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STUDY OF THE DIP CONTENT IN TIRE TEXTILE REINFORCEMENTS

TD-NMR AS A METHOD OF ANALYSIS OF THE DIP CONTENT

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Abstract

The tire is a highly complex product, with numerous materials in its composition, and plays a fundamental role in the comfort and safety of most transports. One of the elementary components of a tire is textile reinforcements. These perform a structural role, provide flexibility, durability and safety, and are present in multiple layers that constitute the tire. Thus, one of the biggest concerns associated with their production is that these adhere correctly to the rubber. The adhesion between textiles and rubber does not occur naturally. Therefore, it is necessary to treat the textiles with a chemical bath that facilitates the bonding between the two components.

Since the dipping solution used in the chemical bath is, in its most normal formulation, highly toxic, a consequence of the presence of formaldehyde and resorcinol in its chemical composition (dip RFL), it is important to measure the dip content in the textiles, to assure is sufficient to allow the adhesion, but not excessive, to avoid economic and environmental implications associated with its waste. This measurement, called Dip Pick-Up, is commonly done using a wet-chemical method but the Time Domain Nuclear Magnetic Resonance (TD-NMR) has proven advantageous compared to the chemical method. This dissertation will focus on the calibration of the TD-NMR device to measure the dip content, since it is the most advantageous for now, using the values obtained through the wet-chemical method to build a calibration curve for two different materials: rayon and nylon.

Due to the environmental and sanitary disadvantages of the RFL dipping solution used until now, Continental AG, in collaboration with the company Kordsa, joined forces to find an alternative to this dip. This effort resulted in a new dip formulation, the Cokoon, considerably more sustainable in all aspects. This new chemical formulation is recent but will completely replace the RFL dip in the future and so it has been starting to be used in some of the textile reinforcements produced at Continental-ITA.

During this dissertation project the TD-NMR device was calibrated to measure the dip content of a range of RFL-dipped nylon fabrics, enabling this alternative instead of the traditional method. An attempt to calibrate the device for a Cokoon-dipped rayon fabric was made, but the curve did not meet the DPU prediction specifications. Although it was not possible to calibrate the Cokoon dipped rayon fabric, the data showed that current methods need to be adapted for this new dip, as the chemicals used in the wet-chemical method may interfere with the Cokoon formulation. It was also proved that this new dip is not adversely affecting the mechanical properties of stiffness and elongation of the rayon fiber.

Keywords: Tire**;** Textile reinforcements; Dip Pick-Up; RFL dip; Cokoon; TD-NMR

Resumo

O pneu é um produto de complexidade elevada, com inúmeros materiais na sua composição, e que desempenha um papel fundamental no conforto e segurança da maioria dos transportes. Um dos componentes elementares do pneu são os reforços têxteis. Estes desempenham um papel estrutural, proporcionam flexibilidade, durabilidade e segurança, e estão presentes em várias das camadas que constituem o pneu. Assim, uma das maiores preocupações associadas à sua produção é a garantia de que estes reforços aderem adequadamente à borracha. Como a adesão entre os têxteis e a borracha não ocorre naturalmente, é necessário tratar os têxteis com um banho químico que permite a ligação química entre os dois componentes.

A solução de imersão utilizada no banho químico é altamente tóxica, consequência da presença de formaldeído e resorcinol na sua composição química (solução RFL), pelo que é importante medir a quantidade de solução retida nos têxteis, de forma a assegurar que é suficiente para garantir a adesão, mas não excessiva, para evitar implicações económicas e ambientais associadas aos seus resíduos. A medição da quantidade de solução retida nos têxteis é habitualmente feita usando um método químico, mas a Ressonância Magnética Nuclear no Domínio do Tempo (TD-NMR) tem-se mostrado vantajosa em relação ao método químico. Esta dissertação incidirá na calibração do dispositivo TD-NMR para fazer a medição do teor de imersão, uma vez que é mais vantajosa, utilizando os valores obtidos através do método químico para construir uma curva de calibração para dois materiais diferentes: rayon e nylon.

Devido às desvantagens ambientais e para a saúde humana da solução RFL utilizada até agora, a Continental AG, em colaboração com a empresa Kordsa, desenvolveram uma nova formulação para a solução de imersão, nomeada *Cokoon*. Esta nova solução é consideravelmente mais sustentável pois elimina totalmente o uso de formaldeído e resorcinol. Apesar de recente, o Cokoon substituirá completamente a solução RFL no futuro, e está, inclusivamente, a começar a ser utilizado em alguns dos reforços têxteis produzidos na Continental-ITA.

Durante este projeto de dissertação, o aparelho de TD-NMR foi calibrado para medir o teor de solução retida nos têxteis de uma gama de tecidos de nylon impregnados com a solução RFL. Foi, também, feita uma tentativa de calibrar o dispositivo para um tecido de rayon impregnado com Cokoon, mas a curva não cumpria os critérios de aprovação. Embora não tenha sido possível calibrar o tecido impregnado com *Cokoon*, os dados mostraram que os métodos atuais precisam ser adaptados para esta nova solução, pois os produtos químicos usados no método químico podem estar a interferir na formulação do *Cokoon*. Também foi comprovado que esta nova formulação não está a afetar negativamente as propriedades mecânicas de rigidez e alongamento da fibra de rayon.

Palavras-chave: Pneu; Reforços têxteis; solução RFL; *Cokoon*; TD-NMR;

Declaration

I hereby declare, under word of honor, that this work is original and that all non-original contributions are indicated and due reference is given to the author and source

2022, April 29

Catarina S. Neves

Sign and date

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Notation and Glossary

dtex	decitex	g/ 10000 m
$\mathrm{DPU}_{\mathrm{dipped\ cord}}$	mass fraction of dip per mass of dipped cord	%
$\mathrm{DPU}_{\mathrm{greige\ cord}}$	mass fraction of dip per mass greige cord	%
m_{dip}	mass of dipping solution	g
$m_{\mathrm{dipped\ cord}}$	mass of dipped cord	g
$m_{\mathrm{greige\ cord}}$	mass of greige cord	g
m	slope of the calibration curve	
n	number of paired calibration points	
N	number of repeated measurements for the sample	
R	coefficient of correlation	
R^2	coefficient of determination	
s_{R}	residual standard error	
$t_{\alpha/2}$	values of the two-tailed t-Student distribution for a α significance level and $n-2$ degrees of freedom	
x_i	value of the $x-\mathrm{axis}$	
$\bar{x}$	mean of the $x_i$values	
$\bar{y}$	mean of the y values for the calibration standards	
$\bar{y}_0$	mean of N repeat measurements of y for the sample	
y_i	observed value of y for a given value of x_i	
$\hat{y}_{\mathrm{i}}$	value of y predicted by the calibration curve for a given value of x_{i}	
y_{TDNMR}	instrumental response (signal) of the TD-NMR device	

Greek Letters

α	significance level of the statistical hypothesis test
β	probability of rejecting the null hypothesis when it is false
θ	population's parameter

List of Acronyms

CI	Confidence Interval
C-ITA	Continental – Indústria Têxtil do Ave, S.A
DPU	Dip pick-up
LDU	Lab Dipping Unit
LTL	Low Target Limit
LTU	Lab Twisting Unit
PET	Polyethylene Terephthalate
RFL	Resorcinol-Formaldehyde-Latex
TD-NMR	Time-Domain Nuclear Magnetic Resonance
UTL	Upper Target Limit

1 Introduction

1.1 Framing and presentation of the work

When thinking about the engineering associated with the automotive industry, one major product is the tire. Tires are high-tech products with several layers of materials and techniques involved, that must provide a wide range of functions in the more diverse conditions. Since tires are the only connection between the car and the road, its functions go from guaranteeing the proper distribution of the forces resulting from braking, accelerating, and maneuvering the car, which assures the safety of passengers and cargo, to improve performance and enabling the most comfortable experience of driving as possible (Continental AG, 2013).

One of the most important components are textile reinforcements. Textile reinforcements are fibers in the form of cords or fabric that are inlaid in rubber and whose primary function is to improve the mechanical properties, maintain shape, support the load and contain the inflation gas. Textile reinforcements also increase the resistance and durability of the tire, performing a major role regarding the performance of tires (Nokyan tyres, n.d.).

The main difficulty regarding the textiles is the adhesion to the rubber. Because of the inert nature of most fibers that constitute the textile reinforcements, they must undergo a treatment called dipping process, where the fibers are dipped in a solution that acts as a bond between the cords and the rubber. The difficulty associated with this process is measuring and understanding the ideal amount of dip. Not sufficient dip results in a deficient adhesion between the cords and the rubber, which compromises the safety and performance; too much dip results in financial and environmental waste, especially because the dip must be disposed carefully due to its toxicity. Therefore, the measurement of the amount of dipping solution infused in the cords after the process of dipping is crucial, and the optimization of the methods for this assessment, as well as the development of better methods to facilitate and increase the precision of the measurements have been a continuous focus in this industry.

The primary method for the measurement of the dip content in cords is the wet-chemical method, which consists in the dissolution of the fiber to obtain the mass of dip. This method brings disadvantages related to the use of strong chemicals and big margin of error associated. The time-domain nuclear magnetic resonance has been gaining popularity as a better method to assess the dip content of textiles, but it requires the construction of a calibration curve. The work being presented in this thesis focus on the construction of such curves to enable the measurement of the dip content of two different materials using TD-NMR.

This dissertation also includes a study of the stiffness and elongation properties of a Cokoon-dipped material, since there was evidence that this dip could be influencing these properties, which would negatively affect the material performance.

1.2 Presentation of the company

Continental was first established in Hannover, Germany, in 1871, as a joint stock company, initially producing soft rubber products, rubberized fabrics and solid tires for carriages and bicycles. Now, 150 years later, it's present in 560 locations, in a total of 58 countries, offering a variety of solutions and innovative technologies for automotive and industrial applications, from technical textiles to chassis and electronics (Continental AG, n.d.-d).

In 1993, Continental acquired Indústria Têxtil do Ave and Mabor, both in Lousado, Portugal, which became Continental – Indústria Têxtil do Ave (C-ITA) and Continental Mabor, respectively. The former company Mabor was already specialized in producing pneumatic tires and Indústria Têxtil do Ave had been found in 1950 to supply its needs of textile reinforcements. After being acquired, C-ITA became also specialized in technical fabrics for vehicle interiors, besides the textile reinforcements for tires. This site supplies textile reinforcements for other Continental's sites all over the globe, as well as technical fabric for automobile interiors, being one of the only two Continental's factories producing textile reinforcements.

Continental is divided into two main units: automotive technologies and rubber technologies. The second unit is focused on rubber products and divided into two sectors: Tires and Contitech. Contitech is responsible for the development of materials, products or systems made of rubber together with other materials to be used in several different applications besides car tires (Continental AG, n.d.-b).

The work developed during this dissertation fits into the rubber technologies unit, and concerns products from both segments - Tires and Contitech.

1.3 Contribution of the author to the work

The work I present here is a continuation of previous Master Thesis', in which have been studied new ways to evaluate, improve and optimize the process of assessing the dip content in dipped cords.

More in detail, I focused on continuing the preparation of the TD-NMR device to serve as the primary method of measurement for the dip content, calibrating it for two different materials. The calibration of the device was first made to a group of nylon fabric treated with the RFL dipping solution. This calibration was approved so the dip pick-up for these materials can now be made through TD-NMR, more easily and faster than it was using the chemical method.

For the second material, made of rayon and treated with a new dipping solution called Cokoon, I developed a calibration curve and studied two different properties for this fiber. Since there was a previous calibration curve that was not being used due to problems in its validation, I started by studying the filtration step of the wet-chemical method and concluded that the previous optimization of this step, that included glass wool, was introducing errors in the results, so I proceeded with a new calibration. Regarding the calibration curve I developed, although it was not possible to approve it, and it is noteworthy that no material treated with the Cokoon dipping solution has ever been calibrated for the TD-NMR device before, the work I developed showed that the methods of assessing the dip content must be reevaluated for materials dipped in Cokoon. I developed a method to obtain samples of cured dip only and performed the wet-chemical method with these samples, instead of using samples of dipped textiles, in order to study the influence of the wet-chemical method in the dip. The data proved that further studies must be conducted to understand which methods are compatible with this dip, since there is evidence that the method is changing the true mass of dip present in the cords.

1.4 Organization of the dissertation

This thesis is composed of 7 chapters with subdivisions according to the needs for each of them. **Chapter 1** is the **Introduction** chapter, which briefly explains the needs that led to the development of this work, the company where it was developed and the main accomplishments. **Chapter 2** presents the **Context and State-of-the-art**, where a contextualization of the theme of the project and an insight of the most important concepts related to the field of study is given. **Chapter 3** is related to the **Materials and Methods** and describes all the methodologies applied during this project. **Chapter 4** is the **Results and Discussion** section, dedicated to presenting and discussing all the relevant results and consequent conclusions obtained. **Chapter 5** presents the **Conclusion**, where all the work developed and what was achieved is summarized. **Chapter 6**, named **Assessment of the work done**, offers a general appreciation of the project. The last section, **Chapter 7**, is the **References** chapter, and displays a list of all the bibliographic references used throughout this thesis.

2 Context and State of the art

2.1 Tire

Tires have come a long way since their primordial design. The tires of the first car were basically a spoked wooden wheel with a rubber coat. Since then, the automotive industry, and the concept and meanings of mobility evolved greatly, so the tire had to keep up with this evolution until it became the complex and optimized product that it is today (Continental AG, 2013).

The production of tires involves five main stages: sourcing of materials and production of compounds, manufacturing of components, building the tire, vulcanization and quality control. The work developed in C-ITA fits in the second stage – manufacturing of components – where the textile, that later will be vulcanized into the rubber, is made (Continental AG, n.d.-c).

Looking closer to the composition of the tire, we can divide its components in two main structural groups: the tread and belt, and the casing. The different layers can be seen in Figure 2.1 and are detailed next.



Figure 2.1 - Representation of a tire constitution (adapted from Continental AG, n.d.-a).

The tread and belt contain the following layers:

1. **Tread**, the main rubber (natural or synthetic) component responsible for the grip, wear-resistance and directional stability;
2. **Jointless cap plies**, a layer of textile reinforcements (usually nylon) embedded in rubber that ensures stability when traveling at high speed;

3. **Steel cord belt ply**, whose function is manly shape retention, directional stability, ensuring performance and reducing rolling resistance.

The casing is composed of the following layers:

4. **Textile cord ply**, a layer of textile (usually rayon or polyester) that controls the air pressure and maintains the shape;
5. **Inner liner**, a layer of rubber responsible for sealing the air chamber and controlling the internal pressure;
6. **Sidewall**, exterior rubber wall of the tire that offers protection from external damage and atmospheric conditions;

Another part of the casing is the Tire bead, a group of three different parts that are responsible for connecting the tire to the car's wheel, constituted by:

7. **Bead reinforcement**, a layer of strong and heat-resistant fibers (nylon or aramid) that enhances directional stability and facilitates steering response;
8. **Bead apex**, a stabilizing wedge of synthetic rubber that provides additional steering comfort;
9. **Bead core**, made of steel wire embedded in rubber to ensure the tire is firmly locked on the wheel rim (Continental AG, n.d.-a).

The arrangement between the belt plies (3) and the body ply (4) dictates the type of the tire. There are three possible arrangements, shown in Figure 2.2, that result in three different types of tires: diagonal bias tires, belted bias tires and radial tires. The position of these components affects the properties and adequacy of the tires to different types of conditions.

Diagonal bias tires have the simplest construction and are consequently easier to manufacture. These tires have the body ply cords laid diagonally (hence the name) in relation to the tread centerline. As result, when the tire deflects, shear occurs between body plies, generating heat and resulting in fast wear. Usually, this type of tire is used for trucks, trailers and farm applications.

Belted bias tires have the same characteristics as a diagonal tire but with the addition of a belt in the tread region. This extra layer restricts the expansion of the body carcass, making it stronger and more stable. As result, belted bias tires have less wear and improved stiffness in the tread area than diagonal tires.

Radial tires are the most common and most adequate to passenger cars. Instead of a diagonal orientation, body plies are laid nominally at 90º to the centerline of the tread, while two or more belts are oriented diagonally in the tread region to stabilize it. The radial body cords

deflect more easily under load resulting in less heat generation, lower rolling resistance, better high-speed performance and less wear. Naturally, the more complex structure increases the materials and manufacturing costs.

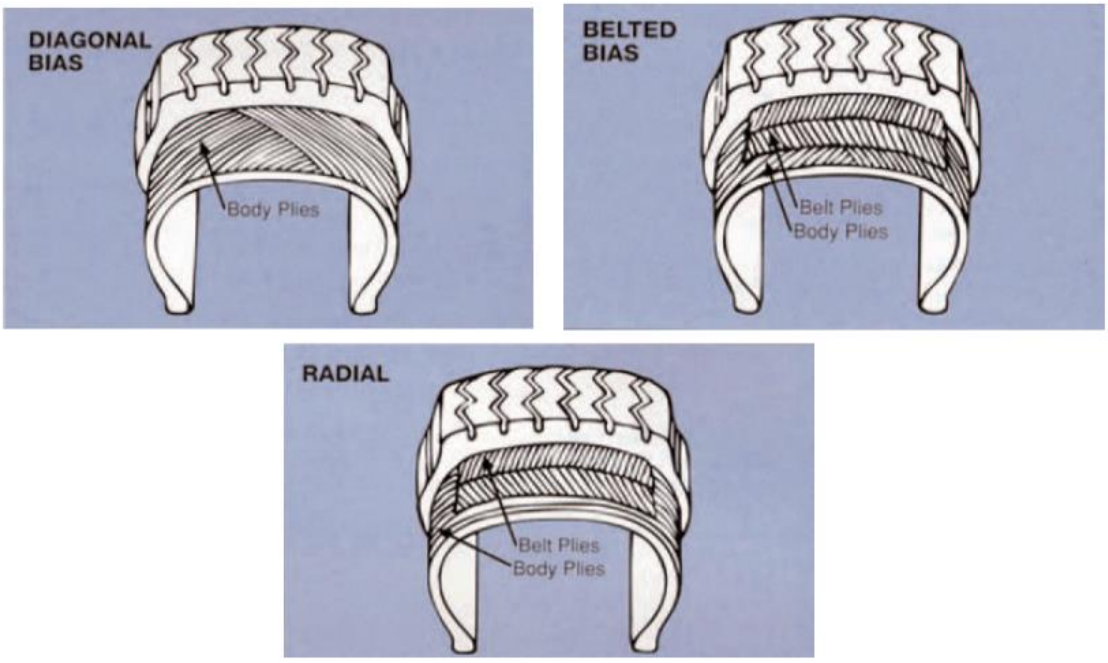


Figure 2.2 -Representation of the arrangement of the belt and body plies in the different types of tires (adapted from Gent & Walter, 2005).

2.2 Textile Reinforcements

Tires are composed of over a dozen of compounds with different functions. Aside from the basic materials like polymers, fillers or antidegradants, there are also reinforcement materials. The main purpose of the reinforcements added to the tire is to provide strength, stability and shape, and keep internal pressure constant. These materials can be textile reinforcements or bead wire. This section will focus on textile reinforcements, specifically the fibers used in the cords that compose them (Fleming & Livingston, 1979).

Before any further development, it is important to understand the meaning of cord and establish some concepts regarding the textiles. The essential concepts and terminology related to textile reinforcements are presented in Table 2.1.

The cords for textile reinforcements are created by twisting two or three yarns of one or two different fibers. The filaments are generally twisted in the direction “Z” to form the yarns, that are lately twisted together in the opposite direction, “S”, to form cords.

Depending on the cord construction, the twist level, twist direction and fiber that composes the yarn, the textile cords present different properties and characteristics (Gent & Walter, 1898; Nokyan tyres, n.d.).

Table 2.1 – Textile terminology (adapted from Gent & Walter, 2005)

Fiber	Material with high strength in the fiber axis direction and length at least 100 times greater than its diameter
Filament	Smallest continuous element of a tire cord
Yarn	Assembly of filaments twisted lightly and rolled up
Cord	Twisted or formed structure composed of two or more yarns
Decitex	Linear density of a textile item defined as the weight in grams of a length of 10000 meters
Twist Level	The number of 360˚ turns per unit length of yarn or cord
Twist Direction	Twist direction is termed "S" if the spiral turns clockwise from top to bottom for a vertically held cord and "Z" for a similar counterclockwise turning
Strength	Tensile load required to rupture a cord at a given rate of extension
Load	Force applied

In section 2.1 it was already stated that different materials are used for each structural part of the tire. This is related to the mechanical properties of each type of fiber and so, different fibers have different behaviours, and the needed characteristics for a given textile reinforcement vary depending on the part of the tire it will constitute. An example of such variety of characteristics is given in Table 2.2.

Table 2.2 - Cord's properties required for carcass' cords and belt's cords (adapted from Gent & Walter, 2005)

Cord properties	
Body ply / Carcass	Belt ply
Dimensional stability	High tensile strength
High tensile strength and modulus	Ultra-high tensile modulus
Low bending stiffness modulus	High bending stiffness modulus
High durability	High compression modulus
High toughness	High adhesion to rubber
Low hysteresis	Good resistance to chemical attack

As seen in the example, depending on the zone of the tire, cords must present specific characteristics to perform different functions. Consequently, not all fibers are suited to a specific function and so, there are usually pre-defined fibers more suitable for each zone.

In most cases, textile reinforcements are used in the form of fabric instead of single cords. In these cases, the cords go through a process of weaving that results in a warp of cords intertwined with a weft. Fabrics can be constructed with different patterns of threads, structure and dimensions, depending on the needs (Nokyan tyres, n.d.).

2.2.1 Rayon

Rayon is a fiber descendant of cellulose. It presents good dimension stability at elevated temperatures, is generally heat resistant until 150 ºC, has medium tenacity and elongation, low stiffness and medium toughness. The downsides are that it is expensive, is not mechanically strong (low resilience), is sensitive to moisture and its process of manufacturing has environmental issues (Dai, 2006; Gent & Walter, 1898).

The most common usage for this fiber is as body ply cord or belt reinforcement (Gent & Walter, 1898; Nokyan tyres, n.d.).

2.2.2 Nylon

The name nylon is used to represent linear aliphatic polyamides (PA), synthetic long chain polymers that can be divided into two main groups: PA 6 or Nylon 6, which contains 6 carbon atoms, and PA 6.6 or Nylon 6.6, which has 6 monomers, each one with 6 carbon atoms.

Regarding its properties, nylon is generally quite heat resistant to temperatures up to 180 ºC, has high tenacity, high elongation, medium stiffness, high resilience, high toughness and is not very sensitive to moisture. As disadvantages it presents bad dimension stability at elevated temperatures and presents heat set during cooling (flatspotting) (Dai, 2006; Gent & Walter, 1898).

Usually, this fiber is used in the cap, overlay ply, belt edge cap or body plies (but with some limitations in this last one) (Gent & Walter, 1898; Nokyan tyres, n.d.).

2.2.3 Polyester

Polyester, the common name to the polyethylene terephthalate (PET), is a long chain synthetic polymer with high tenacity and elongation, low shrinkage, medium stiffness, high resilience, high toughness, and low service growth as well as low heat set and low cost. The drawback of this fiber is its lower heat resistance compared to nylon and rayon (Dai, 2006; Gent & Walter, 1898).

It is mainly used in radial body plies and, with some limitations, can be used in belt plies as well (Nokyan tyres, n.d.).

2.2.4 Aramid

Aramid is a synthetic organic fiber similar to aliphatic polyamides. It is a remarkably inert fiber, two or three times stronger than polyester and nylon, with very good heat resistance and dimension stability but presents a low fatigue resistance, high cost and difficult to cut.

It can be used for belt or stabilizer ply material as an alternative to steel cord (Gent & Walter, 1898; Nokyan tyres, n.d.).

2.2.5 Hybrid

Besides the cords of each one of the fibers presented, it is also possible to combine two or more yarns from different fibers to create a hybrid cord. The most common combination for hybrid cord is aramid and nylon, making it possible to combine the best properties of each of these fibers.

Combining two yarns of nylon and one of aramid it is obtained what is called a Strong Hybrid.

2.3 The Textile-Rubber Adhesion

The adhesion between textiles and rubber is fundamental when building a tire. The main purpose of having the adhesion between both components of the matrix is to allow the transference of the load stress from the rubber to the reinforcing cord. Consequently, unless these two materials are properly bonded, the safety and performance of the tire are compromised, which cannot happen in such a high safety product.

2.3.1 Dipping Solution

Untreated fibers have an inert smooth surface, high modulus of elasticity and a polar character, while rubber has low modulus of elasticity and a non-polar character. Lack of compatibility and mechanical interlocks makes the adhesion between the textile reinforcements and the rubber matrix impossible without chemical treatment.

The solution for ensuring the adhesion of the composite cords-rubber is the **Resorcinol Formaldehyde Latex (RFL)** treatment. RFL consists of an emulsion of rubber latex in an aqueous solution of resorcinol and formaldehyde, that is used to coat the textile cords using a dip bath followed by cure. The resorcinol and formaldehyde react and form a strong polar polymer that bonds with the polar cord, or fabric, whereas the latex can form chemical bonds with the rubber, thus allowing a strong adhesion between the two components.

Although the RFL dip can solve the problem of the adhesion to the textile, it does not easily bond with all fibers. This method has proven very efficient with nylon and rayon but, in the case of polyester and aramid, because of their highly inert surface, the fibers became so unreactive that they do not bond with the RFL coating. The solution in those cases is to create a sub coating using a pre-dip solution of isocyanate and epoxy that connects with both the polymeric cords and the RFL dip, allowing the latter formation of the rubber-cord composite (Gent & Walter, 1898; Louis et al., 2014; Wennekes et al., 2008).

The RFL treatment for nylon and rayon cords is then constituted by a RFL dipping bath, followed by the cure of the dipped cord. For aramid and PET fibers this process has an extra initial step, where the cords are pre-treated with a pre-dip followed by the cure of the pre-dipped cord.

Even when dealing with PET and Aramid textiles, it is not always necessary to pre-treat the cords because some suppliers give them a finish coating, with an oil, that performs the same function as the pre-dip, so the cords are already activated.

After the RFL treatment it is necessary to embed the cords into the rubber. For that, the components go through vulcanization, to assure the adhesion between the cords and the rubber. The adhesion process, including the RFL treatment, is schematized in Figure 2.3.

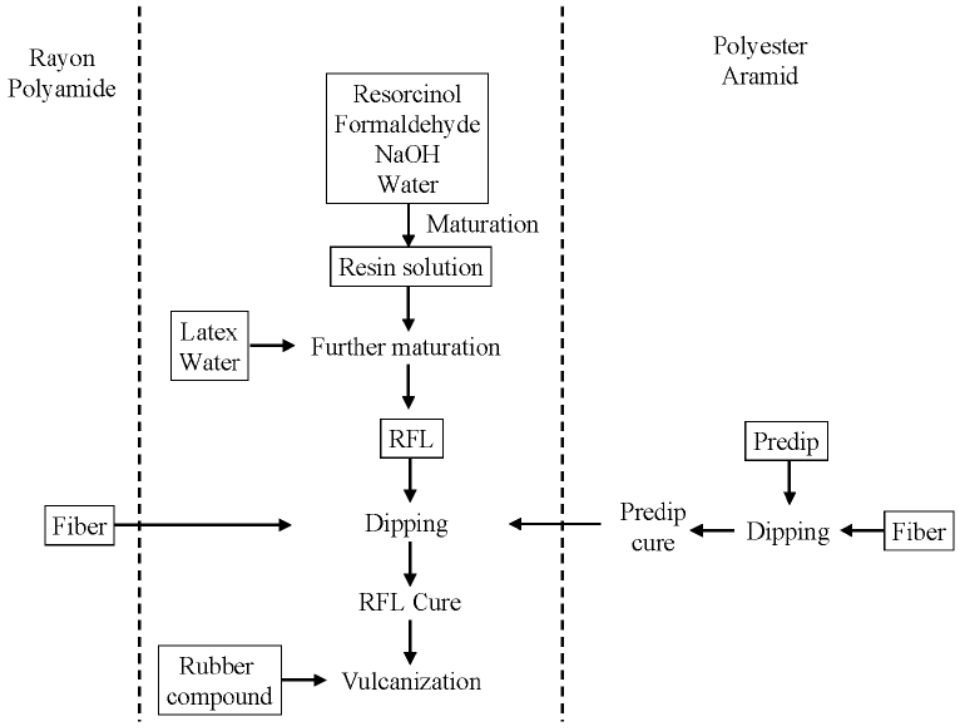


Figure 2.3 – Schematic representation of the adhesion process including the RFL treatment (adapted from Wennekes et al., 2008).

Since the RFL treatment has major disadvantages regarding environmental and health concerns, alternatives have been studied to replace this dipping solution proving that acrylic

resins could be a viable alternative to the standard RFL dipping if the cords were previously activated (Solomon, 1982).

To create a viable RFL-free dip that could assure proper adhesion, Continental in partnership with Kordsa developed a new dip based on an acrylic resin called Cokoon. This new bonding technology is slowly starting to be used in production and the goal is to keep researching and optimizing the recipe until it is possible to fully substitute the RFL treatment with this eco-friendly option (Goodchild, 2020).

2.3.2 Single End and Zell

In C-ITA, the dipping process described in the previous sub section occurs in a production machine called Single-End, in the case of dipping cords, or in the Zell, in the case of dipping fabric.

The single-end machine, schematized in Figure 2.4, owes its name to the fact that the process starts and ends in the same place. The cords without treatment – greige cords – are untwined and stretched in tensioning rollers until entering the dip bath. The machine has two baths, one for the pre-dip and one for the RFL dip, depending on the needs of the fiber. Following the baths, there are four ovens. If the cords do not need to be activated with the pre-dip, they go directly to the dip bath and proceed to be dried and cured in the first and second oven. If the cords need a pre-dip bath, they go through the first bath (with pre-dip), pass through the first and second oven to dry and cure, return to the second bath to be dipped with the RFL solution and then enter the third and fourth oven. After completing the cure, the cords are rolled back in bobbins.

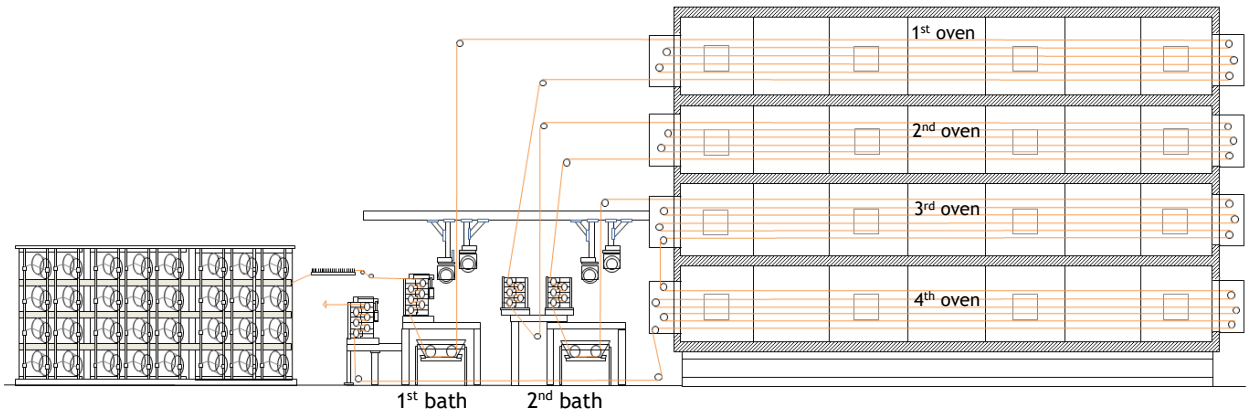


Figure 2.4 – Single-End machine schematization (adapted from Martins, 2013).

The dipping process of fabric is similar but with a few differences. Dipped fabric is not winded in the same place where the greige fabric is unfolded and, instead of dipping several units at once, as it happens in the single-end machine that allows the dipping of 108 cords at once, in

the Zell machine, showed in Figure 2.5, the fabric is dipped one at a time. Apart from that, the process follows the same order of steps with the only difference of needing more ovens – Zell has a total of 7 ovens (de Almeida Rocha, 2019; Peixoto da Silva, 2019).

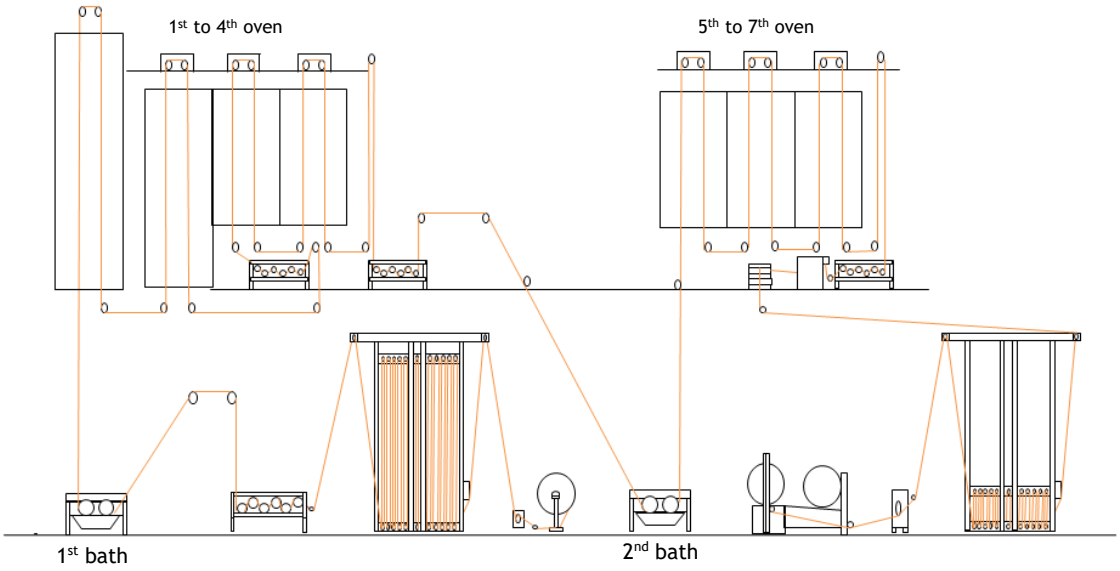


Figure 2.5 – Zell machine schematization (adapted from Martins, 2013).

For research purposes and control, C-ITA has available a model at laboratory-scale of a machine called Lab Dipping Unit – LDU, that can simulate the dipping process of the Single-End and Zell machine. There is also a laboratory-scale machine that replicates the twisting in the construction phase of the cords. This device is called LTU – Lab twisting unit.

2.4 Assessment of Mechanical Properties

As it happens in every industry, the process and the resultant product must be controlled to ensure its quality and guarantee that it respects the specifications.

To assess the quality of the cords produced, several tests are performed to evaluate if the mechanic characteristics and behavior of these are within the parameters established by the company. Mechanical tests are performed using different test machines depending on the parameter being tested.

Some of the most important parameters studied during the quality control of the textile reinforcement produced in C-ITA are the adhesion, through the peel test, the elongation through the force elongation test and the stiffness through the bending stiffness test.

2.5 Dip Pick-Up

As well as the adhesion evaluation, it is crucial to assess the dip amount that is being retained in the dipping process. As already mentioned, insufficient dip compromises the adhesion, but an excessive amount implies a waste of resources, so the dip pick-up percentage per greige cord (from now on denominated DPU), which is the amount of dip that is being retained per greige cord, is another parameter evaluated to control the process. DPU can be calculated from three different methods: wet-chemical method, weighing method and time-domain nuclear magnetic resonance.

2.5.1 Wet-Chemical Method

The wet chemical method is one of the most well-established methods to measure the DPU. It is one of the official methods used in C-ITA and, although it is not the most used, specially by the production department where the textiles are analyzed through TD-NMR, it is an indispensable method, since it is the source of the DPU reference values for the calibration of the TD-NMR.

This method requires the dissolution of dipped cords followed by filtration to recover the dip that does not dissolve, to compare the mass of the dip with the mass of the cord. Besides being a destructive method, it is very time-consuming as some fibers can take days to dissolve, requires strong chemicals and has high associated errors.

2.5.2 Weighing Method

In the weighing method, the samples of the dipped cord are dried and weighed to compare the mass of the dipped cord in relation with the greige cords, allowing to assess the mass of dipped that was retained by the cords and calculate the DPU.

The weighing method is not the most desirable, as it presents more errors associated with the results, and it is easily affected by the humidity sensitivity of the fibers. Even so, it is a lot less time-consuming than the wet-chemical method, which can be an advantage when dealing with fibers that require a long time to dissolve, as it happens with aramid (Peixoto da Silva, 2019).

2.5.3 TD-NMR

The phenomenon analyzed in NMR is related to a natural property of atoms called spin angular moment. The spin angular moment is an intrinsic property of the elementary particles existent in the atom's nucleus (neutrons and protons), related to the motion of the mass, that can only assume the value ±½. Although electrons have spin, the NMR, as the name implies, only focuses on the nuclei, which means that this technology only takes into account atoms with nuclear spin different from 0 (Simpson, 2012).

In a normal state, the nucleus' particles are randomly aligned and the magnetization vector resultant from all the nucleus of the sample is zero. Because of the magnetic moment resultant from the nuclear spin, when placed in a magnetic field, the nuclei behave like small magnets. Each individual spin aligns in parallel (spin number of ½) or in antiparallel (spin number of -½) to the magnetic field where it is placed and the magnetization vector of the nucleus ceases to be null. Because of these different alignments, the magnetic vector resultant is described by one longitudinal and one transversal component. Because the vector is not parallel to the external magnetic field, the transversal component causes the vector to rotate around the direction of the magnetic field. This movement is called precession, and the Larmor frequency translates the relation between the precession frequency and the magnetic field strength. Different elements present different magnetization and, consequently, different Larmor frequency.(Simpson, 2012)

The precessing movement induces stages of lower or higher energy, depending on the energy level in which the particles are and its alignment regarding the magnetic field. If electromagnetic waves with energy equal to the energy difference between two levels of energy are applied to the sample at the Larmor frequency, transition of particles to higher energy states occurs. With transitions between the levels, the populations in each energy state change and, consequently, the magnetization vector of the sample is changed as well.(Simpson, 2012)

After the energy applied in the resonance frequency ceases, each nucleus starts to return to its initial position, to a state of lower energy, by emitting photons in the form of electromagnetic waves. This process is called relaxation and the time taken for the particles to return to its lower stage is called relaxation time, or spin lattice relaxation (Longmore, 1989; Simpson, 2012).

The electromagnetic waves resultant from the relaxation, and the time of relaxation, can give information regarding the nucleus. The NMR device creates magnetic pulses with a 90º or 180º angle to alternate the net magnetization and make the nuclei transition between higher and lower states of energy with periods of relaxation. Then, the device reads the waves resulting from the relaxation, that vary in time. Based on this information, NMR spectroscopy allows the study of physical, chemical, and biological properties of different types of matter. Different types of pulses allow the study of different characteristics (Hornak, 1997; Simpson, 2012).

In the NMR relaxometry, or time-domain NMR, the analysis of the relaxation phenomenon is made in terms of relaxation times. Since the relaxation time depends on the nature of the particles, the interaction of the nucleus with the surrounding environment and the number of particles, this type of spectroscopy can determine a lot of information regarding the sample being analyzed. For example, the larger the sample, the greater the number of atoms and,

therefore, the more intense is the signal of the wave. Also, fast decays imply slow moving molecules and slow decays, consequently, means fast molecular motion. This technique is an accurate and highly recognized methodology that allows the measurements of the molecular content of a sample by analyzing the characteristics of its nuclear magnetic signal (Bruker BioSpin, 2018; Niumag Corporation, 2021; Simpson, 2012).

Because the DIP and the fibers have different compositions, and originate different signals and relaxation times, the TD-NMR device used by C-ITA is calibrated to account for fiber signal and subtract it, presenting only the measurement correspondent to the dip. This allows the measurement of the dip amount existing in the sample.(Pereira Coutinho, 2021)

Although there are other methods to analyze the DPU, like the wet-chemical and weighing methods, TD-NMR has considerable advantages over the others, for being non-destructive, faster, stable, free of chemicals and accurate. However, this technique requires the calibration of the device for the different types of fiber and dip samples (Niumag Corporation, 2021).

2.6 Assessment of previous work

From the past few years until now, the TD-NMR has been a strong and reliable method to assess the dip content of cords at C-ITA. So far, almost every material in frequent production has a calibration curve developed for the TD-NMR device, so their dip content can be analysed through NMR relaxometry instead of resorting to less consistent methods.

At the moment of this study, all the nylon materials being produced with the purpose of serving as textile reinforcements in tires had already been calibrated and validated to the TD-NMR device. However, a group of nylon materials that, although were not meant to be used in tires but were rather part of the Contitech unit, were being produced with some recurrence, so there was a need for the calibration of these materials.

Beside the nylon materials from Contitech, a rayon material was also objective of study during this dissertation, since previous work had already been initiated regarding this material. A calibration curve had already been developed, but hadn´t been validated due to big differences between the DPU obtained in the production and the DPU obtained through TD-NMR. The previous calibration curve, that ended up being discarded, consisted in the first attempt of calibration of a material dipped with a RFL-free dip, so, although this was a continuation of a first attempt, the calibration of a material dipped with Cokoon was, until now, unprecedent.

3 Materials and Methods

3.1 Materials

The materials studied were rayon and nylon. Both materials are fabrics in their final form but, for study and test purposes, were used in the form of single cords.

The rayon fabric is composed by cords with 1840 dtex, and a double construction.

The group of nylon materials studied was composed by four fabrics with equal construction characteristics – monoply cords of 940 dtex -, same type of fiber (nylon) from the same supplier and treated with the same RFL dip. These fabrics only differ in the specifications of production of each fabric, like the width and length. None of these characteristics affect the dip content, the variances in the specifications are only related to the needs for each of their applications, so it does not affect the calibration curve. For that reason, one of the fabric variations was chosen as a reference, and a single calibration curve was developed to fit the entire group.

Neither of the materials were in production at the moment of its study, so it was necessary to twist new greige cords. Using the LTU, the yarns of each fiber were twisted, and the cords were constructed according to the respective specifications.

3.2 Dipping process

As mentioned in chapter 2.3.2, C-ITA has a machine that simulates the chemical treatment of cords or fabric. This unit can be used to optimize, test, and replicate the dipping process.

For the construction of the calibration curve was necessary to study a wide range of DPU so several cords, of both materials, were dipped using dipping solutions with different concentrations. The velocity, temperature and tension conditions were adapted to each cord in question, depending on the conditions of operation used in the Zell machine. The scale down factor was taken in account.

Neither of the cords studied needed pre-activation, so no pre-dip was needed. All the ovens were used.

3.3 Wet-Chemical Method

In C-ITA, the TD-NMR is the most used method by the production sector, but this requires that every material analyzed has a calibration curve stored in the TD-NMR device. The standard samples used as reference for the calibration curve are obtained through the wet-chemical method.

This dissertation project required the realization of many DPU analyses with the ultimate goal of calibrating the TD-NMR device, so the wet chemical method was one of the most used. This method obeys the following procedure:

1. Cut the cord in pieces less than 5 millimeters long until the sample is between one and two grams
2. Dry the sample in the oven at 105 ºC for at least one hour.
3. Let the sample cool in the desiccator, weigh it and register the mass (m_1).
4. Dissolve the sample with a suitable solvent using temperature and agitation, until the cord is completely dissolved.
5. Weigh and register the mass (m_2) of a crucible previously dried for four hours and cooled in the desiccator.
6. Filtrate the dissolution mixture using the crucible and a pump system. Wash it well with previously heated washing fluids.
7. Dry the crucible with the dip for at least two hours.
8. Weigh it after cooling in the desiccator and register the mass (m_3).

The dip content is then calculated using Equation 3.1.

$$\mathrm{DPU}_{\text{greige cord}} = \frac{m_3 - m_2}{m_1 - (m_3 - m_2)} \tag{3.1}$$

During this project, two different fibers were studied: rayon and nylon. The solvents, duration of dissolution and washing fluids for each one of them are presented in Table 3.1.

Table 3.1 – Materials and time of dissolution of the wet chemical method for each material

Cord Fiber	Dissolution time (h)	Dissolution agent	Washing Fluid
Rayon	1	50 ml of formic acid, 98 %, with zinc chloride, 50 $g.L^{-1}$	50 ml of formic acid, 85 %; 50 mL of water
Nylon	1	50 ml of formic acid, 85 %	50 ml of formic acid, 85 %; 50 mL of water

Through Continental standards, the assessment of dip pick-up should be made in triple and the standard variation within samples should not be superior to 0.4 %, otherwise the measurement is not valid.

3.4 Validation of the filtration method for rayon calibration curve

Both in production and TD-NMR calibration, the dip content is assessed using the wet chemical method, which involves a filtration step. During the analysis of the previously made calibration curve for the Cokoon-dipped rayon, it was noticed that this filtration process had been

optimized by introducing glass wool in the crucibles, with the purpose of facilitating the filtration (Pereira Coutinho, 2021). However, the filtration process carried out by the production department remained the same. Because the calibration curve previously developed for rayon had been rejected, and the only factor that stood out from the standard procedure was the filtration method, the first step for correcting this rayon calibration curve was to evaluate the impact that the filtration method could have on the results.

To validate the filtration process, a preliminary study of a cord with high dip content was carried out to analyze the impact of the glass wool in the filtration time, and possible variations in the results. Then, four samples from production were collected and tested, using the wet chemical method with and without glass wool in the filtration process. Five tests were made for each one of the test parameters – five tests with glass wool and five tests without glass wool – and the standard deviation within the results was studied to understand if the use of glass wool was inducing variations.

3.5 Calibration Curve

The calibration of the TD-NMR device requires the construction of a calibration curve to relate the electrical signal resultant from the device measurement to the amount of dip present in the cords.

The calibration curve requires four points in four different intervals of DPU, depending on the specifications of each fiber. The intervals are defined according to the target, upper target limit (UTL) and lower target limit (LTL), specific parameters for each material, and serve as guides to determine the acceptable values of dip content. The calibration points required for the materials studied are presented in Table 3.2.

Table 3.2 – Calibration points for rayon and nylon

	A	*B*	*C*	*D*
	Between LTL-1% and LTL	Between LTL% and target	Between target and UTL	Between UTL and UTL+1%
Rayon	1 – 2 %	2 – 3.5 %	3.5 – 5 %	5 – 6 %
Nylon	2 – 3 %	3 – 5 %	5 – 8 %	8 – 9 %

To achieve this range of points, cords are treated with a dipping solution, maintaining the general recipe but varying the solid content, which means that the dip is diluted or concentrated in each impregnation. Since there is no linear relationship established between the solids content in the dip and the cord DPU, this process takes place by trial and error, that is, the strings are dipped in the LDU, analyzed by the wet chemical method and the recipe of

the dip for the next treatment is adjusted as necessary until it is obtained one sample correspondent to each point of the curve.

After obtaining the samples, these are analyzed in the TD-NMR device that returns an electrical signal corresponding to the sample's DPU. The calibration curve is built using a linear regression between the DPU and the electrical signal.

The calibration curves must be validated. To make the validation, 30 samples from production are tested in the TD-NMR device, using the calibration curve developed. The dip-pick-up obtained must be compared to the values obtained via the wet-chemical method, standardly realized during quality control after the production phase. The DPU obtained using the two methods cannot differ more than a certain value previously established to approve the calibration curve. This value depends on the decitex and, for the specific materials used, the criteria dictated that the difference cannot be superior to 0.563 % for rayon and 0.938 % for nylon.

One of the studied parameters related to the quality of the calibration was the uncertainty associated with the DPU assessment through analysis of samples in the TD-NMR device.

The prediction standard error, s_{R}, associated with the DPU value, x_0, estimated from a known instrument response, y_0, using a simple linear regression is given by Equation 3.2:

$$s_{x_0} = \frac{s_{\mathrm{R}}}{m}\sqrt{\frac{1}{N}+\frac{1}{n}+\frac{(\bar{y}_0-\bar{y})^2}{m^2\sum_{i=1}^{n}(x_i-\bar{x})^2}} \tag{3.2}$$

Where s_{R} is the residual standard error, m is the slope of the linear regression, N is the number of repeated measurements of each sample analyzed, n is the number of paired calibration points, $\bar{y}_0$ is the mean of N repeated measurements of the y_0 value for the sample, $\bar{y}$ and $\bar{x}$ are the mean of the y and x values of the calibration standards, respectively, and x_i is the ith x value of the calibration sample. The value x_0 with confidence bounds is $x_0 \pm t_{\alpha/2}s_{x_0}$, where $t_{\alpha/2}$ is the two-tailed t-Student value for the significance level desired α and $n-2$ degrees of freedom.

The residual standard deviation, s_{R}, is calculated by Equation 3.3.

$$s_{\mathrm{R}} = \sqrt{\frac{\sum_{i=1}^{n}(y_i-\hat{y}_i)^2}{n-2}} \tag{3.3}$$

The parameter y_i represents the observed value of y for a given value of x_i and $\hat{y}_i$ represents the value of y predicted by the calibration curve equation, for a given value of x_i.

3.6 TD-NMR

The analysis in the TD-NMR device requires the preparation of the samples as it is explained bellow:

1. Cut the cord into pieces until the sample is about 0.5 grams.
2. Weigh and identify a clean, dry tube with its lid and register the mass.
3. Transfer the sample to the tube and let it dry in the oven at 105 ºC, without the lid, for one hour for nylon and one hour and a half in the case of rayon. Filling height must be inferior to two cm.
4. After the drying time is complete, put the lid in the tube within the oven to prevent moisture absorption. Remove the tube and let it cool.
5. Weigh and register the mass of the capped tube plus sample.
6. Heat the sample tube to the measurement temperature (40 ºC) using the heating rack for about five minutes.
7. Insert the tube in the TD-NMR device and proceed with the measurement.

The NMR signals are sensitive to impurities so the whole process of preparing the samples should be executed with gloves to prevent the contamination of the samples and tubes. It is also important to extract all the moisture from the samples, as contemplated in the procedure, not only to avoid disturbances in the readings but also because the mass of the samples must be entered into the NMR software to calculate the DPU concentrations.

Another important aspect is that the DPU concentrations in this device are standardly given as a percent per total mass of cord ($\mathrm{DPU}_{\mathrm{dipped\ cord}}$), while the DPU concentrations obtained from the chemical method are presented as a percent per mass of the greige cord ($\mathrm{DPU}_{\mathrm{greige\ cord}}$). These different forms imply that, when reading the DPU given by the TD-NMR or during the calibration curve construction, and when introducing the correspondent DPU into the TD-NMR, the values need to be converted to the appropriate form.

The dip content per total mass of greige cord is given by equation 3.4.

$$\mathrm{DPU}_{\mathrm{greige\ cord}} = \frac{m_{\mathrm{dip}}}{m_{\mathrm{greige\ cord}}} \times 100 \tag{3.4}$$

The dip content per mass of dipped cord is given by Equation 3.5.

$$\mathrm{DPU}_{\mathrm{dipped\ cord}} = \frac{m_{\mathrm{dip}}}{m_{\mathrm{dipped\ cord}}} \times 100 \tag{3.5}$$

And

$$m_{\mathrm{greige\ cord}} = m_{\mathrm{dipped\ cord}} - m_{\mathrm{dip}} \tag{3.6}$$

So,

$$\frac{m_{\text{dip}}}{\text{DPU}_{\text{greige cord}}} \times 100 = \frac{m_{\text{dip}}}{\text{DPU}_{\text{dipped cord}}} \times 100 - m_{\text{dip}} \quad (3.7)$$

$$\frac{100}{\text{DPU}_{\text{greige cord}}} + 1 = \frac{100}{\text{DPU}_{\text{dipped cord}}} \quad (3.8)$$

From Equation 3.8, it is possible to make the conversion through the following equations

$$\text{DPU}_{\text{dipped cord}} = \frac{100}{\frac{100}{\text{DPU}_{\text{greige cord}}}+1} \quad (3.9)$$

$$\text{DPU}_{\text{greige cord}} = \frac{\text{DPU}_{\text{dipped cord}}}{100-\text{DPU}_{\text{dipped cord}}} \quad (3.10)$$

For purposes of simplification, in the following chapters, when only mentioned DPU, this refers to the dip pick-up percentage per greige cord.

3.7 Study of mechanical properties

3.7.1 Load-Elongation Test

In the force elongation test, the cords are gripped in the jaws of the testing machine and then extended until rupture occurs. This allows the comprehension of the maximum extension, elongation and breaking force of the material (International Standard Organization, 2013).

At Continental ITA the equipment used is the Zwick Z010 with appropriate clamp types depending on the material. The testing procedure for rayon fibers is explained next.

1. Prepare five samples of at least 200 mm longer than the clamping length and let them dry in the oven for one hour at 105 ºC.
2. Introduce the adequate pre-tension following the rule of 0.05 $cN \cdot dtex^{-1}$.
3. Select the clamp pressure in order to avoid slippage of the test sample, but without getting breakage on the clamps.
4. Insert the sample in the clamps following the pulling direction.
5. Execute the test using the software interface.

It is essential that all samples are prepared and handled to avoid the change of properties like loss of twist, sharp bending, and so on.

For reproducibility purposes, five samples must be tested for each study and the samples must be removed from the oven immediately before mounting in the tensile tester. If slippage or breakage occurs, the measurement is no longer valid and the samples must be substituted with a new one.

A illustration of the test montage is shown in Figure 3.1.

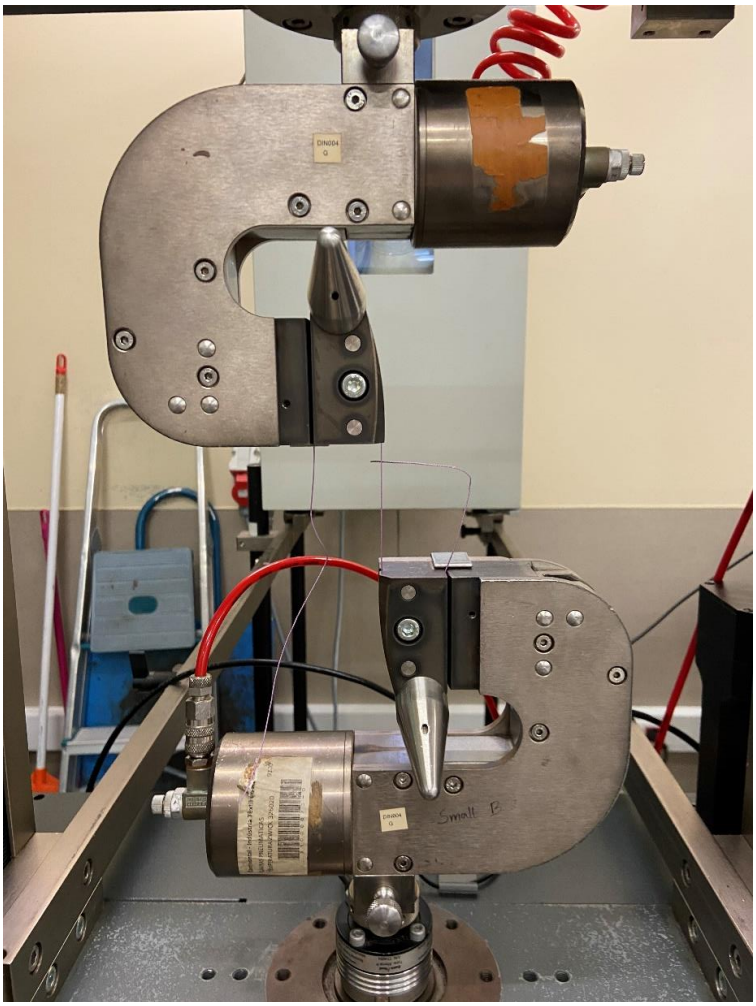


Figure 3.1 – Force-elongation test equipment and assembly.

3.7.2 Bending Stiffness Test

The bending stiffness test evaluates the rigidity of the material and is performed in the same testing machine as the load-elongation test, Zwick Z010, using the clamps shown in Figure 3.3. The procedure for this test is the following:

1. Place 10 cords equally spaced out in the weaving comb, as seen in Figure 3.2 – (a).
2. Mark samples of approximately 7 cm, avoiding the extremities of the comb.
3. Fix the cords with tape, as seen in Figure 3.2 – (b), and cut the samples.
4. Adjust the position of the clamps, if necessary, and place the sample on the support of the upper sample holder, centered and parallel to the support frame.
5. Perform the test using the software interface.

The test requires three samples, but the preparation of samples should be made in quadrupled to prevent in case any sample does not conform. When placing the samples, it must be assured that the cords do not overlay, otherwise the sample must be discarded. It is also important to

avoid touching the surface of the samples or bending it, to avoid interfering with their properties.

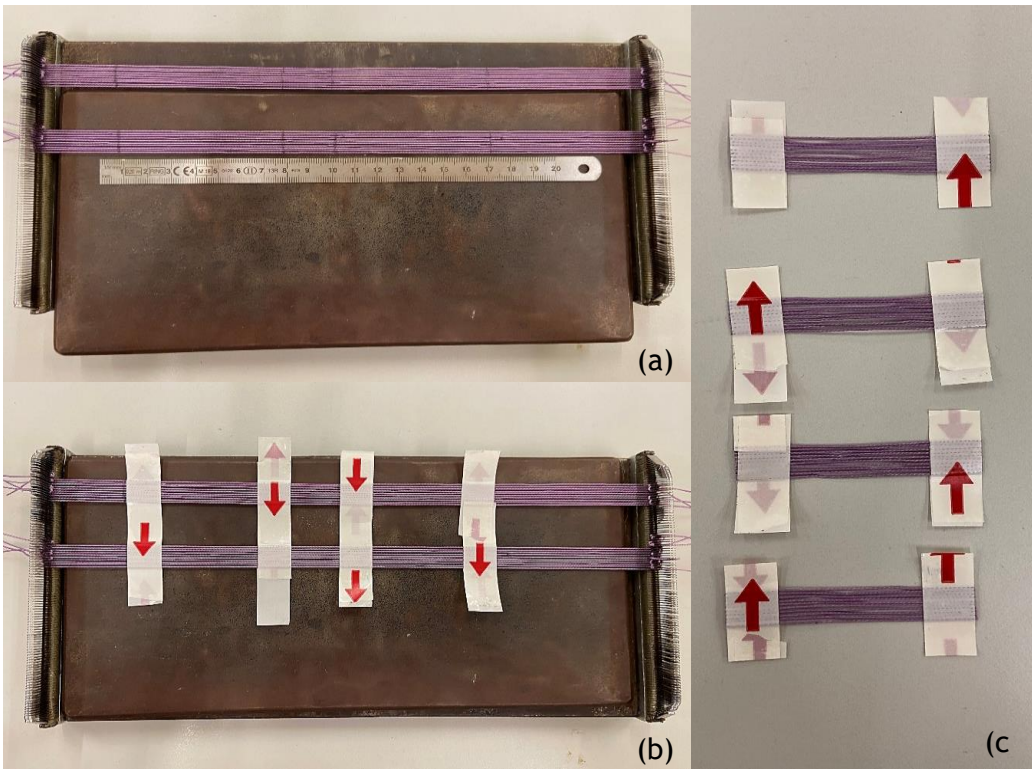


Figure 3.2 – Sample preparation for the stiffness test.

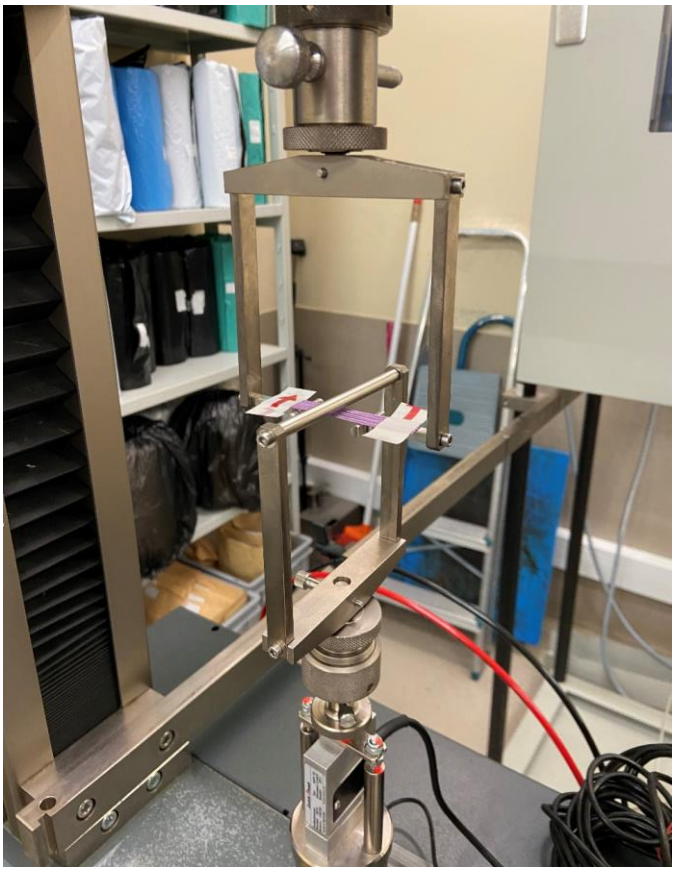


Figure 3.3 – Stiffness test equipment and assembly.

3.8 Statistical Analysis

To conduct reliable analysis and draw thoughtful and duly justified conclusions, several statistical tests were performed during this work.

3.8.1 Confidence interval

The confidence interval is an estimated range of values likely to include the true parameter value with a certain degree of confidence. Although there is no certainty of the true value, it helps bound unknown parameters, allowing one to understand how strong the conclusions are and the degree of certainty regarding the results.

A confidence interval for a particular parameter θ has the form $l \leq \theta \leq u$, where the end-point values are determined through sample data.

The lower- and upper-confidence limit, l and u, are obtained through the estimation of two random variables L and U, respectively. The probability of the parameter θ lie between L and U is $1-\alpha$, as shown by Equation 3.11,

$$P(L \leq \theta \leq U) = 1 - \alpha \tag{3.11}$$

which represents the probability of determining a confidence interval that contains the true value of θ. The value $1-\alpha$ is then called the confidence coefficient (Montgomery & Runger, 2003).

3.8.2 Hypothesis Testing

The hypothesis test is used in comparative experiments to assess the plausibility of some statement about a particular parameter of a population. It can also be described as a statement regarding the probability distribution of a random variable. Independently of the perspective, the goal is always assessing a hypothesis about a parameter of a population.

The test is built under two statements: the null hypothesis, H_0, considered true, and the alternative hypothesis, H_1. Since the hypothesis are related, it is possible to have two different types of alternative hypothesis. If the null hypothesis states that a parameter θ has a certain value ($H_0: \theta = a$), the alternative hypothesis can simply state that the parameter is different from that value ($H_1: \theta \neq a$), a two-sided alternative hypothesis, or it can state that the parameter is bigger or smaller than that value ($H_1: \theta > a$ or $H_1: \theta < a$), which is a one-sided alternative hypothesis.

To determine if the null hypothesis is rejected or not, a statistical test related to the parameter in study is conducted, and the critical values are defined. The critical values are the boundaries

between the no rejection region (interval of values where the null hypothesis is not rejected) and the critical region, (interval in which the null hypothesis is rejected).

When testing a hypothesis, two different errors can occur. The type I error occurs when the null hypothesis is rejected although it is true. The probability of this error happening is defined and transmits the significance level of the test. For example, if $\alpha = 0.057$, this means that there is a probability of 5.7 % of selecting a sample that would lead to a rejection of the null hypothesis, even this being true. Contrariwise, type II errors are characterized by the no rejection of the null hypothesis when this is false and its probability is represented by β. The power of the hypothesis test is the probability $1 - \beta$, which represents the probability of rejecting the null hypothesis when it is false. Usually, the power of the test should be superior to 80 % (Montgomery & Runger, 2003).

3.8.3 Power Curve for two samples t-test

Power curves are statistics tools that allow the study of the impact of the sample size in the power of a statistical test. In the case of testing the difference between two populations' means, these curves involve three parameters: the power of the test, the difference between the populations' means, and the size of the samples involved. Given a significance level α of the test and a specified difference in the means, the curve plots the power of the test versus the samples size, which means that it translates the probability of rejecting the null hypothesis when this is false depending on the size of the samples.

One of the applications of power curves is to determine what size the samples should have for the hypothesis test referred to above can detect a specific difference in the means when this exists (Minitab LLC, n.d.; Montgomery & Runger, 2003).

4 Results and discussion

4.1 Nylon material

The obtention of the calibration curve required the dipping and DPU assessment of several cords, until all four points of the curve, described in Table 4.1, were obtained.

Table 4.1 - Dipping results and dip assessment via wet-chemical method for nylon curve

Curve Points	DPU (%)	Mean (%)	Standard deviation (%)
A	2.31 2.34 2.34	2.33	0.013
B	3.70 3.54 3.70	3.65	0.092
C	5.47 5.40 5.61	5.49	0.10
D	8.24 8.20 8.14	8.12	0.054

After obtaining all the point correspondent cords, each sample was analyzed with TD-NMR, following the appropriate procedure, to build the calibration curve. Using Minitab 18, a linear regression between the TD-NMR signal and the correspondent value of DPU was constructed, obtaining the curve presented in Figure 4.1.

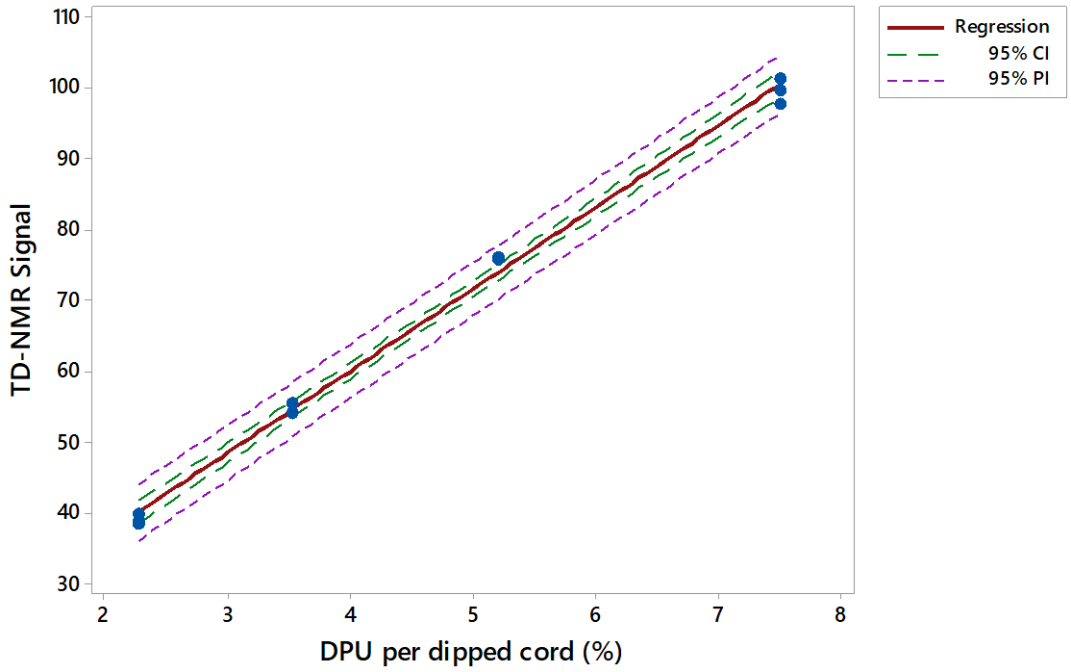


Figure 4.1 - Calibration Curve for nylon with a 95 % confidence and prediction interval.

The resultant data from the wet-chemical method and TD-NMR analysis, as well as sample preparation required, can be consulted in Table A.1 and A.2 of Appendix A.

The residual plots of the calibration curve developed, shown in Figure 4.2, were analyzed to verify the adequacy of the model to the experimental data. This means that, for the model to be adequate, the following assumptions of the linear model have to be fulfilled: errors associated with the regression model fitted were approximately normally distributed, with a mean of zero, random variability, and constant variance. (Montgomery & Runger, 2003).

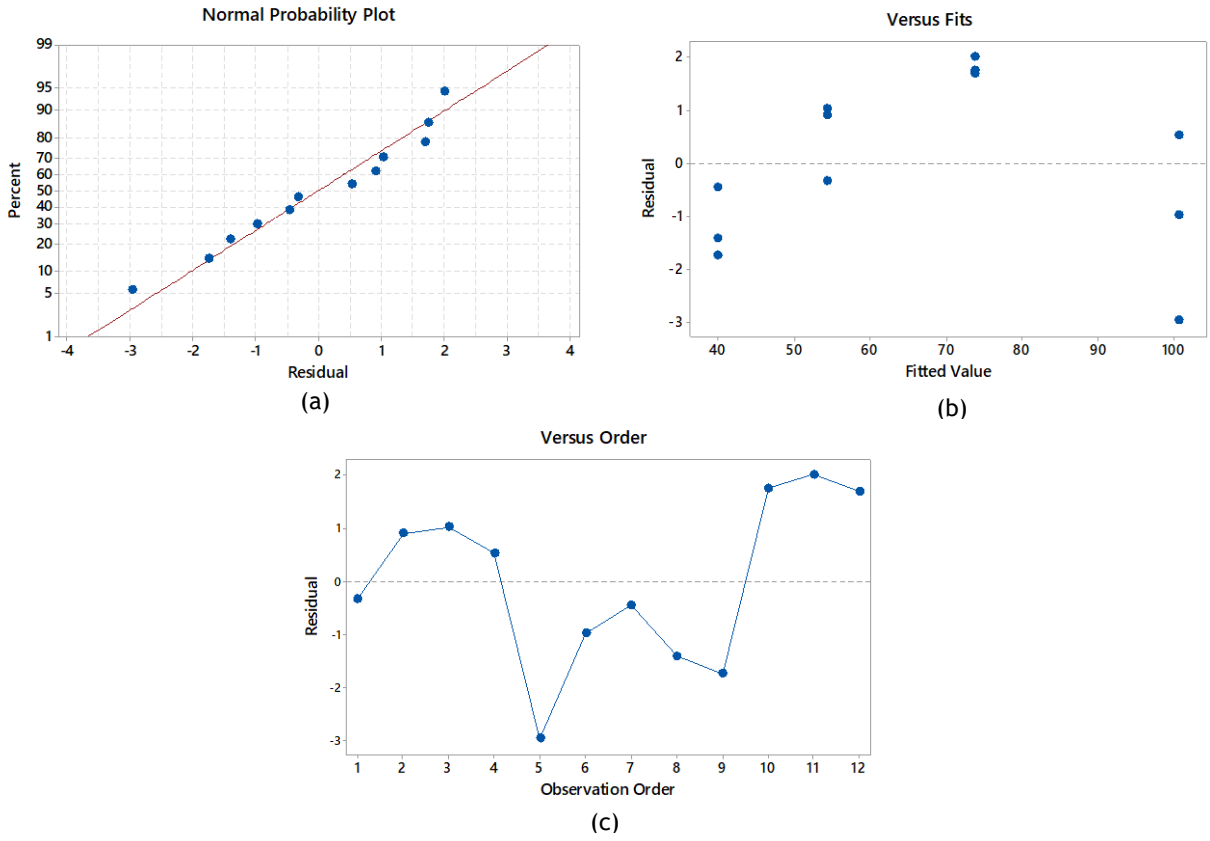


Figure 4.2 – Residuals plots for the linear regression model of the nylon's calibration curve.

The normality residual plot (Figure 4.2 - a) presents the probability distribution of the residuals. Since it displays the points along a straight line, it can be concluded that it does not have major deviations from a normal distribution of the random errors. In the fits residual plot (Figure 4.2 – b), it can be confirmed the assumption that the errors are random, with a mean of zero and constant variance, since the data is nearly equally and random distributed from both sides of the x-axis, without forming any pattern. The order residual plot (Figure 4.2 - c) confirms the assumption of independent errors, because it presents the data distributed in a random pattern around the centerline, indicating they do not depend on the order in which they were obtained. All residual plots confirm that all the assumptions for the linear regression model are satisfied and so, the relation between the predictor (DPU) and the response variable (TD-NMR signal) is well represented by a linear model.

Regarding the statistical characterization of the calibration curve, the coefficients that describe the linear correlations and respective 95 % confidence intervals are presented in Table 4.2.

Table 4.2 – Regression coefficients for the nylon's calibration curve and its statistical characteristics

Term	Coefficients	Standard error	95 % CI	P-Value
Intercept	13.61	1.21	(10.91; 16.30)	$< 10^{-6}$
slope	11.58	0.24	(11.04; 12.11)	$<10^{-12}$

The calibration curve is described by the mathematical equation given in equation 4.1. The coefficients are presented with 95 % interval confidence errors.

$$y_{\mathrm{TDNMR}} = (13.61 \pm 2.70) + (11.58 \pm 0.54)\mathrm{DPU}_{\mathrm{dipped\ cord}} \quad (4.1)$$

From observing the confidence interval for the slope, it can be concluded that the slope estimate is very close to 11.58, so it is significantly different from zero (p-value inferior to 0.05). However, the confidence interval of the intercept is larger because of the greater standard error magnitude of the intercept (1.21).

The statistical parameters for the nylon's regression are presented in Table 4.3

Table 4.3 –Linear regression statistical measures for the nylon calibration curve

s_{R}	R^2 (%)	R
1.64	99.6	0.998

The calibration curve has a residual standard error of 1.6 units of TD-NMR instrument response (Table 4.3), indicating a small deviation of the data from the fitted regression line, which contributes to a narrow mean response confidence interval as can be seen in Figure 4.1.

The coefficient of determination, R^2, has a value of 99.6 % and the correlation coefficient, R, is very close to 1 (0.998), indicating a strong correlation between the signal of TD-NMR and the DPU values in the range of the DPU values considered. All parameters indicate the regression is strong, well-adjusted to the experimental values and produces predictions with minor uncertainties.

Since the purpose of the calibration curve is measuring the dip content of samples in the TD-NMR device, one of the most relevant parameters associated with this calibration was the standard error of the prediction value of DPU given by TD-NMR.

For the calibration curve developed for nylon, a 95 % confidence interval was calculated for a hypothetic sample with a value of $\mathrm{DPU}_{\mathrm{dipped\ cord}}$ of 4.8 %, which corresponds to a $\mathrm{DPU}_{\mathrm{greige\ cord}}$

equal to the target of the material (5 %). The error associated to the prediction was calculated to this value of DPU because the samples measured in production always have dip contents near the target.

For this value of $\mathrm{DPU}_{\mathrm{dipped\ cord}}$, the standard error of prediction, s_{x_0}, is 0.092 %. Since the 0.05 critical value of the two-tailed t-Student distribution with 10 degrees of freedom is 2.228, the 95 % prediction interval for this measurement would be $\mathrm{DPU}_{\mathrm{dipped\ cord}} = (4.76 \pm 0.21)$ %, or, in terms of mass of dip per mass of greige cord, $\mathrm{DPU}_{\mathrm{greige\ cord}} = (5.00 \pm 0.22)$ %.

It is concluded that the uncertainty associated to this measurement is about 4.4 % of the DPU value, which was considered an acceptable amount.

In the validation phase, instead of the 30 samples that the protocol dictates, only 21 samples were obtained since the fabrics under study were not produced frequently. These samples comprised not only the reference fabric, but also the rest of the variations of the Contitech nylon group, otherwise it would not be possible to have enough samples to conduct an appropriate validation. The results of the validation step are presented below in Figure 4.3.

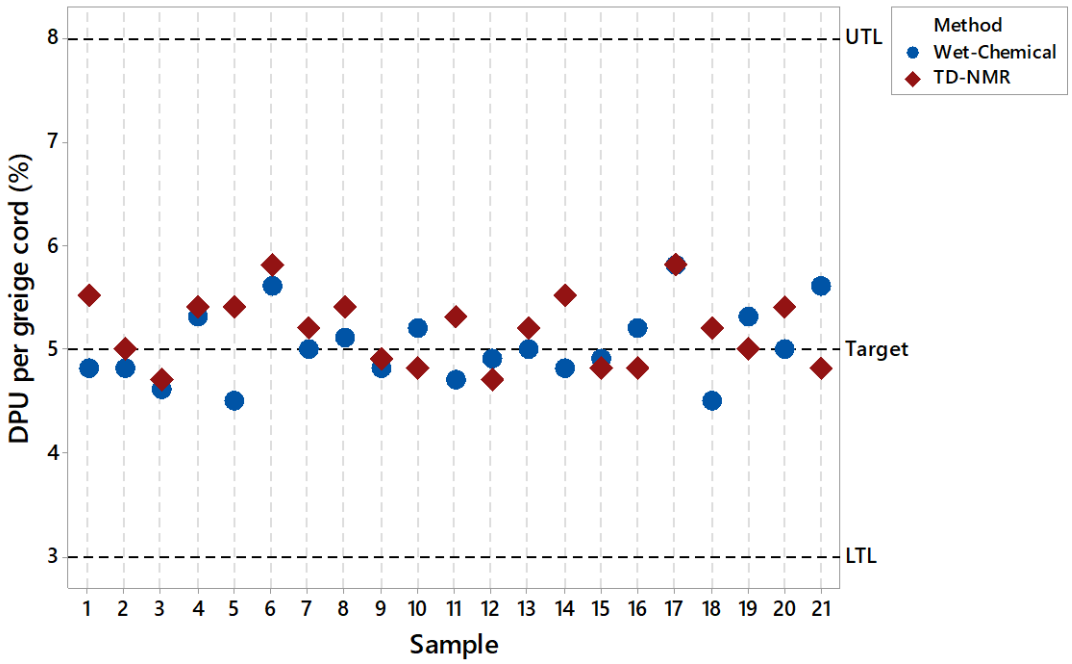


Figure 4.3 - Validation of the calibration curve for nylon: comparison between the TD-NMR measure and the wet-chemical method values.

The data related to the TD-NMR measurements made for the validation phase can be accessed in table A.3 of Appendix A.

It is possible to see that the DPU values obtained using the TD-NMR device round the target (5 %) and are close to the ones obtained from production through the wet-chemical method.

Nevertheless, to be able to consider the calibration curve valid, it was necessary to prove that the two methods did not differ using a statistical test.

Firstly, a hypothesis test was made to verify if both methods produce DPU values with equal variance (see Table A.4 of Appendix A). The test results showed a p-value superior to 0.8, far greater than the significance level defined of 0.05, concluding that nothing indicates that the DPU values from both methods have different variances.

Thus, a two-sample t-test assuming equal variances was conducted to test if the DPU means of both methods differ. The test returned a p-value of 0.179 greater than 0.05, so there is no evidence that both DPU means could be considered different. The results of the test can be better consulted in Table A.5 and Figure A.1 of Appendix A.

Because the number of samples used was inferior to the value established in Continental's protocol, it was important to assure the 21 samples were enough. Power curves were developed for 21 and 30 samples with a difference in means of 0.938, following the criteria of approval for the material in study, and an assumed standard deviation of 0.35, based on the dispersion of the data. These power curves are presented in Figure 4.4.

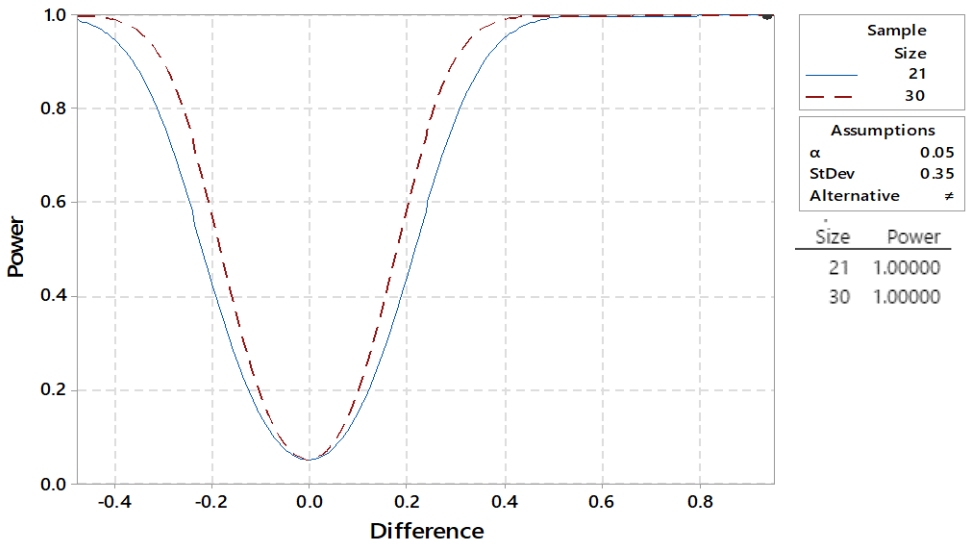


Figure 4.4 – Power curves for sample size of 21 and 30 for α of 0.05, standard deviation of 0.35 and difference of 0.938.

The power curves obtained show that a sample size of 21 had the same power as sample size of 30, so 21 samples were sufficient to perform the validation of the curve. With this, it was concluded that the curve respected all the criteria for approval.

4.2 Rayon material

4.2.1 Validation of the filtration method

To assess if the glass wool had a major influence in the filtration step of the wet-chemical method, a sample was treated with a high dip concentration, followed by its dip content assessment using the wet chemical method with and without glass wool. The results from this first study are presented in Table 4.4.

Table 4.4 – Preliminary study for the filtration step of the wet-chemical method: results of the filtration with and without glass wool

Filtration step	DPU (%)	Mean (%)	Standard Deviation (%)
Without Glass wool	6.14 5.95 6.02	6.04	0.096
With Glass Wool	7.05 6.85 6.03	6.64	0.54

In the absence of glass wool, the filtration was very time consuming because of the high concentration of dip that caused the clog of the crucible, taking between 10 to 25 minutes instead of mere seconds when using glass wool. However, from the results was possible to notice that, when filtrated with glass wool, the sample presented a higher DPU value and showed a larger deviation. To determine if this difference was significant and resultant from the use of glass wool, a further study was conducted.

A total of 4 samples from production were tested using the wet-chemical method with and without glass wool in the filtration step. Five trials were made to each of the possibilities. The results are presented in Table 4.5.

Since the production conditions are always more or less the same in relation to the dip recipes and operation conditions, the samples were considered as replicas and the results were divided between two populations: results of DPU tested with glass wool and results of DPU tested without glass wool.

Table 4.5 – Results from the study of the influence of the glass wool in the DPU

	Without Glass Wool			With Glass Wool		
Sample	DPU (%)	Mean (%)	Standard deviation (%)	DPU (%)	Mean (%)	Standard deviation (%)
A	3.14 2.90 3.28 3.05 2.83	3.04	0.18	4.65 4.01 5.26 5.23 4.22	4.67	0.57
B	3.25 3.53 3.54 3.14 3.25	3.34	0.18	4.50 5.08 3.96 4.51 6.08	4.83	0.81
C	3.10 3.15 3.05 3.02 3.12	3.09	0.05	3.08 3.88 3.42 3.24 3.91	3.51	0.38
D	3.51 3.61 3.44 3.50 3.62	3.54	0.08	4.10 3.76 3.81 4.04 4.88	4.12	0.45

A hypothesis test was conducted to assess if the DPU variances obtained with and without glass wool could be considered equal. The p-value obtained was inferior to the significance level, indicating that the variances were significantly different. Results of this test can be consulted in Table A.6 from Appendix A. Therefore, the data obtained were analyzed using a two-Sample t-test, assuming the variances were not equal, to evaluate the difference in the means. The output of the test devolved a p-value of 7.3×10^{-6}, far lower than the standard significance level defined, showing that the difference between the two population' means is significant. The DPU means presented an estimated difference of 1.03 % with a confidence interval of (0.66;1.39) %.

Once it was proved that the use of glass wool led to mean values of DPU significantly inflated, the standard deviations of the populations were studied to quantify the disparity within the results. The standard deviations obtained were 0.750 with a 95 % CI of (0.544;1.146) for the method with glass wool and 0.241 with a 95 % CI of (0.198;0.325) for the method without glass wool. It was concluded that the use of glass wool caused about three times more variability (standard deviation) in the results. Table A.7 of Appendix A shows the results of the test.

The considerable dispersion in results obtained using glass wool can be explained by the drying time that proceeds the filtration. The standard procedure dictates that the crucibles must be dried for 2 hours after filtration, but this procedure only considers the crucible with the

filtrated mixture. It is possible that, when introducing glass wool, this drying time becomes inadequate and is not sufficient to guarantee the total drying of the wool, introducing variations in the final mass of the crucible and, consequently, in the DPU results.

The use of glass wool was introduced because of the difficulty in the filtration on samples with high DPU, since the crucible would clog with the amount of dip. In practice, it is only necessary to evaluate samples with such high concentrations of dip when developing a calibration curve for the TD-NMR device. During normal production, the dip content is always around the target (3.5 %), so it is always in intermediate ranges of DPU. Consequently, it was concluded that it would not be beneficial to change the method and adjust the procedure just for the realization of the calibration curve, especially as such tests would not have to be repeated after the completion of the calibration. Thereby, it was necessary to remake the previous calibration curve using the filtration without glass wool.

4.2.2 Calibration curve and validation

For the construction of the calibration curve, numerous dipping treatments and DPU assessments were made until the 4 points presented in Table 4.6 were reached.

Table 4.6 – Dipping results and dip assessment via wet-chemical method for rayon curve

Curve Points	DPU (%)	Mean (%)	Standard deviation (%)
A	1.63 1.45 1.43	1.50	0.11
B	3.08 3.37 3.12	3.19	0.16
C	4.46 4.15 4.22	4.27	0.16
D	5.19 5.13 5.28	5.20	0.073

Following the same procedure as before, three samples from each point correspondent cord were analyzed in the TD-NMR (see Table A.8 and A.9 of Appendix A) and a linear regression correlating the TD-NMR signal and the DPU values was constructed using Minitab 18, to obtain the curve shown in Figure 4.5.

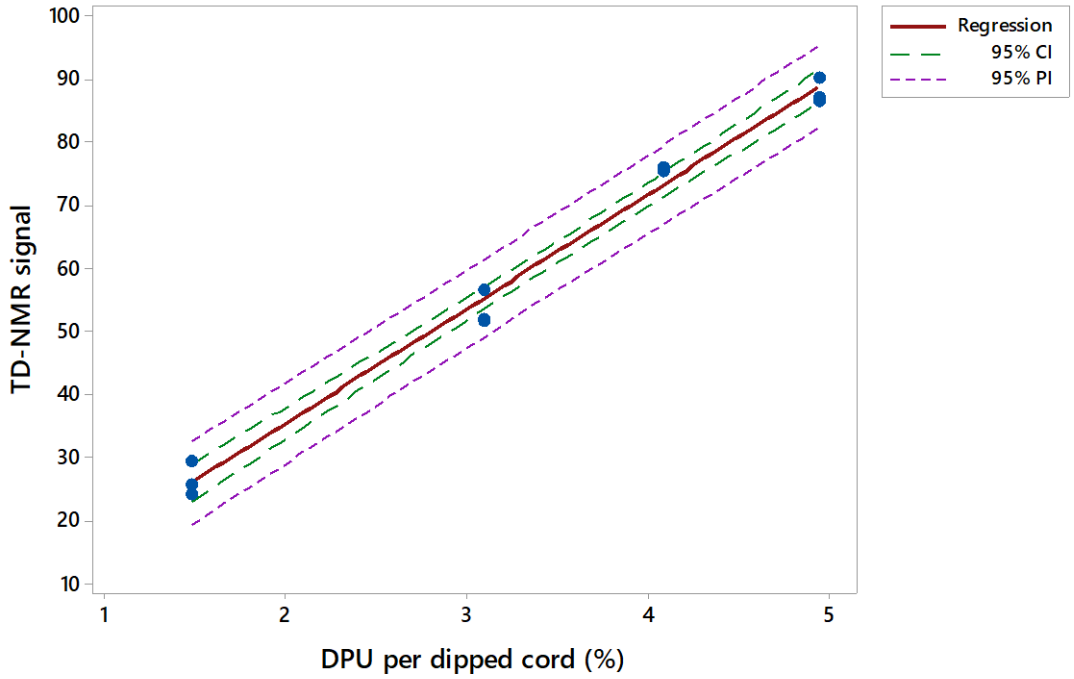


Figure 4.5 – Calibration curve for rayon treated with cokoon, with a 95% confidence and prediction interval.

The residual plots for this calibration curve are displayed in Figure 4.6. These graphs were studied to confirm the assumptions for the linear model (errors approximately normally distributed, with a mean of zero, random variability, and constant variance).

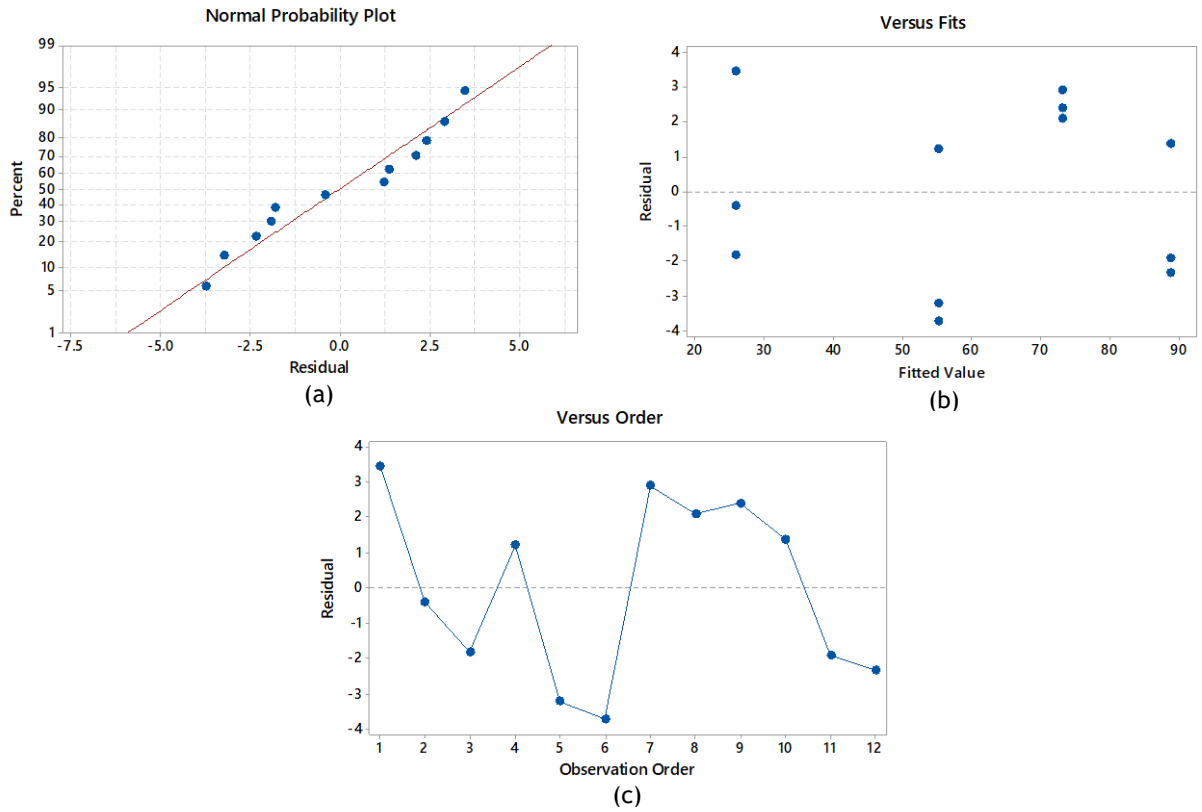


Figure 4.6 – Residuals plots for the linear regression model of the rayon's calibration curve.

From the residuals, it is possible to confirm that the calibration curve meets the assumptions of the linear regression model: the errors appear to follow a normal distribution, as the points are distributed along a straight line in in the normal probability plot (Figure 4.6 – a), seem to be random, with a mean of zero and constant variance, since the points in the fit plot (Figure 4.6 – b) are equally distributed between both sides of the x-axis, without forming a pattern, and are independent from the order in which were obtained, as it is indicated by the random pattern in the order residual plot (Figure 4.6 – c). The linear model was considered adequate, based on this analysis.

The coefficients obtained for this curve, with respective 95 % confidence intervals, are shown in Table 4.7.

Table 4.7 - Regression coefficients for the rayon's calibration curve and its statistical characteristics

Term	Coefficient	Standard Error	95% CI	P-Value
Intercept	-1.08	2.17	(-5.91; 3.75)	0.63
Slope	18.19	0.60	(16.86; 19.52)	$3x10^{-11}$

The mathematical expression that translates the calibration curve obtained for rayon dipped in Cokoon is presented in Equation 4.2.

$$y_{\mathrm{TDNMR}} = (-1.08 \pm 4.83) + (18.19 \pm 1.33)\mathrm{DPU}_{\mathrm{dipped\ cord}} \qquad (4.2)$$

It can be seen, from Table 4.7, that the linear regression is significant because the p-value associated with the slope is inferior to 0.05. The small amplitude of the confidence interval for the slope of the curve indicates a precise estimation for this parameter. Regarding the intercept term, the considerable uncertainty associated is due to the greater magnitude of the standard error of intercept (2.17).

The parameters that characterize this linear regression are displayed in Table 4.8.

Table 4.8 - Linear regression statistical measures for the Cokoon-dipped rayon's calibration curve

s_{R}	R^2 (%)	R
2.66	98.9	0.994

The statistical measures presented in Table 4.8 show evidence of a strong correlation between the signal of TD-NMR and the DPU values in the range of the DPU values considered, translated by a value of 98.9 % and a correlation coefficient of 0.994, very close to 1. The residual standard error of 2.66 does not indicate a considerable deviation of the data from the fitted line. It was concluded the calibration curve achieved showed indicators of good capability.

The uncertainty of the dip content measurement by TD-NMR using the calibration curve developed was calculated, following the same procedure it was used for the nylon calibration curve. Following the specifications for the target of this material, the prediction interval was calculated to a $\mathrm{DPU}_{\mathrm{dipped\ cord}}$ of 3.38 %, which corresponds to a $\mathrm{DPU}_{\mathrm{greige\ cord}}$ equal to the target of the material (3.5 %). The prediction standard error, s_{x_0}, obtained was 0.094 %.

Using the critical value of the two-tailed t-Student distribution for a significance level of 0.05 and 10 degrees of freedom (2.228), the 95 % prediction interval for this measurement would be $\mathrm{DPU}_{\mathrm{dipped\ cord}} = (3.38 \pm 0.21)$ %, or, in terms of mass of dip per mass of greige cord, $\mathrm{DPU}_{\mathrm{greige\ cord}} = (3.5 \pm 0.22)$ %. The TD-NMR measurements of samples with a dip content equal to the target have an uncertainty of about 6.4 % of the DPU value, which was also considered an acceptable amount, although it would be preferred a lower value for this uncertainty.

When proceeding to the validation phase and facing the DPU results of the samples from production, it was noticed that the values were higher than expected and had a lot of variation. For that reason, it was decided that it was prudent to repeat the dip pick-up assessment of such samples. Since the validation should be made with 30 samples and the wet-chemical method implies the realization of the method in triple, the repetition of the DPU assessment through this method for 30 samples would be very time consuming and unsustainable. As a result, and following the reasoning applied to the nylon material, the number of samples necessary to validate the rayon calibration curve was studied using power curves.

To conduct the power test, the difference considered corresponded to the criteria established for the maximum deviation between the TD-NMR and the Wet-chemical results, that, in case of this rayon material, was 0.563. Regarding the standard deviation, it was considered the same variation that was observed for the nylon validation (0.35). The power curves obtained are presented in Figure 4.7.

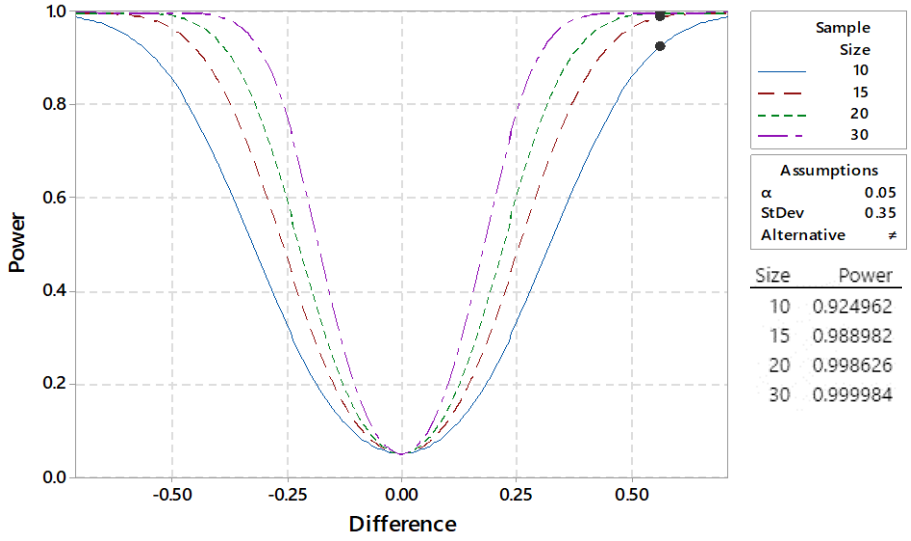


Figure 4.7 - Power curves for sample size of 10, 15, 20 and 30 for α of 0.05, assumed standard deviation of 0.35 and difference of 0.563.

As an outcome from the power test developed, it was decided that 15 samples would be tested and used in the validation, instead of the 30 samples initially proposed. This decision was based on the fact that half the number of samples would considerably reduce the time needed to remake the calculations of DPU, without compromising the accuracy, since reducing the number of samples to 15 would only diminish the power of the test by about 1 %.

Continuing the process of validation, 15 samples from production were tested using the wet-chemical method to re-evaluate the DPU. Appendix A contains the results from the DPU assessment in Table A.10 and from the sample preparation for the TD-NMR measurements in Table A.11. The comparison between the wet-chemical method results and the TD-NMR measurements are presented in Figure 4.8.

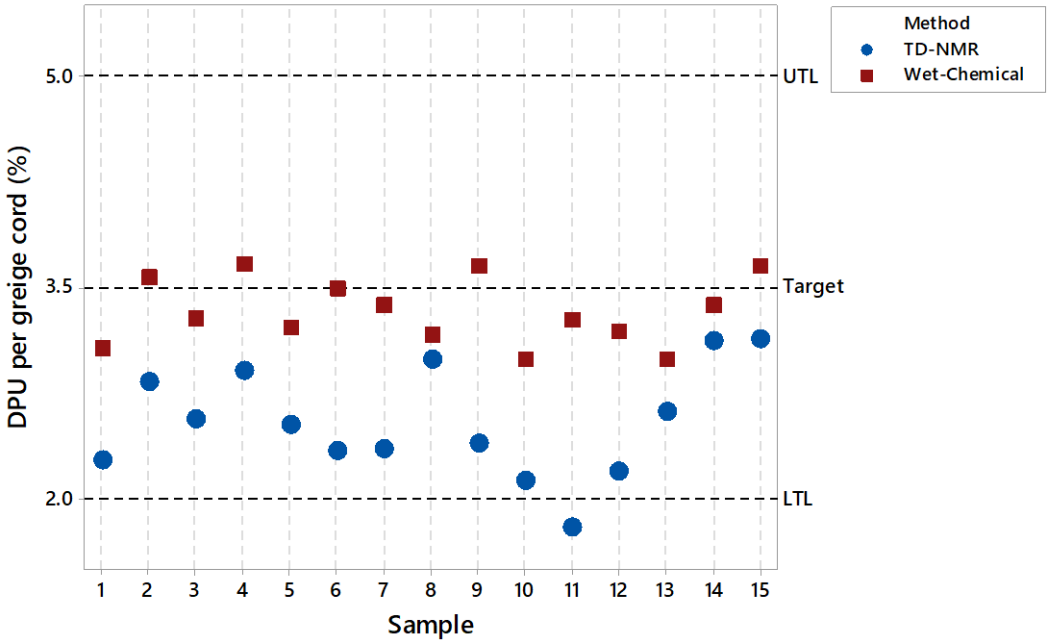


Figure 4.8 - Validation of the calibration curve for rayon: comparison between the TD-NMR measure and the wet-chemical method values.

From observation of Figure 4.8 it is possible to notice that the values obtained through TD-NMR show larger variation and a tendency to be considerably lower than those obtained through the wet-chemical method. Because of these observations, the statistical analysis for this validation was made by conducting a two-sample t-test (see Table A.12 and Figure A.2 of Appendix A), to evaluate the means of both populations, but the variances were not assumed to be equal. The p-value of the test was $10^{-6,}$ indicating that the means differ. The estimated difference is 0.783 with a 95 % mean difference confidence interval of (0.545;1.034). These results proved that the DPU means of both methods could not be considered equal and there is evidence that the difference between them is possibly superior to the criteria established (0.563), so it was concluded that the calibration curve developed did not meet the criteria for approval.

The calibration curve illustrated in Figure 4.5 was not the first one developed during this project. Numerous attempts were made to obtain a group of points that would lead to a well-adjusted linear regression within a meaningful range of DPU values. Figure 4.9 illustrates two different calibration curves, the final curve obtained and one of the discarded trials made with a different group of samples in the same range of DPU. The final curve that is shown in Figure 4.5 was the result of multiple trials and is the one that led to better TD-NMR measurements. Still, the results from the validation phase disclosed and the disparity seen in the different trials, as seen in Figure 4.9, suggests that the TD-NMR calibration obtained does not represent a solid method to assess the dip content of the Cokoon-dipped rayon material.

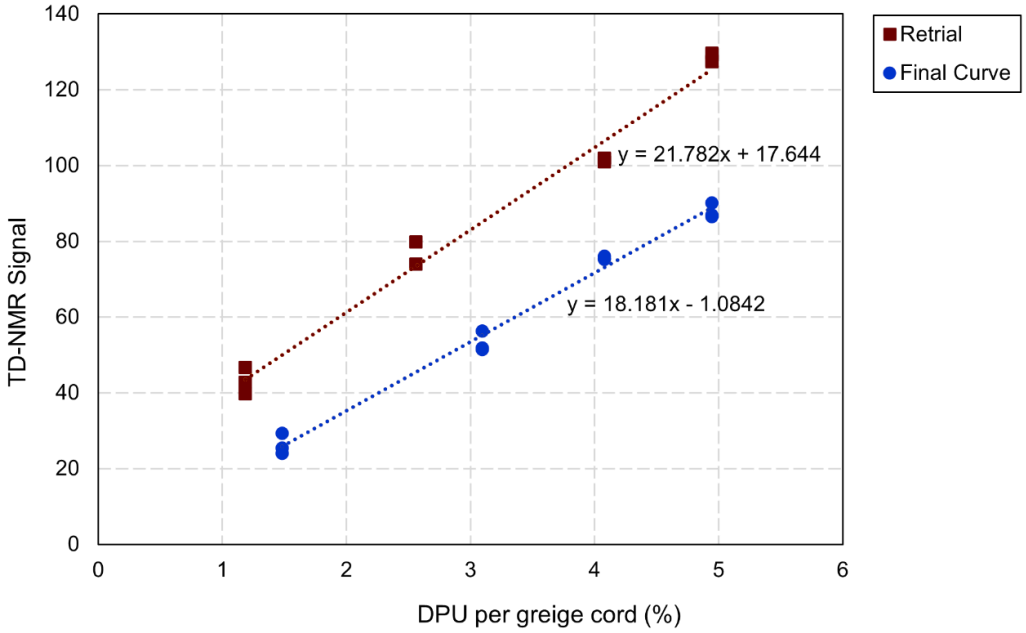


Figure 4.9 – Comparison between two different calibration curves obtained for the same rayon material, from different groups of samples.

The data related to the points of the retrial calibration curve can be consulted in Table A.13 of Appendix A.

4.2.3 Study of the influence of the wet-chemical method on the Cokoon

The work developed for the rayon material was a remake of a previous attempt to calibrate the TD-NMR device that resulted in a calibration curve that could not meet the criteria because of significant variations between the results obtained through TD-NMR and the results obtained through the wet-chemical method.

Initially, the optimization of the filtration step with the addition of glass wool was studied in the belief that it could be the cause of such variations in the results. After repeating the whole process of development of a new curve and respective validation, it was concluded that the calibration curve was, yet again, failing the criteria for approval. Since the curve developed

followed the procedure established, all steps were carefully made and even repeated several times to obtain a curve with the smaller variation possible and, taking into account that the TD-NMR device was never calibrated for any material treated with the Cokoon dip before, it was established that the difficulties encountered with the calibration for this material could be associated with the dip itself.

The Cokoon dip has a composition significantly different from the standard dipping solution that has been used until now. This could mean that the wet-chemical method, developed for the RFL dip, might not be compatible with the constituents of the Cokoon. It can also be happening that the measurement by TD-NMR might be influenced by some components in this new dip and it is in need of further optimization.

In an effort to understand if the wet-chemical method was influencing the results of DPU when testing cords treated with Cokoon, a study was developed in which the method was applied to dip only. The goal was to compare the initial mass of the dip sample with its final mass, after completion of the method, to understand if the method was influencing the mass of dip present in the dipped cords. For that, samples of dip were dried and cured at the temperatures used in the normal production of the cords and the chemical method was normally followed.

Figure 4.10 shows the preparation of the samples and the appearance of the dip after the process of drying and curing. The conditions used in this step are presented in Table 4.9 and the results are shown in Table 4.10.

Table 4.9 – Conditions for preparation of dip samples

Step of preparation	Temperature (˚C)	Duration (min)
Drying	170	10 to 13
Cure	190	10 to 13

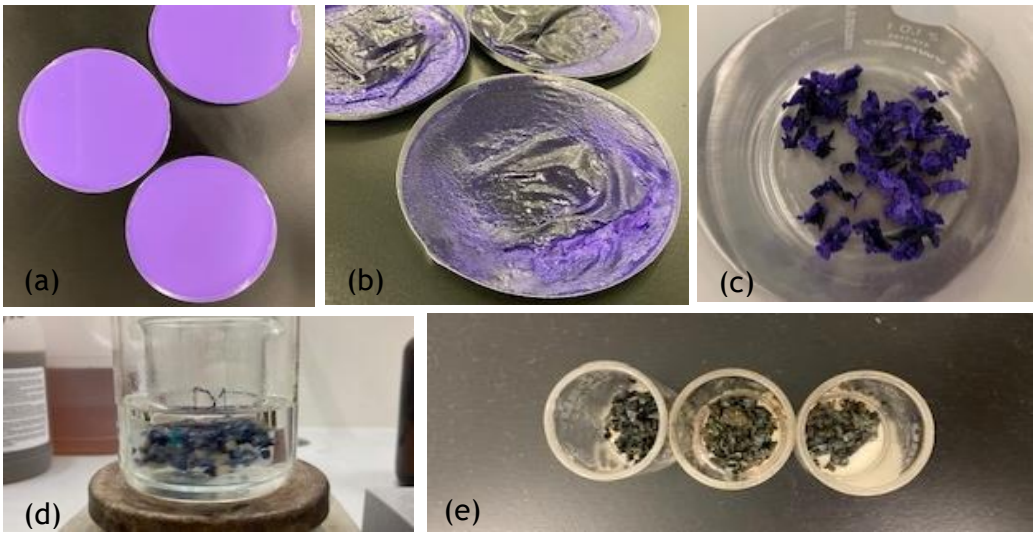


Figure 4.10 – Wet-chemical method applied to dip samples only, from preparation of samples – (a), (b), (c) – to realization of the chemical method – (d), (e) -.

Table 4.10 – Results from the study of the influence of the wet-chemical method in the Cokoon dip

Initial mass of dip (g)	Final mass of dip (g)	Mass variation (%)
0.8607	0.9535	10.8
0.8613	0.9577	11.2
0.8543	0.9415	10.2
0.9429	1.0415	10.5
1.0967	1.1416	4.1
1.1660	1.2294	5.4
0.8028	0.8119	1.1
0.6608	0.7706	16.6
1.0429	1.1215	7.5

The results indicate that the samples are gaining mass during the wet-chemical method. This may be in the cause of the major variations observed during the construction of the calibration curve. For groups of samples within the same range of DPU, the calibration curves obtained had major variation regarding the intercept, as seen in Figure 4.7, consequence of TD-NMR measurements with magnitudes considerably different for the sample with approximately the same DPU. Assuming that this method of assessment of the dip content is influencing the mass of dip in the cords that are tested, the reference values given to the TD-NMR device when constructing the calibration curve, would be more or less discrepant from the real value, depending on the mass variation that occurred, and so, two different attempts of obtaining a calibration curve would present main differences from one to another, as it was contemplated.

These increments of mass may be related to the solution of acid formic with zinc chloride that is used in the dissolution of the cords. It is possible that the zinc ion is reacting with the dip and changing its chemical composition to a product with higher molecular weight, or, it can be adsorbing in the dip, increasing the sample weight. Further studies should be conducted to understand what is in the cause of this increment of mass, and if it is the reason for such variation in the calibration curve and how to resolve this problem.

4.2.4 Study of mechanical properties

Since the Cokoon dip is starting to be used in the normal production of some materials, like the rayon fabric that has been object of study in this master thesis, it is important to assure that it does not compromise the performance and characteristics of such materials.

In the early stages of tests with Cokoon, it was noticed that the rayon cords, when increasing the dip content in the cords, presented atypical values of breaking force, below the minimal defined in the specifications. To assure this situation wasn´t persisting and would not influence the performance of the material in the future, this mechanical property was studied.

Although these abnormal values were only seen in the breaking force, tests of stiffness were also conducted because it was noticed some rigidity and apparent lack of malleability in cords with higher dip content. The results of force elongation and stiffness can be consulted in Figure 4.11 and 4.12, respectively. Table A.14 of Appendix A shows the data of the stiffness and elongation tests conducted.

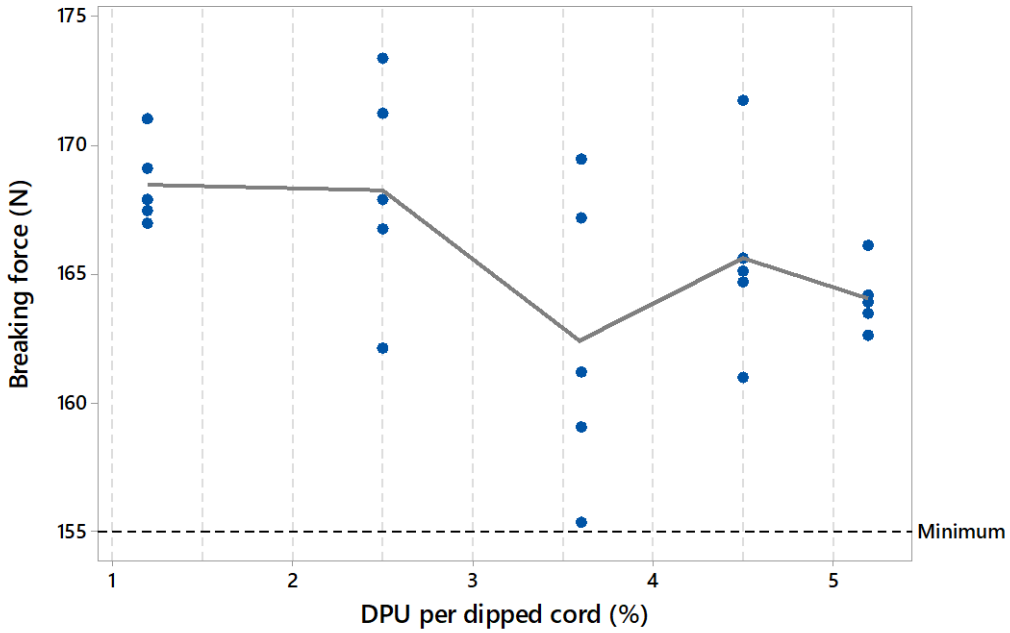


Figure 4.11 - Results for the Load-Elongation study and mean values for each sample.

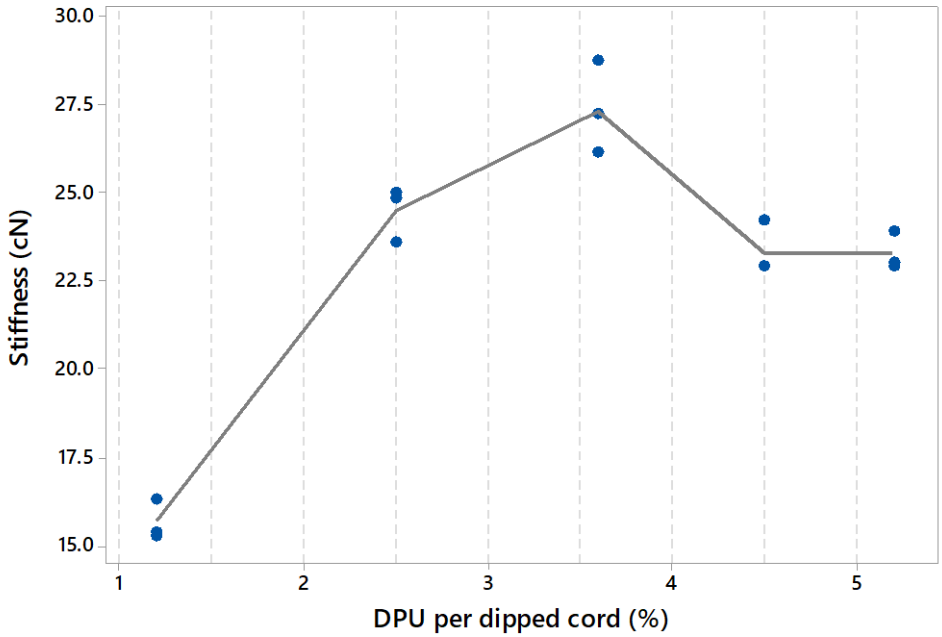


Figure 4.12 – Results of the Bending Stiffness study and mean values for each sample

The purpose of the elongation study was to prove that this property was not being influenced by the dip content of the cords, as it should not. For that, an ANOVA was conducted, obtaining a p-value of 0.085, superior to 0.05, which proves that all means are equal (consult table A.15 of Appendix A). Therefore, it was concluded that the dip content is no longer significantly influencing the elongation of the cords.

For the study of stiffness, the goal was only to check if there was a big increase on the stiffness for cords with high content of dip. With the increase in the DPU, there was a palpable increase in the rigidity of the cords but Figure 4.12 shows that, although there was a considerable increase in the stiffness values from the lowest value until the mid-range of DPU, the values stagnated after that. The stiffness property is not specified in the specification sheet for the rayon material, which means that there is not a minimum and maximum value that it must obey, so the observation of the values and the recognition that the bending stiffness values did not escalate exponentially with the increase of DPU, remaining at relatively low values, is enough to conclude that this material does not present abnormal behaviour regarding this property.

5 Conclusion

This master dissertation had two initially defined goals: calibration of the TD-NMR device for an RFL-treated group of nylon fabrics and a rayon fabric treated with the new Cokoon dip.

Regarding the nylon materials, the goals were achieved. The linear regression that constitutes the calibration curve presented both coefficient of determination, R^2 and correlation coefficient, R, above 0.99, and confidence and prediction intervals very narrow, so all the parameters of the curve indicated a strong linear adjustment.

To determine the precision of the calibration developed, the 95 % confidence bounds associated with the measurement of a sample with a DPU equal to the nylon's target were calculated, obtaining a value of $\mathrm{DPU}_{\mathrm{greige\ cord}} = (5.00 \pm 0.22)$ %, so the uncertainty associated with this measurement is about 4.4 % of the DPU value.

The validation for the nylon's calibration curve was made with 21 samples instead of the 30 that should normally compose the validation because there were no more samples available. It was confirmed that this reduction did not affect the power of the validation. The TD-NMR measurements were compared with the DPU values obtained through the chemical method, and the statistical analysis of the data concluded that the two methods were not considerably different.

Since the calibration curve obtained for the nylon materials was well adjusted and the validation results fitted all the criteria for approval, the calibration was successfully completed. The DPU assessment for these materials can, from this moment, be made through TD-NMR spectroscopy, which implies less time and more reliable assessments.

For the rayon fabric dipped with Cokoon, the goal of enabling its dip content assessment through TD-NMR was not achieved. The filtration step of the wet-chemical method was first studied to understand if the use of glass wool could be the origin of the difficulties related to the previously made calibration curve for this material. It was concluded that the use of glass wool was influencing the results (about three times more variability and inflated DPU values) and the calibration curve should be remade without it.

The calibration curve remade for the Cokoon-dipped rayon showed a value around 0.99 and a narrow confidence and prediction interval. Using the calibration curve developed to assess the dip content of a sample with a DPU equal to the target of the material, the 95 % confidence bounds of the measurement would be $\mathrm{DPU}_{\mathrm{greige\ cord}} = (3.50 \pm 0.22)$ %, which corresponds to an uncertainty of about 6.4 % of the DPU value.

The validation was carried out with only 15 samples because it was concluded that it would be enough to detect differences between the methods without significantly compromising the power of the test (1% less). The results of the validation phase did not allow the validation of the curve since it showed that the means of both populations had a potential difference of 0.783, superior to the criteria established for the material (0.563). It was concluded that the calibration curve developed did not meet the criteria for approval.

Since it was not possible to conclude the calibration of the TD-NMR device for the Cokoon-dipped rayon, and because there were major differences between the various attempts of constructing a calibration curve, the wet-chemical method was applied to samples of dip only to determine if this method could be interfering with the amount of dip in the cords, justifying the difficulties in the calibration. The results indicated a gain of mass between 1 % and 17 % in the dip samples after going through the wet-chemical method. The increase in the sample's mass may be caused by a chemical reaction or adsorption of a component during the dissolution phase of the method, particularly because of the use of Zinc Chloride in the dissolution acid, as the zinc ion is quite reactive. It was agreed that further studies must be conducted to confirm what is in the cause of such mass gains and how extensively this affects the process of calibration.

Because there were reports of abnormal behavior on the force-elongation parameter, tests for this and the stiffness property were conducted to determine if the DPU values influenced these. The force-elongation results were analyzed, and it was proved that the means of the results obtained for different DPU amounts could all be considered equal. Concerning the bending-stiffness tests, although there was an apparent increase in rigidity, the motive for which the study included this mechanical property, it was possible to determine that, for higher ranges of DPU, the bending force obtained was stable and did not differ significantly between samples. It was concluded that none of these properties were influenced by the amount of Cokoon dip in the cord.

6 Assessment of the work done

6.1 Objectives Achieved

The calibration of the Contitech nylon fabrics was successfully developed and approved, meaning that the dip content of these nylon fabrics can be tested using TD-NMR from now on. This alternative will reduce the time consumed testing the samples, while improving the precision of the results.

Regarding the rayon fabric treated with Cokoon, it was not possible to obtain a viable calibration curve. However, through the work developed, it was concluded that it is necessary to re-evaluate the methods and procedures normally used before proceeding to the analysis of materials treated with the Cokoon dip, and new needs for future work emerged.

6.2 Limitations and future work

The major limitation throughout this work was the time. The dip content assessment through the wet-chemical method takes about 4 hours per sample and, although it was possible to make more than one dip pick-up simultaneously, the limit was always three, at the same time the laboratory must be shared with others so the normal activities of the company can carry on. Because of the need to coordinate the material and since more than 200 DPU were made in the course of this project, the limitations of time did not allow the work to be completed to the extent that would be the most advantageous.

From the work developed for rayon, it became clear that it is necessary to conduct further studies regarding the application of the wet-chemical method in cords treated with the Cokoon dip, and so, to rule out any possibility, it would be advantageous to do the following experiments:

- Perform the same study of the chemical method on samples of RFL and compare results;
- Perform a calorimetry test for the samples before and after the wet-chemical study, with the purpose of understanding if there are changes in the composition (allow the understanding if the dip is reacting with the acid solution);
- Perform the wet-chemical method with different dissolution agents, such as sulphuric acid instead of formic acid, as happens in other textile companies;
- Perform the calibration of the TD-NMR with reference values obtained through the weighing method and see if the calibration is more stable;
- Analyse the possibility of the composition of the Cokoon being influencing the TD-NMR measurement.

6.3 Final Assessment

During the around 4 months of practical work that culminated in this dissertation, there were numerous difficulties and setbacks. Weeks of works ended up in dead-ends and results that should lead to conclusions were, a lot of times, an arouse of new problems. The work developed for the rayon material was very challenging and required a lot of effort and countless remakes and retrials. These difficulties are the reason I am the proudest of this dissertation and the most grateful for having the opportunity to embrace this particular theme and face this challenge. I hope that future thesis continues the studies that were developed and carry on the work that was left to be made, and that Continental benefits from these, as I benefited from this experience.

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Appendix A

A.I Nylon Calibration Curve

Table A. 1 – DPU values for nylon calibration points through wet-chemical method

Curve Point	m_1 (g)	m_2 (g)	m_3 (g)	DPU $_{per\ greige\ cord}$ (%)	Mean (%)	Standard deviation (%)
A	1.0523	30.4305	30.4543	2.31	2.33	0.01
	1.1562	30.3983	30.4247	2.34		
	1.1078	30.526	30.5513	2.34		
B	1.1123	30.3979	30.4376	3.70	3.65	0.09
	1.0411	26.3339	26.3695	3.54		
	1.0846	26.6875	26.7262	3.70		
C	1.0900	30.4146	30.4711	5.47	5.49	0.11
	1.0761	30.5275	30.5826	5.40		
	1.0891	30.2936	30.3514	5.60		
D	1.0848	30.4353	30.5179	8.24	8.12	0.05
	1.1594	30.4384	30.5263	8.20		
	1.0621	30.3969	30.4768	8.13		

Table A. 2 – Nylon's calibration curve points resultant from the TD-NMR measurement of the calibration samples

Sample	$m_{tube+lid}$ (g)	$m_{tube+lid+sample}$ (g)	m_{sample} (g)	DPU $_{per\ greige\ cord}$ (%)	DPU $_{per\ dipped\ cord}$ (%)	Signal
A1	16.3331	16.7308	0.3977	2.33	2.28	39.510
A2	16.2294	16.6608	0.4314		2.28	38.555
A3	16.2503	16.7145	0.4642		2.28	38.222
B1	16.2970	16.7575	0.4605	3.65	3.52	54.040
B2	16.3489	16.8399	0.4910		3.52	55.272
B3	16.1892	16.5721	0.3829		3.52	55.389
C1	16.3574	16.8558	0.4984	5.49	5.20	75.576
C2	16.1566	16.5751	0.4185		5.20	75.832
C3	16.2986	16.6949	0.3963		5.20	75.516
D1	16.190	16.6891	0.4991	8.12	7.51	101.107
D2	16.2482	16.7134	0.4652		7.51	97.620
D3	16.2354	16.6826	0.4472		7.51	99.604

Table A. 3 – Preparation of samples for the validation of the nylon calibration curve, respective measure in the TD-NMR device and conversion

Sample	$m_{tube+lid}$ (g)	$m_{tube+lid+sample}$ (g)	m_{sample} (g)	$DPU_{per\ dipped\ cord}$ (%)	$DPU_{per\ greige\ cord}$ (%)	Mean (%)
1	16.2878	16.7088	0.421	5.182	5.465	5.50
				5.194	5.479	
				5.259	5.551	
2	16.2315	16.6805	0.449	4.728	4.963	5.00
				4.759	4.997	
				4.795	5.037	
3	16.1200	16.5849	0.465	4.603	4.825	4.74
				4.506	4.719	
				4.470	4.679	
4	16.1630	16.5775	0.415	5.198	5.483	5.45
				5.173	5.455	
				5.129	5.406	
5	16.2097	16.6763	0.467	5.09	5.363	5.37
				5.102	5.376	
				5.084	5.356	
6	16.2762	16.7331	0.457	5.320	5.619	5.83
				5.568	5.896	
				5.628	5.964	
7	16.2626	16.7429	0.480	4.884	5.135	5.19
				4.945	5.202	
				4.973	5.233	
8	16.2286	16.6787	0.450	5.081	5.353	5.36
				5.043	5.311	
				5.14	5.419	
9	16.2802	16.7608	0.481	4.589	4.810	4.85
				4.643	4.869	
				4.647	4.873	
10	16.1689	16.6140	0.445	4.551	4.768	4.80
				4.575	4.794	
				4.607	4.829	
11	16.3662	16.7877	0.422	5.095	5.369	5.31
				5.041	5.309	
				4.991	5.253	
12	16.2961	16.7035	0.407	4.537	4.753	4.74
				4.518	4.732	
				4.526	4.741	
13	16.2667	16.7510	0.484	4.956	5.214	5.23
				4.979	5.240	
				4.971	5.231	
14	16.3372	16.7953	0.458	5.151	5.431	5.47
				5.188	5.472	
				5.207	5.493	
15	16.3623	16.8197	0.457	4.537	4.753	4.81
				4.668	4.897	
				4.55	4.767	

16	16.2525	16.7605	0.508	4.603	4.825	4.77
				4.508	4.721	
				4.541	4.757	
17	16.3141	16.7743	0.460	5.485	5.803	5.82
				5.457	5.772	
				5.553	5.879	
18	16.2142	16.6501	0.436	4.929	5.185	5.17
				4.886	5.137	
				4.925	5.180	
19	16.1412	16.6455	0.504	4.718	4.952	4.95
				4.730	4.965	
				4.712	4.945	
20	16.2124	16.6943	0.482	5.111	5.386	5.41
				5.142	5.421	
				5.141	5.420	
21	16.2059	16.6013	0.395	4.582	4.802	4.78
				4.508	4.721	
				4.596	4.817	

Table A. 4 – Results of the study of variances for the validation of nylon's calibration curve

Variable	StDev	Variance	95% CI for variance
TD-NMR	0.344	0.118	(0.277; 0.470)
Wet-Chemical	0.357	0.128	(0.268; 0.526)

Null hypothesis	$H_0: \sigma_1 / \sigma_2 = 1$
Alternative hypothesis	$H_1: \sigma_1 / \sigma_2 \neq 1$
Significance level	$\alpha = 0.05$

Method	Statistic	DF1	DF2	P-value
Bonett	0.04	1	40	0.847
Levene	0.02	1		0.879

Table A. 5 – Results of the Two-Samples T-Test, assuming equal variances, for the validation of nylon's calibration curve

Sample	Mean	StDev	SE Mean	Difference	Pooled StDev	95% CI for Difference
TD-NMR	5.168	0.347	0.076	0.149	0.352	(-0.071; 0.368)
Wet-Chemical	5.019	0.357	0.078			

Null hypothesis	$H_0: \mu_1 - \mu_2 = 0$
Alternative hypothesis	$H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
1.37	40	0.179

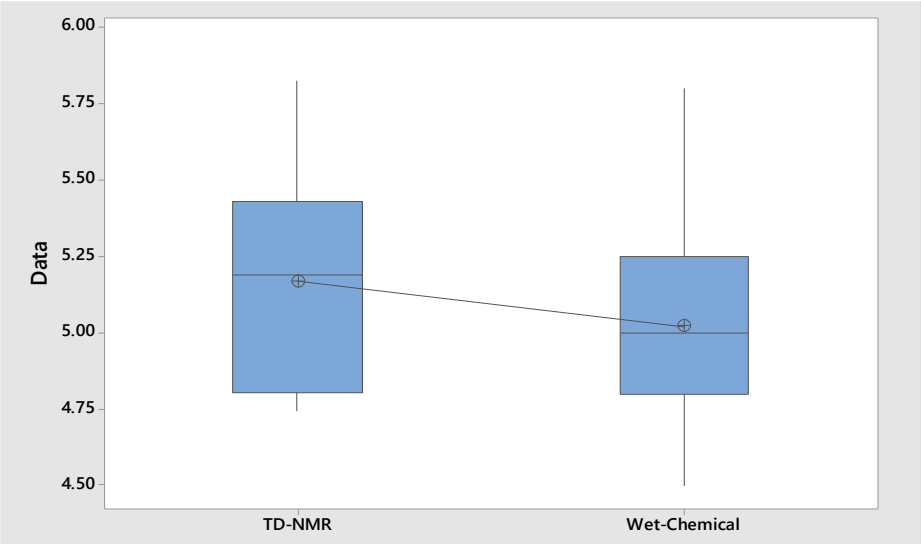


Figure A. 1- Boxplot of the comparison between the TD-NMR and the wet-chemical values for the validation phase of the nylon calibration curve.

A.IStudy of the filtration step of the wet-chemical method for rayon

Table A. 6 – Results for the test of two variances for the validation of the filtration step

Variable	N	Standard deviation	95 % CI	Estimated ratio	Variance
With glass wool	20	0.750	(0.544;1.146)	3.116	0.562
Without glass wool	20	0.241	(0.198;0.325)		0.058
Null hypothesis			H_0: $\sigma_1 / \sigma_2 = 1$		
Alternative hypothesis			H_1: $\sigma_1 / \sigma_2 \neq 1$		
Significance level			$\alpha = 0.05$		

Method	Statistic	DF1	DF2	P-Value
Bonett	11.51	1		0.001
Levene	9.56	1	38	0.004

Table A. 7 – Result of the Two-Sample T-Test, not assuming equal variances, for the validation of the filtration step

Sample	N	Mean	StDev	SE Mean	Difference	95% CI for Difference
With wool	20	4.281	0.750	0.17	1.029	(0.664; 1.394)
Without wool	20	3.252	0.241	0.054		
Null hypothesis				H_0: $\mu_1 - \mu_2 = 0$		
Alternative hypothesis				H_1: $\mu_1 - \mu_2 \neq 0$		

T-Value	DF	P-Value
5.84	22	0.00000703

A.II Rayon Calibration Curve

Table A. 8 - DPU for rayon calibration points

Curve Point	m_1 (g)	m_2 (g)	m_3 (g)	DPU $_{per\ greige\ cord}$ (%)	Mean (%)	Standard deviation (%)
A	1.1395	30.3299	30.3482	1.63	1.50	0.11
	1.3344	26.6871	26.7062	1.45		
	1.4016	26.5061	26.5258	1.43		
B	1.0534	30.4364	30.4679	3.08	3.19	0.16
	1.1000	30.3974	30.4333	3.37		
	1.1767	26.5104	26.546	3.12		
C	1.3129	30.4004	30.4558	4.41	4.25	0.14
	1.246	30.4401	30.4898	4.15		
	1.372	30.4314	30.4866	4.19		
D	1.1875	26.6872	26.7458	5.19	5.20	0.07
	1.047	26.2192	26.2703	5.13		
	1.109	26.3325	26.3881	5.28		

Table A. 9 – Rayon's calibration curve points resultant from the TD-NMR measurement of the calibration samples

Sample	m $_{tube+lid}$ (g)	m $_{tube+lid+sample}$ (g)	m $_{sample}$ (g)	DPU $_{per\ greige\ cord}$ (%)	DPU $_{per\ dipped\ cord}$ (%)	Signal
A1	16.2661	16.6717	0.4056	1.50	1.48	29.290
A2	16.3432	16.7829	0.4397		1.48	25.430
A3	16.2096	16.6539	0.4443		1.48	24.016
B1	16.1988	16.6478	0.449	3.19	3.09	56.319
B2	16.1393	16.6057	0.4664		3.09	51.892
B3	16.1238	16.59	0.4662		3.09	51.392
C1	16.2255	16.6958	0.4703	4.25	4.08	75.215
C2	16.3545	16.7843	0.4298		4.08	75.518
C3	16.3640	16.8109	0.4469		4.078	76.015
D1	16.1187	16.5919	0.4732	5.20	4.94	90.135
D2	16.2632	16.6951	0.4319		4.94	86.841
D3	16.2605	16.6893	0.4288		4.94	86.430

Table A. 10 – DPU through wet-chemical method for the validation samples of rayon

Sample	m_1 (g)	m_2 (g)	m_3 (g)	$DPU_{\text{per dipped cord}}$ (%)	Mean (%)	Standard deviation (%)
1	1.0525	30.4186	30.4498	3.05	3.06	0.04
	1.0228	30.3308	30.3608	3.02		
	1.2128	26.1126	26.1491	3.10		
2	1.0209	30.4018	30.4377	3.64	3.57	0.14
	1.1342	26.3256	26.363	3.41		
	1.1164	26.2133	26.2526	3.65		
3	1.1216	30.4415	30.4775	3.32	3.28	0.16
	1.2306	30.5455	30.5826	3.11		
	1.1971	30.5457	30.5852	3.41		
4	1.2155	26.4768	26.5200	3.69	3.66	0.04
	1.1146	26.6863	26.7252	3.62		
	1.0910	26.4996	26.5382	3.67		
5	1.0202	26.3403	26.3724	3.25	3.21	0.06
	1.0940	30.4410	30.4754	3.25		
	1.3375	30.4391	30.4798	3.14		
6	1.1112	30.4418	30.4795	3.51	3.48	0.04
	1.0149	26.2163	26.2506	3.50		
	1.3256	30.4178	30.4619	3.44		
7	1.0216	30.5194	30.555	3.61	3.37	0.34
	1.1978	30.4315	30.4723	3.53		
	1.0473	30.4165	30.4468	2.98		
8	1.1991	30.4305	30.4671	3.15	3.15	0.11
	1.0236	30.4039	30.4341	3.04		
	1.2652	30.4304	30.4704	3.26		
9	1.1455	26.686	26.7264	3.66	3.64	0.02
	1.1749	30.4207	30.462	3.64		
	1.0919	30.4007	30.4389	3.63		
10	1.0425	30.3295	30.3605	3.06	2.98	012
	1.3658	30.3278	30.3679	3.02		
	0.9791	26.1076	26.1347	2.85		
11	1.3237	26.501	26.5422	3.21	3.26	0.05
	1.1863	26.2121	26.2496	3.26		
	1.0552	26.4978	26.5316	3.31		
12	1.3302	26.501	26.5422	3.20	3.18	0.02
	0.9658	30.4008	30.4303	3.15		
	1.0736	30.4018	30.4349	3.18		
13	1.2452	30.4386	30.4744	2.96	2.98	0.13
	1.3220	30.4006	30.4405	3.11		
	1.1926	26.2547	26.2878	2.85		
14	1.0916	30.4408	30.4765	3.38	3.37	0.05
	1.1068	26.2142	26.2507	3.41		
	1.0458	26.1088	26.1424	3.32		

15	1.0173	30.3296	30.3653	3.64	3.64	0.11
	1.0511	26.3245	26.3624	3.74		
	1.0271	30.4258	30.4608	3.53		

Table A. 11 – Preparation of samples for the validation of the rayon calibration curve, respective measure in the TD-NMR device and conversion

Sample	$m_{tube+lid}$ (g)	$m_{tube+lid+sample}$ (g)	m_{sample} (g)	$DPU_{per\ dipped\ cord}$ (%)	$DPU_{per\ greige\ cord}$ (%)	Mean (%)
1	16.2393	16.6283	0.389	2.182	2.231	2.27
				2.263	2.315	
				2.223	2.274	
2	16.1635	16.5387	0.375	2.742	2.819	2.82
				2.782	2.862	
				2.717	2.793	
3	16.1302	16.5093	0.379	2.462	2.524	2.56
				2.547	2.614	
				2.471	2.534	
4	16.257	16.6217	0.365	2.831	2.913	2.91
				2.810	2.891	
				2.838	2.921	
5	16.2888	16.6488	0.360	2.51	2.575	2.52
				2.448	2.509	
				2.427	2.487	
6	16.1757	16.5315	0.356	2.266	2.319	2.33
				2.282	2.335	
				2.277	2.330	
7	16.1889	16.5416	0.353	2.334	2.390	2.35
				2.270	2.323	
				2.295	2.349	
8	16.2975	16.6699	0.372	2.812	2.893	2.99
				2.959	3.049	
				2.925	3.013	
9	16.2468	16.6167	0.370	2.324	2.379	2.39
				2.330	2.386	
				2.344	2.400	
10	16.1617	16.5344	0.373	2.081	2.125	2.12
				2.056	2.099	
				2.085	2.129	
11	16.1895	16.5595	0.370	1.712	1.742	1.79
				1.795	1.828	
				1.763	1.795	
12	16.3376	16.7133	0.376	2.132	2.178	2.18
				2.141	2.188	
				2.134	2.181	
13	16.2304	16.5944	0.364	2.613	2.683	2.61
				2.503	2.567	
				2.524	2.589	
				2.945	3.034	

14	16.1182	16.4863	0.368	3.036	3.131	3.11
				3.078	3.176	
15	16.2543	16.6042	0.350	3.012	3.106	3.13
				3.031	3.126	
				3.075	3.173	

Table A. 12 - Results of the Two-Samples T-Test, not assuming equal variances, for the validation of rayon's calibration curve

Sample	Mean	StDev	SE Mean	Difference	95% CI for Difference
TD-NMR	2.539	0.392	010	-0.790	(-0.071; 0.368)
Wet-Chemical	3.329	0.235	0.061		

Null hypothesis $H_0: \mu_1 - \mu_2 = 0$

Alternative hypothesis $H_1: \mu_1 - \mu_2 \neq 0$

T-Value	DF	P-Value
-6.69	22	0.000001

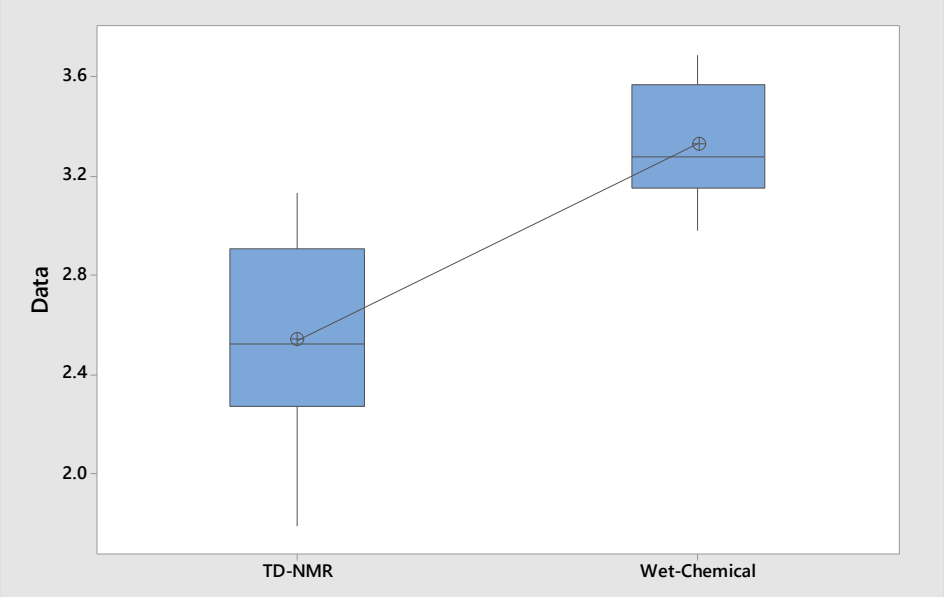


Figure A. 2 - Boxplot of the comparison between the TD-NMR and the wet-chemical values for the validation phase of the rayon calibration curve.

Table A. 13 – Points for the retrial calibration curve of rayon (resultant from the TD-NMR measurement of a new set of calibration samples)

Sample	$m_{tube+lid}$ (g)	$m_{tube+lid+sample}$ (g)	m_{sample} (g)	$DPU_{per\ greige\ cord}$ (%)	$DPU_{per\ dipped\ cord}$ (%)	Signal
A1	16.3454	16.7017	0.3563	1.20	1.48	29.290
A2	16.1422	16.4923	0.3501		1.48	25.430
A3	16.2145	16.5524	0.3379		1.48	24.016
B1	16.3261	16.6588	0.3327	2.63	3.09	56.319
B2	16.277	16.6232	0.3462		3.09	51.892
B3	16.2018	16.6093	0.4075		3.09	51.392
C1	16.2371	16.5958	0.3587	4.25	4.08	75.215
C2	16.3581	16.7272	0.3691		4.08	75.518
C3	16.2973	16.6356	0.3383		4.078	76.015
D1	16.2235	16.5775	0.3540	5.20	4.94	90.135
D2	16.3387	16.6797	0.3410		4.94	86.841
D3	16.3684	16.7160	0.3476		4.94	86.430

A.III Rayon Mechanical Properties

Table A. 14 - Values of breaking force and stiffness resultant from the load-elongation and bending stiffness test, respectively.

DPU (%)	Breaking Force (N)	Mean (N)	Stiffness (cN)	Mean (cN)
1.2	166.97 167.85 171.04 169.11 167.46	168.49	16.3 15.3 15.4	15.7
2.5	166.71 162.11 173.38 171.22 167.87	168.26	24.8 25.0 23.6	24.5
3.6	169.48 167.20 161.16 155.31 159.06	162.44	27.2 28.7 26.1	27.3

4.5	165.09 160.95 165.59 164.66 171.70	165.60	22.9 24.2 22.9	23.3
5.2	163.90 166.08 163.45 162.58 164.18	164.04	22.9 23.9 23.0	23.3

Table A. 15 – results of the ANOVA test for the force-elongation study

Source	Degrees of freedom	Sum of Squares	Contribution	Mean Sum of Squares	P-value
DPU	4	138.4	32.39 %	34.59	0.085
Error	20	288.8	67.61 %	14.44	
Total	24	427.2	100.00%		