

Chemical Engineering Integrated Master

Non Rubberized Cap-Ply Reinforcements

Master Thesis

by

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Abstract

This master thesis was developed at Continental - Indústria Têxtil do Ave, S.A. (C-ITA) in cooperation with Faculty of Engineering at the University of Porto (FEUP). C-ITA core business is the production of textile reinforcements for the rubber industry, specifically for tires produced by Continental Corporation.

Tires are complex objects that combine different reinforcing materials with rubber parts. Rubber provides adherence to the ground and gives the structure to the tire. However, since rubber is elastic, reinforcing materials are needed to hold the rubber parts within defined dimensional limits, especially when the tire is rolling at high speed and temperature. The layer responsible for the capacity to restrict expansion from centrifugal forces is cap-ply.

The introduction of textile reinforcement materials in a tire is a complex process. The cap-ply is made of a textile layer coated with rubber and then sandwiched between a rubber layer and a steel reinforced rubber layer. This project addresses a long-standing question: is it possible to remove the rubber coating layer from the cap-ply? In order to answer this question, and the other questions it was necessary to test textile materials traditionally used on this layer, nylon and hybrid cords of nylon and aramid, with the rubbers from layers under and above the cap-ply.

The results from the trials performed along these five months allowed to answer the principal question of the project: yes, it is possible to remove this layer of rubber. Further tests have to be performed to fully understand on underneath aspects of this unexpected though very relevant conclusion.

Key words: Tires; Reinforcement materials; Cap-Ply; Adhesion.

Resumo

Esta dissertação de mestrado foi desenvolvida na Continental - Indústria Têxtil do Ave, S.A. (C-ITA), em colaboração com a Faculdade de Engenharia da Universidade do Porto (FEUP). A atividade principal da C-ITA é a produção de reforços têxteis para a indústria de borracha, especialmente para pneus produzidos pelo grupo Continental.

Os pneus são objetos complexos, que combinam diferentes materiais de reforço com outros componentes de borracha. A borracha fornece aderência ao solo e permite que a estrutura do pneu se mantenha. No entanto, uma vez que é a borracha é um material elástico, são necessários materiais de reforço para sustentar os componentes de borracha dentro de limites dimensionais definidos, especialmente quando o pneu está a rodar a alta velocidade e temperatura. A camada responsável pela capacidade de limitar a expansão de forças centrífugas é o *cap-ply*.

A introdução de materiais de reforço têxtil num pneu é um processo complexo. O *cap-ply* é constituído por uma camada têxtil revestida com borracha que, de seguida, é ensanduichada entre uma camada de borracha e uma camada de aço reforçado com borracha. Este projeto aborda uma questão de longa data: é possível remover a camada de revestimento de borracha do *cap-ply*? Para responder a esta pergunta, e as outras questões, foi necessário testar os materiais têxteis tradicionalmente utilizados nesta camada, o *nylon* e as cordas híbridas de *nylon* e aramida, com as borrachas das camadas abaixo e acima do *cap-ply*.

Os resultados dos ensaios realizados ao longo destes cinco meses fizeram com que fosse possível responder à principal questão do projeto: sim, é possível remover esta camada de borracha. Outros testes devem ser realizados para compreender plenamente os aspetos desta inesperada, embora muito relevante, conclusão.

Palavras-chave: Pneus; Materiais de reforço; *Cap-ply*; Adesão.

Statement

I declare, on oath, that this work is original and that all non-original contributions were properly referenced with identification of the source.

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Glossary and Acronyms

Glossary

Breaking force: Maximum force needed to break a cord, in Newton.

Decitex (dtex): Linear density in grams per 10000 meters of fiber.

Elastomer: Molecules of irregular structure, weak intermolecular attractive forces and very flexible polymer chains.

Elongation at break: Percentage of elongated cord on the breaking time of the cord.

Glass temperature (T_g): Temperature at which the amorphous domains of a polymer take on the properties of the glassy state: brittleness, stiffness, and rigidity.

Young modulus: Also known as elastic modulus, it is given by the initial linear portion of the curve, within which Hooke's law is obeyed.

List of Acronyms

ASTM	American Society for Testing and Materials
C-ITA	Continental - Indústria Têxtil do Ave
DOE	Design of Experiments
FEUP	Faculty of Engineering of University of Porto
ITA	Indústria Têxtil do Ave, S.A.
LDU	Laboratory Dipping Unit
PET	Polyethylene terephthalate
RF	Resorcinol Formaldehyde
RFL	Resorcinol Formaldehyde Latex
VP	Vinylpyridine

1 Introduction

1.1 Framework

Founded in 1871 in Hannover, Germany, Continental is divided in five major divisions: Chassis & Safety, Powertrain, Interiors, Tires and ContiTech. Since the beginning of the production of plane tires for passenger cars, Continental Corporation has constantly evolved to meet the continuous demand of the automotive industry by studying and applying new techniques, products and equipments.

Indústria Têxtil do Ave, S.A. (ITA), was founded in 1950 in Lousado, Portugal, and became part of Continental Corporation in 1993. Continental - Indústria Têxtil do Ave, S.A. (C-ITA) has as main business the production of textile reinforcements for the rubber industry, specifically for tires produced in Continental. (Continental Corporation, 2014)

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 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. (Lindenmuth, 2006)

The history of pneumatic tires started in the late 1800's in Great Britain as an upgrade of solid rubber tires. As the time passed, pneumatic tires have evolved and in early 1920's, a larger balloon tire was introduced in the market. An improvement of this kind of tires was the tubeless tires, introduced in the 1950's. Since then, the technology in tires has been constantly evolving. Nowadays, it is possible to find three types of tires: diagonal bias, belted bias and radial. The main difference between bias and radial tires is that bias tires have body ply cords that are laid at angles substantially less than 90° to the tread centreline and radial tires body ply cords are laid radially from bead to bead, nominally at 90° to the centreline of the tread. (Lindenmuth, 2006)

Diagonal tires are still used today, especially in trucks and agriculture vehicles. They have a simple construction and they are easy to manufacture. Belted bias are tires with belts (breaker plies) added in the tread region and this belts have the function of restrict the expansion of the body carcass, stabilizing and strengthening the tread region. Belted bias improve wear and handling (due to the stiffness in the tread). Implemented in the 1970's, radial tires deflect more easily under load, generating less heat, giving lower rolling resistance and better high-speed performance. (Lindenmuth, 2006)

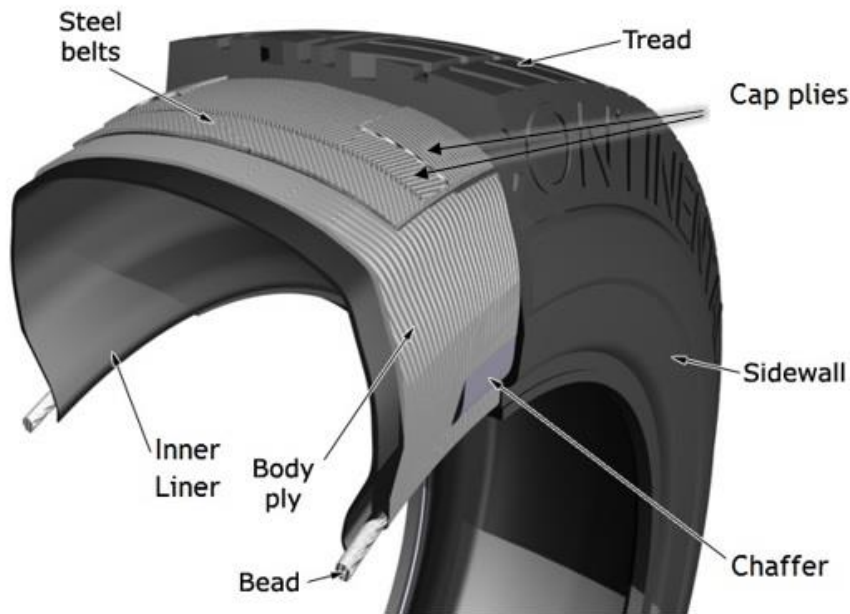


Figure 1 - Radial Tire Construction (adapted from (Conti-Online, 2014))

As it is possible to see in Figure 1, tires are composed by many layers and all of them have a specific chore. The inner liner is a thin compound that is capable to improve the air retention in tubeless tires, lowering the air permeability through the tire. The following component is the body ply, and this section is the rubber coating that encapsulates the radial textile reinforcements. This layer wrap around the bead wire bundle, passing radially across the tire. Providing sidewall impact resistance and strength to contain the air pressure, the body ply is usually used as one layer, however, in larger sizes is common to use two body ply layers. (Lindenmuth, 2006)

To serve as an anchor to inflated tire to the wheel rim is the bead bundles. This section is individual bronze plated wires coated by rubber. On top of the bead bundles are applied the bead fillers and depending on the filler height and hardness, this affects tire ride and handling characteristics. The bead fillers also have the capacity to fill the void between the inner body plies and the body ply ends on the outside. The sidewall rubber has the capacity to protect the body plies from impact, abrasion and flex fatigue. The rubber compound is designed to resist cracking (due to ozone, oxygen, heat and UV radiation). To improve tire handling and stability, some reinforcements are added to the sidewall. These components are also called as chippers or flippers. (Lindenmuth, 2006)

On the top of the body ply and under the tread, two steel belts are applied in opposite angles of one another. These two layers restrict the expansion of the body ply cords, provide impact resistance and stabilize the tread area. In some cases, fatigue resistant components are added between the belts, near the edges of the top belt. These components have the capacity to reduce the interplay shear at the belt edge as the tire rolls and deflects. The

tread is the responsible section to provide the traction for driving, cornering and braking. The rubber compound in this section is formulated to offer a balance between wear, handling, traction and rolling resistance. In cooperation, the rubber compound and tread design should have a good performance in several driving conditions, such as wet, snow or dry surfaces, and also meeting customer expectations for wear resistance, good ride quality and low noise. In the tread area there is also the subtread and the undertread. The subtread improves rolling resistance and can also be used to fine-tune ride quality, handling and noise. The undertread is used to improve adhesion of the tread and to stabilize plies during tire assembly. (Lindenmuth, 2006)

Cap-ply or cap-strips are commonly used in higher speed tires. They are applied on top of the steel belts and they have the capacity to restrict expansion from centrifugal forces during the high speeds. In some cases, the cap-ply is used only to cover the belt edges. (Lindenmuth, 2006)

The main focus of the Continental Corporation is to increase production while simultaneously reducing the costs of production and increasing the performance and safety of the tire, always having environmental safety in mind.

At the present time there is no scientific knowledge that supports the relevance of the supplement of rubber in the textile reinforcement. These project results of the necessity to evaluate the importance of the rubber used in the cap-ply.

1.2 Project Goals

The main goal of this project is to eliminate rubber from the cap-ply, reducing rolling resistance and the total weight of the tire and, therefore, reducing the total CO₂ emissions of the car. Furthermore it is proposed to study the interactions between different types of components by exploring diverse combinations.

1.3 Work Contributions

The main objective of this project, as stated earlier, is studying the possibility of eliminating the rubber coat of the textile reinforcement on cap-ply targeting the reduction of manufacturing costs, the total weight of the tire with direct positive environment benefits.

Since this was the first approach to this project, all the obstacles inherent to it were overcome. The results from this project correspond to all initially proposed goals.

1.4 Thesis Organization

This document is organized in 7 chapters. A brief explanation of each chapter is presented.

1. **Introduction:** description of the Continental Corporation as well as a description of tire industry and technology.
 2. **State of the Art:** description of scientific knowledge about reinforcing materials, chemical treatments on fibers and test methodology.
 3. **Materials and Methods:** explanation of all materials used along this master thesis, and also the explanation of the procedure of test methodology used.
 4. **Results and Discussion:** exhibition of the results of the trials performed and their discussion.
 5. **Conclusions:** presentation of the main conclusions of this master thesis.
 6. **Project Assessments:** information about the achievements of the proposed goals for this project, limitations and suggestions of future work.
 7. **References:** presentation of all references used along this project.
- Appendix:** presentation of additional information.

2 State of the Art

2.1 Reinforcement Materials

The most important part of a tire is its reinforcement, since it provides the strength and stability needed containing, as well, the air pressure. There are three types of reinforcing materials: textile, metal and rubber compounds. (Lindenmuth, 2006) Due to the relevance for this project, metal reinforcements are not going to be discussed.

2.1.1 Textile

One of the most commonly used synthetic polymers in the world is **Nylon**. First produced in 1935 by Wallace Carothers at DuPont Experimental Station, nylon was introduced as a fabric, becoming the first successfully synthetic thermoplastic polymer. Also known as polyamide, nylon is made out of repeating units linked by amide bonds. Initially it was intended to replace silk when it became scarce during World War II, so it was used in parachutes, flak vests and it was also used in many types of vehicle tires. (Palmer, 2001) Nylons are long chain polymers produced by continuous spinning or melt spinning and they are used in applications requiring toughness, chemical inertness, durability, electrical insulating properties, abrasion, low frictional resistance, and self-lubricating properties. Having this qualities, nylon is used in radial passenger tires as cap, or overlay ply, or belt edge cap strip material, with some limited applications as body plies. (Lindenmuth, 2006)

Aramid is the term used to describe the group of aromatic polyamides developed to improve some properties of nylon, namely, the flammability and heat resistance. The first commercial application was a meta-aramid fiber introduced by DuPont in early 1960's under the name Nomex. After some investigation work, a para-aramid emerged under the name Kevlar. Aramids are prepared by the reaction between an amine group and a carboxylic acid halide group, and are produced by spinning the dissolved polymer into a solid fiber from a liquid chemical blend. This material has evolved and has an exceptional strength-to-weight property, a high Young's modulus, high tenacity, low creep and low elongation at break. (Ebewele, 2000)

Rayon is the first semi-synthetic fiber made from the cellulose fiber and it was primarily produced in the 1890's by Georges Audemars. This material can be produced by four different methods: nitrocellulose, acetate, cuprammonium and viscose. The main difference between these methods is the solvent used in each one. It is produced by wet spinning and has some disadvantages, like being expensive and having some environmental manufacturing issues, although there are more advantages, since it is heat resistant, have good handling

characteristics and stable dimensions. Because of this characteristic, this material is used in body ply cord and belt reinforcement. (Lindenmuth, 2006)

Polyethylene terephthalate (PET) is a thermoplastic polymer resin commonly used in synthetic fibers and this polyester was patented in 1941 by DuPont. In its natural state, PET is a semi-crystalline resin, however depending on its production it acquires other physical properties. PET is produced from ethylene glycol and dimethyl terephthalate or terephthalic acid, since it can be produced by two different processes: reaction with dimethyl terephthalate in a two-step process or by reaction with terephthalic acid in a one-step process. It is produced by spinning or melt spinning and is mostly used in radial body plies and has as an advantage its high strength with low shrinkage, low heat set and low cost, however, when compared with nylon or rayon, PET it is not as heat resistant. (Lindenmuth, 2006)

Figure 2 presents the stress/strain properties of the fibers reinforcements referenced before.

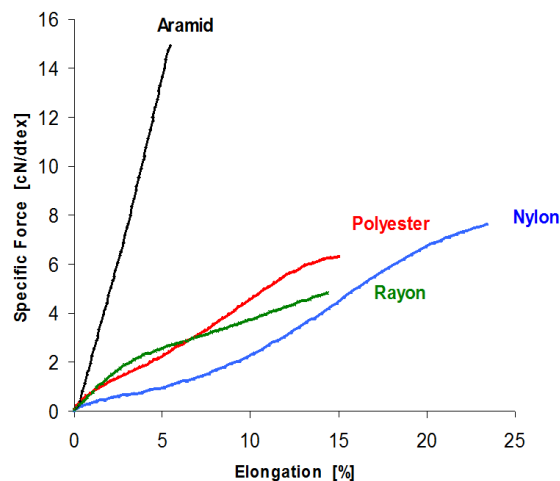


Figure 2 - Stress/Strain properties of different fibers (adapted from (Wahl, 2006))

Hybrid Cords are the combination between two or more different types of yarns twisted together. This combination will provide a new set of properties that in other way were impossible to obtain. With this new technology it is possible to have a cord construction with better properties and with lower production cost. Having as an example the aramid-nylon hybrid cord, this construction will have better properties than the aramid-aramid construction. It will have an improved fatigue resistance, higher elongation, lower raw material cost and controlled shrinkage. When compared with the nylon-nylon construction, the hybrid cord will have a lower shrinkage, improved handling and cornering stability, speed performance and rolling resistance. (Pinto, 2013)

In Figure 3 is it possible to observe the schematic structure of a hybrid cord.

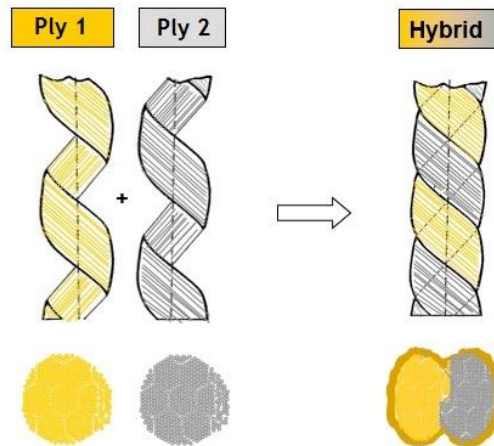


Figure 3 - Structure of a hybrid cord (adapted from (Wahl, 2006))

2.1.2 Rubber

Over the years, the mixture of substances to improve rubber characteristics has evolved. There are many additives and some of them have multiple functions, and because of that, it became more important to select the correct products and more difficult to understand each product available. Currently, rubber products are well-defined substances, personalised for a specific requirement and composed of detailed raw materials. (Rubber Handbook, 2004)

Any substance that is used to improve the processing characteristics of the rubber without affecting significantly its physical properties is called processing additives. They have the capacity to influence chemically or physically the nature of the composites produced. In the beginning the main processing additives used were mostly homogenisers, peptizers and lubricants. Throughout time, the importance of this kind of materials has grown, due to the fast development of modern processing of rubber articles and to the increasing of quality requirements. (Rubber Handbook, 2004)

Lubricants are one of the largest groups of the modern processing additives. The essential raw materials for this kind of products are the ones that improve the flowability of rubber, for example, low molecular weight polyethylene or polypropylene, because of their wax-like character. All lubricants for rubber compounds associate internal and external lubricating effects. This influence depends not only of their chemical structure but also on the characteristics of the polymer they are used in. However, the solubility in the elastomer is the determining factor. When a product is acting as an internal lubricant, it will serve as a bulk viscosity modifier and improve filler dispersion. When acting as an external lubricant, this product has the capacity to improve slip and reduce friction between the elastomer and the metal surfaces of the processing equipment. When used in higher dosage, lubricants can lead to an over concentration and to a subsequent blooming. (Rubber Handbook, 2004)

Peptization and Mastication are process stages where viscosity of rubber is reduced to such a level, which facilitates additional processing or even makes possible to have the main processing. Chemical peptization conceives a faster incorporation of fillers and other compounding ingredients, improving their dispersion. Nowadays, most of synthetic rubbers are supplied with easy to process viscosity levels, and because of that, peptizers are mostly used in natural rubber. (Fries & Pandit, 1982)

Homogenizing Agents are resin based mixtures with the capacity to improve the homogeneity of elastomers that are difficult to blend. They also assist on the incorporation of other compounding materials. These products demonstrate good compatibility with several elastomers and facilitate blending by softening and wetting the polymer interfaces. This type of components are able to make polymer blends to coalesce more easily, making the mixing more effective and consequently reducing mixing times. They also promote blending of elastomers, batch to batch uniformity, filler incorporation and dispersion, and they also increase green tack of many compounds and the efficiency of tackifying agents. Homogenizing resins are divided into hydrocarbon resins (applied as fillers and tackifiers), rosins (applied as emulsifiers and tackifiers), phenolic resins (applied as reinforcements and fillers), coumarone resins (applied as dispersing agents, fillers and tackifiers), petroleum resins (applied as viscosity reducers, fillers and tackifiers), copolymers (applied to help the processing of high hardness polymers), terpene resins (applied ageing performance and resistance against oxidation), asphalt and bitumen (applied as fillers, tackifiers and viscosity reducers). (Rubber Handbook, 2004)

Dispersing Agents have a way of action very similar to the lubricants (described previously) since they are mostly fatty acid derivatives. This components improve dispersion of solid compounding materials, reducing mixing time and they also have a helpful influence on the consequent stages of the processing. The product produced between dispersing agents and fillers is one with low melting point, which helps on the incorporation, so this two components are frequently added together. (Miscellaneous Ingredients, 1993)

Tackifiers are chemical substances used to improve the tack of most of synthetic rubbers, since they are typically less tacky than natural rubber. They are usually low-molecular weight compounds with high glass transition temperature. However, they tend to have low molecular weight, glass transition and softening temperature above room temperature, providing them with suitable viscoelastic properties. (Heinrich, Kluppel, & Vilgis, 2007) This substances lead to the improvement of uncured ply adhesion and facilitate processing, since the viscosity of rubber is reduced. (Rubber Handbook, 2004)

Plasticizers are low molecular weight compounds added to polymeric materials such as adhesives or plastics, to improve their flexibility. In addition, they enhance softness, adhesion

and also have the capacity to lower the glass temperature (T_g). These components interact with the polymer on the molecular level, speeding the viscoelastic response or increasing chain mobility. Plasticizers can be classified as external or internal. An external plasticizer is introduced to a resin or rubber compound and an internal plasticizer is incorporated during the polymerization process. Besides this classification, plasticizers can also be divided as primary or secondary. A primary plasticizer is one that is more compatible to a certain resin than a secondary one. When combined, it is possible to have a reduction of costs and an improvement in electrical and low temperature properties. (Wypych, 2012)

The process of conversion of a raw rubber into a lightly cross-linked network is called **vulcanization**. Most rubbers are soft and have a low modulus, after vulcanization they tend to have a higher stiffness, strength, elasticity and to resist to solvent swelling. The most common method of vulcanization is sulphur vulcanization, especially in natural rubber. The use of various metal oxides (zinc oxide in particular) speeds up the process, and these organic accelerators are almost universally used in addition, as they not only ensure that the sulphur is used efficiently but they also give faster rates of vulcanization. When vulcanization is very active, it is necessary to prevent premature vulcanization during the compounding and shaping stages. This tendency should be reduced with the use of a retarder. When the vulcanization time is too long, there is a diminution in tensile strength or modulus. (Alger, 1997)

2.2 Resorcinol Formaldehyde Latex (RFL) Treatment

Unlike natural fibers such as cotton, man-made fibers have a smooth surface, and because of that there is no connecting of filaments. The strength of adhesion between rubber and man-made fibers is very low because there is an important difference in polarity between the textile reinforcements and the rubber matrix. This fact created the need of a new mechanism to improve the strength of adhesion, the RFL treatment. (Wennekes, 2008) The schematic representation of this treatment is present in Figure 4.

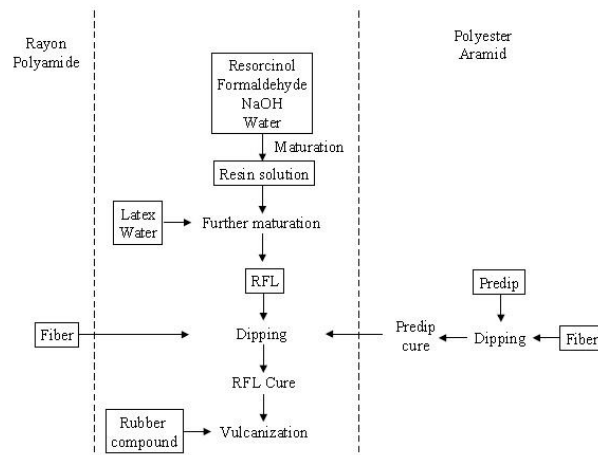


Figure 4 - Schematic representation of the RFL treatment (Adapted from (Wennekes, 2008))

The RFL impregnating emulsion (dip) is composed of a rubber latex on a solution of resorcinol and formaldehyde in water. This emulsion is prepared in two stages. The first stage is the preparation of the aqueous solution of resorcinol and formaldehyde. In this solution is also added sodium hydroxide or ammonium hydroxide to make the mixture basic. This first stage will increase the polarity and mechanical properties of the textile. The second stage is the addition of a solution of latex and water into the solution made in the first step. The latex alone would provide a good interaction with rubber compound, but not with the fiber. In Figure 5 it is possible to observe the proposed RFL chemical structure. (Wennekes, 2008)

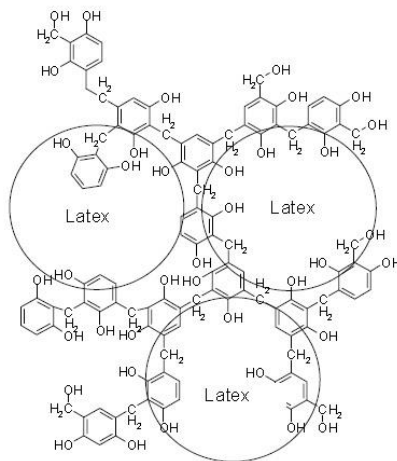


Figure 5 - RFL chemical structure. (Adapted from (Wennekes, 2008))

There are some important parameters to consider regarding the influence in the adhesion rubber to textile reinforcement. The main parameters are: formaldehyde to resorcinol ratio, resin to latex ratio, type of rubber latex and dip pick-up. (Wennekes, 2008)

The formaldehyde to resorcinol ratio is a very important parameter since increasing this ratio increases the degree of condensation and branching. By increasing the amount of formaldehyde, there is an increasing of methylol formation. Methylol functionalities increases

the interactions on the fiber side of the dip by hydrogen bonds, for example. Several studies were made, and all of them showed that there is an optimum value of this ratio. (Wennekes, 2008)

When resin is added to latex in the dip, the strength of adhesion increases significantly. This ratio is a very important one, because if latex is applied to the cord by itself, the bonding force would be very low, and several tests showed that there is an optimum ratio between resin and latex. (Wennekes, 2008)

Although there is no scientific explanation for the fact, it is believed that the vinylpyridine monomer is essential for a good rubber adhesion. For that, the most commonly used latex is based on a terpolymer of styrene, butadiene and vinylpyridine (VP), VP-latex. There are three possible explanations for this good performance: the high polarity of VP-monomer (increasing the interactions with the fiber), the high strength of vulcanized VP-latex, the fact that VP-monomer improves the interactions resorcinol formaldehyde resin. (Wennekes, 2008)

The dip pick-up is the amount of impregnating emulsion on the cord after the impregnating process. This amount of solution in the cord will make the adhesion increase up to a saturation point, approximately 7 wt%. (Wennekes, 2008)

Some fibers (like polyester or aramid) don't have many reactive functional groups, therefore, the standard RFL solution would not have a good adhesion. The solution for this problem was to create a two-step impregnating process, in which the first step would be a solution with isocyanates and epoxy (that improves the film formation). (Wennekes, 2008)

When adding isocyanates to latex, there is a significant improvement of the adhesion to the rubber. These isocyanates must be added in the form of blocked isocyanates, because of its fast reaction in water and toxicity. Therefore, after the reaction of isocyanates with blocking agents, the "new" compounds are stable at normal temperatures, and above 100 °C, they dissociate, originating free isocyanates locally. (US Patent No. 4462855 A, 1984)

2.3 Test Methodology

There are several test methods to use in textile and rubber reinforcements, however, concerning the study of adhesion between rubber and textile reinforcements, the key test methods are the Peel adhesion and H tests.

2.3.1 Peel adhesion test

The peel adhesion test is frequently used when studying tire cords or tire cords fabrics. It covers the determination of peel adhesion of textile reinforcements that are bonded to rubber compounds and it is applicable to either woven or parallel cord textile structures. This test method can be applied not only to textile reinforcements but also steel cords, and it is

used to evaluate the adhesives on the textile reinforcements, metallic coatings on steel cords and the process of adhesive reaction on the cord. (ASTM International, 2004)

This test method can be applied to single cords or to woven fabric. The single cords method is widely used in laboratories, due to its ability to facilitate the study of a large number of adhesion variables at minimum cost. It is considered a good method because it allows a comparison of variables on adhesion, since it provides the peel force value over several linear centimetres of cord and the overall appearance of the peeled area. The woven fabric test is used for a fast adhesion testing on the textile fabric that is being produced in large quantities. (ASTM International, 2004)

The samples for the peel adhesion test, should be assembled in the following order, as seen in Figure 6: Calendered Reinforcing Fabric, Rubber Compound and Textile Sample. In the middle of the sample must be inserted a foil to allow the separation of the mould using the grips of the testing device. (ASTM International, 2004)

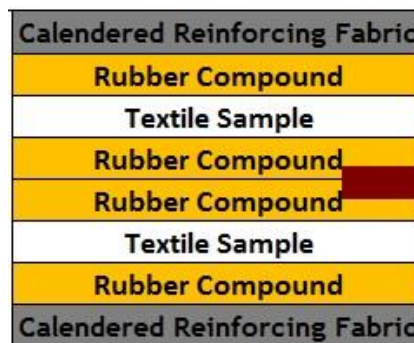


Figure 6 - Assembly of the components into a pad

As said before, the peel adhesion test has as result several information that must be taken in consideration, such as average force of rubber/cord interface, adhesion force and the appearance rating of the peeled area. The average force of rubber/cord interface is given by multiplying the average level of force by the distance to produce this area. The adhesion force is the average strap peel force of the specimen in newton units. The determination of the appearance of the peeled area is judge visually by rating from 1 to 5 the coverage of the fabric, being 1 the lower value and 5 the maximum one. (ASTM International, 2004)

2.3.2 H test

The H test is a test method that is able to cover the capacity of adhesion of reinforcing cords that are bonded to rubber compounds. This technique is used to evaluate tire cords and there are many variables that can contribute to the success or failure of this method, such as fiber type, construction of the cord, adhesive type, cure and application procedure as well as the rubber type, cure and thickness. It is applicable to textile cord structures from natural or manmade fibers. (ASTM International, 2009)

This method has been considered to measure the force required to pull a cord in the direction of its axis from one of the two strips of rubber in which the cord is inserted. This test is commonly used on industry as an acceptance testing of reinforcing cords, however, the precision of this method is incomplete, and, because of that and to determine if there is a statistical bias, more tests are recommended. (ASTM International, 2009)

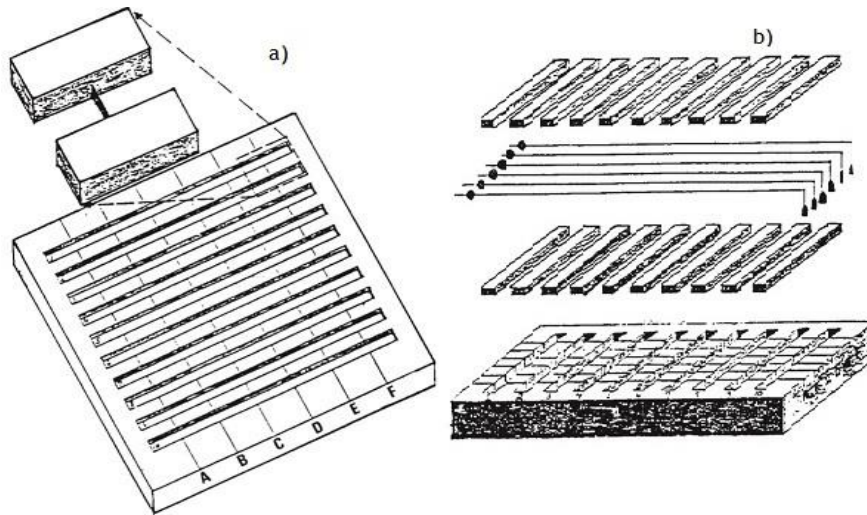


Figure 7 - H test specimen (a) and mould loading (b) (adapted from (ASTM International, 2009))

As it is possible to observe in Figure 7, the test mould has the cord specimen inserted between two layers of rubber compound and this sample forms a model that resembles the letter H. The preparation of the samples should be very fast and meticulous. It is used a pre heated mould and that fact will alter the specific curing conditions of the rubber. The cords ought to be placed with sufficient overhang that allows the attaching of the masses (50 g) and a knot in each one. It is also needed a special care to prevent the loss of the cord twist. (ASTM International, 2009)

The “H” samples are tested in a tension testing machine with special grips. This method allows measuring the adhesion of thin cords with a linear density of less than 6000 dtex. As a result, it is possible to have the shearing force acting in the rubber to cord interface. (ASTM International, 2009)

2.3.3 Other tests

Besides the test methods presented before, there are many other, such as T test, modified T test, modified peel test, combination of peel and T test and the unwinding test. The most commonly used method is the T test, and this trial have the capacity to assess the force required to pull a cord from a block of rubber, in the direction of its axis. The property measured is the shearing force in the cord to rubber interface. (ASTM International, 2010)

The modified T test has the same testing conditions as the traditional method, however the rubber is vulcanized without pressure. This test method measures also the shearing force. In the modified peel test, the mould has only a strip of fabric pressed between the thermoplastic elastomer and this test measures the force to pull of the elastomer from the fabric. By combining the modified T test and the modified peel test, under high temperature and pressure, it is possible to have the pull out and pull off forces. The unwinding test measures the force needed to unwind the cords wrapped on the adhesive. (Flachenecker, A., 2001)

2.3.4 New peel test

Based in an already existent test method, this adaptation of the T peel test provides information of the interactions between the rubber and the textile reinforcements. The main focus of the T peel test is to determine the relative peel resistance of adhesive bonds between flexible adherents. The test mould is made in a very similar way to the peel test one, though this mould have no textile reinforcement trapped in it, as it is possible to observe in Figure 8. It consists in two flexible adherents bonded together. (ASTM International, 2001)

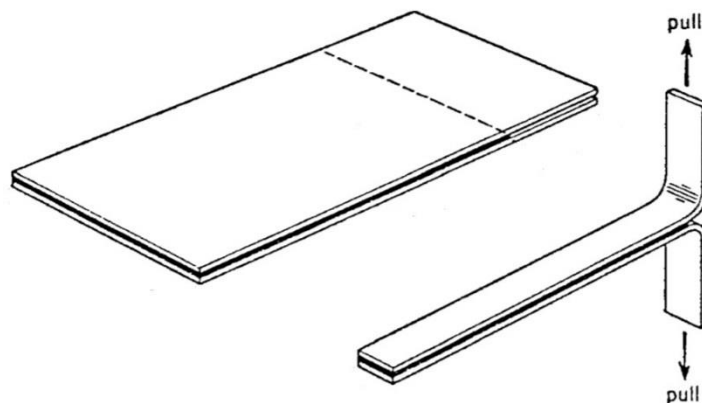


Figure 8 - T peel test panel and test specimen (adapted from (ASTM International, 2001))

Instead of having the two flexible adhesives bonded together, the new test method is the combination of this T peel test and the peel test, having the textile reinforcements in between the rubber compounds, as it is possible to observe at Figure 9. This alternative test makes possible to confirm the adhesion between the different combinations of rubber.

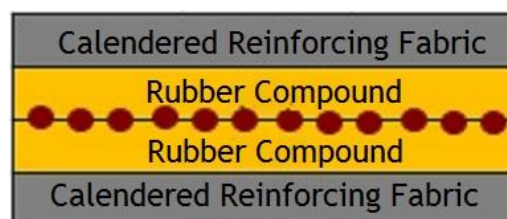


Figure 9 - Component assembly of the new peel test method

3 Experimental

This chapter describes all materials used, the methodology and technical applied throughout this master thesis.

3.1 Materials

Nylon

As mentioned in Chapter 2, nylon is a polyamide with great characteristics for applications on automotive industry, especially as textile reinforcement for tires. In cap-ply, nylon used has as typical load/elongation curve as represented in Figure 10. This curve provides relevant information, the most important one being the breaking force. For the impregnated cord of nylon used in cap-ply, the breaking force is typically ca. 150 N.

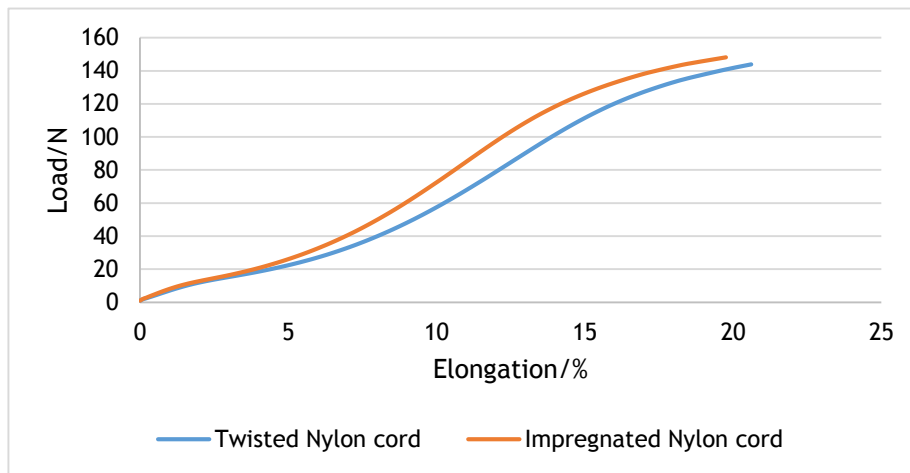


Figure 10 - Load as a function of elongation curve for the Nylon cord used

There are some other important characteristics, such as shrinkage, shrinkage force, dip pick-up and adhesion, which typical values are given in Table 1.

Table 1 - Characteristics of impregnated Nylon cord.

Properties	Standard Value
Shrinkage	5 %
Shrinkage Force	4 N
Dip pick-up	5.5 %
Adhesion	190 N

Hybrid Cord

Hybrid cords are the combination of different types of yarns twisted together, providing excellent properties in no other way possible to obtain. In cap-ply, the hybrid cords used have

as typical load/elongation curve as represented in Figure 11. For the impregnated hybrid cord used in cap-ply, the breaking force is typically ca. 300 N.

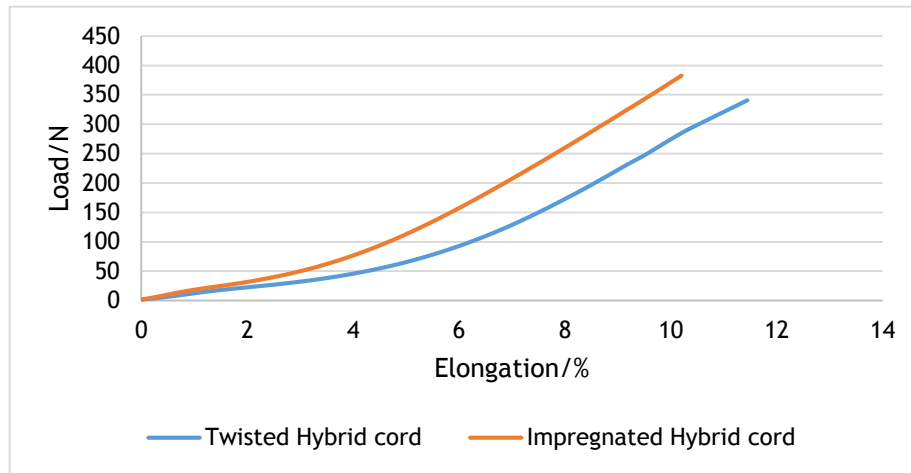


Figure 11 - Load as a function of elongation curve for the hybrid cord used

The shrinkage, shrinkage force and adhesion are also very important characteristics, which values are given in Table 2.

Table 2 - Characteristics of impregnated hybrid cord.

Properties	Standard Value
Shrinkage	4 %
Shrinkage Force	5 N
Adhesion	170 N

Rubber

Nowadays, the rubber used in the cap-ply skim coat is type C. The component from the layer below the cap-ply, the belt skim compound, is type A and the compound from the layer above the cap-ply, the tread, is type B. The main difference between these three components is their composition. However, type C and type A rubber parts are very similar to each other, when compared to type B rubber, since this has no resorcinol. The importance of this parameter will be discussed in Chapter 4.

When it comes to physical properties, all three rubbers show very similar behaviours. All rubbers utilized in this project are currently used in all passenger and light truck tires.

3.2 Laboratory dipping unit and pressing device

Laboratory Dipping Unit (LDU) is used to study the dipping process without interfering to production process. This machine was used during this project to simulate the industrial production of impregnated cords to cap-ply reinforcements, and to optimize the parameters that influenced the most the adhesion between rubber and reinforcement.



Figure 12 - Laboratory dipping unit

As it is possible to observe in Figure 12, the greige cord on the spool goes through the 1st bath and then the temperature and stretch level are controlled at the oven zone. The residence time in each oven is controlled by the speed and by the number of turns inside the oven. The stretch level is controlled by the difference of the rotating speed of the rolls, placed before and after each oven.

A hydraulic pressing device is used to make the vulcanization. In order to have a proper vulcanization, it is required that the press reaches 170 °C and, after stabilization, the test mould is subjected to a constant press force of 4 kN for 10 minutes. The hydraulic press used in this project is in Figure 13.



Figure 13 - Hydraulic press used

3.3 Procedure

Peel Adhesion Test Method

The peel adhesion trials were executed according to standard ASTM D4393-04. The samples preparation was performed on the hydraulic press and tested on a tensiometer device. Before testing, the samples have to be conditioned for at least 3 hours and pre-heated at 120 °C for 30 min \pm 30 s.

H Test Method

The samples from the H test were prepared according to standard ASTM D4779-09. The preparation of the samples was performed in the hydraulic press and then the samples were tested in a tensiometer device. Before testing the samples, they have to be conditioned for at least 3 hours.

New Peel Test Method

The testing procedure for the new test method was similar to the one used in the peel adhesion test.

3.4 Design of Experiments (DOE)

The design of experiments has as main goal define what data, in what quantity and in what conditions should be gathered during an experiment, satisfying two major goals: higher statistical precision possible in the response and the lowest time.

It is therefore a technique of extreme importance for the industry since its use allow more reliable results, saving time. Its application in the development of new products is very important, since it is necessary to have a higher quality of test results. The design of experiments will ensure that the performed trials provide valuable data that can be considered and from where it is possible to make better decisions.

The two textile reinforcements used in cap-ply are nylon and a hybrid construction of nylon-aramid, and to simulate rubber elimination from the cap-ply, the textile reinforcement was directly placed between the two layers of rubber from the tire belt and the tread. For this reason, this project considers three rubber types, the cap-ply rubber, type C, the tire belt rubber, type A, and the tread rubber, type B.

As said previously, the most commonly used test methods are the peel adhesion and the H test. The implementation of the new test method in this trials helps to understand the failures of the peel adhesion trials. So, in this case, it is needed to do three different designs, one for the peel adhesion test, one for the H test and one for the new test method. Since it is necessary to do all the trials, the selected DOE for the three designs is the full factorial

design. A full factorial design allows the measurement of the response variable in all possible combinations of all factor levels.

For the peel adhesion test there are three categorical factors, the three rubber types; there were considered four levels. The number of experiments is then $3^4 = 81$. However, since order is not important some of the generated combinations are similar and can be eliminated. The final number of different trials is 12.

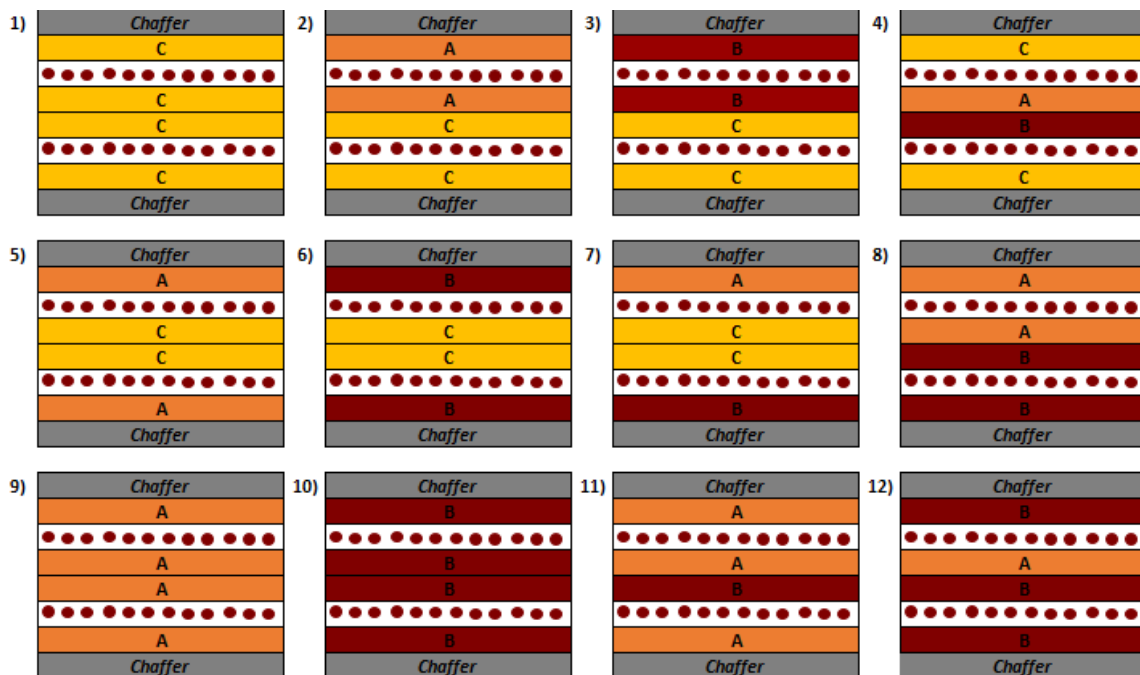


Figure 14 - Schematic representation of the trials performed for peel adhesion

At Figure 14 are the result trials of the DOE for the peel adhesion test. For these trials, the references to consider are trials 1, 9 and 10. These trials are the ones that provide the information about the interactions between the rubber and the textile reinforcement, without any other interference, i.e. these trials are the comparison base of all other trials.

A description of the trials performed for the peel adhesion test will be presented next:

- Trial 1 - This trial is the reference for rubber C;
- Trial 2 - Provides information about the interaction between rubber C and A;
- Trial 3 - Delivers the interaction between rubber C and B;
- Trial 4 - This trial provides the interactions between the two middle layers (containing rubbers A and B) with the edge layers (containing rubber C);
- Trial 5 - This trial assess the interactions between the two middle layers (containing rubber C) with the edge layers (containing rubber A);
- Trial 6 - This trial evaluate the interactions between the two middle layers (containing rubber C) with the edge layers (containing rubber B);

- Trial 7 - Provides interactions between the two middle layers (containing rubber C) with the edge layers (containing rubbers A and B);
- Trial 8 - Provides the interaction between rubber A and B;
- Trial 9 - This trial is the reference for rubber A;
- Trial 10 - This trial is the reference for rubber B;
- Trial 11 - This trial provides the interactions between the two middle layers (containing rubbers A and B) with the edge layers (containing rubber A);
- Trial 12 - This trial provides the interactions between the two middle layers (containing rubbers A and B) with the edge layers (containing rubber B);

Trials 2, 3 and 8 allow assessing the interactions between rubbers, when compared with the reference arrangements. The interface role can be assessed comparing reference trial 1, with trials 5, 6 and 7, and when comparing reference trials 9 and 10, with trials 4, 11 and 12.

For the H test, there are the same three rubbers, but since it is not possible to make mixtures of rubbers, it is only possible to make three trials. At Figure 15 are the result trials of the DOE for the H test.

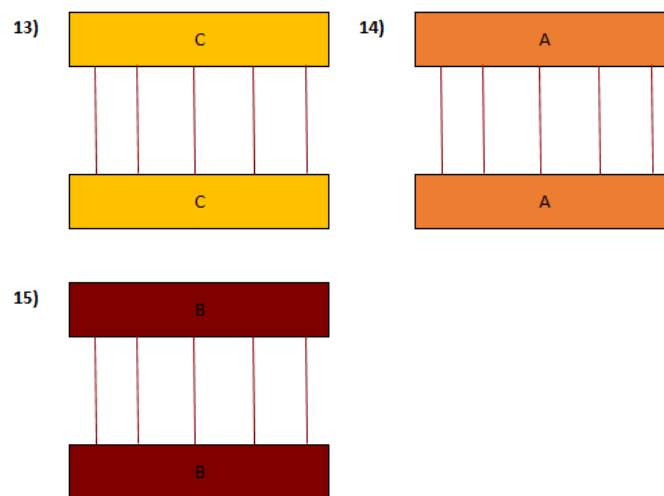


Figure 15 - Schematic representation of the trials performed for H test

For the new peel adhesion test there are three categorical factors, the three rubbers, and two levels, the two levels of rubber in this type of trials. The result is $3^2 = 9$, however, the order is not important, so the repetitions are excluded, resulting in 6 different samples.

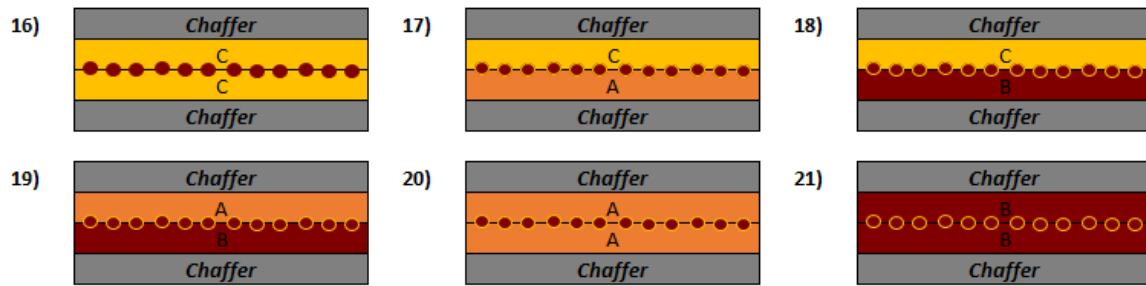


Figure 16 - Schematic representation of the trials performed for the new test method

At Figure 16 are the result trials of the DOE for the peel adhesion test. For this test method, the base references are the trials 16, 20 and 21. The other trials allow the comparison of the interfaces with the base references.

A description of the trials performed for the new peel adhesion test will be presented next:

- Trial 16 - This trial is the reference for rubber C;
- Trial 17 - Provides information about the interaction between rubber C and A;
- Trial 18 - Delivers the interaction between rubber C and B;
- Trial 19 - Assess the interactions between rubbers A and B;
- Trial 20 - This trial is the reference for rubber A;
- Trial 21 - This trial is the reference for rubber B;

To improve the precision of the trials measurements were performed 5 times.

4 Results and Discussion

This work assesses the possibility of not using the rubber coat on the cap-ply textile. The textile was treated with different dips before being made in contact with upper and down rubber parts and the adhesion of these two parts to the textile is assessed.

Emulsion I (dip I) was the target of the first set of tests since it is the currently used impregnating emulsion for nylon cords. Emulsions I and III (dip III) are made of water, RF resin, VP latex, ammonia and formaldehyde. Emulsions II (dip II) and an experimental emulsion made consist of the same components as dip I and III, however in these emulsions isocyanates are added. The pre-activating solution is composed by water and isocyanates. Emulsion II is similar to emulsion III but with the pre-activation on it, i.e., the mixture between these two parts. The experimental emulsion has the same principle of emulsion II, however in this case it is the mixture of emulsion I and the pre-activation.

4.1 Nylon cord with dip I

Peel test

Considering the peel adhesion test, the first results that are important to present are the ones from trials 1, 9 and 10, since those are the base references of this study. Table 3 shows the peel adhesion results of these trials for dip I.

Table 3 - Peel adhesion test results from reference trials with dip I

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 1	192 ± 7	83 ± 1	5.0
Trial 9	151 ± 9	80 ± 3	5.0
Trial 10	93 ± 14	85 ± 4	1.0

The results from Table 3 show that there is a better adhesion for the nylon cord with the rubbers C and A than for the rubber B. The difference of the appearances is visible on Figure 17.



Figure 17 - Peel adhesion samples from the reference trials for nylon cord with dip I

In order to observe the interactions between the rubbers, it is important to compare the results of trials 2, 3 and 8 with the corresponding reference ones - Tables 4, 5 and 6.

Table 4 - Peel adhesion test results from trials 1, 2 and 3 with dip I

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 1	192 ± 7	83 ± 1	5.0
Trial 2	176 ± 4	81 ± 1	5.0
Trial 3	92 ± 7	82 ± 2	1.0

Table 5 - Peel adhesion test results from trials 9, 2 and 8 with dip I

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 9	151 ± 9	80 ± 3	5.0
Trial 2	176 ± 4	81 ± 1	5.0
Trial 8	86 ± 8	80 ± 1	1.0

Table 6 - Peel adhesion test results from trials 10, 3 and 8 with dip I

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 10	93 ± 14	85 ± 4	1.0
Trial 3	92 ± 7	82 ± 2	1.0
Trial 8	86 ± 8	80 ± 1	1.0

As it is possible to observe from the results above, the interaction between the rubber C and A is very good, although, the interaction between these two rubbers and the rubber B is very weak.

To assess the adhesion between interfaces, the comparisons between the references (trials 1, 9 and 10) and trials 4, 5, 6, 7, 11 and 12 are also important - Tables 7, 8 and 9.

Table 7 - Peel adhesion test results from trials 1, 5, 6 and 7 with dip I

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 1	192 ± 7	83 ± 1	5.0
Trial 5	187 ± 6	81 ± 1	5.0
Trial 6	198 ± 6	81 ± 1	5.0
Trial 7	190 ± 7	80 ± 1	5.0

The peel adhesion results from trials 1, 5, 6 and 7 are very similar, because in this case the interaction at the middle interface is dominant, and, therefore, all the changes made in any other layer is not relevant.

Table 8 - Peel adhesion test results from trials 9, 4, 11 and 12 with dip I

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 9	151 ± 9	80 ± 3	5.0
Trial 4	45 ± 5	79 ± 1	1.0
Trial 11	51 ± 7	80 ± 1	1.0
Trial 12	73 ± 12	81 ± 1	1.0

Table 9 - Peel adhesion test results from trials 10, 4, 11 and 12 with dip I

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 10	93 ± 14	85 ± 4	1.0
Trial 4	45 ± 5	79 ± 1	1.0
Trial 11	51 ± 7	80 ± 1	1.0
Trial 12	73 ± 12	81 ± 1	1.0

For trials 4, 11 and 12, when compared to trials 9 and 10, it is possible to observe that the interactions with rubber B are very weak. In Table 9, it is possible to perceive that all trials with rubber B in it have similar results.

H-test

The following tests that were made were the H tests, presented in Table 10. These tests reveal the adhesion between the cord and the rubber.

Table 10 - Shearing force on the rubber to cord interface for dip I

Dip I			
	Rubber C	Rubber A	Rubber B
Force/N	138 ± 10	145 ± 13	61 ± 10

H test results show that rubbers C and A have a very similar adhesion to the nylon cord and that rubber B have almost no adhesion to the cord.

New peel test

Considering the new peel adhesion test, as in the peel adhesion test, the first results that are important to consider are the ones from the base references, trials 16, 20 and 21 - Table 11.

Table 11 - New peel adhesion results for the reference trials

	Force/N	Distance/mm
Trial 16	169 ± 10	81 ± 1
Trial 20	172 ± 6	80 ± 2
Trial 21	91 ± 9	80 ± 1

In order to compare the interfaces, it is necessary to relate the trials 17, 18 and 19 with the base references for this test method - Tables 12, 13 and 14.

Table 12 - New peel adhesion results for the trials 16, 17 and 18

	Force/N	Distance/mm
Trial 16	169 ± 10	81 ± 1
Trial 17	171 ± 8	82 ± 1
Trial 18	58 ± 6	79 ± 1

Table 13 - New peel adhesion results for the trials 20, 17 and 19

	Force/N	Distance/mm
Trial 20	172 ± 6	80 ± 2
Trial 17	171 ± 8	82 ± 1
Trial 19	152 ± 37	81 ± 2

Table 14 - New peel adhesion results for the trials 21, 18 and 19

	Force/N	Distance/mm
Trial 21	91 ± 9	80 ± 1
Trial 18	58 ± 6	79 ± 1
Trial 19	152 ± 37	81 ± 2

For these comparisons it is also possible to conclude that rubbers C and A show similar responses and trials using rubber B show worse results.

To confirm the failures of the rubbers it is needed to compare trials 17, 18 and 19 with the references, trials 16, 20 and 21 - Tables 15, 16 and 17.

Table 15 - New peel adhesion results for the trials 17, 16 and 20

	Force/N	Distance/mm
Trial 17	171 ± 8	82 ± 1
Trial 16	169 ± 10	81 ± 1
Trial 20	172 ± 6	80 ± 2

Table 16 - New peel adhesion results for the trials 18, 16 and 21

	Force/N	Distance/mm
Trial 18	58 ± 6	79 ± 1
Trial 16	169 ± 10	81 ± 1
Trial 21	91 ± 9	80 ± 1

Table 17 - New peel adhesion results for the trials 19, 20 and 21

	Force/N	Distance/mm
Trial 19	152 ± 37	81 ± 2
Trial 20	172 ± 6	80 ± 2
Trial 21	91 ± 9	80 ± 1

In Table 15, the results show that trial 17 has results similar to both references (trials 16 and 20), and in Table 17 it is also possible to observe that trial 19 is between references 20 and 21, though trial 19 has a great precision error. On Table 16, it is possible to observe that the trial 18 is very similar to the reference 21.

Peel, new peel and H tests results show generically a large difference between adhesion values obtained for the rubbers A and C compared to the results obtained for the rubber B. This is due to the fact that the composition of rubbers C and A is quite similar, whereas rubber B has no resorcinol, a component that seems to have a great role on the adhesion process.

For tests performed with dip I and for rubbers C and A, the adhesion between cord and rubbers should be related to (Durairaj, 2005):

- Resorcinol in rubber binds with the sulphur from rubber;
- VP latex of the impregnation solution attaches with the rubber latex;
- RF of the impregnation solution binds to the sulphur in rubber.

For rubber B, since there is no resorcinol on the rubber side, the only binding process are the VP-latex of the impregnation solution that binds with the rubber latex and the RF impregnation solution that binds to sulphur rubber.

It is possible to observe the load-strain graphics concerning the comparisons made for these trials performed on Appendix.

4.2 Screening tests with nylon cord

After obtaining the results for nylon cord with dip I, it is possible to verify that these results do not match the expectations. It is, therefore, necessary to continue the study with a set of screening tests.

Initially it was thought to change the composition of the rubber B, since this is the one that has worse results. However, this requires a larger set of tests. The approach then was to change the impregnation emulsion.

Then the tests began with the emulsion normally used with PET, pre-activating solution with impregnating emulsion III. The tests proceeded with a pre-activation with emulsion I, emulsion II, and an experimental emulsion. In Tables 18 and 19 it is possible to observe the peel adhesion force and shearing force for trials with pre-activation ad dip III.

Table 18 - Peel adhesion force results for the trials with pre-activation and dip III

Pre-Activation with dip III			
	Force/N	Distance/mm	Appearance (1 to 5)
Rubber C	198 ± 6	81 ± 1	5.0
Rubber A	191 ± 2	82 ± 1	5.0
Rubber B	142 ± 0	80 ± 1	3.5/4.0

Table 19 - Shearing force on the interface for the pre-activation with dip III

Pre-Activation with dip III			
	Rubber C	Rubber A	Rubber B
Force/N	153 ± 5	154 ± 12	131 ± 11

From the peel adhesion and shearing force tests for the trials performed with nylon cord and pre-activation with dip III, the results showed an improvement on the adhesion between the cord and mainly rubber B. However, the impregnating conditions for these trials are not the best for nylon cords. In Tables 20 and 21 it is possible to observe the peel adhesion force and shearing force for trials with pre-activation ad dip I.

Table 20 - Peel adhesion force results for the trials with pre-activation and dip I

Pre-Activation with dip I			
	Force/N	Distance/mm	Appearance (1 to 5)
Rubber C	194 ± 1	81 ± 1	5.0
Rubber A	194 ± 5	81 ± 1	5.0
Rubber B	153 ± 1	82 ± 0	3.5/4.0

Table 21 - Shearing force on the interface for the pre-activation with dip I

Pre-activation with dip I			
	Rubber C	Rubber A	Rubber B
Force/N	150 ± 4	159 ± 4	142 ± 5

As said before, although the impregnating conditions are not the best ones for the nylon cord, the results from the peel adhesion and shearing force tests showed an improvement on the adhesion between the cord and mainly rubber B.

Table 22 - Peel adhesion force results for the trials with dip II

Dip II			
	Force/N	Distance/mm	Appearance (1 to 5)
Rubber C	183 ± 1	81 ± 0	5.0
Rubber A	146 ± 4	79 ± 1	5.0
Rubber B	154 ± 2	82 ± 0	4.0

Table 23 - Shearing force on the interface for the dip II

Dip II			
	Rubber C	Rubber A	Rubber B
Force/N	148 ± 9	160 ± 4	145 ± 7

The trial results on Table 22 and Table 23 exposed the best adhesion of the three rubbers to the nylon cord and, also, the impregnating conditions for these trials are the same ones used traditionally on production.

To see if it was possible to improve the adhesion between the rubber B and the nylon cord, an experimental impregnating emulsion was made. The results of these trials are on Table 24 and Table 25.

Table 24 - Peel adhesion force results for the trials with experimental emulsion

Experimental emulsion			
	Force/N	Distance/mm	Appearance (1 to 5)
Rubber C	199 ± 2	82 ± 1	5.0
Rubber A	146 ± 3	80 ± 1	4.0
Rubber B	161 ± 2	81 ± 1	3.5/4.0

Table 25 - Shearing force on the interface for the experimental emulsion

Experimental			
	Rubber C	Rubber A	Rubber B
Force/N	151 ± 9	164 ± 3	142 ± 8

In Figure 18 it is visible the evolution of the appearance for the screening trials made of the rubber B. Since the results have not showed an improvement on the results, the following trials made were with dip II.

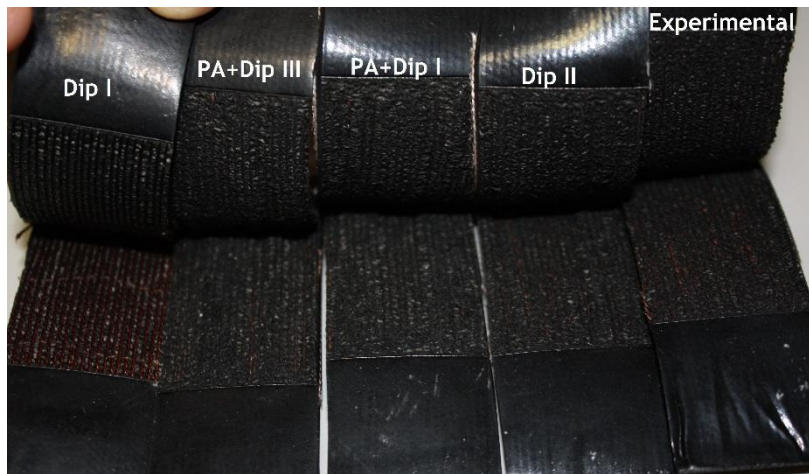


Figure 18 - Peel adhesion samples for the rubber B for the screening tests

All the impregnating emulsions used in these screening tests contain isocyanates, and this component makes possible the improvement of the performance of the rubber B. Isocyanates promote the links between the VP-latex present on the solution in the cord and the latex on the rubber, i.e. the adhesion of specimens will improve in the presence of these components.

Several studies were made under this subject before this master thesis. However, to prove that this concept is correct, a trial was performed where there was no resorcinol formaldehyde resin on the impregnating emulsion, only latex, water and ammonia (to control the pH of solution) - Table 26.

Table 26 - Peel adhesion force results for the trial with no RF resin

	Force/N	Distance/mm	Appearance (1 to 5)
Rubber C	162 ± 9	81 ± 1	3.5
Rubber A	145 ± 11	80 ± 0	3.0
Rubber B	125 ± 5	80 ± 0	1.0

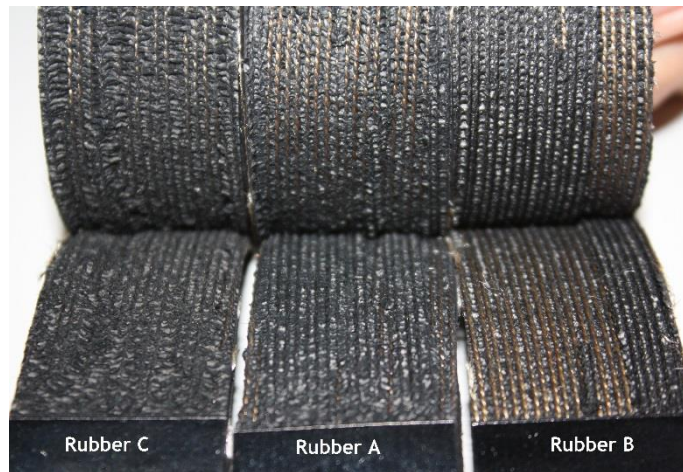


Figure 19 - Peel adhesion samples from the trial with no RF resin

As it is possible to assess from Figure 19, the results show that without RF resin in the impregnating emulsion, adhesion has lower results as well as adhesion force. Proving that the concept studied before this project is correct.

4.3 Nylon cord with dip II

As shown by the results presented before, the set that gives the best results is the set with the impregnation emulsion II - dip II.

From the set of tests presented in DOE, the tests that relate to the peel adhesion test that will not be carried out are the tests 5, 6 and 7. From the results presented before it is possible to observe that they have similar behaviours on the interface. Trials 16 to 21, corresponding to the new peel adhesion test, also will not be realized since they are used to confirm the failure of rubber into the study.

The first results that are important to see are the ones from the trials 1, 9 and 10, since those are the base references - Table 27.

Table 27 - Peel adhesion test results from trials 1, 9 and 10 with dip II

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 1	188 ± 5	81 ± 1	5.0
Trial 9	145 ± 6	80 ± 1	5.0
Trial 10	156 ± 5	85 ± 4	4.0

As said before, it is visible the improvement of the adhesion and appearance for the rubber B and the nylon cord - Figure 20.



Figure 20 - Peel adhesion samples from the reference trials for nylon cord with dip II

To see the interactions between the rubbers it is important to compare the trials 2, 3 and 8 with the base references - Tables 28, 29 and 30.

Table 28 - Peel adhesion test results from trials 1, 2 and 3 with dip II

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 1	188 ± 5	81 ± 1	5.0
Trial 2	168 ± 5	80 ± 1	5.0
Trial 3	167 ± 8	81 ± 1	4.0

Table 29 - Peel adhesion test results from trials 9, 2 and 8 with dip II

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 9	145 ± 6	80 ± 1	5.0
Trial 2	168 ± 5	80 ± 1	5.0
Trial 8	155 ± 4	80 ± 1	4.0

Table 30 - Peel adhesion test results from trials 10, 3 and 8 with dip II

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 10	156 ± 5	85 ± 4	4.0
Trial 3	167 ± 8	81 ± 1	4.0
Trial 8	155 ± 4	80 ± 1	4.0

As it is possible to observe from the results from tables above, the interactions between the rubbers are very similar, since all average forces are around the same values and the appearance from the trials are very alike.

Comparing trials 4, 11 and 12 with reference trials 9 and 10 allow to assess the degree of adhesion at the interface between the rubber types - Tables 31 and 32.

Table 31 - Peel adhesion test results from trials 9, 4, 11 and 12 with dip II

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 9	145 ± 6	80 ± 1	5.0
Trial 4	139 ± 13	80 ± 1	4.0
Trial 11	151 ± 12	80 ± 1	4.0
Trial 12	126 ± 5	81 ± 1	4.0

Table 32 - Peel adhesion test results from trials 10, 4, 11 and 12 with dip II

	Force/N	Distance/mm	Appearance (1 to 5)
Trial 10	156 ± 5	85 ± 4	4.0
Trial 4	139 ± 13	80 ± 1	4.0
Trial 11	151 ± 12	80 ± 1	4.0
Trial 12	126 ± 5	81 ± 1	4.0

As it is possible to observe by the results showed above, the adhesion force between the interfaces is very similar for all the trials performed.

All load/strain graphics concerning the comparisons made for these trials performed can be seen in Appendix.

4.4 Hybrid cord with dip I and with dip II

In the industrial process, the impregnating emulsion used on hybrid cords is the same used on nylon cords, and, because of that, the first trials performed on hybrid cords were with the same impregnating emulsion.

Table 33 - Peel adhesion force results for the trials with hybrid cord with dip I

Dip I			
	Force/N	Distance/mm	Appearance (1 to 5)
Rubber C	168 ± 8	80 ± 0	5.0
Rubber A	127 ± 5	78 ± 0	3.5/4.0
Rubber B	97 ± 3	84 ± 1	1.0

As it is possible to observe from Table 33, as on nylon cord, on hybrid cord, the adhesion between the rubber B is the weakest, although for this material, the rubber A has also a lower adhesion force.



Figure 21 - Peel adhesion samples from the reference trials for hybrid cord with dip I

To verify if the same principle is applied to this material, the next impregnating emulsion used was emulsion II - Table 34.

Table 34- Peel adhesion force results for the trials with hybrid cord with dip II

Dip II			
	Force/N	Distance/mm	Appearance (1 to 5)
Rubber C	188 ± 4	81 ± 1	5.0
Rubber A	135 ± 3	79 ± 0	3.5/4.0
Rubber B	140 ± 3	81 ± 0	3.5/4.0

As on nylon cord, the adhesion for hybrid cord improved significantly with this solution. The appearance for this set of tests is in Figure 22.

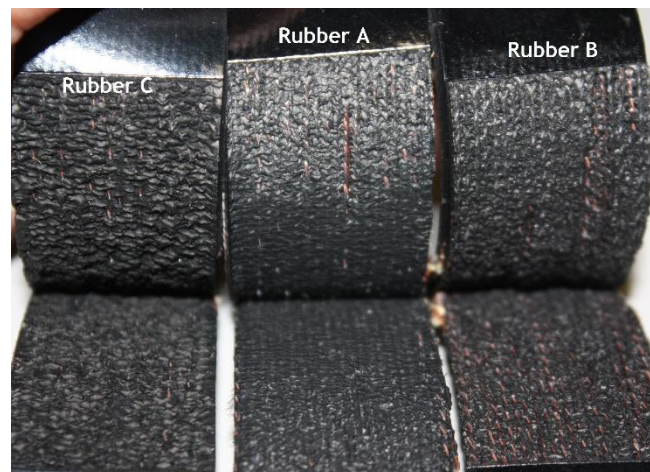


Figure 22 - Peel adhesion samples from the reference trials for hybrid cord with dip II

This study showed some interesting results since the results obtained for hybrid cord with emulsion I showed similar results to the ones obtained for nylon cord. For hybrid cords with emulsion II, the results showed an improvements, however further tests have to be done in order to approach these results to the specifications.

5 Conclusions

The results obtained on the trials performed throughout this project were very successful, since they were able to answer the main question of this project: is it possible to remove the layer of rubber from the cap-ply? The results showed that it is in fact possible to remove this layer, however, further test have to be done in order to assess the influence of this removal on the tire resistance.

The elimination of one layer of rubber will bring several advantages, beginning with the reduce of rolling resistance, the environmental aspects and ending on the financial aspects, since with this project it will be possible to reduce the amount of raw materials used and this fact will lead to a reduction of the production costs.

The first results obtained were for nylon cord with dip I. These results did not corresponded to the expectations, since they showed that with the current impregnating emulsion used on nylon cord it was not possible to remove the layer of rubber from the cap-ply. What caused this was the inexistence on rubber B of one of the major component responsible for adhesion, resorcinol.

After the first results for nylon cord with dip I, it was needed to do screening tests. These trials were needed to assess the influence of other parameters, such as isocyanates, on rubber/cord adhesion. The results from this screening tests showed that the combination that led to better results was, for nylon cords, the impregnation with dip II. The trials for this combination exhibited a significant improvement of adhesion and shearing force. This improvement was assigned to the addition of isocyanates to the impregnating emulsion. This component is able, on the rubber without resorcinol, to promote the bond of VP-latex on the impregnating emulsion with rubber. With this outcome it is possible to conclude that for nylon cord impregnated with dip II it is possible to remove the layer of rubber currently used.

After these trials, the reference trials for hybrid cords were performed. This study showed some interesting results for future work on this subject. The results obtained for hybrid cord with dip I (currently used impregnating emulsion for the cap-ply) showed similar results to the ones obtained for nylon cord, and this is probably due to the same fact: the absence of resorcinol on rubber side.

Trials with dip II and hybrid cords showed improvement results. Further investigation, however, should be done since target adhesion values were not able to reach within this dissertation.

The main difficulties found on the development of this project were the lack of previous knowledge on this subject; the design of experiments was a complex task to do, as it was needed to evaluate different interactions not previously described.

6 Project Assessments

6.1 Achieved Objectives

The main goal of this project was to eliminate rubber from the cap-ply, reducing rolling resistance and the total weight of the tire and, therefore, reducing the total CO₂ emissions of the car. Furthermore it was proposed to study the interactions between different types of components by exploring diverse combinations.

It was decided that the first fiber to be studied was nylon, since this is the fiber used in cap-ply for a longer time. Initial results did not meet the proposed objectives, however, subsequent assays showed that the changes made for this material makes possible to remove the rubber layer existing on cap-ply.

Subsequently, the initial tests for hybrid cords were made. For reasons of time constraints, the tests for this material have not been more extensive, however, the study of this material was not originally a project goal. The results showed that for this material the changes required any other type of nature besides the changes made on nylon cord.

6.2 Limitations and Future Work

The main limitation existing in the preparation of this master thesis was undoubtedly the time that all this work was done. Having started without a starting basis, all the research work of the testing methodology and the planning of all experiments were a major limiting steps of this project. The test methodology used was also one of the limiting steps, which is progression-free for a few years.

This being the beginning of a massive project, it is clear that there is still much work ahead. The main points to focus on immediate are:

- Test the other materials used in cap-ply, namely hybrid cords;
- Investigate the necessary modifications to make in the rubber or in the impregnation emulsion when using resins without resorcinol formaldehyde.

6.3 Final Assessment

From the beginning, this project has been challenging both personally and professionally. Starting from scratch a project of this size is really something very exciting, especially when this work is the target of my master thesis.

From the beginning of master course I knew I wanted to do the dissertation in entrepreneurial environment and, in fact, was a very enriching experience, even with all the inherent ups and downs!

I feel at the end of these five months of intensive work, that all my commitment was reciprocated, because the results are plain to see.

7 References

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Appendix

- Nylon cord with dip I - Peel adhesion test

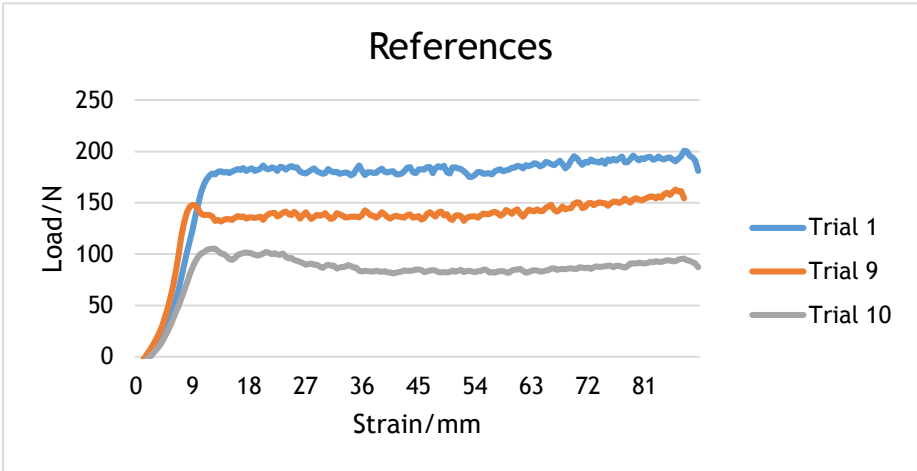


Figure 23 - Load/Strain curve from the references

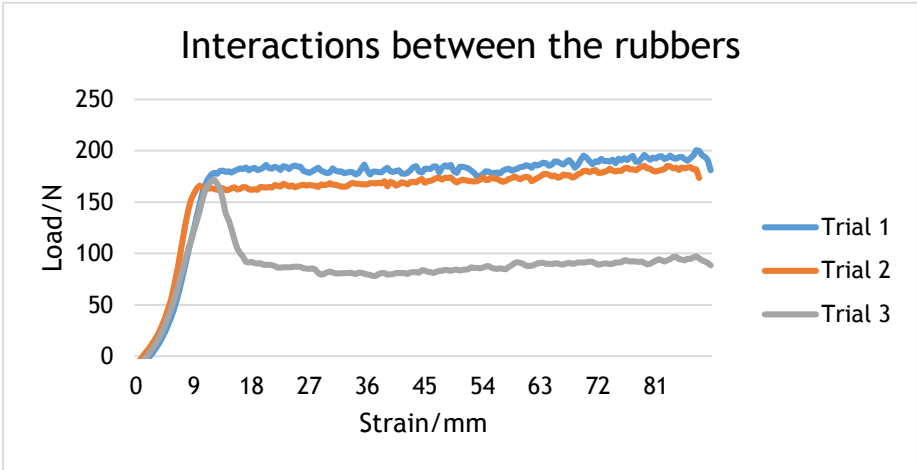


Figure 24 - Load/Strain curve from the trials 1, 2 and 3

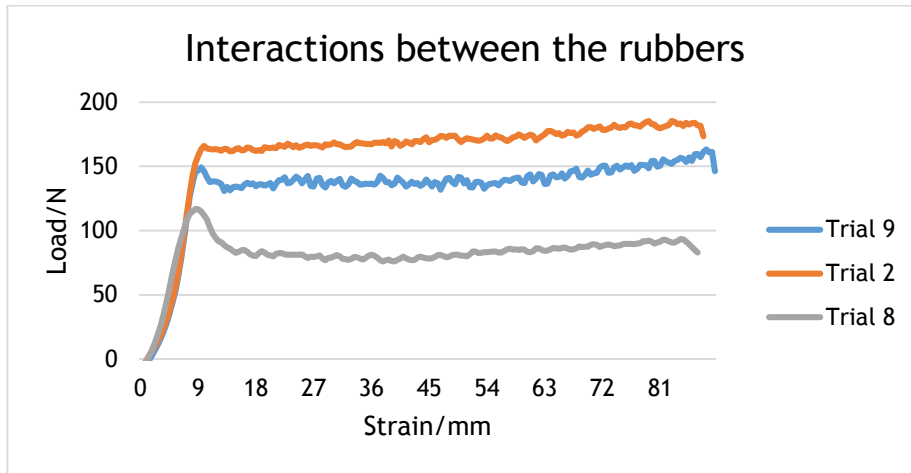


Figure 25 - Load/Strain curve from the trials 9, 2 and 8

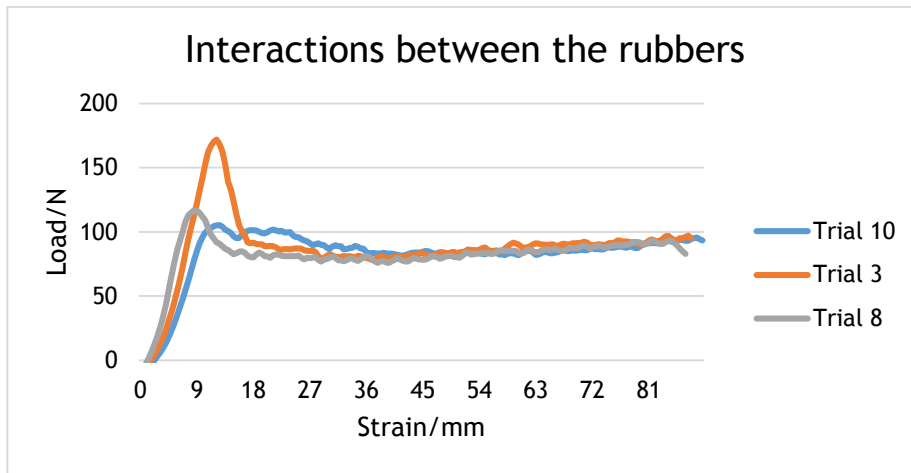


Figure 26 - Load/Strain curve from the trials 10, 3 and 8

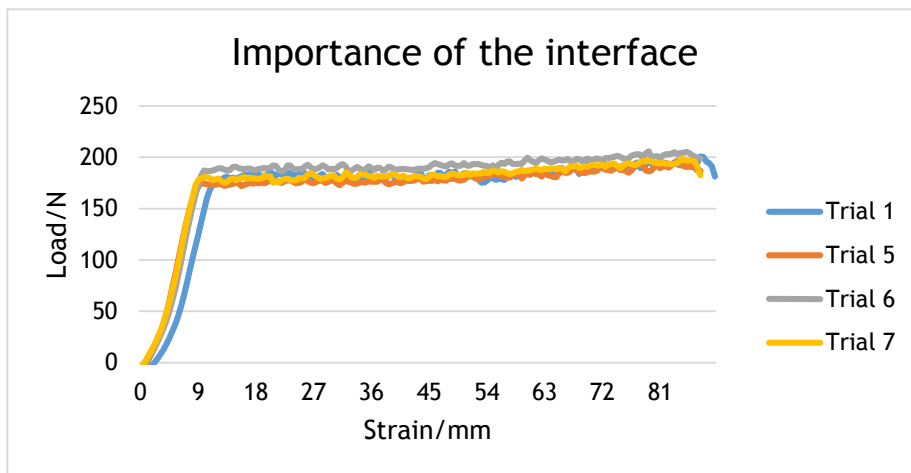


Figure 27 - Load/Strain curve from the trials 1, 5, 6 and 7

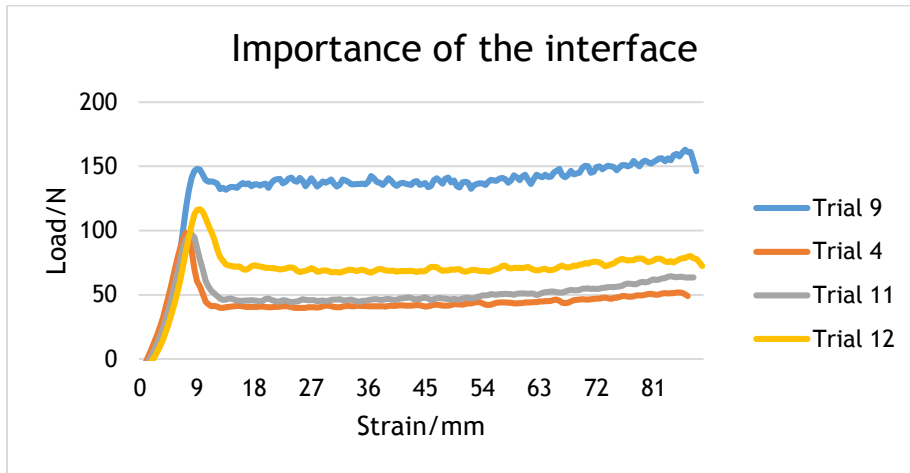


Figure 28 - Load/Strain curve from the trials 9, 4, 11 and 12

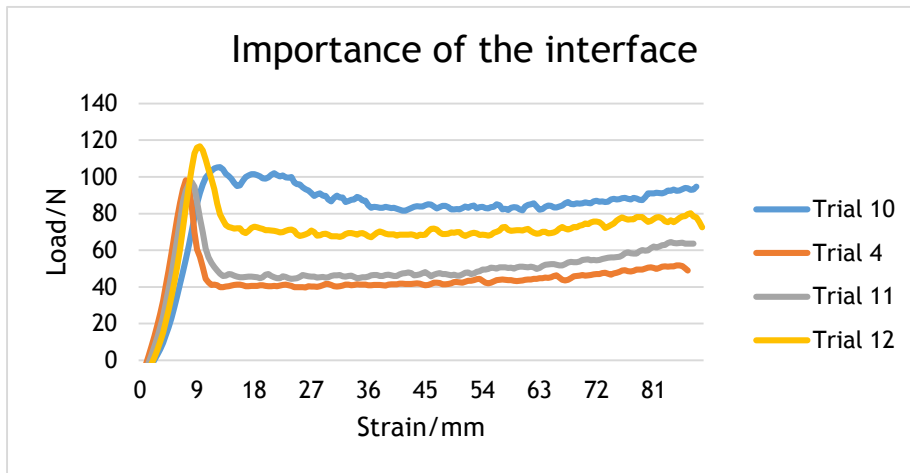


Figure 29 - Load/Strain curve from the trials 10, 4, 11 and 12

- Nylon cord with dip I - New peel adhesion test

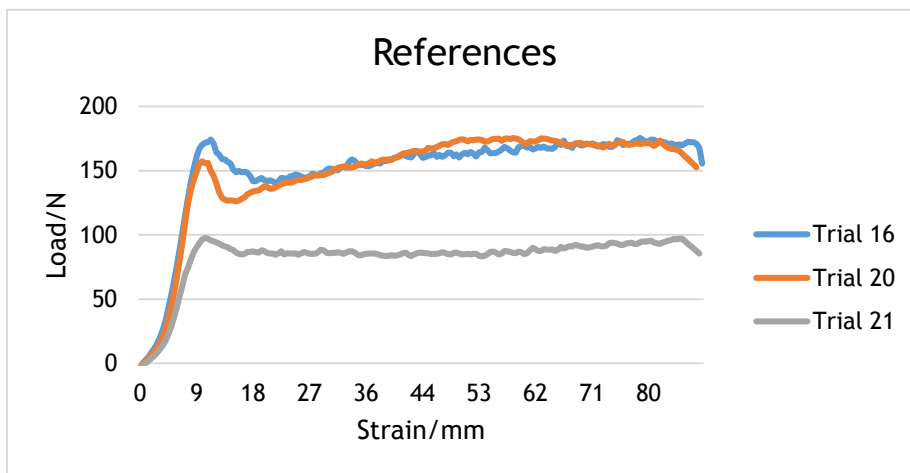


Figure 30 - Load/Strain curve from the trials 16, 20 and 21

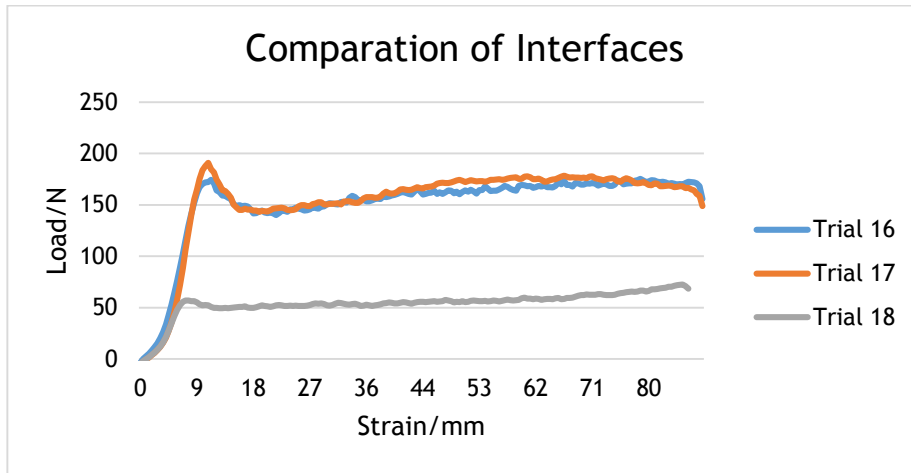


Figure 31 - Load/Strain curve from the trials 16, 17 and 18

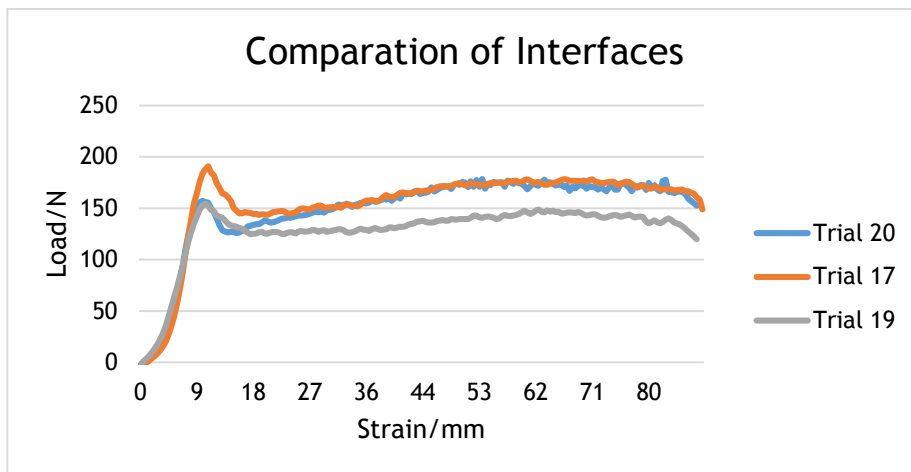


Figure 32 - Load/Strain curve from the trials 20, 17 and 19

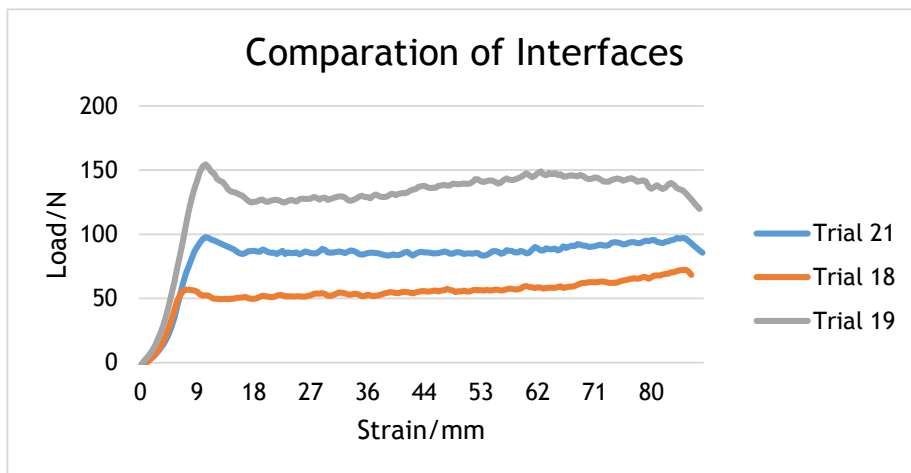


Figure 33 - Load/Strain curve from the trials 21, 18 and 19

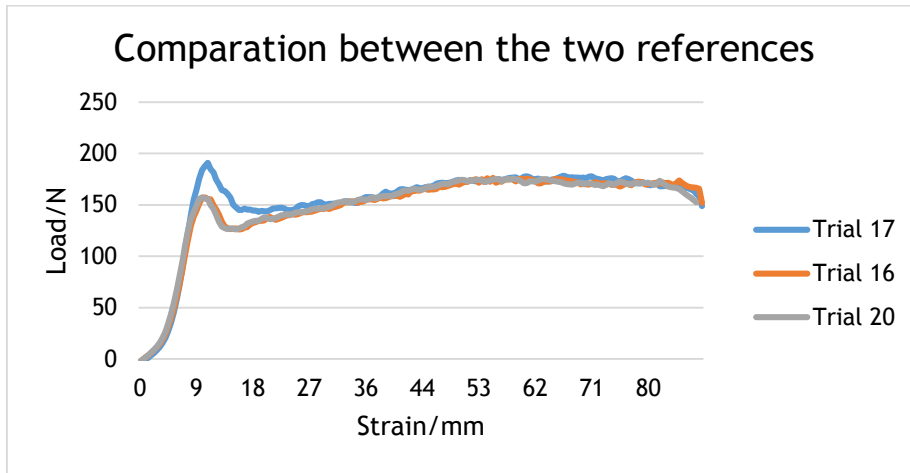


Figure 34 - Load/Strain curve from the trials 17, 16 and 20

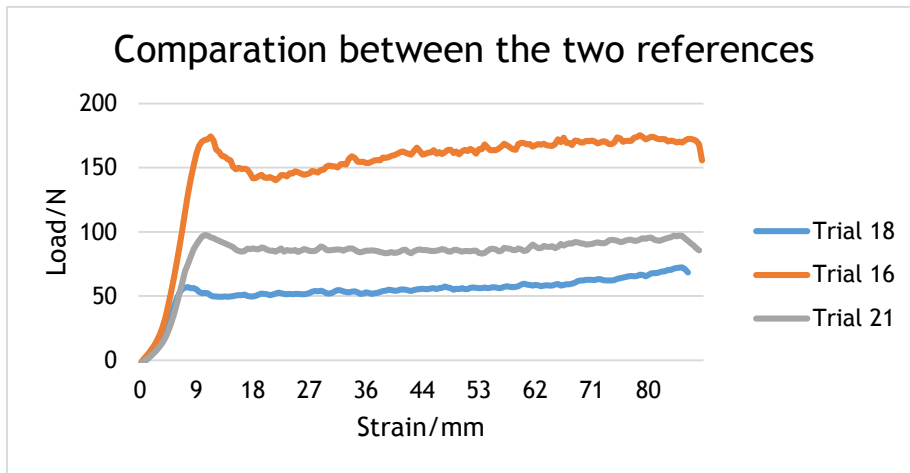


Figure 35 - Load/Strain curve from the trials 18, 16 and 21

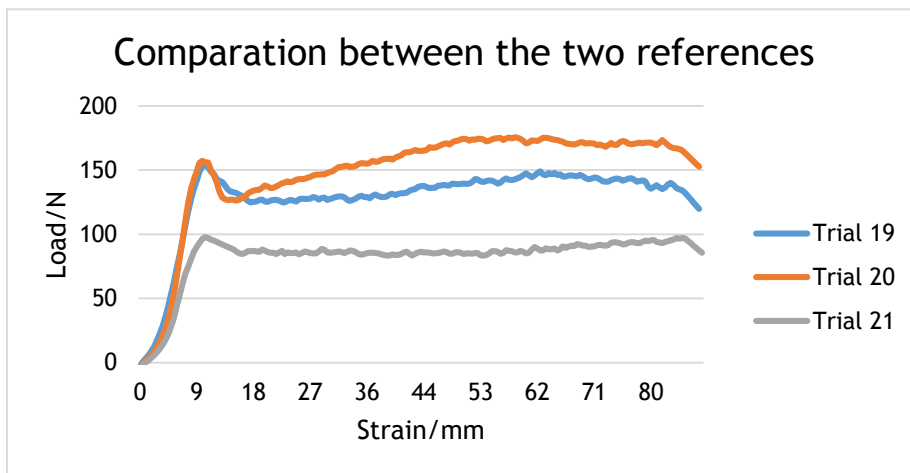


Figure 36 - Load/Strain curve from the trials 19, 20 and 21

- Nylon cord with dip II - Peel adhesion test

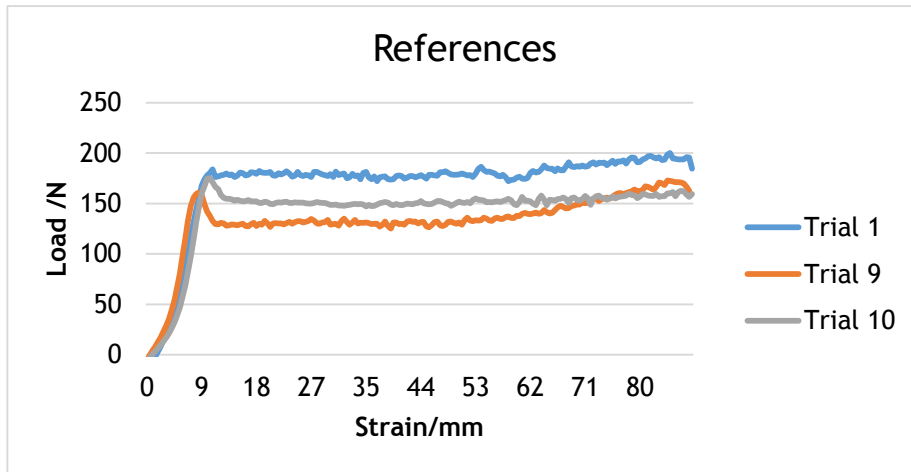


Figure 37 - Load/Strain curve from the references with dip II

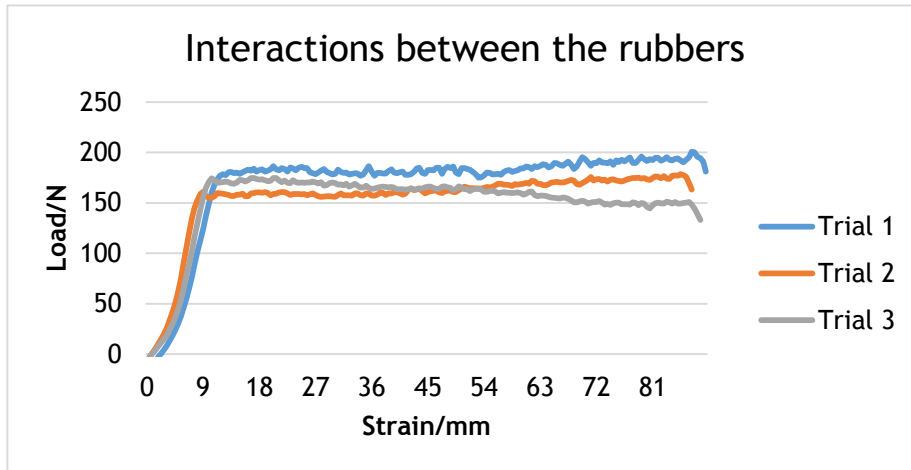


Figure 38 - Load/Strain curve from the trials 1, 2 and 3 with dip II

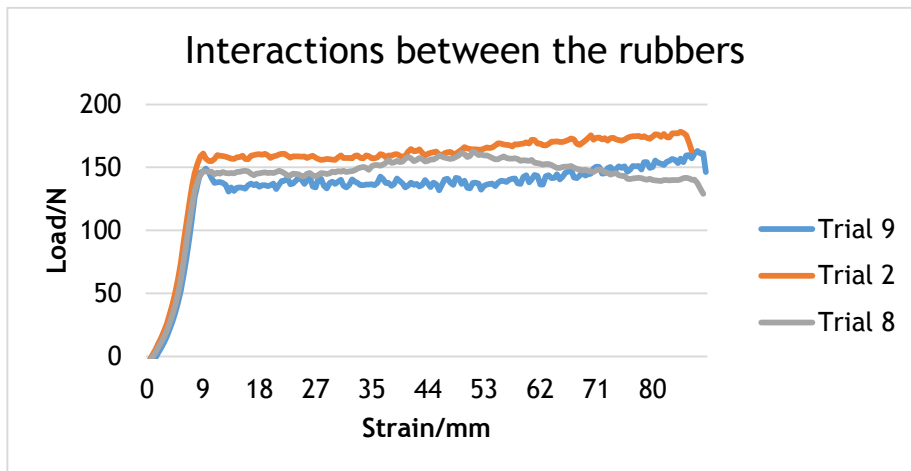


Figure 39 - Load/Strain curve from the trials 9, 2 and 8 with dip II

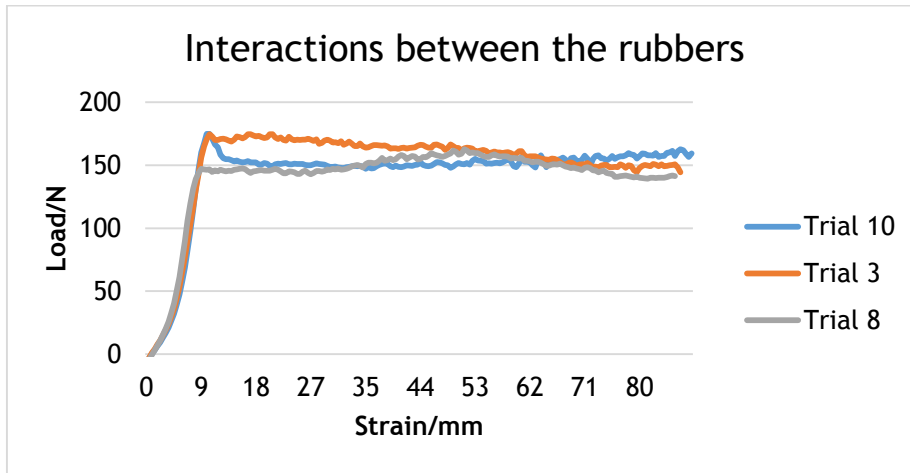


Figure 40 - Load/Strain curve from the trials 10, 3 and 8 with dip II

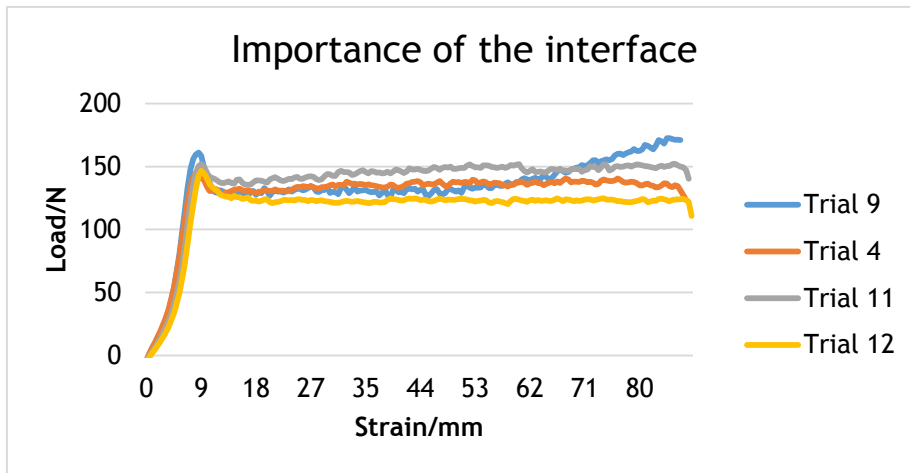


Figure 41- Load/Strain curve from the trials 9, 4, 11 and 12 with dip II

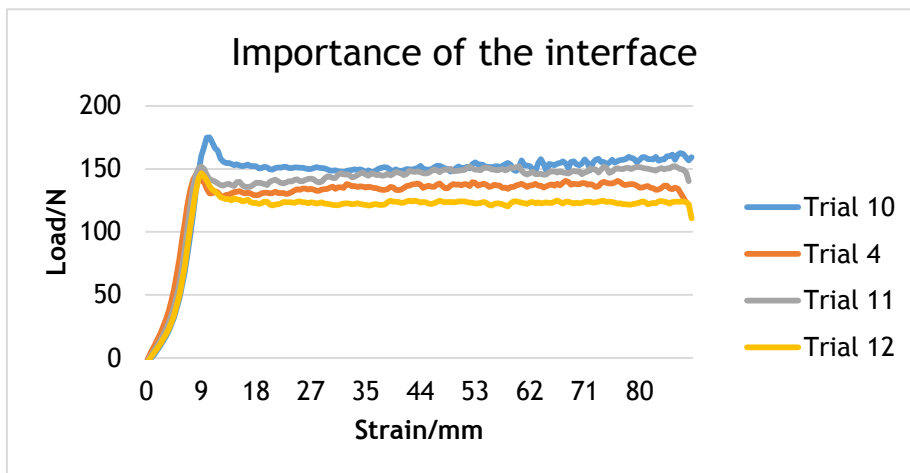


Figure 42- Load/Strain curve from the trials 10, 4, 11 and 12 with dip II