Universidade do Minho
Escola de Ciências

Ângela Maria Gonçalves Rodrigues

Adhesion promoters for tire textiles reinforcements

Outubro de 2016

Ângela Maria Gonçalves Rodrigues **Adhesion promoters for tire textiles reinforcements**

UMinho | 2016

University of Minho
School of Science

Ângela Maria Gonçalves Rodrigues

Adhesion promoters for tire textiles reinforcements

Master's Dissertation
Master in Techniques of Characterisation and Chemical Analysis

Under the supervision of
Prof. Dr. Gabriela Botelho
and
Eng. Carla Pires
and
Dr. Thomas Kramer

October 2016

DECLARAÇÃO

Nome
Ângela Maria Gonçalves Rodrigues

Endereço eletrónico
angelamgrodrigues3@gmail.com

Número do Cartão de Cidadão
14103583

Título da dissertação
Adhesion promoters for tire textiles reinforcements

Orientadores
Professora Doutora Gabriela Botelho
Engenheira Carla Pires
Doutor Thomas Kramer

Ano de conclusão
2016

Designação do mestrado
Mestrado em Técnicas de Caracterização e Análise Química

Universidade do Minho, ___/ ___/ _____

Assinatrura:____

“The dictionary is the only place that success comes before work.

Hard work is the price we must pay for success.

I think you can accomplish anything if you're willing to pay the price.”

Vince Lombardi

Acknowledgements

Completed ... Another step completed! It's time to thank all those who contributed directly or indirectly to the end of another stage of my academic life, without whom this process wouldn’t have been a rewarding and enriching experience it was. I would like to thank them for their contribution. The effort was too much, but the reward will be even greater, I don´t have doubt about that. It took months of work, but the reward will be certainly for the rest of my life. No work, dedication and critical thinking anything is possible. I can say it wasn't easy, but with the help of all everything has become less bitter.

First of all, I have to thank the Eng. Eduardo Diniz and Mr. Manuel Pinheiro for the opportunity to develop my master’s thesis in such great work ambiance, making this experience pleasant and very instructive. I'm also very grateful to Eng. Carla Pires, my supervisor in C-ITA, for the support and trust in my work.

I have to thank the Professor Gabriela Botelho, my supervisor in University of Minho, for all the scientific guidance, help and support. For the encouragement, her willingness to teach and the magnificent work on the collaboration between university and industry.

I have to give very special thanks to Dr. Thomas Kramer for the support during this project, following my work attentively and also for the opportunity to visit Continental R&D in Hannover.

It was a long journey. A very enriching journey of ten months in an environment until then unknown. And like in all journeys, there are good and bad moments. However, and thanks to the people I worked with directly, all the good times overshadowed the bad ones. Therefore, I owe a huge thanks to Eng. Diana Pinto, for all the words of encouragement and for all the good advice always at the right time. I am also grateful for all the assistance provided and all the criticism, always constructive.

I have to give special thanks to Eng. Alexandre Gomes for giving me freedom to explore all my ideas and for his help and support. For Eng. Ana Martins a big thanks for all the teachings, the huge encouragement and the will to help always.

A special thanks to my colleagues in this journey, Master Mafalda Flores, Eng. Pedro Cordeiro, Eng. Raul Falcão and Eng. Ricardo Peixoto for the friendship, knowledge exchange and team spirit. You made this journey much more enjoyable, with hilarious moments for later recall.

I have to thank my all friends, always present.

I also thank to Mr. Noman Mughal and Mrs. Esther Rohleder for sharing knowledge and to answer all my doubts about a large part of this project.

I have also to thank to the Quality team, Mr. Araújo, Mr. Carlos, Mr. Serra, Mr. Miguel and Mr. Vasco, for sharing their work experience with me and for collaborating with my project whenever I needed. Thanks also too many other production workers that have always been available to help me in any situation.

At last but not the least, I would like to thank my parents Maria Leopoldina and Abílio Rodrigues, my sister Sara Rodrigues, for the unconditional support in everyday life and for making me believe I could go further. Thanks to you, I never gave up my goal. I owe a special thanks to Fábio Pereira and his parents, who constantly motivated me and helped me over all these months. I can't forget the one who makes my life more colourful, knows the best and the worst of me, but still is always by my side. Thank you, Fábio, for all the love, encouragement and motivation. For always make me smile in the worst moments, for believe in me and especially for being always available to listen to me.

Abstract

The tire, often looked as a simple rubber item, is actually a complex aggregation of various rubber compounds and reinforcement materials (metallic and textile). Reinforcement materials play a great influence on structural stability, performance, safety and, consequently, on tires overall quality rate.

The textile reinforcement usage involves textile fibres application, among which, one must point out: nylon, aramid, rayon and polyester. Initially, the fibres are subjected to chemical and physical treatments and then integrated in rubber compounds, through a vulcanization process.

This master thesis was developed at Continental - Indústria Têxtil do Ave, S.A. (C-ITA) in cooperation with the Chemistry Department in the University of Minho (UM). C-ITA is a company that belongs to the Continental group, whose main activity is to use fibre (from several suppliers) in textile reinforcements for tires.

The main goal of this project was reformulating the aqueous dipping solutions (dips), composed mainly by resorcinol-formaldehyde-latex (RFL), to obtain a robust adhesion between the fibres and the rubber-matrix. Since resorcinol is a dangerous compound, experiments were tested in order to replace it in dips. To this end, one resorcinol-free resin was tested (Resin-A). The resin used show good results regarding the adhesion of the textile reinforcement to the rubber matrix. Therefore, replacement of the RFL impregnation solutions is possible.

Another aim was to study adhesion promoters to improve adhesion of textile reinforcements for rubber matrix. These promoters activate the surfaces of the cords in a first dip, after this treatment the cords go through another chemical bath consisting of a solution also free of resorcinol. When the fibres passed by a first chemical bath containing adhesion promoters, better results was obtained in relation to the fibres that didn't receive such treatment.

Another method for activation of the surfaces of the cords has also been studied, plasma treatment. This approach is environmentally and economically advantageous, since it reduces the number of large quantity of used solutions and reagents. In addition to these advantages, this treatment was effective in the adhesion of textile reinforcements.

Key words: Adhesion, textiles reinforcements, dipping, plasma treatment.

Resumo

O pneu, muitas vezes encarado como um simples objeto de borracha, é na realidade um complexo aglomerado de vários compostos de borracha e materiais de reforço (metálico e têxtil). Os materiais de reforço presentes no pneu têm um papel fulcral na estabilidade estrutural, desempenho, segurança e, consequentemente, na qualidade do produto. A utilização de reforços têxteis passa pela utilização de fibras têxteis, entre as quais se podem destacar: o nylon, a aramida, o rayon e o poliéster. Inicialmente, as fibras são sujeitas a um tratamento químico e físico e posteriormente integradas nos compostos de borracha, por meio de um processo de vulcanização.

Esta tese de metrado foi desenvolvida na Continental – Indústria Têxtil do Ave, S.A. (C-ITA) em cooperação com a Universidade do Minho (UM). C-ITA é uma empresa que pertence ao grupo Continental e tem como atividade principal a conversão de fibras (fornecidas por vários fornecedores) em reforços têxteis para pneus.

O principal objetivo deste projeto foi a substituição de soluções aquosas de impregnação (*dips*) à base de latex-resorcinol-formaldeído (RFL), por outro mergulho sem RFL, a fim de obter de uma adesão eficaz entre o reforço têxtil e a matriz de borracha. Uma vez que o resorcinol é um composto perigoso, foram efetuados estudos de forma a proceder à sua substituição nos *dips*. Para este fim, foi estudada uma resina sem resorcinol (Resina-A). A resina utilizada mostrou bons resultados no que diz respeito à adesão do reforço têxtil à matriz de borracha. Portanto, é possível a substituição do RFL nas soluções de impregnação.

Outro dos objetivos foi estudar promotores de adesão para melhorar a aderência dos reforços têxteis à matriz de borracha. Estes promotores ativam a superfície das cordas num primeiro mergulho, após este tratamento as cordas passam por outro banho químico que consiste numa solução também ela livre de resorcinol. Quando se fizeram passar as fibras por um primeiro banho químico contendo promotores de adesão, os resultados obtidos foram melhores em relação às fibras que não receberam este tipo de tratamento.

Um outro método para a ativação das superfícies das cordas foi ainda estudado, tratamento por plasma. Este método é ambiental e economicamente vantajoso, uma vez que, reduz em grande número a quantidade de soluções e reagentes utilizados. Além destas vantagens, este tratamento é eficaz na adesão dos reforços têxteis.

Palavras-chave: Adesão, reforços têxteis, impregnação, plasma.

Table of contents

Glossary

dtex	decitex	g/10000 m

List of Acronyms

AG	Automotive Group
C-ITA	Continental - Indústria Têxtil do Ave, S.A.
DOE	Design of experiments
ENR	Epoxidized Natural Rubber
ENR/Latex	Epoxidized Natural Rubber to Latex ratio
IUPAC	International Union of Pure an Applied Chemistry
LDU	Laboratory Dipping Unit
NR	Natural Rubber
RF	Resorcinol Formaldehyde
RFL	Resorcinol Formaldehyde Latex
R/L	Resin to Latex ratio
PET	Polyethylene terephthalate
PI	Product Industrialization
SBR	Styrene Butadiene Rubber
UM	Universidade do Minho

List of Figures

List of Tables

CHAPTER 1. Introduction

1.1 Project presentation and framework

For the general consumer, the most common impression about tires is that they are a piece of rubber with almost no technology associated. However, tires are highly engineered composites with about 20 different components (steel wire and textile cords) and 15 or more rubber compounds. The main function of tires is the capacity to provide the interface between the road and the vehicle, although they also have the capability to support the load of the vehicle and absorb the road irregularities.

The market is increasingly demanding, leading the automotive industry to overcome every day. Being the textiles reinforcements an area where there's room for further developments in both physical (impact resistance, maintenance of shape e.g.), as chemical properties (improving fibres adhesion to rubber), to attend this development this area had to undergo some changes, and to be able to innovate.

The main role of the textile components is to provide the shape and structure to the tire, but is also important to assure the mechanical properties when the tire is subjected to extreme forces during the vehicle motion.

During this master thesis several dipping solutions have been tested in two different fibres. The LDU (Laboratory Dipping Unit) was used for dipping all fibres, followed by a thermal treatment. It was possible to simulate the dipping process at a low scale, quickly and effectively thus not affecting the normal production of the company. After this process, parameters like rubber-cord-rubber interfacial appearance were tested and inspected.

1.2 Project goals

The main goal of this project is focused on the study of aqueous solutions used in the dipping process and key parameters, such as temperature, exposure time in the oven. All solutions are possible alternatives to current dip solution used for impregnation of all the textile reinforcements, composed mainly by resorcinol-formaldehyde-latex (RFL). Another objective of this work is the study of other treatment of textile fibres that does not involve any solvents, namely the plasma treatment.

1.3 Company presentation

The Company *Continental AG* was founded in Hanover in 1871 and started to produce rubber articles. Nowadays, the *Continental AG* belongs to the top five suppliers in the automobile industry worldwide, and is number two in Europe. The Continental Corporation is divided into the Automotive Group and the Rubber Group, and consists of five divisions: Chassis & Safety, Powertrain and Interior which belong to the automotive group, Tires and ContiTech which belong to the rubber group (1).

Indústria Têxtil do Ave, S.A. (ITA) belongs to the rubber group, was founded in 1950 in Lousado, Portugal, and became part of Continental Corporation in 1987 (Figure 1). Continental - Indústria Têxtil do Ave, S.A. (C-ITA) mainly produces textile reinforcements for the rubber industry, specifically for tires produced in Continental (2). This master thesis was developed in C-ITA, more specifically in the Product Industrialization (PI) department.

Figure 1 - Continental - Indústria Têxtil do Ave, Lousado and *Continental* logo (adapted from (2)).

More than half the company's production is now for export out of Portugal, mainly to other Continental plants in Europe. The reinforcements are semi-finished goods for tires and car interiors, such as seats, dashboards and doors. ITA increased their production capacity significantly after an investment of EUR 4.5 million in 2002.

Indústria Têxtil do Ave, S.A. currently employs close to 200 workers. Its work politics is based on the four *Continental* values: trust “We earn the trust we give”, passion to win “We have the passion to win", freedom to act "We grow with freedom and its responsibility" and one for another "We attain top value with our team spirit as one Continental". Its vision is to search for the best solutions and to create the most developed technologies of transport and mobility without neglecting safety, because tires are the beginning of the stability of a vehicle, and the environment (after all, it was the first company to produce environmental friendly tires, 20 years ago). Its goal is to render a safer, more sustainable, more comfortable, individual and affordable mobility (2).

1.4 Thesis outline

This thesis is organized in seven different chapters:

Chapter 1. Introduction

In this chapter, the aim of the project is presented, as well as, the company where the work was developed.

Chapter 2. Theoretical Basis

All the theoretical fundamentals for understanding this work are presented.

Chapter 3. Procedure and technical description

In this chapter, the methods used throughout the project are presented and explained.

Chapter 4. Results and discussion

The initial status results that triggered the project and the subsequent experimental findings obtained with this study are discussed in this chapter.

Chapter 5. Conclusions

In this chapter, the main conclusions are summarized and the open points and suggestions for future work are proposed.

Chapter 6. Project assessments

All limitations found during the work are presented in this chapter, as well as, some suggestions as future work and the final assessments.

Chapter 7. References

In this chapter, the literature references consulted throughout the project are presented, even as the experimental test method specifications of the company for the experiments done.

CHAPTER 2. Theoretical basis

2.1 Tire Industry

The most common impression about tires, for the general consumer, is that they are a piece of rubber with almost no technology associated. Contrary to popular belief, a tire does not consist only of cured rubber. Those with an opportunity to tour a tire production facility are surprised to learn that there are 20 or more components (steel wire and textile cords), with 15 or more rubber compounds at the massive amount of machinery and processing involved to achieve the finished product (3).

Historically, the pneumatic tire was invented later, firstly for bicycles, by John Dunlop in 1888 and subsequently for automobiles (4). In 1898, Continental started producing so called “pneumatics”, tyres capable of giving a more comfortable ride and enabling automobiles to travel at higher speeds.

The tire is a complex technical component of today’s motor cars and must perform a variety of functions. It must cushion, damp, assure good directional stability, and provide long-term service (5). All tires include three types of reinforcements: rubber compounds, steel and textile cords. The application of textile reinforcements in tires is necessary to avoid rubber deformations when excessive forces are applied. These forces result from air pressure of the tire and when accelerating, breaking and cornering of the car. Textile reinforcements are mainly applied on the carcass and cap-ply. There are three basic types of tires, named for the three main ways of constructing a tire, differentiated by the way the carcass plies are oriented (Figure 2).

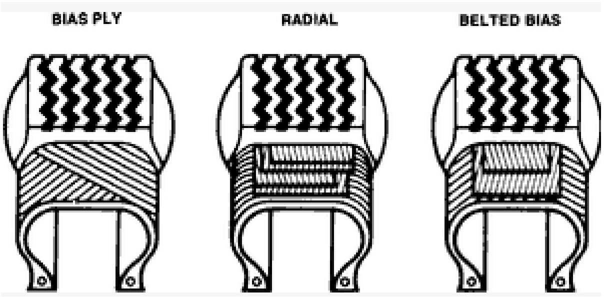


Figure 2 - Tire types (5).

In a typical radial tire there are up to 25 diverse structural parts and as many as 12 different rubber compounds. Radial tires have body ply cords that are laid radially from bead to bead, nominally at 90° to the centerline of the tread. Two or more belts are laid diagonally in the tread region to add strength and stability. Variations of this tire construction are used in modern passenger vehicle tire. The typical radial tire cross section is shown in Figure 3.

Radial body cords have advantages like deflecting more easily under load, thus they generate less heat, give lower rolling resistance and better high-speed performance. Increased tread stiffness from the belt significantly improves wear and handling.

On the other hand, has a disadvantage like complex construction, increasing material and manufacturing costs.

Figure 3 - Typical radial tire cross section (adapted from (5)).

The **tread** is designed and compounded for abrasion resistance, traction, low rolling resistance, durability and protection of the casing. It provides frictional contact for transmission of driving, braking, and cornering forces. The tread pattern is designed to provide uniform wear, to channel water out of the footprint, and to minimize pattern noise on a variety of road surfaces. It is molded during vulcanization step or curing.

Both the tread compound and the tread design must perform effectively in a multitude of driving conditions, including wet, dry or snow covered surfaces, while also meeting customer expectations for acceptable wear resistance, low noise, and good ride quality (6).

Jointless cap plies, consist mostly of nylon embedded in rubber. They have function enhance high speed suitability and act as a barrier restricting migration of chemicals from the tread to the belt (5).

Steel-cord belt plies are high-strength steel cords which provide rigidity and a stable foundation to the tread region which enhances performance, vehicle stability, simultaneously protecting ply cords.

The textile ply or carcass controls internal pressure and also maintains the tyres shape, providing strength and stability to the sidewall. Therefore the carcass is a very important element in tire because it ensures that the tyre keeps in shape even with high inflation pressure.

Inner liner consists of a butyl rubber compound and is formulated to provide good air and moisture permeability, flex fatigue resistance, and aged durability.

Side wall is formulated for resistance to weathering, ozone, abrasion, tear, radial and circumferential cracking, and for good fatigue life. It is composed for natural rubber.

Bead reinforcements are layers of textile composed of nylon or aramid, attached in the bead area directly to the carcass. The main purpose is to stiffen the lower sidewall/bead area to influence the driving behaviour and the high speed durability of the tyre.

Bead apex is a synthetic rubber which enhances directional stability it is responsible for the steering precision and improves the comfort during the trip. It is formulated for good dynamic stiffness, tear strength, adhesion, and durability.

Bead core consists of a set of steel cord embedded in rubber, arranged in a square shape and its main purpose is to guarantee the connection between the tyre and the rim.

2.2 Rubber

As previously noted, the rubber is a major constituent of a tire, and therefore it is the most important and widely used natural polymer from the industrial standpoint. It was used for centuries by the Mayans in the Western Hemisphere before it was introduced into Europe by Columbus (7).

Rubber is a fascinating material, with unique properties that make it an essential component of a pneumatic tire: it is soft, elastic, resistant to cutting and scraping, with a high coefficient of friction and low permeability to gases (3).

Natural rubber (NR) is derived directly from the latex of the *Hevea brasiliensis* (rubber tree), which is grown in regions close to the equator. The main form of natural rubber is structurally almost identical to *cis*-1,4-polyisoprene (Figure 4) (8).

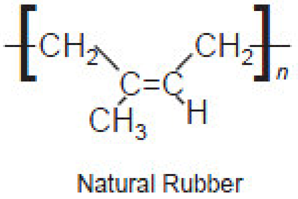
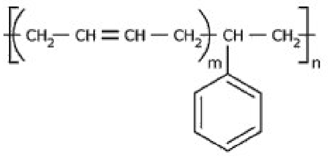
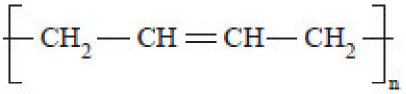
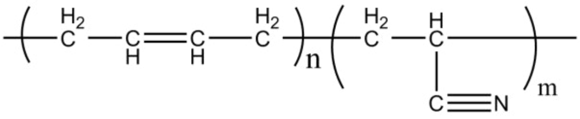


Figure 4 - Chemical structure of *cis*-1,4-polyisoprene (adapted from (8)).

Excessive consumption of natural rubber led to the need of laboratory and industrial synthesis of other forms of rubber by countries that did not have access to its natural form (7). Once it was discovered that the basic unit was isoprene, other types of monomers were quickly developed (Table 1) (9).

Table 1 – Different types of Rubber, wherein *n* and *m* are the numbers of repeating units.

Rubber	**Chemical Structure**
Styrene Butadiene Rubber (SBR)	
Polybutadiene Rubber (BR)	
Nitrile Rubber (NBR)	

Synthetic rubber consists not only of one type of units but can be also copolymeric, which means that different monomers can be conjugated. The double bonds in the structure are crucial for the vulcanization reaction since it is through these bonds that the crosslinking occurs (8).

Vulcanization

To produce rubber articles, like tires and mechanical goods, it is necessary to vulcanize the green rubber.

In 19th century Thomas Goodyear discovered the rubber vulcanization process, making the rubber the perfect material for tires. Chemically, vulcanization, involves the generation of crosslinks between the elastomer molecules and sulphur. Unvulcanized rubber is generally not strong, does not retract essentially to its original shape after a large deformation, and it can be very sticky. In short, unvulcanized rubber can have the same consistency as chewing gum. In other words, the vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a molecular crosslinking network (Figure 5) (10).

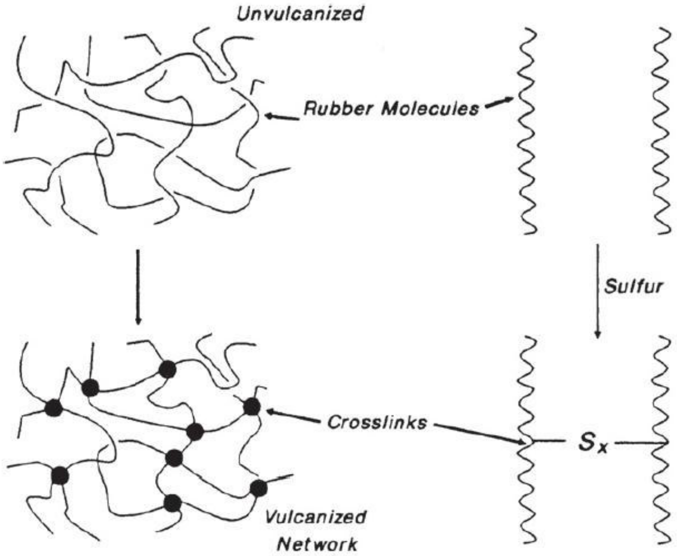


Figure 5 - Schematic representation of crosslink molecular network formation (10).

Thus, the vulcanization is a process of chemically producing network junctures by the insertion of crosslinks between polymer chains. The crosslinks may vary, can be a group of sulfur atoms in a short chain, a carbon-to-carbon bond, a single sulfur atom, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. This process is usually carried out by heating the rubber, this rise in temperature causes a chemical reaction to occur in the rubber compounds whereby the long polymer molecules become crosslinked together by sulfur or other vulcanizing agents, in a mold under pressure (8).

2.3 Textile Reinforcing Materials

As previously stated, the tire is composed of textile reinforcements that provide strength and stability to the sidewall, as well as, contain the air pressure.

There are, at the present, five main types of organic fibres (cotton, rayon, nylon, polyester and aramid) used in reinforcements for rubbers (11).

Fibres are characterized by having high strength, good elongation and a host of other properties depending on their usefulness. There are two main natural fibres: cotton and wool, the former the polysaccharide cellulose (Figure 6), and the later protein (12).

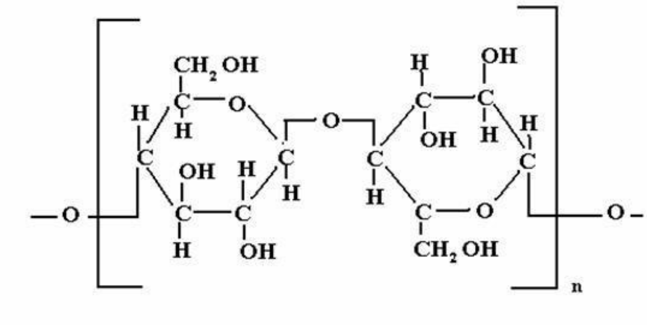


Figure 6 - Chemical structure of cellulose, wherein *n* is the number of repeating units (12).

Following the pioneering work of Carothers at the DuPont Corporation (13), and with the increasing availability of low-cost raw materials, the synthetic fibres industry developed rapidly as demand for textiles outstripped production of cotton and wool. The world production of all fibres exceeds 36 million metric tons a year, with approximately 50 % being synthetic. Production of synthetic fibres overtook that of cotton in late 1970s (14).

Fibre to rubber adhesion is an important subject in rubber composite industry. It is well known that surface physical, mechanical and chemical treatments are effective methods to improve interfacial bonding.

2.3.1 Rayon

Rayon is a manufactured regenerated cellulose fibre. It is made from purified cellulose, primarily from wood pulp, which is chemically converted into a soluble compound (12). A scheme of the viscose rayon process chemistry is given in Figure 7. As can be seen, the basic structure of the cellulose is essentially unchanged and the various stages are primarily to solubilise and regenerate the cellulose (15).

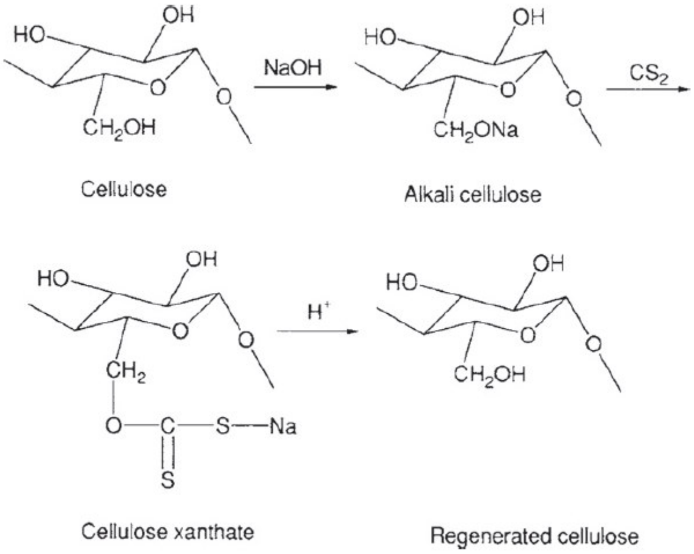


Figure 7 - Viscose rayon synthesis (adapted from (15)).

Rayon is more expensive than PET, more sensitive to moisture and has environmental manufacturing issues. On the other hand, rayon has advantages, like stable dimensions, heat resistance and good handling characteristics (16).

2.3.2 Nylon

Nylon is the generic name for the linear aliphatic polyamides characterized by the presence of amide groups —(CO–NH)— in the main polymer chain.

There are a wide variety of nylon polymers but only two types are applied to tires, nylon 6,6 and nylon 6 (15).

The synthesis of nylon 6,6 is shown in Figure 8, it can be obtained from the polycondensation of hexamethylenediamine and adipic acid, each monomer containing six carbon atoms so giving the designation of nylon 6.6 (11).

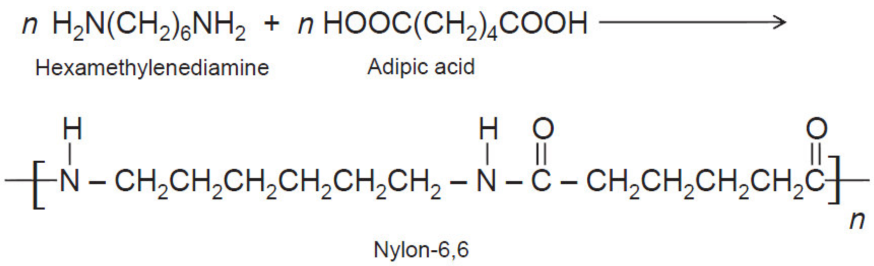


Figure 8 - Synthesis of nylon 6,6, wherein *n* is the number of repeating units (adapted from (8)).

On the other hand, nylon 6 is produced from just one monomer (a homopolymer version of nylon), which contains 6 carbon atoms, hence giving the designation nylon 6. It is derived from caprolactam, by a ring-opening polymerization as seen in Figure 9.

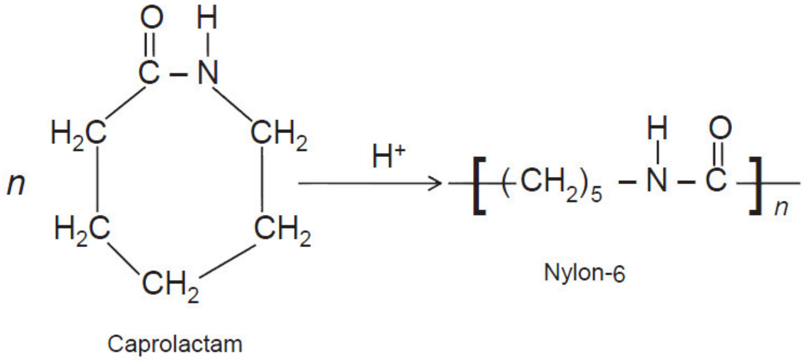


Figure 9 - Production of nylon-6 from caprolactam, wherein *n* is the number of repeating units (adapted from (8)).

In the tire industry, nylon 6,6 is used more extensively than nylon-6 because nylon-6,6 has a higher melting point.

2.3.3 Polyethylene terephthalate (PET)

Such as nylon 6,6, polyester is formed by a condensation polymerization reaction but in this case the monomers are dimethyl terephthalate and ethylene glycol (Figure 10).

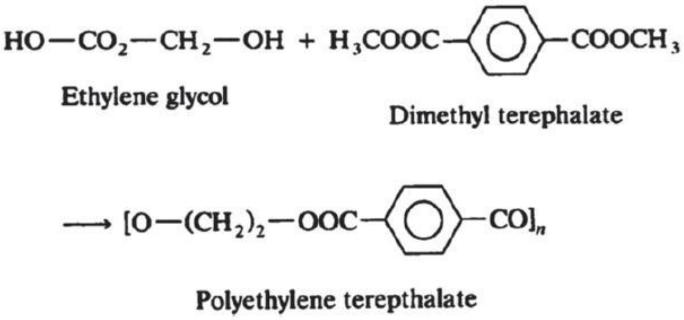


Figure 10 - Polymerization of polyethylene terephthalate, wherein n is the number of repeating units (adapted from (15)).

Polyester is the highest volume synthetic textile material used in the world (15). About 12 % of this fibre is used in the tyre industry to make cords to reinforce for rubber tires. Almost all polyester yarns used in this industry are filament yarns of polyethylene terephthalate (PET). It is also used extensively in other applications as conveyor belts, hose, clothing, home textiles, and carpets and rugs (8). PET isn't as heat resistant as nylon or rayon.

2.3.4 Aramid

Aramid is another class of the fibres that finds applications in tire industry. Kevlar is the trade name of the polymer that has found most extensive use among the aramid. Aramid is like nylon in that it contains the amide bond —(CO–NH)— it is manufactured from *para*-phenylenediamine and terephthaloyl chloride (Figure 11). The substitution of the aliphatic carbon backbone by aromatic groups brings about considerable changes in the properties of the resultant fibres (15).

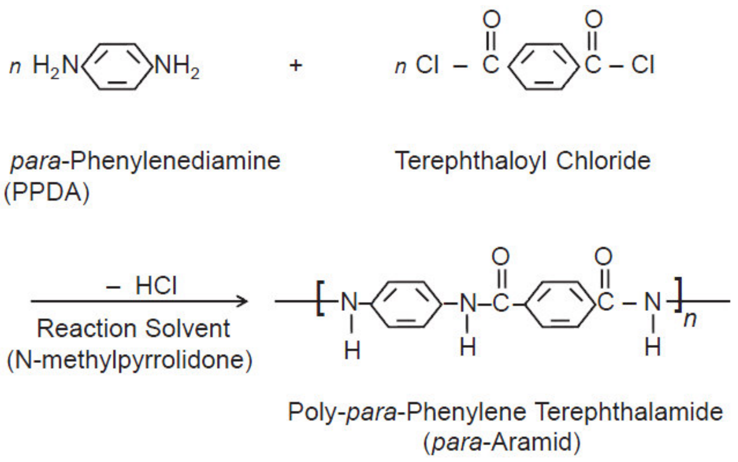


Figure 11 - Synthesis of aramid, wherein *n* is the number of repeating units (adapted from (8)).

This polymer has extremely high strength, as a fibre, and was originally introduced for use as tire cord. It is two to three times stronger than polyester and nylon. However, because of its extraordinary properties, over half of its production now goes into “bulletproof” ballistic protection for police and military applications, aerospace composites, boat hulls, protective clothing, an asbestos substitute for protective coverings for underground optical fibres and special ropes (8).

The major disadvantages on the production of aramid are the processing constraints (difficult to cut) and the cost (16).

2.4 Yarn and cord processing in C-ITA

There are various processes which fibres can subjected to before being part of a tire namely **twisting**, **weaving** and **dipping**. In C-ITA the process begins with twisting and finish with dipping, in this particular case, spinning process completed outside C-ITA by the yarn suppliers.

The yarn is the basis for all subsequent procedures. So, the first procedure in the reinforcement textiles formation is the yarn production by spinning process (17). There are different types of spinning such as dry spinning, wet spinning, gel spinning and melt spinning that are applied to each fibre depending on physical and chemical properties (3).

It follows the **twisting** process, first process in C-ITA. The greige yarn (yarn without treatment), is twisted in order to increase the elongation and improve the fatigue resistance of the textile. In the twisted cord the yarns are more compact and the filaments more firmly held, which gives greater resistance to damage from abrasion (11). The cord construction begins with twisting the yarns individually in the Z direction (counter-clockwise) followed by the twisting of multiple yarns in the S direction thus constructing a cord as shown in Figure 12.

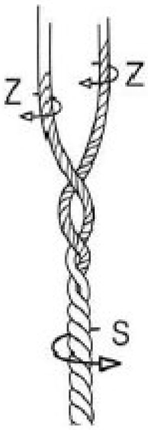


Figure 12 - Twist directions in a greige cord (11).

According to the number of yarns forming the cord, this can have different types of construction, for example a rope with a 1x2 construction, means one cord constituted by two yarns (Figure 13).

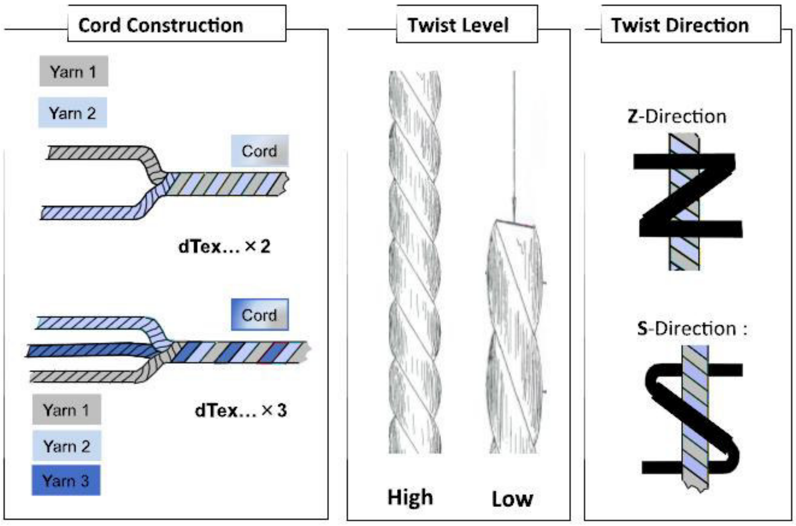


Figure 13 - Cord design (18).

Weaving is the next process. Woven fabrics generally consist of two sets of yarns that are interlaced and lie at right angles to each other. In this process the two types of yarns are warp (run parallel to the weaving machine) and weft (run perpendicular to the machine) are intertwined (19). This process occurs depending on the application intended, i.e., fabric, or simply the single cord. After preparing the reinforcement textile it is necessary a physical and chemical treatment to ensure adhesion cord and rubber in tire. This process step called **dipping**.

Dipping

At C-ITA there are two impregnation machines being one for single cords (Figure 14) and the other one for textile fabrics. The dipping process has the objective of providing good adhesion properties to the cord or fabric. In this process, reinforcement textiles are subjected to high temperatures (thermo-fixation) and tension over a specific amount of time stabilizing the textile materials (11). Heat is applied in the ovens and tension is controlled by the difference of the rotating speed of the rolls that pull the cord. It has four ovens, being the first and third one responsible to dry the cord, reason why it is called first and second dry zone; the second and fourth one are the stretching zones (hot stretch zone and normalizing zone), where temperature and mechanical devices will give to fibre/cord the physical properties intended (20). These conditions are used to improve the mechanical properties of polymer.

The cords also suffer a chemical treatment where they are dipped in a specific solution which will provide the effective adhesion rate between the fibre and rubber.

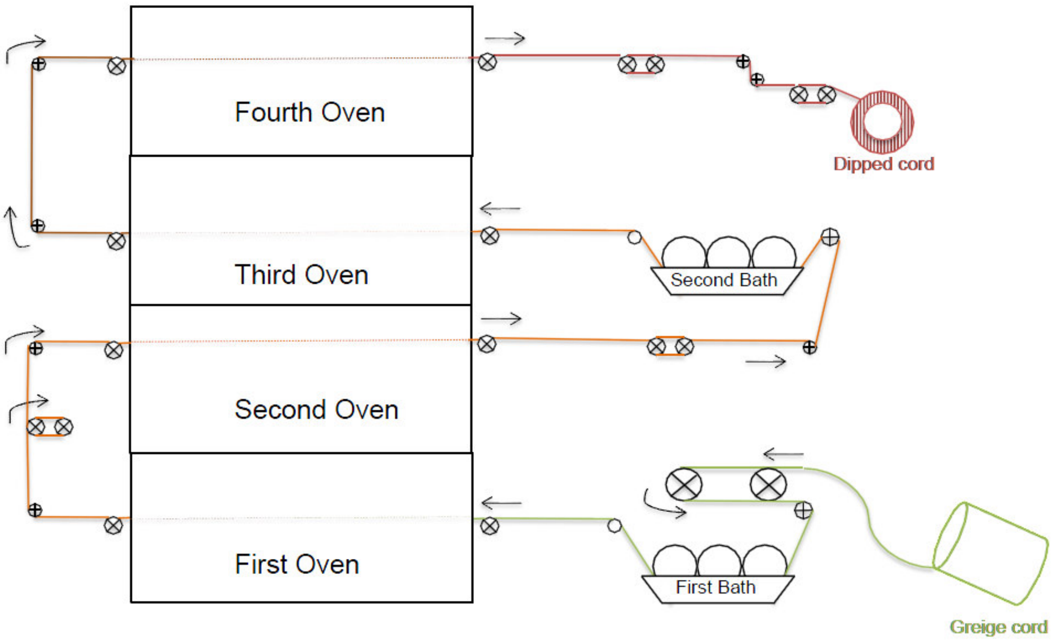


Figure 14 - Dipping and heat treatment process (18).

Chemically, the heat treatment/curing process is associated to the formation of a cross-linked network structure, increasing the interaction between the fibre and the adhesive. This process although time consuming and being high energetically expensive is absolutely necessary for fibres life service behaviour's, ensuring the necessary characteristics for its key role on tire (21).

2.5 Adhesion

In this subchapter, the main characteristics of the components responsible for the adhesion of the textile material to rubber matrix will be discussed. As mentioned earlier, the main objective of this work is to test possible substituents for the RFL dip system. In this chapter some of the possible alternatives will be presented.

Adhesion is of fundamental importance to the textile industries, it is necessary in nearly every type of textile-based product. This is an important factor in using fibres together with rubber as well as the individual properties of each material. (22) An adequate bonding of textile fibres to elastomeric matrices is essential for a satisfactory performance, improving durability and shape's maintenance of the composite material of many heavy duty mechanical rubber products, like tires (23).

Adhesion is defined as an attraction of two different substances resulting from intermolecular forces between the substances. In this case, these substances are the adhesive material. These adhesion forces are manifested when the substances are brought into contact (Figure 15), and work is required to separate them (24).

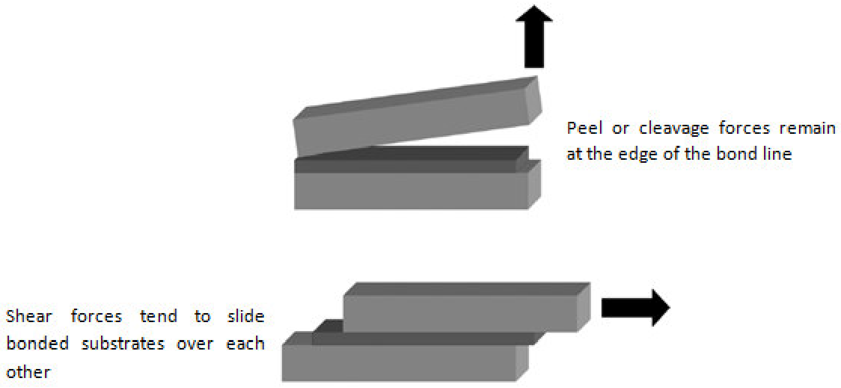


Figure 15 - Illustrations of shear and peel forces to which adhesive bonds are often subjected. (adapted from (24))

Tires are used under severe conditions; therefore a very high level of adhesion is required. The adhesion between untreated fibres and rubber is always low, because there is a significant difference in modulus and polarity between the reinforcing fibres and the rubber matrix (21). In general, strong adhesion is obtained through adhesive treatment of the textile or through addition of bonding agents to the rubber compound. The type of adhesive treatment is dependent on the type of fibre used.

2.5.1 Resorcinol Formaldehyde Latex (RFL)

Before synthetic textile cord had been developed, the rubber industry was using casein or animal blood to promote adhesion between cotton cords and rubber (22). But the introduction of synthetic fibres as reinforcements in rubber composites identified the need for an improved adhesives and adhesion promoters for the enhancement of strength between rubbers and fibres. An improved adhesion requirement for the tire, conveyer and transmission belt applications had led to the development of resorcinol (R) formaldehyde (F) latex (L) adhesives what is today referred to as an “RFL dip” (8).

The nature of the fibre plays the most important role in RFL treatment of tire cords. In practice it has been recognized that rayon and nylon cords are easy to bond to rubber by RFL treatment, but with polyester cord this is extremely difficult. This should be attributed to the nature of the polymer structures. Rayon and nylon contain reactive groups –OH and amide groups –CONH-. But polyester has a less reactive structure, and it does not have so called active hydrogen in the polymer chain. So, for polyester fibres, the RFL-treatment alone is not sufficient due to the lack of polar and hydrogen bonding groups. In case of aramid fibres, the bulky aromatic groups sterically hindered the amide functionalities. These fibres are not-activated fibres. Therefore, both polyester and aramid fibres are treated with a pre-dip before being treated with a standard RFL-dip (Figure 16) (21).

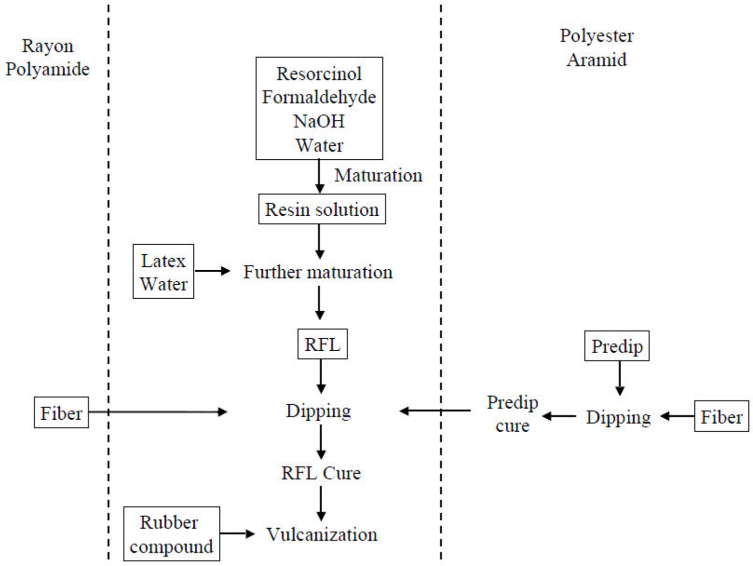


Figure 16 - Schematic representation of fibre treatments, including RFL-treatment and the adhesion to rubber compounds. (adapted from ((21)).

The RFL-dip is an emulsion of rubber latex in a solution of resorcinol and formaldehyde in water. The objective of resorcinol formaldehyde resin is to achieve good adhesion to the organic fibre substrate whether it is rayon, nylon, or polyester. RF resins used to prepare RFL dips are the product of a chemical reaction between resorcinol and formaldehyde (Figure 17).

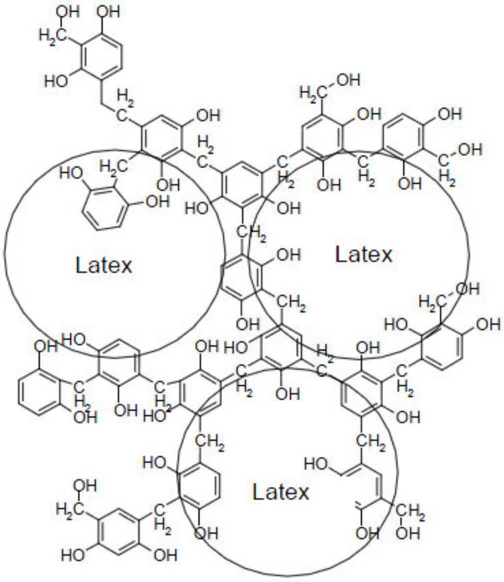


Figure 17 - Proposed RFL morphology (adapted from (21)).

On the other hand, the rubber latex portion can be natural rubber latex or styrene butadiene vinylpyridine (terpolymer) latex or even neoprene latex. Although the efforts and studies that had been made, the latex based on the ter-polymer 2-vinylpyridine-styrene-butadiene (so called VP-latex) still the choice for the RFL system. The pyridine nuclei facilitate the interaction between the RF film and fibre through hydrogen bonding (25). This rubber latex is present to achieve good adhesion with the rubber matrix itself. If latex alone is employed as an adhesive, wouldn't be possible a good rubber to textile adhesion because of lack of active groups in latex. It also provides the dipped cord with flexibility properties. This “rubber-resin molecule” then combines with the functional groups on fibre surface through methylol groups, creating a sort of mesh, which will act as the bonding agent between all the compounds. So, the RFL allows good adhesion between the rubber and the textile cord reinforcement. Several studies have shown that the structure of the cured RFL consists of a continuous resin phase and dispersed latex particles (21).

RF resin

The most important component in the RFL-dip is the RF-resin (Resorcinol Formaldehyde resin). Pre-condensed resins are the ones currently used in the industry, allowing resorcinol and formaldehyde to be partially condensed in dilute aqueous alkali solution, before being added to the latex (20). The adhesion of the textile substrate with immersion formulation is believed to be due to the composition of the resin itself, being the methylol groups the ones responsible for establishing reaction between them and the hydroxyl groups on fibres surface, forming covalent bonds.

Benzene-1,3-diol (Figure 18) IUPAC name for Resorcinol, is one of the most acclaimed chemicals in organic chemistry and is widely used in the development of many areas, like chemistry, technology and medicine.

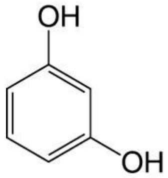


Figure 18 - Chemical structure of Resorcinol.

Resorcinol has a very specific structure, this molecule with two hydroxyl groups in the aromatic structure, located at their meta-positions with respect to each other. The location of these two groups in the benzene ring provides a high reactivity. In spite of its widely use in composite applications, the reaction mechanism between resorcinol and formaldehyde is not completely understood (21).

RF resins can be classified into two major groups, novolaks and resoles. In the presence of an acid or alkaline catalyst conditions and formaldehyde concentration less than one mol per mol of resorcinol, the resin contains essentially novolak type structures. In presence of an acid catalyst, condensation between resorcinol and formaldehyde can lead to the production of a methylene bridge resorcinolic resin structure, being known as novolak resins (Figure 19) (25).

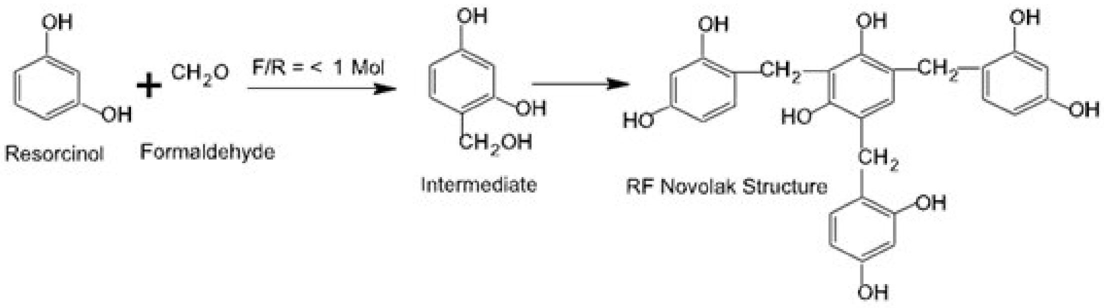


Figure 19 - Novolak resin structure (adapted from (25)).

However, an increase in formaldehyde concentration at room temperature or lower and alkaline conditions, will favour the formation of methylol groups in the resin structure, forming resoles resin structures (Figure 20) (25).

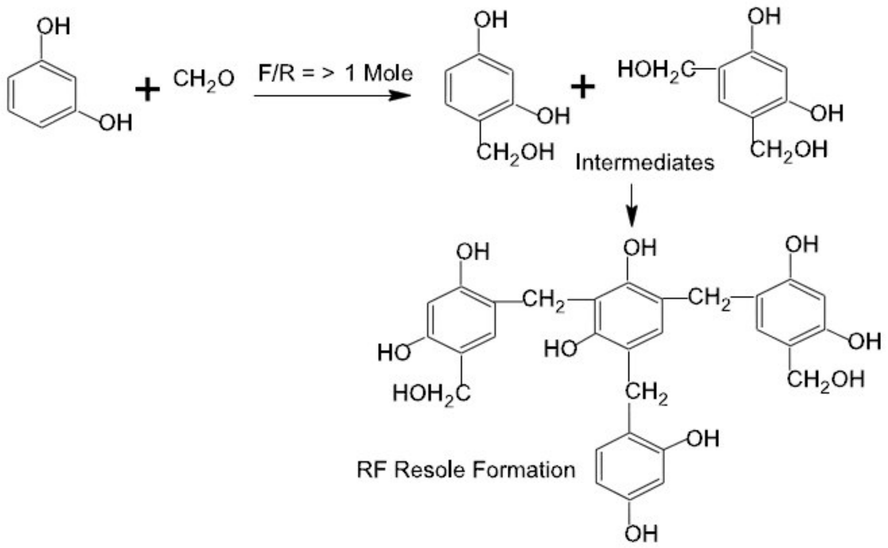


Figure 20 - Resole resin structure (adapted from (25)).

A standard RFL is prepared in two major steps. The first step consists of a reaction between resorcinol and formaldehyde to produce a "resole" type molecules. The second step is primarily the introduction of latex into the first step RF resin.

The textile cord or fabric is first immersed in the RFL dip suspension and then passed through a vertical oven under tension at a predetermined elevated temperature and time. This process is called heat setting, where the adhesive dries and coats the cord or fabric while under tension.

2.5.2 Maleinized polybutadiene (Resin-A)

Resin A is a maleinized polybutadiene dispersion (Figure 21) which is used as an adhesion promoter. Liquid polybutadienes obtained by anionic polymerization of 1,3-butadiene have been investigated since many years because of their commercial importance in the field of adhesives and coatings (26).

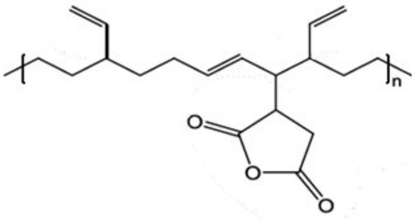


Figure 21 - Chemical structure of maleinized polybutadiene.

The polybutadienes are modified by three possible industrial processes: maleinization (Figure 22), epoxidation and chlorination. The maleinized products contain anhydride groups randomly distributed along the polymer chain. Using polybutadiene to replace RF-resins requires other additives. At least one acid group of maleinized polybutadiene must be modified with a hydrophilic group to increase water solubility. This modification needs to consider the chemical compatibility between the adhesion promoter and the polymeric material.

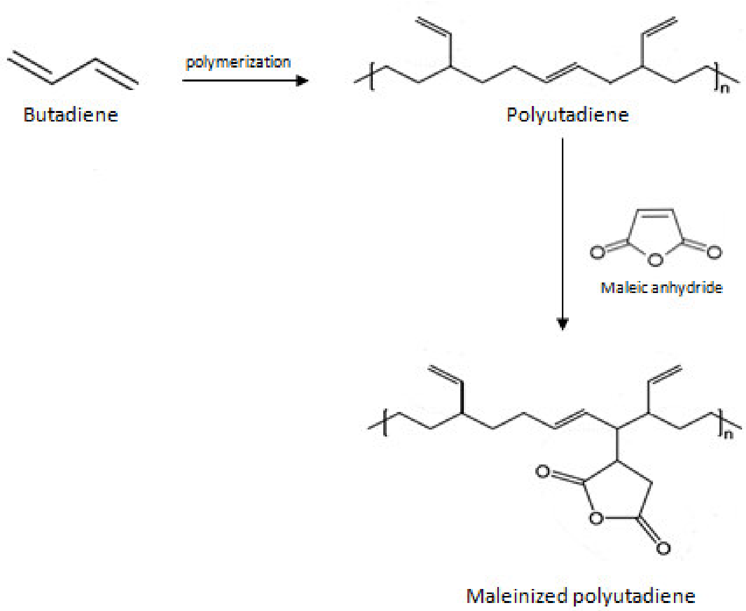


Figure 22 – Maleinization of polybutadienes.

Reactive groups on the copolymer react with the fibrous material, by covalent bonding, to attach to the material. This reaction (curing) can take place before, during or after the treated textile is dried, although it is generally preferred that the cure occur after the drying step. The process (cure) temperature can vary widely, depending on the reactivity of the reactants. However, the temperature should not be so high as to decompose the reactants or so low as to cause inhibition of the reaction or freezing of the solvent. Unless specified to the contrary, the curing process described herein takes place at atmospheric pressure over a temperature range from about 110 °C to about 250 °C (27).

These resins being water-based are environment-friendly and show good adhesion on various substrates including steel and synthetic fabrics (26).

2.5.3 Pre-dip (nAA's fibres activation)

As mentioned earlier, certain textile cords, such as PET and aramid, do not have sufficient surface activity to properly react with the RFL dip. To promote adhesion of polyesters and aramid, a two-bath impregnating process was developed. A preliminary impregnating step is carried out before the RFL-dip, in which a blocked isocyanate is applied in combination with a polyepoxide (epoxy resins). After which they are heat treated and dried before the RFL dipping procedure. In this initial treatment, a variety of different chemicals are used (28). One problem with some of these chemical agents is toxicity in the workplace. For this reason blocked isocyanates have been used instead of free isocyanates.

Blocked isocyanates

Polyfunctional isocyanates were used frequently in the rubber industry as crosslinking agents and adhesion promoters in the 1940s and 1950s. They have been widely replaced by RFL-dip. The reason for this is the restriction of handling organic solvents (in which the polyfunctional isocyanates are dissolved) and the much lower storage stability of the isocyanate dip prior to treatment with the rubber compound compared to RFL and treated textiles. They are renowned for their high reactivity and selectivity towards various functional polymers, and absence of side reactions and by-products (28).

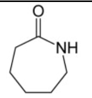
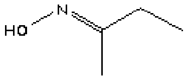
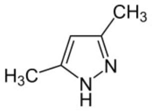
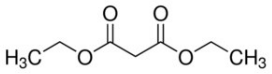
However, their reactivity also leads to severe drawbacks for use:

- compounds containing multiple free isocyanate groups cannot be used in stable formulations
- they are highly sensitive to atmospheric moisture and traces of water e.g. in coating solvents/ingredient
- free isocyanate compounds, especially diisocyanate monomers, can be extremely hazardous to health.

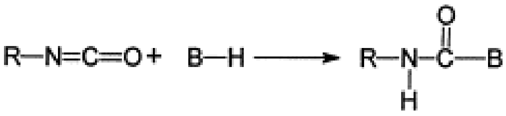
Blocking technology was developed to overcome compounding limitations, and provide a safe working environment (29).

There are several methods in which the isocyanate functional group can be "blocked" by a blocking agent. The type and nature of the blocking agent can vary, but they have a common characteristic: contains at least one active hydrogen atom in the molecule (Table 2).

Table 2 - Blocking agents (adapted from (29)).

Blocking Agent	**Chemical structure**	**Unblocking Range (˚C)**	**Melting Point (˚C)**	**Boiling Point (˚C)**
ε-caprolactam (ε-CAP)		160 - 180	72	138
methylethylketoxime (MEKO)		140 - 160	-30	152
3,5-dimethylpyrazole (DMP)		110 - 120	106	218
Diethylmalonate (DEM)		100 - 120	-50	199

In the first case (Figure 23) the isocyanate group reacts with an active hydrogen compound. Upon heating and in the presence of a nucleophile, the product is obtained (30).



$$R{-}N{=}C{=}O + B{-}H \longrightarrow R{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}B$$

Figure 23 - A blocked isocyanate by reaction with active hydrogen compounds (adapted from (30)).

In the case of active methylene groups, such as those of malonic esters, the reaction occurs with the methylene group, formed by two active hydrogens. This type of blocked isocyanate is produced by addition of the isocyanate to the active methylene site (Figure 24).

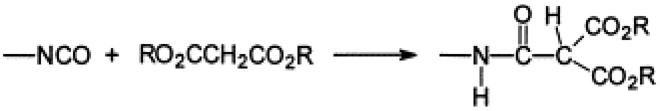


Figure 24 - Reaction of an isocyanate with a malonic ester (adapted from (30)).

The unblocking mechanism (1) is simply the reverse reaction of that used to manufacture the blocked isocyanate (2) as show in Figure 25:

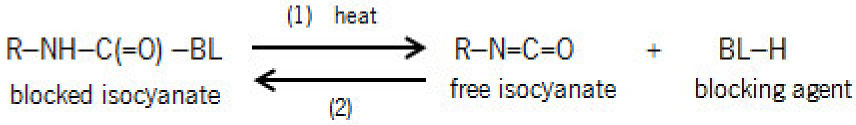


Figure 25 - Unblocking mechanism (adapted from (29))

Blocked isocyanates are inert and not dangerous at ambient temperatures. After unblocking reaction the free isocyanate groups can be reacting with hydroxyl or other functional groups on the polymer (31).

In C-ITA the activation process is made using an specific blocked isocyanate, but in order to improve the adhesion between the fibres it were tested three other types of isocyanates.

Epoxy resins

Epoxy resins thermosetting comprise the group of polymers most widely used as adhesives and matrix in high performance composites, and form one of the most important classes of structural adhesives. In general, these resins are used under various mechanical stresses, which may include situations where the material is subjected to high strain rates. Due to excellent mechanical properties, epoxy resins have been used in a wide range of industrial applications, including structural adhesives, coatings and matrix resins in fibre reinforced composites as well as in the aviation and aerospace applications (32).

Epoxy resins undergo a transformation called curing upon heating or exposure to a variety of reagents, usually acids or bases. The result is an extremely hard solid. Most resins contain two epoxy groups. The versatility of these resins is connected to the great reactivity of the epoxy group. The epoxy ring (Figure 26) is a highly deformed structure in which the angles of CO bonds worth approximately 60 ° and are considerably smaller than the angle of the tetrahedral carbon, 109.5 °, or the angle of oxygen leads 110 °, in ethers open chain. Furthermore, the epoxy ring carbon atoms are positively charged due to the greater electron affinity of the oxygen atom.

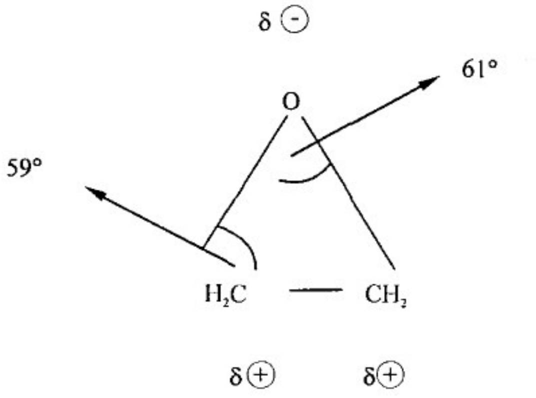


Figure 26 - Epoxy ring (adapted from (33)).

These characteristics make the epoxy ring unstable, favouring its opening by different types of chemical functionalities. When curing takes place in contact with a surface containing hydroxy groups, surface bonding occurs though covalent linkages: the resin acts as a strong adhesive.

2.5.4 Epoxidized natural rubber (ENR)

Epoxidized natural rubber (ENR) is a derivative of natural rubber with two reactive sites namely the unsaturated isoprene and epoxidized isoprene units which are randomly distributed on the polymer backbone (Figure 27). The epoxidation of natural rubber is one of the most important and promising ways to obtain new polymeric materials from a renewable resource, due to the high performances and good properties of epoxidized natural rubber. ENR is a polymer with good elasticity and adhesive properties (34,35).

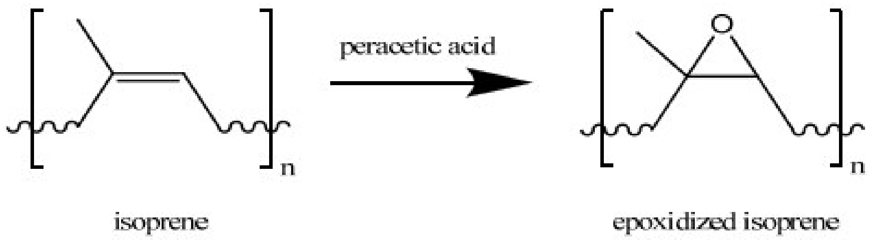


Figure 27 - Modification of NR to ENR (adapted from (34)).

ENR is polar and exhibits properties similar to other synthetic elastomers. ENR's polarity increases to the presence of epoxide groups in the structure. The epoxy ring structure becomes more reactive and capable of reacting with the hydroxyl groups present on the surface of the fibres. Owing to the polarity, the ENR is miscible with others polar polymers (36).

2.5.5 Plasma treatment

The methods of surface modification of materials can be divided into four categories: mechanical, chemical, flame, and plasma. With textile fibres, chemical and plasma treatments are most widely used since the mechanical and flame treatment process will often degrade thin fibres (23,37).

Plasma treatment is an alternative method to chemical treatment (with similar surface changes). The pre-treatment of textiles by plasma technologies becomes more and more popular as a surface modification technique (38). Plasma surface modification does not require the use of water and chemicals, resulting in a more economical and ecological process (39). The enormous advantage of plasma processes concerns the drastic reduction in pollutants and a corresponding cost reduction for effluent treatment, so it can be considered as an environmentally benign technology (40). In addition, the plasma treatment increases the hydrophilic character of the fibres. This application has been done on all possible fibre types, with varying success. The treatment aims at the introduction of water compatible functional groups such as $-COOH$, $-OH$ and $-NH_2$. Of all plasma effects, this is without a doubt the most studied because it influences many plasma applications (39).

Silanes

The study of reactive functional silanes and polysiloxanes, mostly involving compounds with carbofunctional groups has been developed considerably due to its varied applications, such as adhesion promoters, crosslinking agents, dispersing agents, coupling agents, and surface modifiers. They are used in many fields of science, and especially in materials science and a chemical technology. Silanes used in the rubber industry are generally bifunctional organic silicon compounds with two reactive groups (41).

Silicon is in the same family of elements as carbon in the periodic table. In their most stable state, silicon and carbon will both conveniently bond to four other atoms; but silicon-based chemicals exhibit significant physical and chemical differences compared to analogous carbon-based chemicals. Silicon is more electropositive than carbon, does not form stable double bonds, and is capable of very special and useful chemical reactions. Silicon-based chemicals include several types of monomeric and polymeric materials (40).

Silane coupling agents are compounds whose contain functional groups that bond organic and inorganic materials (Figure 28). It acts as a sort of intermediary which bonds organic materials to inorganic materials. This characteristic that makes silane coupling useful for improving the mechanical strength of composite materials, for improving adhesion, and for resin modification and surface modification. The individual molecules of silane coupling agents contain two types of reactive functional groups characterized by different kinds of reactivity (42).

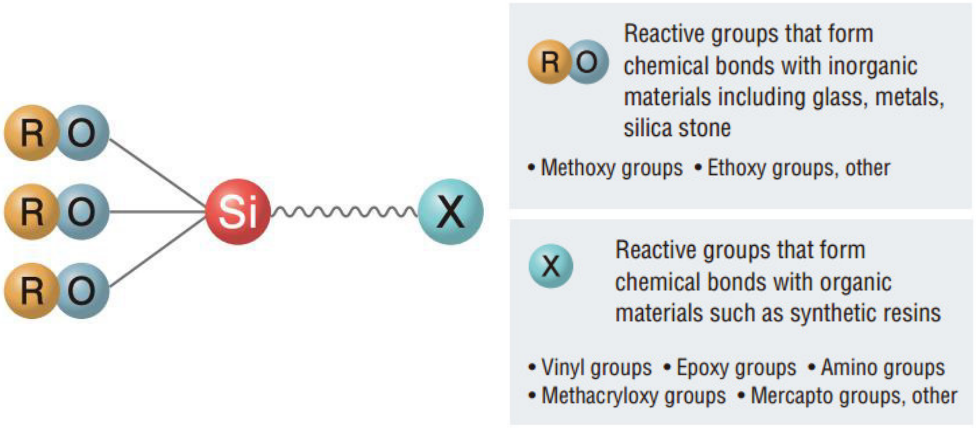


Figure 28 - Molecules of silane coupling agents (42).

Silane coupling agents are hydrolysed to form silanol groups, and oligomers are formed through partial condensation. The silanol oligomers then hydrogen bond to the surface of the inorganic material. Finally, the inorganic material put through a drying process and robust chemical bonds are formed through a dehydration condensation reaction (Figure 29).

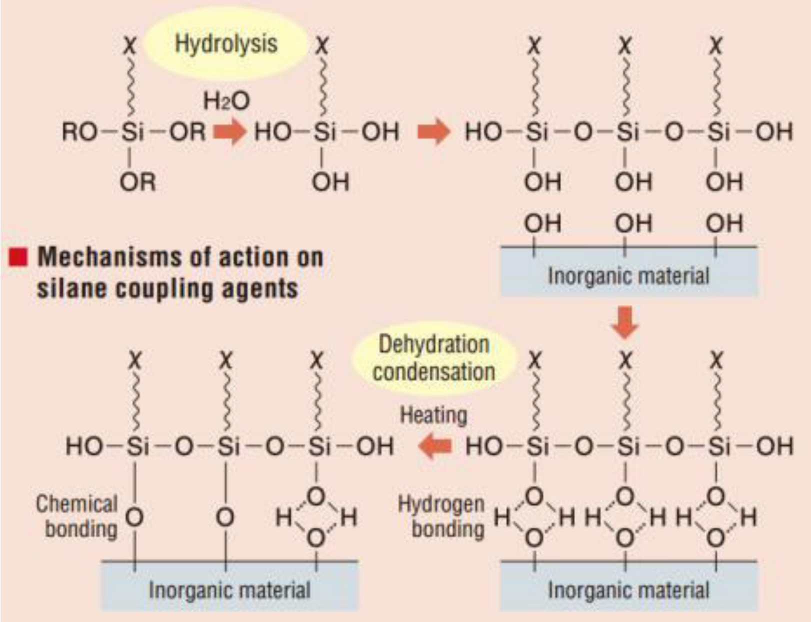


Figure 29 - Mechanisms of action on silanes coupling agent (43).

These compounds were used in the main dip after plasma treatment. Silanes were used in replacement of RFL dip.

CHAPTER 3. Procedure and technical description

3.1 Materials and reagents

In order to achieve the main objective of this project it was necessary to perform a task sequence (Figure 30) with the use of selected materials and reagents. So, this subchapter describes the methodology and the techniques used in the development of this project.

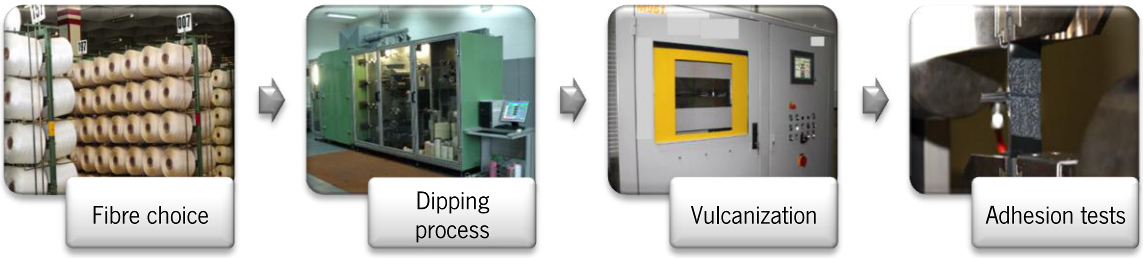


Figure 30 - Step by step used during the experimental procedure.

3.1.1 Fibres

Throughout this project, the trials were performed with different types of fibres like nylon and polyester. Table 3, shows the different fibres used during this work and their characteristics.

Table 3 - Fibre characteristics used.

Fibre	**dtex**[1]
nylon	940
polyester	1440

[1] *Decitex (dtex)* – Linear density in grams per 10 000 meters of fibre

The fibres have certain specifications that must be met according to each customer. So, for this study these specifications were taken into account throughout the C-ITA specifications, as well as, the production values (Table 4). For the peel force, the minimum value taken into account is 120 N and for appearance test is 3.5.

Table 4 - Peel forces achieved at the production.

Fibre	**Peel forces achieved at the production [N/25mm]**
nylon	139-151
PET	189-216

3.1.2 Reagents used in dips preparation

Continental ITA has distinct dip formulations for each fibre. The reagents used in all formulations tested during the practical work are listed in Table 5. The respective concentrations used, as well as the exact composition of each solution were being optimized during the entire project. For confidentiality reasons only present the reagents that make up the dips.

Table 5 - Reagents used in all formulations tested.

Dip formulations (reagents)	Fibres
Latex	nylon PET
Resin-A	
RF- Resin	
Epoxy resin	
Isocyanate	

Dipping preparation and methodology

The dipping process consists in the preparation of water-based dip solutions, both pre-dip (for all non activated cords) and dip. Pre-dip solution is the first to be prepared by adding an epoxy polymer and an isocyanate solution to water. After that, comes the RFL dip or Resin-A dip. A normal RFL dip preparation includes three steps; latex aqueous dispersion, alkaline resin solution, formaldehyde addition, but also considering some preparation techniques. Latex aqueous dispersion must be performed under controled conditions, namely water pH and mechanical agitation. During latex blend preparation, air capture must be avoided otherwise it will promote foam formation and oxygen presence on dip, leading to latex destabilization (oxidative cure). At the same time resin is diluted on water with ammonia for pH adjustment. At this stage, agitation also plays an important role by increasing solubility at room temperature. The resin must be visually inspected if there are non-reacted parts or coagulate formation. Higher resin age life will result on less solubility; it means there will be non-reacted resin parts on dip tray and attached to final cord.

The final step is formaldehyde addition, will endorse cross linking between resin and latex. Formaldehyde should be added carefully and slowly, and preferably into bulk solution rather on its surface, in order to avoid agglomeration. The Resin-A dip preparation is simpler and includes an only step; it is composed of Resin-A, latex and water. Latex aqueous dispersion must be performed under control conditions, namely water pH and mechanical agitation; the resin A is incorporated in the solution carefully.

After mixing, all dips must stay at rest between 10 and 30 minutes.

Dip analysis was performed after usage, for some trials. The pH and solid content (S.C / %) (Equation 1) were measured. The pH is a parameter that may influence the adhesion between the fibre and the rubber matrix, therefore it has to be controlled. The solid content is quantified in order to determine the residual matter after the evaporation of the volatile chemicals (44).

$$\text{Solid Content}/\% = 100\ \frac{dry\ weight}{wet\ weight}\quad \text{[Equation 1]}$$

To measure the solid content, a minimum of 0.5 grams of dip is weighted (to an accuracy of 0.001 g). Then, the weighted matter is placed an aluminium plate at the moisture analyser. So, C-ITA has a restricted specification for each dip, regarding to pH and solid content.

All dipping formulations were tested in each fibre for an evaluation of peel force and appearance (during this stage, force-elongation tests were also applied to evaluate if there was any significant variation on the mechanical behaviour when changing the dip formulation). Next study step consisted in a systematic approach, where distinct new formulations were tested, taking in consideration the knowledge achieved during prior studies (45,46), C-ITA know-how and literature (Figure 31). The adhesion was then tested by peel-test method (ASTM method) (47), aiming for an optimized formulation compatible with the fibres under study.

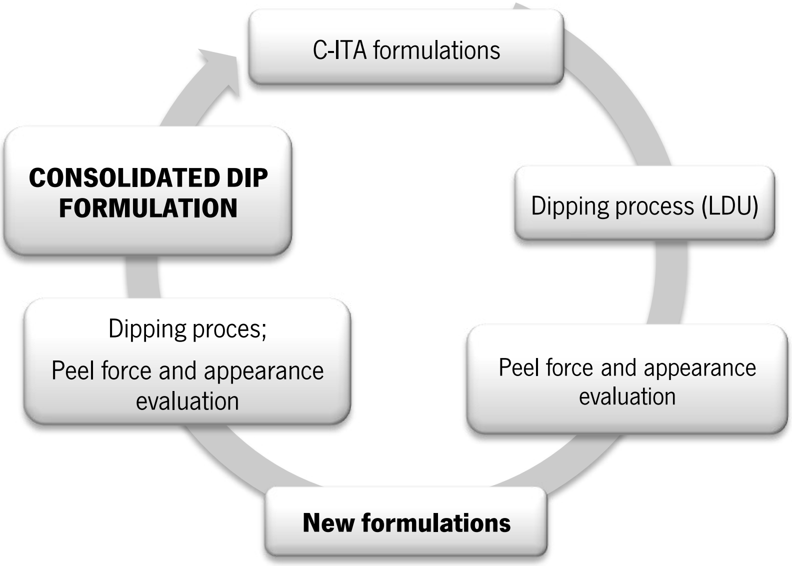


Figure 31 - Scheme of methodology applied in all dipping formulations.

3.2 Equipments

Throughout this project some equipment were necessary, namely the LDU, the plasma machine, tensile test machine (Zwick Roell) and vulcanization press.

In this subchapter will be presented in detail the LDU well as the plasma machine. These devices were crucial for the preparation / optimization of all samples. They allow changing the working conditions in order to achieve the best result.

3.2.1 Laboratory Dipping Unit (LDU)

After dips preparation follows the impregnation process. The trials were performed in the Laboratory Dipping Unit (LDU) at ITA. This machine allows identifying, improving and optimizing the ideal conditions in the impregnation of cords (Figure 32). This dipping unit is very similar to the production single cord dipping unit. However, as the ITA is 24 hours of continuous operation, it is impossible to interrupt the normal course of immersion production units. So LDU offers the possibility to simulate on a small scale, different production configurations/setups; it allows running experiments on an optimization scope or to improve and search for new dipping setups in any fibre.

Figure 32 - Laboratory Dipping Unit (LDU) at ITA (48).

In this step the greige fabric (or single cords) is emerged in one or two solutions depending if the cord is activated or not. The pre-activation step should be considered whenever non-adhesion activated fibres (nAA's) are processed. After passing through the solutions the cords will go pass the ovens for drying process.

The operating conditions employed are shown in Table 6. According to the results for each trial, the conditions have been optimized.

Table 6 - Operating conditions in LDU.

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

3.2.2 Plasma treatment

As mentioned above, the plasma treatment was used as the surface activation of the strings. In these tests the rope passes first through the plasma machine and then proceeds to the LDU. Low-pressure plasma technology was used in all experiments with this treatment. The most important components of a system are the vacuum chamber, the vacuum pump and a high-frequency generator for plasma creation (Figure 33).

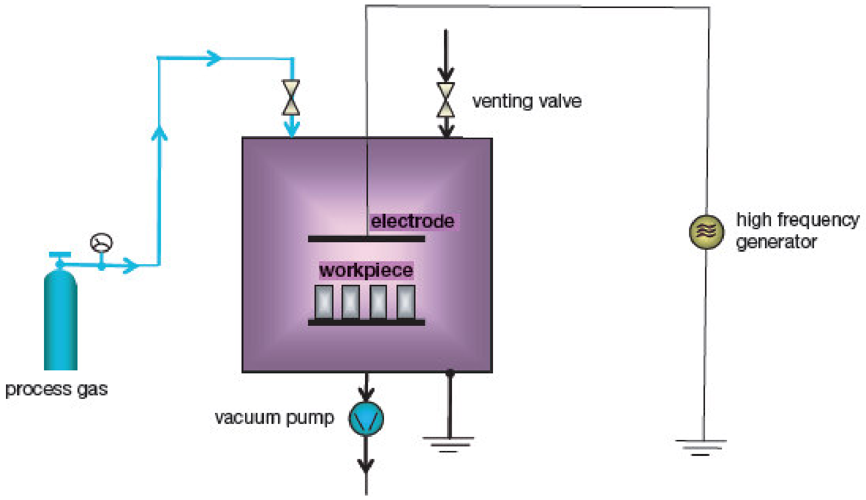


Figure 33 - Plasma system scheme (49).

In addition to the operating conditions shown in Table 6 (LDU settings) were further optimized the pressure (mbar) and power (%) (plasma machine settings). The complete test procedure for this equipment was developed, however, for confidentiality reasons cannot be disclosed.

3.3 Testing methods

The dipped cords have to be tested in order to measure the adhesion rate between rubber and the cords, an essential parameter on this study. The cords are submitted to the peel-test method, which determines the force required to separate two layers of cords bonded together by an intermediate rubber layer.

Peel test

The peel test is performed at C-ITA according the ASTM 4313 method (47). This test is a very important criterion for the material approval, since it determines the force required to separate two layers of cords bonded together by a layer of rubber and a calendered reinforcing fabric called shaffer, as well as, the coverage, this is the ratio between the bare fabric and the portion covered by rubber.

The separated areas of the test samples are inspected visually using the coverage rating between 1 to 5 (Table 7). The side with the poorest coverage is used for the evaluation.

Table 7 - Coverage rating for visual inspection.

Classification *	**Rubber coverage / %**	**Cords description**
1	0	completely free of rubber
2	25	mainly free of rubber
3	50	half covered by rubber
4	75	mainly covered by rubber
5	100	completely covered by rubber

*In determining the coverage rating, half ratings (i.e., 3.5) are also acceptable.

As any other test method, its samples have to be closest as possible to product application. So, it is crucial and necessary to simulate fabrics creating a handmade fabric with dipped cords, which are passed through a textile comb (Figure 34).

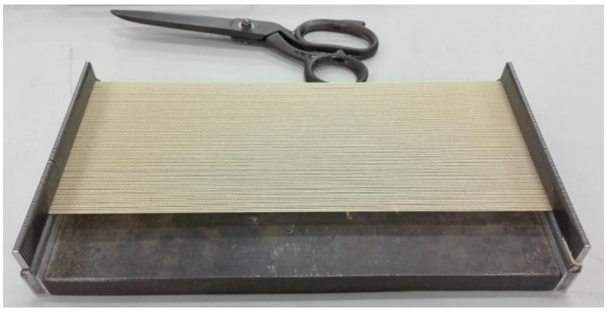


Figure 34 - Textile comb with nylon 940x2 dipped cord.

When the textile comb is sufficiently filled for the mould dimensions, a piece of chaffer (i.e. protective rubber-cord layer) is cut and attached to compound and then another piece of skim compound is then added on the top of the cords (Figure 35).

Figure 35 - Peel test specimen preparation.

The resulting specimen need to be pressurized and then cut in two samples with mould dimensions, according to test standards (ASTM D 4393-00) (47) which are joined to form a rubber-cord “sandwich” (Figure 36).

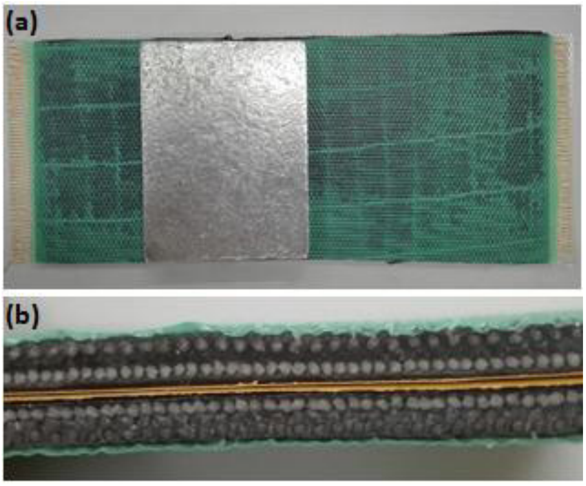


Figure 36 - (a) Peel test specimen after pressurized; (b) lateral view and materials identification.

The sample is incorporated in the mould and then vulcanized in a curing press at controlled temperature, pressure and time. Temperature was set on 170 °C and pressure on 8 – 10 bar during 10 minutes. On the end, vulcanized specimen must be removed from the hot mould and air-cooled for a minimum period of 3 hours before testing. After air-cooling period, the specimen are cut on three parts and kept at 120 °C for 30 minutes.

The testing occurs in a tensile machine (Zwick Roell) that pulls one half of the specimen at a constant speed of 100 mm / min while the other half is fixed (Figure 37), and at same time peaks of force are recorded – the mean value of these peaks is the peel-adhesion force for that specimen (ASTM D 4393-00) (47).

Figure 37 - Tensile machine separating the rubber specimen.

CHAPTER 4. Results and discussion

4.1 Resin-A

As previously said one of the goals of this project is the replacement of the resorcinol resins used in dips once these resins represent environmental problems and probably their use will be prohibited in the coming years. Thus, the Continental group has a resorcinol free resin as alternative to the common RF-resin. In this work, this resin will be called Resin-A. For this, the dipping solutions and LDU settings were varied to find the best result. After the dipping process, peel force and appearance rate were evaluated.

The main goal for the study of this resin is to find the best pre-dip recipe (the common pre-dip constitution: water, epoxy and isocyanate) and the optimal treatment conditions. The nylon fibres used in these studies were twisted with 940 dTex and a 1x2 construction.

Some studies with this resin have been developed in the company in other research projects (18,45,46). The best dip formulation for nylon was based on previous studies. In these same studies a pre-dip solution was used to improve the results with this resin. The adhesion between nylon and the rubber matrix was increased by these modifications, but the chemical reaction between this new dip and the fibre has not yet been fully understood. Although, it was concluded that the Resin-A has less affinity with nylon than the RF-resin. To improve this affinity and to promote the bonding between the dip and the fibre, a pre-dip with isocyanates is required. It means, the nylon fibre was dipped passing first through a pre-dip and then through a dip solution. However, the adhesion wasn't good. To solve this problem, three other type of isocyanate (A, B and C) at different temperatures were tested.

The objective was to decrease the temperature of second oven, because the only disadvantage is that two baths at high temperatures are needed.

The nylon cords treated with RFL-dip requires the usage of two ovens (the first at 160 °C and the second at 218 °C). Using two baths it will be necessary to use four ovens and higher temperatures. The melting temperature of nylon is 250 °C. By using two ovens with a temperature of 235 °C, the nylon's melting temperature is closer. This can be a problem when carrying out these tests in production, once there are temperature fluctuations. Another problem with the elevation of temperature in the dipping process is the influence on the fibres physical properties. Thus, by increasing the temperatures and using more ovens, the nylon properties can transcend the specifications. To find the best conditions for the nylon's fibre treatment with this new dip some trials were performed.

The greige cords were first treated with a previously recipe determined (for comparative purposes) and after with Dip A. The treatment conditions used for all trials are shown in Table 8. These ideal conditions were obtained after several trials.

Table 8 - Parameters in the dipping process on LDU.

LDU Setup

	Temperature (˚C)	**Exposure time (s)**	**Stretch (%)**	**Speed (m / min)**
1st Dry (T1 °C)	165	64	2.5	9.8
Hot Stretch (T2 °C)	210/225	45	4.0	
2nd Dry (T3 °C)	140	28	0	
Normalizing (T4 °C)	235	45	0	

The reference trial (Ref.) was performed with the isocyanate normally used in pre-dip, at two different temperatures. The following trials were performed by switching the type of isocyanate (A, B and C). Each trial was done in duplicate at different temperatures. The results are shown in the following table (Table 9).

Table 9 - Results of adhesion for all trials.

Results - Adhesion (Peel Test)

Trial	**1 Ref.**	**2 Ref.**	**3 Type A**	**4 Type A**	**5 Type B**	**6 Type B**	**7 Type C**	**8 Type C**
T2 º C	210	225	210	225	210	225	210	225
Peel force ± Δ peel force [N / 25mm]	188 ± 3	191 ± 2	184 ± 5	189 ± 2	180 ± 3	195 ± 7	181 ± 2	186 ± 6
Appearance (1-5)	3.5	3.5	3.5	3.7	3.5	4.5	3.0	3.5

After all the tests, it was concluded that it is possible to replace RF-resin by Resin-A. However, the best result was obtained for the trial number six, which means that the best isocyanate is the B at 225 °C temperature. As stated before, the isocyanates are unblocked when there is an increase of temperature, therefore and according to the isocyanates tested under these operating conditions, isocyanate B acts as the best adhesion promoter.

This resin was able to promote the bonding between nylon groups and the functional groups of the rubber matrix. Therefore, it is a viable hypothesis for replacing resorcinol resin but needs more reformulations in order to achieve the best result for appearance value.

4.2 Epoxidized Natural Rubber (ENR)

For this study nylon fibres with 940 dTex and a 1x2 construction were used. The objective of this study was to determine the best results with this new dip formulation. This new formulation is constituted of ENR, latex and water.

Two different solutions were prepared. One contains water, latex and ENR and the other contains only water and ENR. The trials were repeated where the temperature of the fourth oven was modified. All other conditions remained constants (speed, stretch and exposure time) (Table 10). These trials were realized with and without pre-dip. But the adhesion between the rubber and the cords, without pre-dip, didn't show good results. So, after this first result it is possible to conclude that this new chemical compound (ENR) doesn't work without pre-dip. The common pre-dip (water, epoxy and isocyanate) was used.

Table 10 – Design of experiments and results.

Trials	**ENR/Latex**	**Temperatures º C (4th oven)**	**Results**	
			Adhesion (Peel Test)	
			Peel force ± Δ peel force [N/25mm]	**Appearance (1-5)**
1	1:0	200	226 ± 3	1.0
2		250	228 ± 5	1.5
3	1:1	225	190 ± 1	3.5
4	0:1	200	211 ± 4	1.0
5		250	184 ± 2	2.5

Firstly, it can be seen that there is an improvement of the results when using ENR together with latex (trial number three). As previously stated, if latex alone was applied to the fibre material, an interaction between rubber matrix of the compound would be provided, though not with the fibre itself (trials number four and five). The same happens when only the ENR is in solution (trials number one and two). On the other hand, after the introduction of an epoxy group with the latex gives better results. This happens because after the opening of the ring, achieves a connection with the active groups of the fibre while the latex, in turn, allows adhesion to rubber.

4.3 Plasma treatment

The purpose of this treatment is to activate the surface of the strings, making them pass into the plasma chamber. After this process the cord goes to the LDU which receives the second treatment.

4.3.1 Elimination of pre-dip in PET cords (using normal RFL dip)

As said earlier, PET cords are not activated so, they need an additional treatment (pre-dip) to make the surface of the cords activated. This additional treatment was replaced by plasma activation. The common RFL dip was used, as well as all other conditions of treatment (LDU settings). PET cords (non-activated) were twisted with 1440 dTex and a 1x2 construction.

Were made four trials (Table 11). In one of them, the greige cords were first treated with a common pre-dip solution and after treated with a RFL (resorcinol-formaldehyde-latex) adhesive dipping bath (for comparative purposes). Standard treatment conditions were used. The second test was conducted in the same manner, however the speed was set to 4m / min. Several test trials were necessary to conclude that this was the best operating speed of the equipment, the optimal speed. So for better comparison of results the reference test was made at the same speed. In the third trial, the greige cords first passed by the plasma chamber and then treated with a common RFL dip in LDU. The LDU conditions were different (compared to trials one and two), once were used only two ovens.

In order to keep the exposure time equal for all experiments since the speed is equal to 4m / min was necessary to fix the first zone in the 65 seconds (exposure time) so the number of the first oven laps reduced from 7 to 3. Once the speed has been reduced, the number of turns must also be reduced. If the number of turns were equal, the cord would spend more time in the oven (bigger exposure time) in relation to the reference trials, changing the properties of the cord.

Table 11 - Key parameters in the dipping process on LDU and plasma machine for PET cords.

LDU Setup

Trials	**1** Normal pre-dip + RFL dip (normal conditions)	**2** Normal pre-dip + RFL dip	**3** Plasma treatment + RFL dip (without pre-dip)	**4** RFL dip (without plasma treatment and pre-dip)
Temperature / ºC				
1st Dry	160	160	160	160
Hot Stretch	235	235	235	235
2nd Dry	135	135		
Normalizing	235	235		
Turns	7/5/3/5	7/5/3/5	3/3	3/3
Speed / m.min-1	10.2	4.2	4.2	4.2
Plasma power / %	-	-	50	50

In this case, the aim is to compare the effects caused by plasma treatment with commonly used method of activation (pre-dip).

In the last trial (number four) the cord only passed by RFL dip, so didn’t have any treatment for activation. This trial is to important so proving if the cord really activated after plasma treatment. The results obtained are show in Table 12.

Table 12 - Results for PET cords with RFL treatment, activated by plasma.

Results - Adhesion (Peel Test)

Trials	**1** Normal pre-dip + RFL dip (normal conditions)	**2** Normal pre-dip + RFL dip	**3** Plasma treatment + RFL dip (without pre-dip)	**4** RFL dip (without plasma treatment and pre-dip)
Peel force ± Δ peel force [N/25mm]	258 ± 2	210 ± 5	182 ± 7	89 ± 4
Appearance (1-5)	5.0 	5.0 	4.0 	1.5 

After these results it is evident that the plasma treatment was efficient, allowing the activation of the surface of the PET cords. This statement is improved by observing results of the trials number two and three. In the trial number two, the normal pre-dip was used, obtaining a result that would be expected. However, the test number three activation was achieved by plasma treatment, obtaining a good result for PET cords. The fourth trial, without any activation allows demonstrating the effect of plasma treatment.

4.3.2 Silanes dip - replacement of RFL dip

The aim of this study was the replacement of the main dip (RFL dip) with a silane solution. After activating the surface of the cord, by plasma treatment, the cord was dipped in this solution in order to obtain good results in the coverage values. The nylon fibres used in this study were twisted with 940 dTex and a 1x2 construction.

A lot of trials were performed to achieve a result that was above the minimum values. In the first one, the greige cords were first treated with a common pre-dip solution and after treated with a RFL adhesive dipping bath for comparative purposes. For this trial, standard treatment conditions were used (Table 11, trial number one). In other trials the speed was changed to 4m / min and were used only two ovens at different temperatures. After several trials, it was possible to adjust the impregnation conditions until you find the optimal conditions. The silanes recipes have also changed over the trials. The results (Table 13) show that it is possible to replace the RFL dip, by silanes solution. It is also observed that without the plasma treatment the silane solution is not effective, since the values obtained for the appearance and peel force are too far from acceptable values.

Table 13 - Results for nylon cords with silanes dip, activated by plasma.

Results – Adhesion (Peel Test)

Trials	**1** Normal pre-dip + RFL dip (normal conditions)	**2** Plasma treatment + Silanes dip	**3** Silanes dip (without plasma treatment)
Peel force ± Δ peel force [N/25mm]	258 ± 3	189 ± 5	113 ± 2
Appearance (1-5)	5.0 	4.3 	1.5 

As previously stated, silane coupling agents are compounds with high reactivity it acts as a sort of intermediary which bonds organic materials to inorganic materials. This characteristic makes silane coupling agent useful for improving adhesion between cords and the rubber.

4.3.3 Ageing behaviour

This procedure is of utmost importance, since the treated cords are not used immediately, will be stored. So, it is necessary to estimate how long the treatment is maintained and which are the best storage conditions.

With this work was possible to observe how long is that the effect of plasma treatment remained in the treated cords. For this, adhesion tests were performed over three days. It was possible to observe a decrease in the peel force as well as in coverage (Figure 38).

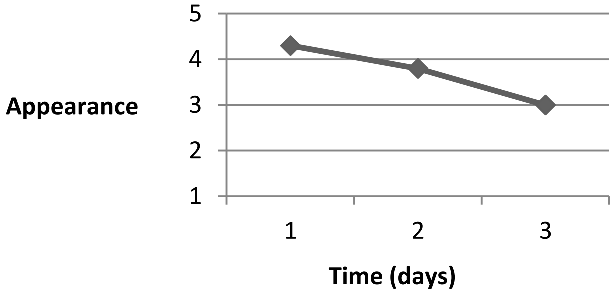


Figure 38 - Effect of plasma treatment during three days.

Once the light effect may influence in the active groups generated on the surface of the strings and eliminate this effect, the treated cord was kept in the dark in a black bag, during all procedure. The adhesion tests were done day after day, until to be observed a decrease in peel force and coverage values. After 46 days of cord storage there was a decrease in the coverage value as well as the peel force (Figure 39). So this is the maximum time that the cord should be stored without any changes to their properties.

This means that an additional treatment must be done to accurately determine the maximum number of days that the rope can be stored (since the first day after impregnation up to 46 days later). Many factors may lead to an abrupt lowering of peel force values (for values below specification) as well as the appearance value.

	First day of tratment	**46 days after treatment**
Peel force ± Δ peel force [N/25mm]	166 ± 3	149 ± 2
Appearance (1-5)	4.0	3.0

Figure 39 - Evolution of coverage values and peel force during storage time.

One factor comes down to an error during the impregnation that has damaged this part of the rope. Another of which may be due to operator error during the preparation of the comb to the test execution.

Once the bag is opened in each test, the atmosphere inside the same may have changed dramatically, influencing the properties of the cord.

CHAPTER 5. Conclusions

This project focused on the study of reinforcement-to-rubber adhesion properties and on the different dips used to the fibres treatment.

The results obtained on the trials performed throughout this project were successfully accomplished, since they were able to answer the biggest question of this project: is it possible to replace RF-resin in the dip solutions? The results showed that it is in fact possible to replace this resin by another resin (Resin A).

Concerning the resorcinol-formaldehyde replacement, the best formulation to Resin-A for nylon fibres and the key parameters for the dipping process on the LDU were studied. The samples tested showed good results concerning the adhesion level between the cord and the rubber. These results are obtained when using isocyanate B. It can be concluded that the resin A shows good results when used together with isocyanate B. Therefore, it is possible to replace the RF-resin in the dip solutions.

With the same goal (replacing the RFL dip) several solutions were tested composed of ENR and latex. Satisfactory results were achieved when the ENR was in solution with the latex, even so, the results were not good enough. A future study is needed to improve these results.

The second objective of this master's thesis was to study another method that did not involve the use of aqueous solutions for activation of the surfaces of the cords. After several tests, which were varied experimental conditions, such as speed, exposure time and aqueous solutions recipes, good results were obtained regarding the adhesion between the textile and the rubber matrix. This method has a great advantage since it decreased the amount of solution required for the treatment of textile fibres, as well as, the energy required in the LDU once only one solution is required (main dip) and a single oven.

Regarding to the study of the aging behaviour, it was possible to conclude that in fact the ropes after plasma treatment followed dipping treatment, can be stored without a modification in their properties. However, must be stored in the dark without contact with light, for a maximum of 46 days after treatment.

CHAPTER 6. Project assessments

6.1 Limitations and future work

The objectives were achieved in a quite satisfactory manner, however, as in any other work, there are some limitations and even a possible future work in order to get even better results. This being an ongoing project, there was always something to improve and further testing were required, though the time was not enough to test all the new ideas. Time was a crucial factor in this development work, since for some of the tests the process of soaking and tests were very time consuming, not allowing an optimization / improvement for all of them.

Concerning the replacement of resorcinol, Resin A should be tested for all fibres used in C-ITA, as well as the testing should be performed on the machine production in order to obtain the same results. The conditions must be optimized in order to achieve the same values that in the LDU. This is a very promising alternative but there is a way to go before Resin A replaces the RF-Resin. To obtain better results it is crucial to understand all the mechanisms, so it is important to study also the rubber component, as well.

In the study of ENR, it may be possible to obtain better results if normal isocyanate was replaced by the three other isocyanates tested in the study of Resin A. Test the three types would be the first step, and then optimize the best result.

For all studies; tests in the production are required and also reproducibility studies should be done.

6.2 Final assessment

Once completed all the experimental work, it is now possible to make a very positive assessment. As in all projects some unexpected problems and many challenges, but it is in these situations that can grow overcoming all adversities found. It was an exciting and challenging experience, with a personal and professional growth. This work contributed to further develop the expertise related with textile reinforcements and with the tire's knowledge and still have a sense of what is happening at industrial level, from conception to the end product. No doubt, a very enriching experience at all levels.

All this work is very useful, because in the course of this study was generated extensive information that may be important for the starting point for other projects.

Therefore, it was important for all parties involved in this work, since the main objectives were successfully achieved.

CHAPTER 7. Bibliography

1. Continental [Internet]. [cited 2015 Dec 10]. Available from: http://www.continental-corporation.com/www/portal_com_en/themes/continental/history/
2. Continental [Internet]. [cited 2015 Dec 10]. Available from: http://www.continental-corporation.com/www/portal_com_en/themes/continental/history/1971_1995.html
3. Gent AN, Walter JD. The Pneumatic Tire. Rubber World. U.S. Department of Transportation; 2006. 18-170 p.
4. King EF, Clark S. Mechanics of Pneumatic Tires. Oxford University. 1981. 352 p.
5. Continental. Tyre Basics: Passenger Car Tyres. Tdc 06/2008. 2010;1–30.
6. Wulfhorst B, Gries T, Veit D. Textile Technology. Text Technol. 2006;315–20.
7. White JL, Bumm SH. Polymer Blend Compounding and Processing. In: Encyclopedia of Polymer Blends. 2011. p. 12–54.
8. Dick JS, Rader CP. Raw Materials Supply Chain for Rubber Products. Advanced Elastomer Systems. Munich: Hanser Publishers; 2014. 25-228 p.
9. Ebewele RO. Polymer Science and Technology. United States of America: Polymer science and technology; 2000. 12-58-315 p.
10. Coran AY. Vulcanization. The Science and Technology of Rubber. 2013. 337-381 p.
11. Wootton DB. The Application of Textiles in Rubber. Vol. 44, Rapra Technology Limited. 2001.
12. Rodgers B. Reinforcing Material in Rubber Products. Goodyear Tire Rubber Co. 2001;11–89.
13. Fung W, Hardcastle M. Textiles in Automotive Engineering. In: The Textile Institute. Cambridge: Woodhead Publishing Limited; 2001. p. 44–156.
14. Stevens MP. Polymer Chemistry: An Introduction. Third edit. Oxford University Press; 1999. 13-87 p.
15. Rodgers B, Waddell W. Tire Engineering. Fourth. The Science and Technology of Rubber. Elsevier; 2013. 653-695 p.
16. Lindenmuth BE. An Overview of Tire Technology. The Pneumatic Tire. 2006. 231-285 p.
17. Fangueiro R, Soutinho F. Yarn imaging and advances in measuring yarn characteristics. Woodhead Publ Ser Text. 2010;232–56.
18. Marques R. Dip improvement on textile reinforcement for tire application. Tese de Mestrado, Faculdade de Ciências da Universidade do Porto; 2014.
19. Horrocks AR, Anand SC. HANDBOOK OF TECHNICAL TEXTILES. Cambridge: Woodhead

Publishing Limited; 2000.

20. Pelton DA. Adhesive composition and method for adhering textiles to epdm rubber. WO01/68784A1, 2001. p. 1–26.

21. W. B. Wennekes. Adhesion of RFL-treated cords to rubber: new insights into interfacial phenomena. Ph.D. thesis, University of Twente, Enschede; 2008.

22. Takeyama T, Matsui J. Recent Developments with Tire Cords and Cord-to-Rubber Bonding. Vol. 42, Rubber Chemistry and Technology. 1969. p. 159–256.

23. Stammen E, Dilger K. Adhesive bonding of textiles: applications. Joining Textiles. Woodhead Publishing; 2013. 275-308 p.

24. Petrie EM. Adhesive bonding of textiles: principles, types of adhesive and methods of use. Woodhead Publishing Series in Textiles. 2013. 225-274 p.

25. Durairaj RB. Resorcinol: Chemistry, Technology and Applications. Springer; 2005.

26. Ferrero F. Solvent effect in grafting of liquid polybutadienes with maleic anhydride. Prog Org Coatings. 2005;50–5.

27. Stefanoiu F, Candy L, Vaca-Garcia C, Borredon E. Kinetics and mechanism of the reaction between maleic anhydride and fatty acid esters and the structure of the products. Eur J Lipid Sci Technol. 2008;441–7.

28. Engels H-W, Weidenhaupt H-J, Pieroth M, Hofmann W, Menting K-H, Mergenhagen T, et al. Rubber, 9. Chemicals and Additives. Ullmann's Encyclopedia of Industrial Chemistry. 2011.

29. Baxenden Chemicals Ltd. Urethane Surface Coatings – Blocked Isocyanates. Chemtura Corpuration. 2012;

30. Wicks DA, Wicks ZW. Blocked isocyanates III: Part A. Mechanisms and chemistry. Prog Org Coatings. 1999;148–72.

31. H. Hughes A, Topham A. Blocked Isocyanate. 5,246,557, 1993. p. 1–6.

32. Jin FL, Li X, Park SJ. Synthesis and application of epoxy resins: A review. J Ind Eng Chem. The Korean Society of Industrial and Engineering Chemistry; 2015;1–11.

33. D'Almeida JRM, Monteiro SN. Efeito da Variação da Razaão Resina/Endurecedor sobre a Resistência ao Impacto de uma Resina Epóxi. Polímeros Ciência e Tecnol. 1996;44–9.

34. Hamzah R, Bakar MA, Khairuddean M, Mohammed IA, Adnan R. A structural study of epoxidized natural rubber (ENR-50) and its cyclic dithiocarbonate derivative using NMR spectroscopy techniques. Molecules. 2012;10974–93.

35. Mohammad SF, Zainal N, Ibrahim S, Mohamed NS. Conductivity Enhancement of (Epoxidized Natural Rubber 50)/Poly(Ethyl Methacrylate)–Ionic Liquid-Ammonium Triflate. Int J Electrochem Sci. 2013;1–9.
36. Ismail H, Ooi ZX. The Effect of Epoxidized Natural Rubber (ENR-50) as a Compatibilizer on Properties of High-Density Polyethylene/Soya Powder Blends. Polym Plast Technol Eng. 2010;
37. Jones and G. K. Stylios. Joining textiles - Principles and applications. The Textile Institute and Woodhead Publishing; 2012. 223-347 p.
38. Zille A, Oliveira FR, Souto AP. Plasma Treatment in Textile Industry. Plasma Process Polym. 2014;1–34.
39. Shishoo R. Plasma technologies for textiles. The Textile Institute and Woodhead Publishing; 2007. 1-78-222 p.
40. Ebnesajjad S. Handbook of Adhesives and Surface Preparation: Technology, Applications and Manufacturing. Elsevier; 2010. 5-130 p.
41. Chruściel JJ, Leśniak E. Modification of epoxy resins with functional silanes, polysiloxanes, silsesquioxanes, silica and silicates. Prog Polym Sci. 2014;67–121.
42. Kash L. Mittal. Silanes and Other Coupling Agents, Volume 4. 1st ed. 2007.
43. Shin-Etsu Chemical Ltd. Silane Coupling Agents. 2015;1–24.
44. Test methods manual. Assoc Connect Electron Ind. (2):1–9.
45. Flores MS. One fits all – The unified dip solution recipe for. Tese de Mestrado, Faculdade de Ciências da Universidade do Porto; 2015.
46. Freitas A. Correlation between the reinforcement-to-rubber adhesion properties and latex dip formulations. Tese de Mestrado, Faculdade de Engenharia da Universidade do Porto; 2012.
47. ASTM - Standard Practice for Conditioning and Testing Textiles. In Annual Book od ASTM Standards. Continental- internal information; 2013.
48. Cordeiro P. Test method development for textile helix cord angle analysis. Tese de Mestrado, Faculdade de Engenharia da Universidade do Porto; 2016.
49. Diener electronic. Plasma Technology. Plasma-Surface-Technology. 2007;7–49.