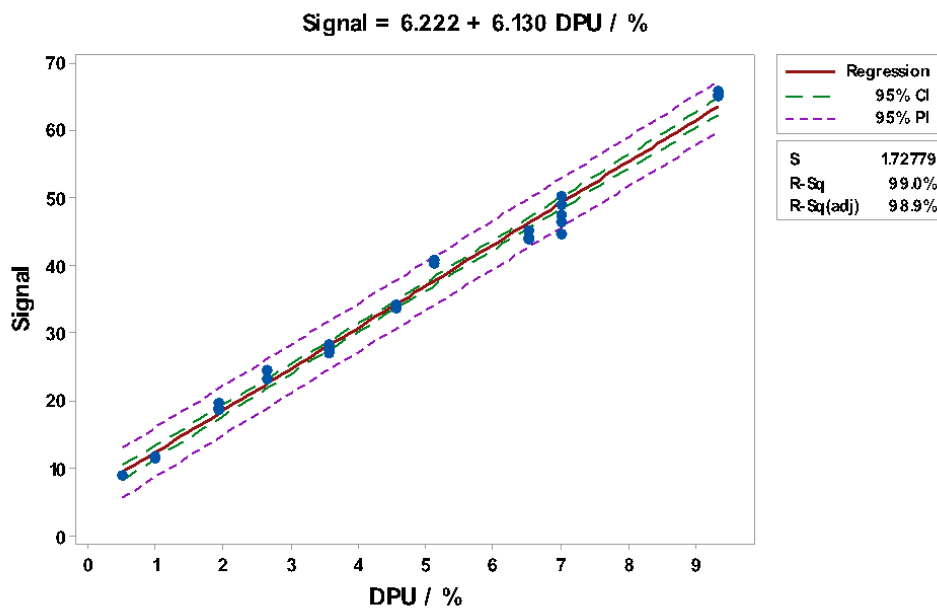


Figure A.4.4 - Fitted line plot for combined hybrid/aramid's calibration curve.