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STUDY OF DIP CONTENT IN THE TIRE TEXTILE REINFORCEMENT

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À FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO EM
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held in

Continental - Indústria Têxtil do Ave, S. A.

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Abstract

Tire textile reinforcements improve tire performance and security, yet integrating such components in rubber is not easily achieved. Preparing textiles involves a coating method using a dip solution that confers the capability of adhesion, however it is necessary to study if the amount of solution in the cords is within established specifications to guarantee tire quality and passenger security.

Continental – Indústria Têxtil do Ave, S.A, producer of textile reinforcements has a strong commitment in having the highest quality products and the best characterization equipment. Currently, to assess the amount of solids in the cord it is performed a chemical method which is very time-consuming and lacks precision.

To overcome the challenging task of determining the amount of dip in the cords, a Time Domain-Nuclear Magnetic Resonance (TD-NMR) has been recently acquired, and a methodology was established, which has been validated by the previous author. Whether the methodology can successfully analyse cords with distinct characteristics or which conditions may interfere with the correct attainment of the amount of dip in the cord, are yet to be studied.

This project aims on the study of the applicability of the current TD-NMR analysis method to cords with different constructions and supplier. Furthermore, it aims to identify and study its influence of which preparation steps may produce interferences with the result. Due to time constrains, this project will only focus on nylon and hybrid cords.

In order to study these aspects, the amount of solids in the cords was assessed by TD-NMR on samples from different constructions and/or different suppliers. In addition, the influence of inappropriate samples drying and sample manipulation without gloves was studied, both having increasing effects, yet inappropriate drying having the greater influence.

It was confirmed the applicability of the nylon calibration in distinct cords by comparing the results obtained via TD-NMR and the results obtained through the chemical method. Moreover, it was confirmed the necessity to properly dry samples and manipulate them with gloves to avoid interferences.

Such results support the conviction of having an easier and quicker methodology to determine Dip Pick-up introduced by the previous author.

Key words: tires, textiles reinforcements, TD-NMR, quality control, dip coating

Resumo

Os reforços têxteis de pneus melhoram o desempenho e segurança dos pneus, mas a integração desses componentes em borracha não é facilmente alcançada. A preparação de têxteis envolve um método de revestimento usando uma solução que confere capacidade de adesão, porém é necessário estudar se a quantidade de sólidos nas cordas está dentro das especificações estabelecidas para garantir a qualidade dos pneus e a segurança do passageiro.

Continental - Indústria Têxtil do Ave, S.A, produtora de reforços têxteis tem um forte compromisso em ter produtos de alta qualidade e os melhores equipamentos de caracterização. Atualmente, para avaliar a quantidade de solução nas cordas é realizado um método químico com um tempo de execução bastante elevado e com baixa precisão.

Para superar a tarefa desafiadora de determinar a quantidade de solutos nas cordas, foi adquirido recentemente um equipamento de Ressonância Magnética Nuclear no Domínio do Tempo (TD-NMR) e foi estabelecida uma metodologia que foi validada pelo autor anterior. Se a metodologia pode analisar com sucesso cordas com características distintas ou quais condições podem interferir com a correta obtenção da quantidade de soluto na corda, ainda não foi estudado.

Este projeto visa o estudo da aplicabilidade do atual método de análise TD-NMR em cordas com diferentes construções e fornecedores. Além disso, visa identificar e estudar a influência das etapas de preparação que podem produzir interferências no resultado. Devido a restrições de tempo, este projeto apenas estudará cordas de nylon e híbridos.

Para estudar estes pontos, a quantidade de sólidos nas cordas foi avaliada por TD-NMR em amostras com diferentes construções e/ou fornecedores diferentes. Além disso, estudou-se a influência da secagem incorreta das amostras e a sua manipulação sem luvas, verificando-se que ambos produziam efeitos aumentativos no resultado, tendo a secagem incorreta maior influência.

Foi confirmada a aplicabilidade da calibração de nylon em cordas distintas comparando os resultados obtidos através do TD-NMR e os resultados obtidos através do método químico. Além disso, foi confirmada a necessidade de secar adequadamente amostras e a sua manipulação deve ser feita com luvas para evitar interferências.

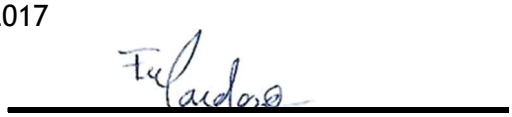
Tais resultados suportam a afirmação de ter uma metodologia mais fácil e rápida para determinar a quantidade de solutos na corda introduzido pelo autor anterior.

Palavras-chave: pneu, reforços têxteis, TD-NMR, controlo qualidade, revestimento têxtil

Declaration

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

Porto, 3 of July of 2017



(Francisco Monteiro Cardoso)

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Notation and Glossary

dtex	Decitex	g/10000 m
%DPU	Dip Pick-up Percentage	%
m_{dip}	Mass of dip placed in plate	g
$m_{dipped\ cord}$	Mass of dipped cord	g
m_1	Mass of dipped cord before dissolution	g
$m_{greige\ cord}$	Mass of heatset greige cord	g
m_{solids}	Mass of residues after evaporation of volatile compounds	g
m_3	Mass of the crucible containing solid dip	g
m_2	Mass of the empty crucible	g
%SC	Solid Content Percentage	%
tex	Tex	g/1000 m

List of Acronyms

CL	Confidence Level
C-ITA	Continental – Indústria Têxtil do Ave, S. A.
DPU	Dip Pick-up
FEUP	Faculdade de Engenharia da Universidade do Porto
FID	Free Induction Decay
LDU	Lab Dipping Unit
PET	Polyethylene Terephthalate
TD-NMR	Time Domain Nuclear Magnetic Resonance

1 Introduction

1.1 Framing and presentation of the work

Continental is a renowned tire manufacture, producing high performance and high-quality tires for several types of vehicles. First established in Hanover, Germany in 1871, Continental started as a producer of rubbery products and solid tires for carriages and bicycles. Always committed in making technological developments, cutting-edge tires and other innovative rubbery products were produced through the years. Responsible for the first patterned tread tire for automobiles, major developments in hoses productions and innovative eco-friendly tires, being at the forefront of technology was always a priority ("Continental," 2017).

Continental acquired many plants all over the world throughout the years allowing higher production and even specialized plant units. In 1990 a joint venture was set up with a Portuguese company for tire production and a unit for textile cord production in Lousado, making 1993 the year for complete takeover ("Continental" 2017).

Continental – Indústria Têxtil do Ave, S.A. (C-ITA) is responsible for the entire production of textiles for nearly 70% of other Continental production units in Europe. Receiving the raw materials and transforming the yarns in cords, C-ITA is also responsible for the dipping process making the cords ready for its final task.

While driving, tires are expected to provide grip, allow the best handling while ensuring safety to the passengers, and ultimately with the longest lifetime. Contrary to what it seems, present time pneumatic tire is quite complex and a combination of several components and materials, some of which, rubber, steel and textiles reinforcements, the latter being the focus of this project (Brewer et al., 2006; Continental, 2010).

Tire textile reinforcements have its main application in the carcass and cap-ply, both a composite of rubber and cord, yet with different objectives and location in tire. Thus, it is important to produce a composite which has the properties of the both materials and function as one. To do so, it is necessary to incorporate the textiles in the rubber, however, due to the non-reactive nature of cords, without a proper adhesive, cohesion is not possible.

Textiles must undergo a number of transformations and treatments before being ready for its insertion in the tire. Textile dipping is regarded as one of the most important steps during the preparations of fibres to achieve its final properties. Not only it will confer its final mechanical properties, but it will allow proper adhesion to rubber, thus conferring the ability to insert the cords in the tire. Having the correct amount of dip in the cord is important since

if it is lower to what is expected, adhesion will not be effective and if such cord is inserted in a tire, failure may occur. On the other hand, if the amount of dip is excessive, not only will it be costlier for the company, but since the dip contains non-environment friendly substances, it will damage the environment (Brewer et al., 2006).

Quality control is a crucial step in the manufacture process at C-ITA. To release a product to the customer, distinct parameters must be verified to guarantee they are within the specifications of the product. Parameters like stiffness, maximum elongation and adhesion are verified to assure the quality of the product. One parameter tested is the Dip Pick-up (DPU), however, the validated method is very time-consuming and has some errors intrinsic to the technique, yet it is the only validated method available. Having this in mind, C-ITA acquired an equipment that could possible substitute this method, a Time Domain Nuclear Magnetic Resonance (TD-NMR).

In this context, this project will focus on the study of this newly acquired equipment, to ultimately be used in the quality control of C-ITA's products, tire textile reinforcements. It will be conducted studies to understand how the nylon calibration will perform while measuring cords with distinct constructions and suppliers that differ from the cord used for calibration of the equipment, carried out before this project, and in what degree may preparation conditions affect the results.

1.2 Contributions of the Work

This project will carry on the study of Dip Pick-up of C-ITA cords using a TD-NMR device, to provide further understanding how the equipment will perform in various situations. Where previous work established a methodology, proceeded to demonstrate the capability of the equipment and validated a nylon and Hybrid calibration, no other study was conducted (Silva, 2017).

To allow an easier adaptation and to complement the previous understanding of how the equipment works, I proposed an alteration to the established methodology to allow quicker adaptation and worked towards the objective of understanding which properties can lead to an interference with the result. Moreover, in this thesis I studied the capability of the equipment to measure different cords, making a great step in full implementation of TD-NMR in quality Control at C-ITA.

1.3 Organization of the thesis

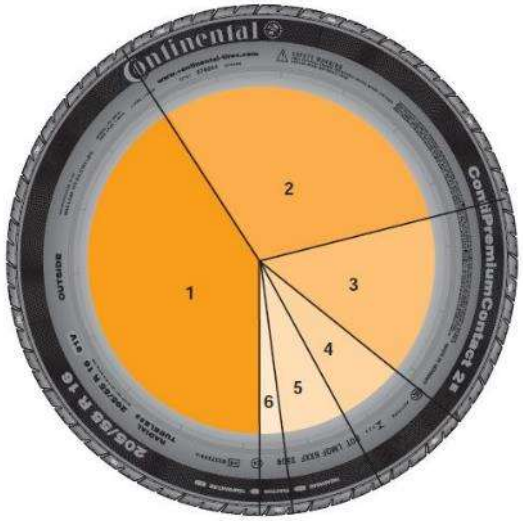
This thesis is divided in 7 chapters, which will be briefly described next:

1. **Introduction** – Continental presentation and tire industry and technology. Brief contextualization of the problem and thesis objectives.
2. **Context and State of the art** – Contextualization of the project, describing tire and tire textile reinforcements industry. Presentation of the currently methodology and equipment in study.
3. **Technical Description** – Description of equipment and methodology used during the course of this project for each conducted study.
4. **Results and Discussion** – Presentation and discussion of the results achieved.
5. **Conclusion** – Presentation of the conclusions established from results obtained.
6. **Assessment of the work done** – Global appreciation of the developed work.
7. **References** – Listing of references used during this project.

2 Context and State of the art

2.1 Tires - piece of engineering

In modern car manufacture, many aspects are taken into account in order to continuously improve several attributes of the car. Ranging from speed, fuel consumption to design, one of the most important aspects when designing a new car model is security of the passengers. Tires solely purpose is to provide security to the passenger. To strengthen this statement, the reader must be reminded that the only part of the vehicle in contact with the ground is a small area of each tire. Given its importance to the driver and other occupants of the vehicle, tires underwent many changes since its first production. Ever since the development of the first pneumatic tire many upgrades transformed the tire from a quite simplistic rubbery product to a complex piece of engineering (Clark & Administration, 1971).



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

Figure 1 - Different materials to produce a modern tire (adapted from Continental, 2010).

Pneumatic tires served as an upgrade for solid rubber tires during the late 1800s. In early 1950s tubeless tires were introduced after improvements in rim design, and only in the late 1960s belted bias tires were developed. Until present days, different types of tires were developed and the main difference being the bias layer arrangement: diagonal bias and radial, where belted bias has similar construction as diagonal bias tires with the addition of belts to its construction (Brewer et al., 2006).

Radial tires, which are the predilect construction used in passenger car tires at present time, can be separated into different layers, each with different functionalities, properties and materials. A modern radial tire is mainly a composition of a tread, cap-ply, sidewall, carcass, belts and beads.

1. Tread
2. Cap-ply
3. Steel belts
4. Carcass
5. Bead

Figure 2 - Tire components (adapted from Continental, 2010).

The outer layer of the tire, the surface that it is in contact with ground is designated tread and is responsible for the required traction during breaking, cornering and driving. Furthermore, it is designed to channel out water, minimize sounds while driving and provide uniform wear even in different weather conditions while maintaining traction (Brewer et al., 2006; Continental, 2010).

To allow proper inflation of the tire, air must be tightly enclosed inside the tire. In the inner part of the tire there is a specially formulated compound to reduce permeation of air through the tire called inner liner. In addition to this component, the carcass provides the strength required to withstand the air pressure. A compound of textile cords and rubber, it extends from bead to bead and serves as primary reinforcement material in the tire casing. These cords are placed perpendicularly to the movement of the tire, in other words radially, thus giving the name of the construction of the tire (Brewer et al., 2006; Continental, 2010).

The sidewall rubber serves to protect the body plies from abrasion, flex fatigue and impact. Also carries information about the tire, like size, maximum speed and weather suitability. To correctly secure the tire to the wheel rim there are two beads, one on each side of the tire that consists in a carbon wire covered in rubber that clamp on the wheel rim (Brewer et al., 2006).

There are two steel belts, placed with opposite angles on top of the body plies and under the tread restricting the expansion of the body ply cords and providing impact resistance. In order to further restrict expansion of the belts due to centrifugal forces during high speed driving, a layer of textiles is applied on top, the cap-ply (Brewer et al., 2006).

As mentioned before, there are several types of tires, with similar materials, however with different constructions. Usually it is the arrangement of the body plies that dictates the type of the tire – Figure 3.

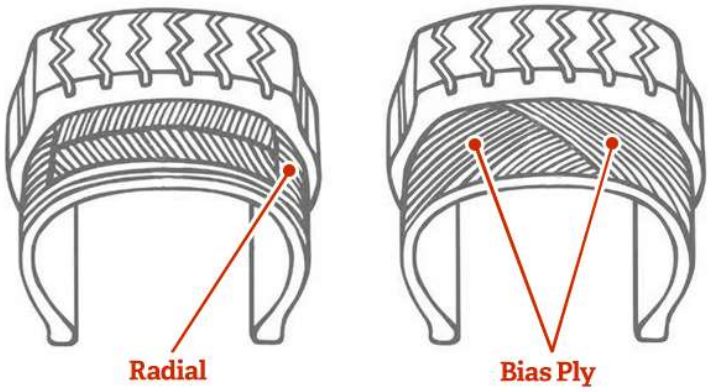


Figure 3 - Radial and Bias Ply tire comparison (Ennis, 2014).

Diagonal bias tires are simpler than the other constructions since there are no belts in it. The body ply cords are laid at angles substantially less than 90º to the tread centreline, from bead to bead. Belted bias tires use the same construction as the diagonal bias tires with the addition of belts in tread region (Brewer et al., 2006).

Radial tires, the most complex construction, have body ply laid radially from bead to bead. To strengthen the tire, steel belts are laid diagonally in the tread region, helping in the stability of the tire during the cornering. Although its construction is more expensive and complex, radial body cords allow easier deflection under load, meaning less heat will be generated, give lower rolling resistance and better high-speed performance. Plus, increasing tread stiffness from belts improves wear and handling significantly (Brewer et al., 2006).

2.2 Textile Reinforcement

Textiles have strong influence in the structure and functionality of the tire. When applied in a tire component, these materials should confer a specific property depending on its function, for example textiles used in the carcass should allow the tire to withstand the air pressure inside the tire, by providing extra resistance to the composite. Thus, the material used to produce the cord must be carefully studied and an optimal construction should be developed to provide the best characteristics, yet endure the conditions tires are subject to.

C-ITA principal products are textiles used in Continental's tire manufactured in Lousado and in 70% of Continental tire plants across Europe, which are applied in the carcass and cap-ply. At the moment, there are four different fibres used in C-ITA as raw materials: nylon, aramid, rayon and polyethylene terephthalate (PET). It is also possible to produce hybrid cords and currently at C-ITA hybrid cords are constructed using aramid and nylon, making a total of 5 different cords (in terms of raw material) (C-ITA, 2016).

Nylon fibres are synthetic chains of polymer with their main usage being in radial tires as cap or overlay ply. Although it has good heat resistance, strength and low sensitivity to moisture, it suffers high service growth (Brewer et al., 2006).

Aramid is also a synthetic fibre with high tenacity, about 2 to 3 times stronger than polyester and nylon. It can be used as an alternative for steel cords or for belts. Its strength leads to a disadvantage since it is quite difficult to cut the fibres, becoming a processing constrain, plus this material is very costly (Brewer et al., 2006).

Polyester or PET are synthetic fibres with a very common presence in radial body plies. They have very good mechanical properties like low shrinkage and low service growth, have low heat set and reduced cost, however are not as heat resistant as nylon or rayon (Brewer et al., 2006).

Rayon is a fibre produced from cellulose normally used on body plies that presents good heat resistance and good handling characteristics. With high cost and great sensitivity to moisture as its down sides (Brewer et al., 2006).

Fibres can be grouped into four levels of complexity: filaments, yarn, cord and fabric, being filament the simplest unit. A yarn is a group of filaments, and it can be twisted into cord, afterwards it is possible to weave fabric with cords using weaving machines – Figure 4. C-ITA receives yarn spools of four distinct materials from several suppliers and twist them into cords using several twisting units at the plant. Cords can be a single yarn twisted, a combination of two or more, moreover, varied materials can be used in twisting units making it a hybrid cord as it was said previously (Clark & Administration, 1971).

Figure 4 – Weaving machine.

Twisting can be applied in two distinct directions, clockwise and counter-clockwise. If the cord is winded in counter-clockwise direction it is said it was twisted in “Z”, the other way

around, in clockwise it is called in “S”, as seen in Figure 5. Usually, yarns are twisted in “Z” and afterwards when twisting the yarns together to form a cord, they are twisted in “S” (C-ITA, 2016).

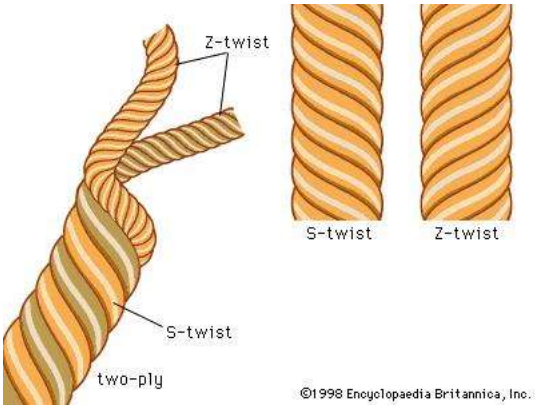


Figure 5 - "S" and "Z" twisting (“Types of yarn,” 1998).

It is possible to produce cords with different twists and in contrary directions. Associated with producing cords from varied materials it is possible to produce many different cords, each with its set of properties and applications just by combining yarns with different twist.

Cord are defined by the materials they are made of, the number of yarns twisted together and linear density. Linear mass is defined by tex that is the grams in 1000 meters of cord, however the typical subunit used in industry is decitex, the grams in 10000 meters of cord. Each combination of characteristics mentioned above is known as the construction of the cord (Clark & Administration, 1971).

As mentioned above, depending on the final application of the textiles, it may be required to produce fabric, for example, textiles used in the tire carcass are fabrics.

2.2.1 Textiles dipping

Upon production, textiles should be shipped to tire plant to become part of the tire. However, due to the inert nature of the cords, proper adhesion is not obtained simply by the insertion of the cord in the middle of the rubber followed by vulcanization.

To allow cord-to-rubber adhesion, cords are dipped with a solution that will serve as an intermediary, bonding together cord and rubber. Resorcinol-Formaldehyde-Latex (RFL) solution consists of a resin (a mixture of resorcinol and formaldehyde) which allows the adhesion between cord and rubber (Figure 6) due to its ability to create mainly covalent bonds and latex which serves as a matrix (Fidan, Kleffmann, Scharr, & Schombacher, 2002).

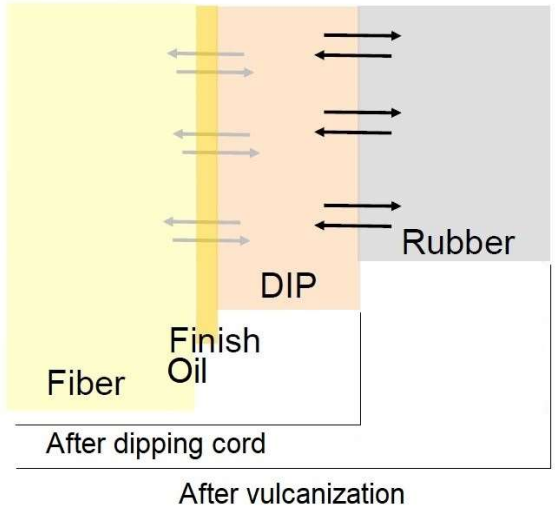


Figure 6 - Schematic representing dip as ligand (adapted from Kramer, 2013*).*

Nevertheless, some materials may require a 2-step process to successfully create this bonding matrix. Being extremely non-reactive, a pre-dip (solution of epoxy resin and isocyanate) is used to functionalize the cord and properly connect to the dip. Some suppliers may imbibe the fibres with an oil finishing that will make the functionalization of the cord, making it unnecessary to use the 2-step process.

Once the fabric is inserted in the rubber and it is vulcanized, it is expected to stay as a single piece while keeping the mechanical, physical and chemical properties required for the tire to endure all conditions it will be exposed to.

The equipment used by C-ITA for cords impregnation is called Single-end (Figure 7) receiving its name for its arrangement; as greige cord enters in one side and the dipped cords is wound up on the same side. As the cord enters the machine, pulled by tensioning rollers that give the correct stretch, it is dipped in the first bath and introduced into the first oven where the dip is dried, then cord enters in a second oven where it is hot-stretched, gaining its final properties.

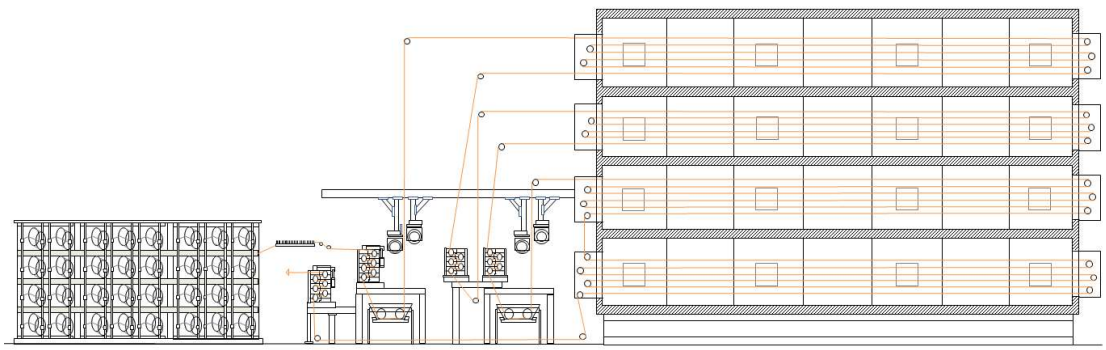


Figure 7 - Schematic representation of Single-End.

For some materials, as for example aramid, it is necessary to use an activation pre-dip, the first bath will contain the pre-dip, and the second bath the dip. In this case, the first oven is responsible for pre-dip drying and second oven will have the same functions as for the other situation, it will heatset the cords. Moreover, the third oven will dry the dip and the fourth oven will be used for cord normalization respectively, i.e., to allow stabilization of the cord. The dipped and dried cord is then wound up in bobbins and is ready for shipping.

C-ITA is equipped with a machine capable of dipping rolls of fabric named Zell (Figure 8). Contrary to Single-end the finished product is not wound up in the same side as the greige product, and it can only dip one roll at a time. On the other hand, Single-end can dip several spools at a time.

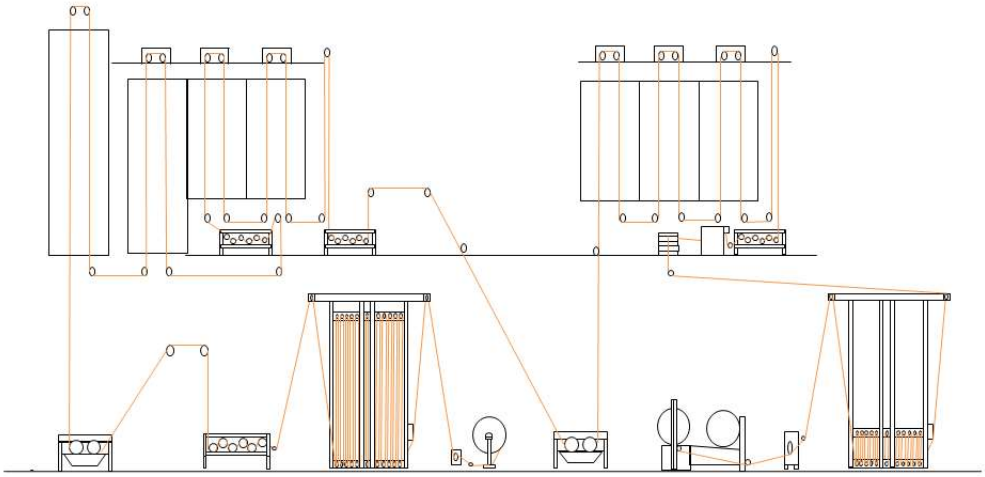


Figure 8 – Schematic representation of Zell.

Every product requires specific conditions of impregnation (temperature, speed, stretch, dip recipes), which have been previously established by C-ITA after extensive studies, during product development.

To guarantee the quality of the products it is necessary to perform several tests that will ensure textiles will function properly. Cord functionality is linked to the amount of dip in the cord, thus proper determination of the amount of dip is crucial. Less dip in the cord will result in poor adhesion, while larger amount of dip will be a waste of resources and not environmentally friendly.

In Figure 9 can be observed the final result of a test to study the cord adhesion to rubber, and can be concluded the importance of a correct adhesion cord-to-rubber. If this problem was not addressed, the rubber would easily be torn apart during its action in the car, as can been seen in Figure 9 – Left, where cord was separated from rubber, showing a weak rubber-to-cord adhesion. On the other hand, if cord is properly inserted in rubber, the test will

result in full cord coverage by rubber, as demonstrated by Figure 9 – Right, allowing to conclude that the cord successfully adhered to rubber.

Figure 9 - Bad rubber-to-cord adhesion (left) Good rubber-to-cord adhesion (right).

2.3 Quality control and the TD-NMR

Quality control department in C-ITA performs several tests to verify if the final product meets the requirements. From stiffness, maximum elongation, force and adhesion to rubber, the shipped product will be fully characterised.

One test quality facilitators run is the DPU measurement. This test measures the amount of dip that is impregnated in the cord. There are two developed methods for DPU measurement, the standard method and TD-NMR method.

2.3.1 Standard Method

The method applied by Continental to measure the %DPU in the cord is based on mass differences (gravimetric method) and determines the %DPU per greige cord, having a specific experimental procedure for each type of material. It is a wet chemical method involving the following steps: (i) dissolution of fibres, (ii) solvent removal by filtration and recover the dip (solid), (iii) dry the dip, and (iv) weight the solid dip. The %DPU is then calculated by applying Equation 1.

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

Where:

m_1 the mass of dipped cord before dissolution;

m_2 the mass of the empty crucible;

m_3 the final mass of the crucible containing the solid dip.

Due to the hygroscopic nature of the cords, they must be dried up in the oven before any weighting. However, some materials like PET have very low hygroscopic nature, meaning that its weight will not be affected by humidity. Therefore, there is not any difficulty in

weighting cord mass, so %DPU can be measured by a weighting method that does not involve dissolution of fibres. For instance, it is used the mass of a heatset greige cord as a reference value, as it can be observed in Equation 2.

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

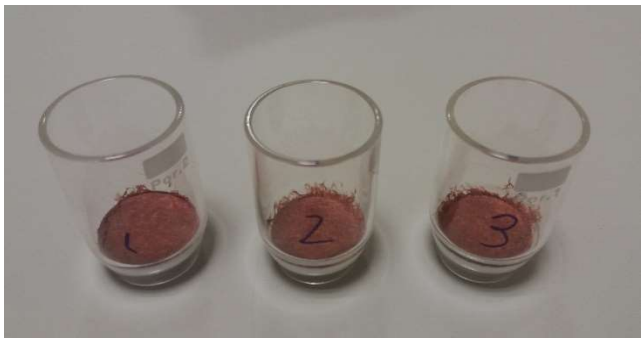


Figure 10 - Result of filtrating the dissolved fibres.

The standard method is very time-consuming and the it has intrinsic errors in its several steps, resulting in great variation associated with it, having the most common error the incorrect dissolution of fibres which will result in a higher result of %DPU. Nevertheless, it is the extension of the execution time that makes this method such an impractical quality control technique for a company. For example, to test nylon or rayon, it takes about five hours to obtain the %DPU, but to test %DPU for aramid or hybrid it takes three to five days to obtain.

2.3.2 Time Domain-Nuclear Magnetic Resonance

As already said, TD-NMR is being studied as a new method to measure %DPU in dipped cords. TD-NMR equipment used during this project is based on the same principle as the conventional NMR but with a distinctive characteristic: instead of comparing the chemical shift of an isotope in the compound, it measures the energy released by compound's protons after being exposed to a low frequency magnetic field. The resulting signal varies through time and it is related with the number of protons present, therefore, higher concentration of dip in cords will result in a higher signal obtained.

TD-NMR has been used in many industries for quality control, as it is a device that can make rapid tests, it is non-destructive and has no need for specialised personnel. The equipment detects radiation that it is emitted in a decay curve known as Free Induction Decay (FID) – Figure 11.

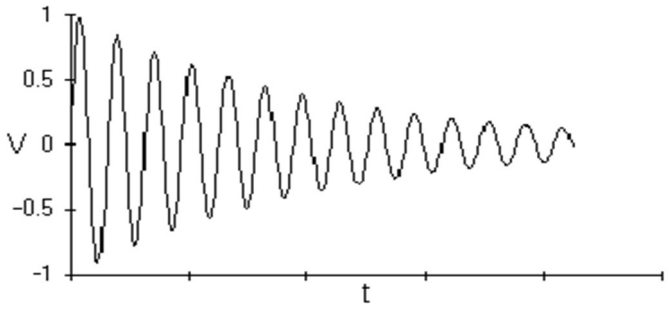


Figure 11 - Free Induction Decay curve (adapted from CDRH Magnetic Resonance Working Group, 1997)

In addition, the equipment can produce magnetic pulses with different angles (90º and 180º), each affecting the spins of protons in distinct ways. This disturbance is known as the Hahn echo sequence. After the deactivation of a pulse, the spins return to their equilibrium position, emitting the received energy. This energy, can be represented in the time domain and is proportional to the number of protons that are affected. Furthermore, different protons have different relaxation times giving different graphics (Hornak, 1997).

Some suppliers of yarn use oil to help the filaments to stay together. This treatment is called spin-finishing and the amount of oil on the fibres can be determined by a TD-NMR. Since the fibre has a different physical state, solid, and has a typically short relaxation time, and the spin-finish oil, which is an oil-type liquid and has a typically large relaxation time, distinct peaks can be observed. A Hahn echo sequence is applied to the sample, meaning it will first be exposed to a 90 º pulse and then to a 180 º pulse proceeded by the reading of the signal emitted by the sample. Bruker personnel have already optimized the echo time in such a way that the solid-type signal will have already decayed by the time the spin-finish signal occurs. Such optimization will allow highly trustworthy measurements and sensitive measurements (Dalitz, Cudaj, Maiwald, & Guthausen, 2012).

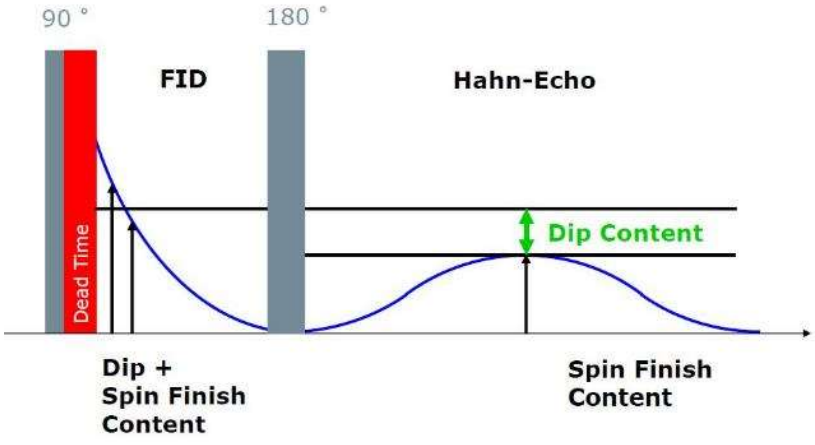


Figure 12 - Schematic representing how the equipment determines %DPU (Bruker, 2016).

There are similarities observed between the Oil pick-up analysis and Dip pick-up analysis, so the challenge that is proposed is the implementation of a TD-NMR in the determination of DPUs. With the assistance of the supplier of the device, it was developed a software, with optimized variables to determine DPUs. Furthermore, in case the yarn has some spin-finish oil, the software application subtracts its signal as well as the one from yarn, resulting in a dip measurement only, as it is demonstrated in Figure 12 (Bruker, 2016).

3 Technical Description

This chapter describes the studies performed in this project as well as the methods applied. Firstly, it is proposed some alterations to the established method of sample preparation to provide an easier adaptation to quality facilitators in C-ITA when the TD-NMR equipment is implemented. After that the following aspects were studied:

- The influence of the handling conditions during sample preparation on the %DPU determination;
- The influence of the samples drying on the %DPU determination;
- If the calibration method developed for the original cord (reference cord) can be used to measure %DPU of cords with different properties (construction and supplier);

C-ITA produces cords consisting of four different raw materials (nylon, PET, aramid and rayon), due to time constraints, this project focuses on the study of nylon and hybrid cords.

3.1 Sample preparation method (for TD-NMR)

On TD-NMR acquisition by C-ITA, it was necessary to calibrate the equipment and validate the method for some representative materials produced in the plant. Currently the TD-NMR equipment is calibrated for one nylon cord, a hybrid cord and a PET cord, with fixed construction and supplier. This equipment is furnished with a detector capable of measuring samples, having a maximum height limit of 2 cm for proper detection. Thus, samples are required to be below this limit to avoid incorrect detection. Due to the length of the samples, it is difficult to prepare the sample in order to obey to the height limit. Silva (2017) proposed a procedure for sample preparation which allows correct arrangement in the TD-NMR tubes. However, it was not successfully implemented since it proved impractical after getting the plant operators' feedback, since the methodology is quite difficult. For this reason, it was necessary to search for an easier but as efficient method. To this end, alternative ways of preparing the samples were considered in this project, which led to finding a new method for sample preparation.

This new method, which is illustrated in Figure 13 allows sample preparation in a quick and straightforward way. The procedure involves the following steps: (i) approximately 1 g of cord is curled around the operator fingers (Figure 13-1), (ii) the sample is cut off the bobbin (Figure 13-2), (iii) the sample is folded to obtain a sample with smaller diameter (Figure 13-3), (iv) fixing the sample with loose tips (Figure 13-4), (v) given a knot with the tips of the cord (Figure 13-5) and (vi) introducing the sample in the tube assuring it has not more than 2 cm inside the tube (Figure 13-6).

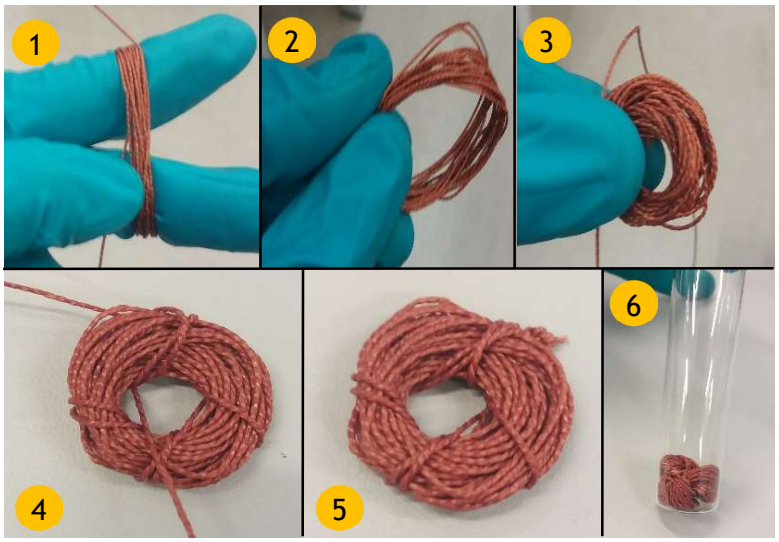


Figure 13 - New sample preparation method.

It is important to have in consideration that these samples may be part of a bobbin (that is, one single cord) or a fabric. The same preparation procedure is applied in both cases, however, the sample from a fabric is made up of several cords, which are stripped from the fabric, instead of a single one. Thus, once the weft is removed, the tips of the different cords are tied together, as seen in Figure 14, and the tied cords are prepared in the same way as a single cord (as shown in Figure 13).

Figure 14 - Sample of fabric with tips tied together.

Despite Bruker recommendations established the necessity of handling not only samples but also the tubes with gloves, it was proposed to identify all possible interferences with %DPU measurement. Therefore, this is identified as a possible interference in %DPU measurement since external particles present in the sample should increase its signal.

In order to identify the influence of not using gloves in %DPU determination, a series of 50 samples of nylon and hybrid cords were prepared, previously dipped using the LDU. Half of the samples were prepared following the established guideline for the sample preparation

procedure, that is, using gloves during all process. In contrast, the other 25 samples were prepared without gloves. The %DPU was then determined for both sample groups and the results were compared, as detailed in section 4.1.

3.2 Dip Pick-up Measurements (%DPU)

As mentioned before, in this project the DPU measurements have been performed using the TD-NMR method. TD-NMR measurements were conducted on a Minispec mq20 from Bruker (Figure 15). The equipment is controlled by Minispec Plus software that allows equipment settings, create calibrations and perform measurements according to the applications created by Bruker.

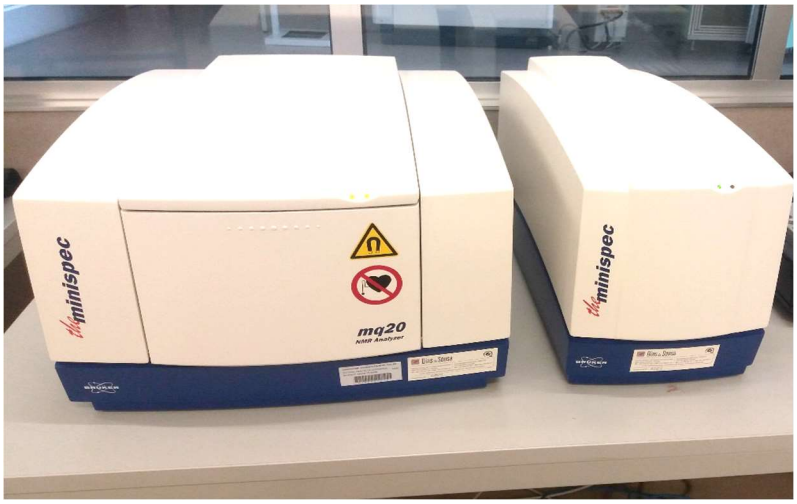


Figure 15 – Minispec mq20 from Bruker.

Bruker developed an application for C-ITA to measure dip pick-up on cords. This process and its conditions were properly studied and optimized by the equipment manufacture personnel so that the measurements can be efficient.

Before the insertion of the tubes in the equipment and measuring %DPU, it is required proper sample drying to avoid the interference of humidity, therefore, a drying step must be performed. Continental has established a procedure, which involves the following steps: (i) dry the samples in an oven at 105 ºC for at least 60 minutes, (ii) cover the tube before removing the sample from the oven, (iii) allow the sample to cool to ambient temperature (25 ºC), (iv) weight the sample, and, (v) heat the sample to 40 ºC for 30 minutes (the analysis temperature) (Hussmann, 2015).

After following the mentioned steps, the samples are ready for DPU measurements using TD-NMR. In Figure 16 is illustrated the data acquisition in progress, where it is measured the signal of the sample, and later returning a DPU measurement.

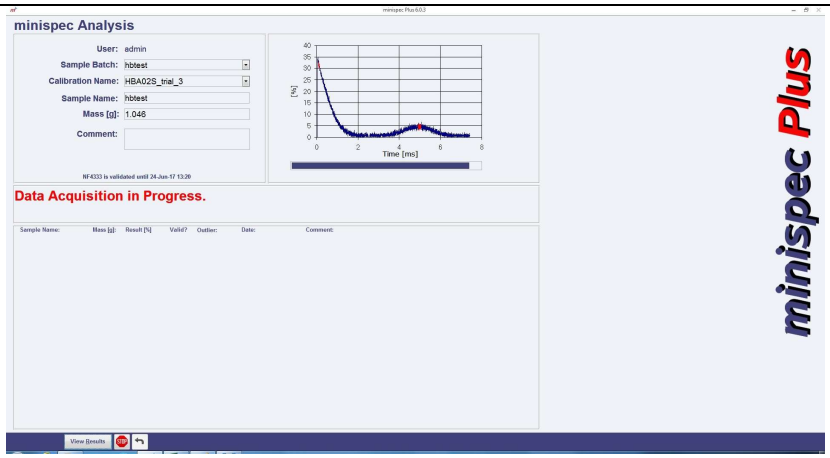


Figure 16 - DPU measurement

As mentioned above, it is essential to perform the drying of the samples correctly since it is expected that the measurement of %DPU can be altered by the presence of humidity. Thus, for this study, two groups of 25 samples were prepared: the first is the reference group and the second the study group. For the reference group of samples %DPU was measured following the established method, and the study group followed the same methodology, but skipping step (i), that is, the drying step.

In Figure 17 is possible to observe samples being cooled to ambient temperature before sample analysis.

Figure 17 - Samples ready for measurement.

3.3 Cord dipping

C-ITA is equipped with a machine that can replicate Single End in a laboratory scale, known as Lab Dipping Unit (LDU) – Figure 19. This equipment is used to dip coat one cord at a time and the impregnation of some of the cords used in this project were performed on this equipment.

Specifically, nylon and hybrid cords with the same properties as the reference cords (construction and supplier) were dipped using the LDU. These cords are shown in Figure 18.

Figure 18 – Nylon and hybrid cords dipped using the LDU.

Before running the LDU equipment, the operating conditions (oven temperature, stretch or tension applied and speed) must be properly set, since they will dictate the mechanical properties of the cord.

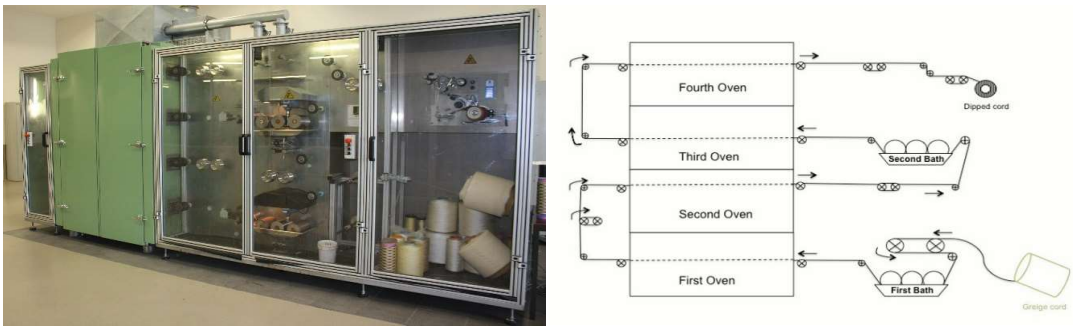


Figure 19 - LDU (left) and LDU Schematics (right).

In addition, it is required to prepare and place the dip in the equipment in the appropriate position. However, before the dipping process, it is necessary to measure dip's solid content (%SC) to verify if it matches C-ITA specifications.

The %DPU of a cord is related to the %SC of the dip used during the dipping process. The higher %SC will, the higher %DPU. Therefore, measuring the dip's solid content will provide information in what will be the cord's %DPU. In other words, to guarantee the %DPU will be in agreement with specifications, firstly the dip's %SC must within the specifications. For example, if a certain cord is dipped in an aqueous solution with approximately 17% SC, it should have a %DPU around 5%. Thus, if the specification for the cord's %DPU is lower than 5%, then it is required to have a dip with %SC lower than 17%. However, this relation is not inter-materials, since using the same dip in cords of different materials will results in cords with different DPU.

The equipment used to measure %SC is a solid measuring device, Sartorius MA100. Using a pre-set program with established conditions by Continental's Reference Laboratory, around 1 g of solution is placed directly in the aluminium plate shown in Figure 20 and the equipment is ready to start. Dip is heated to 105 ºC, allowing the evaporation of the solvent.

Figure 20 - Sartorius MA100.

The solids that remain in the plate represent the solid content of the solution. The mass of the solid is then divided by the mass of the solution (around 1 g), and the solid content fraction is calculated following Equation 3.

$$\%SC = \frac{m_{solids}}{m_{dip}} \times 100 \quad (3)$$

Where:

m_{solids} the mass of residues after evaporation;
m_{dip} the mass of dip placed in plate at the beginning of the test.

3.4 Minitab 17 statistical software

Minitab 17 is a statistical software used by Continental that allows quick and effective statistical analysis of results. In this project, Minitab 17 will be used to validate the experimental results obtained.

In a statistical analyse of results, a hypothesis test can be used to compare two values obtained by two different methods, allowing to determine the difference between the two values. However, since the objective of this study was to determine if the results obtained were equivalent, the traditional hypothesis test will not provide the necessary information to

conclude with confidence and precision if, in fact, the results are equivalent. Therefore, it was performed an equivalence test.

The equivalence test differs from the traditional hypothesis test, in which the results are tested for significant difference, whereas in this case the results are tested for similarities, within a range of equivalence. In other words, a maximum deviation between the two results is pre-defined, and by applying the equivalence test it is possible to check if the results have a deviation inferior to the maximum value established (DeCook, 2015).

In this project context, the range of equivalence is defined as ±0.5%.

3.5 Different Nylon cords with a single calibration

In the previous work developed by Silva (2017), the TD-NMR was successfully calibrated for a nylon cord, hereinafter referred to as reference cord. One of the objectives of this work is to study if the validated calibration can be applied to all nylon cords, or if it is required a new calibration for every cord. Essentially, C-ITA uses raw materials from different suppliers and produces cords with different constructions. Knowing if the TD-NMR calibration validated for reference cord can be confidently applied to all cords produced with the same material regardless of its origin and construction will help to the implementation of the TD-NMR method in quality control.

To study the applicability of the nylon calibration in nylon cords with distinct characteristics, firstly was studied a cord with different construction from the reference cord, designated Cord A.

Then, it was studied a cord with the same construction as reference cord, but with different supplier, designated Cord B.

Finally, it was studied a cord which has different construction from reference cord and Cord A, furthermore, it has a different supplier from Reference cord and Cord B. This cord will be designated Cord C.

For every cord, Cord A, Cord B and Cord C, samples were collected from fabrics that were previously validated by the chemical method and shipped to clients. Resorting to C-ITA database, the results obtained through chemical method by quality facilitators were collected. Then, the samples were analysed using TD-NMR and the obtained results were compared to the collected data. This process is illustrated in a simple scheme seen on Figure 21.

After comparing results obtained for each cord, a statistical analysis was performed to assess the equivalence between the values obtained through the two different methods.

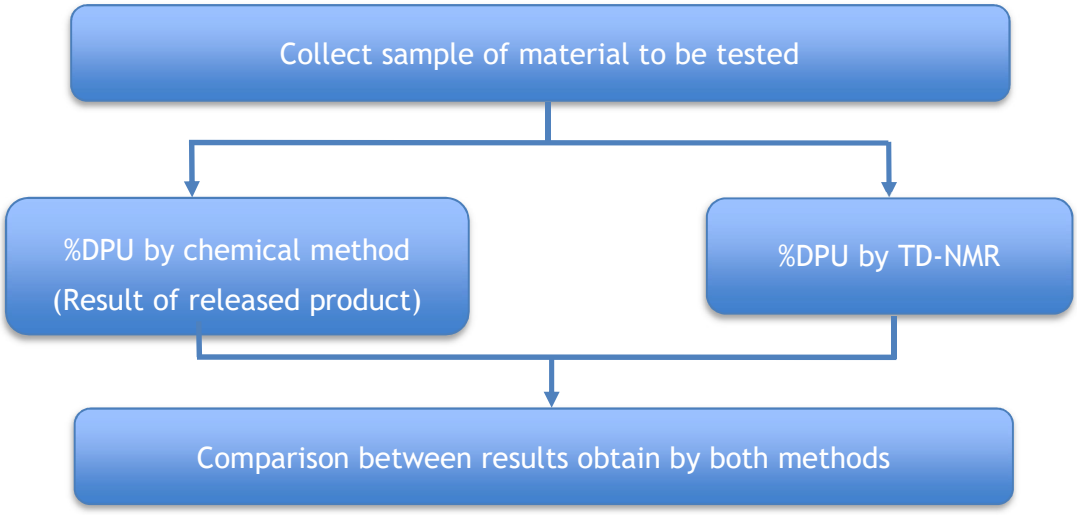


Figure 21 - Schematic of the methodology for studying different cords.

4 Results and discussion

4.1 Influence of handling the samples without gloves

As previously mentioned, one of the objectives of this work was to study the influence of handling samples with or without gloves during the sample preparation (explained on chapter 3.1) on the %DPU determination. To this end, a series of samples was prepared using gloves before placing them into tubes for TD-NMR tests. In this way, the skin from the operator's hands did not touch the samples. Another series of samples was prepared without gloves. Therefore, these samples were in direct contact with the skin, which may leave foreign particles on the surface of the samples, transferred from the operator's hands. The results were then compared in order to understand if this factor affects the %DPU (Figure 22). The series of samples handled with gloves is referred to as "Reference", and the series of samples handled without gloves is called "No gloves".

The samples were collected from a bobbin, therefore, sample number 1 was the first sample collected, from the outer part of the bobbin, thus corresponding to the last instant in the dipping process. Sample number 2 was collected after sample number 1, so it corresponds to the piece of cord that was dipped exactly before the sample 1.

As the sample number increases, the closer the sample is to centre of the bobbin.

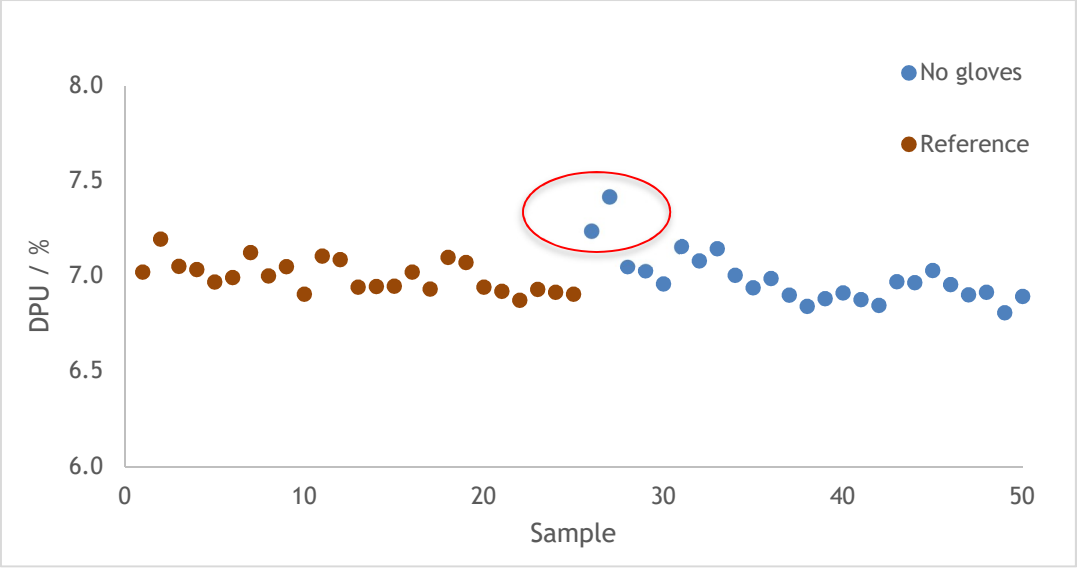


Figure 22 - Comparison between "Reference" and "No gloves" series for nylon cords dipped with 22% SC dip.

The results in Figure 22 seems to suggest that, there was no significant difference between the two sets of points, indicating the samples were not significantly affected by any external particle/grease.

However, it could be verified that the first two samples of the No gloves series (points identified in Figure 22) had a higher %DPU compared to the rest of the samples series, allowing to speculate that, this alteration might be related to the preparation of the samples method. Since the samples were prepared in a sequential order and without interruptions, any dirtiness present in the operator's hand might have been transferred to the cord during the preparation of the first two samples, which would affect the rest of the samples to a lesser extent. As a consequence, the results would not be appreciably influenced.

Besides, considering only the Reference values (Figure 23) it was possible to identify a characteristic pattern in the evolution of %DPU values. Samples that represent an earlier stage in the dipping process, had lower values %DPU. For example, as mentioned before, sample number 2 corresponds to the piece of cord that was dipped exactly before the number sample 1. So, the %DPU of sample number 2 was lower than the %DPU of sample number 1. This behaviour was not predicted and went unnoticed since the verification of this patterns implies the performance of a significantly big number of sample measurement, and this kind of analysis was not performed before. Further explanation is presented in Section 4.1.2.

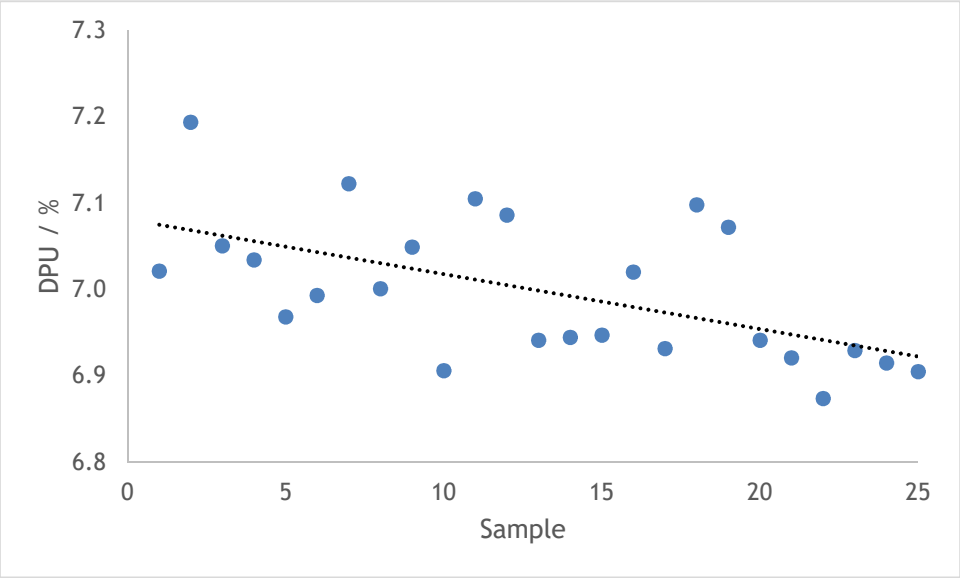


Figure 23 - Reference values of DPU for nylon 22% SC with tendency line (dotted line).

Nevertheless, in order to verify this trend, another spool of nylon was dipped and a new group of Reference samples was prepared. Figure 24 represents the result of the measurements conducted for the new Reference samples and the behaviour exhibited is similar to the one described before: a linear decrease of DPU occurs from the left to the right of the x-axis. The left side of this axis corresponds to the first samples analysed, sample number 1, sample

number 2, etc. As mentioned before, these samples were the last ones to be dipped so they are the farthest from the centre of the bobbin.

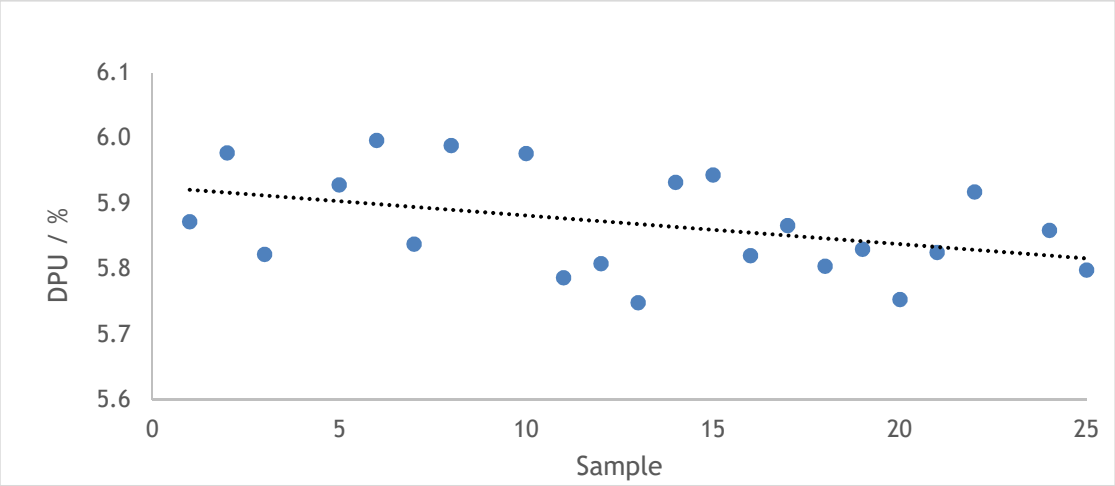


Figure 24 - Results of Reference samples of nylon 17% SC bobbin with tendency line obtained from linear regression in Excel (dotted line).

In summary, two series of Reference samples were analysed (Figure 23 and Figure 24) and the results obtained exhibited the same behaviour: a decrease in %DPU occurs from the samples that correspond to the last moments in the dipping process to the ones that correspond to the beginning of the process. Hence, as the results of %DPU of two independent bobbins exhibited identical, it led to the conclusion that all samples should follow this behaviour.

The objective of this study was to understand if samples prepared using gloves had similar value of %DPU to that of the samples prepared without gloves. One way of verifying the similarity of the two groups is to compare the average %DPU result since it was expected a constant %DPU in all cord. However, such a method cannot be applied. Attending to the trending observed (Figure 23 and Figure 24) for %DPU values through the cord, a comparison between samples that represent an earlier dipping stage and samples that represent a later dipping stage would result in an error. Since it is expected samples from earlier dipping moments to have lower values, direct comparison between their results with results from samples representing later dipping moments would result in a difference.

Given this, the trend observed cannot be ignored and it was necessary to determine a method that allowed the comparison between the results obtained for samples of the same cord through its entire length.

It was proposed a method to predict the range of values in which the following samples' %DPU would vary. Firstly, it was required to determine in which range the Reference samples' %DPU varied. To do so, it was calculated the maximum difference between all %DPU values of Reference samples and its tendency line equation. Posteriorly, to obtain the top limit of the range, it was represented a line with the same slope as the tendency line, obtained by adding

half of the maximum difference to the tendency line. To obtain the lower limit of the range the same procedure was followed, except it was subtracted half of maximum difference.

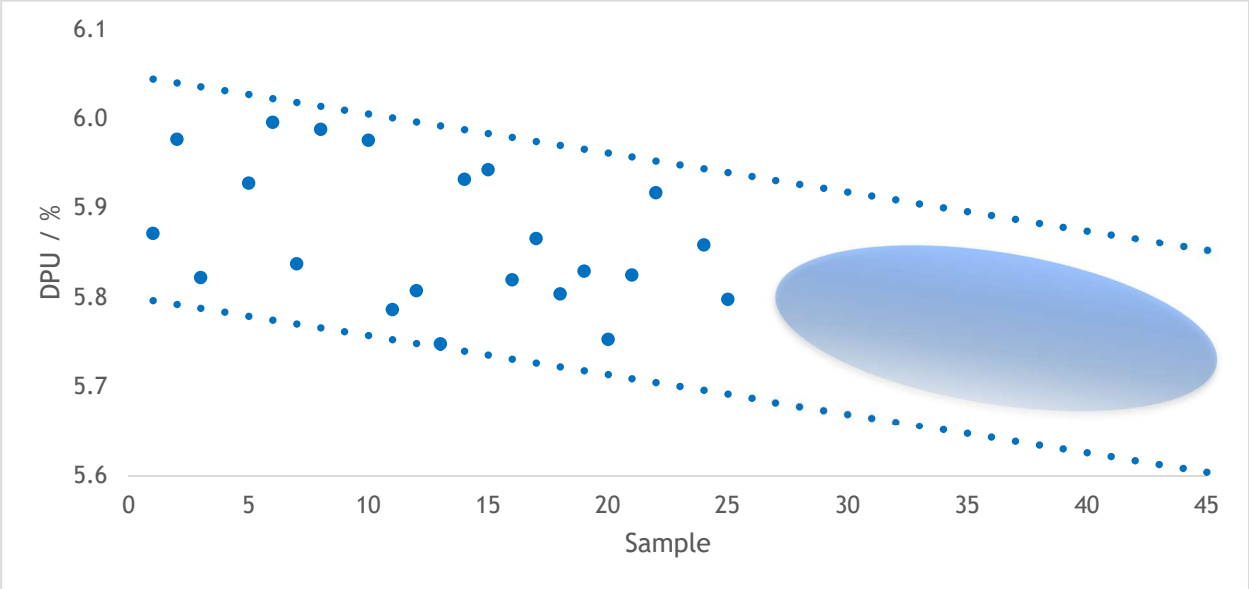


Figure 25 - Prediction of next samples' results (blue region).

The area limited between the two lines obtained, demonstrated by the blue area in Figure 25, represents the area of the samples collected after the 25 reference samples should have its %DPU value represented. A more detailed explanation is found in Appendix 2.

After the determination of this area, it was possible to compare the results obtained considering the trend.

After examining the data from the first group of samples in Figure 22, it was concluded that the results of most samples were not affected by the manipulation without gloves, since the values from the Reference series of samples were similar to the No gloves series. It was speculated that this was due to the fact that the external particles that came from the operator's hands were transferred to the cord by the first samples that were prepared, so, since all samples are prepared consecutively, only the first ones are affect by the presence of these particles on the operator's hand. Therefore, a new study was conducted with a slight change: instead of an uninterrupted preparation of all samples, the process was stopped and other tasks and activities were performed after the preparation of a sample. In this way, it was possible to guarantee that when the preparation of the next sample was performed, the operator's hands were as dirty as they were for the previous sample.

By applying this alteration to the methodology and the prediction range, it was clear that manipulating the samples without gloves would cause alterations to the DPU value obtained through the TD-NMR, as showed is Figure 26. Approximately half of the samples appear

above the maximum value predicted by the calculated model, while the rest of the samples appear within the prediction area, yet close to the limit.

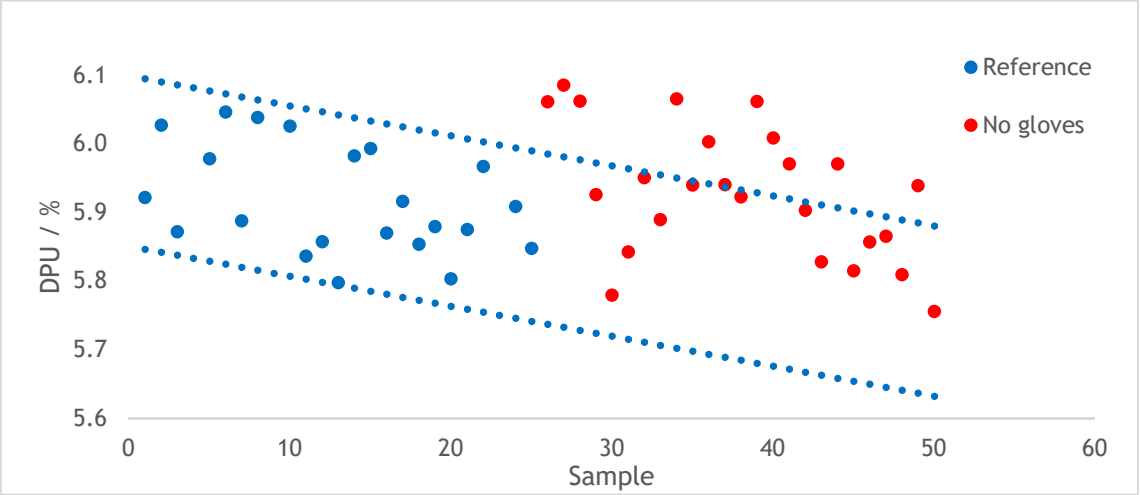


Figure 26 - Comparison between Reference samples and No glove samples for nylon 17% SC bobbin.

Representing the same range calculated for the reference samples, but adjusting it to the No glove series, most of the samples fitted in the defined range, as it can be seen in Figure 27. This leads to the conclusion that the %DPU of samples handheld without gloves underwent a shift. This was interpreted as a constant influence in the results that was consequence of the presence of external particles, since the equipment was not capable of removing any external signal present in the sample. Additionally, the same behaviour of decreasing in the %DPU for the samples closer to the bobbin centre was maintained.

Essentially, it was possible to see that the handling of the samples without gloves resulted in an increase in the %DPU. For this series of samples, samples from the No gloves series had its dip pick-up percentage increased in approximately 0.13% when compared to the Reference samples. However, it was considered that this alteration happens due to external particles in the hands of the operator. So, each analysis may have a different increase in the %DPU of the samples, due to variation of type and quantity of this external particles for each operator.

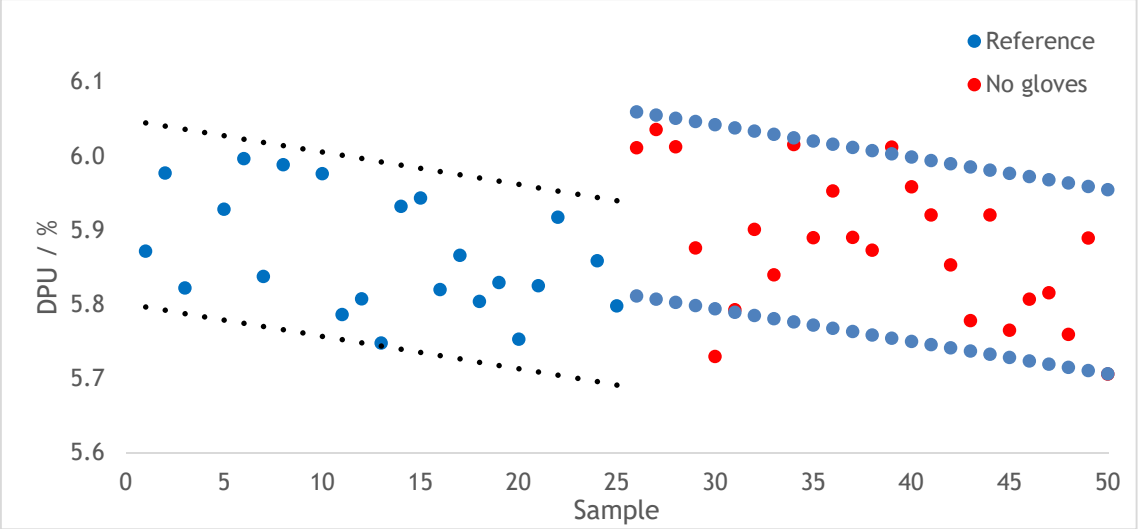


Figure 27 - Deviation from the predicted area showing a shift in No gloves sample group.

Since it was possible to prove that nylon samples are affected by unprotected hand manipulation, it was performed the same study in a hybrid cord in order to understand if the results were similar. Therefore, the same procedure described previously was applied to the hybrid cord and its results can be seen in Figure 28. As expected, it was possible to observe an increase in %DPU in the series of samples handled without gloves, during their preparation, in comparison to Reference samples.

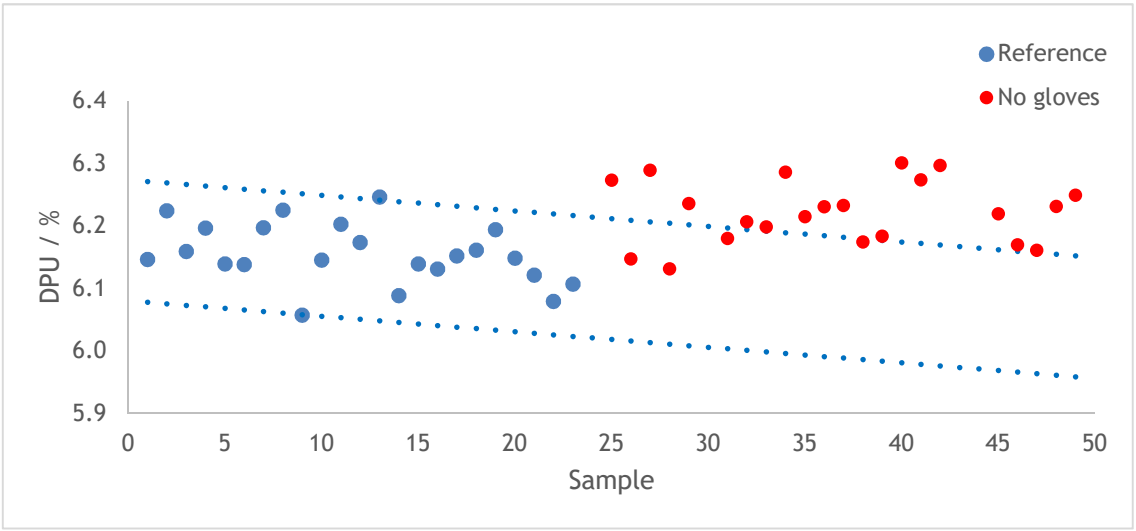


Figure 28 - Result of No glove samples for hybrid bobbin.

The results in Figure 28 supported previous conclusions achieved for nylon cord, specifically that handling the samples without gloves will undoubtedly influence the %DPU result. Nevertheless, it will not affect in great magnitude the results. In other words, in case a sample is prepared without proper handling (that is, using gloves), the results will not be largely changed, since the maximum difference observed was inferior to 0,2%. However, to achieve a

more faithful result, the manufacture's indications should be correctly applied, so, gloves should be used.

4.1.1 Influence of the operator

As mention before, it was considered that every analysis may have a different increase in the %DPU of the samples, due to variation of type and quantity of external particles, which means that different operators performing the preparation of the samples might lead to different results. So, it was performed a study to understand how manipulation by different operators can influence the results of the test. Five operators were selected and each uninterruptedly prepared 5 samples of nylon 17% SC bobbin without gloves. The five selected operators work on the same department, performing different tasks. Also, the group includes different ages and genders. Operator 1 prepared the samples 1 to 5, Operator 2 prepared the samples 6 to 10, Operator 3 prepared the samples 11 to 15, Operator 4 prepared the samples 16 to 20 and Operator 5 prepared the samples 21 to 25. Afterwards, each sample was analysed and its results can be seen in Figure 29.

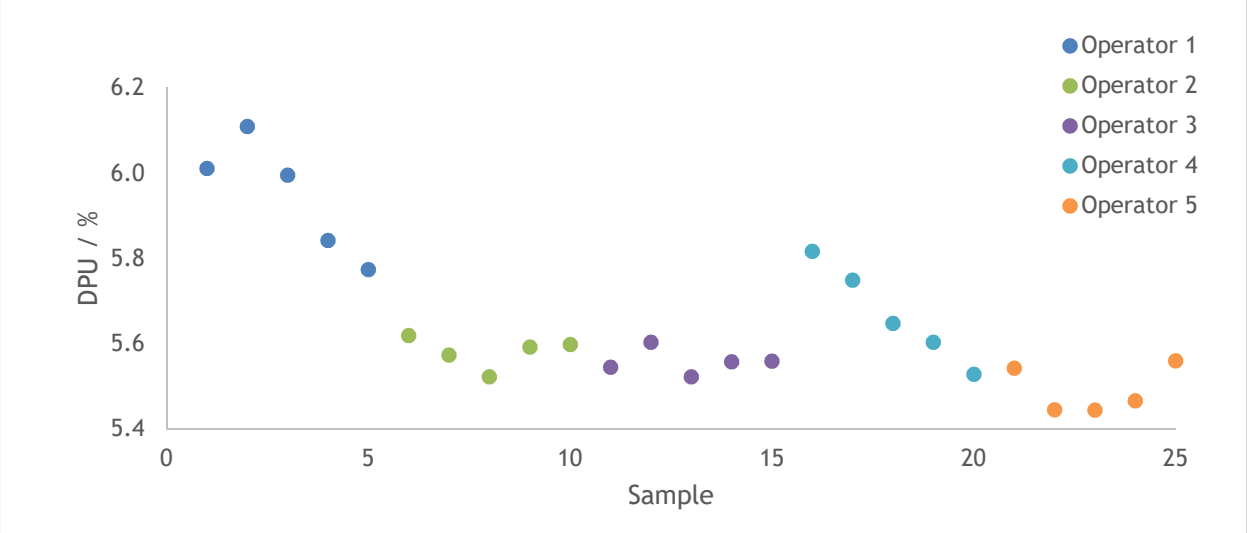


Figure 29 - Results of nylon 17% SC samples handheld by different operators.

By observation of Figure 29 it is not possible to identify any trend, which supports the idea that each operator has its own influence on the samples. In this case, the samples handled by Operator 1 and Operator 4 showed higher values of %DPU. Also, the first samples prepared by these operators show higher values and a decreasing tendency, reinforcing the previous statement that preparing samples without stops leads to a decreasing of the influence through sequential samples. On the other hand, Operator 2, Operator 3 and Operator 5 have almost no interference with the results. Therefore, while it was possible to conclude that there was an influence resulting from the handling of samples without gloves, this will depend on the quantity of external particles that come in contact with the cord. In addition, the selected

operators work in a cleaner environment than quality facilitators, thus the latter may increase the influence in the DPU if they prepare samples without using gloves.

4.1.2 Solid Content variation

As previously mentioned, the trend observed in the %DPU results was not expected to find. That is, the decreasing values of DPU from the samples that correspond to the last moments in the dipping process, to the ones that correspond to the begging of the process. In other words, from the samples that are the farthest from the centre to the ones that are on the centre of the bobbin. In an attempt to find the reasoning for this trend, while operating the LDU, several measurements of %SC of the dip were performed. Normally only one measurement is performed, before starting dipping the cord. Since it is known that the %SC and the %DPU are related, for this study several measurements were performed in order to determinate if the %SC varies through the process of dipping the entire cord.

Samples of dip were collected at specific moments during the dipping of two bobbins of cords, one nylon bobbin and one hybrid bobbin. Given the fact that both materials were dipped with the same dip, it made changing solutions unnecessary.

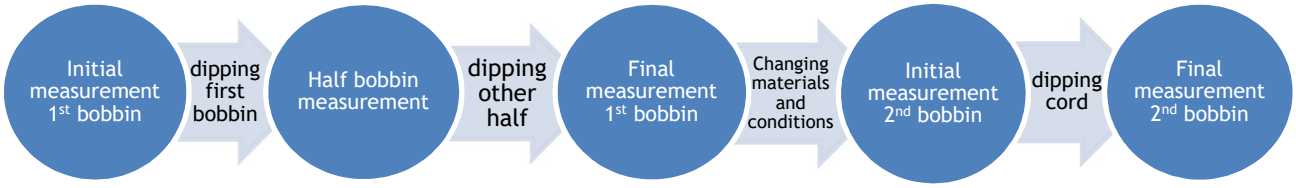


Figure 30 - Schematic demonstration of the several %SC measurements.

Initially it was performed the traditional measurement before the dipping of cord started, followed by another when half of the dipping of the first bobbin was done and another when the dipping of the first bobbin was completed. Following the end of the dipping of the nylon bobbin, the conditions of the LDU had to be changed since the second bobbin was of different material, a hybrid cord. After a period of stabilisation, a measurement of the %SC was made before starting the second dipping. Next, a second one was performed when at the end of the second bobbin dipping process. Figure 31 illustrates the five measurements made, giving the evolution of the dip %SC.

A gradual increase of the concentration of the dip with time can be seen on the results showed in Figure 31. This data corroborated the behaviour of the %DPU observed in the bobbins that were analysed.

As previously mentioned, a higher %SC in the dip solution results a higher %DPU of the dipped sample. Then, according to the data given by the measurements of %SC, the first samples taken from the bobbin, that represent the final moments of the impregnation, should

have %DPU higher than that of the last samples taken from the bobbin, which represents an earlier moment of the impregnation process.

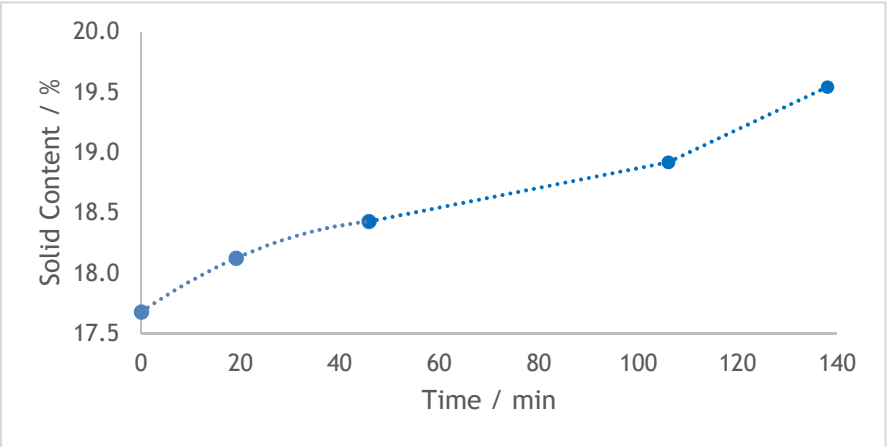


Figure 31 - Variation of Solid Content of dip during dipping process.

Given the obtained results, it is believed evaporation of the solvent takes key role in the increasing concentration, since the dip is an aqueous solution.

4.2 Influence of inappropriate drying of samples

In order to understand how important performing a correct drying of the samples is to the determination of %DPU by TD-NMR, this step was removed from the process so that the results could be studied. Following the methodology described in the Chapter 3, the samples were prepared and its %DPU was measure without drying them in the oven.

It was expected to see an increase in the %DPU of the sample that had not been dried up, since moisture works as a contaminant to the sample and the equipment is not prepared to subtract its signal, using Bruker's application to measure %DPU.

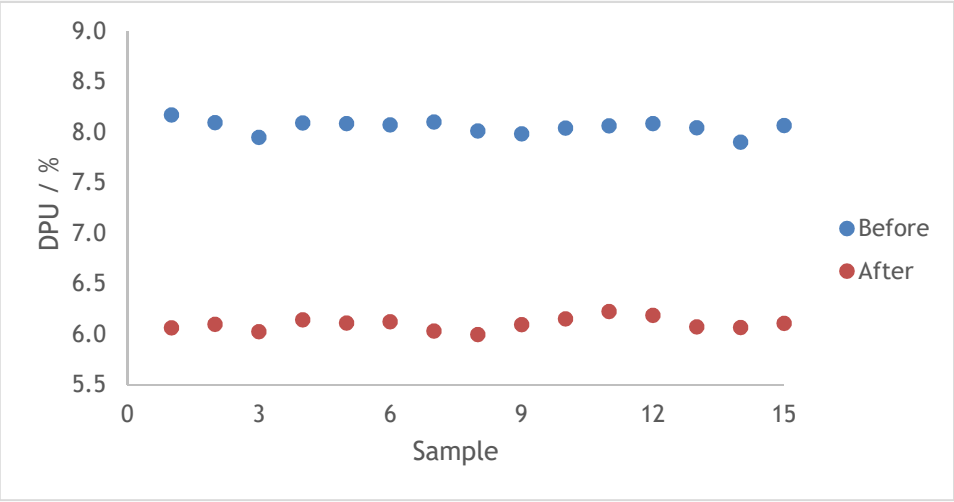


Figure 32 - Results of %DPU before and after being dried at 105 ºC for 1 h.

In Figure 32 it is compared the %DPU of the samples before and after being dried. There is a clear difference between the results of the same sample before and after due to the presence of humidity on the cord. For this set of samples, there was a decrease of nearly 2% of the %DPU value due to moisture removal. Thus, proving the drying of cords of major importance in sample preparation.

While performing the %DPU, it was possible to understand if the samples were properly dried. More specifically, while heating samples to the analysis temperature in the heatblocks, droplets began to form in the tubes, meaning humidity was still present. This was very visible during the performance of this study, as it can be seen in Figure 33.

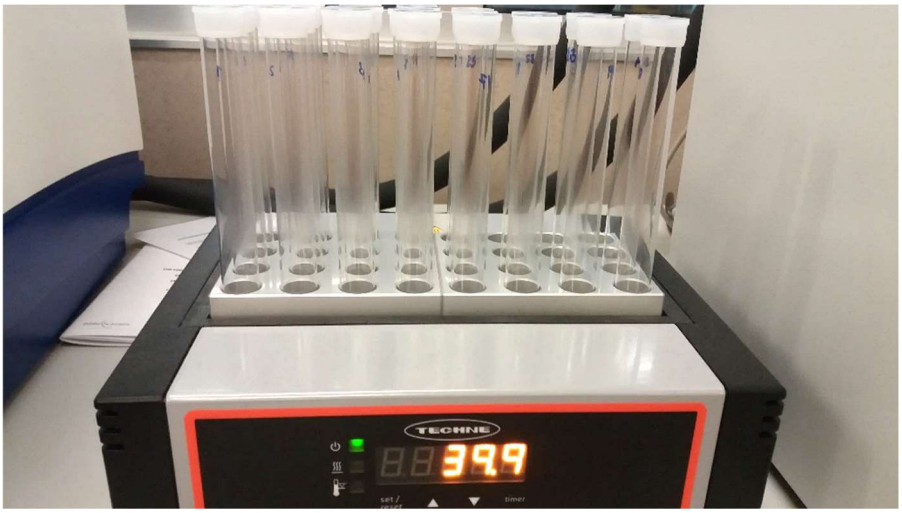


Figure 33 - Visible presence of humidity in tubes due to insufficient drying of samples.

4.3 Study of different construction and Suppliers for nylon cords

As mentioned in section 3.5, currently there is a validated calibration for a nylon cord (reference cord). The applicability of this nylon calibration to the analysis of cords with different construction and suppliers was studied, according with the methodology established in the same section. The interference of these two factors in study, construction of the cord and the supplier of the material will be evaluated, firstly individually and later combined in one cord.

In this section, it will only be studied nylon cords due to the fact that, currently, C-ITA only produces one hybrid cord. Thus, rendering this study for hybrid cords not required.

4.3.1 Cord with different construction

To study the applicability of the calibration to nylon cords with different construction from the Reference Cord, it was chosen a cord with the same supplier as Reference Cord, but with different construction, which is designated Cord A.

A total of 22 samples were collected, prepared and analysed using the TD-NMR. Figure 34 represents the comparison between results of production (values in C-ITA database obtained by quality facilitators using the standard method) and those obtained by TD-NMR. Plus, it is represented the limits of the specification and target value for %DPU for Cord A.

The results show there was no tendency, in other words, the %DPU obtained from TD-NMR may be slightly higher or lower than the %DPU determined by quality facilitators.

Moreover, all values are within the specifications limits. However, as mentioned before, the chemical method has an associated error intrinsic to its steps, therefore, it is possible some production results, which values are near the limits of specification, may be off such specification. These results help to fortify Continental objective to have a controlled method that allows to achieve good results for its products.

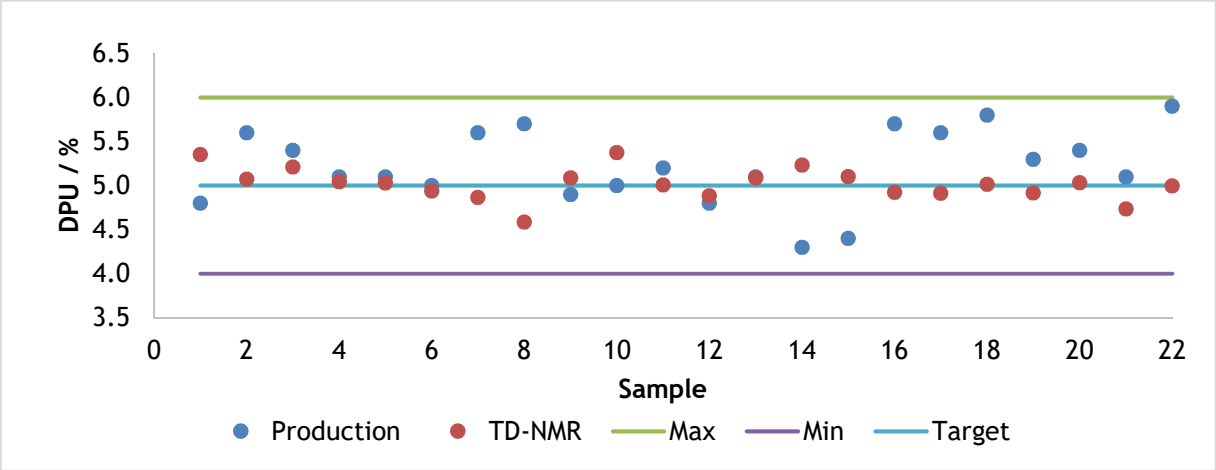


Figure 34 - Comparison of TD-NMR with Production results for Cord A.

Until present time, no error was established for TD-NMR methodology, as it is still required further studies to determine this value. However, it is expected this equipment is able to measure %DPU with a small deviation from the standard method.

A curious aspect can be seen, TD-NMR results depict a very stable result of the %DPU around the target (value the %DPU should be according C-ITA specifications), while Production's values, by the contrary, portray a more instable result. This may demonstrate that the dipping process may be more stable than is currently thought to be.

In order to validate the suggestion that the use of two methods are equivalent, statistical analysis was performed. It was performed an equivalence test between results from Production, as the reference values, and TD-NMR results as the tested values. This test differs from the traditional hypothesis test, in which is tested for significant difference, whereas the selected test tests for similarities, within a range of equivalence.

To perform an equivalence test, first it is required to establish an equivalence range, a range that limits the maximum error in which the tested values are still accepted as equivalent. The equivalence range is set as ±0.3% by C-ITA.

Figure 35 represents the test executed for a 95% Confidence Level (CL). It was possible to conclude that it cannot be claimed equivalent since the resulting p-value is 0.162 higher than 0.05, which is the maximum value for which is possible to claim equivalence.

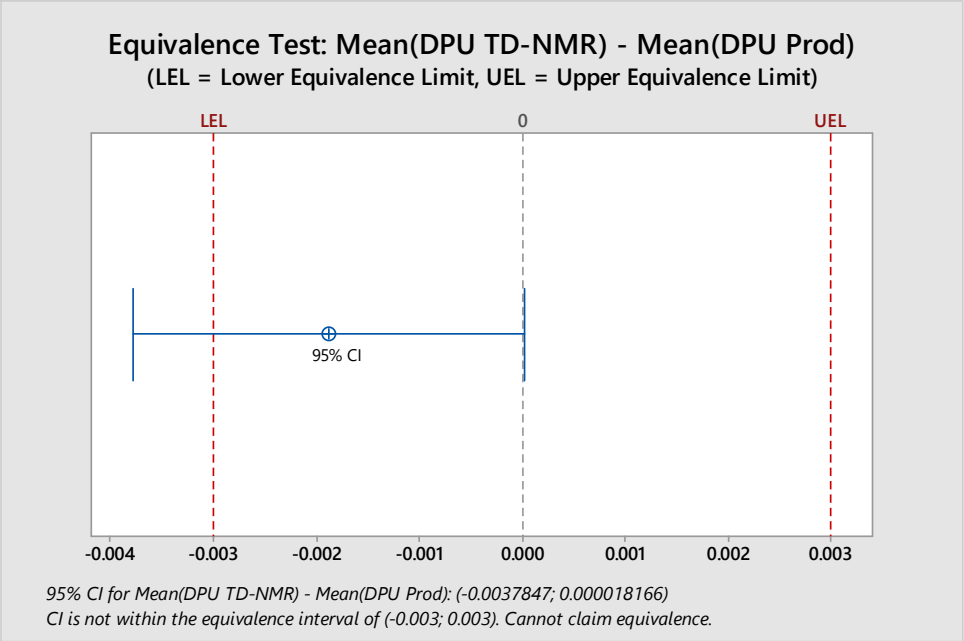


Figure 35 - Equivalence test for Cord A samples with ±0.3% equivalence range and 95% CL.

The test was performed calculating $'Mean\ of\ TD-NMR\ results' - 'Mean\ of\ Production\ results'$, resulting in a negative value. Therefore, there is a tendency for the value of %DPU from production to be higher than the obtained by TD-NMR, as it is shown in the previous figure. Such a tendency can be explained by the resulting effect errors that may occur during the execution of chemical method, for example in case proper dissolution of fibres is not achieved the resulting %DPU will be higher. Having this tendency in consideration, it was then proposed an alteration to the equivalence range, increasing it to ±0.5%. Although, it is possible to keep the upper limit without affecting the results (test only failed due to lower limit).

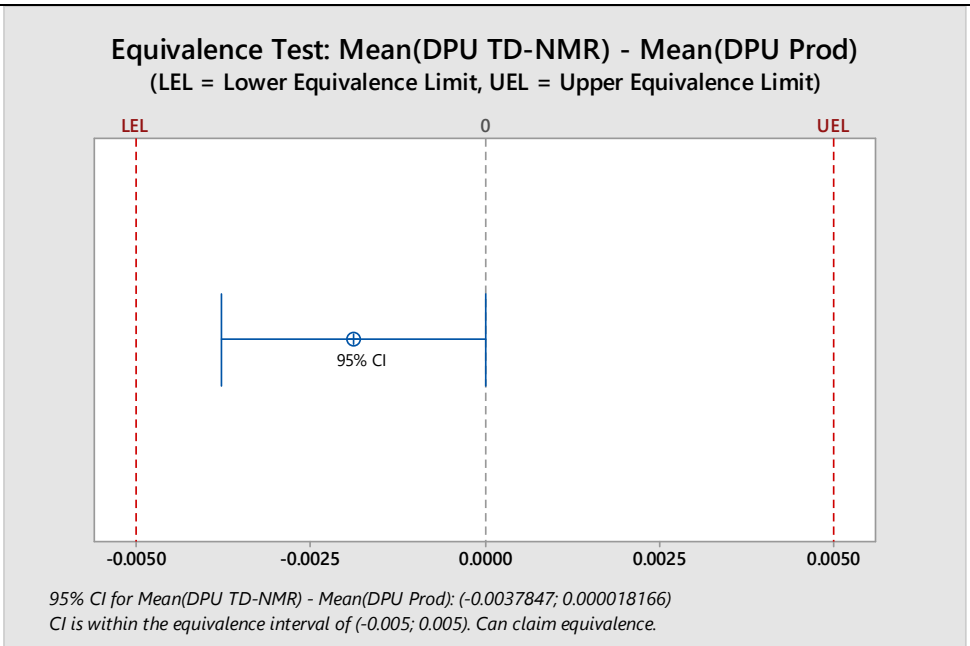


Figure 36 - Equivalence test for Cord A samples with ±0.5% equivalence range and 99% CL.

The test was repeated test with the newly proposed equivalence range, and it is represented in Figure 36, achieving a p-value of 0.005. Since it was lower than 0.05, it was possible to claim for equivalence between samples' results.

Although a good result was achieved, it was only possible since the range of equivalence was enlarged. Therefore, to minimise the possibility of error, the same test was performed (with equivalence range of ±0.5%), but this time with an increase in the CL, changing it to 99%.

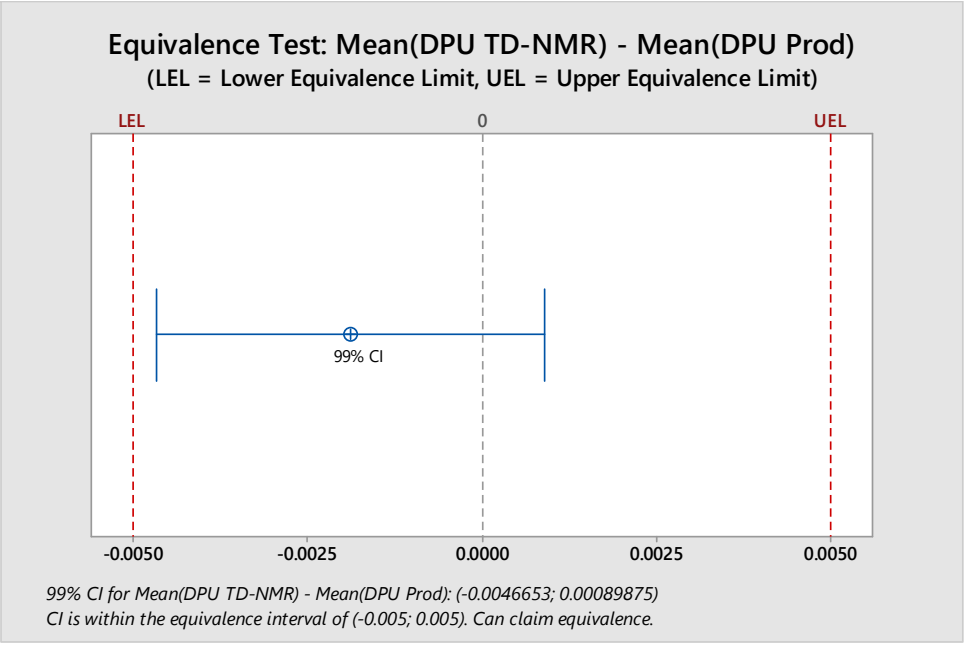


Figure 37 - Equivalence test for Cord A samples with ±0.5% equivalence range and 99% CL.

Figure 37 shows the results obtained for the equivalence test, where a p-value of 0.005 was obtained. Since the resulting p-value was inferior to the new maximum value, 0.01, it was possible to claim that the results obtained by TD-NMR and results obtained by quality facilitators are equivalent with 99% of certainty.

It was then possible to conclude that the equipment can measure %DPU using the calibration for the Reference Cord and have great confidence in its results.

4.3.2 Different supplier

Testing different suppliers is of great importance to understand if the equipment has the ability to measure different types of cords. Mainly because the source of the material used to twist cord and later dipping it may have great influence in the obtained results via TD-NMR. As mentioned before, each supplier may apply spin finishing oil and the equipment should be able to cancel out its signal, however some interference to the final result may be possible.

Given this, samples from Cord B, a cord with different supplier from Reference Cord, but with the same construction, were collected. Having collected a total of 20 samples, %DPU results obtained through both methods are represented in Figure 38.

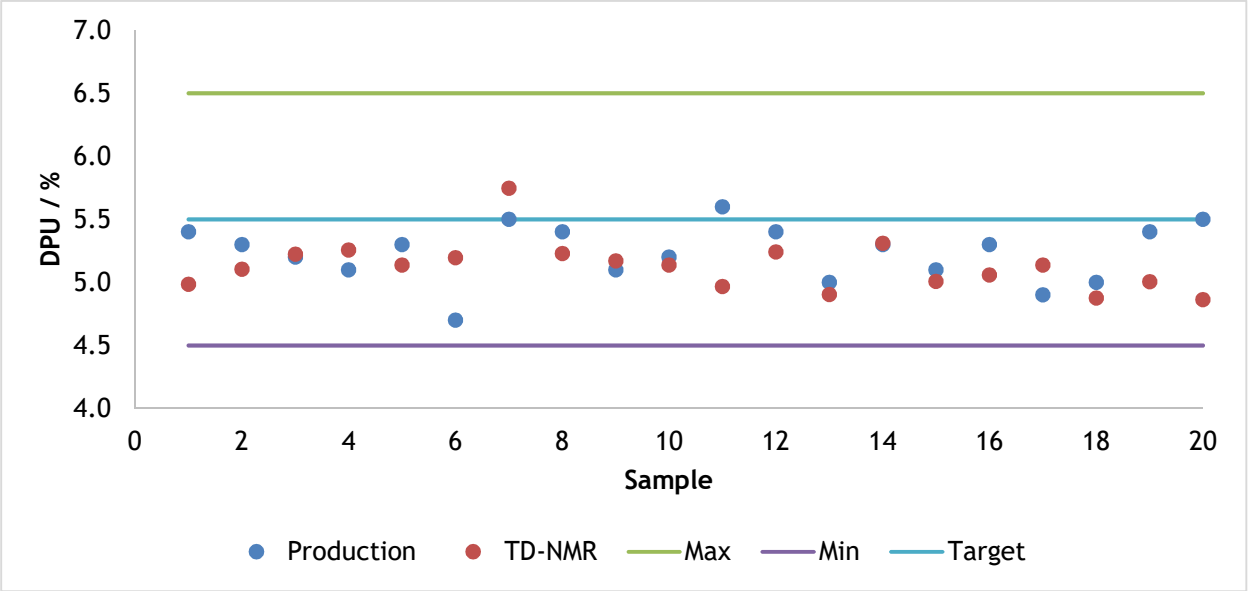


Figure 38 - Comparison of TD-NMR with Production results Cord B.

For Cord B, it appears not to be great divergence between the two groups of results, and as the results achieved in the previous section, there was not a visual trend in the difference between values of %DPU. Such results may be interpreted as an indication of similarity between group of results. However, to verify the equivalence of the results, and potentially validate the calibration for cords with different suppliers, an equivalence test must be performed.

The test was performed using the established equivalence range of ±0.5% and using a 99% CL, having its results displayed in Figure 39. It was obtained a p-value of 0.003 demonstrating the equivalence of both methods' results (p-value lower than 0.01). Thus, it is possible to perform %DPU measurements using the reference cord calibration for cords with a different supplier.

Nevertheless, it is important to state that the supplier which was tested is one of many in C-ITA. Thus, it is possible that a particular supplier provides other interferences that are not contemplated in all samples collected until this point. In conclusion, this study should be continued and further suppliers should be tested.

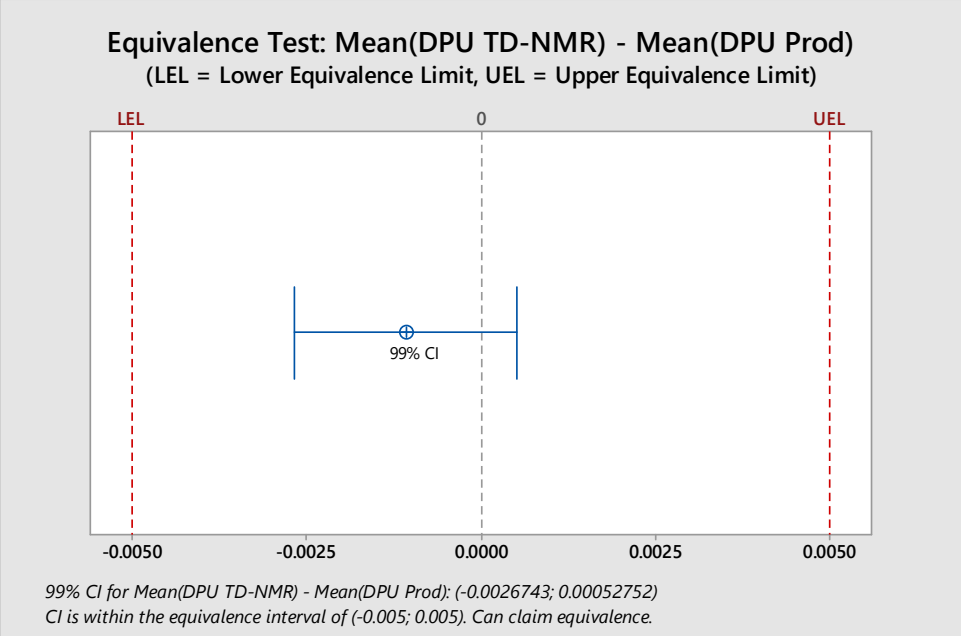


Figure 39 - Equivalence test for Cord B samples with ±0.5% equivalence range and 99% CL.

4.3.3 Different construction and supplier

At this moment, it was proved the calibration can be successfully applied to measure the %DPU of cords with different constructions and %DPU of cords from different suppliers. The next logical step should be proceeding with the same methodology for a cord with different construction and different supplier from the Reference Cord. In addition, as mentioned before, only a different supplier, besides the one from the Reference Cord is tested and studied. Therefore, when selecting Cord C, it was chosen carefully, not only to have a different construction and supplier from the Reference Cord and different construction from Cord A, but also to have a different supplier from Cord B.

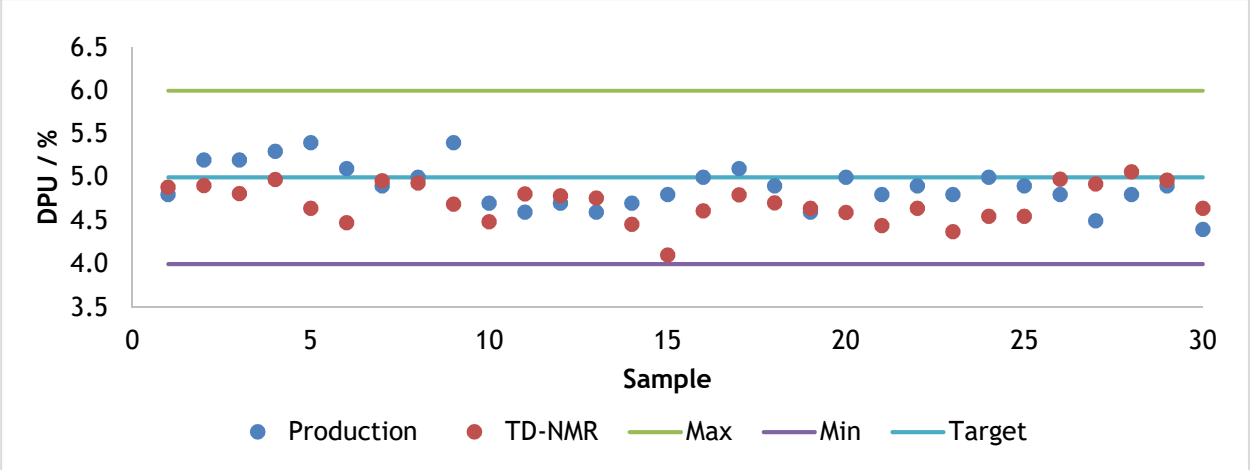


Figure 40 - Comparison of TD-NMR with Production's results for Cord C.

A total of 30 samples were collected and measured its %DPU having the comparison between results displayed in Figure 40.

As the previous studies, there are no visible differences or tendency between the two sets of samples. Results obtained with TD-NMR may be higher or lower than results obtained by quality facilitators, allowing the suggestion that results from both methods may be similar.

In order to ascertain the previous statement, proof must be gathered. It was then performed an equivalence test between %DPU results obtained in C-ITA database and %DPU results obtained using the equipment in study. Figure 41 displays the resulting information of the performed equivalence test.

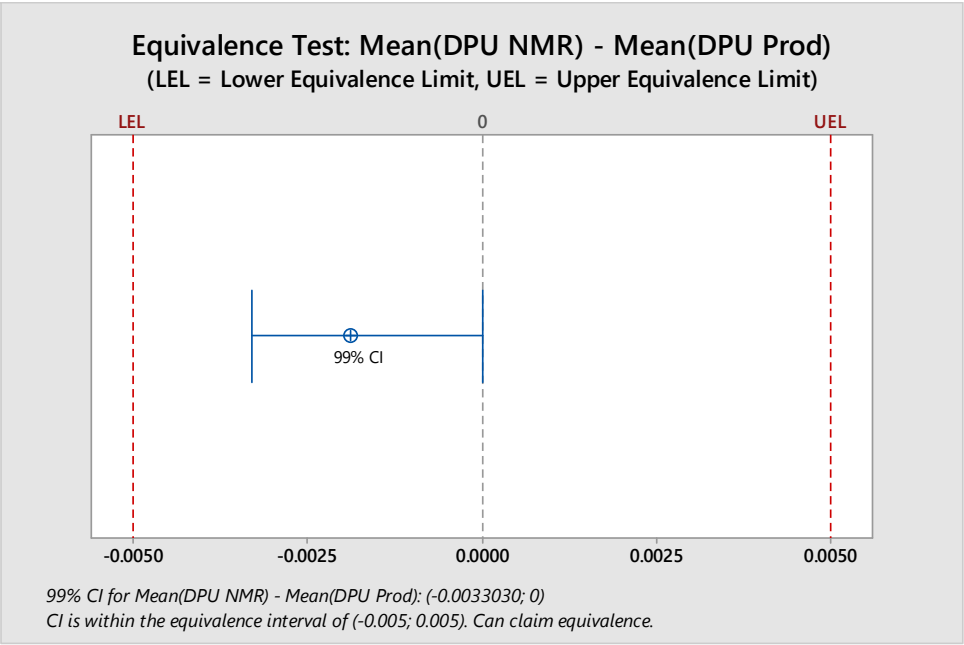


Figure 41 - Equivalence test for Cord C samples with ±0.5% equivalence range and 99% CL.

The results from this statistical test proved what was suggested from the analysis of Figure 40. The two sets of results are very similar, as the resulting p-value was inferior to 0.01.

For this test, Minitab 17 could not return a p-value with higher precision, thus it was obtained a p-value of 0.000, allowing to claim with 99% of certainty that these samples have equivalent results.

It is then possible to claim that the calibration can be satisfactorily applied for the determination of %DPU in samples with different construction and supplier from the Reference Cord without major differences from the results obtained by the standard method. However, as it was said before, throughout this project, besides the Reference Cord supplier, only two suppliers were tested, allowing space for doubt in what concerns different suppliers. Therefore, it is required further studies to understand if other suppliers spin-finishing oils can interfere with the results.

5 Conclusion

This project will provide more information on the use of a TD-NMR for %DPU measurement on nylon and hybrid cords at C-ITA, equipment that will strongly influence the quality control of its products.

Trying to identify which factors in measurement %DPU could most affect the results obtained, three potential situations were identified: contamination of the material during sample preparation in case no gloves were used, inappropriate sample drying and improper placement of sample in TD-NMR tube, being the latter solely dependent of the operator care, thus not being conducted any study. In order to understand the effects and its magnitude, a series of tests was performed for each situation. It was possible to conclude that, although not in a large scale, contaminants from hand can affect the results, resulting in %DPU overestimation, and it is recommended to wear gloves for manipulating both the samples and the material used to perform the measurement.

At the same time, as it was expected, it was observed that inappropriate drying of samples resulted in higher values for %DPU, which evidences the importance of this step on the %DPU determination.

Another point of major importance to C-ITA was to understand if there was a need to create calibrations for each nylon cords with different properties from Reference Cord used for nylon calibration. Three different cords with three different properties were studied: a cord with different construction from the original nylon cord, another with different supplier and a cord that combined both differences. To perform statistical analysis, it was proposed an equivalence range of ±0.5%. It was proved that for every type of cord tested, all results could be claimed equivalent. Furthermore, it was proved with a great confidence since all cords can be claimed equivalent with 99% CL. Therefore, it is possible to conclude that different cords of nylon can be measured using the same calibration method established and validated for the reference nylon cord.

Such results are important to C-ITA since it shows that the implementation of the equipment in its quality control can be simplified. Also, it was possible to conclude that, in case proper preparation of samples is not attained, results may be influenced, thus requiring care.

This project had great importance in Continental's commitment to have a method that allows rigorous measurements of the properties of its products, thus ensuring the quality of the latter, however, more studies must be performed to deepen the knowledge involved in dip-content study via TD-NMR.

6 Assessment of the work done

6.1 Objectives Achieved

At the beginning of this project it was proposed to identify which factors in sample preparation could influence the result returned by a TD-NMR. In addition, it was proposed a study to understand if the equipment could be used to measure %DPU in nylon cords with distinct characteristics from the original cord used to calibrate the equipment.

For each objective, several studies were conducted, each with specific methodologies allowing to achieve essential information and results. In what concerns preparation conditions, the main influences were identified and its magnitude was determined.

When studying cords with different properties, it was successfully established the utility of a single calibration for a diverse group of cords in %DPU determination.

6.2 Other Work Carried Out

Besides the work described in this document, other smaller tests were conducted. Minor studies were conducted with experimental products, performing %DPU measurements using the two described methodologies, to understand how varied materials with very distinct characteristics could alter the result of the equipment and its integration in C-ITA production environment. Moreover, other tasks were executed to obtained a greater knowledge of C-ITA procedures and works.

6.3 Limitations and Future Work

In terms of limitations to this project, it mainly concerns the study of cords with different characteristics. The methodology involved collecting samples of materials already expedited, and C-ITA only stores samples until a maximum of 6 months. Given the fact that C-ITA produces a numerous amount of materials, with a wide range of characteristics, it was a difficulty to collect a great number of samples of the desired characteristics within the duration of this project.

As it was mentioned before, it should be continued the testing of different suppliers, from those studied, to understand if there could be any influence due to the finishing products that suppliers apply to their products.

Finally, it remains as future work to perform the calibrations and validation for all the remaining materials used at C-ITA. Although different nylon cords did not show much interference with the TD-NMR results, there should be taken into account that for other

materials the same conclusion may not be achieved, leaving for future work this same study for cords of other materials.

6.4 Final Assessment

Looking back to the beginning of this internship, it is clear the major step it was taken in the implementation of this equipment at C-ITA production process. It is rewarding to be part of such step that will certainly lead to more rigorous measurement of Dip Pick-up.

7 References

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Appendix 1 - %DPU throughout the bobbin

During the performance of the studies mention in Chapter 4, many samples of one bobbin were collected. Since it is possible to calculate that the handling of samples without using gloves resulted in an increase in %DPU of 0,13%, it is possible to adjusted the results to illustrate the results that would be obtained if all the cord samples were handled with gloves. In addition to those values, some samples from the study of the influence of handling by different operators that did not show deviation from the Reference values are also included.

The main purpose of representation this graphic display is to, once more, demonstrate the evolution of the %DPU throughout the bobbin.

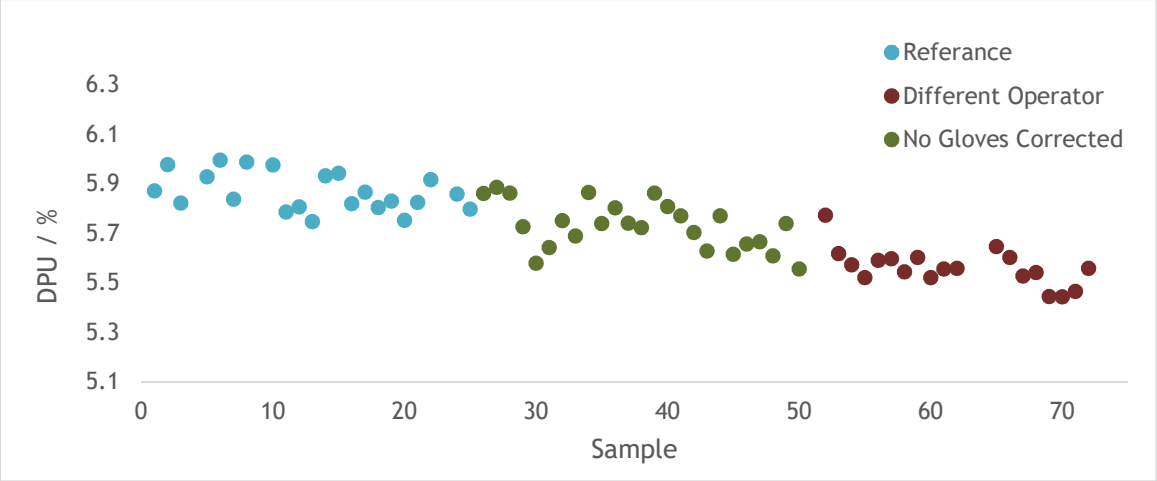

Figure 42 - Evolution of the DPU throughout the bobbin.

Appendix 2 - Calculus example

It was proposed a method to predict the range of values in which the following samples' %DPU will vary. To provide a clear explanation, a calculus example will be demonstrated.

Firstly, it is required to determine in which range the Reference samples' %DPU varies. First it is determined the maximum value of all %DPU results, represented by Max and posteriorly the minumum value of the same results represented by Min.

$$Max - Min = Diff \tag{4}$$

Where $Diff$ is the maximum difference between results. The following step is determining the tendency line of the obtained results which has the equation:

$$y = mx + b \tag{5}$$

Finally, two equations are represented: The top range equation and lower range equation. To obtain both equation, it is necessary to add half of $Diff$ for top range equation, and to subtract half of $Diff$ to obtain the lower range eqaution:

$$y = mx + b + \frac{Diff}{2} \tag{6}$$

$$y = mx + b - \frac{Diff}{2} \tag{7}$$

Finally, having both limiting equations, it is just required to calculate the values for the following samples. The resulting range, demonstrated by the blue area in the previous figure, represents the area where samples collected after the Reference samples should have its %DPU value represented.

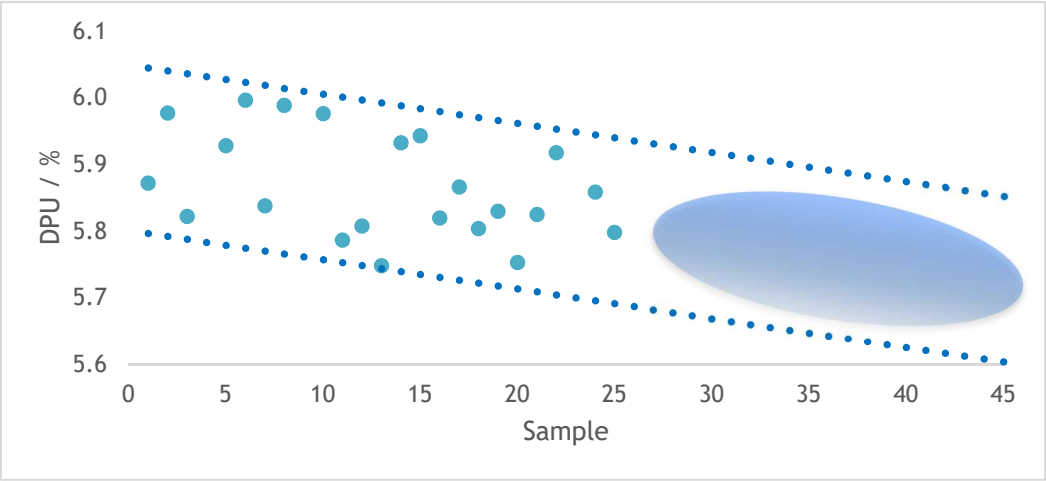

Figure 43 - Example of calculated limits