Adhesion optimization by new Latex-Blends on Rayon reinforcement for tyre application.

Master’s Thesis
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Abstract

This thesis frames within the collaboration between C-ITA (Continental - Indústria Têxtil do Ave) and FEUP (Faculdade de Engenharia da Universidade do Porto).

C-ITA belongs to Continental AG, which stands out in tyre industry as a leader and mainly as a reflection of constant technological improvement and innovation.

Tyre, often looked as a simply commodity, is nowadays a high-tech item; Compared to a molecule, where all the components must be well balanced and bonded together. Reinforcement materials are one of the areas, on tyres development, where there is space for significant improvements. This work is part of that effort bringing crucial information concerning adhesion between textile reinforcement elements and compound.

This study deals about the optimization of dipping formulations for being used with Rayon fabrics. Three base formulations were optimized: a) original resorcinol, formaldehyde and latexes-dip (RFL-dip) formulation; b) original rayon base formulation; and c) recently improved rayon base formulation. These formulations are made of resorcinol, formaldehyde and latexes, where latexes are natural rubber, styrene butadiene rubber and vinyl pyridine.

There are many variables involved in the preparation and processing of an RFL dip bath. A change in one or more of these variables can exhibit a profound effect on the functionality of the dip. The knowledge on how these variables affect the performance of the dipping is then of crucial importance; a thoroughly literature survey was made targeting to clarify the role of each component in the dip and of the dip composition.

Fibre dipping process was simulated in the LDU (Lab Dipping Unit), while the adhesion level was tested using standard methods as H-test and peel test.

The optimized dip formulation for rayon fibers contains only one latex, vinyl pyridine, and performs significantly better then the recently improved formulation by the company. The new formulation has also the potential to have a general-purpose application; however, tests should now be performed. Net financial benefits for the company of this work are on a maximum 15 % cost saving by changing for the optimized formulation.

**Key words:** tyre, textile reinforcement materials, dipping, adhesion, Rayon, Nylon, cost saving
Resumo

Esta tese resulta da colaboração entre a Continental - Indústria Têxtil do Ave (C-ITA) e a Faculdade de Engenharia da Universidade do Porto (FEUP).

A C-ITA pertence ao grupo Continental AG, que se destaca na indústria de pneus através da sua liderança e maioria por ser um reflexo de constante aprimoramento tecnológico e inovação.

O pneu, normalmente considerado um bem de consumo comum, é hoje, um produto de alta tecnologia; comparado a uma molécula, onde todos os seus componentes deverão estar bem balanceados e interligados.

Os materiais de reforço são uma das áreas, no desenvolvimento do produto (pneu), onde existe espaço para consideráveis desenvolvimentos. Este trabalho é, em si mesmo, parte desse esforço, contribuindo com informação crucial sobre a adesão entre elementos de reforço têxtil e o composto de borracha.

Este estudo trata da otimização de soluções de impregnação a ser usadas para tecidos de Raião. Três formulações base foram otimizadas: a) a solução de impregnação RFL (Resorcinol, Formaldeído, Latex) base; b) a formulação usada atualmente para a impregnação de raião; e c) a melhor formulação para impregnação de raião. Estas formulações são constituídas por resorcinol, formaldeído e latex, em que estes são: latex natural, borracha de estireno butadieno e vinil piridina.

Há muitas variáveis envolvidas na preparação e processamento de uma solução de impregnação RFL. A alteração de uma ou mais destas variáveis podem apresentar um efeito profundo sobre a funcionalidade do soluto. O conhecimento sobre como essas variáveis afetam o desempenho da impregnação é, então, de uma importância crucial. Um exaustivo levantamento bibliográfico foi realizado, visando esclarecer o papel de cada componente na solução e da composição da solução de impregnação. A impregnação da fibra foi simulada na máquina de impregnação de pequena escala, denominada por LDU (Lab Dipping Unit), enquanto o nível de adesão foi testado recorrendo a métodos de teste estandardizados como o método H e o método de Peel.

A formulação otimizada para a impregnação de raião contém apenas um tipo de látex, vinil piridina, sendo o seu desempenho significativamente melhor do que a formulação recentemente encontrada pela empresa. A nova formulação tem também o potencial de levar a uma aplicação de uso geral.

Palavras-chave: Pneu, Materiais de Reforço Têxtil, impregnação, Adesão, Raião, Nylon, Redução de custos.
Official Statement

I declare, under honour commitment, that the present work is original and that every non-original contribution was properly referred, by identifying its source.
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<th>Description</th>
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<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>AG</td>
<td>Automotive Group</td>
</tr>
<tr>
<td>FEUP</td>
<td>Faculdade de Engenharia da Universidade do Porto</td>
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<tr>
<td>F/R</td>
<td>Formaldehyde to Resorcinol ratio</td>
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<tr>
<td>C-ITA</td>
<td>Continental - Indústria Têxtil do Ave</td>
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<tr>
<td>LDU</td>
<td>Lab Dipping Unit</td>
</tr>
<tr>
<td>MRO</td>
<td>Maintenance, Repair and Operation</td>
</tr>
<tr>
<td>NR</td>
<td>Natural Rubber</td>
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<tr>
<td>PDU</td>
<td>Production Dipping Unit</td>
</tr>
<tr>
<td>RFL</td>
<td>Resorcinol Formaldehyde Latex</td>
</tr>
<tr>
<td>RF</td>
<td>Resorcinol Formaldehyde</td>
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<td>R/F</td>
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<td>RF/L</td>
<td>Resin to Latex ratio</td>
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<tr>
<td>Ry</td>
<td>Rayon</td>
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<tr>
<td>SBR</td>
<td>Styrene Butadiene Rubber</td>
</tr>
<tr>
<td>TRM</td>
<td>Textile Reinforcement Material(s)</td>
</tr>
<tr>
<td>VP/SBR</td>
<td>VP Latex to SBR ratio</td>
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<tr>
<td>VP/NR</td>
<td>VP Latex to NR ratio</td>
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<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
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1 Introduction

1.1 Project Presentation & framework

The goals for automotive industry have been changed... Manufacturer corporations claim to offer new driving experiences. People’s mobility evolved to other level; the question is no longer mobility itself but sustainability (i.e. “economics for life”); this means people need to move but want to do it efficiently. Economical and environmental sustainability plays a crucial role nowadays.

Tyre manufacturers should be able to upgrade their product to satisfy a new market demand. Consumers who often consider tyres as a low-tech commodity now recognize the importance of a correct tyre choice. (1) Nowadays, internet and aggressive marketing campaigns lead tyres know-how directly to consumers and as a result they start to make purchasing decisions not based solely on price.

Continental tyres are at this moment available with the European tyre label (Figure 1). With effect from 2012, tyres will be marked with an “energy label” (similar to the one seen on new fridges); It’s good that the EU has defined a tyre label with regards to energy efficiency, wet grip and noise. With it, drivers can obtain some information about a tyre’s properties. The statutory labeling however cannot replace the comprehensive and detailed ADAC tyre test as the best source of information to assist a purchase decision. (2)

![Image of EU tyre label](image-url)

*Figure 1 - “Check and Balance”, EU tyre label. (1)*
From the last paragraph it is concluded that an inevitably tyre development policy must be taken. As a complex product (fit-for-purpose), several upgrades on rubber and tyre shape had been made. Nowadays a continuous upgrade on reinforcement materials is still needed by assuring rigorous chemical and mechanical properties in the final product.

At the present time, one of the top five automotive groups, Continental was founded in 1871 in Hannover, Germany, and started producing in 1898 the so called “pneumatics”, tyres capable of giving a more comfortable (cushioned) ride and enabling automobiles to travel at higher speeds. (1)

Since then, it has developed important knowledge on automotive rubber goods; some other companies had been acquired as a strategic approach to increase Continental group business areas and technology.

In fact tyres manufactured by Continental are nothing less than high-tech products. With 150,000 employees and 193 production sites in between R&D centers, there are two textiles reinforcement’s producers. One is located in the USA and the other one is C-ITA.

Founded in Lousado, Portugal, on 1950’s, C-ITA is a corporation with textile manufacturing as core-business, especially oriented for tyre industry. Operating as an industrial cluster with Mabor (actually Continental Mabor S.A.) it had a well established knowledge, providing high quality standards to textile reinforcement materials. This explains the main reason why Continental AG decided to acquire C-ITA in 1993.

Textile reinforcements materials (TRM) are composed of metal and textile materials on rubber. Both textile and metal, must guarantee that tyres keep their structure, even in extreme conditions like hot weather or low pressure. They are the load carriers of the tyre, offering stability and strength to the sidewall and tread as well as containing the air pressure inside the tyre. (3)

Textile (or metals) on itself doesn’t have any effect on tyre performance unless they are fully linked on rubber lattices. Basically, a dipping process must be promoted to ensure a robust adhesion between fibers and rubber. In Figure 2, the adhesion interchange mechanism is represented; it is now clear one of the main goals of this project, to enable chemical bonding between rubber lattices and dipped fiber (single cord or fabric).
1 Introduction

Dipping solutions are commonly known as RFL solutions. The three major components are resorcinol (R), formaldehyde (F) and latex (L), dispersed on water. On parallel with chemical bonding insurance there is another goal: searching for a well balanced latex composition to get maximum adhesion force and coverage. In fact, this goal is the main challenge of this assignment. Rayon dipping solution is the only constituted by a blend of three different types of latex: vinyl pyridine latex (VP), styrene butadiene rubber (SBR) and natural rubber (NR). The reason why this latex blend and its proportions are used remains unclear. Rayon recipes can present agglomeration problems as well as destabilization during preparation when compared with other dip solutions at C-ITA.

Studying dip formulations is important because it makes easier to adapt to new adhesion requirements, provides tools for cost optimization and makes the changes to different raw materials faster and cheaper. Dipping process must be adjusted to fiber type depending on if it is a non-adhesion activated (nAA) or activated (AA) one, due to its characteristics as a finished cord and also to achieve the physical properties required to its role in the tyre.

Running trials with a selected cord on a small-scale dipping machine (LDU) will led to obtain different adhesion levels according to the dip solution being used. It has lower costs per trial than running in the Production Dipping Units (PDU) being possible to scale up the results trend.

Figure 2 - Adhesion interchange mechanism. (4)
1.2 Work contributions

The present work was developed after several preliminary works on the proportions of main components of the dip formulation. It not only goes further than previous work by optimizing the latex content on rayon recipe and adjusting it in order to get maximum adhesion but also by comparing with other C-ITA recipes; it means, dip’s standardization possibility can be checked.

Despite the fact it is an “unending” work, it defines two possible changes on rayon dipping; one regarding an optimized recipe (latex blend); and the other, on dip standardization direction. Both founded possibilities have superior adhesion performance and cost effectiveness.

The time to develop this study was a crucial factor, although for a six month period, strong results had been achieved.

1.3 Thesis organisation

This thesis is organised in 7 chapters, being each of them outlined on the next paragraphs:

Chapter 1, Introduction gives an initial approach to automotive industries market, with an important reference to Continental AG role on global tire market, its efforts for being a market leader and reinforcement materials importance on final product.

Chapter 2, State of the Art-- a deeper introduction to tyres technology and C-ITA production is made. Furthermore, cord to rubber adhesion mechanisms are enunciated on RFL technology and impregnation techniques.

Chapter 3, Procedure and Technical Description - explains the methodology used both for dip elaboration and adhesion testing, the design of experiments and author’s knowledge from production day-by-day.

Chapter 4, Results and discussion - refers all the experimental work results, its discussion, based on literature and external contributions, as well as providing tools for product industrialization.

Chapter 5, Conclusions - point out all the main aspects strongly sustained by this work.

Chapter 6, Project Assessment - describes all the pending subjects that will provide information for this work scope improving even more RFL treatments know-how.

Chapter 7, Bibliography - is a complete list of all the references used throughout this work.
2 State of the Art

2.1 Tyre

A typical car tyre uses about 60 raw materials. However, the tyre compounder quickly learns that adjusting one of the properties often affects other performance areas. Thus, compounds must be “engineered” or “balanced” to meet performance criteria for both original equipment vehicle manufacturer and the aftermarket customer. (5)

Tyres assumed different types, going from belted bias to radial, which are now leaders of the passenger tyre market. Compared with diagonal tyres, radial tyres show less rolling resistance and wear, better traction, and a smoother elasticity at high speed. As said before, tyres are high-tech products, with several layers expected to perform all sorts of functions like being able to cushion or dampen but also assuring good direction stability and long term service. Tread and sidewall is the directly viewed layer, responsible for the direct contact with the road; the first will provide the necessary grip, ensuring high mileage and water expulsion while sidewall will protect the body plies from abrasion. These two parts are only made of rubber compounds.

![Cross section of a tyre](image)

*Figure 3 - Cross section of a tyre, indicating the areas for fibre reinforcement and its locations related to tyre constituents.*

Going deeper on tyre, the cap-ply is responsible to provide strength and stability to the sidewall and tread; like carcass, made to control internal pressure and maintain tyre shape, is composed by textile reinforcement materials linked to rubber compounds. These are the tyre parts where fibre-to-rubber adhesion know-how will be applied.
Steel-cord belt plies exist to optimize directional stability and rolling resistance obtained from the rubber-to-steel adhesion.

The components of a modern radial tyre for passenger cars contain diverse ingredients in differing amounts, varying by tyre size or type. For a regular summer tyre, it is interesting to know that 15% of its ingredients are reinforcing materials. (1)

2.2 From fibers to TRM

Textile reinforcing materials (TRM) on tyres starts from simple fibers to final dipped cords, or fabrics, to use on tyre plants (calendaring). Fibers can be organized into four levels of design: filament, yarn, cord and fabric. A group of filaments spun together constitutes a yarn. The yarn after being twisted (alone or with more yarns) forms a cord. Depending on the application, the cord can be weaved into fabric or not.

C-ITA is divided on three different production areas, fiber and yarn twisting, weaving, and dipping. Twisting process improves final cord fatigue resistance and elongation by sharing tensile properties between filaments cooperative interactions. (4)

The raw cords are weaved in looms to produce fabrics. In this process cords are distributed by the comb, parallel to others, only connected transversally with a weft material (cotton yarn or elastic weft).

Rayon fabric is used on carcass as reinforcement and it is made from cellulose produced by wet spinning (possibly named as viscose or regenerated cellulose). It is often used in Europe and in some run-flat tyres as body ply material. As advantages it has heat resistance and good
handling conditions. As main disadvantage it presents a high cost, is more sensitive to moisture besides environmental manufacturing issues. Even when heat is excessive in the tyre, rayon and polyester manage to keep the tyre in the perfect round shape thanks to reduced thermal shrinkage (practically inexistent on rayon), resulting in a comfortable ride. (5)

The (semi) man-made fibres such as regenerated cellulose have a smooth surface; therefore, there is no interlocking of filaments. Furthermore, the mechanical properties of these fibres are higher compared to cotton and as a result a higher strength of the adhesion is required. This resulted in the Resorcinol Formaldehyde Latex treatment invented by Charch and Maney. (6)

2.3 Dipping process

Adhesion is an important factor in using textile materials together with rubber as well as the individual properties of each material. Roles of adhesion may be to give desirable properties, improve durability and maintain the shape of the composite material. (5)

All parameters on dipping process; like cure temperature of the dips, tensile forces on cords and residence times on ovens; need optimization for every type of reinforcing fibre, the type of RFL and the type of rubber to adhere to. It is therefore not surprising that the knowledge of cord to rubber adhesion to date is very pragmatic rather than scientific. (6)

2.3.1 RFL – dip solution

As a result of Rayon filament introduction a reclaimed rubber-casein-latex adhesive was examined to improve this defect, but it failed to satisfy requirements of the tyre industry. Thereafter, studies of adhesives based on latex and thermosetting resin progressed and led to actual RFL dipping. (Adapted from (5)).

The usual RFL formulation has the following ingredients: Water, Latex, Resorcinol (“in situ” resin or pre-condensed resin), Formaldehyde and an alkaline solution as Ammonia or Sodium Hydroxide.

Using water instead of an organic solvent has many advantages: water is cheaper, easier to treat and not harmful to health. All dipping solutions on C-ITA are water based ones.

If latex alone is employed as an adhesive, good rubber to textile adhesion cannot be obtained because of lack of active groups in latex and weak tensile properties of the adhesive coating film. Latex bonds both to the resin and to the rubber. It also provides the dipped cord with flexibility properties. (5)

Resorcinol has been chosen as the phenolic molecule of choice among other derivatives in the adhesive formulation of fiber-rubber composite applications, due to its water solubility,
enhanced reactivity with formaldehyde at room temperature and basic conditions. (7). A precondensed resin is used on C-ITA, allowing resorcinol and formaldehyde to be partially condensed in dilute aqueous alkali solution before being added to latex.

The precondensed resin dispersion contains resorcinol “trimers” having methylol groups (called resoles) with some mono and dimers of resorcinol. The term trimer means that three resorcinol molecules are connected through a methylene (-CH₂-) bridge. (7)

![Precondensed resin](image)

**Figure 5 - Schematic approach to trimethylol resorcinol (RF resole) formation/presence on precondensed resin.**

Besides its facility of handling and enhanced storage stability, plus reduced maturation and fuming exposure, which means on the final, superior adhesion potential; this type of resin keeps ammonia from reacting with formaldehyde during RFL-dip preparation, preventing the formation of hexamethylenetetramine, which may interfere in the resin’s formation, by limiting its extent. It may also be responsible for the latex colloidal destabilization. (8)

Increasing formaldehyde concentration, on RFL solution, at low temperature (preferably room temperature or lower) and alkaline conditions will promote the formation of methylol groups in the resin structure. Formaldehyde will work as a crosslinking promoter.

The formation and stability of methylol derivatives of resorcinol and RF-resins are important to develop and strengthen the bond between the fibres and RFL adhesives. (7)

Ammonia is required to keep the pH in an alkaline level (of about 9 to 10). A strict pH control is needed while working with polymeric compounds like latexes and resins resoles otherwise it will result on partially condensed reaction products, changing the desirable course for the chemical reaction.
2.3.2 Production Dipping Units (PDU)

RFL treatment will be outlined below. Generally, greige cord or fabric is immersed in an RFL dip bath, and squeezed by passing through a roll unit, vacuum unit, or beater to adjust the pickup of the adhesive. Then cord or fabric is introduced into air ovens where are dried and RFL baking is accomplished. (5)

Figure 6 - Schematic drawing of fabric impregnation machine (In general, the same can be used to describe single cords impregnation). (Adapted; (6))

Generically it is easy to find dipping processes descriptions on specialized literature. Although real design and operating conditions are specific of each plant and oriented to its production. Main parameters on dipping machinery are the same, temperature, stretch level, exposure time and the dip solution being used. Exposure time together with temperature will interfere on curative process of the dip on fibers. Temperature plays a triple role: it de-humidifies the fibre, it cures the RFL treatment and it gives the final mechanical properties jointly with stretch.

Dipped fabrics or cords, besides its adhesion level and all characteristics affected to dip (tackiness, stiffness and moisture content) must also regard some physical properties needed to achieve costumer’s specifications. On quality control laboratories, properties like elongation (at a specific load), break force and thermal shrinkage are measured and certified to use by costumers. Elongation measures the fiber’s length increase when subjected to a force; at the end the cord will break, that force is called the Break Force. Thermal Shrinkage
Adhesion optimization by new latex blends on Rayon reinforcement for tyre application.

will give as an output, how much cord shrinks when it is subjected to a high temperature during a certain period of time.

2.3.2.1 Lab Dipping Machine (LDU)

C-ITA has a small scale dipping machine on its development laboratory. With it, it is possible to perform studies in a much, faster and cheaper way, as it will not interrupt the normal operation of the production units (Zell and Single-End).

![Lab Dipping Machine](image)

**Figure 7 - Lab dipping unit (and zoom in).**

LDU operating scheme is similar to production dipping machines but reduced to a small scale. At the beginning, greige cord will go thru mechanical devices which stabilizes and guides the cord to the first stretching area, then it passes on the first dip tray; it can be used for an activation bath (in this case the second dip tray will be used to the regular dip), or normally, for the single stage dip. 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 fiber/cord the physical properties intended as long as RFL treatment is cured.

2.3.3 Adhesion Mechanisms

There are many opinions on how RFL functions with rayon: Hydrogen bonding between phenolic hydroxyl groups in RFL resin and electronegative groups on fibers (9), condensation reaction between methylol group of RF resin and active hydrogen in the fiber (10), dipole-dipole interaction (11) and molecular entanglement (12)
However, the evidence has been insufficient for any of those bonding mechanisms to gain wide acceptance. For convenience of explanation, reaction theory is presented as an example: (12), proposed the following possible bonding diagram between RFL and rayon.

Formaldehyde reacts to the resorcinol resin to form methylol derivatives as mentioned before. Further condensation forms methylol derivatives in which four to five resorcinol nuclei are combined through methylene -CH₃- and methylene ether -CH₂-O-CH₂ bonds. Rayon’s hydroxyl groups (-OH) behave as nucleophile center originating methylene ether bonds between rayon (polymeric chain) and resin resole.

Formaldehyde to resin ratio (F/R) increases both the degree of condensation and the degree of branching. The concentration, the maturation time and temperature of resin solution, as well as the curing time and temperature of the RFL-dip influence the rate of condensation. When the styrene butadiene copolymer is used for the latex component of RFL, adhesion decreases with the increase of styrene.

Also many opinions have been presented for the rubber to RFL bond: interdiffusion between RFL and rubber, co-vulcanization of carbon-carbon double bonds in RFL with rubber, ionic interaction, chemical reaction between RF resin and rubber. (5)

These proposed mechanisms (...) are very diverse and based on assumptions rather than scientific research. One of the mechanisms commonly proposed is co-vulcanization of the RFL-rubber interface. Very few authors experimentally verified this by performing an in-depth study of the RFL-rubber interface. (6)

The bond between resorcinol formaldehyde resin and rubber has generally been deemed to be the same as other phenolic resin rubber linkage,
Greth proposed that phenol formaldehyde resin reacts with the double bond in the isoprene unit of natural rubber to form chromanes.

![Greth and Hultzsch mechanism for adhesion chemistry on RFL - compound.](image)

Van der Meer proposed generation of methylene quinine intermediate which then reacted at the methylene group adjacent to the unsaturated carbon in natural rubber.

![van der Meer mechanism for adhesion chemistry on RFL - compound.](image)

As an overview, a possible bonding scheme, between Rayon, resin and latex is suggested, based on (12) and (7) publications.

![Schematic representation the adhesion mechanism between Rayon, RF resin, Latexes and rubber compound (Adapted; (5)).](image)
3 Procedure and Technical Description

3.1 Introduction

*Greige cord, dipped cord, moisture control, compound, vulcanization, test...*

Many variables must be controlled within these concepts. Adhesion can be seen as the sum of these parts: It means a systematic approach was realized always considering literature, Continental group research and author’s experience during this work.

3.2 Fibre

The fibre used for the latex blend study was rayon, with a linear density of 2440 dtex (decitex) and a cord construction by 1x2. As previously stated, rayon is a TRM with high advantages to use on carcass, although it is considered a half-synthetic material, because the raw material is still a natural polymer: cellulose. Rayon can be easily bonded to rubber comparing to PET or Aramid but its hydrophilic behaviour will affect both dip concentration on cord (dip pickup) and moisture capture.

3.2.1 LDU Setup

LDU offer the possibility to simulate in lab different production configurations. It means different cords and setups can be used. On latex blend study, it is important to fix a strict configuration for LDU as closest to production unit. The setup configuration, present on Table 1, is the one according to C-ITA knowledge, which would give results closest to the production unit.

A controlled cord stretch or tension was fixed as well as passages and running speed, ensuring this way the desirable residence time on oven. Temperature and vacuum could be controlled by the operator, however, on this work, these parameters remained constant. An oven length is 1.5 m and process trials runs at 15 meters per minute.

*Table 1 - Lab dipping unit setup for trials performed.*

<table>
<thead>
<tr>
<th>Zones</th>
<th>Temperature / °C</th>
<th>Exposure time / s</th>
<th>Stretch / %</th>
<th>Passages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Dry</td>
<td>135</td>
<td>30</td>
<td>0.9</td>
<td>5</td>
</tr>
<tr>
<td>Hot Stretch</td>
<td>165</td>
<td>30</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>2nd Dry</td>
<td>175</td>
<td>18</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Normalizing</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>
Finished trials had about 150 meters of dipped cord. This was the necessary length for the process to stabilize and to have enough cord to perform all the required tests. These cords must take a stabilization period of 24 hours, in a conditioned room at about 23 °C and 53 % of air humidity. At the end of this period, cords final properties are considered as stable.

3.2.2 Moisture control

A major disadvantage of rayon is its sensitivity to moisture. In moist conditions, its loss in strength is significant. In fact, moisture will affect not only cord (or fabric) properties but also adhesion force and coverage. Moisture effect analysis is beyond this thesis scope; however a special attention was given to its interference on results.

Rayon is dried at temperature ranging from 150 °C to 200 °C. Insufficient heat can lead to poor interaction of RFL with cord while excessive heat can crosslink the dip to a state that impairs compatibility with the rubber compound. Oven dried cords were used for all samples preparation; these cords are exposed at 105 °C during one hour.

3.3 Dipping preparation and methodology

Dip preparation can easily be taken as a non-important stage; that idea, normally linked to technical literature “three stages recipe” explanations, is completely wrong. It should follow the main steps; latex aqueous dispersion, alkaline resin solution, formaldehyde addition, but also considering some preparation techniques.

Latex dispersion must be realized with pH controlled water, adding the different kind of latexes with care while controlling agitation. Mixing interferes on solution temperature and also on molecular entanglement. 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).

While preparing the latex dispersion, resin is diluted on water with ammonia; at this stage, agitation also plays an important role by increasing solubility. Resin must be visually inspected if there are non-reacted parts or coagulates. 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.

Formaldehyde addition, will endorse cross linking between resin and latexes. If this addition occurs to quickly it will affect dip stability. 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 were measured.
3.3.1 Design of experiments

C-ITA developed a dipping formulation for rayon impregnation - reference rayon formulation. Based on this formulation the improved formulation was obtained by changing the latexes composition and keeping constant the resorcinolic to formaldehyde weight ratio ($RF/L =$ constant).

Instead of molar concentrations, weight ratios of dried raw materials were used; following, VP Latex to SBR and VP Latex to NR ratios were chose as independent variables on optimizing the dipping formulation. Continuously increasing VP Latex amount will lead to an extreme case on latex blend, which recipe will only have VP Latex on its content. The contrary will happen while continuously decreasing the VP Latex amount and the new recipes will have a maximum content of SBR or NR. The extreme formulations will be called as Max VP and Min VP respectively, and compared with the reference recipe.

Seven formulations were set changing one ratio each time; these formulations were then prepared and used for coating rayon fabric samples. Finally, the adhesion of the coated fabric samples to compound was assessed (by H-test and Peel Test) and the formulation showing the highest adhesion obtained - optimized formulation.

![Diagram of design of experiments](image)

*Figure 12 - Integrative scheme to obtain the design of experiments.*

The stability range of the formulations was also assessed during the adhesion optimization procedure.
Dip solid content (S.C. / %) was used as a control parameter because it directly affects the adhesion. Starting with a minimum of 15 wt. % two more experiments were performed for 18 wt. % and 22 wt. %. Solid content was decreased by adding water (diluting the dip).

Concerning the RFL formulation, only ammonia (25 wt. %) and formaldehyde (37 wt. %) were considered as non contributing for the solid content; ammonia is used for pH control and evaporates easily; formaldehyde is consumed during methylol group's formation.

### 3.3.2 Production analysis and Formulations

An important task, before running the experimental trials, is to completely join workers experience on dip elaboration and impregnation process. It resulted on some empirical contributions that must be considered under a more scientific spec. Some contributions were already written on the beginning of this point (3.3 Dipping preparation and methodology).

Usually, workforce prefer to prepare rayon dipping solution during the night shift for two main reasons: it takes more time to prepare than other dips (slowly formaldehyde addition) and mainly due to temperature interference (at night is cooler). While preparing the dip, they also pay some external attention to its viscosity level and possibly agglomeration; unfortunately they cannot control this phenomenon, which means it must be controlled on recipe formulation stage.

Several problems occur with high viscosity or dip instability: fibre pick up augment; cord (or fabric) has a tacky touch and it is “glued” together on roll; it means that the final product did not obey to the specifications and, subsequently, costs will increase. In fact, a similar issue occurred almost a year ago in production; it resulted on a dip recipe modification.

### 3.4 Testing Methods

The dipped fibers have to be tested in order to measure the adhesion (i.e. on this case, the latex blend formulation effect). Two methods are used in this assignment: Peel test and H-test. Despite their differences, they both consist of vulcanizing rubber with cords and then testing the rubber-cord force in a dynamometer.

#### 3.4.1 Peel Test

Peel test determines the force required to separate two layers of cords bonded together by an intermediate layer of rubber. In contrast with H-test, peel test does not imply any cord breakage.
3.4.1.1 Peel Test samples preparation

As a test method, its samples have to be closest as possible to product application. So, it is crucial to simulate fabrics by creating a handmade fabric consisting of a series of test cords, which are passed through a textile comb (Figure 13).

![Textile comb with Rayon 2440x1x2 dipped cord.](image)

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. Another piece of skim compound is then added on the top of fabric, and finally marked to cut with mould dimensions according to test standards (ASTDM D 4393-00) (Figure 14). Protective layers must remain during sample preparation and must only be removed when necessary; avoiding this way, grease and humidity presence on rubber and rubber to cord interface.

![Peel test specimen preparation; chaffer - skim compound - cord green adhesion with mould outline.](image)
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The resulting specimen (Figure 14) needs to be pressurized and then cut in two samples, which are joined to form a rubber-cord “sandwich” as presented on Figure 15.

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 is cut on three parts. Before tensile testing, the specimens should be kept at 120 °C for 30 minutes. The testing occurs in a tensile machine that pulls one half of the specimen at a constant speed of 100 mm/min, while the other half is fixed. During pulling, peaks of force are registered. The mean value of these peaks is the peel-adhesion force for that specimen. (ASTDM D 4393-00).

The peel-test experiments performed on this work were according to C - ITA quality control. Rubber to cord appearance is also a quality parameter. It is visually inspected and classified in a 1 - 5 rank according to the number of cords that are covered by rubber.

Figure 15 - Peel test rubber sample; lateral view and materials identification.

Figure 16 - After testing peel test sample with good appearance for Rayon cords.
3.4.2 H-test

H-test is another standard test (ASTM D 4776-04) for testing cord to rubber adhesion; it gives the H-pullout force value. It is basically described as cord samples bounded between two layers of vulcanized rubber, on a mould, which will be later cut on H forms (because of the blocks of rubber linked by a piece of cord).

3.4.2.1 H-test sample preparation

The test specimen sandwich is cut to create an H-test specimen consisting of a single cord with each end embedded in the center of a tab end of the rubber test block.

![H-test sample preparation](image)

Figure 17 - H-test sample preparation; steps: from rubber compound to final sample.

H forms were tested in a pull out tester, which has grips that take the top rubber part of the H upside while the other part is fixed. On this test, cord will be removed from the upper rubber block, which may cause cord breakage or simply failure on cord to rubber linkage.

The maximum force yielded is the H-test adhesion force or H-pullout force. Rubber compound used on this test is supplied by Continental. It is a testing compound made for adhesion studies.

Like peel test, the vulcanization stage also occurs in a curing device at controlled press, temperature and time. The pressure is 60 bar, at 170 ºC for 10 minutes. Caution must be taken in sampling and handling so that samples receive minimum exposure to ambient atmosphere and light prior to rubber embedment. Rayon is particularly sensitive to moisture pick-up (which negatively affects adhesion) and should be handled accordingly. (14)
4 Results and discussion

As affirmed on design of experiments chapter (3.3.1), experiments must be based on the production recipe for Rayon 2440x1x2. The first DoE was obtained from 902 PS dip solution by changing its solid content and latex blend proportions; to achieve these new formulations, a MSExcel routine was made using Solver tool. Several calculation parameters were initially defined so its output was accordingly to this work purpose.

Firstly, recipe’s total mass fraction must be equal to one. Components mass fraction is obtained by multiplying the mass in component percentage by its total amount on dip. Resorcinol-Formaldehyde to Latex ratio must be constant and equal, in value, to the standard dip (902 PS); it means, step number 2 and 3, of dip elaboration, is equal in all recipes (Only varying on latex blend step). (3.3).

The routine inputs are both latex blend ratios (VP/SBR and VP/NR ratios) and the recipe desirable solid content percentage (S.C. / %); Solid content must be defined on a range between the previously defined values, normally the solid content percentage ± 1 %).

Extreme points definition, Max and Min VP content, were given by a very high or low numerical value respectively; On Figure 18, ratios modification plan is expressed. Values like 0.00 and 300 were only used for tool manipulation; it has no physical mean (expressed as zero or infinite).

With conditions and inputs fixed, the output (new formulation) is provided by changing the latex amounts while equalizing the recipe total mass fraction to one.

**Figure 18 - Latex blend scenarios, MSExcel-Solver routine; first DoE trials - 902PS recipe.**
This tool is used to get all the new blends formulations considered on this work. Whenever other manipulations occur, it will be expressed on this paper.

Starting with 22 wt. % solid content recipes, extreme recipes were defined; It were also calculated the ones for 18 wt. % and 15 wt. % solid content.

For 15 wt. % solid content solutions, several problems with its elaboration occurred. While preparing the dips, the viscosity level, on the beginning of the third stage, was very high, resulting on an increased air capture during agitation. (First and second stage preparation strictly obeyed to the methodology present on 3.3.)

While promoting formaldehyde addition, although it was done very carefully, some molecular entanglement was observed on aqueous dispersions surface. This phenomenon occurs independently of the stirring level (using mechanical agitator, manual agitation, very slow agitation); with mechanical, there is no directly viewed phenomenon on the surface, due to solution turbulent stirring, but few seconds later, some solid material starts to be formed on container’s base.

On 902 PS Min VP -15 %, several minutes after its elaboration, it became completely solidified (Figure 19). For 902 PS 15 %, viscosity level was lower, nevertheless, during an aging period it started to agglomerate as well (Figure 19 - right side).

![Figure 19 - Dip instability and solid particles agglomeration on containers base.](image)

Being impossible to work with those dips, it was necessary to improve its elaboration; several hypothesis were considered for new attempts. Latexes and resin were substituted for new ones hindering storage problems or age life effects; mechanical agitation was stopped so air capture was minimized (no anti-foaming use); mixing temperature was controlled (around 17 ºC) and pH was measured (2.3.1) before and after formaldehyde addition. Lowering the agitation level and changing resin sample, by other with lower age life, was crucial for a stable dip preparation. However, at this moment, there is a non formulated explanation for this, rather than an empirical. Using the same formulation, chemicals and operator, two dips were performed at different room temperatures, at 15 ºC and 21 ºC respectively.
From results, one may positively state that room temperature interfere on 902 PS dip stability (Figure 20); in reality, this fact is coherent with the problems announced on 3.3.2. Production analysis and Formulations chapter (elaboration during the night shift).

Formulations stability range was also assessed during the adhesion optimization procedure. Dip solid content (S.C. / %) was used as a control parameter because it directly affects the adhesion. Starting with a minimum of 15 wt. % two more experiments were performed for 18 wt. % and 22 wt. %. Solid content was decreased by adding water (diluting the dip).

Concerning the RFL formulation, only ammonia (25 wt. %) and formaldehyde (37 wt. %) were considered as no contributing for the solid content; ammonia is used for pH control and evaporates easily; formaldehyde is consumed during methylol group’s formation.

*Figure 20 - Room temperature effect on 902 PS solutions stability.*

Fixing agitation level, setting temperature on 15 °C range, using brand new chemicals and the same operator, 902 PS dip recipes were newly performed.

For 15% S.C., 902 PS dip, did not presented agglomeration although it showed a high viscosity level, resulting on a high tackiness final cord; for 902 Min VP, the prepared dip was stable, but started to agglomerate on LDU dip tray (*Figure 21*), during impregnation, resulting on a non homogenously dipped cord.

*Figure 21 - Dip agglomeration, high viscosity dip and logistics problems with machine running dirtier.*
Maximum VP-Latex content formulation, 902 Max VP 15%, was also characterized with high viscosity but without instability problems. Its superior stability could be related to VP-Latex single presence.

All dipped cords showed high tackiness and low length samples; it means less than 100 meters were perfectly dipped, being lower to the critical length needed for process stabilization (3.2.1 LDU Setup). For 18 % and 22 % S.C formulations, same problems occurred, nevertheless trials were carefully executed; dipping process was done during the first hours of the morning (low temperature) and dip maturation time was extended.
4.1 902PS DIP - results

Nevertheless, with a very careful approach and time taking methodology, trials were performed. On Table 2, results are presented. For 22% solid content solutioning, it was impossible to get homogenously dipped cords due to non stability effects. Based on obtained appearance levels, results cannot be considered as expressible. Adhesion force reaches a very high value for both Min VP formulations, conflicting with literature references: “For RFL dips used to promote adhesion to thermoset elastomer types such as NR, NR/SBR and SBR, the best performance is obtained by using VP-Latex, which is a terpolymer of vinylpiridine, styrene and butadiene(...)” (15)

Table 2 - Results for the first DoE trials, Peel test and H test results for different latex blends and solid contents percentage. Dip pH control.

<table>
<thead>
<tr>
<th>Latex Blend</th>
<th>902 PSA</th>
<th>902 Max VP</th>
<th>902 Min VP</th>
<th>902 PSA</th>
<th>902 Max VP</th>
<th>902 Min VP</th>
<th>902 PSA</th>
<th>902 Max VP</th>
<th>902 Min VP</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.C. / %</td>
<td>21.41</td>
<td>22.09</td>
<td>22.09</td>
<td>18.00</td>
<td>18.00</td>
<td>18.00</td>
<td>15.00</td>
<td>15.00</td>
<td>15.00</td>
</tr>
<tr>
<td>RF/L</td>
<td>0.265</td>
<td>0.2548</td>
<td>0.255</td>
<td>0.265</td>
<td>0.2548</td>
<td>0.255</td>
<td>0.265</td>
<td>0.2548</td>
<td>0.255</td>
</tr>
<tr>
<td>VP/SBR</td>
<td>0.507</td>
<td>Infinite</td>
<td>No VP</td>
<td>0.507</td>
<td>Infinite</td>
<td>No VP</td>
<td>0.507</td>
<td>Infinite</td>
<td>No VP</td>
</tr>
<tr>
<td>VP/NR</td>
<td>0.570</td>
<td>Infinite</td>
<td>No VP</td>
<td>0.570</td>
<td>Infinite</td>
<td>No VP</td>
<td>0.570</td>
<td>Infinite</td>
<td>No VP</td>
</tr>
<tr>
<td>Peel Test / N</td>
<td>Non-stable</td>
<td>184 ± 18</td>
<td>196 ± 7</td>
<td>243 ± 15</td>
<td>174 ± 9</td>
<td>186 ± 9</td>
<td>226 ± 16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>App. (1-5)</td>
<td>Non-stable</td>
<td>1.5</td>
<td>2.0</td>
<td>1.0</td>
<td>1.5</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H - Test / N</td>
<td>Non-Stable</td>
<td>99 ± 16</td>
<td>124 ± 11</td>
<td>86 ± 5</td>
<td>101 ± 6</td>
<td>113 ± 12</td>
<td>66 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final pH</td>
<td>Non-Stable</td>
<td>7.39</td>
<td>8.22</td>
<td>8.76</td>
<td>8.89</td>
<td>8.15</td>
<td>8.88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
On literature, (7), it is settled: “The presence of pyridine nuclei in the rubber latex molecule facilitates the interaction between the resin and fibre through hydrogen bonding mechanism. It was also observed that a maximum adhesion could be achieved with a 2-vinyl pyridine content at about 15 % (VP-Latex)”.

Although peel test results, for Min VP content, were very high, (almost rubber-to-rubber peel force values), H-Pullout force results, for same trials, were completely contradictory; H-test procedure does not undergo as much errors as peel test, it is performed at room temperature, and cords are oven dried before its elaboration, avoiding this way high temperatures interference comparatively to peel test.

Nevertheless, H-test results are the lower ones when peel force reaches the maximum. In fact, the standard deviation within H-test trials is usually very elevated, but it is impossible to validate these trials, not only because of its results but also due to its non reproducibility. Accordingly to (2.3.1), pH control is essential to improve adhesion; Miller and Robinson stated that adhesion of cord to rubber depends on the pH of RFL adhesives. Too high or too low pH is inadequate. Adhesion is affected by the degree of condensation of the resorcinolic resin. And condensation conditions are affected by alkali concentration. Thus, the dependence of adhesion on pH may be brought about by change of RF resin condensation. As the optimum maturing conditions is affected by concentration of RF solution, type of latex, and heat treatment after dipping, the most advantageous conditions for RFL preparation should be decided empirically. (5)

Going forward and trying to give a scientific explanation for the succeeded, pH had been measured, before and after formaldehyde addition (Final pH; Table 2). In fact, pH values were accordingly to literature (5) when using butyl latex or SBR latexes keeping suspended the explanation for dip non stabilization.

Being the first trials, performed with few practice on dipping and adhesion testing, methodology has been inquired by comparing author’s results with those of an experienced operator, using a new greige cord sample and repeating all the standard formulations for the three different solid contents. Results indicated the same problems trend, as reported on Table 3.

Unfortunately, the conventional RFL adhesive system is a highly sensitive system.

In effect, the system is too sensitive to processing variables. (…) This may be due to any of a series of variables, such as temperature, concentration of components in the dip, finish on the fiber (sizing), etc. This failure of the textile to develop good adhesion with conventional adhesive system results in rejection of that batch of textile by the rubber fabricator and the
textile has to be sold off at a fraction of its true value, for other uses where adhesion is no
critical, at a great economical loss. (16)

Table 3 - First trials remake results for 902PS dip.

<table>
<thead>
<tr>
<th></th>
<th>902 PS</th>
<th>902 18 %</th>
<th>902 15 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.C. / %</td>
<td>21.41</td>
<td>18.00</td>
<td>15.00</td>
</tr>
<tr>
<td>Remake (Peel Test / N)</td>
<td>183 ± 14</td>
<td>171 ± 14</td>
<td>153 ± 3</td>
</tr>
<tr>
<td>App. (1 - 5)</td>
<td>1.0</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>New Cord Sample (Peel Test / N)</td>
<td>184 ± 7</td>
<td>120 ± 9</td>
<td>162 ± 8</td>
</tr>
<tr>
<td>App. (1 - 5)</td>
<td>2.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>New Operator (Peel Test / N)</td>
<td>169 ± 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>App. (1 - 5)</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In fact, some answers can be found on literature: When the formaldehyde concentration is higher, the viscosity of the resin solution is also increased due to the formation of higher molecular weight products. The maturing conditions necessary to prepare a stabilized dip depends on the R/F solution concentration, amount and type of catalyst and also latex blend.

Longer maturation for RF reaction or after blending with the latex is detrimental because condensation of resorcinol and formaldehyde continues and decreases progressively with the number of reactive sites or groups. With the pre-condensed resin based dip, too long maturation may decrease the adhesion.

When the resin solution is prepared with ammonia, formaldehyde could react with ammonia to produce methylolated amines first, which in turn reacts with resorcinolic resin to produce an insoluble material. Ammonia is more reactive towards formaldehyde, and therefore the formation of insoluble material cannot be avoided. (Figure 19) (7)

Nevertheless, this must be considered a hypothetical explanation; ammonia phase equilibrium is preferential to gas phase, meaning that possible reactivity with formaldehyde will be lower being affected by agitation, and also, its solubility in water, decreases with an increase on temperature (47 % for 0 ºC and 31 % for 25 ºC); this way, solid material formation will be minimized. (3.3.1).

In fact, (8), related RFL dip stabilization with preventing ammonia to react with formaldehyde, being hexamethylenetetramine responsible for limiting resin’s formation extent and latex colloidal destabilization.(2.3.1)
Formaldehyde possibly reacts with ammonia, leading to imines formation; imines is a functional group or chemical compound containing a carbon-nitrogen double bond. On the considered reactive medium, it will react to form the called methylolated amines, by being affected from the phenolic species presence (Resorcinol - precondensed resin), which will act as a nucleophile, by breaking the double bond, leading to the insoluble material compounds formation.

Alkaline medium, inspected by pH values, posted on Table 2, promotes the nucleophile addition reaction.

The presented mechanism, on Figure 22, must be considered as an attempt to explain the phenomenon; In fact, results analysis gives an interaction between factors (temperature, compounds reactivity, pH deviation, stirring effect, etc.) rather than a simpler reaction mechanism, for dip instability. Not being this thesis purpose, one could say that know how was built and several information was collected.

Figure 22 - Possible reaction mechanism for insoluble material formation.
4.2 902PS Modified DIP

As stated on 4.1, 902 PS formulations were modified, on C-ITA, by changing its latex blend proportions and maintaining other components amounts. Chemicals used on these formulations are the same. The new recipe was named 902 PS Modified. At first impression, one may say that empirical knowledge led to this decision, giving to latex (preferably SBR and NR) destabilization the main reason for all issues previously identified.

Table 4 - Comparison between 902 PS and 902 PS Modified recipes.

<table>
<thead>
<tr>
<th>Component Data in Recipe</th>
<th>902 PS - Modified</th>
<th>902 PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step</td>
<td>Component</td>
<td>Wt.%</td>
</tr>
<tr>
<td>1</td>
<td>Water</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>VP - Latex</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>SBR</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Natural Rubber</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Ammonia 25%</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>RF-Resin 75%</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Formaldehyde 37%</td>
<td>37</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Solid Content</td>
<td>%</td>
<td>22.00</td>
</tr>
</tbody>
</table>

RF/L | 0.255 | 0.265 |
VP/SBR | 1.440 | 0.462 |
VP/NR | 2.357 | 0.570 |

Changing the latex content by increasing VP-Latex while reducing SBR and NR amounts, has positively affected dip stability and enhanced adhesion force and coverage. One may say that previous chapter technical hitches were completely solved, however, this new formulation is only stable when prepared on a high volume tank (Figure 23), with agitation, and all elaboration techniques cited on 3.3, not being when only a small volume sample is prepared.

![Figure 23 - C-ITA dip preparation area; Agitator "zoom in" for 902PS Mod.](image)
In fact, when prepared to use on LDU, it showed high viscosity at room temperature, resulting on a higher tackiness dipped cord. It is not correct to infer that it also occurs on production; PDU’s have compress rolls and a vacuum system which provides a dip pick up adjustment. High tackiness it is not necessarily bad, in fact, it is desirable for some customers while promoting green adhesion (low thermal adhesion).

Based on previous information, if resin to formaldehyde ratio (R/F) had been modified, by diminishing formaldehyde amount, viscosity could be reduced (4.1). From C-ITA know-how, is known that a decrease of R/F seems to cause an increase on adhesion (optimum level in between 1.5 and 2.2, although, for other recipes and fibres). (17) In effect, it is a contradictory situation that is beyond this paper scope; production results are the ones, so, trying to change recipe’s formulation in order to achieve a better result on LDU is an erroneous approach.

Figure 24 - 902 PS Modified 22% dip on LDU, high viscosity dip.

Homogeneously dipped cords were obtained for 902 PS Modified trials, regarding the same systematic methodology as explained on the beginning of this chapter. Trials were performed for 22% solid content.

Table 5 - Second DoE trials results for 902 PS Modified.

<table>
<thead>
<tr>
<th>S.C. / %</th>
<th>21.56</th>
<th>22.09</th>
<th>22.09</th>
<th>21.31</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF/L</td>
<td>0.263</td>
<td>0.255</td>
<td>0.255</td>
<td>0.267</td>
</tr>
<tr>
<td>VP/SBR</td>
<td>1.582</td>
<td>0.462</td>
<td>Infinite</td>
<td>0.000</td>
</tr>
<tr>
<td>VP/NR</td>
<td>1.838</td>
<td>0.570</td>
<td>Infinite</td>
<td>0.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peel Test / N</th>
<th>196 ± 3</th>
<th>174 ± 5</th>
<th>202 ± 8</th>
<th>225 ± 26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ap. (1 - 5)</td>
<td>4</td>
<td>2</td>
<td>3.5</td>
<td>2</td>
</tr>
</tbody>
</table>
For those trials on Table 5, only peel test was executed, by saving time and as a manner to conclude if there are good adhesion levels for 902 PS dip by using vacuum, if 902 PS - Modified dip gives good adhesion and coverage levels and what were the results for the extreme recipes. It also permitted to see if dip instability persists.

Using vacuum on LDU as a manner to reduce dip concentration on cord, definitely helped machine to run cleaner although both adhesion force and appearance were at a low level. Obviously, dip pickup has a direct effect on the adhesion of treated cords to rubber. (...) There should be enough penetration of the dip into the fibres to ensure good anchorage. In his study, Dietrick showed that adhesion increases as dip pickup increases but a saturation point is reached where increased pickup does not substantially improve adhesion. Also, high dip pickup will stiffen the treated cord and may compromise its flexibility and/or durability. (13). However, for 902 PS Modified based trials, dip pick up was not studied; dip pick up and solid content remained on values based on production know-how.

For the standard and maximum VP content recipes, 902 PS - Modified and 902 PS - Modified Max VP respectively, higher appearance levels was reached, as well as peel force; it means, once again, that a good adhesion level was reached while increasing VP-latex content on 20 % from initial recipe or continuously increasing to an extreme scenario as 902 PS Modified Max VP. In fact, it seems to be on the same adhesion level although one may pay special attention because its appearance level is inferior, and there is no SBR or NR on its formulation, being sooner to achieve a conclusion.

### 4.2.1 Stability range

902 PS Modified Min VP results, showed that dip completely failed on cord to rubber adhesion; its peel force value is considerably higher than 902 PS Modified being on a rubber to rubber strap peel force level; it means that mainly occurred a rubber-to-rubber separation. Cord coverage was completely affected and there were not a thin rubber film on cords surface as a synonym of dip effectiveness, as showed on Figure 25.

*Figure 25 - Peel Test samples with weak cord coverage for 902 PS Modified Min VP.*
Adhesion optimization by new latex blends on Rayon reinforcement for tyre application.

As referred on 3.2.2, excessive temperature can crosslink the dip resulting on poor adhesion between rubber and fibre; it could be a explanation for 902 PS Modified Min VP results, leading to repeat the peel test for this trial. Results were the same, and expected, to a non VP-Latex presence formulation.

Results from Table 5 were viewed like a turning point. Hence, a new DoE was made for 902 PS Modified recipe, considering a predictable range based on previous results, where good adhesion levels would be reached; it was named as dip stability range, defined for ratios in between 902 PS Modified and Max VP formulation.

4.2.2 902 PS Modified New DoE

As previously explained, the same methodology was used to define the new DoE. All the recipes, considered for impregnation on LDU, plus adhesion testing, were the ones, selected by the author that will give an effective variation on amounts resulting on measurable adhesion samples (excluding those who give little mass variations).

Consequently, among standard recipe (902 PS Modified) and extreme recipe (Max VP), 4 new formulations were considered, corresponding to VP/SBR variations, and another 4, to VP/NR respectively. For a constant RF/L ratio, strong results were achieved resulting on a latex optimization trend.

During those trials, external information and literature survey was taken, leading the experimental work to a different direction.

Wootton reported that a blend of 80% VP with 20% SBR latex results in an optimum adhesion for Rayon tire cord. (...) Adhesion was measured to a NR compound. (18)

Takeyama and Matsui suggested 80% SBR blended with 20% VP latex provides adequate Rayon adhesion. (15)

In fact, it seems contradictory information, nevertheless, it must be analyzed; Wootton proposal is coherent with the so far achieved results, by increasing VP latex amount, adhesion level increases. The suggested formulation excludes adding natural rubber to dip and refers the compound type where adhesion was tested. It may led to think that it is a non-reproducible formulation although a NR compound is used; The compound used on C-ITA for adhesion trials can contain NR on its constitution, besides other lattices. This suggestion will be considered on this work scope, by the same methodology, considering amounts on dry weight and the same chemicals as other formulations.

Takeyama and Matsui recipe is up to date comparatively to Wootton’s, leading us to think on a more customized formulation, for mechanical rubber goods and more economically effective.
In fact, SBR started to be mainly produced, on Germany, during Second World War period as a substitute for NR, whose existence in Europe was minored due to Asian commercial block. Cost purposes effects, on nowadays latex blends formulations, will be inspected lately on this paper. Takeyama’s formulation won’t be considered for adhesion testing.

Wooton formulation was named 902 PS 80/20, and it is obtained from 902 PS Modified by changing VP-latex and SBR amounts, on an 80/20 relation, excluding NR presence. Resin and Formaldehyde steps remained equal.

RF/L ratio for this formulation was lower than the considered for DoE trials; nevertheless, 80/20 results will be shown on Figure 26. Although, there is no trend line represented between 902PS Modified (reference) point (VP/SBR = 1.44) and the first DoE recipe result considered on the stability range (VP/SBR = 2.50) otherwise it were comparing non-comparable formulations (different RF/L).

![Figure 26 - Adhesion results for VP/SBR modification](image)

On Figure 26, adhesion peel force and cords appearance are organised on an increasing VP/SBR ratio tendency; it robustly specifies that VP-Latex single presence will led to adhesion and coverage results on the same level as reference formulation. Wooton formulation gave a 5 N or 7 N superior force comparing to 902 PS Max VP or 902 PS Modified, but it lacks coverage; this formulation can be compared with DoE trials because it excludes NR from its formulation, but one may suggest that its fault is not promoting appearance.

Same analysis was done to the VP/NR ratio variation. (Figure 27)
Without SBR on its formulation, dipped cords were tested. Coverage results presented a homogeneous trend for VP/NR = 50; VP/NR = 200, clearly distinguishing these samples from the lower values ratio.

![Figure 27 - Adhesion results for VP/NR modification](image)

Peel force values are inferior when compared to those posted on VP/SBR chart on Figure 26, although, results trend was, once again, peel force and coverage maximized while increasing VP-Latex content and reducing other latexes content on formulation. VP/NR ratio started on VP/NR = 5 because for an inferior value, like VP/NR = 2.50, dip started to agglomerate, being analogous to succeeded on 4.1.

![Figure 28 - Peel test samples comparison for 902PS Modified new DoE.](image)
Being earlier to conclude NR interference on cord coverage, but comparing results from Figure 26 and Figure 27 and author’s visual inspection, it seems appearance level is higher for an optimized amount of NR, which must be considered on a two criteria interception; it means NR amount should be the one promoting good cord coverage but at the same time minimizing the occurrence of instability on dip. This discussion is both supported by 4.2.1 results and results trend for VP/NR ratio (higher NR amount).

As mentioned on 3.4, on parallel with peel test, adhesion level was also inferred by H- Pullout force versus VP/SBR and VP/NR ratios.

**Figure 29 - Adhesion for R/F=0.255 (in mass), for VP/SBR different ratios.**

**Figure 30 - H- test samples for ratios modification on 902PS Modified dip.**
From Figure 29, latex optimization is newly secured by 902 PS Modified Max VP; for this formulation, H-pullout force achieves its higher value. Its results trend was according to one obtained for the same ratio variation on peel test. Absence of SBR leaded pullout force to increase 20 N on its value comparing to the standard formulation (902 PS Modified VP/SBR = 1.44).

On Figure 30, there are two important aspects resulting from visual inspection that helped to secure last paragraphs statements: On 902 PS Modified and 902 PS Modified Max VP samples, upper rubber block was removed letting rubber attached to cord, conferring its black rounded aspect; it means, failure occurred on rubber to rubber interface rather than dip to rubber linkage. Another aspect is cord failure and the way it gets off from the upper block; in fact, for VP/SBR = 5 ratio, cord was pulled out from rubber block like there was no bond between those materials. As an effect, a low pullout force value was obtained.

![Figure 31](image)

*Figure 31 - Adhesion for R/F=0.255 (in mass), for VP/NR different ratios.*

H-test was also realized for VP/NR variation samples. Figure 31 must be analyzed jointly with previous information. NR presence on formulation granted higher pullout force for lower ratio values. Although, while reducing its presence till the extreme case scenario, pullout force continuously increased, once again, on the same previously mentioned results trend (Max VP).

Special attention must be given to H-pullout force for VP/NR = 200, because it registered a 40 N deviation from its locals. It was considered as a no evident peak, being 90 % of the results indicating that adhesion level reaches its maximum for VP-latex single presence formulation. Accordingly to 4.1, “(...) standard deviation within H-test trials is usually very elevated”, being a possible reason to this off-trend result. (Figure 32)
4.3 902PS Modified to 701PS DIP

Based on last chapter conclusions it may seem repetitive to say that the choice of the latex component has a pronounced effect on adhesion, but in fact, for (5) vinyl-pyridine terpolymer latex only or a mixture of vinylpyridine latex and SBR latex are widely accepted for preparing RFL adhesive for tyre fabric to use on tyre carcass.

Table 6 - Comparison of effect of latex type on adhesion of Rayon and Nylon to rubber.
(adapted from (5))

<table>
<thead>
<tr>
<th>Latex</th>
<th>Rayon / %</th>
<th>Nylon / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR latex</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td>Natural latex</td>
<td>75</td>
<td>55</td>
</tr>
<tr>
<td>Blend of 80% SBR and 20% VP latex</td>
<td>95</td>
<td>80</td>
</tr>
<tr>
<td>Vinylpyridine latex</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

While nylon requires 100% vinylpyridine latex for maximum adhesion (Table 6), there is an optimum mixture of vinylpyridine-SBR latex for rayon. Single vinyl-pyridine latex use is superior for adhesion as previously described, but is not favorable for fatigue of textiles. (5)

Although literature opinion was set like last paragraph, results from 4.2.2 showed that by only using VP-Latex on Rayon dip formulation, strong adhesion results were obtained.

![Graphic representation of the comparison between 902 PS Modified formulation and selected recipes](image)

Figure 32 - Adhesion level comparison between 902 PS Modified formulation and selected recipes (from lower VP - Latex amounts to maximum content).

On Figure 32, an illustrative line, indicating 902 PS Modified result was sketched, intercepting the new formulations peel test results, which provided better results comparing to reference; recipe number 3 and 902 PS Modified Max VP.
Adhesion optimization by new latex blends on Rayon reinforcement for tyre application.

On it, peel force side deviation results were also presented. It was helpful by showing that recipe number 3 has a considerable deviation on it result, being considered less reliable than single VP-Latex formulation, which has a side deviation of only 2 N.

During this report some minimal references had been done to nylon. Nevertheless, a special attention must be given both for literature (mechanisms 2.3.3, Table 6) and C-ITA knowledge. In fact, 902 PS Modified Max VP dip formulation, for 22 wt. %, is nearly equal to Nylon dip latex blend used, at date, on C-ITA. On Table 7, a comparison between those recipes is done.

Table 7 - Comparison between 902 PS Modified and 701 PS recipes

<table>
<thead>
<tr>
<th>Component in Recipe</th>
<th>902 PS - Modified Max VP</th>
<th>701 PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0%</td>
<td>-</td>
</tr>
<tr>
<td>VP - Latex</td>
<td>40%</td>
<td>-</td>
</tr>
<tr>
<td>SBR</td>
<td>67%</td>
<td>-</td>
</tr>
<tr>
<td>Natural Rubber</td>
<td>60%</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>0%</td>
<td>-</td>
</tr>
<tr>
<td>Ammonia 25%</td>
<td>25%</td>
<td>-</td>
</tr>
<tr>
<td>RF-Resin 75%</td>
<td>75%</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>0%</td>
<td>-</td>
</tr>
<tr>
<td>Formaldehyde 37%</td>
<td>37%</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>1.00</td>
</tr>
<tr>
<td>Solid Content</td>
<td>%</td>
<td>22.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>902 PS - Modified Max VP</th>
<th>701 PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF/L</td>
<td>0.255</td>
<td>0.206</td>
</tr>
<tr>
<td>VP/SBR</td>
<td>1.440</td>
<td>-</td>
</tr>
<tr>
<td>VP/NR</td>
<td>2.357</td>
<td>-</td>
</tr>
</tbody>
</table>

4.3.1 RF/L adjustment

Nylon formulation, 701 PS, presents a lower value for RF/L ratio but it is only constituted by VP-Latex. Rayon cord was dipped with 701 PS retrieving an adhesion result that is better than reference formulation (902 PS Modified) and even better than 902 PS Modified Max VP. Excluding, for now, dip standardization as an economical and product engineering improvement, it is important to note that RF modification together with VP-Latex increased amount (+5 % on wt. %) leaded to improve the last chapter best result (902 PS Modified Max VP).

Starting with the same methodology, as realized on other DoE’s, recipes were defined to inspect resin interference on adhesion; based now on 902 PS Modified Max VP formulation, latex composition was fixed, varying resin proportions (RF/L) from a minimum resin content
(above 902 PS Max VP) and a maximum content, upper to 701 PS dip and setting formulations in between (RF/L = 0.199 and RF/L = 0.237).

![Graph showing peel force (N) vs. RF/L for different resin formulations.](image)

**Figure 33 - RF/L modification for Rayon cord dipping with 701 PS dip and new formulations.**

![Graph showing appearance results for different resin formulations.](image)

**Figure 34 - Appearance results for RF/L modifications in between 902 PS Modified dip and 701 PS.**

Results trend, observed on Figure 33, absolutely states that changing rayon dipping for 701 PS results on a 30N higher peel force, a maximum appearance level and a better result when compared with reference recipe, RF/L = 0.255.
On Figure 34, peel test samples appearance level is represented for all tested formulations; 701 PS dip, nylon dip, presented the higher value.

Although it is going out from this paper main subject, these conclusions confirmed a possibility to dip standardization. Special attention must be given to NR and SBR absence.

### 4.3.2 Cord Properties

In fact, one may say that going for 701 PS solution for rayon dipping did not certify that final cords properties will be just like those for 902 PS Modified and final costumer’s specifications will be respected. Hence, dipped cords testing were promoted to analyse its interference; Elongation at 45 N, stiffness and shrinkage were the main parameters tested. It corroborates that 701 PS is the best formulation.

Table 8 - Cord characteristics for 902 PS Modified and 701 PS formulations.

<table>
<thead>
<tr>
<th>Cord characteristics</th>
<th>902PS Mod</th>
<th>701 PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peel</td>
<td>195</td>
<td>223</td>
</tr>
<tr>
<td>Appearance</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Breaking load</td>
<td>242</td>
<td>222</td>
</tr>
<tr>
<td>Elongation @ 45N</td>
<td>1.24</td>
<td>1.22</td>
</tr>
<tr>
<td>Break elongation</td>
<td>13.7</td>
<td>12.7</td>
</tr>
<tr>
<td>Stiffness / cN</td>
<td>10</td>
<td>16</td>
</tr>
<tr>
<td>Shrinkage</td>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Force + Pretension / cN</td>
<td>537.7</td>
<td>569.3</td>
</tr>
</tbody>
</table>

New peel test were realized with same cord samples that will be tested, offering this way the possibility to check if results are reproducible. In fact, adhesion force for 701 PS dipping continued on the same level (compare with Figure 33) and cord coverage slightly augmented, reaching its maximum level. Elongation, breaking load and breaking elongation results for both cords did not show significant deviation on between. Thermal shrinkage was tested, but results were like expected for rayon (2.2). Increased stiffness on 701 PS dip is thought to be related to the high modulus of vinylpiridine terpolymer itself. (19) Although its difference on 6 N it is not significant accordingly to C-ITA knowhow.
4.3.3 Cost saving

Dip raw materials costs were analysed on a year-to-date basis. Considering all the prices flotation’s and suppliers different offers; a 15% cost reduction, (on recipe), formulation was found when using 701 PS for rayon dipping. (Figure 35)

In fact, dip standardization will minimize process costs not only by eliminating two expensive chemicals, SBR and NR, but mostly by reducing its effects on maintenance, repair and operation; In fact, SBR and NR are respectively 48% and 40% more expensive than VP - Latex (on € / ton basis).

SBR and NR are these days affected by a continuously decreasing availability and increasing cost. It creates incentives to identify suitable alternatives to natural rubber. Adhesive formulators have blended natural rubber latex with small amounts of styrene butadiene latex albeit with a negative impact on adhesive performance. For pressure sensitive adhesive applications, like tyre cord applications, natural rubber has been hard to replace due to its superior auto adhesion characteristics, low tack and good compatibility with tackifiers. (20)

Hence, going for a single VP Latex dip bath will avoid its use when impregnating Rayon and Nylon, being an interesting alternative to minimize formulations associated costs.

When the operative effect is referred, it means that C-ITA dipping unit could use the same dip and will only have to change its thermo-mechanical setup for the different fabrics. Time gain between changing dip, maintenance operations, ovens cleaning operations and liner passing will increase its production level.
4.3.4 Dip standardization

Several other trials were performed using C-ITA dipping formulations for different fibres impregnation. From those, it were selected the ones which has a similar constitution when compared with rayon standard recipe. There were also been considered different solid content formulations like 701 PS 17% and F801 20%. Once again, 701 PS 22% dip, showed the best adhesion results.

Figure 36 - Rayon cord adhesion level by using different dips used on C-ITA.

Figure 37 - Appearance results for Rayon dipping formulations; Reference recipe (902 PS Modified) compared with and other dips at C-ITA.
4.4 902PS Modified - Best formulation

From chapter 4.2, DoE’s were performed by only changing one of the ratios and fixing the other. It allowed inferring both SBR and NR independent interference on dipping and it final porpouse - adhesion level between fabrics and rubber. Working with a blend inevitably takes the adhesive formulator to consider a variation of both compounds (SBR and NR). Software like JMP Application 10 offers the possibility to prepare a DoE for mixtures. Nevertheless, with a short time period to run several trials, a different methodology was used by considering previous chapter’s results. On Figure 38, previously enunciated results are expressed together. From recipes 3 and 7, a new formulation was set using VP/SBR ratio from recipe 3 and VP/NR ratio from recipe 7.

Starting with the initial formulation, VP/SBR = 10; VP/NR = 50, trials were performed. Best results were observed for VP/SBR = 4.9; VP/NR = 50 ratios. Adhesion peel force was $213 \pm 3$ N with good cord coverage (appearance 4). The best trial formulation overcame the one used in production in every single time. The adhesion results showed a side deviation value of only 3 N. It increased 902 PS Modified adhesion level on a gap of 8 N and cord coverage remained. Attention must be paid while looking for LDU dipped cords results; there is always an increase on peel force values from cords to production fabrics testing. When “scaled up”, adhesion results for the tested configuration are higher on LDU when compared to production.

During these work trials same rubber batch had been used for both peel and H test.

Figure 38 - Schematic representation of adhesion levels expected for combined formulations.

4 - Results and Discussion
4.4.1 Best formulation cost saving

Adhesive formulators using NR latex have seen significant price fluctuations in their raw materials in the last few years. Continued price volatility and uncertainty should be considered when formulating decisions are made. The best experimental formulation (“Best Formulation”) is compared to 902 PS Modified, in terms of chemicals content and final cost.

Table 9 - Best Formulation modifications and economics.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>902 PS Modified</th>
<th>Best Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>VP-Latex</td>
<td>-</td>
<td>-1.60</td>
</tr>
<tr>
<td>SBR</td>
<td>-</td>
<td>-3</td>
</tr>
<tr>
<td>NR</td>
<td>-</td>
<td>-6.5</td>
</tr>
<tr>
<td>Others components</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RF/L</td>
<td>0.235</td>
<td>0.235</td>
</tr>
<tr>
<td>Total Cost / €</td>
<td>-</td>
<td>-3.2%</td>
</tr>
</tbody>
</table>

Advantages come out by definitely reducing NR and SBR percentage, allied to a cost saving of 3%.

Moreover, and mostly important, the presently used cord dip compositions containing the resorcinol-formaldehyde resins must be aged before use, and their useful lifetime, once prepared, is a matter of only a few days at best. Depending on the ambient temperature at which they are stored.

Therefore, a cord dip composition in which the resorcinol-formaldehyde resin is replaced, which provides at least as good adhesion of cord to rubber as the present RFL system, at lower cost and which does not require aging would solve a long-felt need.
5 Conclusions

This project embraces textile reinforcement materials (TRM) studies, at C-ITA, by defining several conclusions on the dipping area. The results, its reproducibility, as well as being part of an intensive research on specific literature, validated all the formulations previously announced.

The optimization process was initiated with a particularly instable dipping solution; nevertheless, strong results had been achieved. Two main conclusions were born from this study: The first, an optimized formulation based on nowadays dip, 902 PS Modified for rayon, where adhesion level is increased on 8 - 12 N, using a VP-Latex/SBR/NR blend with a cost reduction on formulation of 3%. It must be seen as an alternative while studying NR absence effects on tyre cords fatigue and age life. Nearby, C-ITA could implement this alternative.

The second, and a considerably more interesting one, is the possibility of dip standardization by using the same dip for two different textile reinforcement materials - Nylon and Rayon. On this possibility, a 15 % cost reduction is estimated, although MRO costs were not considered; it means this reduction is only calculated on a compounds cost basis and not on an overall scenario, where product industrialization issues are considered. As main advantages, it offers the possibility to eliminate 902 PS Modified dip from C-ITA dip list, led to a time gain between changing dip, maintenance operations, ovens cleaning and liner passing, increasing this way C-ITA production capacity. With 701 PS dip, Rayon presented a 211 ± 1 N peel force, maximum cord coverage level (5 in a 1 - 5 scale) and a H - Pullout force value of 144 N.

Information was collected and know-how achieved while trying to describe dip instability, conferring to this document an extra value for decision taking on C-ITA dipping process.

RFL technology is the core of tyre cords application during the years, and several innovations have been made, however, alternatives to formaldehyde use (there was no possibility to analyse VOC level present on the process) as also as resorcinol resins must be found, not only by reducing workforce exposure to its harmful content, but also regarding greener products and production processes.
6 Project Assessment

6.1 Accomplished Objectives

This work was initially thought as a method to inspect latexes blend function on all C-ITA dips. The unanswered question was: What is the improvement on fibre to rubber adhesion by changing actual dip solutions on its latex blend?

In fact, VP-Latex is present on all C-ITA dips, and it is questionable, if SBR and NR absence on dipping formulations, are leading to final fabrics (or cords) all the desirable properties. Rayon dip is the only containing a VP-Latex/SBR/NR blend.

To properly answer last paragraphs question, two different approaches could be done; to previously set a cord type and change its dipping formulation by adding SBR and NR latexes to it. Then the same procedure must be repeated for other cords.

Or, starting with rayon cords and its dipping formulation, now considered as obsolete 902 PS dip, and optimize its blend. Whenever an optimized formulation was set, cord type will be changed and adhesion level newly inspected. This approach was the selected one and inevitably leaded to a different route for this work than the initially thought.

First trials (902 PS dip) problems and discussion obligate to spend almost 2 of the 6 months period for this work.

Going to actual rayon dipping formulation, 902 PS Modified, and experiencing, on a small scale, all those problems inherent to its use on production, quickly was percept that going from 902 PS basis to other dips optimization was a wrong approach. The contrary seemed to be the wanted; to verify rayon adhesion level, on single VP-latex formulations.

On parallel there were two more central handled issues, cost saving and product industrialization. Very strong results were achieved on it, by concluding that adhesion level for rayon is promoted while using a dip without SBR and NR. Increasing this way dip cost effectiveness and achieving standardization possibility for dipping Rayon and Nylon. It is clear the advantage to produce this both fabrics, without changing dip, and most of all, without stop and maintenance periods among both fabrics production.

These work main goals had been accomplished by proving that maximum adhesion and appearance levels were reached by two different optimizations on latex formulations constitution; one can be considered a short time decision/alternative to nowadays reference dip, the best formulation. Other, considered a long time one, due to its necessity to be more deeply tested, is Nylon dip, providing the possibility to Nylon and Rayon dip standardization.
6.2 Limitations and future work

As mentioned on 1.2 Work contributions chapter, time was a crucial factor on this work development conferring to it an “unended” nature.

Working with rayon, its necessity to work with oven dried cords (moisture), and testing adhesion by two different methods, clearly consumed the time and opportunities to study other cords on optimized dip formulations. This work clearly defined that latexes blend increases dip cost and interferes on production level. Nevertheless, dip standardization proposal must be seen as a strong opportunity, and aging tests are needed, as a way of proving that NR absence is not interfering with cords age life and fatigue resistance on tire.

On 902 PS Modified to 701 PS formulation changing there was an apparent effect on changing RF/L ratio; it means resin proportion must be optimized.

By using other cords, like Rayon 1650 dtex and other cords types (Nylon, PET, Hibrids and Aramid), dip standardization must be analysed, none forgetting the dip solid content variations.

6.3 Final Assessment

Working on such a vast area, with so many variables and a huge impact on final product characteristics seemed overwhelming for a chemical engineering trainee. In fact, first months were very hard with all the uncertainty that dip non stabilization as delivered. Although, these work supervisors were capable to guide the author on a desirable way. It somehow seemed like “Don’t look for the next opportunity. The one you have in hand is the opportunity.”

In fact, on dip instability, dip standardization possibility and the best formulation were born, being at the same time, cost saving formulations.

It offered the possibility to eliminate rayon dip, 902 PS Modified, from C-ITA dip list with several advantages for maintenance, repair and operation (MRO).

Progress has undoubtedly been made; once again, this work must be seen as a promoter for further works on dipping process at C-ITA by always keeping in mind improvement and innovation.
Adhesion optimization by new latex blends on Rayon reinforcement for tyre application.

7 Bibliography


17. Direito, F. *Know-how and process key parameters for water based latex dip formulations to get robust reinforcement to rubber adhesion in passenger car tires*. 2011.


