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Kevin Anthony Oliveira Rodrigues **Adhesion promoters for tire textile reinforcements**

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Escola de Ciências

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Master's Dissertation
Master in Chemical Analysis and Characterisation Techniques

Under the supervision of
Eng. Diana Pinto
and
Dr. Thomas Kramer
and
Prof. Dr. Susana Costa

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DECLARAÇÃO

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Adhesion promoters for tire textile reinforcements

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Abstract

Tires are much more than round pieces of rubber, they are in fact complex engineering products with more than twenty components like rubber, steel wire and textile fabrics. This last group plays a crucial role in tire's performance allowing tires to maintain air pressure and stability. However in order to be inserted in tire textile fabrics must undergo a chemical and physical treatment that provides adhesive properties between them and rubber. This chemical treatment is based on the use of specific aqueous solutions (dips) that will activate the surface of the fibres making them bond to rubber through a process called vulcanization. Continental - Indústria Têxtil do Ave, S.A. (C-ITA) is a company devoted to the production of tire textile reinforcements and was the place, in combination with the Department of Chemistry of the University of Minho, where this master thesis was developed. One of the purposes of this project was to study more environmental friendly dip solutions that could replace the current resorcinol-formaldehyde-latex (RFL) dip solution, providing the same satisfying adhesion results. To fulfil this purpose two different solutions were tested (resin A dip and resin B dip) and both provided satisfying adhesion results, indicating that RFL dip can be in fact replaced. The other aim of this project was to study the chemical properties of all compounds involved in this study and try to determine the reaction mechanism of the cord-resin A dip-rubber complex. Therefore through the use of proton Nuclear Magnetic Resonance (^{1}H-NMR) and Infrared (IR) spectroscopies it was possible to confirm the chemical structure of many C-ITA reagents and solutions. Regarding the cord-resin A dip-rubber complex a reaction mechanism was proposed, however further studies must be conducted in order to validate it.

Keywords: tire, textile reinforcements, alternative dip solutions, adhesion, chemical characterization.

Resumo

Os pneus são muito mais que objetos de borracha redondos, são de fato complexos produtos de engenharia com mais de vinte componentes entre os quais borracha, fios de aço e reforços têxteis. Estes reforços têxteis possuem um papel crucial no desempenho do pneu, permitindo a manutenção da sua pressão interior e conferindo estabilidade ao mesmo. Contudo, para serem inseridos no pneu os reforços têxteis devem ser submetidos a um tratamento químico e físico que lhes confere propriedades adesivas com a borracha. O tratamento químico baseia-se no uso de soluções aquosas específicas (dips) que ativarão a superfície das fibras, possibilitando a sua ligação à borracha através do processo de vulcanização. A Continental - Indústria Têxtil do Ave, S.A. (C-ITA) é uma empresa dedicada à produção de reforços têxteis para pneus e foi o local, em combinação com o Departamento de Química da Universidade do Minho, onde esta tese de mestrado foi desenvolvida. Um dos propósitos deste projeto foi estudar dips com propriedades amigas do ambiente capazes de substituir a atual solução de resorcinol-formaldeído-látex (RFL), fornecendo os mesmos resultados satisfatórios de adesão. Para cumprir este objetivo, foram testadas duas soluções distintas (dip de resina A e dip de resina B) e ambas proporcionaram resultados de adesão satisfatórios, indicando que o dip de RFL pode de fato ser substituído. O outro objetivo deste projeto foi estudar as propriedades químicas de todos os compostos envolvidos neste estudo e tentar determinar o mecanismo de reação do complexo corda-dip de resina A-borracha. Através da utilização de espetroscopia de ressonância magnética nuclear de protão (^{1}H RMN) e de espetroscopia de infravermelho (IV) foi possível confirmar a estrutura química de muitos dos reagentes e soluções da C-ITA. No que diz respeito ao complexo corda-dip de resina A-borracha um mecanismo de reação foi proposto, porém um estudo mais extensivo é necessário para a sua validação.

Palavras-chave: Pneu; reforços têxteis; soluções alternativas de impregnação; adesão; caracterização química.

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List of Acronyms

AG	Automotive Group
BR	Butadiene rubber
C-ITA	Continental - Indústria Têxtil do Ave, S.A.
CNSL	Caju Nut Shell Liquid
dtex	Decitex (g/10000 m)
EDS	Energy Dispersion spectroscopy
ENR	Epoxidized Natural Rubber
IR	Infrared spectroscopy
LDU	Laboratory Dipping Unit
MS	Mass spectrometry
NR	Natural Rubber
NMR	Nuclear Magnetic Resonance
PET	Polyethylene terephthalate
PI	Product Industrialization
RF	Resorcinol Formaldehyde
RFL	Resorcinol Formaldehyde Latex
SEM	Scanning Electron Microscopy
VP	Vinyl pyridine

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CHAPTER 1. Introduction

1.1. Project presentation and framework

Since the inventing of the wheel, humankind is searching for new and more effective ways to move. Mobility evolved to another level and although the general consumer wants to travel in a comfortable and fast way, he still does not understand why a round piece of rubber can be so expensive. Tires are much more than round pieces of rubber, they are in fact complex engineering products with more than twenty components like rubber, steel wire and textile fabrics [1].

The continuous growing of the market and marketing campaigns lead the consumer to obtain more information about tires, leading to a tire purchase not only price based. This forces tire companies to improve their tire manufacturing, being textile reinforcements clearly an area that can be explored.

Textile reinforcements are a crucial part of the tire in the way that they are responsible by maintaining tires air pressure and sidewall stability, so they play an important role in tires structure and mechanical properties. Textile reinforcements are introduced in the tire by being impregnated with specific solutions called “dips”.

Therefore during this master thesis different dip solutions were tested in four different fibers, through the use of a Lab Dipping Unit (LDU). Besides dip solutions chemical interactions with fibers and rubber were studied by the use of different chemical characterization techniques like mass spectrometry, nuclear magnetic resonance (NMR) and Infrared (IR) spectroscopy. Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) analyses were also performed in order to study a specific dipped nylon cord.

1.2. Project goals

The main goal of this project was to study the chemical properties of the compounds used in C-ITA and determine the reaction mechanism of the cord-dip-rubber complex for the current alternative dip solution used in the impregnation of textile reinforcements, mainly constituted by maleinized butadiene (Resin A) and latex. Another goal of this project was to study more environmental friendly solutions for textile reinforcement's impregnation, in alternative to the current resorcinol-formaldehyde-latex (RFL) dip solution that is being used.

1.3. Company presentation

Continental AG was founded in 1871 in Hannover, Germany, and began to produce different rubber articles. In 1898, Continental produces the first called "pneumatic" tire, and since then the company continued to increase its expertise in tire technology. Nowadays the company has 193 working locations around the world, relying in two textiles reinforcement producers [2].

One of these producers is C-ITA, founded in Lousado in 1950, this company produces mostly textile reinforcements for tire industry, mainly to Continental [2]. Since its foundation, C-ITA continued to grow and nowadays is not only a textile industry that supplies the rubber industry, but is also a company that focuses on textile development and investigation. Product Industrialization (PI) is the department responsible for textile development in C-ITA, and where this master thesis was developed.

1.4. Thesis Organization

This thesis is organized in seven different chapters:

Chapter 1. Introduction:

The goals of the project and the company where it was developed are presented in this chapter.

Chapter 2. State of Art:

In this chapter, all the theoretical basics for understanding this work are presented.

Chapter 3. Procedure and technical description:

All the techniques and methods used during this project are described in this chapter.

Chapter 4. Results and discussion:

In this chapter the results that were obtained during this project are presented and subjected to a critical analysis.

Chapter 5. Conclusions:

The conclusions obtained from all the findings of this project are presented in this chapter.

Chapter 6. Future work:

In this chapter, the limitations of the work performed are pointed out, and suggestions for future work are proposed.

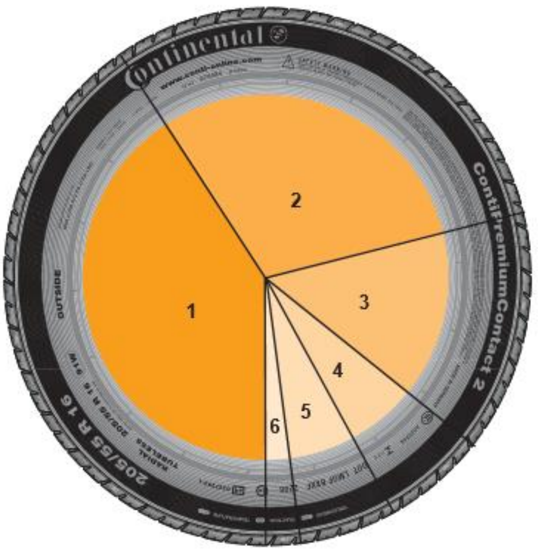
Chapter 7. References:

In this chapter, the literature references consulted throughout the project are presented.

CHAPTER 2. State of the Art

2.1. Tire Industry

Tires are high tech products used in all sort of vehicles; they are much more than just cured rubber. General consumers do not realize that producing a tire involves the combination of many ingredients and materials (Figure 1) that are processed through the use of highly specific machinery [3].



1. Rubber: 41%
2. Fillers (silica, carbon black, chalk): 30 %
3. Reinforcing materials (steel, fibres): 15%
4. Plasticizers (oils and resins): 6%
5. Chemicals for vulcanization (zinc oxide, sulphur): 6%
6. Anti-ageing agents and other chemicals: 2%

Figure 1- Tire composition (adapted from [3]).

Tires include functions such as providing the interface of the vehicle with the road; support the vehicle's load; provide good road friction independent of the road /atmospheric conditions and finally tires must absorb road irregularities giving the driver a comfortable and secure driving experience [4]. Pneumatic tires, created in the end of 1800s provided the last function mentioned, and since that time they continued to develop.

During this development three tire types were commercialized, more specifically diagonal bias, belted bias and radial tires. The main difference between this three tire types is the orientation of the textile reinforcing material [1]. From these three types, radial tires are the most difficult and expensive to produce, however they exhibit the best behaviour in terms of weight distribution and heating resistance, making them more suitable for high speeds. Figure 2 shows an illustration of all the components of a radial tire.

Figure 2- Cross section of a radial tire (adapted from [3])

1. **Tread:** its main function is to provide grip between tyre and road surfaces, allowing the vehicle to move, brake and turn. Tread is also specifically formulated to be resistant to abrasion, to have low rolling resistance and high durability. This component is also responsible for protecting the inner part of the tire and it needs to have a specific pattern in order to fulfil certain goals such as: uniform wear, minimum noise and adaptability to the road surfaces [1].
2. **Jointless cap plies**: they are basically nylon cords cured in rubber and their function is to prevent tire expansion at high speed [1].
3. **Steel-cord belt plies** are high-strength steel cords that protect the tire from any impact and simultaneously they protect the ply cords enhancing vehicle stability [1]
4. **The textile ply:** also called carcass, it has the function of maintaining tires shape by controlling internal pressure, providing strength and stability to the sidewall [3].
5. **Inner liner:** it is basically a rubber layer specifically inserted to provide air retention and reduce permeability outwards the tire [1]
6. **Side wall**: composed by natural rubber, it has the function of provide the tire resistance to tear, abrasion an weathering, in summary its main function is increase tires fatigue resistance [3].
7. **Bead reinforcement:** it represents the layers of textile that are directly attached to the carcass. These layers will strengthen the sidewall/bead area improving driving experience and tire high speed durability [3].

8. **Bead apex:** is a synthetic rubber produced precisely for improving driving comfort, due to the fact that it is responsible for enhancing directional stability and steering precision [3].
9. **Bead core**: is a squared form group of steel cords cured in rubber that assure the connection between the tyre and the rim [3].

2.2. Rubber

Rubber is the main component of tires, and it is one of the resources more explored worldwide. Natural rubber (NR) is the result of the coagulation of the latex produced by *Hevea brasiliensis* tree; this compound with a chemical structure similar to a *cis-1, 4-polyisoprene* (Figure 3) exhibits a high structural regularity, resulting in high tensile strength and abrasion resistance when this compound is crystalized [5]. Besides, rubber is also a material with a high friction coefficient and good elasticity properties, making it the perfect material to be used in tire industry.

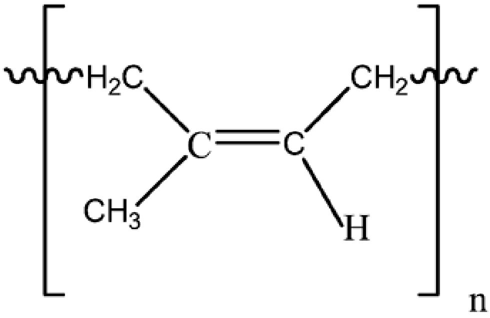


Figure 3-Chemical structure of cis-1, 4-polyisoprene (adapted from [5]).

Hevea brasiliensis tree does not exist in worldwide; it is mainly located in South America and so the necessity of rubber companies to find a substitute for NR appeared. Instead of substituting NR by another component, rubber companies invented a way of producing it in a synthetic way. In fact NR is mainly a polyisoprene, that when modulated lead to the production of different synthetic rubbers such as styrene butadiene rubber (SBR), polybutadiene rubber (BR), nitrile rubber (NBR) and butyl rubber (IIR) [6].

However tire industry does not use rubber in its natural state, in order to have the desired properties rubber must suffer a vulcanization process. Vulcanization is required for the alteration of rubber mechanical properties, giving it more strength, heat resistance, durability and elasticity [7, 8].

Essentially, vulcanization is a process where the rubber is subjected to high pressures and temperatures with the purpose of increasing the number of cross-links between rubber polymeric chains. These cross-links may result from a group of sulphur atoms in a short chain, a carbon-to-carbon bond, a single sulphur atom, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion (Figure 4) [7].

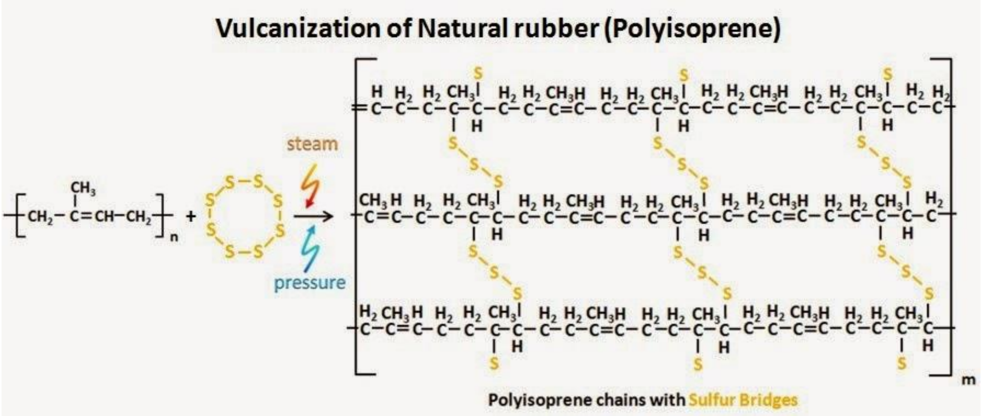


Figure 4-Schematic representation of natural rubber vulcanization process (adapted from [9]).

2.2.1. Epoxidized natural rubber (ENR)

Another very specific type of rubber is epoxidized natural rubber (ENR), this compound is a natural rubber derivative with a polymeric structure that contains unsaturated and epoxidized isoprene [10]. According to the number of epoxidized isoprene units the name of the ENR varies, ENR-25 and ENR-50 are the most relevant for the work that will be presented and as the name indicates ENR-25 has a quarter of its units replaced by an epoxidized isoprene (Figure 5-B) while ENR-50 has fifty percent (Figure 5-A).

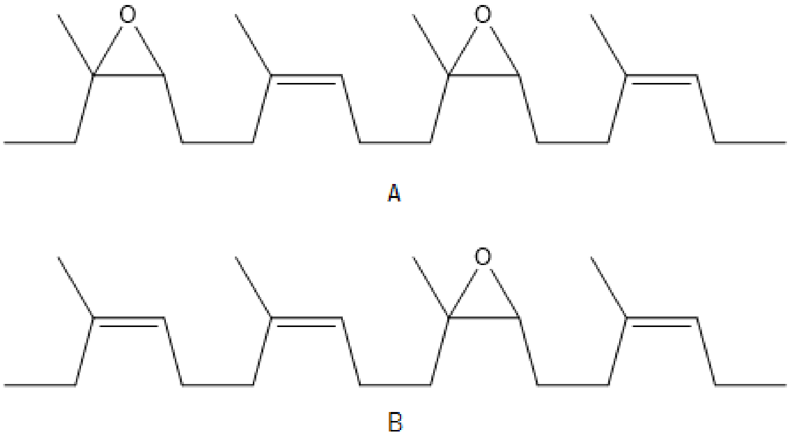


Figure 5- A- ENR-50 chemical structure; B- ENR-25 chemical structure.

Through ENR chemical structure is clearly that the unsaturated and epoxidized isoprene units are responsible for ENR reactivity, allowing this compound to have good adhesive properties. Furthermore, through ENR chemical structure it is also clear that this is a polar compound that increases polarity with the increasing of epoxide groups, making it more miscible with other polar compounds [10].

However, one of ENR major drawbacks is the poor ageing properties exhibited by its vulcanized samples as well as its instability when mixed with other compound. Furthermore this instability issue will be an object of study in this master thesis, more precisely the coagulation problem that was detected when mixing ENR-50 with the latex used in the impregnation process.

2.3. Textile Reinforcement Materials

As previously mentioned, textile reinforcing materials are also a crucial component of tires, providing various functions such as tire stability and good driving experience both in terms of comfort and vehicle performance.

Regarding textiles, many fibres are being currently used in tire manufacturing, however aramid, nylon, rayon and polyethylene terephthalate (PET) are the most commonly used.

2.3.1. Aramid

Poly p-phenylene terephthalamide (PPTA) more known as aramid is one of the most used fibres in tire industry; however this fibre also found its place in armoury equipment, more precisely Kevlar vests. Aramid is manufactured from *para*-phenylene diamine and terephthaloyl chloride [11] (Figure 6).

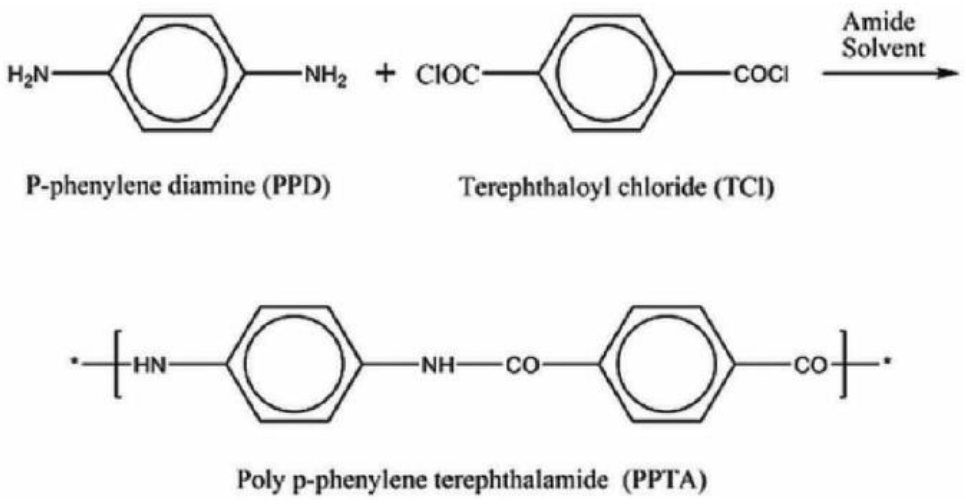


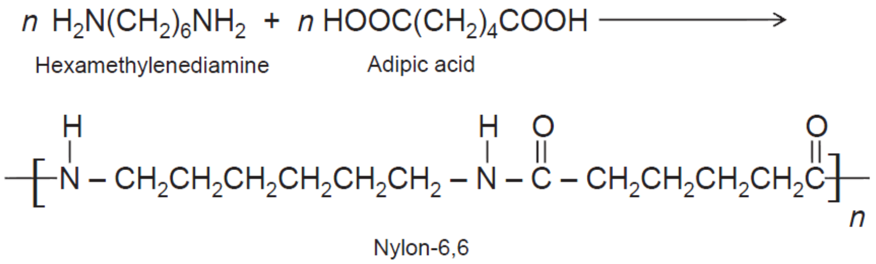
Figure 6 -Aramid synthesis illustration (adapted from [11]).

Due to the presence of a very organize network of aromatic groups aramid has extremely high tensile strength, property that makes this fibre perfect in a large number of fields that vary from armoury equipment, aerospace composites and boat hulls [12]. Nevertheless aramid does not present only benefits because the fabrication process of this fibre is very expensive and difficult to perform.

2.3.2. Nylon

Nylon is a synthetic fibre that is characterized as a linear aliphatic polyamide. This fibre can be produced in multiple ways generating different nylon polymers, however for tyre industry only nylon 6 and nylon 6,6 are used.

Regarding the synthesis of this two fibres, they differ in the way that nylon 6,6 is produced from to monomers while nylon 6 is obtained through only one monomer. Taking into account nylon 6,6 synthesis, this fibre results from the condensation of hexamethylenediamine and adipic acid, and thus each monomer contains six carbon atoms the nylon fibre is designated as nylon 6.6 (Figure 7) [13].



$$n\ H_2N(CH_2)_6NH_2 + n\ HOOC(CH_2)_4COOH \longrightarrow \left[\overset{H}{\overset{|}{N}} - CH_2CH_2CH_2CH_2CH_2CH_2 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}} \right]_n$$

Figure 7- Nylon 6,6 synthesis (adapted from [12]).

As previous mentioned nylon 6 is produced from just one monomer, namely caprolactam that contains 6 carbon atoms, giving this nylon fibre the designation of nylon 6. The ring-opening polymerization of caprolactam results in this fibre production (Figure 8).

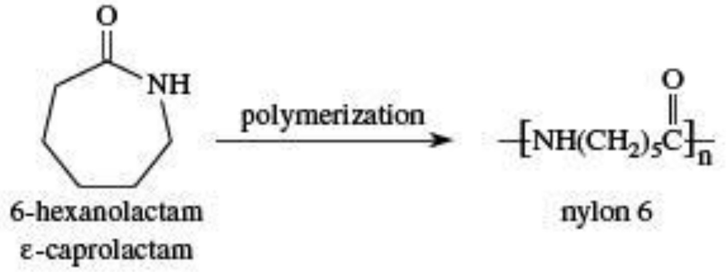


Figure 8- Nylon 6 synthesis (adapted from [12]).

Although nylon-6 and nylon-6,6 are both polyamide fibres, they physically differ in terms of melting point, glass-transition temperature, crystallinity and tensile modulus. Furthermore, nylon 6,6 is more explored by tire industry due to the fact that it possesses a melting point of 262˚C and nylon 6 a melting point of only 219˚C [14].

2.3.3. Rayon

Rayon is a cellulose derived fibre; basically obtained from purified cellulose that is converted into a soluble compound. Due to its viscosity, the purified cellulose needs to go through several chemical processes in order to obtain a regenerated cellulose fibre (rayon). These processes are represented in figure 9, essentially the cellulose is boiled with caustic soda, then is treated with carbon disulphide and coagulated in a sulphuric acid solution [15].

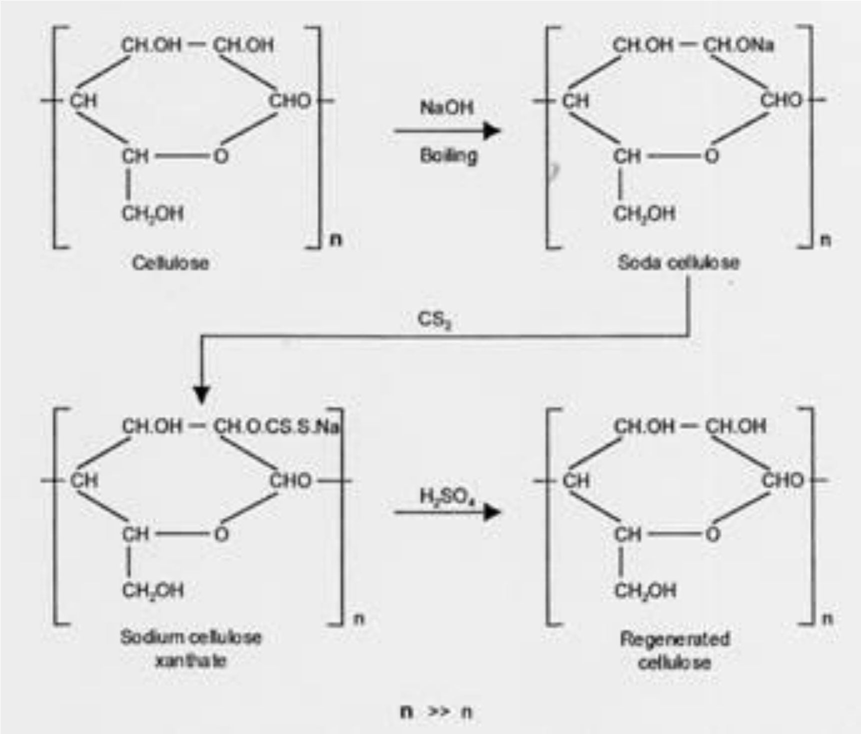


Figure 9- Rayon fibre synthesis (adapted from [16]).

This fibre presents some drawbacks such as its expensive production process and its high moisture sensitivity. However rayon fibre also presents some advantages like good dimensional stability and tensile strength [15].

2.3.4. Polyethylene terephthalate (PET)

Polyethylene terephthalate (PET) is a synthetic fibre related to polyester family, this fibre is formed by the polymerization reaction of dimethyl terephthalate and ethylene glycol (Figure 10).

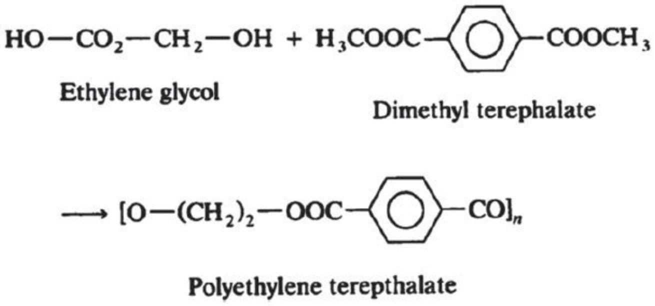


Figure 10- PET fibre synthesis (adapted from [5]).

This reaction occurs under heat and catalysts conditions, allowing the formation of ester groups that function as a link between PET monomers. Aromatic ring presence allows PET fibres to present high tensile strength, making them suitable in a large field of applications such as tyre industry, clothing, seat belts, hose and home textiles. Besides PET can also be used in form of plastic, making this synthetic fibre the most widely produced [5].

2.4. Yarn and cord processing in C-ITA

C-ITA is not responsible for fibre production; the company receives all types of fibres and processes them in order to obtain the final product: impregnated cords and fabrics. Therefore the processes used by C-ITA to obtain quality impregnated cords and fabrics are twisting, weaving and dipping.

Twisting is the first process applied in C-ITA, here the greige yarn will be twisted within controlled parameters, that will result in a cord that presents good elongation and fatigue resistance. Twisting also gives the cord better abrasion resistance in the way that yarns are arranged in a more compact structure [17]. Different cord constructions can be performed according to the desired cord mechanical properties; usually the yarns are individually twisted in Z direction (clockwise) and then twisted together in S direction (counter clockwise) (Figure 11). Cord designation depends of cords construction, for example if the cord is composed by two yarns twisted together it is a considered a 1x2 construction, if it is constituted by three yarns twisted together is considered a 1x3 construction.

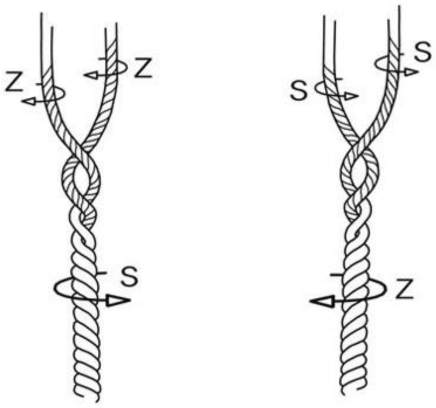


Figure 11- Cord twisting and construction (adapted from [18]).

Hybrid cord is a very specific type of construction in which at least two different fibres are twisted together in order to produce a cord that exhibits both fibre mechanical properties [1], [19] . The hybrid cord mainly produced in C-ITA is composed by one yarn of aramid twisted with one ply of nylon and exhibits high tensile force driven from aramid and high elongation resulting from nylon. Thus the investigation of new hybrid cords with different mechanical properties is a very promising field in textile reinforcement development.

After twisting the weaving process takes place, here the cords are interlaced at right angles in order to form woven fabrics [20]. Weaving process can be performed in different conditions according to the function of the woven fabric. At this stage the woven fabric is ready to the dipping process.

Dipping is the final process used at C-ITA and it is of most importance because without dipping the cords or fabrics will not bond to rubber, compromising tires manufacturing and performance. Dipping process involves both chemical and physical treatment of cords and textile fabrics; chemical treatment is performed by the immersion of the cord in a dip solution that will activate cords surface and thus confer its adhesion to rubber. Physical treatment it's made through high temperatures and tension. This will allow the modification of cords mechanical properties.

Both treatments are applied together in two different C-ITA impregnation machines, one designed for cords and another for fabric impregnation. Basically, as can be seen by figure 12, the heat treatment is applied by the four ovens that constitute the machine while tension results from the presence of traction rolls that rotate at different speeds and pull the cord. In figure 12 it is also clear that the cord can go through two bathing zones, that contain the dip solution required for cords activation (chemical treatment). Depending if the fibre is or is not activated one or two dip solutions must be applied.

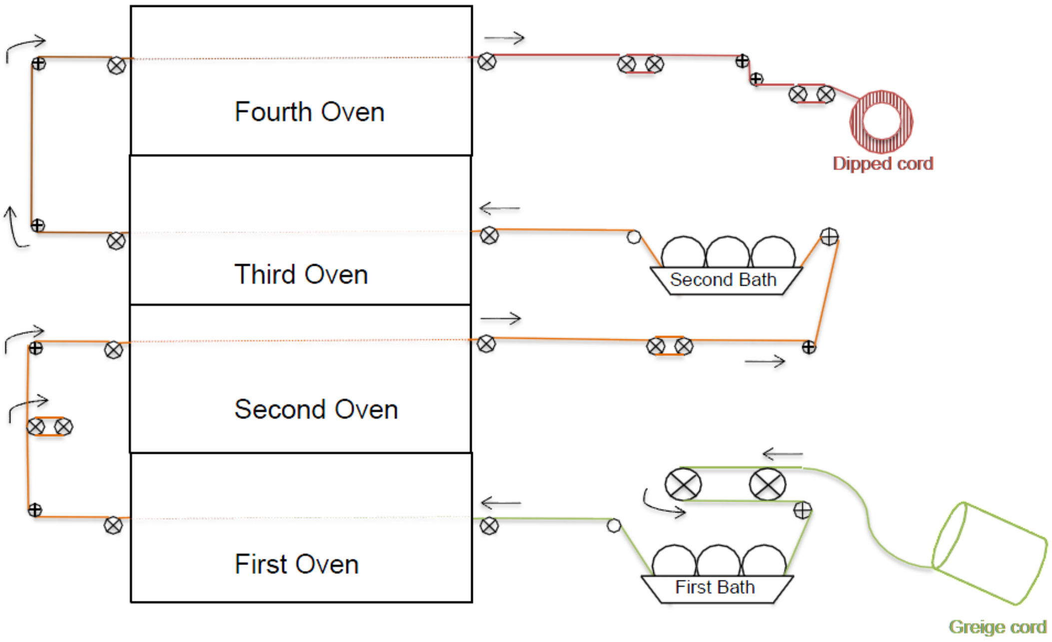


Figure 12- Dipping process (adapted from [21])

After the dipping process, the impregnated cords and textile fabrics have the chemical and physical properties required to assure a good rubber adhesion and a satisfying mechanical performance, therefore they are ready to be introduced in the tire.

2.5. Adhesion

As previously mentioned, textile reinforcements are a crucial component in tires structure and performance, however they can only perform its function when perfectly bonded to the tires rubber. Therefore adhesion is an essential parameter to take into account when producing textile reinforcements and it can be defined as the attraction between two different compounds. This attraction results essentially from the intermolecular forces established between two compounds and textile reinforcement industry goal is to increase the number of this intermolecular bonds in order to enhance the force required two separate the bonded compounds, namely cord and rubber.

So a strong adhesion is required in tire industry due to the fact that tires are subjected to considerable forces and conditions, on the other hand it is known that naturally fibres do not bond to rubber due to the inert characteristics of both substances [22]. Therefore the dipping process is essential to achieve a satisfying adhesion, being dip solutions the main responsible for a perfect cord-rubber bonding [23].

In this subchapter the different dip solutions and cord treatments (plasma) used in cord impregnation will be analysed.

2.5.1. Resorcinol, formaldehyde, latex solution (RFL dip)

Resorcinol, formaldehyde and latex (RFL) are the main components of the solution that is used by C-ITA in order to obtain quality impregnated cords. RFL dip can be divided in two components, namely the RF-resin and the rubber latex emulsion. Regarding RF-Resin, as the name indicates it is constituted essentially by resorcinol and formaldehyde that react together creating the network represented by the chemical structure shown in Figure 13.

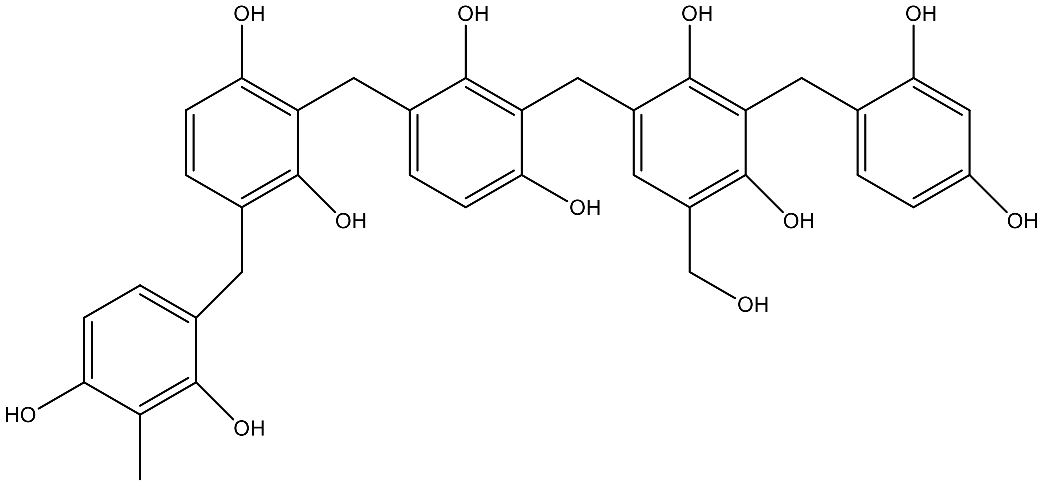


Figure 13- RF-Resin chemical structure.

Resorcinol and formaldehyde are high reactive molecules that are used in a wide field of applications like chemistry and medicine. RF resins can be divided in two groups, novolaks and resoles [24]. Novolak resins are produced in low concentrations of formaldehyde and in the presence of an acid or alkaline catalyst, basically in these conditions the condensation of resorcinol and formaldehyde leads to the formation of the chemical structures represented in Figure 14.

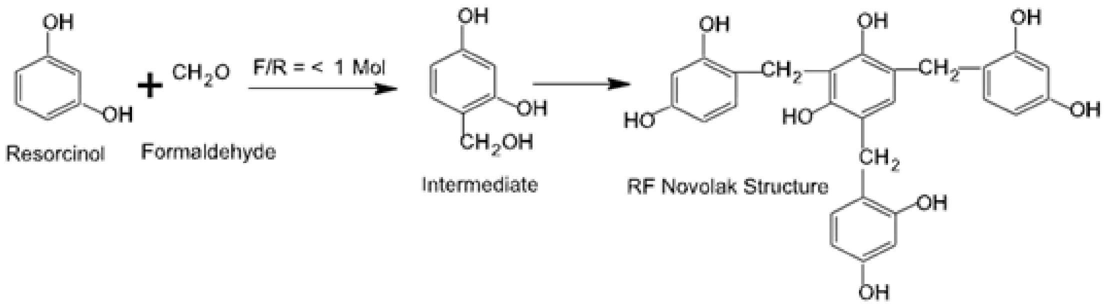


Figure 14- Novolak resin structure (adapted from [24]).

Resole RF-resin are formed when formaldehyde concentration increases or when the solution becomes more alkaline, in this conditions methylol groups are formed leading to the chemical structure presented in Figure 15.

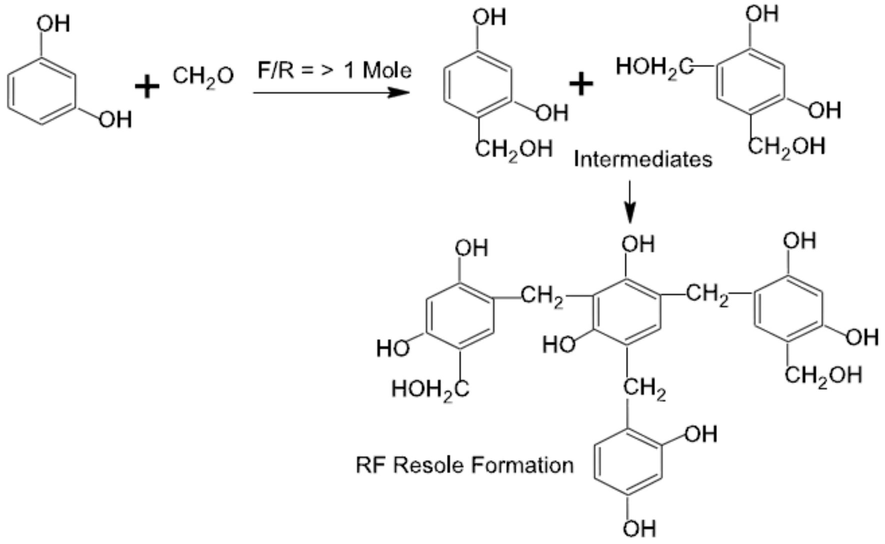


Figure 15- Resole resin structure (adapted from [24]).

The RF-resin is responsible for forming covalent bonds between the cords and the RFL dip, this covalent bond results from the presence of the methylol groups in the resin and the reactive groups (-OH; -CONH) present in the fibre [25]. However not every fibre possesses exposed reactive groups available to react with RF-Resin, in these cases RFL dip is insufficient to obtain a good adhesion. Aramid and PET fibres are an example in which RFL dip impregnation is insufficient, thus these fibres need to be pre-treated with a solution capable of insert reactive groups in these cords, this solution is commonly named as pre-dip [26]. On the other hand fibres such as nylon and rayon are very susceptible to react with RFL dip, do not needing any type of pre-treatment [26].

As previously mentioned, the other component in RFL dip is the rubber latex emulsion, this emulsion is constituted by latex and water. In C-ITA the most commonly used latex is styrene vinyl pyridine latex (VP-Latex) which chemical composition is represented in Figure 16.

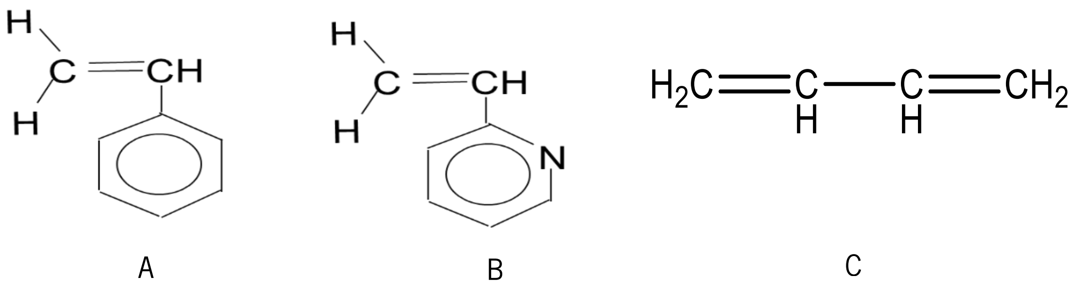


Figure 16- VP-Latex chemical composition. A- Styrene (15 %); B- Vynil pyridine (15%); C- Butadiene (70%)

VP-Latex main function is to facilitate the interaction between the RF resin and fibre and also function as an adhesive between the cord and the rubber [25, 27]. The combination of VP-Latex with RF-resin results in a solution capable of acting as a strong adhesive due to both the presence of a considerable number of reactive groups (methylol groups present in RF-Resin) and latex adhesive properties. The structure of RFL dip is represented in Figure 17, basically this solution is a resin phase combined with dispersed latex particles.

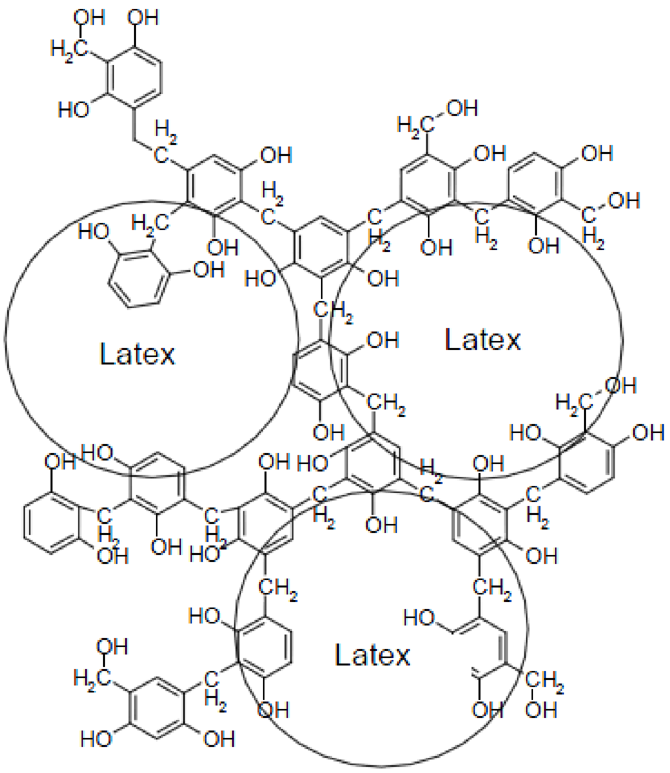


Figure 17- RFL dip structure (adapted from [22])

Due to all its characteristics RFL dip seems to be the perfect solution for cords impregnation, however it presents the severe drawback of containing both resorcinol and formaldehyde, highly reactive species that present considerable human and environmental hazard [28].

2.5.2. Alternative resins

As previously mentioned, RFL dip major drawback is the fact that it is not an environmental friendly solution, so one of textile reinforcements industries concern is the replacement of this solution for more environmental friendly ones. In this subchapter, some alternative solutions will be presented as well as an alternative treatment, namely plasma treatment.

2.5.2.1. Maleinized polybutadiene (Resin A)

Resin A is the most promising solution available for RFL dip replacement. This solution is environmental friendly and is basically a maleinized polybutadiene dispersion (Figure 18), this dispersion presents good chemical properties that are suitable to be used in the adhesion field.

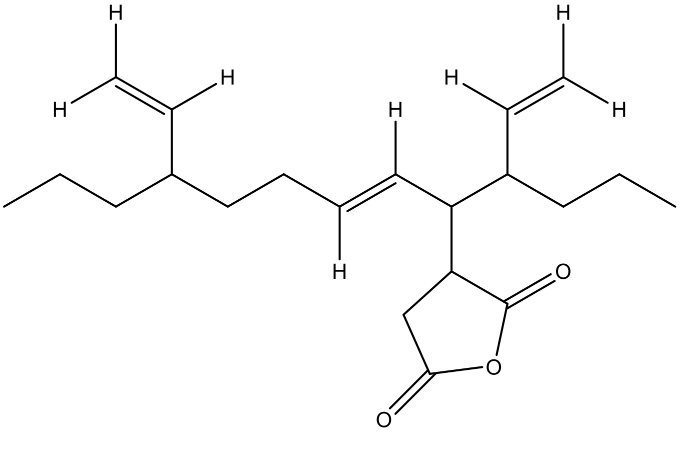


Figure 18- Chemical structure of maleinized polybutadiene (Resin A).

The polybutadiene present in resin A suffered a modification process called maleinization, in this process maleic anhydride reacts with the polybutadiene leading to the random distribution of anhydride groups along the polymer chain (Figure 19). The presence of these anhydride groups changes completely the chemical properties of the polybutadiene, increasing its reactivity and water solubility, making resin A dip an aqueous environmental friendly dip solution.

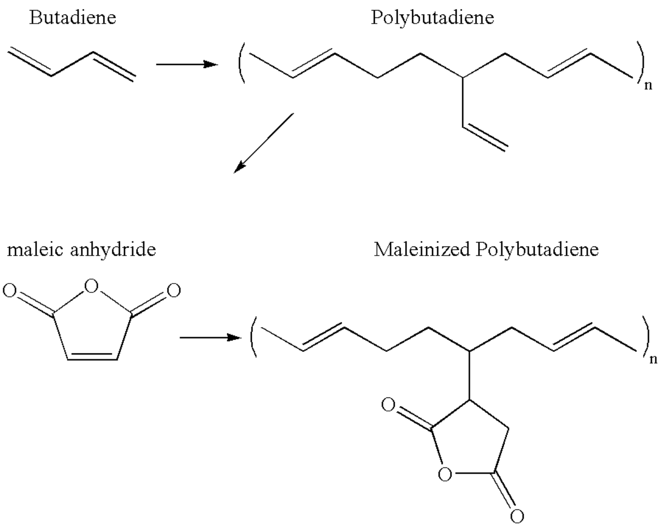


Figure 19- Maleinization of polybutadienes (adapted from [29]).

Furthermore, these anhydride groups that were inserted in the polybutadiene will be the responsible for reacting with the fibre, probably by covalent bonding. This process (cure) is promoted at high temperatures that can vary from 110 °C to about 250 °C [29].

Different studies have shown that resin A dip lead to good adhesion results with different fibres, making it a very good solution to replace RFL dip [30].

2.5.2.2. Phenolic resin (Resin B)

Resin B dip is another alternative to RFL dip; resin B main difference from RF-resin, which is the most commonly used resin in the field of adhesion promoters, relies on the fact that it is constituted by cashew nut shell liquid (CNSL). CNSL is a source of non-isoprenoid lipids that contain anarcadic acid, cardanol, cardol and isomers (Figure 20) [31].

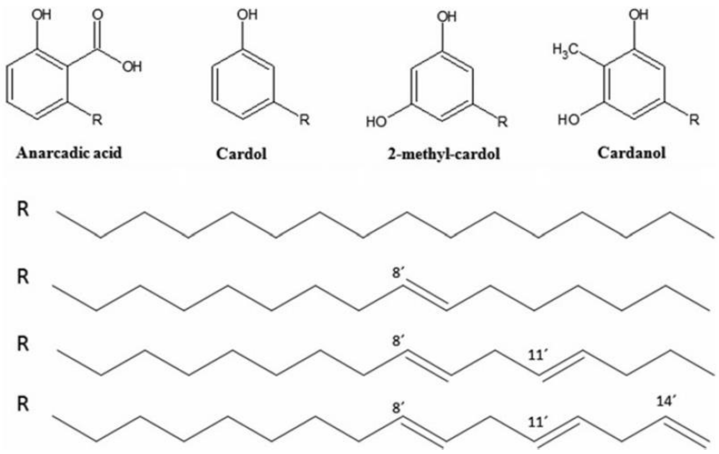


Figure 20- Major components of cashew nut shell liquid (adapted from [31]).

From all this components cardanol is the most relevant, being applied in a wide variety of areas such as plastics additives, surfactants, pharmaceuticals, pesticides and most importantly in resins. Cardanol is a non-toxic component, and so can be used in production and present almost no human hazard [31].

In fact CNLS components share chemical structural similarities with phenol, making them a good option to be used in RFL dip substitution, besides previous studies have shown that when adding CNLS to RF-Resin there is an improvement in the material thermal decomposition resistance and a lower formaldehyde emission [31, 32].

Therefore, the resin B used in this study cannot be considered environmental friendly, because it has formaldehyde and resorcinol in its chemical composition, however due to CNLS presence the emission of formaldehyde is diminished and at the same time, due to cardanol characteristics, less human hazard is generated. Furthermore resin B dip presents the same good adhesion results as standard RFL dip, making it a viable solution to be applied.

2.5.3. Pre-dips

As previously stated, there are some cords that require more than one dip solution in order to obtain a satisfying cord-rubber adhesion. Therefore for the studied cases was necessary the use of two dipping baths in which the last solution used is one of the dips mentioned above. So the first solution, called pre-dip, will be used with the purpose of making the cord more suitable for dip chemical activation. Nowadays, most pre-dip solutions used are a combination of a blocked isocyanate with an epoxy resin [26] . Regarding isocyanates they are high reactive molecules that were commonly used as rubber adhesion promoters [33]. Nevertheless these compounds reactivity presents some drawbacks such as high toxicity, high sensitivity and high solution instability. Due to this fact a blocking system was created in order to diminish isocyanates reactivity drawbacks making them inert and safe at ambient temperatures [33]. At higher temperatures (dipping process) the unblocking reaction of isocyanates occurs, making possible isocyanate groups to react with the functional groups present in the cord, leading to its pre-activation [34].

In this work two different isocyanates were used and analysed, namely isocyanate A (A) and isocyanate B (B). The chemical structure of both blocked isocyanates is shown in Figure 21.

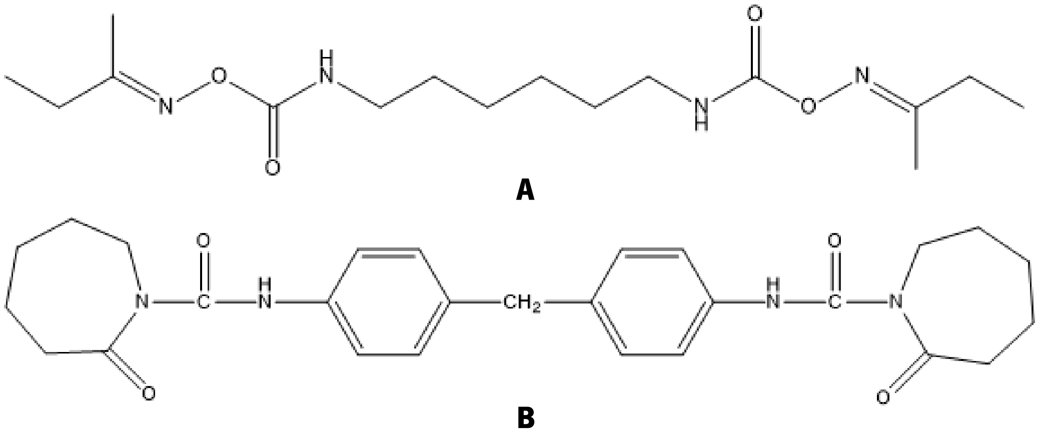


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Figure 21- Isocyanate A (A) and isocyanate B (B) chemical structures.

As mentioned earlier, the other pre-dip component is an epoxy resin. Epoxy resins are one of the most important classes of structural adhesives due to their good mechanical properties and environmental degradation resistance. Furthermore epoxy resins can become hard solid when heated or exposed to certain reagents (acids or bases) in a transformation process called curing [35]. Cured epoxy resins present excellent mechanical strength and water tightness, making this compound ideal not only as an adhesive but also as a water isolator. Regarding epoxy resin chemical structure, as the name indicates the active group present in this compound is an epoxy ring that presents high reactivity. The chemical structure of the epoxy resin is presented in Figure 22.

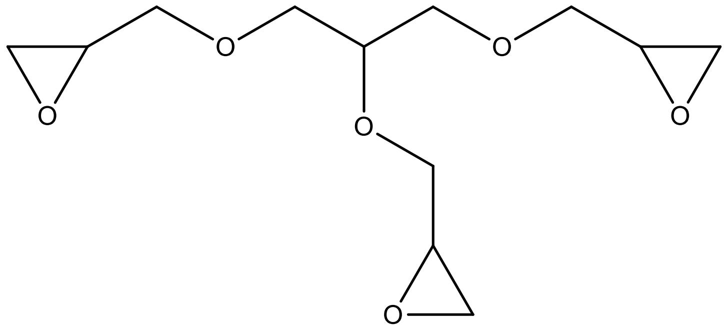


Figure 22- Epoxy resin chemical structure.

Through Figure 22 is clear that each monomer of this epoxy resin is composed by three epoxy groups, therefore high reactivity is expected from this compound. Besides, in the dipping process this resin will be exposed to high temperatures resulting in its curing, leading to the formation of covalent chemical bonds between the epoxy groups present in the resin and the active groups present in the cord [26].

2.5.4 Plasma treatment

Plasma is one of the methods that can be used in order to pre-activate cord surface. Usually this technique is not used in solo, requiring a dip solution to obtain good rubber-cord adhesions [36].

Plasma treatment can act in the cord by four different processes: cleaning, activation, grafting and deposition [37]. The first one refers to plasma ability to remove, via hydrogen abstraction or chain scissoring, any organic contaminants present on cords surface (Figure 23-A). Activation occurs when reactive groups such as hydroxyl are inserted in cords surface, leading to an increasing of polar and hydrophilic entities that increase cords surface energy, resulting in a better adhesion (Figure 23-B). Regarding grafting, this is a process in which plasma is combined with a monomer and through plasma activation the monomer becomes linked (grafted) to the cord, this process usually occurs with argon plasmas using monomers such as allyl amine and allyl alcohol (Figure 23-C). Finally, plasma can be also used as a deposition process, leading to the deposition, through plasma vaporization, of more complex molecules in cord surface.

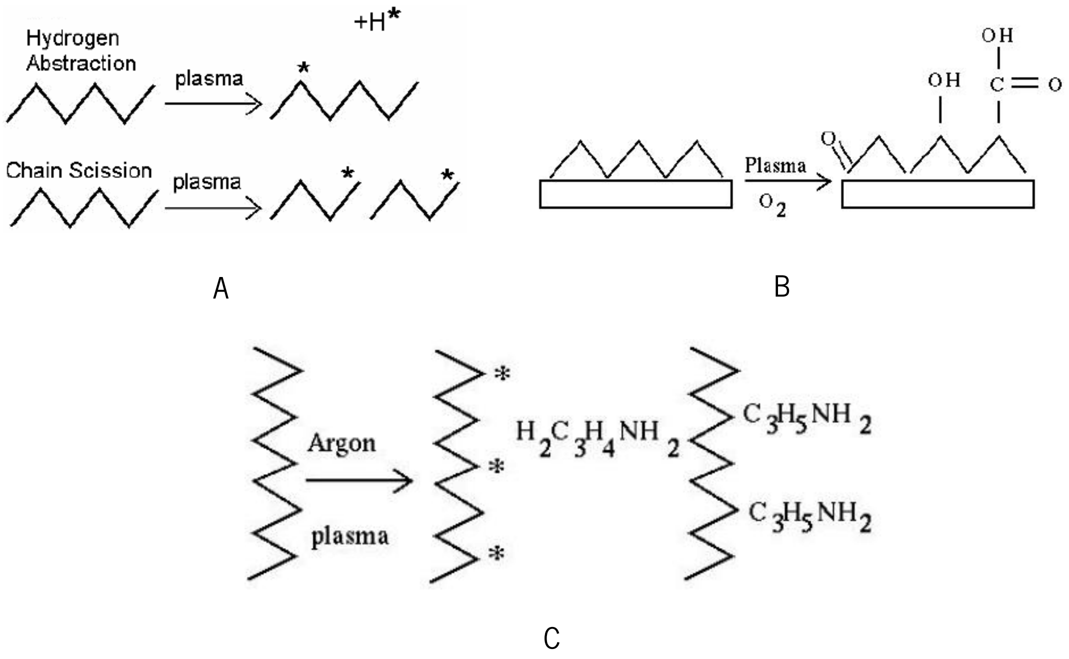


Figure 23- Plasma treatment processes. A- Cleaning; B- Activation; C- Grafting. (Adapted from [37]).

As can be noticed plasma treatment can promote various process in cords surface that enhance cord-rubber adhesion, being cleaning and activation the most relevant ones regarding cord treatments. Besides, as this technique does not require any water or chemicals, it provides great economic and ecologic advantages [38], making it a viable environmental friendly solution to be used in cords impregnation process.

CHAPTER 3. Procedure and technical description

3.1.Material and Reagents

3.1.1. Cords

The cords used during this project have their characteristics represented in table 1.

Table 1- Cords used during this study.

Cord	***dtex***
Nylon	940×2
Polyester	1440×2
Rayon	1840×2
Aramid	1680×2
Hybrid (Aramid + Nylon)	1680×1 + 1400×1

These cords were involved in different tests and were treated with different mechanisms like plasma or dip solutions such as RFL dip and Resin A dip.

3.1.2. Reagents

Throughout this project different dip solutions were tested, according to the study and the type of fibre to be treated. C-ITA has specific dip solutions for each fibre, however due to confidentially reasons the concentrations of each component in the solution must not be revealed, for that reason Table 2 represents all the reagents that were used in this project as well as the cords where they were applied.

Table 2- Reagents used in this project and cords where they were applied.

Reagents	Cords
VP-Latex	All cords
BR-Latex	Not used in cords, only chemical tests
ENR-25/50	Not used in cords, only chemical tests
Resin-A	Except Rayon cord
Resin B	Only Rayon cord
RF-Resin	Except Rayon cord
Epoxy resin	Pre-dip of hybrid, aramid and polyester cords
Isocyanate	Pre-dip of hybrid, aramid and polyester cords

Dip solution preparation is a crucial step to achieve quality impregnated cords. In this project different pre-dip/dip solutions were used, as represented by table 3.

Table 3- Solutions used in this project and cords where they were applied.

Dip formulations	Cords
Pre-dip (Isocyanate A as isocyanate)	Aramid and PET
Pre-dip (Isocyanate B as isocyanate)	Nylon, Rayon and Hybrid
RFL dip	Except Rayon cord
Resin-A dip	Except Rayon cord
Resin B dip	Only Rayon cord

Regarding pre-dip preparation this is an aqueous solution were an isocyanate is mixed with an epoxy resin, so basically these two reagents are directly added to water. RFL dip preparation is more complex and can be divided in three steps. Firstly VP-Latex is added to water, this latex aqueous dispersion is performed in controlled pH conditions and is always under mechanical agitation. The second step is the preparation of the RF-resin solution, in this step RF-resin is diluted in water and ammonia is added to the solution in order to adjust the pH. The final step is the mixture of the latex aqueous dispersion with RF-resin solution and the addition of formaldehyde. Formaldehyde will promote the formation of chemical bonds between RF-resin and VP-Latex, so it must be added very carefully to the mixture to avoid any type of agglomeration that can compromise RFL dip efficiency.

Resin A and resin B dips are much simpler to prepare, in both cases VP-latex aqueous dispersion must be prepared in the same conditions previously mentioned and then it is only necessary the careful addition of the corresponding resin to the mixture.

After pre-dip/dip preparation, two parameters must be evaluated in order to verify dip quality. The first parameter is pH, that can vary from 7-10 according to each dip solution, pH is very important because it affects the curing process and therefore the adhesion between cord and rubber. The second parameter is solid content that can be described as the residual matter that stays in the cord after chemical evaporation of the dip compounds.

$$\text{Solid Content}/\% = 100\,\frac{dry\ weight}{wet\ weight}$$

To measure solid content PI lab has a moisture analyser, in this equipment approximately (1,000±0,001) grams of dip solution are weighted in an aluminium plate and inserted in the device.

3.2. Equipment

During this project different equipments were required to proceed with the investigation and as both chemical and physical analysis were performed, there was a strong collaboration between C-ITA and University of Minho in order to provide all the perfect conditions for the project.

So in C-ITA the equipments used in cord impregnation were the LDU and the atmospheric plasma machine, which allowed the preparation and optimization of all samples required during the project. In addition, a dynamometer machine (Zwick Roel) was also required in order to carry out peel test method.

Regarding University of Minho, different methods were required in order to perform all the chemical analysis, namely the NMR, the HPLC-MS and the IR spectrometer. Is also important to point out that SEM-EDS analysis were performed in collaboration with 3 B’s company.

Therefore, in this subchapter all the equipment required will be presented.

3.2.1. Laboratory Dipping Unit (LDU)

The Laboratory Dipping Unit (LDU) is a small scale copy of the machine that is used in C-ITA in the impregnation process and it's of most importance in all the investigation work that is performed in C-ITA because it allows the impregnation of cords in specific conditions. The modulation of these conditions allows the operator to perform different studies, since testing different temperature/speed/tension programs to using different fibres or dip solutions. For all its versatility LDU is essential to the PI department.

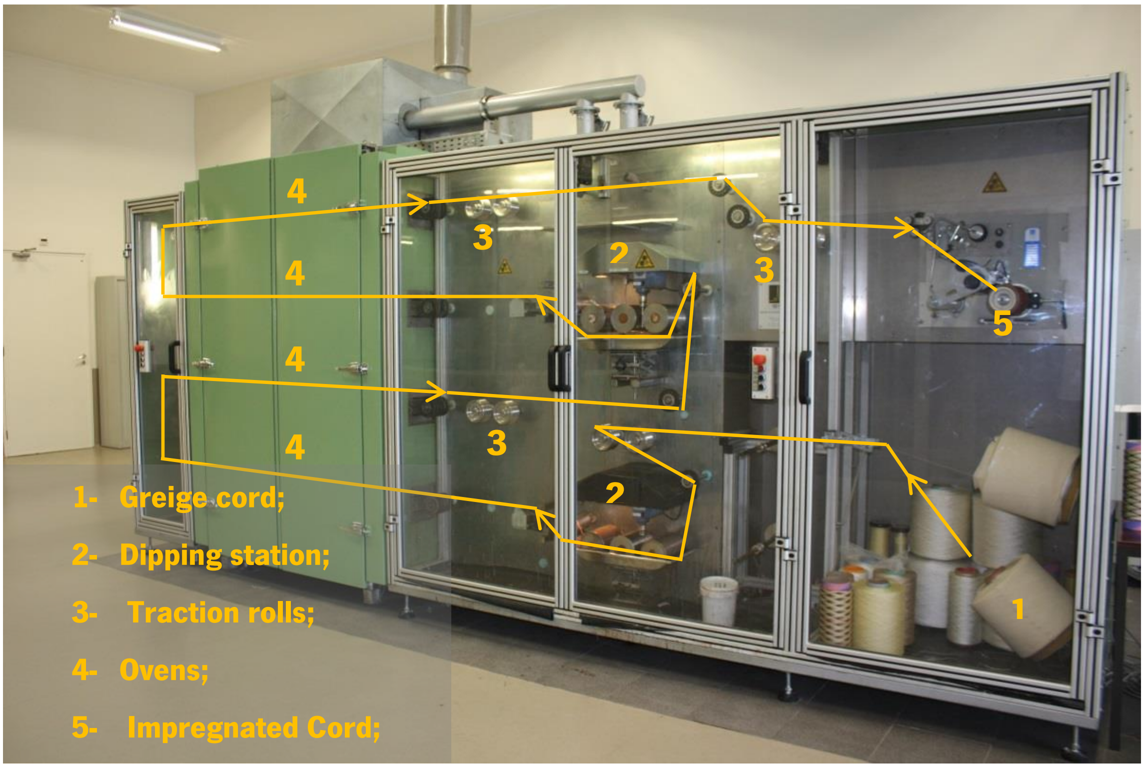


Figure 24- Laboratory Dipping Unit (LDU) representation.

Regarding LDU function (Figure 24), initially the greige cord is inserted in the machine and is emerged in one or two dip solutions depending if it is an activated cord or not. After the emersion the cord will go through the ovens for its drying and curing process. Both these processes are controlled in terms of the temperatures in the ovens as well as the exposure time that the dipped cord is subjected. During its course on the LDU, the cord is subjected to different tensions at a specific speed that will influence the mechanical properties of the cord, increasing in general its tensile strength.

Therefore on the LDU machine there are different operating parameters that can be altered in order to achieve better results, these operating conditions are revealed in Table 4.

Table 4- Operating parameters used in LDU.

Operating parameters	
Temperature	° C
Speed	m / min
Exposure time	s
Tension	N
Stretch level	%

3.2.2. Atmospheric Plasma

Atmospheric Plasma allows treating cords in terms of cleaning and activating its surface . In this equipment two operating conditions can be controlled, namely plasma power (%) and gas flow L/min. The gas that is used in this equipment is compressed air, so it is a mixture of different atoms like carbon, oxygen, nitrogen and hydrogen.

Therefore, atmospheric plasma is an environmental friendly alternative for cord activation, being also a very promising equipment due to the fact that it can be inserted in production in a much more easier way than the vacuum plasmas available in the market.

3.3. Testing methods

After cord impregnation it's necessary to evaluate its quality through the quantification of adhesion appearance and force. The testing method used in this case is called peel test.

Besides, as one of the goals of this project is to understand the interaction between cord and dip, chemical tests must be performed to PI lab compounds, these same tests will be presented in this subchapter.

3.3.1. Peel test

As previously mentioned, peel test is a method used to assess adhesion quality. In this method the two parameters that are evaluated are peel force and coverage. Peel force (N/25 mm) can be defined as the force required to separate two layers of cord bonded together by a rubber surface while coverage illustrates the amount of cord that is covered by rubber in the peel sample.

Coverage evaluation is measured by human eye and it varies between a 1 to 5 range (Table 5).

Table 5- Coverage rating.

Classification	Rubber coverage / %	Cords description
1.0	0	completely free of rubber
2.0	25	mainly free of rubber
3.0	50	half covered by rubber
4.0	75	mainly covered by rubber
5.0	100	completely covered by rubber

Therefore a coverage value of 1 indicates a peel sample where the cord is completely free of rubber while a coverage value of 5 indicates a peel sample where the cord is completely covered by rubber (Figure 25). In C-ITA, the minimum coverage value accepted is 3.5.

A B

Figure 25- Peel test samples. A -Coverage:1.0; B- Coverage: 5.0.

Peel force evaluation is measured with the aid of a Zwick/Roel Z010 machine, and the minimum peel force accepted is 120 N/25 mm independent of the type of rubber used. In C-ITA two type of rubber can be used according to the type of cord, rubber A is used for nylon and hybrid cords while rubber B is used for PET, aramid and rayon cords.

Regarding peel sample preparation several steps must be performed, firstly the impregnated cords must be placed in parallel to each other in order to mimic a textile fabric

(Figure 26), forming a complex of 80 or 90 cords per 10 cm. The complex of 90 cords per 10 cm is only used for hybrid cords.

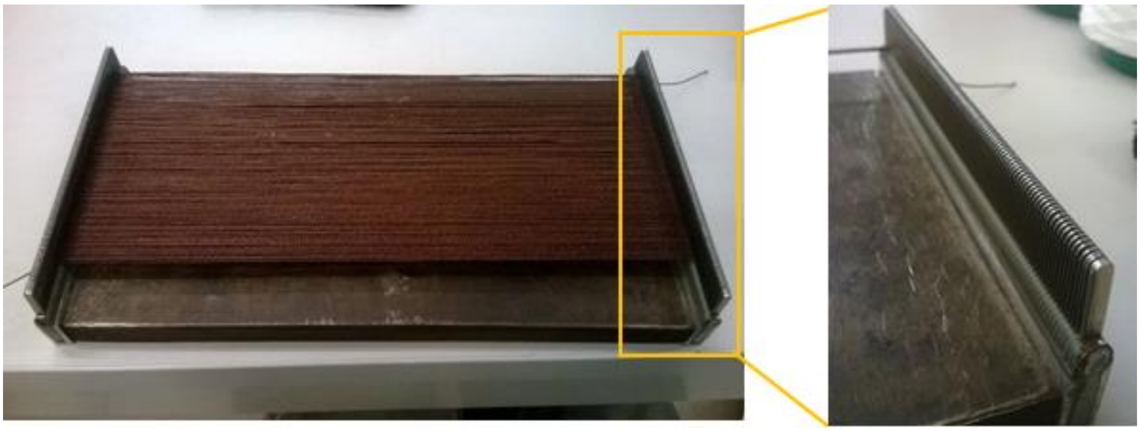
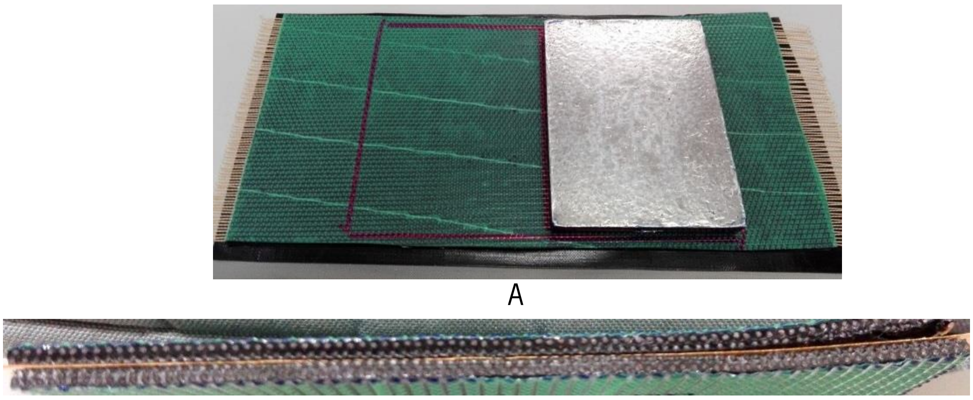


Figure 26- Hybrid 90/10 cm complex.

Secondly, the complex is covered in both sides by a layer of the correspondent rubber, and then in one of the surfaces a protective layer of rubber called chaffer is added. At this point, this cord-rubber-chaffer complex is cut in two equal mould fitting forms that are glued together (Figure 27).



A

B

Figure 27- A- Adhesion mould cutting; B- Adhesion layer overview.

This final complex is then vulcanized in the Wickert 1600S hot press during 10 minutes at 170˚C with a pressing force of 5 kN. After vulcanization, the sample must rest for a minimum period of three hours and then cut in three (2,5×10) cm^2 peel samples according to the ASTM D885 [39].

Peel test occurs at this stage; the peel samples previously prepared are inserted into a oven at 120˚C for a period of thirty minutes and then subjected to a tensile test using the Zwick/Roel Z010 machine. After this test the two sides of the adhesion will be visible, as seen in

Figure 28, and so coverage can be assessed and peel force will be obtained through Zwick equipment

Figure 28- Peel sample subjected to tensile test.

3.3.2. Reagents preparation

As mentioned above, C-ITA has different dip solutions in which different chemical compounds are used and the aim of this project is to understand the chemical properties of all these compounds in order to better understand what sort of chemical reactions are involved in the cord-dip-rubber complex. To understand these chemical reactions it's necessary to know exactly the chemical properties and formulations of each reagent. Mass spectrometry, NMR and IR spectroscopy were the techniques chosen to answer this question.

However the reagents and solutions that C-ITA uses can't be directly analysed by these techniques, so an extraction procedure is necessary because most reagents/solutions are solubilized in a matrix (usually water). Due to this fact all the samples were subjected to a liquid-liquid extraction process using solvents with different polarities. The use of different solvents arises from the lack of information that is known about each reagent, so four extractions were performed in order to see which one provided better results.

Regarding the extraction procedure, the first step was to dilute all samples (1:10) because very sensitive techniques were used and the use of high concentrated extracts would not be advisable. Following the dilution the liquid-liquid extraction was performed using four different solvents: diethyl ether, petroleum ether, ethyl acetate and chloroform. This experimental design can be seen in Figure 29.

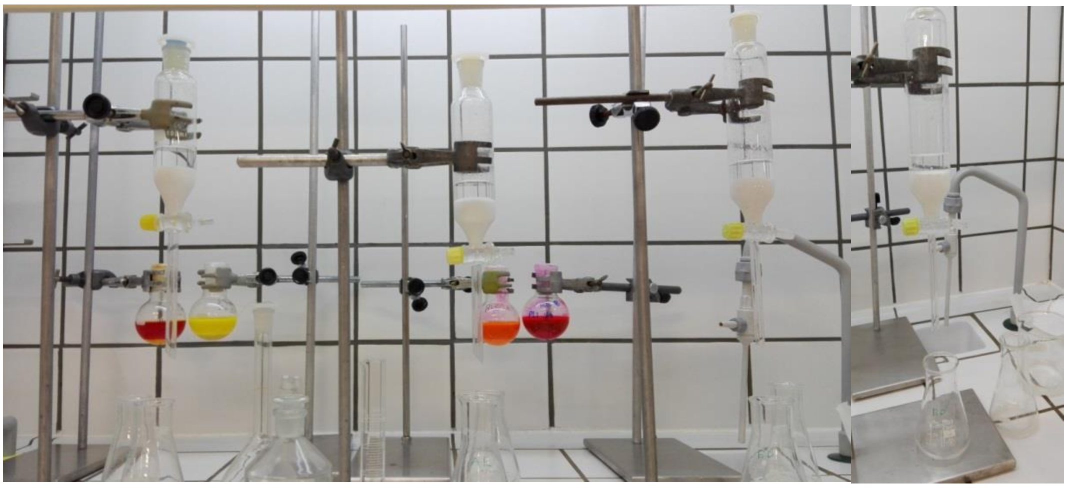


Figure 29- Experimental design of liquid-liquid extraction procedure.

From the liquid-liquid extraction an organic phase containing the corresponding analite was obtained, to this organic phase anhydrous magnesium sulphate was added in order to remove any water traces. The sample was then filtered and evaporated in a rotary evaporator.

This extraction method was applied to many reagents and solutions used in C-ITA, resulting in a total of fifty-two liquid-liquid extractions. All the extraction samples obtained were stored in labelled Eppendorf's. At this point all samples can be directly analysed by the techniques previously mentioned.

3.3.3. ^{1}H Nuclear Magnetic Resonance (NMR) spectroscopy

Nuclear Magnetic Resonance (NMR) is a spectroscopic technique widely used in the study of molecules structure and dynamics. For that reason it was used in this project with the aim to confirm all chemical structures of the reagents and solutions which structure is already identified and give also a clue about the unidentified chemical structures of certain reagents and dip solutions.

Hydrogen NMR spectroscopy analyses were performed in University of Minho using an Ultrashield 400 Plus machine by Bruker (Figure 30-B). The preparation of the NMR samples was very simple due to the previous extraction procedure mentioned above, basically all 76 extracts were dissolved in deuterated chloroform and placed in an NMR tube (Figure 30-A) and then inserted in the NMR equipment.

A B

Figure 30- NMR tubes (A) and NMR equipment (B).

The main advantage of the NMR technique is the fact that it's a non-destructive method, so all samples were recovered after the analysis.

3.3.4. Infrared spectroscopy (IR)

Infrared spectroscopy (IR) was de second spectroscopic technique used in this project and it can almost be considered as a functional group detector. IR spectroscopy is so versatile because it can be used in solid, liquid or gaseous samples, providing results in a very short period of time. The main disadvantage of IR spectroscopy is the fact that, different from NMR, the samples are destroyed during the analysis; this explains why IR spectroscopy was performed after NRM analysis. Besides NMR spectroscopy provided knowledge about the chemical structure of the samples, and this type of information is crucial for the comprehension of IR spectroscopy results.

Regarding IR spectroscopy analysis, they were performed in University of Minho, using a FTLA2000 machine produced by ABB. "Neat" technique was used in all samples, so the basic procedure was to solubilize each sample in dichloromethane and place it between two pure NaCl cells, after dichloromethane evaporation the cells were placed in the support cell (Figure 31-A) and inserted in the equipment (Figure 31-B).

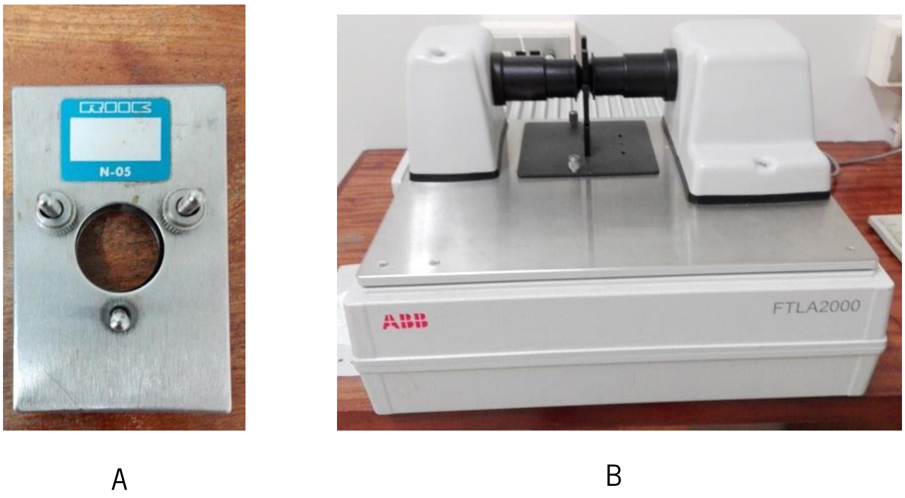


Figure 31- A- Infrared support cell; B- Infrared equipment.

This step was repeated for one sample of each reagent/dip solution (notice that in the extractions four samples of each reagent/dip solution were obtained) taking into account that between each analysis the NaCl cells must be cleaned with dichloromethane. Moreover, at regular intervals the IR spectra of NaCl cells alone was checked in order to verify any contamination problem. For each sample three essays were performed resulting in a total of thirty-six IR spectrums obtained.

3.3.5. Mass spectrometry (MS)

Mass spectrometry (MS) is an analytical technique in which the molecules are ionized and separated according their mass/charge ratio. MS is a very versatile technique because it can be applied to all type of samples and previous knowledge of their composition is not needed. Regarding this work MS analysis is of most importance in order to better understand the composition of the dip solutions used in C-ITA, namely the pre-dips and RFL and Resin A dips.

However due to the problems verified in the MS equipment that will be later addressed, the experimental procedure was only applied to two samples, namely resin A and isocyanate A. Firstly, both samples were solubilized in high performance liquid chromatography (HPLC) graded methanol and filtrated with a 0.02 mm filter (Figure 32-A). Following filtration, the samples were injected in a ThermoFinninganLXQ mass spectrometer equipped with an ion trap analyser (Figure 32-B).

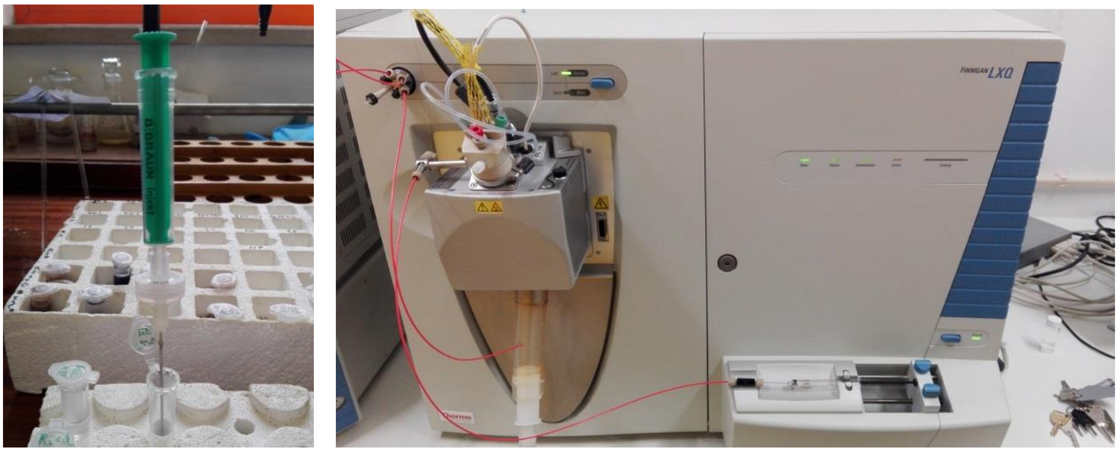


Figure 32- A- Sample filtration; B- Mass spectrometrer.

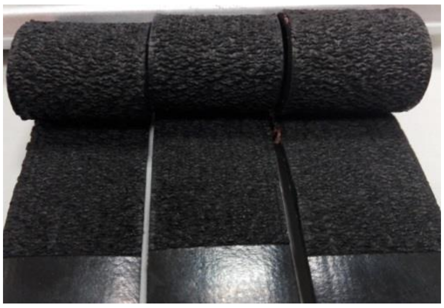
Between each injection the equipment was cleaned with methanol in order to avoid any contamination between samples. Finally, using the MS spectrometer several MS analyses were performed for each sample.

3.3.6. Scanning Electron Microscopy (SEM)-Energy Dispersive Spectrometry (EDS)

Scanning electron microscopy (SEM) is a microscopy technique that allows the visualization of samples with a high resolution and amplification. Usually this technique is applied simultaneously with energy dispersive spectrometry (EDS), making it possible to the operator the determination of several chemical elements present in the sample. Therefore, SEM-EDS analyses were used in this project in order to study a specific resin A nylon dipped cord that presented adhesion impairment at a very fast rate.

The first stage of this method was the preparation of samples, in this case two resin A nylon dipped cords were analysed, one was impregnated one day previous to the SEM-EDS analyses, while the other had been prepared the month before. Furthermore, two peel samples were also analysed, the first one was made from the nylon cord impregnated two days before the analyses, and the other was made using the resin A dipped nylon cord that was kept inside a dark bag during the period of one month (Table 6).

Table 6- Samples used in SEM-EDS analyses. * The cord was kept in a dark plastic bag during the period of one month.

Cords		**Peel samples**
Resin A nylon cord impregnated one day before analysis	⟶	
Resin A nylon cord impregnated one month previous to analysis*	⟶	

Regarding the cords, no previous preparation was required, however the same was not applied for the peel samples, due to their size they do not fit in the SEM support cell, thus they needed to be cut in small sizes. In order to achieve regular cutting surface liquid nitrogen was used; basically the peel samples were immersed in liquid nitrogen and then broken. However this process was not effective in the way that only the rubber existent in peel samples broke, being nylon cords resistant to the breaking force (Figure 33). The solution was to cut the peel samples using a specific textile scissor.

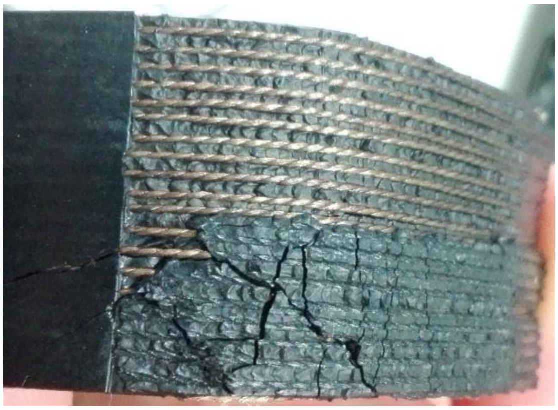
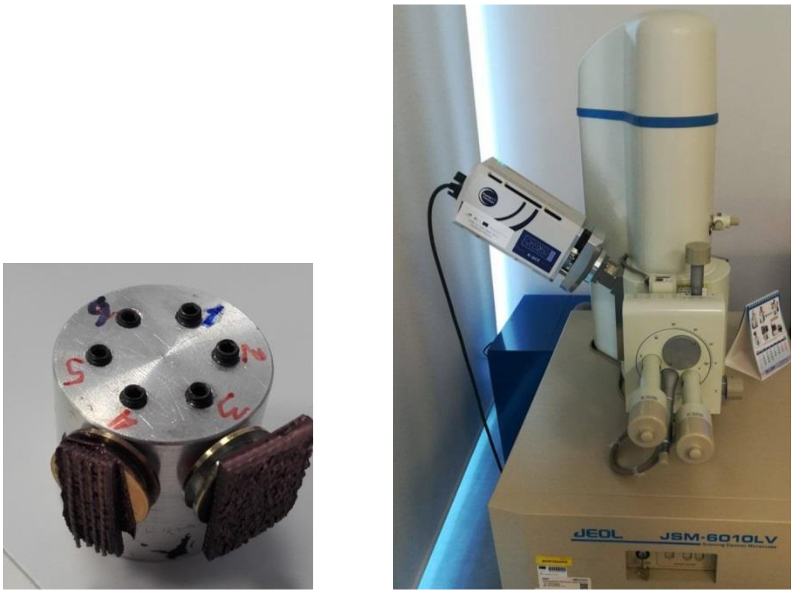


Figure 33- Resin A nylon dipped cord treat with liquid nitrogen.

At this point all samples were ready to be analysed, firstly to perform EDS analyses the samples were assembled in a specific support cell and inserted in the SEM JSM-6010LV from JEOL microscope equipped with an EDS equipment fabricated by Oxford Instruments (Figure 34).



A B

Figure 34- A- SEM support cell; B- SEM-EDS equipment.

After EDS analysis the samples were all coated with gold using a 108auto Cressington Sputter Coater. With all samples coated SEM analysis was performed; at this point the samples were assembled once again in the support cell and inserted in the SEM microscope, with this equipment several results were obtained using different amplifications.

3.3.7. Optical microscopy

Optical microscopy, more precisely reflex microscopy was used, similar to SEM-EDS analysis, to study a specific resin A nylon dipped cord that presented adhesion impairment at a very fast rate. However since SEM-EDS analysis provided longitudinal views of the cord, optical microscopy was only used to study the transversal view of the cord, making possible to see how the dip interacts with the inner fibres of the nylon cord.

Since the sample in question is a cord, some preparation is required in order to study the transversal section. The first step was to place the samples vertically in a mould of cardboard that was then filled with a specific resin, as can be seen in Figure 35.

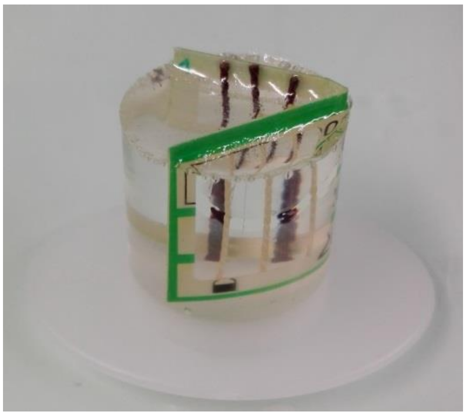


Figure 35- Resin A nylon dipped cord placed in a resin mould.

Following this step the resin mould needs to be polished in order to eliminate the cardboard section and leave only the cord transversal section at the surface of the resin mould. This polish treatment was performed in a Minitech 233 lab polisher machine from Presi, as can be seen in Figure 36.

Figure 36- Polish treatment of the resin mold.

After this step the samples are ready to be studied by optical microscopy, for that purpose it was used a BH2 Olympus reflex microscope, equipped with a Leica DFC280 camera (Figure 37), and several images, at different amplifications, of the cords transversal section were acquired.

Figure 37- Optical reflex microscope equipped with a Leica Camera.

CHAPTER 4. Results and discussion

In this chapter all the results obtained during this master thesis will be exposed and discussed according to the order by which they were performed. Therefore this chapter will be divided in three subchapters where the first one will focus on the alternative resins that were tested in PI; the second one will expose the chemical analysis that were performed in University of Minho and the last one will reveal the chemical reactions that were determined during this work development.

4.1. Alternative Resins

As previously mentioned, RFL dip bares a significant human and environmental hazard that must be addressed, thus one of this master thesis goal is focus on new dip formulations to replace the current RFL dip solution used. In this subchapter two different dip formulations will be exposed as well as all the tests to which they were submitted.

4.1.1. Latex study

The study of the latex based reagents used in C-ITA was the first work performed during this master thesis. This study is based on the fact that VP-Latex, the most commonly used latex in all dip formulations (RFL dip, resin A dip and resin B), shows a high instability when mixed with ENR-50, an epoxy rubber that is being used as a possible solution to dip cords. This high instability translates in terms of the formation of aggregates within the solution. Therefore the purpose of this study was to identify the main responsible for the aggregates appearance.

The first step was to study temperature effect on these compounds in separate due to the fact that in the LDU dip solutions are subjected to high temperatures, making this feature the possible responsible for clot formation in the mixture. Therefore VP-Latex and ENR-50 where heated in separate and the pH of both solutions was controlled (Table 7).

Table 7- VP-Latex and ENR-50 temperature *vs* pH.

VP-Latex		**ENR-50**	
Temperature ˚C (range)	pH (range)	Temperature ˚C (range)	pH (range)
(27.0 – 61.0)	(9.49 – 9.05)	(26.3 – 60.8)	(8.58 – 7.50)

Through Table 7 is clear that an increase in temperature lead to a small pH decrease in both reagents, however no clot formation was observed in both heated samples, indicating that temperature by itself is not the responsible for clot formation in VP-Latex-ENR-50 mixture.

The next step was to study pH variation for the two reagents in separate. In order to perform this study 100 mL of VP-Latex and 100 mL of ENR-50 were titrated in separate with different formic acid 85% volumes. Both samples were maintained at an ambient temperature of 23 ˚C. The results are shown in Figure 38.

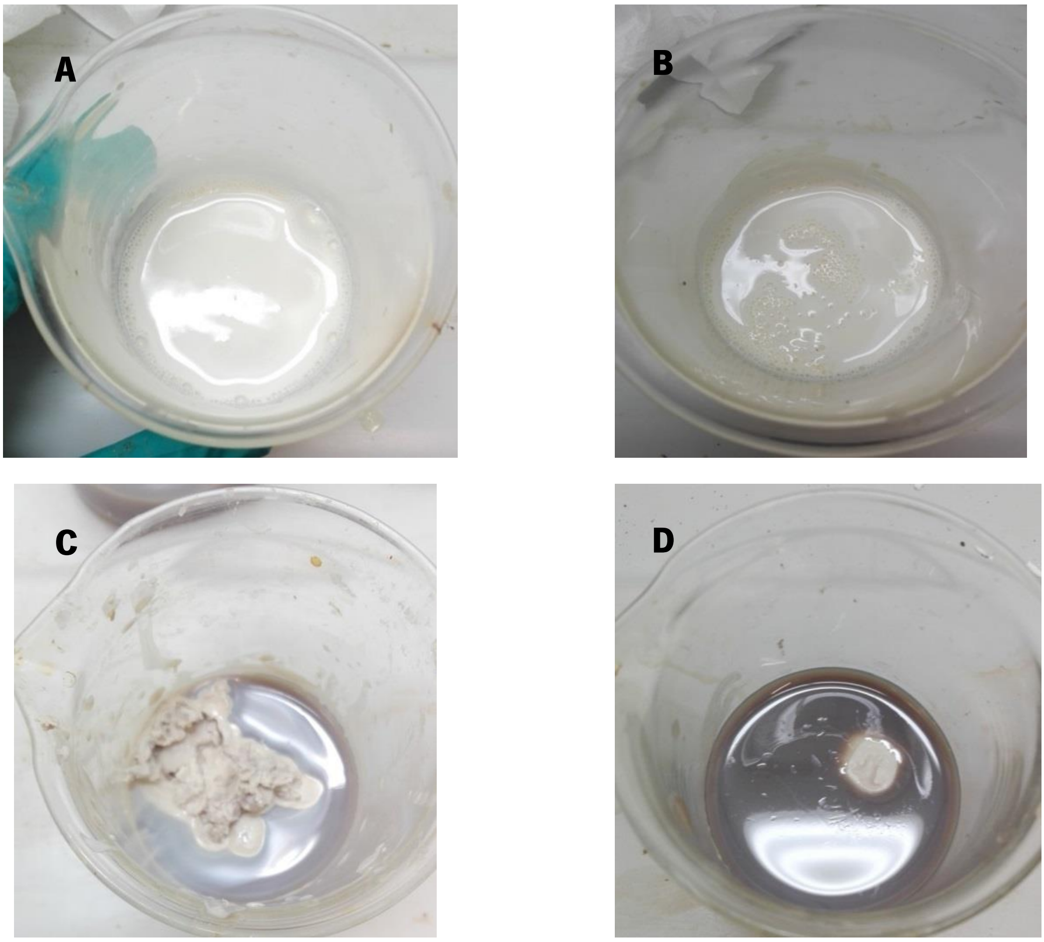


Figure 38- Titration experiment. A- ENR-50 + 1,1 mL of formic acid; B- ENR-50 + 0,4 mL of formic acid; C- VP-Latex + 1,5 mL of formic acid; D-VP-Latex + 0,8 mL of formic acid.

Figure (A+B) illustrates that a decrease in pH does not lead to ENR-50 coagulation. However the opposite is noticed in VP-Latex (Figure C+D), coagulation occurs when adding formic acid to the samples and the extent of this coagulation increases with the amount of formic acid used. This occurs because VP-Latex is stabilized by an anionic solution that is neutralized when in contact with formic acid, leading to VP-Latex particles aggregation [40] (Figure 39).

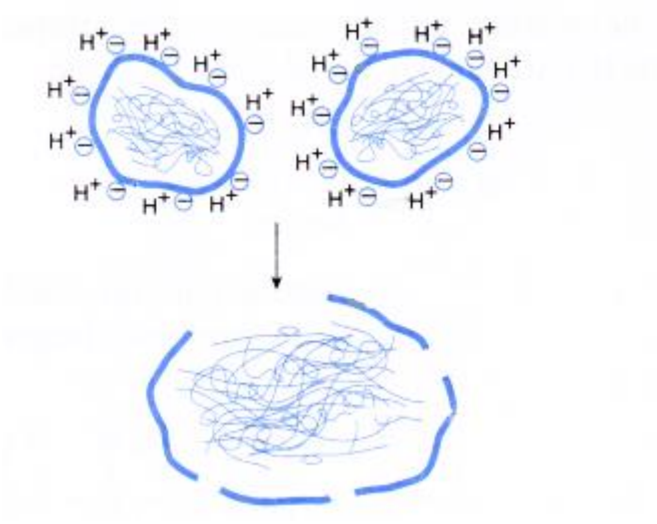


Figure 39- Coagulation mechanism of titrated VP-Latex (adapted from [41])

However in ENR-50/VP-Latex mixture no sudden pH changes occur, thus VP-Latex coagulation when titrated does not seem the correct explanation for mixture coagulation. For that reason the next step was to prepare different ENR-50/VP-Latex mixtures, using different reagent ratios. The trials are exposed in Table 8.

Table 8- VP-Latex/ENR-50 different ratio trials.

Ratio VP-Latex/ENR-50 (mL)	T (˚C)	pH	observations
50/50	23.8	9.37	Clotting
70/30	23.2	9.48	Clotting
85/15	24.2	9.38	Clotting
95/5	24.8	9.36	Clotting
30/70	24.0	9.50	Clotting
5/95	23.6	9.51	Clotting

From Table 8 is clear that all VP-Latex/ENR-50 mixtures coagulated, however the extent of the coagulation was different between the samples. In fact with the increasing of VP-Latex concentration a clear increase in agglomeration extent was noticed, indicating that VP-Latex may be the main responsible for mixtures coagulation. This increase in the extent of the coagulation is shown in Figure 40.

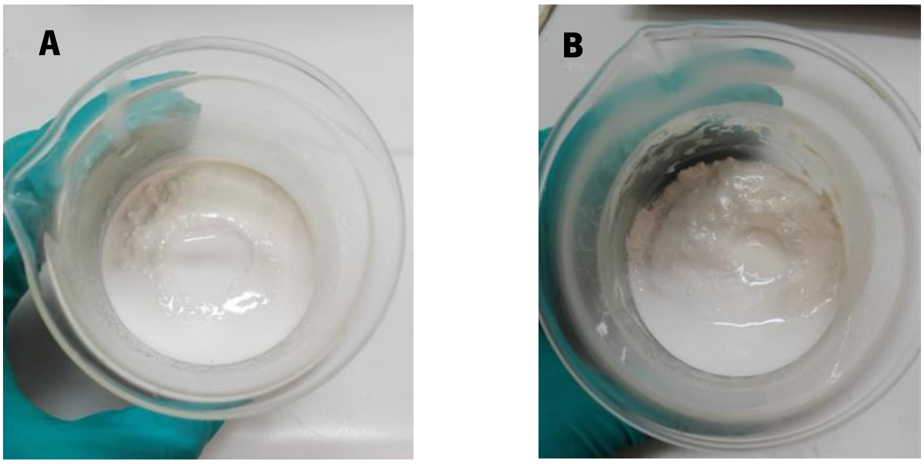


Figure 40- VP-Latex/ENR-mixtures. A- 50/50 mL ratio; B- 70/30 mL ratio.

This coagulation problem can arise from VP-Latex and ENR-50 different chemical properties, as previously mentioned ENR-50 is essentially a polar molecule whose polarity increases with the amount of epoxy groups present in the molecule, besides this compound is stabilized by a non-ionic solution. On the other hand VP-Latex is stabilized by an anionic solution and is mainly constituted by butadiene (70%) a non-polar compound. This difference in polarity can be the key to explain this mixture coagulation problem.

Therefore the next step was to replace VP-Latex for butadiene latex (BR-Latex), a reagent that is stabilized by a non-ionic solution like ENR-50. This difference between the surfactants (non-ionic for BR-Latex and anionic for VP-Latex) could be the solution to this coagulation problem. Thus, different BR-Latex/ENR-50 mixtures were prepared according to Table 9.

Table 9- BR-Latex/ENR-50 mixtures.

Ratio BR-Latex/ENR-50 (mL)	T (˚C)	pH	observations
70/30	23.6	9.35	Clotting
30/70	23.5	9.40	Clotting

Table 9 shows that BR-Latex was not the solution for the coagulation problem, since coagulation was noticed in both mixtures. Furthermore, similar to VP-Latex/ENR-50 mixtures with the increase of BR-Latex there is an increase in coagulation extent, suggesting that VP-Latex and BR-Latex have similar chemical properties. This result can also indicate that the stabilizer solution does not play a significant role in coagulation, since that even being BR-Latex and ENR-50 stabilized by non-ionic surfactant coagulation still occurred.

The final step was to try an ENR with a lower polarity; in this case ENR-25 was the selected reagent. Similar to the previous study, VP-latex/ENR-25 mixtures with different ratios were prepared (Table 10).

Table 10- VP-Latex/ENR-25 mixtures.

Ratio VP-Latex/ENR-25 (mL)	T (˚C)	pH	Observations
50/50	23.8	9.37	Clotting
70/30	23.2	9.48	Clotting
85/15	24.2	9.38	Clotting
95/5	24.8	9.36	Clotting
30/70	24.0	9.50	Clotting
5/95	23.6	9.51	Clotting

Despite having lower polarity, ENR-25 still coagulated with VP-Latex, and similar to the previous study an increase in coagulation extent is clearly noticed with the increasing of VP-Latex concentration.

To conclude, all these results indicate that latex and ENR compounds form aggregates when mixed and the main explanation may be the difference in polarity between this two reagents. However the possible formation of chemical bonds between ENR epoxy groups and VP-Latex molecules must not be excluded since VP-Latex particles possess different sites (double bonds) that can bind to ENR reactive group. Therefore, further studies must be conducted in order to confirm this hypothesis.

4.1.2. Resin A

The first alternative dip tested in this master thesis is the Resin A dip, as previously mentioned this dip formulation is environmental friendly and has already shown good adhesion with many of C-ITA produced cords, namely PET, aramid, Hybrid and nylon cords. Thus in this subchapter the results regarding the new experiments that were conducted using resin A will be exposed. The first study focused on coupled plasma treatment to impregnation with resin A dip while the second study presents an experiment that was performed with the purpose of comparing the ageing behaviour between RFL dipped cords and Resin A dipped cords. Furthermore two studies regarding one specific resin A dipped cord (nylon) will be also discussed.

4.1.2.1. Plasma treatment

As previously mentioned plasma treatment is a new and effective way of pre-treating cords making them more susceptible for dip interaction. Similar to RFL dip, resin A dip by itself is insufficient in the impregnation of certain cords, requiring the use of a pre-dip solution in order to achieve good adhesions. Plasma treatment offers the solution for pre-dip removal, leading to a decrease in the chemicals required to dip cords that will result in a possible reduction in the production cost and also a significant decrease in the environmental impact.

In this study five trials were performed in the atmospheric plasma, between these five trials the only conditions changed were the gas flow and the plasma power that increase from trial to trial. In addition the same resin A dip solution and the same LDU parameters were used in all trials. After impregnation, a peel test was performed to all samples prepared and the results are showed in Table 11.

Table 11- Nylon resin A dipped cord treated with atmospheric plasma.

Trial	**1**	**2**	**3**	**4**	**5**
Peel force (N/25 mm)	173	175	197	197	203
Coverage	1	1	1	1	1

Table 11 clearly shows that none of the five trials achieved satisfying results thus very poor coverage values were obtained, indicating that nylon cord resin A dipping failed. Furthermore, these results show that atmospheric plasma treatment, with the conditions used, is incapable of activating nylon cord in order to react efficiently with resin A dip, providing an acceptable adhesion. Regarding peel force, since very bad coverage values were obtained, this parameter is irrelevant because it only represents the force required to separate rubber from rubber.

The main problem of this equipment is adjusting plasma power and gas flow in order to activate nylon cord without breaking it. However even with the highest plasma power possible nylon cord was not activated (trial 5), indicating that other parameters must be modified. Due to this fact further trials must be performed in order to achieve better results with atmospheric plasma treatment. The second step should be varying the LDU parameters, like increasing the velocity in order to reduce the cord time exposure to plasma treatment making it less susceptible to break. If these trials reveal poor results recipe optimization should be the final step.

In conclusion, despite this study revealed poor results regarding nylon cord impregnation with atmospheric plasma coupled with resin A dipping, it is the first step for the application of atmospheric plasma equipment. Perhaps with the further studies above mentioned this equipment will reveal itself a very useful tool for cord dipping in C-TA.

4.1.2.2. Ageing behaviour

The second study regarding resin A dip solution was an ageing experiment. Essentially the aim of this study was to evaluate if resin A dipped cords present the same ageing behaviour of RFL dipped cords. Figure 41 represents an overview of the experiment conducted, basically four different fibres were used and each one was dipped with two different dip solutions, one the standard RFL dip used by C-ITA and the other the Resin A dip that was used in the tests above mentioned. Besides, the impregnated samples were stored in two different conditions: in order to mimic the cord behaviour inside the tire, in one day six peel samples of each cord were prepared and vulcanized, however peel test was performed to only one of each cord samples, therefore the remaining five samples were "stored in rubber" and on each month one of them was subjected to a peel test. The other condition was to perform one peel test on each month to the dipped cord that is kept in the bobbin inside a dark bag (protect from light). With both studies was possible to assess the ageing behaviour of all dipped cords inside and outside the tire, allowing to know how the adhesion of both dip solutions is influenced during the period of six months.

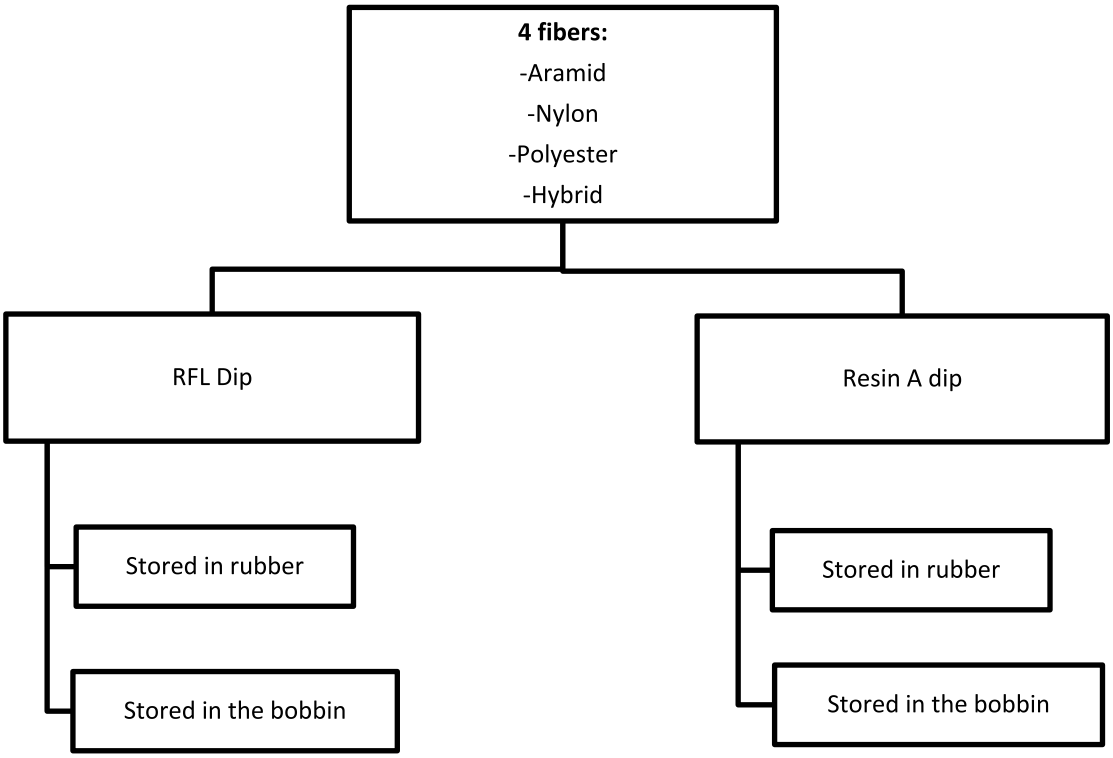


Figure 41- Ageing experiment of RFL and Resin A dipped cords.

Furthermore as previously mentioned in C-ITA two different rubbers can be used in the adhesion, namely rubber A and rubber B. The main difference between them are the polymer blend (rubber B contains SBR), the carbon blacks used and the amount of oil present. In this study rubber B was used to all fibres due to the fact that it provides more precise peel force values. However aramid and hybrid cords revealed poor adhesion values with rubber B, leading to the use of rubber A in this study for only these two cords.

To facilitate reader comprehension, the results of this experiment will be separated by type of cord.

Aramid cord:

Taking into account aramid cord, the first results exposed in Figure 42 represent the ageing behaviour both in terms of coverage and peel force of resin A and RFL aramid dipped cord when stored both in rubber A and B.

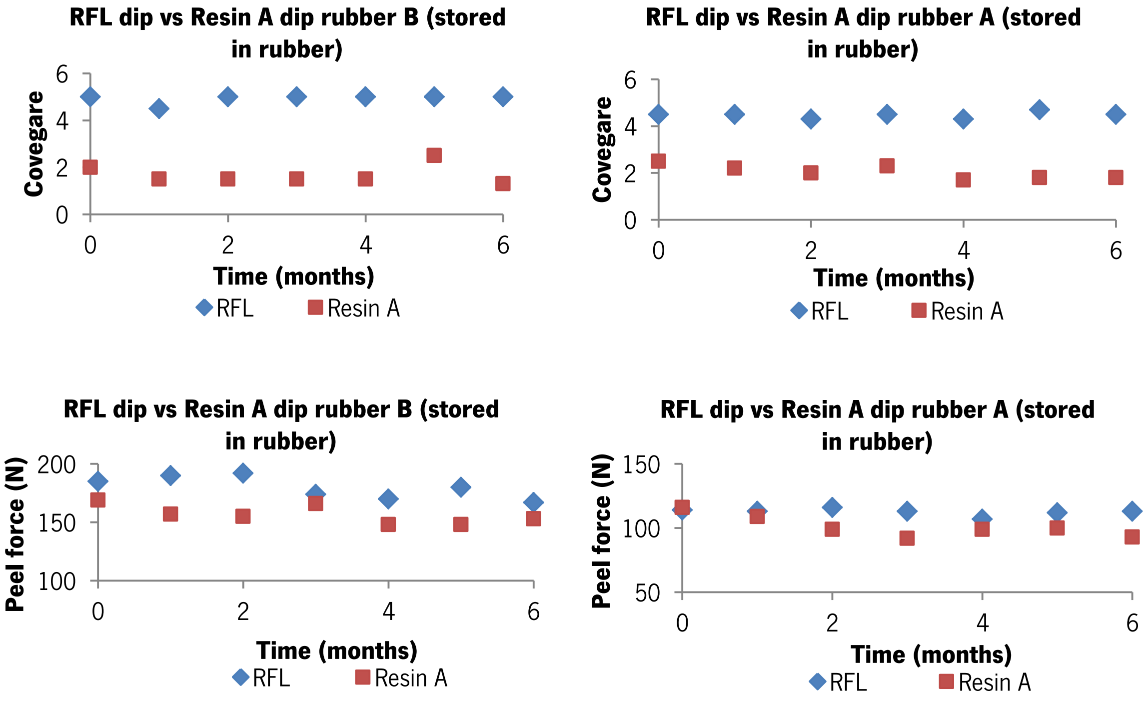


Figure 42- Ageing experiment of aramid cord stored in rubber with the two rubber types used. Note: All peel forces presented are in N/25 mm.

From Figure 42 it can be noticed that RFL aramid dipped cord exhibited good coverage (4.5-5) and good peel forces (>120 N/25mm) for both types of rubber used during the period of six months. This result clearly show why RFL dip is currently used in cord impregnation, thus it provides high adhesion quality that is maintained even during six months. Regarding resin A aramid dipped cord the results obtained were very poor, in fact no ageing behaviour was observed since the initial coverage value (rubber A: 2.5 and rubber B: 2.0) was already lower than the minimum accepted (3.5). Peel force values in this case are irrelevant due to the fact that a very poor adhesion was obtained. Therefore, the results for resin A aramid dipped cord indicate that a problem with cord impregnation might occurred, since previous resin A aramid dipped cords had revealed satisfying adhesion results.

The following study with aramid cord was the influence of the storage in the bobbin for both resin A and RFL aramid dipped cords. These results are showed in Figure 43. In this case since rubber A is more appropriated for aramid the ageing test was only performed with this rubber. Besides, due to insufficient cord, the study was conducted for only three months.

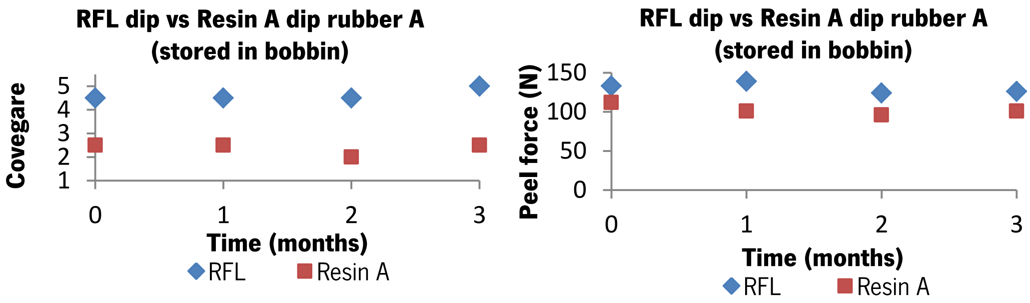


Figure 43- Ageing experiment of aramid cord stored in the bobbin. Note: All peel forces presented are in N/25 mm.

From Figure 43 is possible to conclude that similar to the "storage in rubber" condition resin A dip did not work, resulting in very poor adhesion results. This result supports the claim that a problem in cord dipping might occurred. Taking into account RFL dip results with this condition, they reveal very good coverage and peel force values during the period of three months, therefore it can be concluded that in both conditions RFL dip provides high adhesion quality.

To conclude, for aramid cord this ageing experiment suggested that RFL aramid dipped cord does not suffer any ageing in both storage conditions. Concerning resin A aramid dipped cord no ageing behaviour can be conclude probably due to an incorrect cord impregnation.

Hybrid cord:

As previously mentioned hybrid cord is a cord composed by one yarn of aramid and one yarn of nylon twisted together. Like aramid this cord was tested with both rubbers in the "stored in rubber" condition and the results are present in Figure 44.

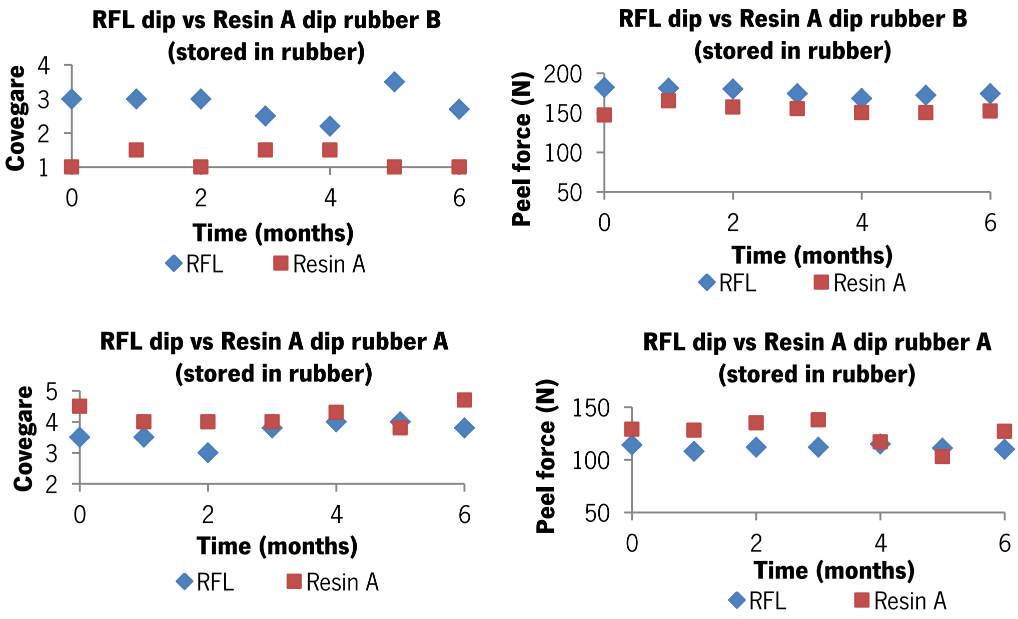


Figure 44- Ageing experiment of hybrid cord stored in rubber with the two rubber types used. Note: All peel forces presented are in N/25 mm.

Figure 44 shows that both RFL and resin A hybrid dipped cords revealed very poor coverage results with rubber B (RFL dip: 3; resin A dip: 1.5), supporting the fact that the most appropriated rubber for hybrid cord is A.

Regarding rubber A results they considerably improved with both dipped cords, in this case RFL hybrid dipped cord revealed an initial coverage of 4.5 while resin A hybrid dipped cord revealed an initial coverage value of 3.5, being this the minimum value accepted. During the period of six months the RFL hybrid dipped cord decreased slightly its coverage value (around 4), however in the last month of the experiment the value obtained was of 4,5, thus indicating that this slight decrease might be more related to the peel sample preparation than with the ageing of the sample. Focusing on the peel force values of RFL hybrid dipped cord with rubber A; all were above the standard (120 N/25 mm) with the exception of the fifth month sample. Overall the results for RFL dip application for hybrid cord are very positive, and no ageing of this dipped cord was detected during the period of six months.

Concerning resin A hybrid dipped cord Figure 44 shows that, for rubber A, during the six months of the study coverage values were around 3.5 and 4, being only the second sample (coverage of 3) below the standard coverage value. Moreover the peel force values obtained by this hybrid dipped cord are superior to 120 N/ 25 mm, being only the fifth month sample lower to the standard. Curiously the fact that both peel force values obtained for the fifth month sample of

RFL and Resin A hybrid dipped cord (with A rubber) are below the standard suggests that a possible calibration error in ZwickRoell machine might occurred, thus affecting both samples peel test. In conclusion, for the "stored in rubber" condition both dip solutions revealed satisfying adhesions with rubber A during the period of six months, so no ageing process was detected.

The next condition to be studied was both hybrid dipped cords kept in the bobbin inside a dark plastic bag. As previously mentioned on each month one peel sample of each cord (resin A dipped and RFL dipped) was prepared and submitted to a peel test. Figure 45 shows the results obtained during the four months of the experiment.

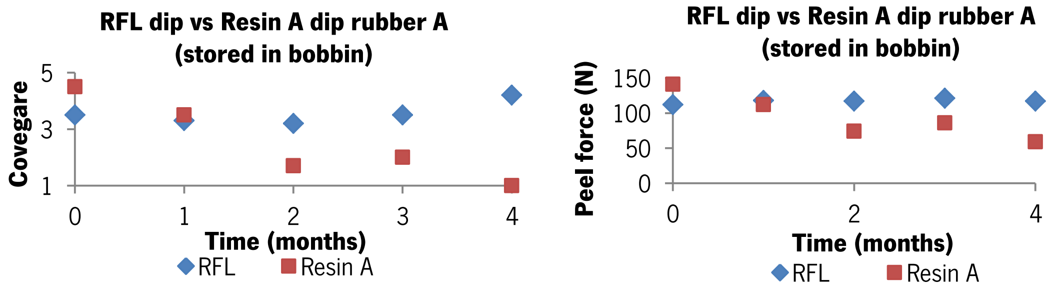


Figure 45- Ageing experiment of hybrid cord stored in the bobbin. Note: All peel forces presented are in N/25 mm

Through figure 45 is clear that during the period of four months RFL hybrid dipped cord do not suffer significant alterations in both coverage and peel force values, thus no ageing process is detected. Besides the coverage values obtained are around 3.5 and 4 indicating that when kept in the bobbin RFL hybrid dipped cord exhibits the same behaviour has when stored in the rubber, giving in both cases satisfying adhesion results. Resin A hybrid dipped cord results show a very curious event, thus in Figure 45 is clear that after the first month both coverage and peel force values decrease considerably, in fact in the fourth month coverage value of resin A hybrid dipped cord is of 1 (the minimum evaluation possible) and the peel force value is of only 59 N/25 mm. So with this storage condition after the period of one month there is considerable adhesion impairment, indicating that resin A dip might be affected when in contact with air.

Overall the ageing study of hybrid dipped cord revealed that when dipped with RFL dip this cord does not exhibit any ageing in both storage conditions. On the other hand when dipped with resin A dip this hybrid cord reveals an ageing behaviour when exposed to air ("stored in the bobbin") that leads to adhesion impairment. If stored in rubber no ageing behaviour of this resin A hybrid dipped cord is observed, indicating that air exposure might be the trigger of cords surface inactivation.

PET cord:

PET cord was the next object of this ageing study, as previously mentioned rubber B was the rubber selected and in Figure 46 the results concerning the condition “stored in rubber” are shown for both resin A and RFL dipped PET cords.

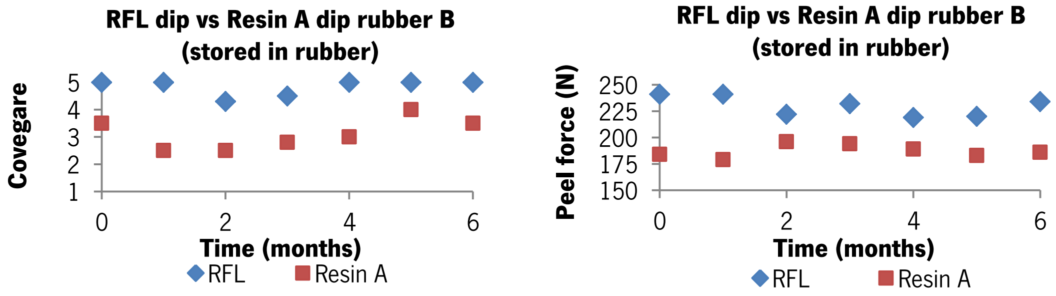


Figure 46- Ageing experiment of PET cord stored in B rubber. Note: All peel forces presented are in N/25 mm

Figure 46 indicates that RFL PET dipped cords show coverage values around 4.5 and 5 during the period of six months, moreover the peel force values obtained are around 220-240 N/25 mm. For this reason RFL dip shows almost perfect adhesion results for PET cord, revealing no ageing behaviour during this six month period. Resin A PET dipped cord results exposed in Figure 46 are considerably different from RFL PET dipped cord results, in the way that both coverage and peel force values are lower. Nevertheless Resin A PET cord present a peel force always higher than the standard one. Concerning coverage value, this one is around 3.5, being the minimum coverage value accepted. However it is important to point out that from the first to the fourth month coverage values fell below the standard reaching values of 2.5 and 3, but as in the fifth and sixth month coverage increases this coverage loss must not be considered has an ageing impact and could be more related with the peel sample preparation. In fact PET was a specific cord that was not produced in the LDU machine, in this case both cord samples (RFL dipped and resin A dipped) were produced in the fabric dipping machine, therefore the peel sample preparation is slightly different in the way that the portion of the fabric must be correctly aligned between the two rubber layers, any deviation can lead to the coverage decrease that was detected in this study. To conclude, when "stored in rubber" both resin A and RFL PET dipped cords do not exhibit ageing impairment.

The following step was to study the condition "stored in the bobbin" in order to see how resin A and RFL PET dipped cords adhesion is influenced during the period of four months. In Figure 47 the results concerning this study are exposed.

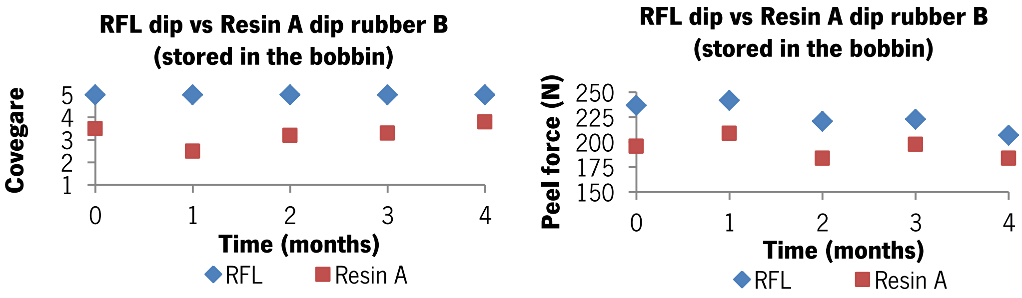


Figure 47- Ageing experiment of PET cord stored in the bobbin. Note: All peel forces presented are in N/25 mm

Through Figure 47 it can be seen that RFL PET dipped cord maintains a coverage value of 5 during all four month of the analysis, moreover peel force values obtained for these adhesion slightly decrease during the same period, however all are considerably higher than the standard 120 N/25 mm. For this reason is clear that RFL PET dipped cord is not influenced by the storage conditions since that both "stored in rubber" and "stored in the bobbin" good adhesions are obtained. Besides, no ageing behaviour of this dipped cord is noticed, supporting the current use of this RFL dip solution in cord impregnation. Taking into account resin A PET dipped cord, Figure 47 shows that in general satisfying coverage values (around 3.5) were obtained during the period of four months. Besides, is clear that despite a coverage decrease in the first month (2.5) the following coverage results remain constant and acceptable, indicating that no PET dipped cord ageing is occurring. Regarding peel force, all five peel samples revealed satisfying results. Both coverage and peel force results for resin A PET dipped cord kept in the bobbin indicate that this cord does not suffer any ageing behaviour, revealing good adhesion quality within this four month period.

In conclusion this RFL and resin A PET dipped cord ageing study revealed that RFL dip leads to a PET dipped cord that provides very good adhesion for both storage conditions. Moreover resin A PET dipped cord provides an adhesion with lower coverage and peel force values, nevertheless it is still considerable an acceptable adhesion thus it fulfils the required standards.

Nylon:

Nylon is the final cord studied by this ageing experiment, similar to PET cord only rubber B was used for this cord ageing experiment. The results concerning the "stored in rubber" condition are exhibited in Figure 48.

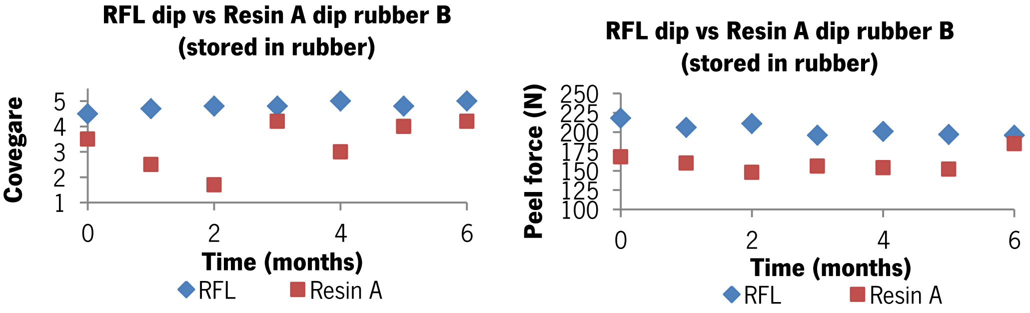


Figure 48- Ageing experiment of Nylon cord stored in rubber B. Note: All peel forces presented are in N/25 mm

Figure 48 represents the behaviour of resin A and RFL nylon dipped cords throughout a six month period of storage in rubber. Focusing on RFL nylon dipped cords is possible to notice that during this period all peel samples presented coverage values around 4.5 and peel force values significantly higher than 120 N/25 mm, therefore with the storage condition used very good adhesion results were obtained and no ageing of the RFL nylon dipped cord was detected. Regarding resin A nylon dipped cords the coverage values obtained during the six months of the experiments present some irregularities, however is possible to see that in general the coverage value around 3.5 and 4.0. Only in the first and second month coverage value is very low (2.5 and 2.0 respectively), nevertheless as this one increases in the following months it is not possible to conclude that resin A nylon dipped cord is ageing. For this reason the coverage values obtained in first and second month must be related with the peel sample preparation. Taking into account the peel force values of this cord, they are all above to the required standard. Overall, within a six month period, both resin A and RFL nylon dipped cords exhibit no ageing behaviour when "stored in rubber" providing satisfying adhesion results.

As all the other cords, nylon cord was also submitted to an ageing experiment with the condition “stored in bobbin”. The results from this experiment are revealed in Figure 49.

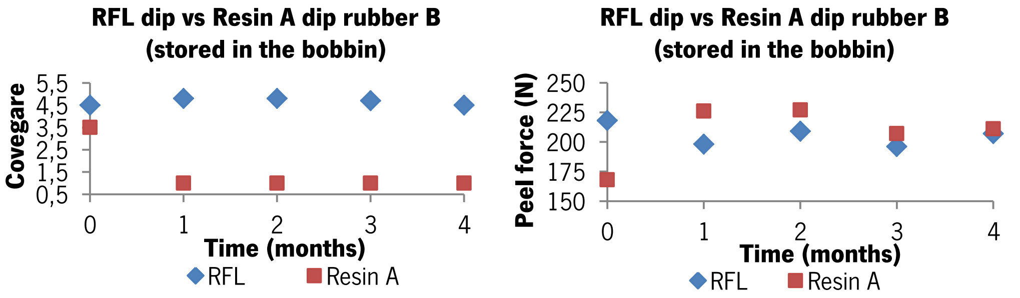


Figure 49- Ageing experiment of Nylon cord stored in the bobbin. Note: All peel forces presented are in N/25 mm

Taking into account RFL nylon dipped cords Figure 49 clearly shows that during a four month period this nylon cord revealed both coverage and peel force values above the required standards. In addition, as no changes in these values are noticed during this period no ageing of the RFL nylon dipped cord occurred. On the other hand, similar results were not obtained for resin A nylon dipped cord, thus after the immediate test (0 month) the coverage values of the peel samples suffer a high decrease (from 3.5 to 1.0). Besides, in the following months this coverage value remain constant at 1.0, suggesting that during only one month this resin A nylon dipped cord suffered a considerable ageing impairment. In order to exclude bad peel sample preparation on the same month more than one peel sample was tested, providing the same 1.0 coverage value. Furthermore this event must not be linked to an incorrect cord impregnation since the first adhesion performed provided a satisfying adhesion (coverage: 3.5; peel force: 160 N). For all these reasons is possible to conclude that resin A nylon dipped cords revealed an ageing behaviour when “stored in the bobbin”, revealing that air exposure might be the trigger behind resin A dip inactivation.

To conclude, once again RFL dip revealed no ageing behaviour, providing good adhesion results in both storage conditions. On the opposite resin A nylon dipped cord revealed no ageing when “stored in rubber”, however ageing impairment was noticed when this nylon dipped cord was “stored in the bobbin”, indicating that air exposure might be affecting resin A dip adhesive properties.

Ageing experiment overview:

Taking into account the results obtained with this ageing experiment for all dipped cords is possible to draw out some conclusions.

Firstly, all RFL dipped cords revealed very good adhesion results and no ageing behaviour in all cords used. In addition no difference was detected in the storage conditions. Therefore this results justify why RFL dip is the most commonly used solution in cord impregnation, thus it provides very good adhesions that keep their chemical and physical properties during a long period of time.

Secondly, is possible to conclude that, excluding aramid, all resin A dipped cords "stored in rubber" revealed satisfying adhesion results and no ageing process. For this reason these results indicate why resin A dip is a good solution for RFL dip substitution, because inside the tire ("stored in rubber") the resin A dipped cords tested provide the required adhesion for a correct tire performance.

Lastly, is possible to conclude that an ageing impairment is detected in resin A hybrid and nylon dipped cords when "stored in the bobbin". Curiously hybrid cords also contain nylon fibres, thus there could be a link between these two results in the way that resin A dip interaction with nylon might not be as effective as in PET cord where no ageing behaviour was detected. In addition, the main difference between the two storage conditions is that in "stored in the bobbin" condition the cords are in contact with air while in "stored in rubber" condition the cords are already bonded to the rubber and are not air exposed. This fact may suggest that air exposure may be the trigger behind this two resin A dipped cords inactivation, however further studies must be conducted in order to obtain more solid conclusions.

4.1.2.3. Nylon resin A dipped cord SEM/EDS analysis

Through ageing experiment, is clear that resin A nylon dipped cord revealed a considerable adhesion impairment when stored in the bobbin. In order to better understand this result two microscopic analysis were performed: SEM-EDS and optic microscopy. The aim was to see if there is any difference between a resin A nylon dipped cord stored in the bobbin during one month and a resin A nylon dipped cord one day old. This study was applied to both cords and peel samples of the dipped cords.

The first part of SEM analysis was focused on the peel samples of both resin A nylon dipped cords. In figure 50 is exposed the view, at two different amplifications, of the peel sample correspondent to the one day old nylon dipped cord. Through the figure is clear that no cord can be seen; besides it can only be observed the presence of rubber and the corresponding cracks resulted from the peel test separation. This result was expected since this peel sample revealed coverage of 5, indicating that only rubber can be observed.

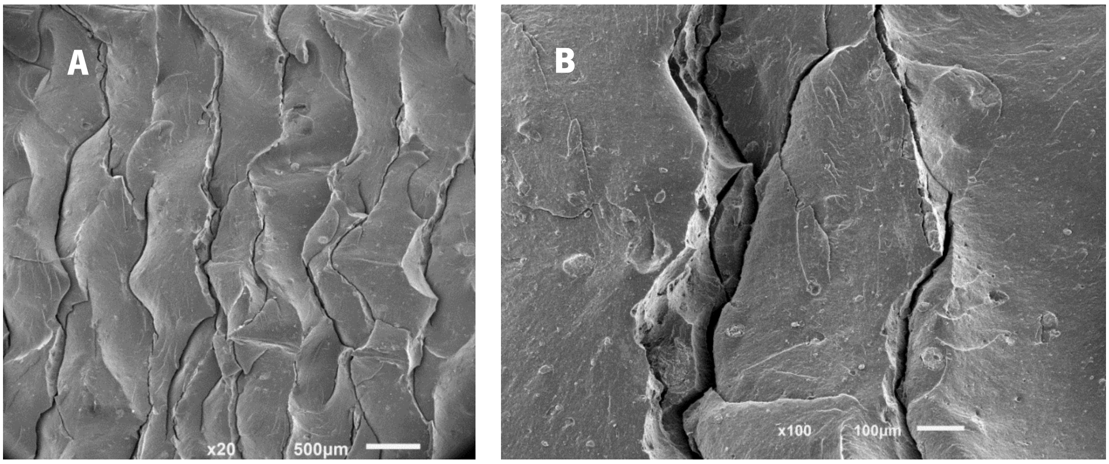


Figure 50- SEM results of the one day old peel sample of resin A nylon dipped cord. A- 20x amplification; B- 100x amplification.

Regarding the one month old nylon cord peel sample, the results are shown in Figure 51. From Figure 51-A the nylon dipped cord can be easily detected supporting the bad coverage value obtained. Besides in Figure 51-B a transversal view of the peel sample is revealed, indicating once again that no layer of rubber is on top of the nylon dipped cords, furthermore in this figure the group of cords situated below corresponds to the chaffer rubber, so it must not be taken in consideration.

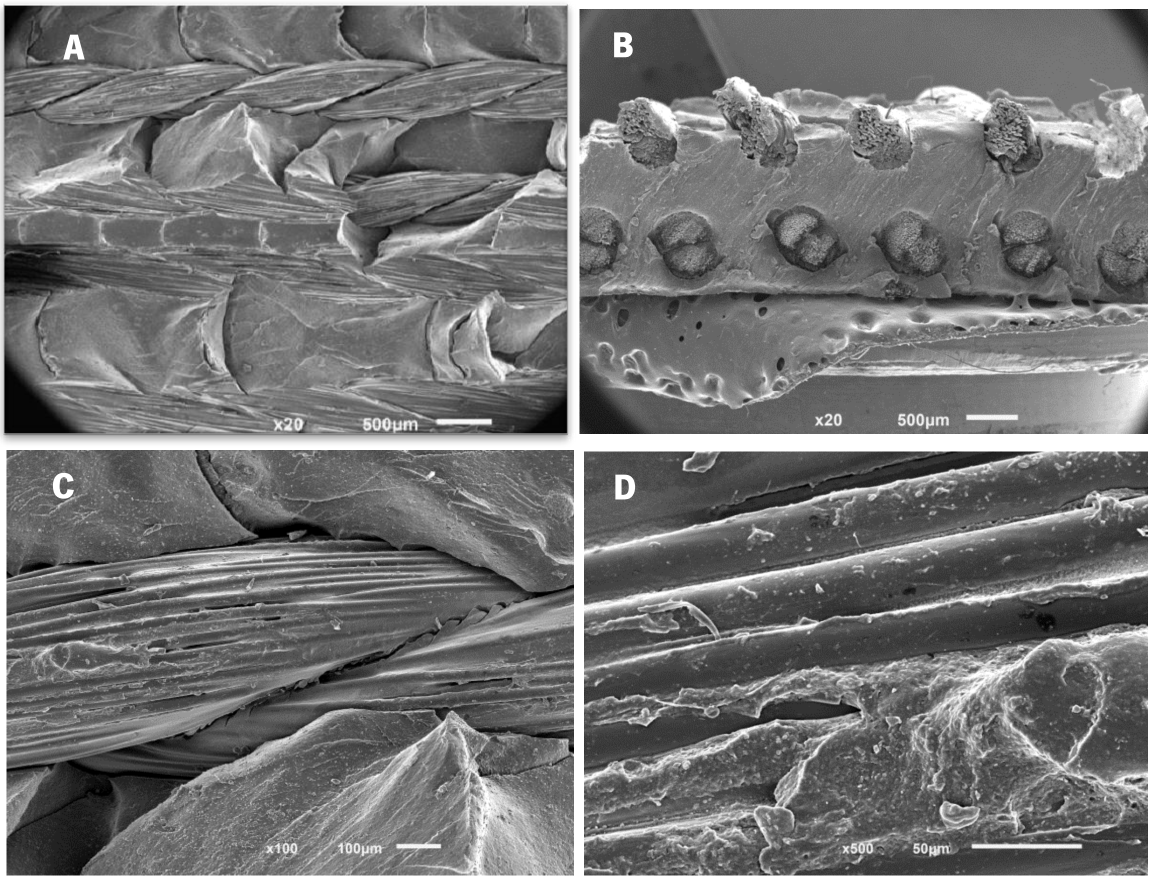


Figure 51- SEM analysis of one month old resin A nylon dipped cord. A- 20x amplification; B- Transversal view of the peel sample, 20x amplification; C- 100x amplification; D- 500x amplification.

Regarding Figure 51-C and Figure 51-D they indicate the presence of small amounts of rubber bounded to the resin A nylon dipped cord, however these small amounts are invisible to human eye, thus they do not enter in coverage value consideration. In general, Figure 51 shows clearly that one month old resin A nylon dipped cord does not achieve a satisfying adhesion, indicating the possibility of resin A dip degradation on cords surface.

The next step was to perform SEM analysis of the two resin A nylon dipped cords in order to inspect the state of the dip in cords surface. The results from SEM analysis of one day old nylon dipped cord are exposed in Figure 52. From this figure it can be noticed a very smooth cord surface with few irregularities and aggregates, thus indicating the presence of resin A dip in cords surface.

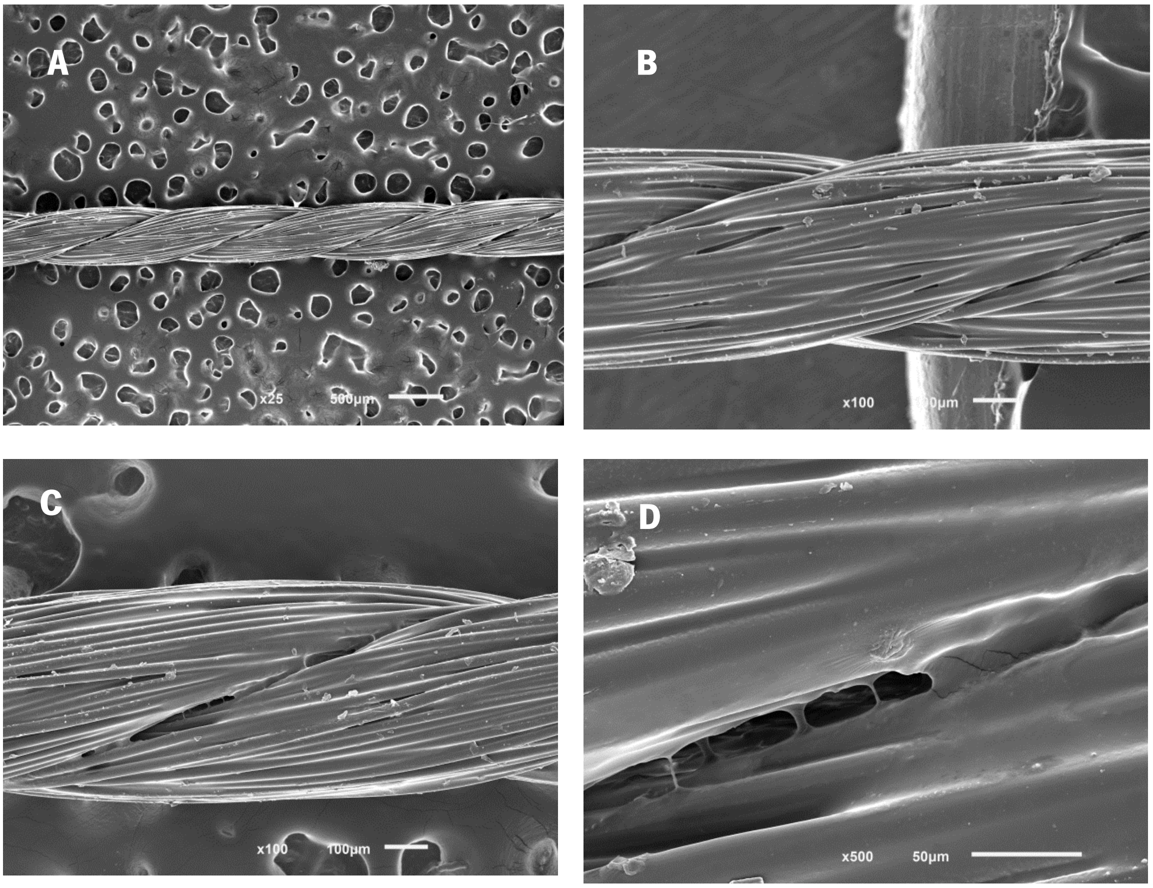


Figure 52- SEM analysis of one day old resin A nylon dipped cord. A- 25x amplification; B- 100x amplification; C- 100x amplification; D- 500x amplification.

Moreover, it can be seen in Figure 52-D a perfect coating of the cord, supporting resin A dip presence and confirming the good adhesion obtained by this resin A nylon dipped cord. For this reason this study confirmed that one day old resin A nylon dipped cord has the perfect conditions to obtain a satisfying adhesion.

However, for one month old resin A nylon dipped cord the same does not occur. Through Figure 53 is clear that the cord presents a rougher surface with a considerable presence of aggregates (Figure 53-B, C and D). This considerable aggregate presence may indicate dip degradation due to one month exposure to the air (when kept in the bobbin), resulting in an adequate resin A nylon dipped cord that does not exhibit good adhesive properties to rubber.

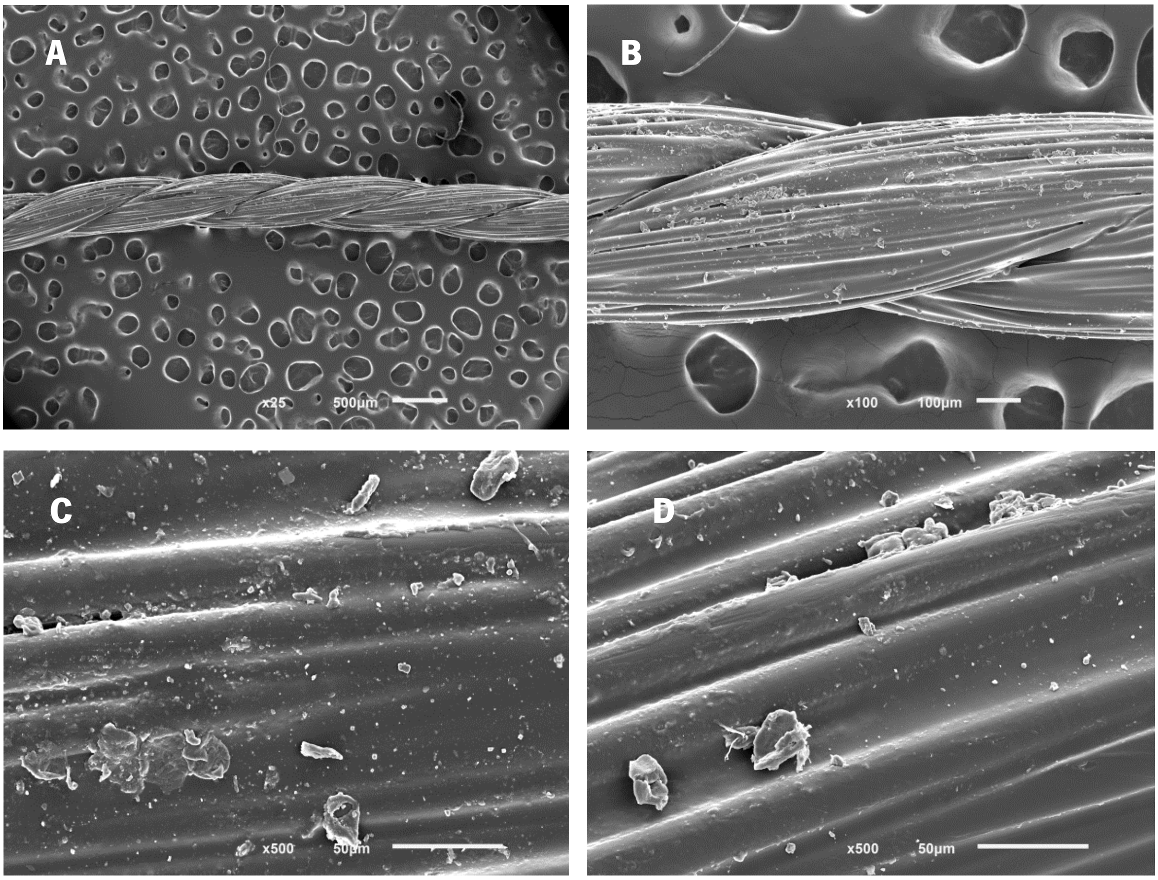


Figure 53- SEM analysis of one month old resin A nylon dipped cord. A- 25x amplification; B- 100x amplification; C- 500 x amplification; D- 500x amplification (another area).

It is important to point out that Figure 53-C and Figure 53-D represent the same amplification of the cord, however in two different areas, showing that this aggregate presence is not sporadic but is in fact verified through all the cord surface.

Comparing the SEM analysis of the two different resin A nylon dipped cords (Figure 52 and Figure 53) is possible to conclude that the main difference between them is aggregates presence, that is playing a significant role in the adhesion behaviour. These results suggest that during the period of one month kept in the bobbin, resin A nylon dipped cord suffers chemical alterations on its surface that clearly compromise adhesion quality.

In order to better understand the chemical changes that resin A nylon dipped cord suffered EDS analysis were performed. Once again these analysis were performed for both cords (one day old and one month old) and for both cords peel samples. It is important to point out that not only one EDS analysis was performed for each sample, in fact different EDS analyses in different areas of each sample were made in order to make certain of the values obtained.

Therefore the values exposed in Table 12 are a mean of all the EDS values obtained for each sample.

Table 12- EDS analysis of resin A nylon dipped cords and their corresponding peel samples.

Sample \ Element %	C %	O %	S %	Si %
1 day old nylon cord	81.3 ± 1.1	18.7 ± 1.1	-	-
1 month old nylon cord	74.9 ± 1.5	25.1 ± 1.5	-	-
1 day old peel sample	87.7 ± 0.8	7.2 ± 0.7	2.4 ± 0.3	1.5 ± 0.2
1 month old peel sample	76.4 ± 3.0	6.6 ± 1.9	5.4 ± 1.3	11.6 ± 1.9

In Table 12 many results are exposed. Firstly, regarding both resin A nylon dipped cords is clear that they only contain carbon and oxygen, this result was expected since nitrogen and hydrogen are not detected by EDS equipment and the only other two elements that should be present are the ones that are detected. Taking into account the relative percentage of each element in the samples it can be seen that oxygen percentage is considerably higher in the one month old nylon dipped cord, this result supports the hypothesis that resin A dip aggregation may occur by oxidative means. Therefore one day old nylon cord presents a lower oxygen percentage that may be an indicator of no resin A dip oxidation. Since it is a relative element percentage, once the oxygen percentage is lower for one day old nylon dipped cord, the carbon element percentage will be higher for this sample. However as carbon does not play a significant role in adhesion it is a secondary element to be considered.

Regarding the peel samples, four different elements were detected by EDS: carbon that is present both in rubber and nylon cord; oxygen that is present mainly in resin A dip but also in the rubber; sulphur that is present in the rubber and essential to vulcanization [8]; and silica that is used as a filler for tire, being present in the rubber [42]. Comparing both peel samples is clear that one day old peel sample has a higher concentration of carbon, which is an indicator of more rubber in cords surface, a fact that was observed by SEM analysis since one day old resin A nylon dipped cord was completely covered by rubber. Due to the fact that one day old nylon dipped cord was completely covered by rubber the EDS analysis do not show the elementary constitution of the resin A dip but they show the elementary constitution of the rubber that covers the nylon cord and as rubber contains both sulphur and silica that is why these elements are detected. Oxygen presence (7.2%) can be explained by the penetration of the electron beam that can detect resin A dip presence.

Taking into account the one month old resin A nylon dipped cord peel sample, most EDS analysis were performed on the cord that is exposed in this peel sample, like this the element percentage that is obtained is representative of cord surface. Nevertheless previous results showed that small quantities of rubber were still bonded to the cord, thus it is not possible to be certain of what is in fact being measured by EDS. In this peel sample it was detected a lower carbon percentage that is an indicator of less rubber presence, however the relative element percentage of silica and sulphur were considerably higher maybe due to the incorrect adhesion that occurred that compromised a homogenous adhesion section, leading to high silica content in certain areas.

To conclude, SEM analysis gave relevant results concerning resin A nylon dipped cord, revealing that when this cord is stored during one month in the bobbin it is severely damaged and this same damage is exhibited by dip aggregation on cord surface. Therefore the storage of resin A nylon dipped cord must be taken into account in order to avoid this problem.

4.1.2.4. Optic microscopy of resin A dipped nylon cords

The second microscopic technique applied to the problem detected in resin A nylon dipped cord was optic reflex microscopy. The purpose of this technique was to see a transversal view of the two nylon cords (one month old and one day old) in order to detect if there is any different dip interaction with the inner fibres of the nylon cord. The results obtained from this analysis are presented in Figure 54.

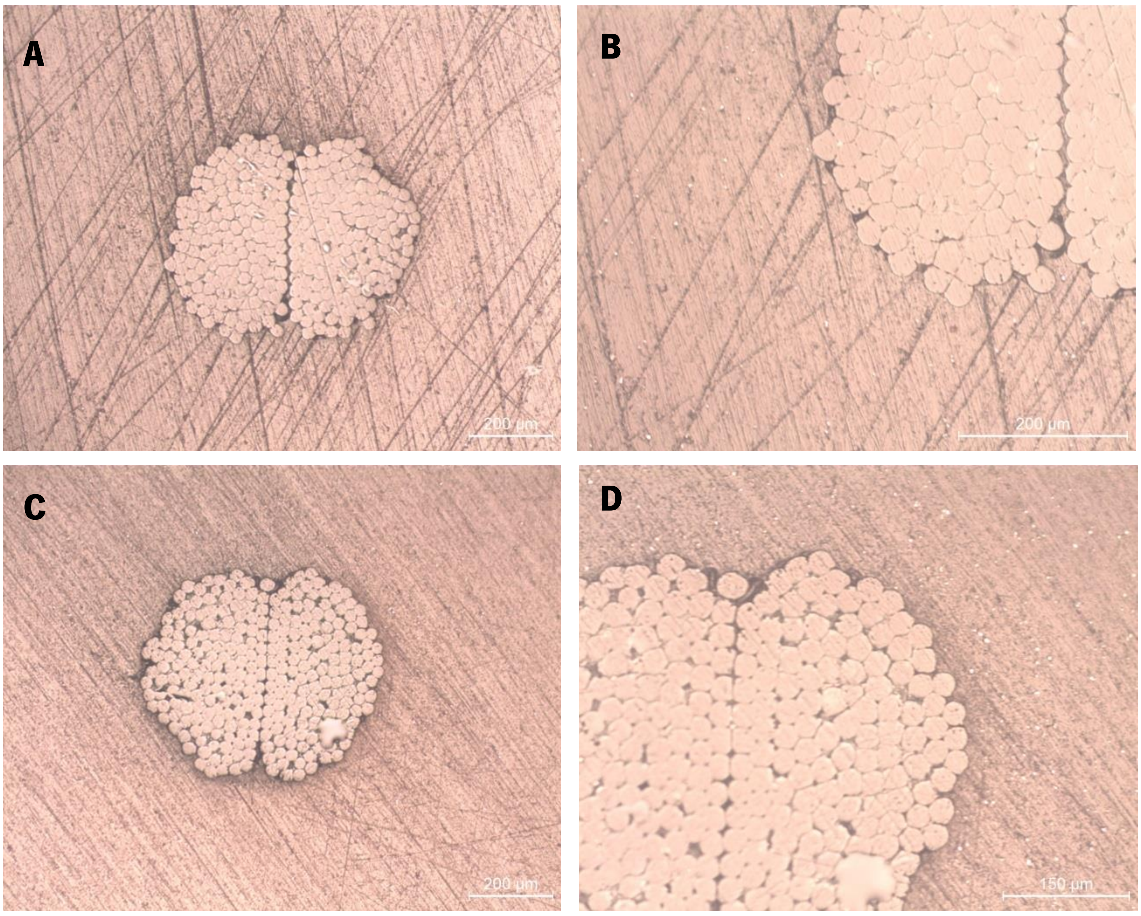


Figure 54- Microscopic optical view of the transversal section of one day old (A+B) and one month old (C+D) resin A nylon dipped cords. A+C- 70x amplification; B+D- 140x amplification.

Through Figure 54 is possible to see clearly that both nylon cords are constituted by two nylon plies that are twisted together. In addition all images contain background scratches that result from the polish treatment, nevertheless this polishment did not compromise the correct visualization of all samples.

From Figure 54 it can be also noticed that the transversal section of one day nylon dipped cord (Figure 54-A+B) and one month old nylon dipped cord (Figure 54 C+D) are very similar and it is not possible to distinguish them. It is important to point out that In Figure 54-C and Figure 54-D there is the presence of a water drop that must not be interpreted as resin A dip. Therefore dip impregnation to the inner part of the cord could not be detected, in fact resin A dip detection was not possible by the use of this optical technique. To conclude, since resin A dip detection was not possible it is expected that in the figure the two nylon cords seem equal due to the fact that they have the same construction (940x2).

4.1.3. Resin B (Phenolic Resin)

Trough resin A study is clear that rayon fibre was not included, that occurred due to the fact that rayon cannot be dipped with resin A dip. This takes place because in order to react with the cord resin A dip needs temperatures between 220˚C-240˚C, however at these high temperatures rayon cords are severely damaged and lose considerable breaking force. Therefore, being a cellulose derived fibre, and according to previous C-ITA trials, rayon cord ideal dipping temperature is around 175˚C.

For that reason the aim of this study was to find a substitute for resin A dip in rayon cord impregnation, however this substitute should maintain the same environmental friendly properties exhibited by the former resin A dip.

Resin B was the selected reagent for this study, despite showing some human and environmental hazard, the presence of CNSL in this dip solution clearly makes it more viable that the current RFL dip used. Nevertheless this resin can only be used in rayon cord impregnation if it achieves satisfying adhesion results.

In a first approach nine different dip recipes were used in rayon dipping. The only difference between these recipes is the Resin B/Formaldehyde ratio. In addition, is important to point out that the dipping process run in the LDU with specific operating parameters for all nine trials. For each of these nine trials one peel test was performed in order to assess adhesion quality. The results are shown in Table 13.

Table 13- Peel test results of the nine trials performed in the LDU using dip recipes with different Resin B/Formaldehyde ratios to dip rayon cord.

Trial	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Peel force (N)	199	169	159	178	179	162	169	177	161
Coverage	1.0	1.0	1.0	1.0	1.5	1.0	1,5	1.0	1.0

From Table 13 is clear that all trials revealed very poor results regarding adhesion quality as the maximum coverage value reached was of only 1.5 and as previously mentioned the minimum coverage value accepted by C-ITA standards is 3.5. Regarding peel force, despite being higher than the required standard of 120 N, this result is not significant since the peel force measured only represents rubber to rubber separation. Therefore all these results indicate that using different Resin B/Formaldehyde ratios does not improve adhesion quality.

For that reason the next step was to prepare two resin B dip solutions using this time different Resin B/VP-Latex ratios. After dipping rayon cord with this two dips a peel test of each trial was once again performed. The results are shown in Table 14.

Table 14- Peel test results of the two trials performed in the LDU using dip recipes with different Resin B/VP-Latex ratios to dip rayon cord.

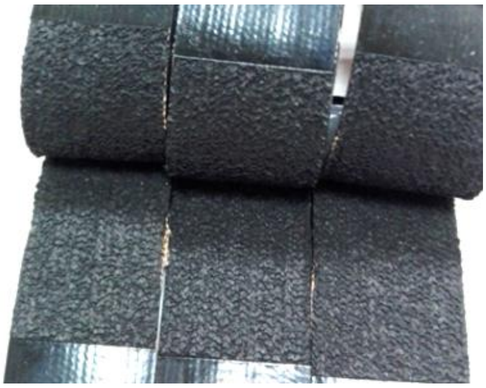
Trial	**10 (Lower Resin B/VP-Latex ratio)**	**11 (Higher Resin B/VP-Latex ratio)**
Peel force (N)	180	228
Coverage	2.5	5.0
		

Table 14 shows that using different Resin B/VP-Latex ratios was the right path to achieve a better adhesion in rayon cord since better results regarding coverage were obtained in both trials. Besides a perfect coverage is obtained when using a higher Resin B/VP-Latex ratio and at the same time the peel force value for this trial is considerable higher than the previous ones obtained, suggesting that this resin B recipe works perfectly in rayon cord. The fact that higher Resin B/VP-Latex ratio provided better results than the lower ratio may suggest that an increase in resin B leads to a higher concentration of active groups that can establish a more strong and effective bond between the cord and the rubber, resulting in a better coverage and a higher peel force.

The final step was to confirm trial 11 and also perform a new trial (Trial 12) using the same resin B recipe but use in the LDU the operating parameters that are currently used in C-ITA for rayon cord dipping with RFL dip. The main difference between the LDU operating parameters of these two trials is that trial 11 uses higher temperatures and lower speeds than rayon RFL dip reference operating parameters. Once again both trials were performed and peel test of each dipped rayon cord was performed (Table 15).

Table 15- Peel test results of the two trials performed in the LDU using two different operating parameters and the same dip recipe to dip rayon cord.

Trial	**11 confirmation**	**12 (Rayon reference operating parameters)**
Peel force (N)	208	163
Coverage	5	4

The results represented in Table 15 indicate that Trial 11 obtained a better coverage and peel force value than trial 12 demonstrating that the operating conditions used in trial 11 are ideal to obtain better dipped rayon cords. However as trial 11 uses lower speeds that will result in a delay in C-ITA dipped rayon cord production leading to a significant increase in the production cost. However trial 12 shows that using Resin B dip with the current C-ITA operating parameters for rayon (higher speeds, lower temperatures) also provides a satisfying adhesion since both coverage and peel force values are superior to the required standards (coverage: 3,5; peel force: 120 N). Therefore this resin B dip recipe can be effectively applied in rayon cord dipping having similar cost production as the current RFL dip solution used but offering more environmental friendly conditions. Besides recipe optimization can be performed, leading to the reduction of resin B, making it even more profitable for the company.

4.2. Chemical and structural analysis

As previously mentioned one of this master thesis main goal is to better understand the chemical mechanisms behind the cord-dip-rubber complex. In order to fulfil this goal three different characterization chemical techniques were used namely NMR spectroscopy, IR spectroscopy and MS spectrometry.

In this subchapter the results obtained through the application of the techniques above mentioned will be revealed and discussed.

4.2.1. ^{1}H NMR spectroscopy

Proton NMR spectroscopy was used in this master thesis with the purpose of identify the chemical structures that are present in the reagents and solutions that are used in C-ITA. As mentioned before the chemical structure of some compounds is already known, nevertheless C-ITA does not receive these compounds in their pure state; some of them contain stabilizers and other additives that are necessary for product commercialization, storage and processing. For that reason all reagents and solutions used in this study were subjected to an extraction procedure (with organic solvents) in order to obtain the target compound. Although it is a fact that this extraction procedure will lead to the loss of some information regarding the sample, it is a necessary process thus it allows having knowledge of at least the most important chemicals present.

Furthermore, as mentioned in the Methods chapter, four extractions were performed for each reagent/solution giving a total of fifty-two NMR spectrums obtained. However in this master thesis it will only be presented for each sample the NMR spectrum that most accurately represents the chemical structure of the compound. It is important to add that in most NMR spectrums an intense signal appears at a chemical shift of 7,270 ppm, which corresponds to deuterated chloroform ($CDCl_3$), solvent used in all NMR analysis. It is also important to point out that signal attribution was performed according to the tables compiled in Silverstein *et al* [43].

<u>VP-Latex:</u>

The first reagent to be analysed by NMR was VP-Latex. This compound is a mixture of styrene, butadiene and vinyl pyridine with a ratio of 15%, 70% and 15%, respectively. In Figure 55 it is represented the NMR spectrum obtained as well as the signal attribution for the different chemical structures.

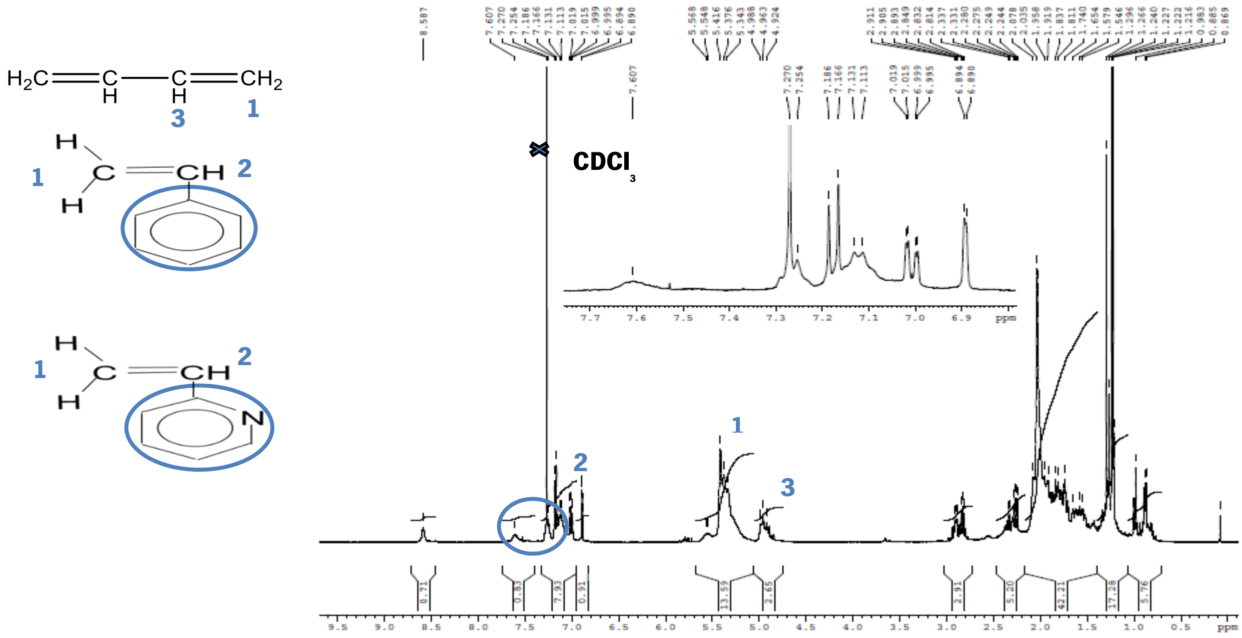


Figure 55- VP-Latex chemical structure and corresponding NMR spectrum.

In Figure 55 is possible to see the different signals generated by the VP-Latex extraction sample. Some of the signals can be easily attributed to the components as they appear at characteristic chemical shifts, considering the structure. For example, at a chemical shift (δ) between 7.50-7.10 ppm it is visible a group of signals that correspond to the aromatic protons present in styrene and vinyl pyridine. At δ 6.90 ppm signal 2 can be ascribed to the vinylic protons in vinyl pyridine and styrene. This large chemical shift is due to the nearby benzene ring, whereas the vinylic protons in butadiene (signal 3) appear at lower chemical shift since there is no electron withdrawing effect. Finally, the CH_2 protons in butadiene (signal 1) are visible at δ 4.23 ppm which is characteristic of this type of protons.

It is also possible to detect a considerable high intensity signal between 3.0-1.5 ppm, which usually indicates the presence of aliphatic groups. However by studying VP-Latex chemical composition it is clear that no aliphatic groups should be detected. These signals cannot be attributed to any of the extraction solvents, therefore this result indicates that some stabilizer or additive may be present in VP-Latex composition.

Overall NMR analysis of VP-Latex confirmed the chemical structure of this reagent thus signals of all three compounds (styrene, butadiene and vinyl pyridine) were detected. Still the presence of aliphatic groups was also noticed, suggesting that VP-Latex reagent might contain other chemicals in its formulation.

BR-Latex:

BR-Latex was the following reagent to be studied by NMR spectroscopy and the main difference between this compound and VP-Latex is the fact that BR-Latex does not contain vinyl pyridine in its composition. NMR spectrum and signal attribution of BR-Latex extraction sample is exposed in Figure 56.

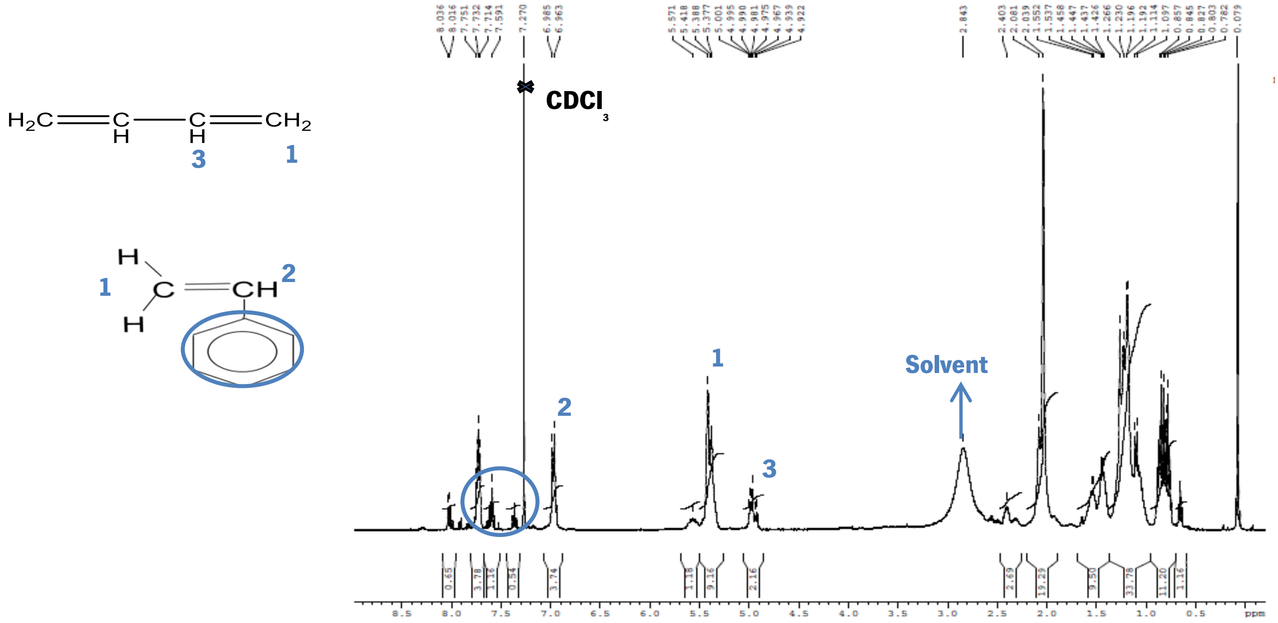


Figure 56- BR-Latex chemical structure (left) and corresponding NMR spectrum.

From Figure 56 is clear that BR-Latex NMR spectrum is very similar to VP-Latex NMR spectrum (Figure 55), in fact the only difference between them is the presence of a solvent signal and the slight increase of the chemical shift of the aromatic groups that in BR-Latex are only present in styrene. Furthermore signals 1, 2 and 3 appear at the exact chemical shift as signals 1,2 and 3 of VP-Latex NMR spectrum, thus confirming the chemical similarity between this two reagents. Another important similarity is the presence of aliphatic groups (3.00 ppm-1.50 ppm), which was not expected and suggests that both BR-Latex and VP-Latex have the same additives on their composition. Therefore this aliphatic group presence might be more related with stabilizer presence than with any contamination problem.

ENR-50:

ENR-50 was the following compound to be analysed by NMR spectroscopy and Figure 57 shows the NMR spectrum obtained for the extraction sample of this compound as well as the most probable signal distribution.

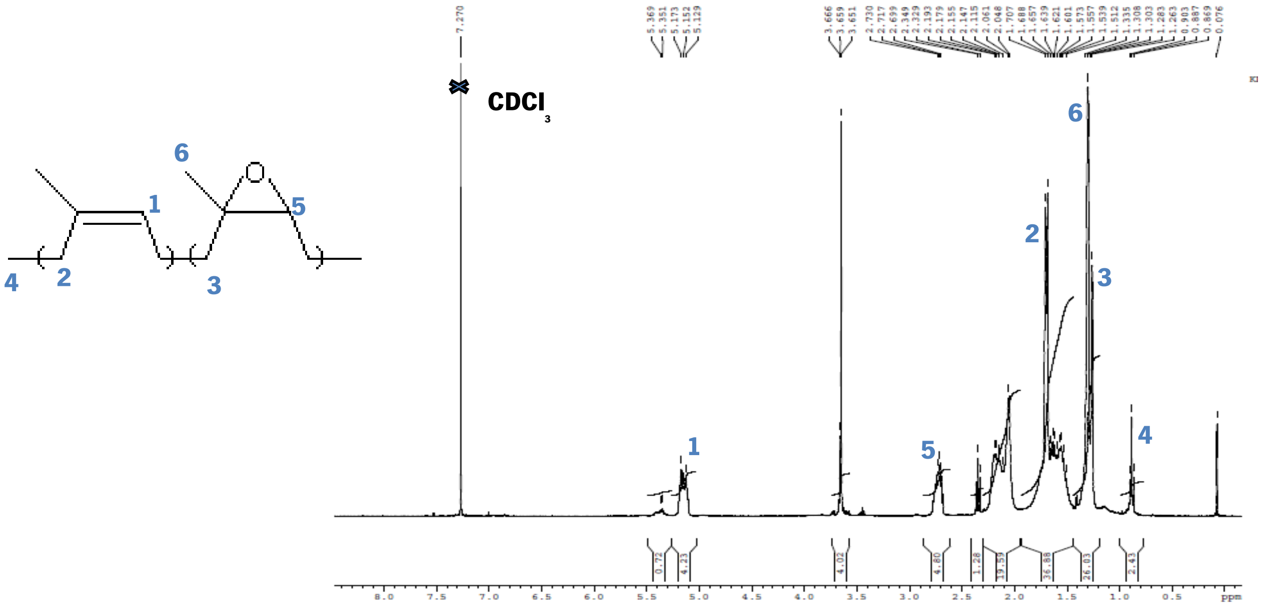


Figure 57- ENR-50 chemical structure (left) and corresponding NMR spectrum.

Through the analysis of ENR-50 NMR spectrum (Figure 57) is possible to detect all the compound's proton signal that are mostly located between 0.80 ppm and 3.00 ppm chemical shifts, confirming the aliphatic structure presented by ENR-50. Additionaly at a higher δ (around 5.25 ppm) signal 1 corresponds to the CH$_2$ protons of the double covalent bond. Although this NMR spectrum confirmed ENR-50 chemical structure, some signals could not be identified (between 2.00 ppm and 2,50 ppm and at 3.65 ppm), indicating that other chemicals might be extracted and are present in ENR-50 composition.

Isocyanate A:

Isocyanate A was the first isocyanate to be studied by NMR spectroscopy. The resulting NMR spectrum of isocyanate A extraction sample is represented in Figure 58. Since isocyanate A is a geometric molecule only half of its chemical structure is presented in Figure 58.

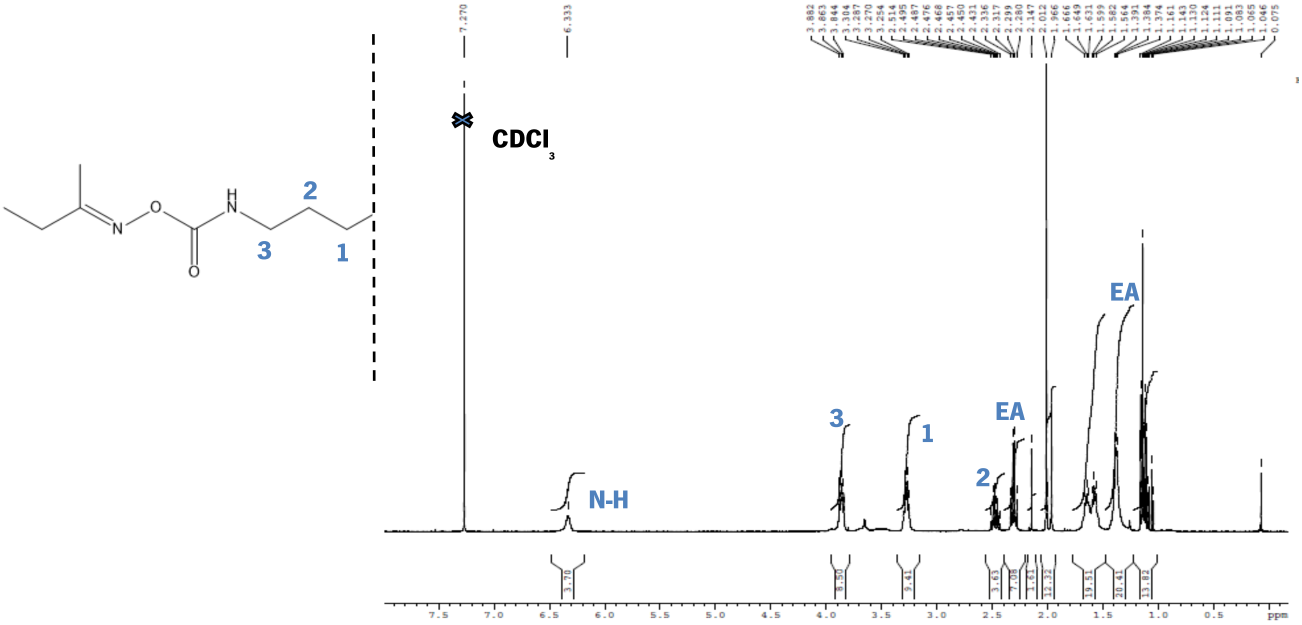


Figure 58- Isocyanate A chemical structure (left) and corresponding NMR spectrum. EA- diethyl acetate (solvent used in the extraction procedure).

Isocyanate A NMR spectrum presented in Figure 58 reveals all the characteristic signals for this compound, thus confirming its chemical structure. Moreover this NMR spectrum also presents diethyl acetate (EA) characteristic signals, which was one of the solvents used in isocyanate A chemical extraction. In this spectrum some signals could not be assigned, suggesting that other components might be extracted, confirming the complexity of isocyanate A reagent.

Isocyanate B:

Isocyanate B was the final isocyanate studied by NMR spectroscopy and the corresponding NMR spectrum obtained from its extraction sample is exhibited in Figure 59.

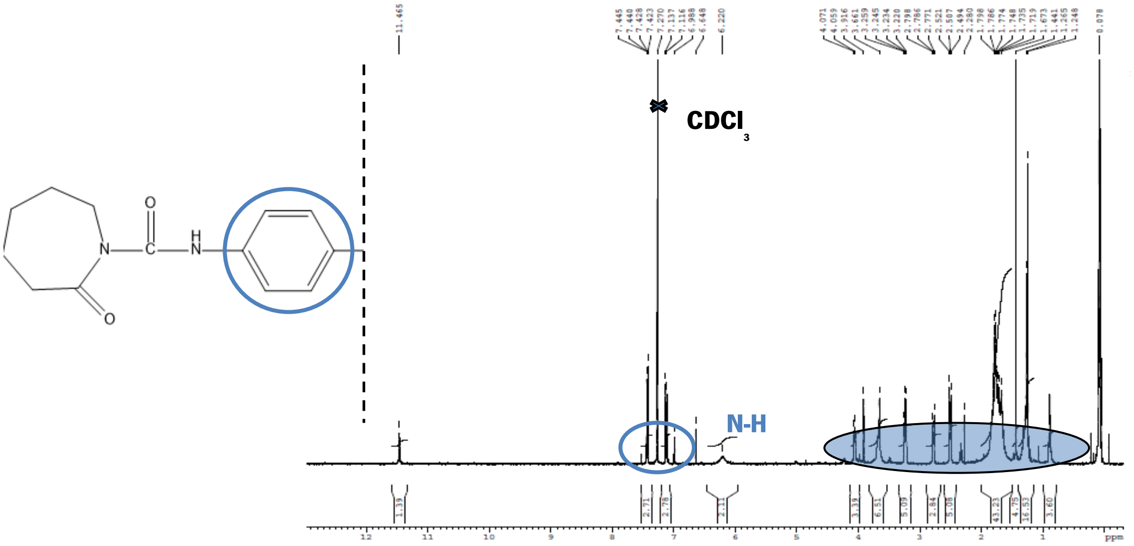


Figure 59- Isocyanate B chemical structure (left) and corresponding NMR spectrum.

In Figure 59 is possible to see the typical NMR signals that characterize isocyanate B chemical structure, namely an N-H signal located at δ 11.465 ppm and a signal for aromatic protons located between 7.45-7.16 ppm. Moreover between 4.00-1.00 ppm NMR signals regarding the caprolactam (blocking agent of isocyanate B) are detected. However more signals in this same interval were not identified, suggesting that other components are present in this reagent.

Epoxy resin:

The NMR spectrum and the signal attribution for the epoxy resin extraction sample are exposed in Figure 60.

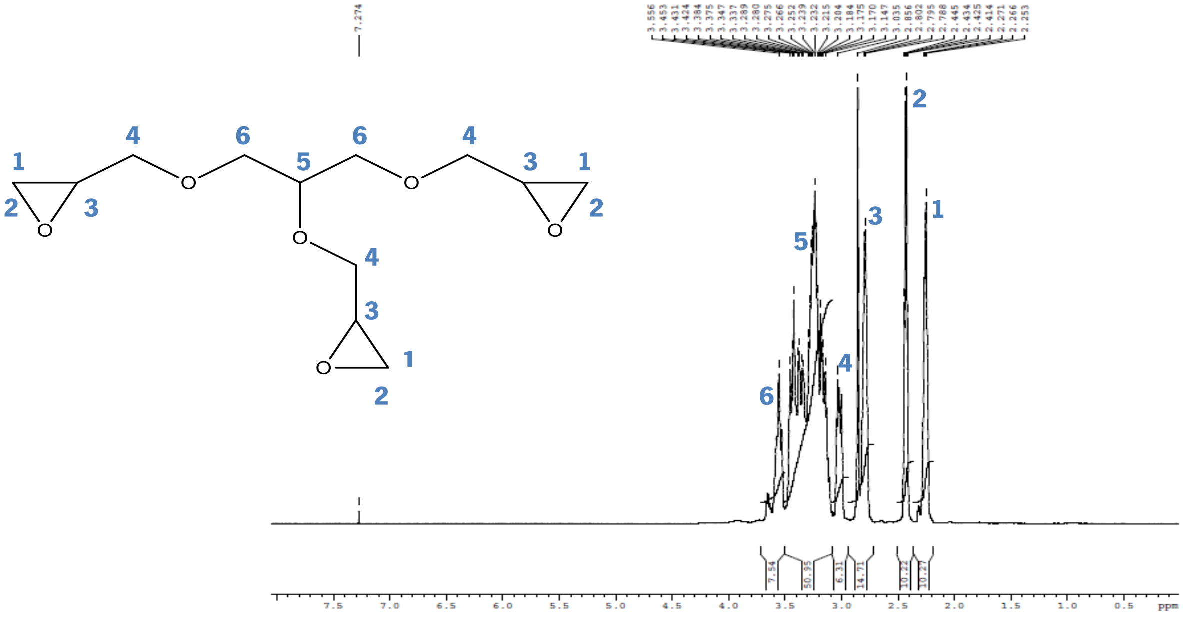


Figure 60- Epoxy resin chemical structure (left) and corresponding NMR spectrum.

In Figure 60 is possible to see that all the characteristic NMR signals ascribed for epoxy resin are present, thus confirming this compound chemical structure. In addition, the presence of other components in this extraction sample is not suggested by this spectrum since no strange signals were obtained. In fact the deshielding effect of oxygen in this compound chemical structure is the cause for signal width between δ 3.50-3.00 ppm.

RF-Resin:

RF-Resin, important constitute of RFL dip, was the following reagent studied by NMR spectroscopy. The resulting NMR spectrum as well as the corresponding signal attribution is exposed in Figure 61.

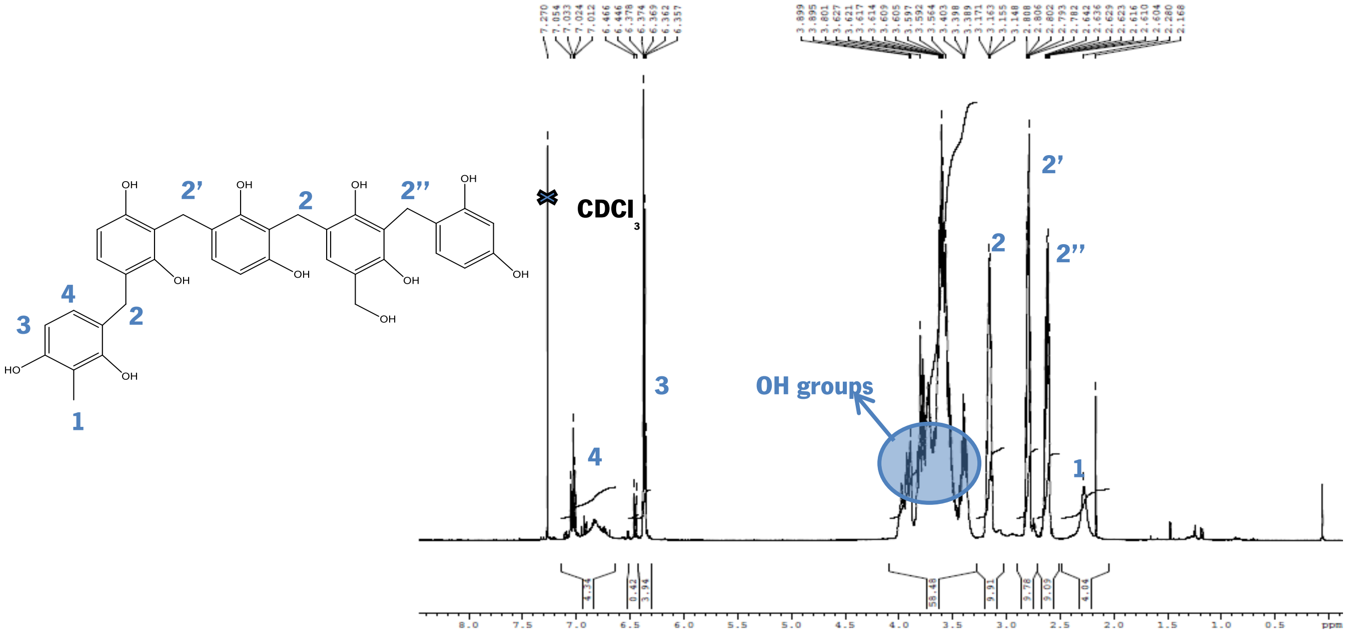


Figure 61- RF-Resin chemical structure (left) and corresponding NMR spectrum.

In the NMR spectrum exposed in Figure 61 is possible to recognize the typical signals ascribed for RF-resin chemical structure, thus the extraction performed for this sample provided successful results. From this spectrum is also important to point out the signal between δ 3.89-3.38 ppm, which is related to the hydroxyl (OH) protons, the reactive groups of RF-Resin reagent. In addition, three different 2 signals were detected (2, 2' and 2''), where the different chemical shift obtained presented arises from the different vicinity in which they are inserted.

Resin A:

As previously stated resin A is one of the most important components in Resin A dip, being the main responsible for cord-rubber adhesion. The extraction sample of this resin was analysed by NMR spectroscopy, being the corresponding spectrum exposed in Figure 62.

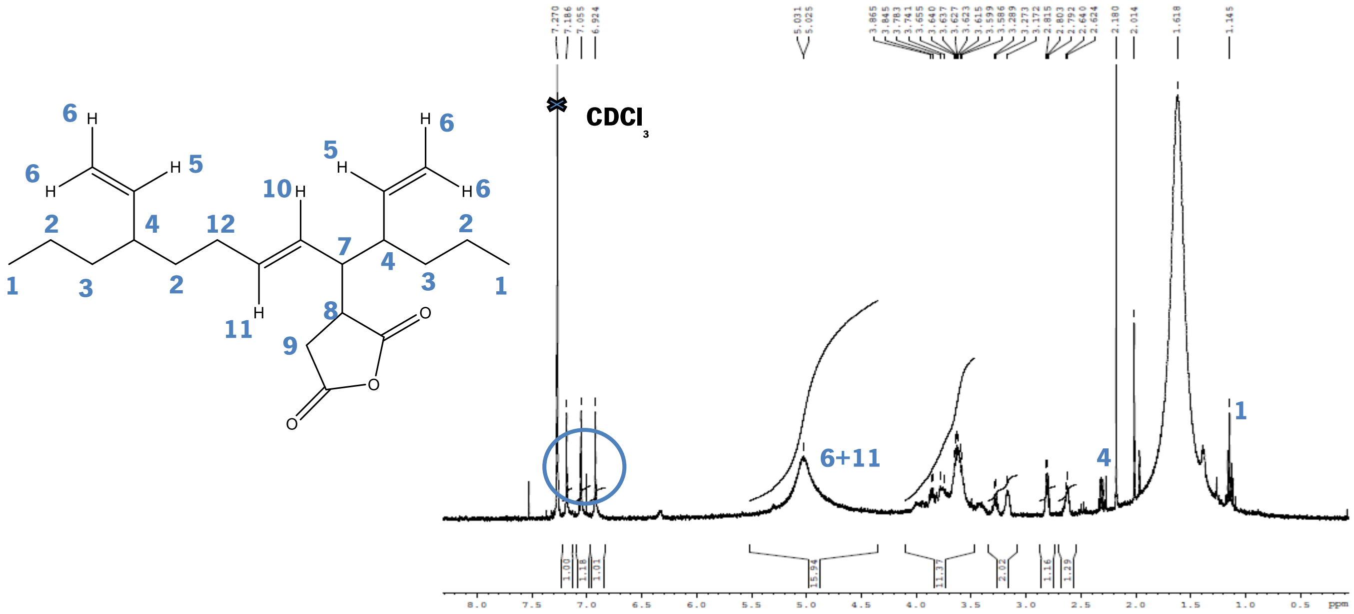


Figure 62- Resin A chemical structure (left) and corresponding NMR spectrum.

Through the NMR spectrum revealed in Figure 62 is possible to see that most of resin A characteristic signals are absent, so it was not possible to confirm this reagent chemical structure. Moreover, the presence of aromatic protons signal (around 7.10 ppm) and other unidentified signals suggests that the extraction procedure used was not effective, leading to the extraction of other undesired resin A matrix compounds.

Resin A pre-dip:

Resin A pre-dip is a mixture of isocyanate A and epoxy resin reagents and its main function is to pre-activate the cords in order to facilitate resin A dip impregnation. For this reason resin A pre-dip analysis is extremely important to better understand cord-dip chemical interaction. In Figure 63 the NMR spectrum of resin A pre-dip extraction sample as well as signal attribution are revealed.

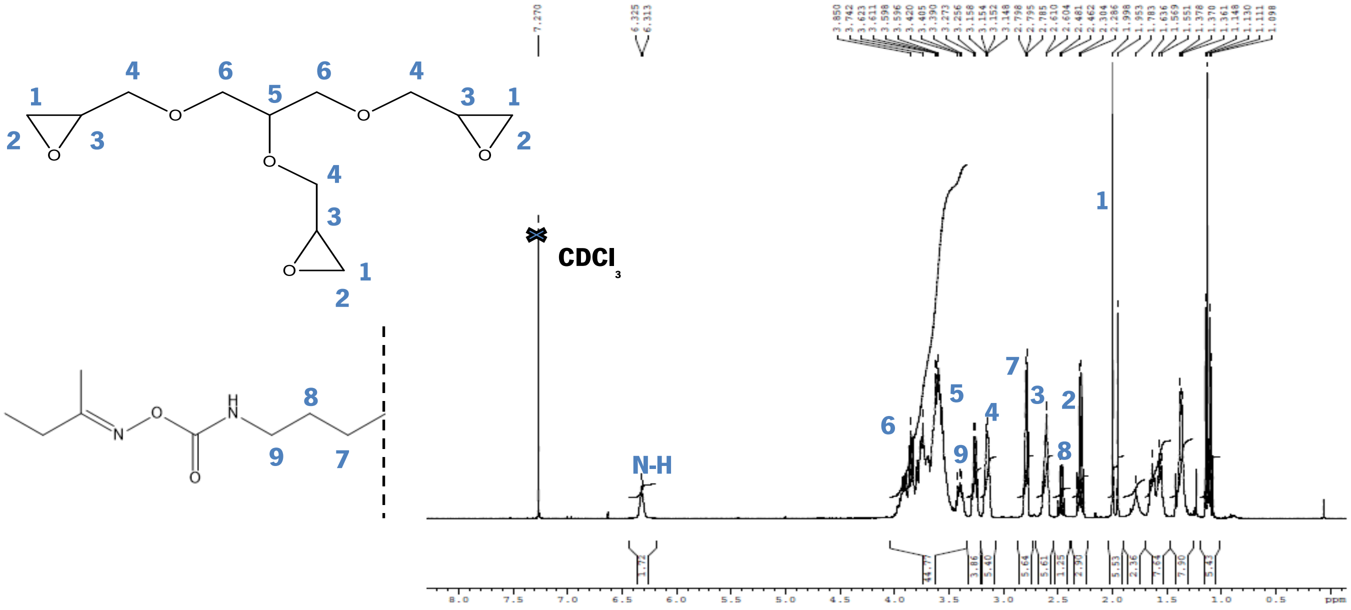


Figure 63- Resin A pre-dip components (left) and corresponding NMR spectrum.

Through Figure 63 is clear that all the characteristic signals for isocyanate A and epoxy resin were detected, thus confirming the chemical composition of resin A pre-dip. Additionally, the signals that were not ascribed had already appeared in isocyanate A NMR spectra (Figure 58), confirming the presence of additives in this compound. To conclude, this NMR analysis validates pre-dip composition, revealing a very effective extraction procedure.

RFL pre-dip:

RFL pre-dip is essentially constituted by isocyanate B and epoxy resin and similar to resin A pre-dip its main function is to pre-activate cords in order to facilitate, in this case, RFL dip cord interaction. RFL pre-dip extraction sample was so analysed by NMR spectroscopy and the results are exposed in Figure 64.

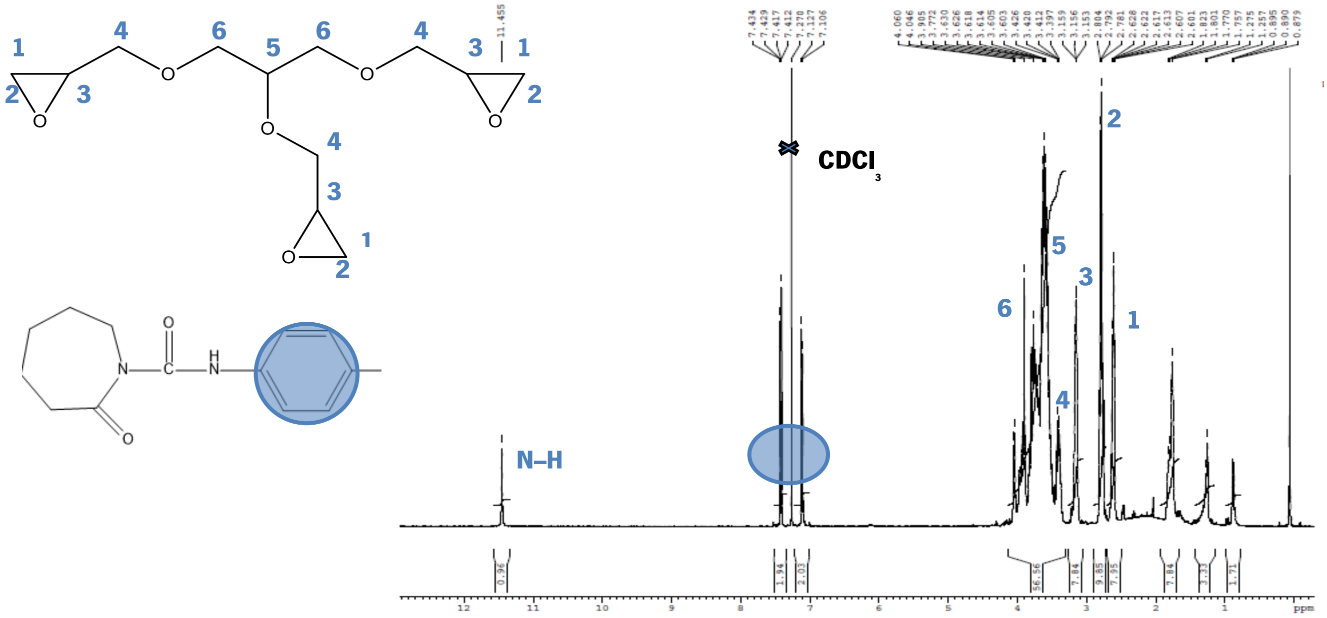


Figure 64- RFL pre-dip components (left) and corresponding NMR spectrum.

The NMR spectrum presented in Figure 64 exhibits the characteristic signals for both isocyanate B and epoxy resin, supporting the chemical composition of RFL pre-dip and confirming the success of the extraction procedure. In addition, is important to point out that the NMR signals not ascribed were already present in isocyanate B spectrum, supporting the presence of other additives in this reagent.

Resin A dip:

Resin A dip solution (mixture of resin A and VP-Latex) is one of the main targets of this NMR analysis since it is the most promising alternative for RFL dip being capable of providing good adhesive properties to cords. The better knowledge of this dip constitution is a very important step to better understand cord-resin A dip chemical interactions. Therefore the resulting NMR spectrum for resin A dip extraction sample is presented in Figure 65.

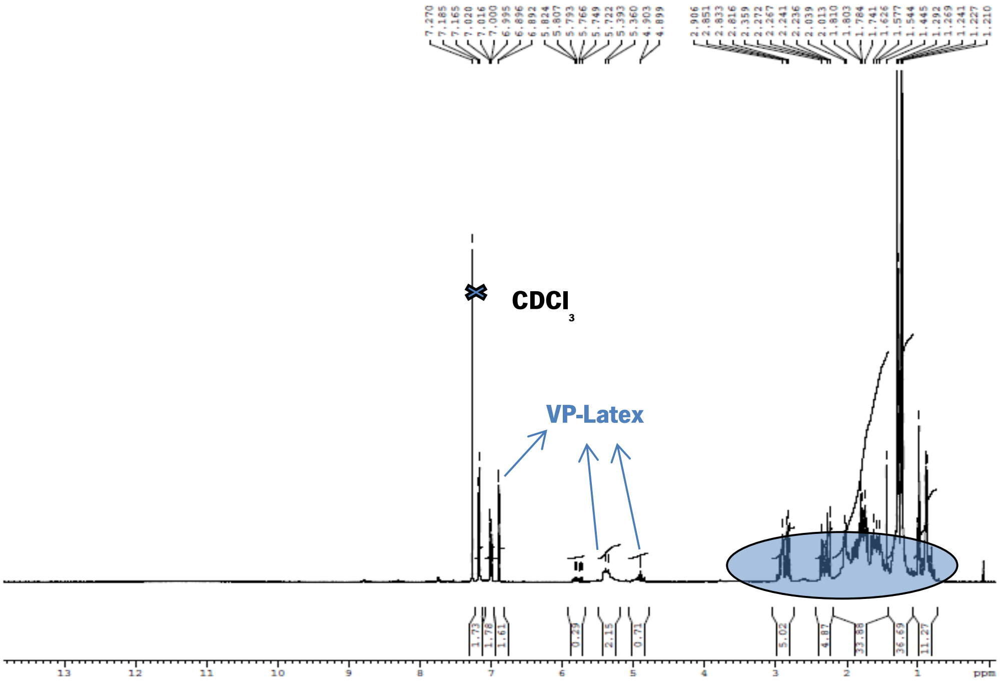


Figure 65- NMR spectrum of resin A dip.

In Figure 65 the NMR spectrum presented only revealed signals corresponding to VP-Latex reagent, not detecting any resin A characteristic signals. In fact even the presence of strange aliphatic groups is detected in this spectrum, supporting the presence of stabilizers in VP-Latex reagents. Regarding resin A signal absence, this result may arise from the fact that resin A NMR spectrum (Figure 62) also failed to identify this resin, leading to the conclusion that in both samples extraction resin A could not be effectively extracted from its matrix. Another possible reason behind resin A signals absence is the low concentration of this compound within resin A dip solution. To conclude, this resin A dip NMR spectrum was unable to confirm resin A dip constitution, revealing only VP-Latex presence.

RFL dip:

RFL dip was the last solution to be studied by NMR spectroscopy. As previously mentioned this solution is very complex, containing different chemicals such as RF-Resin, VP-Latex, ammonia and formaldehyde. For this reason RFL dip was subjected to an extraction procedure and then analysed by NMR, being the results exposed in Figure 66.

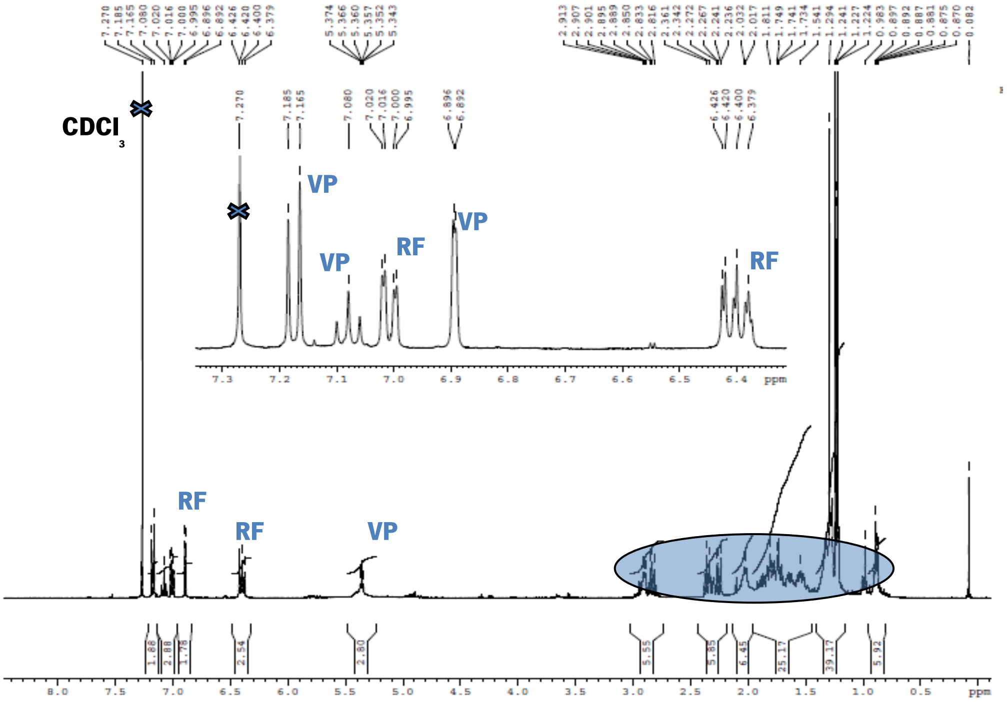


Figure 66- NMR spectrum of RFL dip. VP: VP-Latex; RF: RF-Resin.

The NMR spectrum exposed in Figure 66 represents the characteristic signals ascribed for both RF-Resin and VP-Latex, thus confirming the chemical composition of this solution. Moreover, the detection of both formaldehyde and ammonia was not expected in this analysis since they are highly reactive molecules that certainly reacted within the solution. Taking into account VP-Latex reagent is once again possible to detected aliphatic group presence, confirming once more additives presence in this reagent.

NMR spectroscopy overview:

Overall NMR analysis provided very good results in the way that, with the exception of resin A, all the chemical structures of the reagents used in this master thesis were confirmed. Furthermore NMR analysis revealed the chemical composition of both pre-dips and RFL dip solutions, being only unable of detecting resin A in resin A dip solution. In addition NMR analysis also confirmed the presence of additives in some of the extraction samples analysed, confirming the complex chemical composition of the reagents and solutions used in this master thesis.

4.2.2. IR spectroscopy

As previously mentioned from NMR spectroscopy analysis it was possible to confirm the chemical structure of most reagents and solutions used in this master thesis and due to this fact the next step was to verify which functional groups are present in each sample. This analysis is of most importance since functional groups are usually the main responsible for molecules reactivity, which is related to cord-dip-rubber adhesion. For that reason the technique selected to analyse sample's functional group presence was IR spectroscopy.

It is important to point out that all samples used in this technique are the same used in NMR spectroscopy analysis, since this last technique is a non-destructive analytical method. Therefore like in NMR spectroscopy some information regarding each reagent and solution might be lost. Nevertheless the presence of the targeted reagents (VP-Latex, isocyanate A etc.) within the extraction samples was confirmed by NMR spectroscopy.

Regarding IR analysis, is important to point out that in almost all the IR spectrums that will be presented it was noticed a signal presence around 2750-3250 cm^{-1}. As the reagents and solutions analysed have different chemical structures this signal presence was not expected, however NMR analysis indicated the presence of additives (aliphatic groups) in some one the samples, and this might be the most probable cause for this signal detection. Besides, this strange signal presence cannot be attributed to poor NaCl cell cleaning since from time to time an IR spectrum of only this cell was performed and did not reveal this signal presence. Due to this fact this signal appearance will not be considered in the following IR spectrums analyses. Furthermore, is also important to point out that signal attribution was performed according to the tables compiled in Silverstein *et al* [43].

VP-Latex:

VP-Latex was the first reagent to be analysed by IR spectroscopy and so the obtained IR spectrum is exposed in Figure 67.

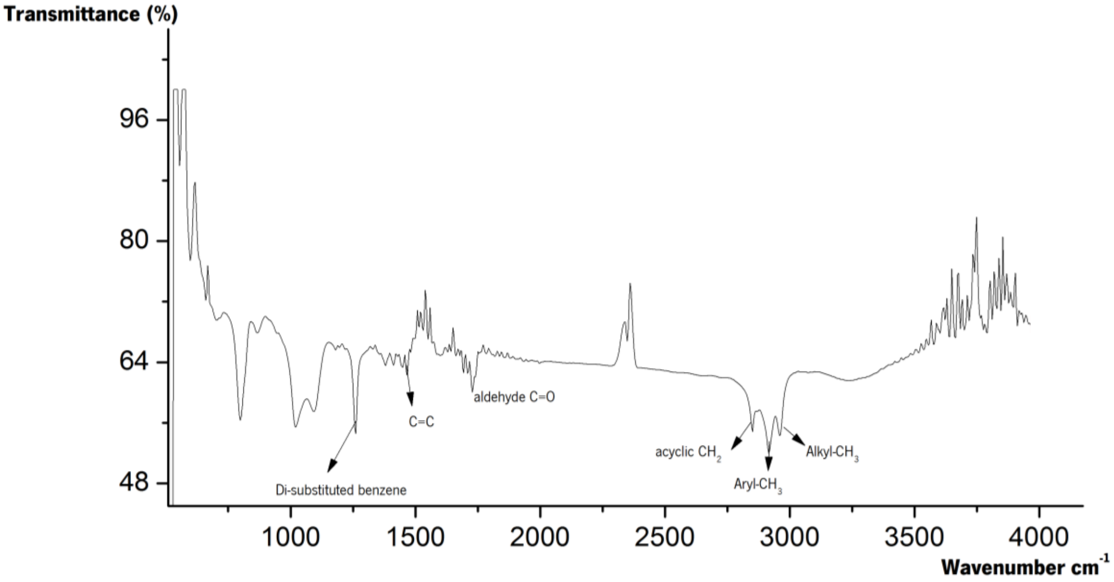


Figure 67- VP-Latex Infrared spectrum.

The IR spectrum represented in Figure 67 shows the presence of some VP-Latex functional groups namely C=C at a wavenumber (υ) of 1500 cm^{-1} and a di-substituted benzene at υ 1260 cm^{-1}. The first functional group is present in butadiene while the second one is present in both vinyl pyridine and styrene, thus this spectrum indicates VP-Latex presence in this extraction sample. Although a signal related to an aldehyde carbonyl group is present and as in VP-Latex chemical structure no carbonyl group is present this signal may arise from the additives that NMR spectroscopy detected in this VP-Latex extraction sample. Besides, this additive presence is corroborated by the signal detection around 2750-3250 cm^{-1}.

BR-Latex

The next reagent submitted to IR spectroscopy analysis was BR-Latex and the corresponding IR spectrum of its extraction sample is presented in Figure 68.

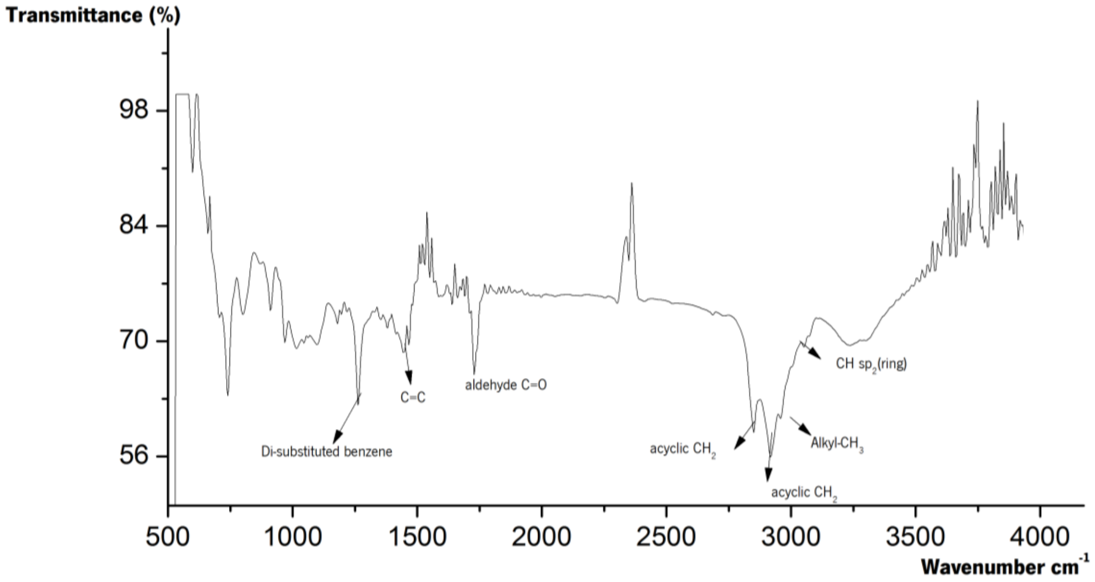


Figure 68- BR-Latex Infrared spectrum.

Through Figure 68 is possible to see the strong similarity between BR-Latex and VP-Latex since in both IR spectrums equivalent functional groups are detected (C=C at υ 1500 cm^{-1} and a di-substituted benzene at υ 1260 cm^{-1}). Besides, it is also seen an aldehyde carbonyl around υ 1700 cm^{-1} that like in VP-Latex it might be related with the additives present in BR-Latex. Therefore, these results (Figure 67 and 68) corroborate the strong chemical similarity between both latex used in this study.

ENR-50

Taking into account ENR-50, the IR spectrum obtained for its extraction sample is exposed in Figure 69.

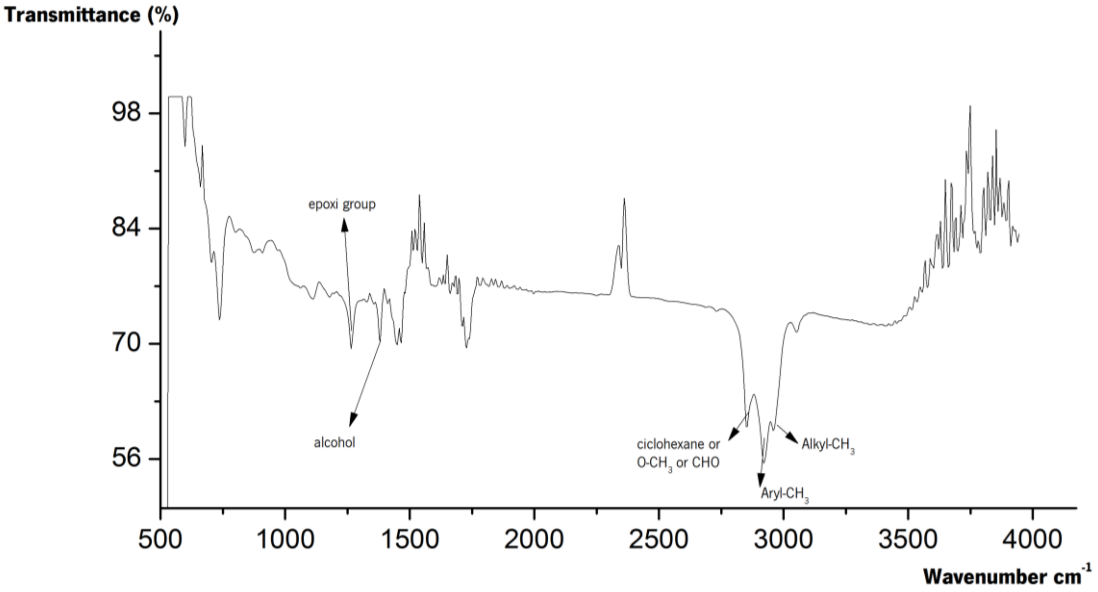


Figure 69 - ENR-50 Infrared spectrum.

The IR spectrum presented in Figure 69 illustrates the main functional group of ENR-50 since around υ 1265 cm^{-1} a signal indicating epoxy group presence is detected. Moreover it is also detected a signal at υ 1380 cm^{-1} that probably corresponds to an alcohol group that may appear through to the interaction of the epoxy group of ENR-50 with the other additives present in the extraction sample. Once again additive presence is confirmed by the signal presence around υ 2750-3250 cm^{-1}.

Isocyanate A

Isocyanate A was also studied by IR spectroscopy and the obtained IR spectrum for the extraction sample of this reagent is presented in Figure 70.

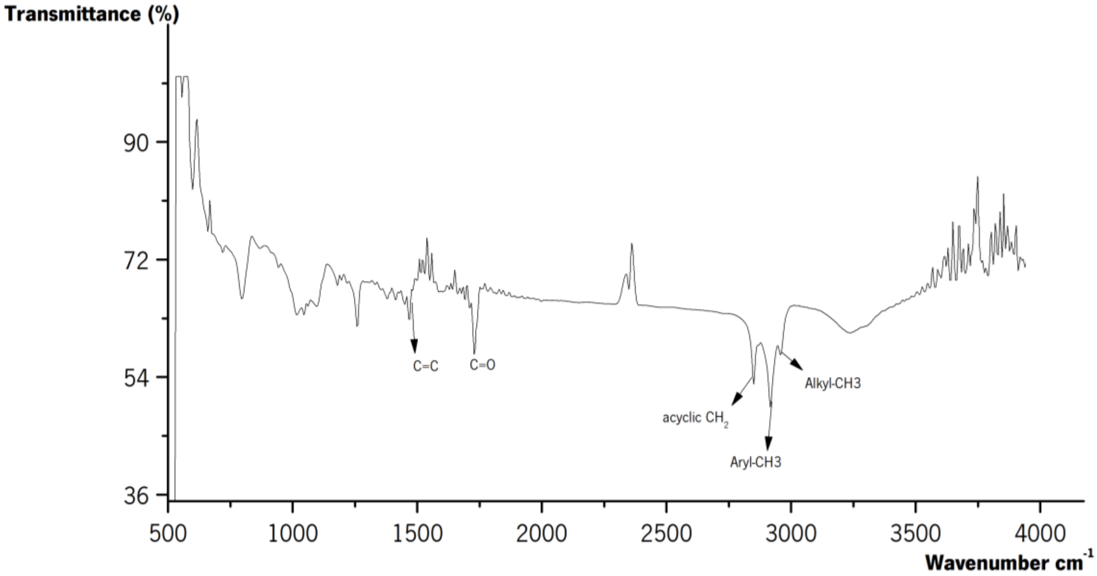


Figure 70- Isocyanate A Infrared spectrum.

Through Figure 70 is clear the presence of a carbonyl group around wavenumber 1780 cm^{-1}, which is one of isocyanate A most important functional groups, allowing its high reactivity. Nevertheless, the presence of abnormal signals is also detected in this IR spectrum, thus indicating that other chemicals were extracted from isocyanate A reagent.

Isocyanate B

The other isocyanate studied by IR spectroscopy was isocyanate B. The corresponding IR spectrum obtained for the extraction sample of this compound is revealed in Figure 71.

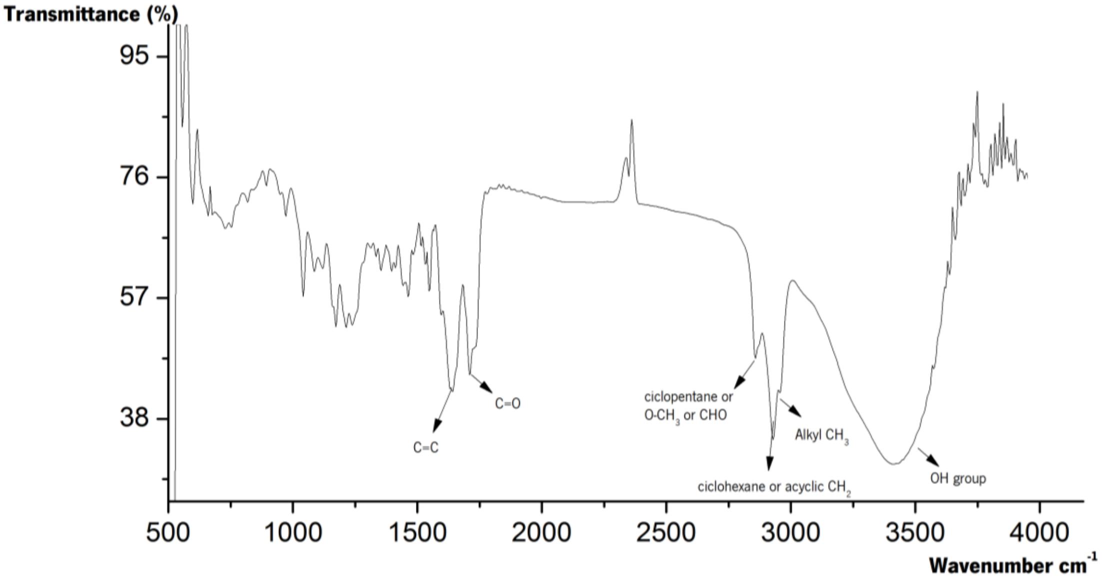


Figure 71- Isocyanate B Infrared spectrum.

In Figure 71 is possible to detect one of isocyanate B main functional group namely the carbonyl group located at υ 1780 cm^{-1}. Besides, the presence of an intense OH signal is detected around υ 325-3500 cm^{-1}, that may be an indicator of isocyanate B reactivity with other additives or it may be also a signal only generated by additives presence. Furthermore, at υ 1630 cm^{-1} a signal is detected and it suggests C=C presence that may arise from the aromatic ring of isocyanate B or it might be also related with additives presence. In summary, carbonyl group detection appears as the most relevant signal here detected due to the fact that it is one of isocyanate B most relevant groups.

Epoxy resin

Concerning epoxy resin the IR spectrum obtained for its extraction sample is presented in Figure 72.

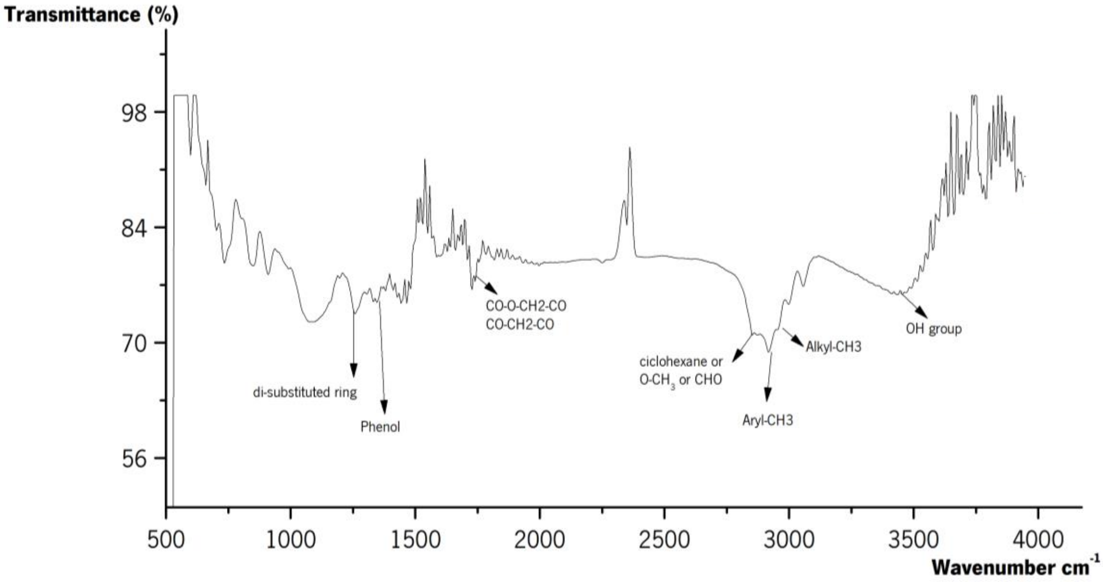


Figure 72- Epoxy resin Infrared spectrum.

From Figure 72 analysis is possible to confirm the presence of some functional groups that are related with epoxy resin chemical structure, more precisely the OH signal detected at wavenumber 3430 cm^{-1} and the CO-CH2-CO signal at υ 1731 cm^{-1}. In addition, a signal related with phenol functional group appears at υ 1350 cm^{-1}, indicating that Epoxy resin might be suffering chemical changes within the extraction samples. Finally, additives presence is once more detected.

RF-Resin

RF-Resin was the second RFL dip component to be analysed by IR spectroscopy (VP-Latex was already analysed) and the corresponding IR spectrum obtained for its extraction sample is exposed in Figure 73.

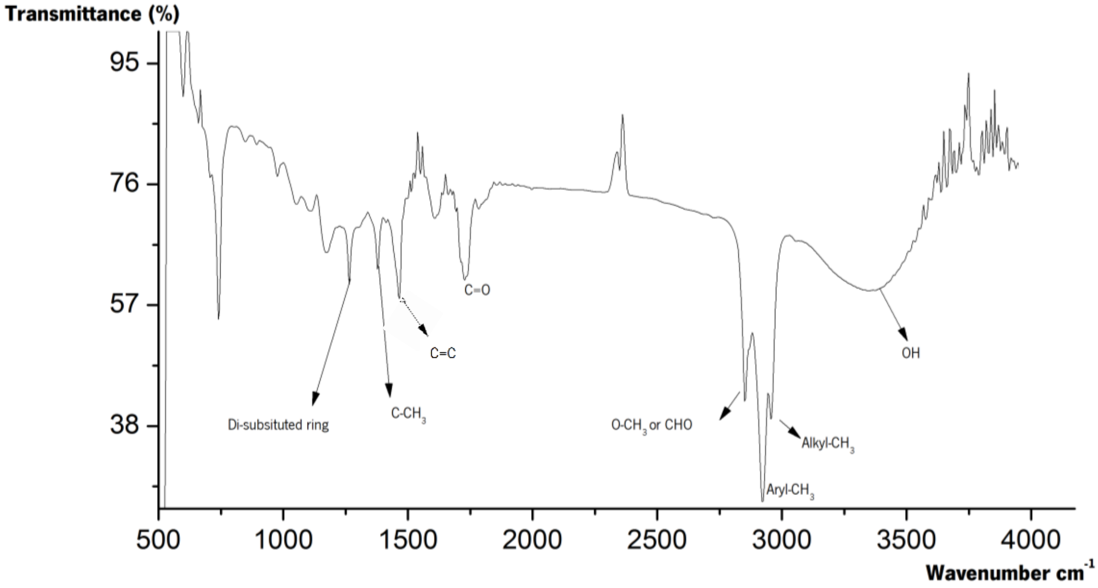


Figure 73- RF-Resin Infrared spectrum.

In the IR spectrum presented by Figure 73 is possible to visualize the presence of some RF-Resin functional groups namely the OH groups at υ 3430 cm^{-1}, the $C\text{-}CH_3$ at υ 1370 cm^{-1} and the C=C group υ 1500 cm^{-1}. These results corroborate the chemical structure of this compound. Similar to the previous analysis, additives presence was noticed by the signal presence previously mentioned (around υ 2750-3250 cm^{-1}).

Resin A

Resin A was the following reagent to be analysed by IR spectroscopy and the IR spectrum of its extraction sample is presented in Figure 74.

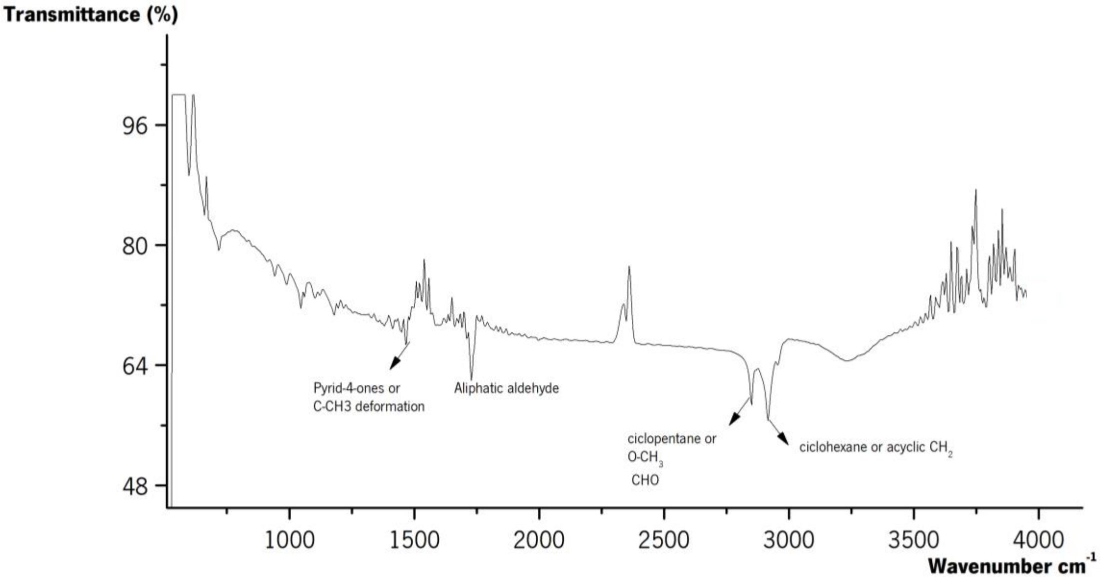


Figure 74- Resin A Infrared spectrum.

Through the IR spectrum exhibited in Figure 74 is clear that no characteristic resin A functional groups were detected, thus supporting the bad extraction that was suggested by the previously mentioned NMR results. Therefore, this IR spectrum is not representative of resin A chemical structure, being more related with the other chemicals that were extracted from resin A reagent. In fact, in this case the IR spectrum obtained is very poor in terms of the functional groups that were detected, suggesting only the presence of an aliphatic aldehyde group (υ 1728 cm^{-1}) and the presence of the signals around υ 2750-3250 cm^{-1}.

Resin A pre-dip

As mentioned before resin A pre-dip is a mixture of isocyanate A and epoxy resin and so IR spectroscopy should detect the functional group of both reagents. Therefore the IR spectrum obtained for resin A pre-dip extraction sample is presented in Figure 75.

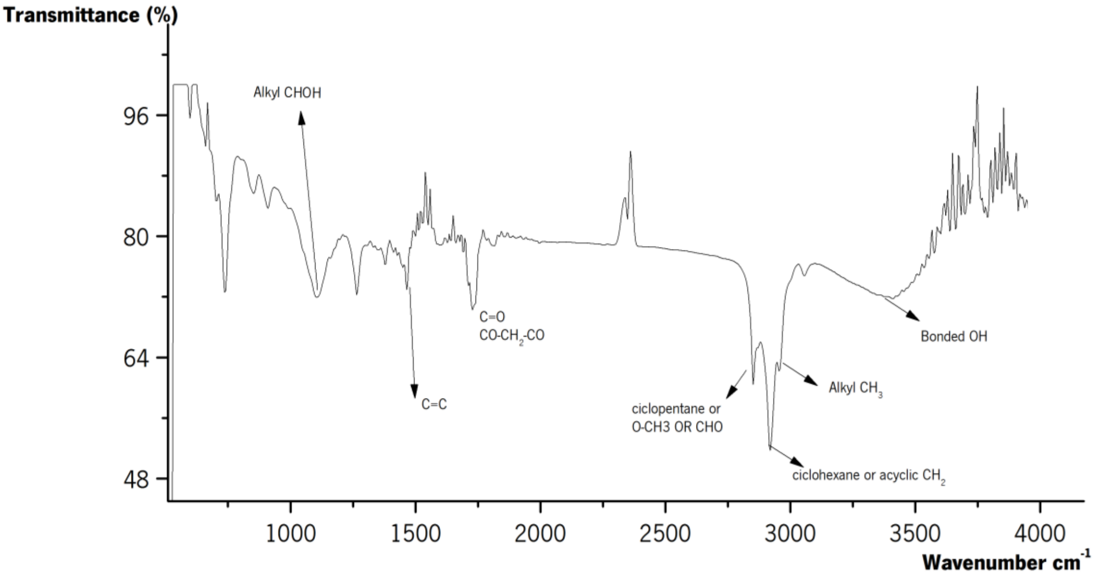


Figure 75- Resin A pre-dip Infrared spectrum.

Figure 75 illustrates all the functional groups that were detected in resin A pre-dip extraction sample, showing some functional groups such as bonded OH (υ 3410 cm^{-1}) and CO-CH$_2$-CO that most probably are related with epoxy resin and isocyanate A chemical structures. Besides, once again it was noticed additives presence in this sample, leading to the resulting IR signals.

RFL pre-dip

The other pre-dip analysed by IR spectroscopy was RFL pre-dip which is a mixture composed by epoxy resin and isocyanate B reagents. The resulting IR spectrum of RFL pre-dip extraction sample is exposed in Figure 76.

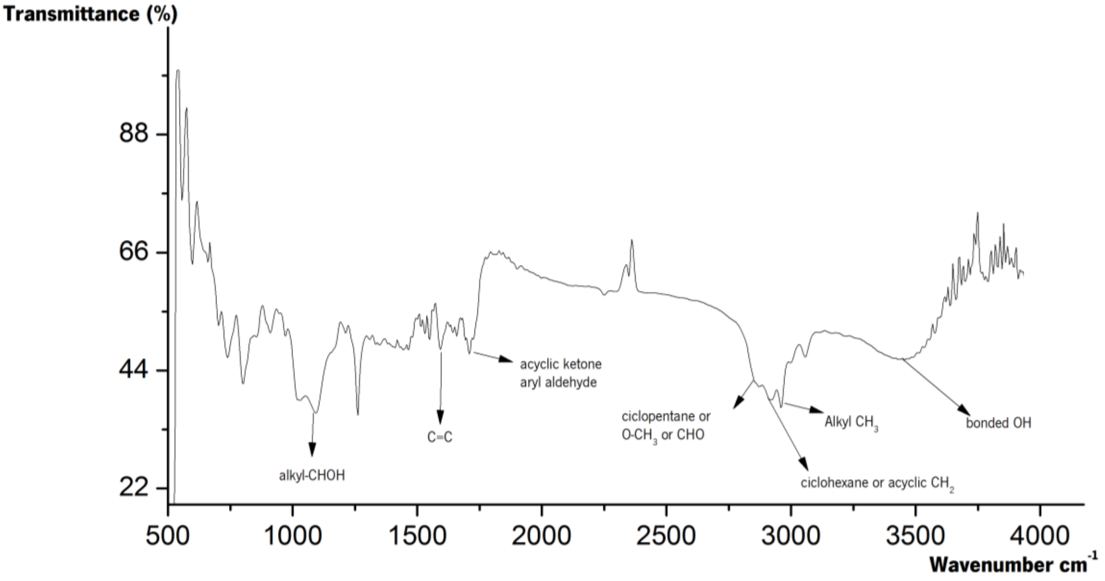


Figure 76- RFL pre-dip Infrared spectrum.

Trough Figure 76 is evident the similarity between RFL and Resin A pre-dips, in the way that similar functional groups were detected within the two spectra. This result is expected since both solutions react in a very similar way given the fact that both contain the epoxy resin and a specific isocyanate (isocyanate A for resin A pre-dip and isocyanate B for RFL pre-dip). However in this spectrum CO-CH$_2$-CO signal (Figure 76) was not detected and instead at a wavenumber of 1700 cm^{-1} a signal was noticed, suggesting the presence of or an acyclic ketone or a aryl aldehyde functional group. Therefore this signal may indicate any chemical interaction between the pre-dips used or it might also be related with the additives present in this extraction sample.

Resin A dip

The following solution to be chemical characterized by IR spectroscopy was Resin A dip, that is the current best alternative for RFL dip substitution. The IR spectrum concerning the extraction sample of this dip solution is presented in Figure 77.

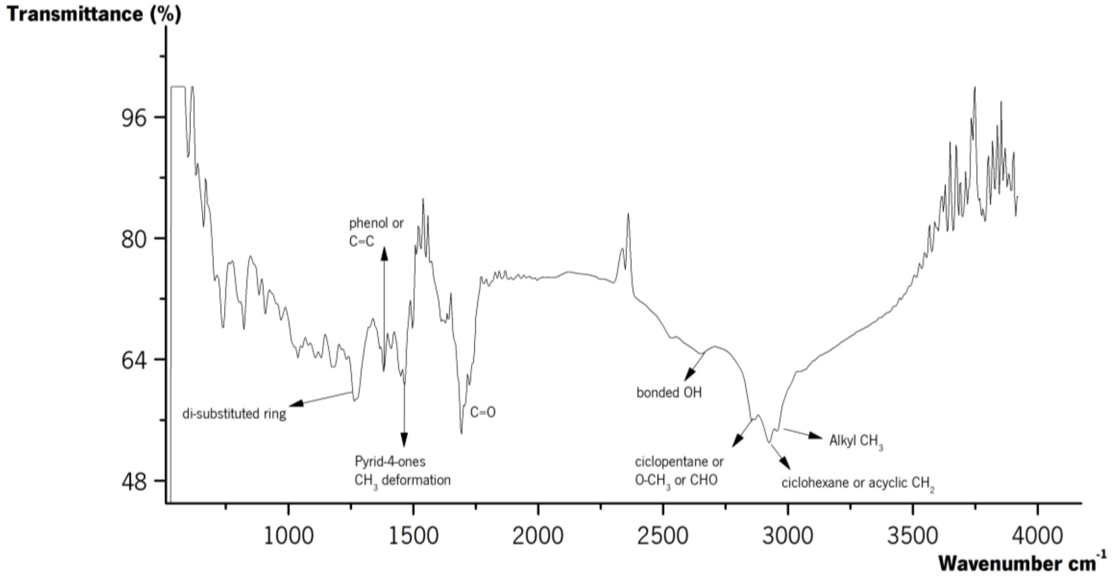


Figure 77- Resin A dip Infrared spectrum.

Through the IR spectrum exposed in Figure 77 is possible to see that a large variety of functional groups was detected. In fact the carbonyl group detected at υ 1680 cm^{-1} could suggest resin A presence within the extraction sample but as NMR analysis did not detect this chemical in the resin A pre-dip extraction sample (Figure 66) it is not possible to be absolutely certain about this signal attribution. Furthermore, in this IR spectrum is also possible to see the presence of some other functional groups such as C=C and di-substituted ring that may be related with VP-Latex presence in the resin A dip extraction sample. Nevertheless the presence of additives was also noticed in this IR spectrum.

RFL dip

As previously stated RFL dip is a solution mainly constituted by RF resin and VP-Latex and it is the currently most used solution for tire cord impregnation. The IR spectrum obtained for its extraction sample is presented in Figure 78.

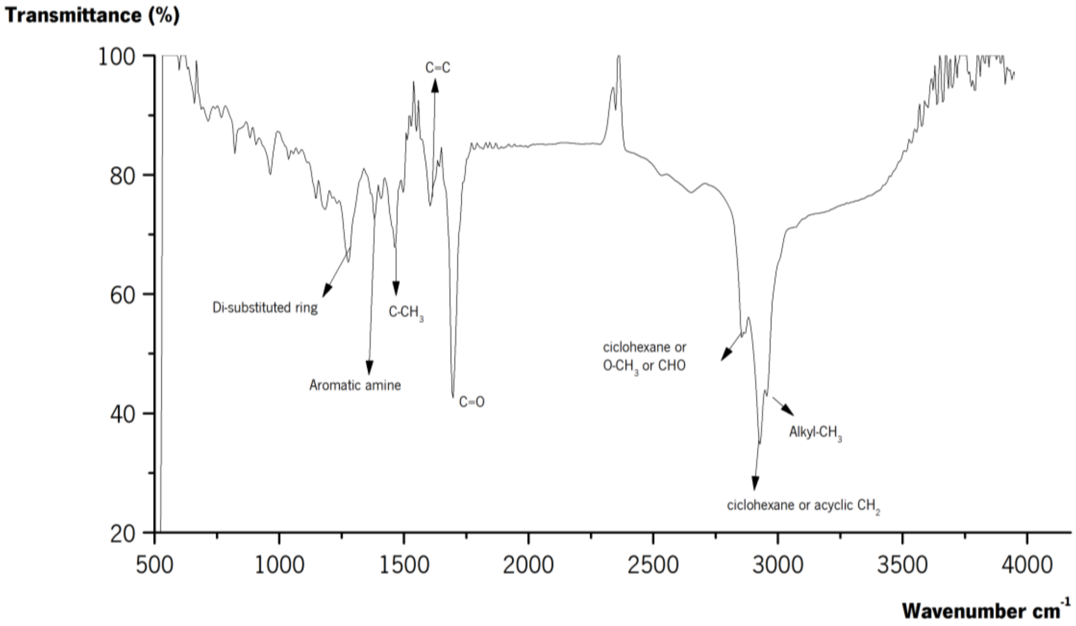


Figure 78- RFL dip Infrared spectrum.

The IR spectrum exhibited in Figure 78 demonstrates the characteristic functional groups of both VP-Latex and RF-Resin (Figure 67 and 73), thus confirming the presence of both compounds within this dip solution. Curiously in this IR spectrum no OH group presence is evident suggesting that some blockage of this group might occurred in the extraction sample. Additionally additives presence is once again detected by this IR spectrum.

IR spectroscopy overview:

In general IR spectroscopy analyses provided very good results in the role of identifying the functional groups present in all samples. Besides the results obtained confirmed the previous NMR results presented, validating the chemical structures of all reagents as well as the chemical composition of all solutions. Similar to NMR spectroscopy results, resin A was the only reagent that was not detected and characterized by both techniques since it seem to be not correctly extracted. Finally additives presence was also confirmed through the use of this characterization technique.

4.2.3. Mass spectrometry

Mass spectrometry (MS) was the final analytical technique used in this master thesis and it was used to study the mass/charge (m/z) ratio of the reagents and solutions used in C-ITA. The aim with this technique was to see if when mixed together the reagents react with each other (for example VP-Latex with Resin A) forming new chemical structures with different m/z ratios. By knowing the m/z ratios of the new compounds formed it might be possible to predict their chemical structure. For that reason the first step was to characterize the reagents alone, using the extractions samples that were obtained for each reagent/solution. But since IR is a destructive technique the extracted samples used in MS analyses were from an extraction with a different solvent (remember that four solvents were used in the extraction) that revealed in NMR spectroscopy equivalent results.

However MS analysis did not occur as expected since only two analysis namely of isocyanate A and resin A were performed. The reason behind this problem is the fact that in general the samples are polymeric and when inserted in the MS spectrometer they contaminated the equipment's column, resulting in long periods of cleaning time with methanol as eluent (more than three days for each sample). Therefore in order to preserve the MS spectrometer no further analyses were performed. For this reason in this subchapter it will be only presented the ion positive MS spectrums obtained for resin A and isocyanate A extraction samples.

Resin A

Resin A is a reagent with a molecular weight of 332 g/mol, however as the MS spectrometry analysis used was ion positive sodium must be added to the molecular weight, therefore resin A signal should be at 356 m/z ratio. The ion positive MS spectrum obtained for the resin A extraction sample is exposed in Figure 79.

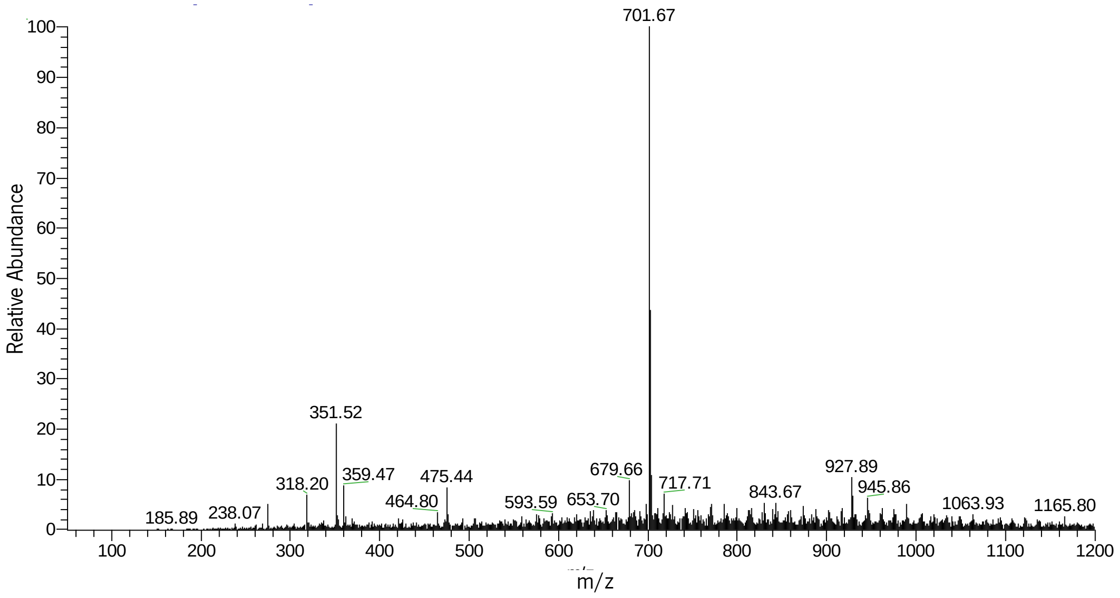


Figure 79- Resin A ion positive MS spectrum.

Through Figure 79 is clear that resin A characteristic signal was not detected, being the most intense signal of this MS spectrum located at 701.67 m/z . Furthermore, from this spectrum no signal can be directly related with resin A, suggesting the absence of this chemical within the extraction sample. This result is corroborated from NMR and IR analyses which also did not detected resin A chemical in the extraction sample. For that reason the MS spectrum that is presented is a representation of the m/z ratio of the additives extracted from resin A reagent.

Isocyanate A

Isocyanate A is an isocyanate with a molecular weight of 339 g/mol, so as it was also subjected to ion positive MS analysis its characteristic signal should appear at 363 m/z. The resulting MS spectrum obtained for isocyanate A extraction sample is presented in Figure 80.

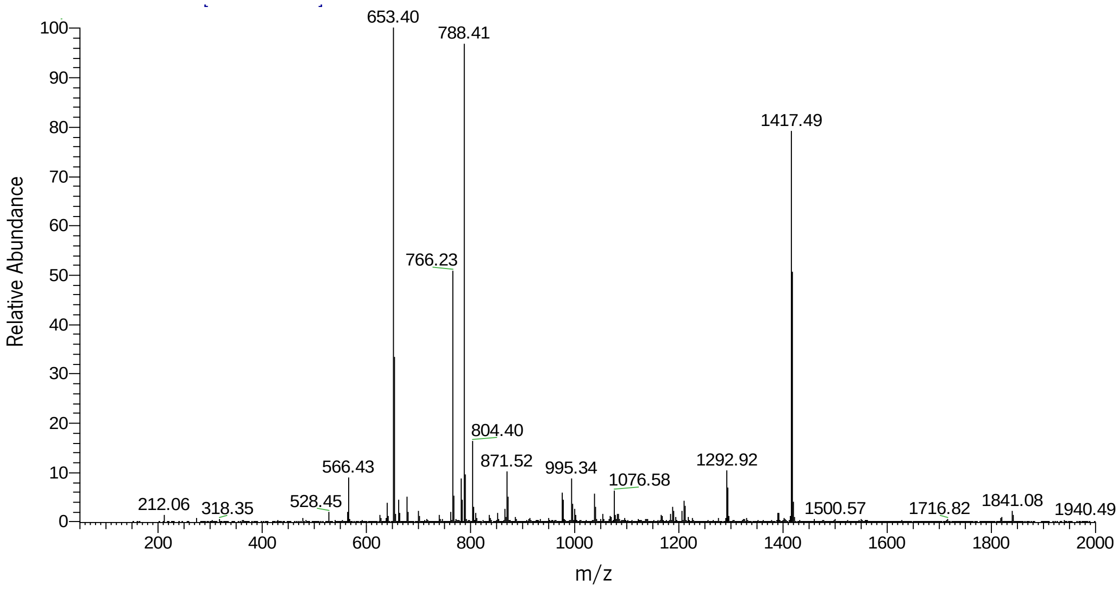


Figure 80- Isocyanate A ion positive MS spectrum.

From the ion positive MS spectrum presented in Figure 80 is possible to verify that isocyanate A typical signal is not detected. In fact the most abundant m/z ratios present are related with considerably higher m/z ratios. This result may arise from isocyanate reactive properties because isocyanates are highly reactive molecules that can easily form dimers and trimers. Thus there is a strong probability of aggregation between the isocyanates present in isocyanate A extraction sample, leading to the abundance of higher m/z ratio compounds.

In summary, both MS analyses were unable to identify the targeted chemical compounds, revealing the presence of high m/z ratio structures that may arise from the additives present in both reagents or from the abnormal aggregation of these same reagents within the extraction sample.

4.3. Chemical mechanisms

As previously mentioned one of this master thesis main goal was to understand the chemical mechanisms that involve the cord-dip-rubber complex and in order to fulfil that goal several characterization techniques (NMR, IR and MS) were used. With these techniques it was possible to confirm both the chemical structure and functional group constitution of C-ITA reagents and solutions. For that reason in this subchapter two chemical mechanisms will be presented focusing on two different issues mentioned in this project, namely the VP-Latex/ENR-50 mixtures coagulation problem and the cord-resin A dip-rubber complex.

4.3.1. VP-Latex/ENR-50 mixtures

Taking into account VP-Latex/ENR-50 mixtures the previous results revealed that when mixture aggregate formation was observed and it was suggested that this aggregate formation might be related with polarity difference among the two reagents or possible chemical interactions between them. Therefore since chemical bonding between ENR-50 and VP-Latex may occur it is proposed a reaction mechanism in Figure 81, which demonstrates how these two reagents may interact resulting in an insoluble chemical structure.

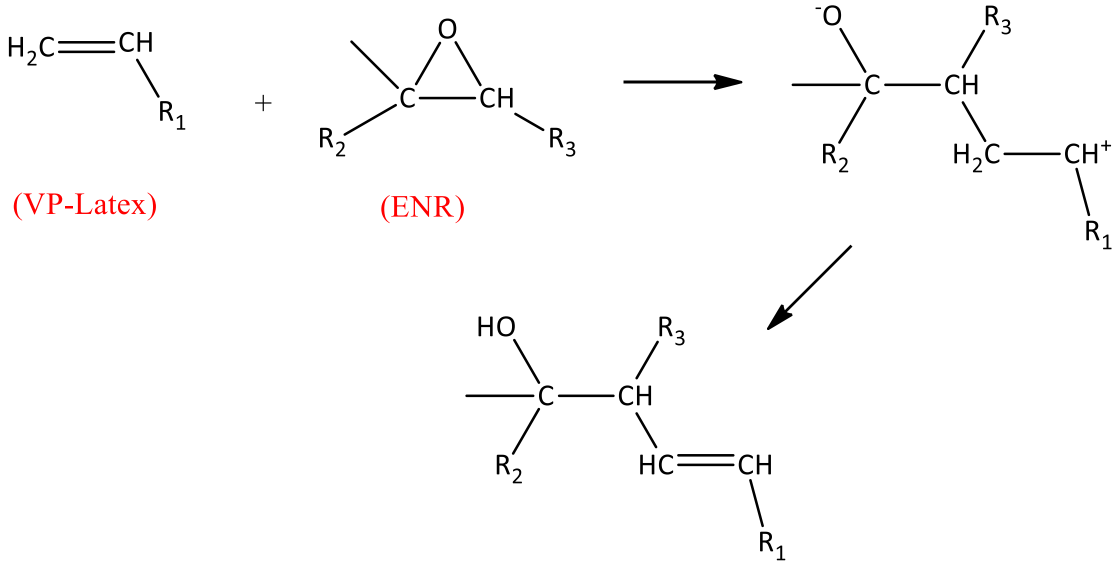


Figure 81- Proposed reaction mechanism between VP-Latex and ENR-50.

Figure 81 shows that the alkene (either the vinyl groups in VP-Latex or the double bonds in the ENR compound) can act as the nucleophile and attack the epoxide which suffers ring opening to yield an alcohol. However it is important to point out that the chemical mechanism above mentioned was not confirmed by any of the analyses performed, it is only a suggestion of what might be occurring within the mixture. Nevertheless it is still a possible hint of what might be occurring in these mixtures.

4.3.2. Cord-Resin A dip-Rubber complex:

The better knowledge about the chemical interactions between cord and resin A dip was one this master thesis main goal, however all the analysis performed did not clearly indicate how the dip interacts with the cord, providing strong chemical bonds that result in the good adhesion results showed. The main reason behind the analyses problem is the fact that resin A was not effectively extracted with the procedure used, resulting in the absence of this chemical in the analyses performed. Moreover since MS analysis was not able to be performed to all the desired samples it was not possible to detect the possible formation of new chemical structures within the resin A dip, resulting in the lack of knowledge about this solution. Nevertheless since it was possible to confirm the chemical properties of some of Resin A dip and pre-dip compounds, a possible reaction mechanism will be exposed. Firstly since all resin A dipped cords required a pre-activation (using an isocyanate A and epoxy resin solution) it will be presented the chemical interactions that might occur between this pre-dip solution and the resin A dip solution (Figure 82).

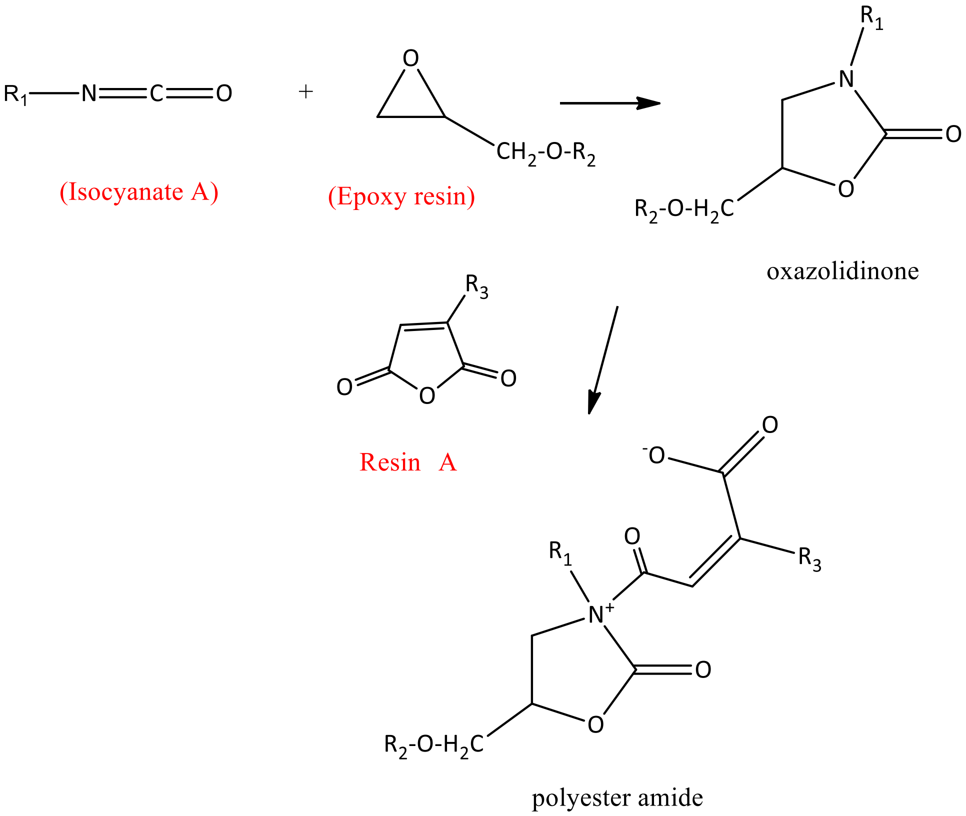


Figure 82- Proposed reaction mechanism for pre-dip (isocyanate B + epoxy resin) and resin A interaction.

From Figure 82 it is proposed that the reaction of the isocyanate with the epoxide by electrophilic attack results in the formation of a cyclic urethane (oxazolidinone) [44]. This species can then undergo attack by the anhydride to yield a charged N- acylated oxazolidinone, a type of polyester amide. Considering the multifunctonality of the isocyanate, epoxide and anhydride (which also possesses reactive double bonds), this ensemble of reagents can result in a highly branched, highly reticulated polymeric material that can result in extensive coverage of the cord surface. Further covalent reaction with the cord cannot be ruled out as multiple reactive sites are available in the polymer (Figure 83).

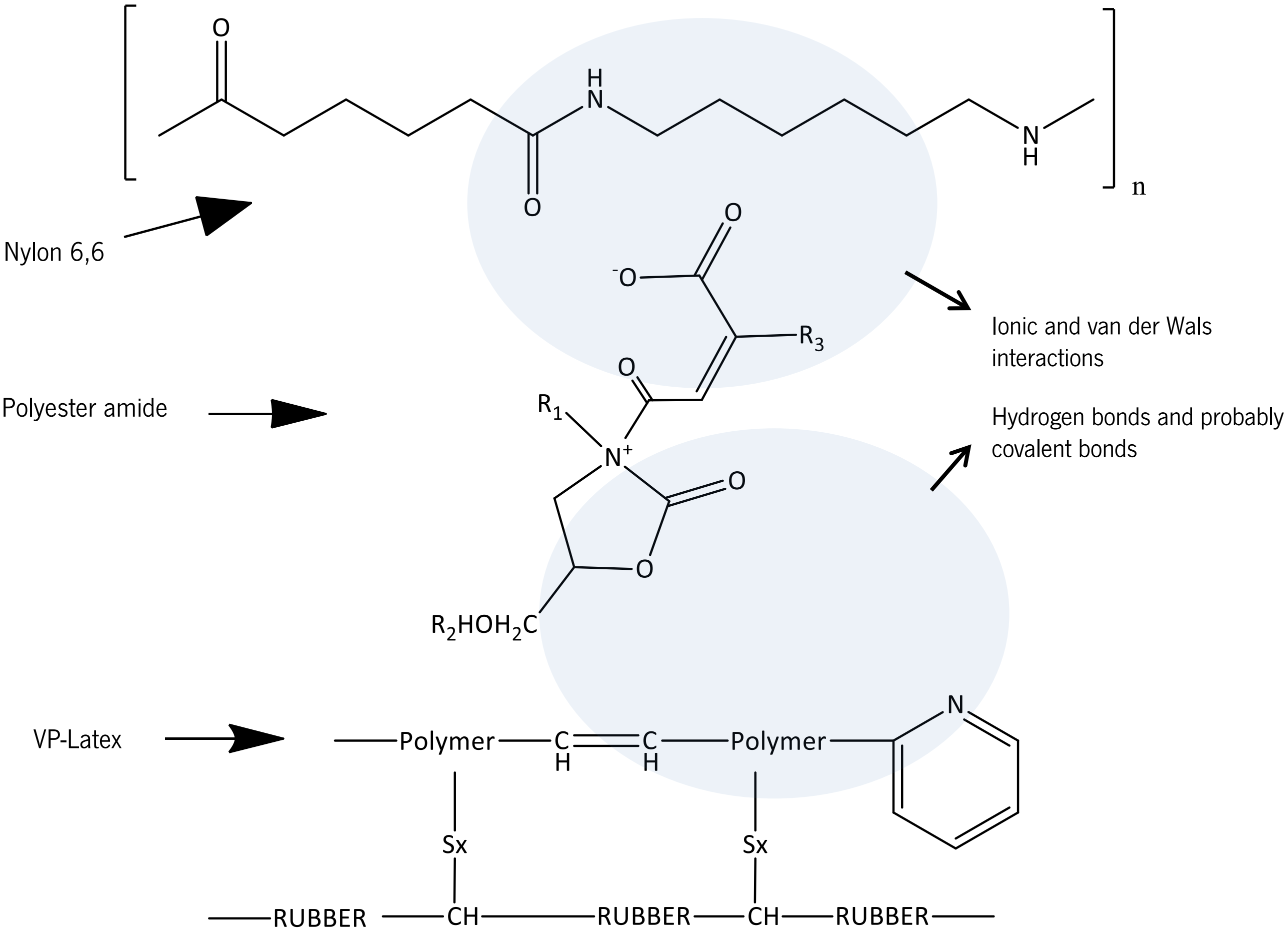


Figure 83- Proposed cord-resin A dip-rubber complex chemical interactions.

From the reaction mechanism proposed in Figure 82 is suggested that the resulting polyester amide can interact with both cord and rubber through both the considerably high number of reactive sites and the high complexity of this molecule. For that reason Figure 83 illustrates how this highly branched molecule may interact both with rubber and cord (nylon 6,6 was used as an example). Similar to RFL dip, VP-Latex main function in resin A dip might be to provide adhesive properties between the dip and the rubber, whereas resin A and pre-dip function (through polyester amide) is mostly related to cord activation and binding through possible ionic and van der walls interactions and also hydrogen and covalent bonds.

In summary it is important to point out that all the chemical mechanisms presented were not confirmed by the analyses performed, being only suggestions of what might be occurring in these solutions. Therefore further studies must be performed in order to confirm the hypothesis mentioned above.

CHAPTER 5. Conclusions

This master thesis project was performed with the aim of studying more environmental friendly alternative dip solutions for RFL dip substitution as well as studying the chemical properties of the reagents/solutions and determine the reaction mechanism surrounding the cord-resin A dip-rubber complex.

The results showed in this project indicated that there are in fact more environmental friendly alternative dip solutions that can replace the current RFL dip solution used in tire textile reinforcements impregnation. Moreover the results showed that both resin A and resin B dips are valid solutions regarding textile reinforcement's impregnation since overall good adhesion results were obtained for both solutions.

Regarding resin A dip the results obtained for its ageing experiment revealed that when impregnating nylon and hybrid cords, more effective storage conditions must be taken into account in other to preserve these cords adhesive properties out of the tire. However regarding resin A dipped PET cords the results obtained revealed no ageing of this cord. In addition the results obtained for coupled atmospheric plasma and resin A dip nylon cord impregnation revealed very poor results, thus future studies are required in order to improve these results.

Concerning resin B dip rayon cord impregnation the results obtained were very successful indicating that this dip solution can effectively replace RFL dip and provide less hazardous effects for both humans and the environment. Nevertheless further studies must be conducted in order to apply this dip in all the remaining fibres impregnation.

Taking into account the second goal of this project is possible to conclude from both NMR and IR analyses that in general the chemical structure of almost all reagents was confirmed and the chemical composition of the pre-dip and dip solutions was clarified. Only resin A and resin A dip revealed inconclusive results suggesting that other approach must be used in order to study these samples chemical properties. Furthermore MS analyses did not reveal significant results due to both sample and equipment limitations.

Finally, from all the chemical analyses performed two reaction mechanisms were suggested, one for VP-Latex/ENR-50 mixtures coagulation problem and other for the cord-resin A dip-rubber complex. However further tests are required to confirm both mechanisms proposed.

CHAPTER 6. Future work

Overall the objectives proposed in this project were successfully achieved; however as in all works performed there is always a space for improvement since some work limitations are always present. The major limitation for this project was time, despite nine months seem a long period all the desired testing and optimization were not possible to be performed since that most of the studies performed, mainly the ageing and the chemical characterization experiments, were very time consuming.

In relation to the resin A dip solution it is required to repeat the ageing experiment for aramid cord thus this cord impregnation was not successful. Moreover, regarding atmospheric plasma treatment further tests must be conducted in order to improve the results obtained, this new tests should focus on both resin A dip recipe and atmospheric plasma/LDU conditions optimization.

Regarding resin B dip solution the next step should be recipe optimization and in the future texting the optimized solution in the impregnation of the remaining C-ITA cords (nylon, PET, aramid and Hybrid).

It is of most importance to point out that for all studies above mentioned both reproducibility and production tests must be performed.

In relation to chemical analyses future work should focus on improving the extraction procedure, allowing the extraction of resin A reagent and reducing the number of additives extracted. Besides MS analysis to all C-ITA compounds should be performed in order to obtain a more profound knowledge. Moreover in order to confirm the chemical reaction mechanisms proposed in this master thesis further characterization techniques should be applied.

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