Mestrado Integrado em Engenharia Química

Tire Cord Properties and Their Dependence on Twisting and Temperature

Master's Thesis

by

Paulo André Carrero Cardoso

Performed at

Continental AG - Body Compound & Reinforcement Technology



Supervisor: Prof. Adélio Mendes

Industrial Coordinator: Dr. Thomas Kramer & Dr. Carole Justine



Departamento de Engenharia Química

Acknowledgments

Now that the thesis has come to an end, it is time to thank and show recognition to every person that one way or another has helped or supported me during this stage of my life. Thereby I would like to properly express my gratitude to:

Professor Adélio Mendes for the guidance and the availability in dealing with any sort of questions.

Dr. Thomas Kramer and Dr. Carole Justine for their supervision, assertiveness and all crucial support to overcome every challenge in the developed work.

The Reinforcements Testing Laboratory crew for the patience and attendance during all the time.

All Body Compound & Reinforcement Technology department for all clarifications and gentleness over these months.

All the Portuguese community, present in Hannover which made this time even more enthusiastic.

Ms. Andreia Cruz for the huge cooperation inside and outside of the company.

Mr. Eduardo Diniz, Mr. Manuel Pinheiro and Mr. Alexandre Gomes for give me the opportunity to be present in Indústria Têxtil do Ave in Lousado for two weeks and for all collaboration during this project.

Mr. Nuno Drumond, Ms. Diana Pinto, Ms. Rute Pacheco and Ms. Ana Martins for so much knowledge in such a short time, which prepared me in the best way to challenges confronted during this thesis.

i

Abstract

The present master thesis was developed at Continental Technology Center in Hannover with the collaboration of Indústria Têxtil do Ave and of the Faculty of Engineering at the University of Porto.

Tires are highly engineered structures, consisting of more than 20 parts with more than 15 rubber compounds. One of the critical sections of the tire are textile layers, formed by a set of textile cords known as fabric. The final performance of the tire is affected by good physical, thermomechanical, adhesion and fatigue properties of tire cords. One of the fundamental properties of cords which helps ensure all of these specifications is the twist.

This thesis studies the effect of twist level on the performance of tire cords targeting to maximize the tenacity, elongation at break, fatigue resistance, and rubber adhesion of the cords. It also addresses to identify the performance differences among the various types of aramid fibers.

Polyester, polyamide 6.6 and aramid fibers have been selected to perform pure cords with different twist levels. As aramid fibers, Nomex, Arselon, Twaron, and Technora were used in this project. The mechanical properties of the cords were obtained from load/elongation at RT, 40 °C, 80 °C, 120 °C and 160 °C, thermal shrinkage, disc fatigue, peel test, creep and relaxation tests.

In the end it was possible to define the optimal twist factor for each cord construction: 210 for PET1100x1x2, 160 for PET550x1x2, 90 for PET225x1x2, 90 for NYLON235x1x2, 200 for ARA1100x1x2 and 60 for ARA220x1x2. Concerning the different types of aramid fibers, Technora and Twaron showed high tenacity although a very low fatigue resistance. On the other hand Nomex showed the highest stability fiber with respect to temperature and showed better results in terms of relaxation but a truly poor adhesion.

Key words: tire cords; reinforcements; twist; temperature; aramid fibers

Resumo

A presente dissertação foi desenvolvida no Centro Tecnológico da Continental em Hannover, em colaboração com a Indústria Têxtil do Ave e com a Faculdade de Engenharia da Universidade do Porto.

Pneus são estruturas complexas, constituídos por mais de 20 componentes com mais de 15 compostos de borracha. Uma das secções críticas do pneu são as camadas têxteis, formadas por um conjunto de cordas têxteis conhecido como tecido. O desempenho final do pneu é afetado pelas boas propriedades físicas, termomecânicas, de adesão e de resistência à fadiga das cordas de pneu. Uma das propriedades fundamentais das cordas de pneus que ajuda a assegurar todas estas especificações é a torção.

Esta tese estuda o efeito do nível da torção no desempenho das cordas de pneu com vista à maximização da tenacidade, alongamento de rutura, resistência à fadiga e adesão à borracha. Aborda ainda a identificação das diferenças no desempenho entre os diferentes tipos de fibras de aramida.

Por forma a construir cordas puras com diferentes níveis de torção foram selecionadas fibras de polyester, de poliamida 6.6 e de aramida. Como fibras de aramida foram usadas Nomex, Arselon, Twaron e Technora. As propriedades mecânicas das cordas foram obtidas a partir de uma série de testes físicos como força/alongamento à temperatura ambiente, 40 °C, 80 °C, 120 °C e 160 °C, shrinkage a elevada temperatura, teste da fadiga, teste da adesão, teste da deformação e ainda o teste de relaxamento.

No final foi possível definir o fator de torção apropriado para cada corda: 210 para PET1100x1x2, 160 para PET550x1x2, 90 para PET225x1x2, 90 para NYLON235x1x2, 200 para ARA1100x1x2 e 60 para ARA220x1x2. Em relação aos diferentes tipos de fibras de aramidas, Technora e Twaron apresentaram alta tenacidade mas muito baixa resistência à fadiga. Por outro lado, Nomex apresentou maior estabilidade em termos de temperatura, apresentou melhores resultados em relação ao relaxamento mas uma adesão bastante pobre.

Palavras chave: cordas de pneu; reforços; torção; temperatura; fibras de aramida

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.

Contents

C	onten	ts	. V
In	dex o	f figures	vii
In	dex o	f tables	, xi
G	lossar	y	xii
1	Int	roduction	. 1
	1.1.	Continental AG and project introduction	. 1
	1.2.	Project motivation and contribution	. 2
	1.3.	Thesis organization	. 2
2	Sta	ite of the art	3
	2.1.	Tire	3
	2.2.	Reinforcement materials	. 4
	2.3.	Terminology used in textile industry	. 4
	2.4.	Manufacture of textile reinforcements	. 6
	2.5.	Tire cords	. 7
	2.5	.1. Cord characterization	7
	2.5	.2. Cord construction	8
3	Ma	terials and methods	10
	3.1.	Cord designs	.10
	3.2.	Test methods	.11
	3.3.	Types of aramid fibers used	.16
4	Re	sults and discussion	17
	4.1.	Twist study	.17
	4.1	.1. Polyester pure cords	17
	4.1	.2. Polyamide 6.6 pure cords	24
	4.1	.3. Aramid pure cords	26
	4.1	.4. Effect of twist and conditioning on shrinkage	31

	4.1	.5. Materials comparison	33
	4.2.	Aramid fibers comparison	39
	4.2	.1. p-aramid vs m-aramid vs p-m-aramid	vs arselon40
5	Cor	nclusions	44
6	Pro	oject assessment	45
	6.1.	Accomplished objectives	45
	6.2.	Limitations and future work	45
	6.3.	Final assessment	45
7	Ref	ferences	47
An	nex A	A - Tire	49
An	nex E	3 - Twist and Fabric	50
			51

Index of figures

Figure 1 - Passenger car tire parts (adapted from [5])
Figure 2 - Cord parts (adapted from [9])6
Figure 3 - Appearance of a cord with low and high twist level (adapted from [7]) 8
Figure 4 - Design of: a) pure cord; b) hybrid cord level (adapted from [11]) 8
Figure 5 - Effect of temperature as a function of twist factor12
Figure 6 - Coverage in peel adhesion samples: a) no coverage, b) full coverage 13
Figure 7 - Beginning of creep test of Nomex1335x1x2 387 tpm14
Figure 8 - Beginning of relaxation test of Nomex1335x1x2 387 tpm
Figure 9 - Molecular structure of: a) para-Aramid, b) meta-Aramid, c) para-meta-Aramid (adapted from [19])
Figure 10 - Tenacity as a function of twist factor of PET1100x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability)
Figure 11 - E@B as a function of twist factor of PET1100x1x2 at RT and 80 $^\circ$ C (lines were added for readability)
Figure 12 - Temperature influence as a function of twist factor of PET1100x1x218
Figure 13 - Residual force as a function of twist factor of PET1100x1x219
Figure 14 - Peel adhesion results as a function of twist factor of PET1100x1x219
Figure 15 - Tenacity as a function of twist factor of PET550x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability)
Figure 16 - E@B as a function of twist factor of PET550x1x2 at RT and 80 $^\circ$ C (lines were added for readability)20
Figure 17 - Temperature influence as a function of twist factor of PET550x1x221
Figure 18 - Peel adhesion results as a function of twist factor of PET550x1x221
Figure 19 - Polyester cords with different twist: a) 200 tpm, b) 350 tpm, 470 tpm (extracted from [10])22
Figure 20 - Tenacity as a function of twist factor of PET225x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability)

Figure 21 - Elongation at Break as a function of twist factor of PET225x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability)
Figure 22 - Temperature influence as a function of twist factor of PET225x1x223
Figure 23 - Peel adhesion results as a function of twist factor of PET225x1x224
Figure 24 - Tenacity as a function of twist factor of NYLON235x1x2 at RT and 80 $^\circ$ C (lines were added for readability).
Figure 25 - E@B as a function of twist factor of NYLON 235x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability)25
Figure 26 - Temperature influence as a function of twist factor of NYLON235x1x2. 25
Figure 27 - Peel adhesion results as a function of twist factor of NYLON235x1x226
Figure 28 - Tenacity as a function of twist factor of ARA1100x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability)
Figure 29 - E@B as a function of twist factor of ARA1100x1x2 at RT and 80 $^\circ$ C (lines were added for readability)27
Figure 30 - Temperature influence as a function of twist factor of ARA1100x1x227
Figure 31 - Residual Force as a function of twist factor of ARA1100x1x228
Figure 32 - Peel adhesion results as a function of twist factor of ARA1100x1x228
Figure 33 - Tenacity as a function of twist factor of ARA220x1x2 at RT and 80 $^\circ$ C (lines were added for readability)
Figure 34 - E@B as a function of twist factor of ARA220x1x2 at RT and 80 $^\circ$ C (lines were added for readability)29
Figure 35 - Temperature influence as a function of twist factor of ARA220x1x230
Figure 36 - Peel adhesion results as a function of twist factor of ARA220x1x230
Figure 37 - Different conditioning state of cords
Figure 38 - Shrinkage results for relaxed and non relaxed conditioning of PET1100x1x2 cords
Figure 39 - Shrinkage results for relaxed and non relaxed conditioning of PET550x1x2 cords
Figure 40 - Shrinkage results for relaxed and non relaxed conditioning of PET225x1x2 cords

Figure 41 - Shrinkage results for relaxed and non relaxed conditioning of polyamide 6.6 235x1x2 cords
Figure 42 - Tenacity as a function of twist factor of PET1100x1x2, PET550x1x2, PET225x1x2, ARAMID1100x1x2, ARAMID220x1x2 and NYLON235x1x2 cords at RT (lines were added for readability)
Figure 43 - Tenacity as a function of twist factor of PET1100x1x2, PET550x1x2, PET225x1x2, ARAMID1100x1x2, ARAMID220x1x2 and NYLON235x1x2 cords at 80 °C (lines were added for readability).
Figure 44 - Polymer chain orientation: (a) Conventional organic fibers; (b) Aramid fiber (adapted from [20])
Figure 45 - Maximum loss of strength with twist at RT and 80 $^{\circ}$ C35
Figure 46 - E@B as a function of twist factor of PET1100x1x2, PET550x1x2, PET225x1x2, ARA1100x1x2, ARA220x1x2 and NYLON235x1x2 cords at RT36
Figure 47 - E@B as a function of twist factor of PET1100x1x2, PET550x1x2, PET225x1x2, ARA1100x1x2, ARA220x1x2 and NYLON235x1x2 cords at 80 $^{\circ}$ C (lines were added for readability)
Figure 48 - Tenacity as a function of twist factor of PET1100x1x2, PET550x1x2 and PET225x1x2 cords at RT (lines were added for readability)
Figure 49 - Tenacity as a function of twist factor of PET1100x1x2, PET550x1x2 and PET225x1x2 cords at 80 °C (lines were added for readability)
Figure 50 - E@B as a function of twist factor of PET1100x1x2, PET550x1x2 and PET225x1x2 cords at RT (lines were added for readability)
Figure 51 - E@B as a function of twist factor of PET1100x1x2, PET550x1x2 and PET225x1x2 cords at 80 °C (lines were added for readability)
Figure 52 - Tenacity as a function of twist factor of ARAMID220x1x2 and PET1100x1x2 cords at 80 °C (lines were added for readability)
Figure 53 - Tenacity as a function of twist factor of ARAMID220x1x2, NYLON235x1x2 and PET225x1x2 cords at 80 °C (lines were added for readability)
Figure 54 - Tenacity as a function of temperature for each type of aramid fiber (lines were added for readability)
Figure 55 - Maximum loss of strength with temperature for each type of aramid
fiber

Figure 56 - E@B as a function of temperature for each type of aramid (lines were
added for readability)41
Figure 57 - Relaxation rate of each type of aramid fiber41
Figure 58 - Creep rate of each type of aramid fiber42
Figure 59 - Shrinkage of each type of aramid fiber42
Figure 60 - Residual force of each type of aramid fiber43
Figure 61 - Peel adhesion results as a function of twist factor of each type of aramid fiber
Figure 62 - Passenger car tire parts (extracted from [5])
Figure 63 - Schematic diagram of tire cords in passenger car tires; a) Conventional; b) Belted bias-ply; c) Radial (extracted from [3])
Figure 64 - Twist directions (extracted from [11])50
Figure 65 - Woven fabric (adapted from [25])50
Figure 66 - Force Elongation test (extracted from [26])51
Figure 67 - Rotating discs in two opposite positions: a) extension; b) compression. 51
Figure 68 - Peel test (extracted from [26])51

Index of tables

Table 1 - Function of the main components of a passenger car tire	3
Table 2 - Textile terminology (adapted from [10])	5
Table 3 - Physical tests performed with cords (adapted from [8])	7
Table 4 - Pure cord constructions used in the twist study	10
Table 5 - Aramid cord constructions used	11

Glossary

List of variables

Γ	Force/Load	N
T_L	Number of turns per meter of a twisted cord or yarn	tpn
α	Twist Factor	
ε	Elongation	%

List of acronyms

ΑG Aktiengesellschaft ARA Aramid **Breaking Force** BF Decitex dtex Ends per decimeter epdm E@B Elongation at Break Elongation at Specific Force E@SF Force at Specific Elongation F@SE ITA Indústria Têxtil do Ave PET Polyester TF Twist factor tpm Turns per meter

1 Introduction

1.1. Continental AG and project introduction

The present Master Thesis was developed at Continental AG Tire Division, Hannover, in collaboration with Indústria Têxtil do Ave (ITA) and with the Faculty of Engineering at the University of Porto (FEUP).

Continental AG is a world leading automotive manufacturing company well known for their tires. In fact tires are the main product commercialized since it was founded in 1871. *Tire Division* is responsible for developing and meeting the needs concerning tires. Besides, there are more five divisions targeting to meet the consumer needs with respect to mobility. *Chassis & Safety Division* deals with integration of active and passive driving safety. *Interior Division* works with all information management related with the car. *Powertrain Division* integrates innovative and efficient system solutions for vehicle powertrains. *Contitech* develops and produces functional parts, components and systems for the automotive and other important industries.[1] [2] This huge and well organized structure employs around 177 000 collaborators distributed among 46 countries.

A tire is not only an integral part of vehicle design but also, the only part that is in contact with road. As such, it has to be able to sustain all kinds of road surface conditions (wet or dry, rough or smooth) and at the same time it has to absorb shocks, dissipate heat and resist to wear and damage. It is remarkable that all the specifications required for a tire would never be even near possible without the aid of textiles.[3] The textile elements that integrate a tire are present in the form of cords and are known as reinforcement materials. As the strength members of a tire, tire cords must define the tire shape, maintain durability against bruise and impact and support the loads. One of the essential cord properties that helps to ensure all of these specifications is twisting. On the other hand, it is also important be aware of performance of tire cords at high temperatures, once that in manufacturing and during the rolling service the tire is submitted to high temperatures. Regarding these concerns, the present project has two focuses: understand the effect of twist on performance of tire cords and clarify the performance of different aramid fibers as tire cords. For this purpose polyester, polyamide 6.6 and aramid fibers were selected to perform different cord constructions. Then for each cord construction were defined different twist levels and performed a wide range of tests as forceelongation, thermal shrinkage, disc fatigue and peel test. At the end was possible to

Introduction 1

define the proper twist for each cord construction and understand the divergence between the different aramid fibers used.

1.2. Project motivation and contribution

Reinforcement materials are the predominant load carrying members of the cord-rubber composite. This means that tire cords are the strength members of a tire.[4] One of the most important properties which provides that strength is twisting. Nevertheless does not imply that a high twist level is better regarding performance of tire cords. On the other hand, it is also significant consider their performance at high temperatures. According to this, find out an optimum twist level for each cord construction and comprise the performance of different aramid fibers was the driving force of the present project.

All the test methods and specimens developed during the present project were performed by the author in collaboration with Reinforcement Lab Testing staff.

1.3. Thesis organization

This thesis is organized in 6 main chapters, as follows:

Chapter 1, *Introduction*, is meant to introduce the company where the work took place, Continental AG, to frame and elucidate the work done.

Chapter 2, State of the art, describes the current knowledge about reinforcement textile materials and tire cords.

Chapter 3, *Materials and Methods*, reports the materials and methods employed in the present work.

Chapter 4, *Results and Discussion*, presents the results of the assignment and their discussion.

Chapter 5, *Conclusions*, presents the important ideas to retain at the end.

Chapter 6, *Project Assessment*, gives an overall judgment about the work performed and some tips to further developments.

Introduction 2

2 State of the art

2.1. Tire

A tire can be defined as a highly engineered structure where various textile components are embedded in a rubber matrix.[3]

Figure 1 illustrates the major sections of a passenger car tire.

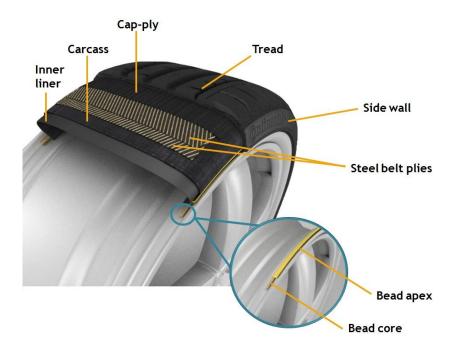


Figure 1 - Passenger car tire parts (adapted from [5]).

Table 1 describes the function of each layer that makes up a passenger car tire (Annex A shows the sequence of all these layers).

Table 1 - Function of the main components of a passenger car tire.

Bead core	Ensures firm tire seating on the rim.
Bead apex	Promotes directional stability, steering and performance.
Inner liner	Ensures the air pressure inside the tire.
Carcass (textile cord ply)	Keeps the tire in shape even with high inflation pressure.
Steel-cord belt plies	Optimize directional stability and rolling distance.
Cap ply	Enable high speeds.
Side wall	Protects the tire from lateral damage.
Tread	Promotes good road grip and enables water expulsion.

Nowadays the tire industry produces mainly two variants of commercially successful structures designated as cross-ply (or bias-ply) tire and radial-ply tire. A third variant designated as bias-belted tire was developed in the sixties but never

became popular commercially (Annex A illustrates these three variants of a tire). Currently most of the tires are a radial-ply construction for being generally considered to be better for rolling resistance, handling and wear resistance.[3] [6]

2.2. Reinforcement materials

The continuous sophistication of the specifications and use of textile materials has led to the adoption of lighter, stronger and more precisely engineered yarns.[7] There are five major fibers that make up the currently reinforcement materials usage - rayon, nylon, polyester, aramid and steel.

Polyester is the condensation polymerization product of ethylene glycol and terephthalic acid. It has become relatively inexpensive, making it a good choice for passenger and small light truck tires. Polyester cords are not recommended for use in high-load/high-speed/high-temperature applications, as in truck and racing tires, due to rapid loss of properties at tire temperatures above about 120 °C.[4]

Rayon is made from cellulose and it is produced by wet spinning. Its properties make it an excellent choice for passenger car tires. Nevertheless rayon has lost market share to polyester due to the higher cost and environmental concerns with production facilities. Rayon has a main application on race tires. [4]

Nylon is a trade name for aliphatic polyamides. Two varieties are used in tire cords - polyamide 6 (polycaprolactam) and polyamide 6.6 (polyhexamethylene adipamide). Despite both materials present similar properties, polyamide 6 is less expensive but more sensitive to moisture. Nylon is preferred in applications such as medium/heavy-duty truck tires and off-road equipment.[4]

Aramid is a wholly aromatic polyamide two to three times stronger than polyester and nylon. The relative high cost has slowed its application as a general radial belt material where steel cords perform well. Aramid is particularly suitable where weight is important, such as in the belts of radial aircraft tires or in overlay plies for premium high-speed tires.[4]

Steel cord is carbon steel wire coated with brass, which has been drawn, plated, twisted and wound into multiple-filament bundles. It is the principal belt ply material used in radial passenger car tires.[4]

This project focused entirely on textile reinforcement materials.

2.3. Terminology used in textile industry

The vocabulary related to textiles presents specific terminology that is important and useful to know before deeper developments. ~

Table 2 presents the terms commonly used in the texile area.

Table 2 - Textile terminology (adapted from [4]).

Fiber A material with high strength in the fiber axis direction and with at least 100 times greater than its diameter.			
Filament	The smallest continuous element of a tire cord.		
Yarn / strand / ply	Assembly of filaments twisted lightly and plied together.		
Cord	Twisted structure composed of two or more yarns.		
Fabric	Structure used in tire manufacture, comprising a sheet of warp cords or yarns with widely spaced weft yarns, woven in the orthogonal direction.		
End count	Number of warp or weft yarns/cords per dm in a fabric (epdm).		
Greige cord	Cord before dipping process.		
Dipped cord	Cord after chemical treatment.		
Pure cord	Cord composed by the same polymer.		
Hybrid cord	Cord composed with different polymers.		
Linear density	tex = g / 1000 m , $dtex = g / 10000 m$		
Twist level	Number of turns per meter (tpm) of a twisted cord or yarn.		
Twist factor	Represents the mathematical correlation between the twist level and titer. $\alpha = T_L \cdot \sqrt{\frac{total\ dtex}{10000}}$		
Twist direction	Is termed "S" direction if the spiral turns clockwise from top to bottom for a vertical held cord and "Z" direction for similar counter clockwise turning.		
Twist balance	If a set of yarns and the resulting cord have same twist it is termed a balanced cord.		
Breaking Force	Maximum force to break a cord and it is expressed in Newton.		
Elongation at Break	Maximum elongation of the cord when it breaks.		
Strength	The tensile load required to rupture a cord. It is expressed in Newton.		
Tenacity	Specific breaking strength per titer. Could be expressed in cN dtex ⁻¹ .		
EASL	Elongation at Specific Load. Can be visualized on the Load-elongation curve and it is expressed in percentage.		
LASE	Load at Specific Elongation. Can be visualized on the Load-elongation curve and it is expressed in Newton.		
Modulus	Slope between the elastic part of the load-elongation curve.		

2.4. Manufacture of textile reinforcements

All textiles used in tires are specially prepared and processed in order to build up structures designated as fabrics. In order to obtain them, a sequence of spinning, twisting, weaving and dipping processes are required.

At the beginning a filament yarn, where each filament runs the whole length of the yarn, is received. Through the **spinning process** it is possible to transform the polymer into yarns with a wide range of linear densities and twists. Single yarns are used in the majority of fabrics for normal textile and clothing applications. In order to obtain special yarn features, particularly high strength and modulus for technical applications, folded yarns are often needed.[7] Thereby, from the first stage of **twisting process** results a folded yarn, usually twisted in the "Z" direction. On the second stage, two or more folded yarns are back twisted in the "S" direction, resulting in a greige cord (Annex B presents in more detail the twist directions). Tire cords are usually balanced with equal twist levels in yarns and cords.[4] Figure 2 shows an example of a cord made through the two processes mentioned above.

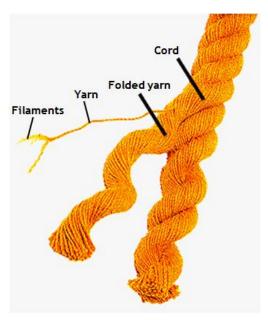


Figure 2 - Cord parts (adapted from [9]).

Through the **weaving process** it is possible to perform a greige woven fabric, which generally consist of two sets of cords that are interlaced. The cords that run along the length of the fabric are known as "warp ends" while the cords that run from selvedge to selvedge are known as "weft picks" (Annex B illustrates these cord directions).

The final step consists in a **dipping process**, in which the greige fabric is passed through a dip solution tank and then dried in an oven. This treatment occurs under

controlled conditions of time, temperature and tension. These parameters are key factors to get good rubber compound-cord adhesion.[10]

Typically the textile reinforcements enter into the tire plants as dipped fabrics, ready to be bonded to the rubber (calendering) and inserted into tires.

This project focused entirely on tire cords (their manufacture does not include the weaving process).

2.5. Tire cords

2.5.1. Cord characterization

The final performance of the tire is affected by the good physical, thermomechanical, adhesion and fatigue properties of the tire cords. However, there are certain primary cord properties that not only influence but determine the resultant tire performance. Among them are the strength, elasticity, creep, adhesion to rubber, heat, moisture and fatigue resistance, weight for equal strength, and stiffness for equal load. In terms of fiber choice, apart from the cost, three other main characteristics determine the use of a particular fiber in an automotive tires: tenacity, shrinkage at high temperature, and heat generation.[3] In order to determine this whole set of properties, a set of physical tests were performed.

Table 3 summarizes the range of physical tests performed.

Table 3 - Physical tests performed with cords (adapted from [8]).

Force Elongation	Measures the relation between force and elongation.	
Thermal Shrinkage Measures the shortening of the testing length caused by temperature, time and pre-tension.		
Disc Fatigue Measures the phenomenon leading to filament fracture under repeated tension/compress stress.		
Peel test	Measures the adhesion of textiles that are bonded to rubber compounds.	
Creep	Measures the increasing deformation while load is constant.	
Relaxation	Measures the decreasing in load while deformation is constant.	

Another significant property which affects performance of tire cords is the twist. Physical and mechanical properties of the cords are greatly dependent on the thickness of yarns and the twist level. The first twist of the individual yarns has a great effect on the physical and mechanical properties. During this first twist the yarns length shortens. When the yarns are twisted together, they are stretched as a result of its twist in the opposite direction to the first twist. Was further discovered that the thickness of the filaments has a pronounced effect on the yarn properties. A

reduction in the dtex of filaments promotes a favorable effect on the fatigue resistance.[10] Thus the greatest advantage of using twisted cords is the increase in fatigue resistance and in some cases the increase in structural elongation as well. Although it is known that twist also promotes a decrease in cord modulus. So the twist applied to the cord will depend on the final application desired.

Figure 3 presents the difference in the appearance between a cord with a high twist and a cord with a low twist.



Figure 3 - Appearance of a cord with low and high twist level (adapted from [7]).

2.5.2. Cord construction

Cords are made by twisting two or more yarns. At the beginning, each yarn is individually twisted, usually in the "Z" direction. This twist is represented as "x1", representing that a unique yarn was twisted around itself, resulting in a folded yarn. Then at least two folded yarns are twisted together, usually in "S" direction. Depending on the yarn material, cords can be distinguished in **pure cords** or **hybrid cords**. Pure cords are constructed by yarns of the same fiber type, while hybrid cords are constructed by more than one fiber type.

Figure 4 illustrates an example of a pure cord and a hybrid cord.

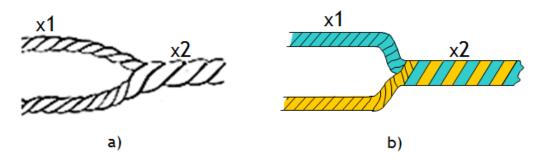


Figure 4 - Design of: a) pure cord; b) hybrid cord level (adapted from [11]).

Regarding pure cords, first is mentioned the fiber which composes the cord. Following appears the linear density of the fiber and then the cord construction. Thus, the pure cord represented above is described as "white dtexx1x2. Regarding hybrid cords it is necessary first indentify the material and then the cords construction. In this case, the hybrid cord pictured above is described as

"blue dtexx1 + yellow dtexx1". The motivation to construct hybrid cords lies in acquiring different properties when the materials, just by themselves, cannot achieve those properties.

In this project only pure cords were studied.

3 Materials and methods

This chapter describes all the techniques and methodologies used in this project. Taking into account the fibers that are currently used to make tire cords, polyester, polyamide 6.6 and aramid fibers were selected.

3.1. Cord designs

This project is divided in the twist study and the study of different types of aramid fibers.

For the twist study it was necessary to set the twist of each cord construction. At this point, it was necessary to keep in mind that it was desired a similar range of twist factor for thin cords and thick cords. In addition, the Laboratory Twisting Unit machine used to make all the cords has a twist limit of 600 tpm. Therefore it was decided to use three different twist levels to thin cords and six twist levels to thick cords.

Table 4 presents the range of twists used in the twist study.

Fiber	Cord construction	Twist level (tpm)
	1100 x 1 x 2	100 / 200 / 300 / 400 / 500 / 600
Polyester	550 x 1 x 2	100 / 200 / 300 / 400 / 500 / 600
	225 x 1 x 2	200 / 400 / 600
Aramid	1100 x 1 x 2	100 / 200 / 300 / 400 / 500 / 600
Arailliu	220 x 1 x 2	200 / 400 / 600
Nylon	235 x 1 x 2	200 / 400 / 600

Table 4 - Pure cord constructions used in the twist study.

Concerning the study of different types of aramid fibers it was necessary to select the yarns for each type of aramid. Then it was selected a Nomex fiber as meta-aramid, a Twaron fiber as para-aramid, a Technora fiber as para-meta-aramid and still another type of aramid fiber known as Arselon. Then in order to be able to compare them, similar yarn dtex were selected and the same twist factor was applied to all cords. Unlike what happened in the twist study, each of these yarns was provided by different suppliers.

Table 5 presents the different aramid cord constructions used in this study.

Table 5 - Aramid cord constructions used.

Fiber	Trade name	Туре	Cord construction	Twist level (tpm)	Twist factor
Aramid	Nomex	m-aramid	1335 x 1 x 2	387	_ 200 _
Aramid	Twaron	p-aramid	1100 x 1 x 2	426	
Aramid	Technora	p-m-aramid	1100 x 1 x 2	426	
Aramid	Arselon	other	970 x 1 x 2	454	

3.2. Test methods

All cords used in this project were dipped and then wounded in spools. It is important to be aware that the wear, abrasion and hence the test results of textile materials are sensitive to numerous factors. Among them stand out the textile material itself, the environment in which the tests are conducted and test conditions. It is then impossible to compare test results if the test conditions were not equal cord to cord.[12] For this reason all the cords have been previously conditioned, maintained and tested in a standard atmosphere at 23 °C with a moisture content of 45 % of relative humidity. Exceptionally the cords used to make the peel test specimens were used without any prior contact with light.

Before describing the tests methods used it is important to realize the specifications associated with tire production and tire service conditions. Thus, in the final stage of the tire building process (vulcanization), the tire is submitted to high temperatures (170 °C - 200 °C) and high pressure (up to 22 bar). After this phase, the textile cords that make up the tire remain with approximately 3.5 % of elongation. This is the reason why the first 20% - 30% of the laod-elongation curve are so important. Thereby is revealed the "secure level" of the cord, even before the tire starts rolling. In relation to the rolling service, a tire can reach temperatures between 23 °C to 200 °C, where the last value represents a completely extreme condition. All test methods used taking into account all these features are described below.

3.2.1. Load-Elongation

It was used a tensile testing machine according to standard ASTM D885.[13] A conditioned cord is clamped in the machine and the pre-load is applied. When the test begins, the cord is stretched until broken (Annex C illustrates this test method). Through this test it is possible to measure directly the breaking force, elongation at break, force at 3.5%, force at 4% and elongation at 45 N. For the twist study trials

were carried out only at RT and 80 °C. With these results it was possible to verify the effect of twist in temperature. For this purpose it was first considered the difference between the results obtained at each temperature. Then this difference was normalized by sample result with lower twist. Finally the results were plotted in a spider chart where zero is the goal for each property represented. Figure 5 shows an example of these results.

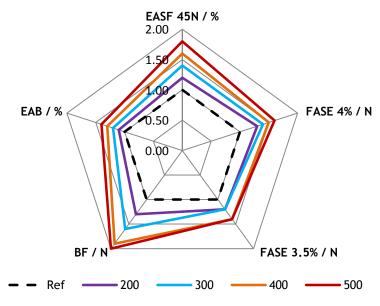


Figure 5 - Effect of temperature as a function of twist factor.

Different types of aramid fibers were characterized at RT, $40\,^{\circ}$ C, $80\,^{\circ}$ C, $120\,^{\circ}$ C and $160\,^{\circ}$ C. To ensure the repeatability of the results an average of five measurements were performed for each cord construction and for each property.

3.2.2. Thermal Shrinkage

All trials were performed according to standard ASTM D4974.[14] First the cord is clamped in one side of the test machine while on the opposite side the pre-load required is applied. Then a portion of the cord is surrounded by an oven. At this point starts to count the time of the test. This test is performed at 180 °C for 2 minutes and allows to directly measure the shrinkage of the cords in percentage. To ensure the repeatability of the results an average of three measurements were performed for each cord construction.

3.2.3. Disc Fatigue

All trials were performed according to standard ASTM D6588.[15] First cord specimens are placed between strips of rubber compound and molded into blocks. Then six samples are tested without suffering the disc fatigue test and for this reason are known as "fresh samples". The other six specimen blocks are mounted between the two rotating discs. These discs are positioned in such a way, that the specimen

will suffer compression and extension as the discs rotate (Annex C illustrates the rotating discs in these two opposite positions). After a specified number of cycles, the specimen blocks are removed from the discs and their breaking force is measured in a tensile testing machine.[16] Specimens that experienced the disc fatigue test are known as "fatigued samples". It is expected that the fresh samples show breaking force values higher than fatigued samples. In this line of reasoning the results are presented in terms of percentage of residual force. This is no more than the loss of strength of the fatigued samples in relation to fresh samples. Regarding disc fatigue results it will be presented only the results for cords with a dtex over 900. For thin cords inconclusive results were obtained.

3.2.4. **Peel test**

All trials were performed according to standard ASTM D4393.[17] Rubber specimens are pre-conditioned in an oven at 120 °C for 30 minutes. After this time the specimen is removed from the oven and clamped directly on the tensile testing machine. When the test starts the sample is opened and the force required to open it is directly measured by the testing machine. This force is known as peel force. (Annex C illustrates this test method. The evaluation of adhesion of textiles is made by measuring the force which textiles bond to the rubber (peel force) and by the rubber cover shown by the cords. Coverage is evaluated by the person who is testing. As described, peel force is directly measured by the testing machine. On the other hand, coverage is evaluated by the operator and is measured on a scale from 1.5 to 5. The lower value represents the total absence of coverage while the highest value represents the full coverage of the cords with rubber. Figure 6 shows an example of these two extreme cases.



Figure 6 - Coverage in peel adhesion samples: a) no coverage, b) full coverage.

The results regarding peel adhesion it will be presented in a bar chart. On the vertical axis is represented the peel force, the different bars represent the cords with different twists and the number in each bar represents the coverage. To ensure the repeatability of the results an average of three measurements were performed for each cord construction.

3.2.5. Creep and relaxation

Both test methods are performed in the same testing machine used for shrinkage with the same procedure. Nevertheless, creep test was conducted at 100 °C with a stress of 20 N statically kept for 2 hours. On the other hand, in the relaxation test a constant deformation of 0.5 % was applied for 20 minutes. The difference between these two testing methods is that relaxation test is based on the strain control while the creep test is based on stress control. Through the creep test is possible to achieve the dimensional changes in terms of elongation occurring over time to a constant load. The degree of creep depends on several factors such as the type of plastic, the magnitude of load, temperature and time.[18]



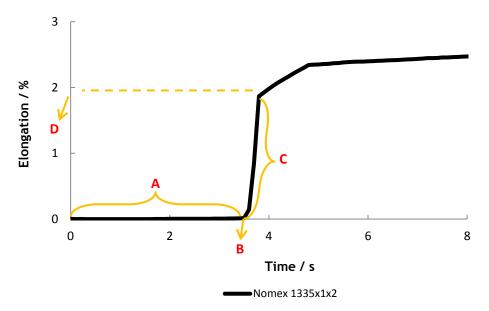


Figure 7 - Beginning of creep test of Nomex1335x1x2 387 tpm.

Zone A represents the period before the application of the load on the cords. Time B represents the time at which the test begins the test starts, which means, when the load is applied to the cords. Zone C represents the immediate dimensional changes that occur in the cord when the load is applied. Elongation D will be the value that will count as initial elongation (ε_i). In the meantime the cord continues to deform and after two hours the elongation value (ε_f) is recorded and the test ends. This makes it possible to determine the creep rate according to Equation 1:

Creep (%) =
$$\varepsilon_f$$
 (%) – ε_i (%) (Equation 1)

In relation to the relaxation test is possible to observe the gradual decrease in stress over time maintaining a constant deformation.

Figure 8 shows the initial instants of relaxation test.

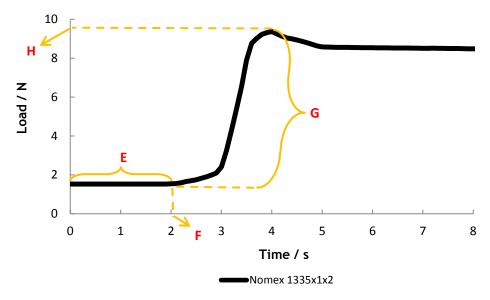


Figure 8 - Beginning of relaxation test of Nomex1335x1x2 387 tpm.

Zone E represents the period prior to the application of deformation on the cords. Time F represents the time when the test begins, this is, when the deformation is applied to the cord. Zone G represents the immediate force experienced by the cord in order to withstand the imposed deformation. The load value represented by the letter H will be the initial load (F_i) . In the meantime the load continues to decrease and after twenty minutes the final load value (F_f) is recorded and the test ends. This makes it possible to determine the creep rate according to Equation 2:

Relaxation (%) =
$$\frac{F_i(N) - F_f(N)}{F_i(N)}$$
 (Equation 2)

Thereby, the obtained results were represented in bar graphs where the closer to zero the better the cord performance in relation to creep and relaxation. To ensure the repeatability of the results an average of three measurements were performed for each cord construction.

3.3. Types of aramid fibers used

The term "aramid" is short for "aromatic polyamide". Aramid fibers are manmade high-performance fibers. The fiber-forming substance is a long chain synthetic polyamide where at least 85% of the amide linkages are attached directly to two aromatic rings.[7] Their molecules are characterized by relatively rigid polymer chains, linked by strong hydrogen bonds that transfer mechanical stress very efficiently.[19] Already the earliest aramid fibers were initially targeted at reinforcement of tires and plastics.[20]

Figure 9 shows the molecular structure of three different types of aramid fibers used in this project.

Figure 9 - Molecular structure of: a) para-Aramid, b) meta-Aramid, c) para-meta-Aramid (adapted from [19]).

It can be seen that para-aramid, meta-aramid and even para-meta-aramid fibers were used. As previously described Nomex fiber was used as meta-aramid, Twaron fiber was used as para-aramid and Technora fiber was used as para-meta-aramid. As the name suggests, the position of linkages that form their molecular structure is the main difference between them. It was also incorporated another type of aramid known as Arselon.

4 Results and discussion

After collecting all the data for the twist study and for the study of different types of aramid fibers the obtained results were organized and discussed as follows.

4.1. Twist study

This study focused exclusively on pure cords. With this it will be possible to develop hybrid cord construction with an exact yarn twist. In order to understand the effect of twist on tire cords made of different fibers polyester, polyamide 6.6 and aramid cords were tested.

First results regarding tenacity, elongation at break and the effect of temperature will be presented. After that the results regarding fatigue resistance and peel adhesion will be presented. These last results represent the mandatory requirements for tires.

4.1.1. Polyester pure cords

Polyester 1100x1x2 cords

As mentioned above, first results regarding tenacity and elongation at break as a function of the twist factor and for two temperatures (RT and $80\,^{\circ}$ C) are presented - Figures 10 and 11.

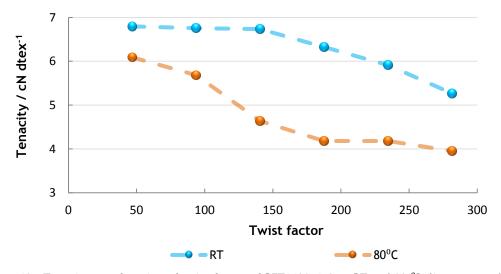


Figure 10 - Tenacity as a function of twist factor of PET1100x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability).

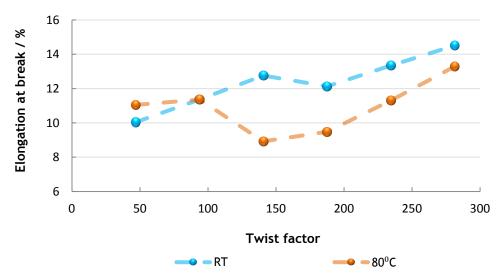


Figure 11 - E@B as a function of twist factor of PET1100x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability).

From Figure 10, a drop in tenacity at RT is observed from a twist factor of 140 while at 80 °C tenacity level outs after a twist factor of 160. It is expected the elongation increases as a function of twist. Figure 11 shows this behavior at RT. However, elongation reaches a minimum before increasing monotonously at 80 °C. The reason for this unexpected result was not identified. It should be emphasized that each experimental value was obtained by the average of 5 measurements.

Figure 12 shows a spider chart illustrating how the temperature affects different cord properties depending on twist.

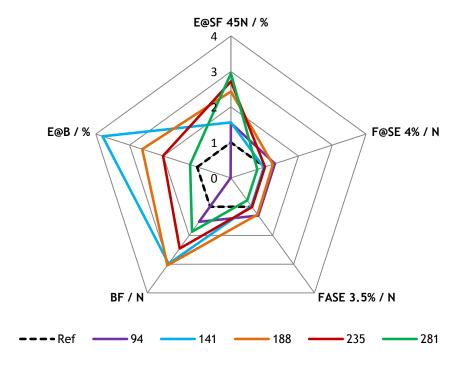
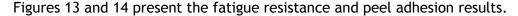


Figure 12 - Temperature influence as a function of twist factor of PET1100x1x2.

From Figure 12, it can be noticed that generically temperature affects less the cord properties as the twist decreases.



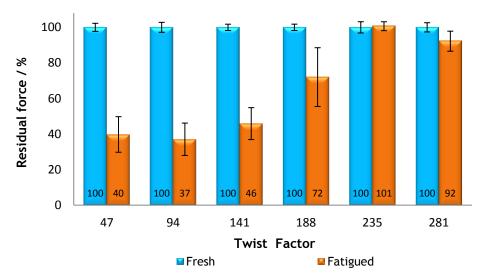


Figure 13 - Residual force as a function of twist factor of PET1100x1x2.

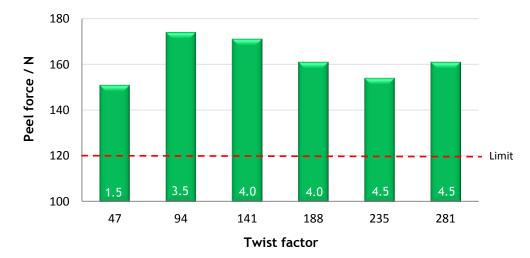


Figure 14 - Peel adhesion results as a function of twist factor of PET1100x1x2.

From Figure 13 it is clear that cords with higher twist present higher fatigue resistance. In fact, this is the reason why the cords forming the textile materials used on tires are twisted. This behavior can be explained by the helix angle because as the twist increases the angle between cord axis and filament axis of cord increases.[10] Thus at high twist, cord behaves like a coil spring, giving it higher fatigue resistance.[21] Then can be retained that for a twist factor over 200 this cord construction suits the fatigue resistance requirements. It can also be retained that fatigue samples present a much higher variation between the obtained results. Regarding peel adhesion results all cords presented a peel force above the limit but

only for a twist factor over 200 a good coverage is reached. Taking into account the obtained results, a twist factor of 200 can be considered suitable for sufficient tire performance requirements.

Polyester 550x1x2 cords

Figure 15, 16 and 17 present the results regarding tenacity, elongation at break and effect of temperature for PET550x1x2 cords construction.

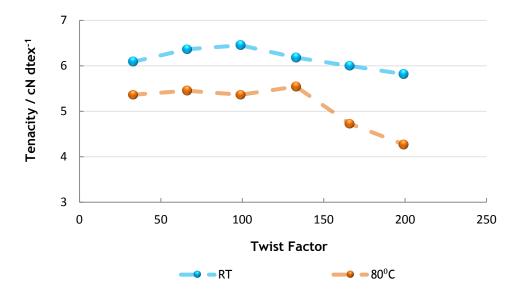


Figure 15 - Tenacity as a function of twist factor of PET550x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability).

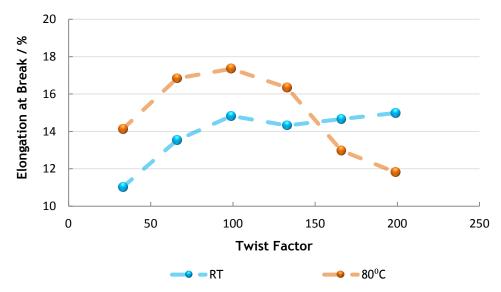


Figure 16 - E@B as a function of twist factor of PET550x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability).

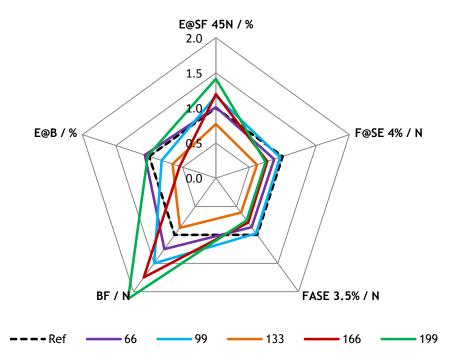
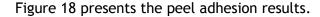


Figure 17 - Temperature influence as a function of twist factor of PET550x1x2.

For this cord construction tenacity is not significantly affected by twist at RT. Although at high temperature a drop in tenacity for a twist factor above 130 is observed. From Figure 16 an increasing of elongation with twist up to a twist factor of 100 at RT can be noted. The same behavior is observed at 80 °C. From Figure 17 it can be seen that a twist factor around 130 is less affected by temperature with respect to all mechanical properties represented. It can be noticed that the effect of temperature on BF increases with twist and it is higher when compared with the effect of temperature on E@B.



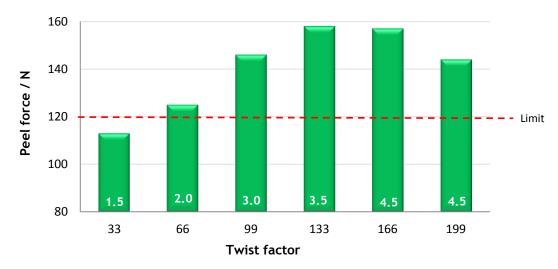


Figure 18 - Peel adhesion results as a function of twist factor of PET550x1x2.

In terms of peel adhesion, acceptable values of peel force are reached for a twist factor over 66. In order to achieve an acceptable coverage a twist factor above ca. 160 is needed. The coverage improvement with twist can be explained once that the number of turns per unit length increase with twist. Therefore the amount of yarn per unit length increases. The filaments are tightened and the contact area of the plies in unit length increases as the twist increases. [10] This fact provides a higher area of contact between fiber, dip solution and rubber. Figure 19 shows in a clear way the increasing of the amount of yarn per unit length with twist.

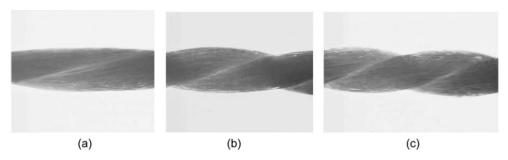


Figure 19 - Polyester cords with different twist: a) 200 tpm, b) 350 tpm, 470 tpm (extracted from [10]).

Taking into consideration the obtained results it was decided that a twist factor of 160 satisfy the tire performance requirements.

Polyester 225x1x2 cords

Figures 20, 21 and 22 present the results regarding tenacity, elongation at break and effect of temperature for PET225x1x2 cord construction.

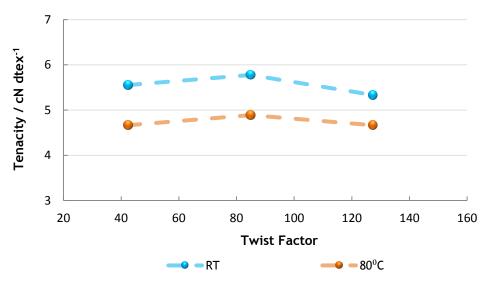


Figure 20 - Tenacity as a function of twist factor of PET225x1x2 at RT and 80 ℃ (lines were added for readability).

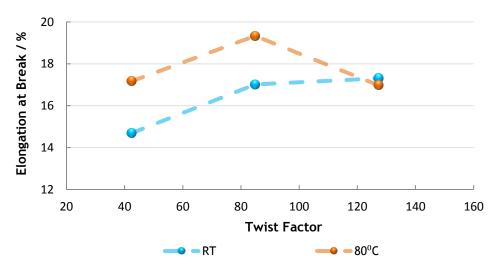


Figure 21 - Elongation at Break as a function of twist factor of PET225x1x2 at RT and 80 $^\circ$ C (lines were added for readability).

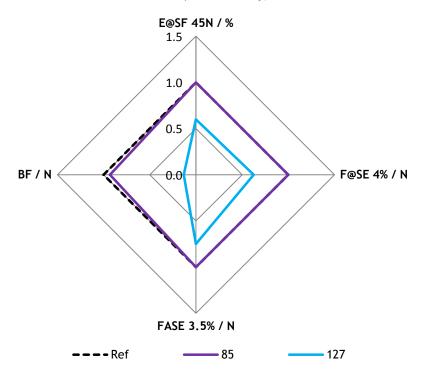


Figure 22 - Temperature influence as a function of twist factor of PET225x1x2.

For this cord construction tenacity is not affected by twist regardless the temperature. From Figure 21 it is possible that is possible to increase the structural elongation with twisting at RT. At high temperature the twist starts to affect negatively the elongation from a twist factor of 85. Then it is clear that a high twist is less affected by temperature regardless the mechanical property.

Figure 23 presents peel adhesion results for this cord construction.

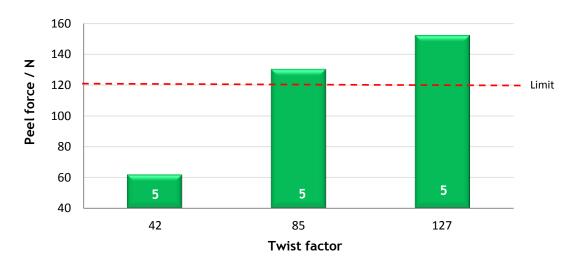


Figure 23 - Peel adhesion results as a function of twist factor of PET225x1x2.

Regarding peel adhesion results all the cords presented very good coverage but peel force is only reasonable above a twist factor of 85. Taking into account the obtained results it was decided that a twist factor of 90 satisfy in a better way the tire requirements.

4.1.2. Polyamide 6.6 pure cords

In order to present an alternative to thin polyester cords, thin polyamide cords were performed.

Polyamide 6.6 235x1x2 cords

Figures 24, 25 and 26 present the results regarding tenacity, elongation at break and effect of temperature for NYLON235x1x2 cord construction.

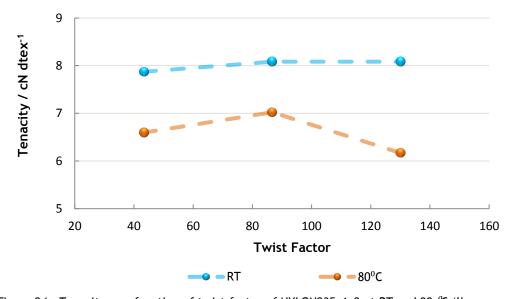


Figure 24 - Tenacity as a function of twist factor of NYLON235x1x2 at RT and 80 $\,^{\circ}\!\text{C}$ (lines were added for readability).

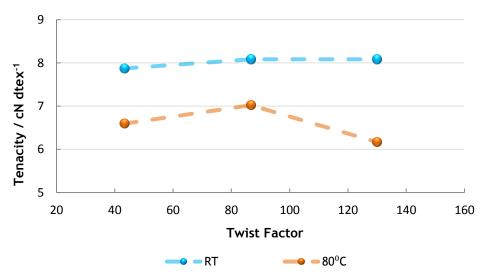


Figure 25 - E@B as a function of twist factor of NYLON 235x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability).

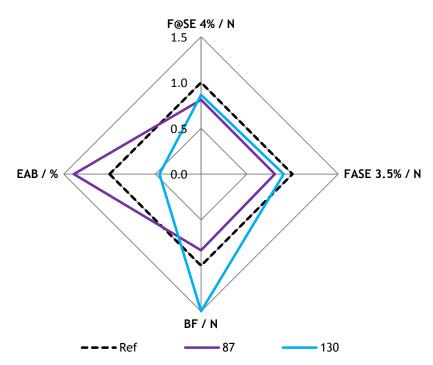


Figure 26 - Temperature influence as a function of twist factor of NYLON235x1x2.

From Figure 24 it can be seen that tenacity is not affected by twist at RT. On the other hand tenacity starts to decrease from a twist factor of 87 at 80 °C. From Figure 25 can be retained that the structural elongation can be increased with twist at RT. At 80 °C a drop in elongation from a twist factor of 87 can be seen. In terms of effect of temperature it was decided to select a twist factor of 87 as the best, once that from this cord construction is desired its structural elongation.

Figure 27 presents the peel adhesion results for this cord construction.

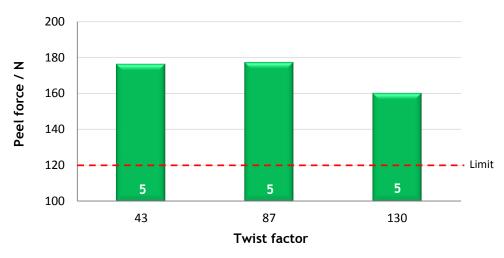


Figure 27 - Peel adhesion results as a function of twist factor of NYLON235x1x2.

Regarding peel adhesion results, all cords present high peel force and very good coverage. According to these results it was decided that a twist factor of 90 satisfy in a better way the tire requirements.

4.1.3. Aramid pure cords

Aramid cords were performed once it is expected that they present high tenacity and fatigue resistance. For this study all cords were performed with Technora fiber.

Aramid 1100x1x2 cords

Figures 28, 29 and 30 present the results regarding tenacity, elongation at break and effect of temperature for ARA1100x1x2 cord construction.

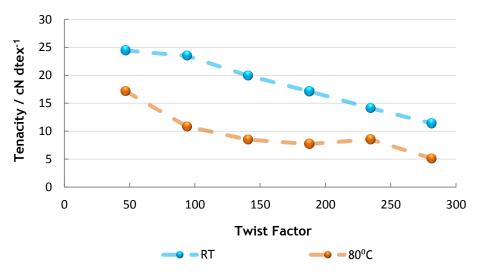


Figure 28 - Tenacity as a function of twist factor of ARA1100x1x2 at RT and 80 $\,^{\circ}$ C (lines were added for readability).

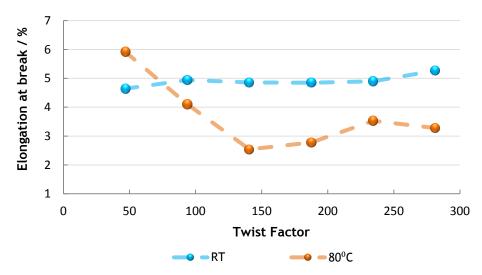


Figure 29 - E@B as a function of twist factor of ARA1100x1x2 at RT and 80 $^{\circ}$ C (lines were added for readability).

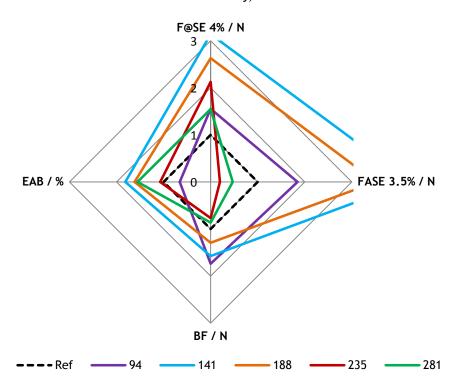


Figure 30 - Temperature influence as a function of twist factor of ARA1100x1x2.

For this cord construction can be seen a continuous decrease in tenacity with twist at RT. At high temperature tenacity starts to decrease less sharply from a twist factor of 141. From Figure 29 it is possible to see that the structural elongation is not affected by twist at RT. At high temperature the structural elongation is once again affected negatively by twist. Regarding the effect of temperature is less remarkable for low and high twists.

Figures 31 and 32 present the fatigue resistance and peel adhesion results.

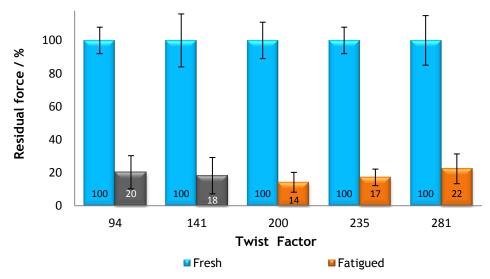


Figure 31 - Residual Force as a function of twist factor of ARA1100x1x2.

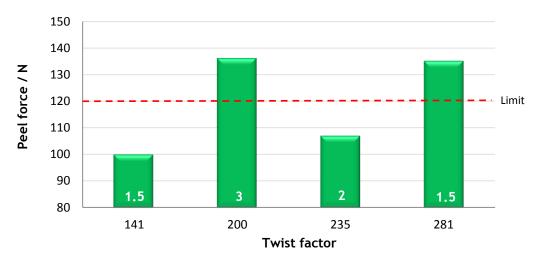


Figure 32 - Peel adhesion results as a function of twist factor of ARA1100x1x2.

Regarding fatigue resistance cords with low twist does not bonded to the rubber specimens. In this case the force measured it was only to split the rubber. Besides this fact it is possible to retain that fatigue resistance increase with twisting. However the cords tested present very low fatigue resistance. From Figure 32 can be assumed that something wrong happened with the specimen with a twist factor of 235. Then it is possible to note the increasing of peel force with twist and that all cords presented poor coverage. This poor coverage explains the fact that all specimens present a significant variation between them, regarding the fatigue resistance results. Taking into account the obtained results it was decided that a twist factor of 200 satisfy in a better way the tire requirements.

Aramid 220x1x2 cords

Figures 33, 34 and 35 present the results regarding tenacity, elongation at break and effect of temperature for ARA220x1x2 cord construction.

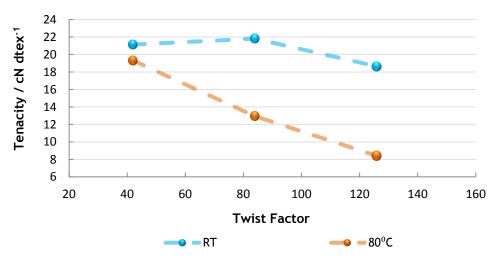


Figure 33 - Tenacity as a function of twist factor of ARA220x1x2 at RT and 80 $\,^{\circ}\!C$ (lines were added for readability).

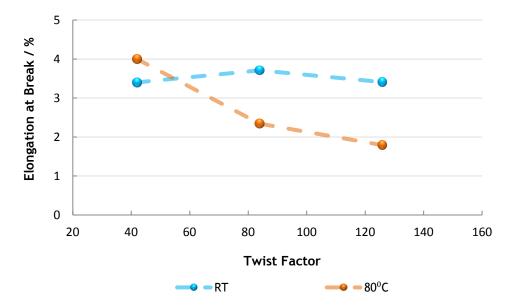


Figure 34 - E@B as a function of twist factor of ARA220x1x2 at RT and 80 $\,^{\circ}\!\text{C}$ (lines were added for readability).

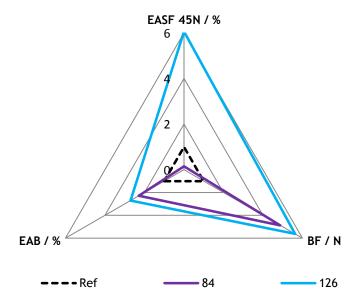


Figure 35 - Temperature influence as a function of twist factor of ARA220x1x2.

For this cord construction tenacity starts to decrease from a twist factor of 84 at RT. At high temperature tenacity only decreases with twist. Regarding elongation, it is not affected by twist at RT. At high temperature is affected negatively by twist. In terms of effect of temperature is less pronounced at low twist.

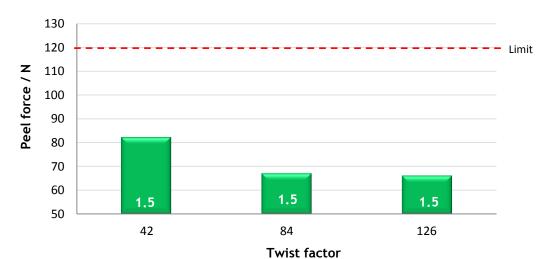


Figure 36 presents the peel adhesion results.

Figure 36 - Peel adhesion results as a function of twist factor of ARA220x1x2.

In terms of peel adhesion results, all cords presented very low peel force and poor coverage. Taking into account the obtained results it was decided that a twist factor of 60 satisfy in a better way the tire requirements.

4.1.4. Effect of twist and conditioning on shrinkage

In order to understand the effect of conditioning on shrinkage were used materials in two different states. Part of the material was taken from the spool and directly tested. Other material portion was taken from the spool, allowed to stand during a period of 24 hours and then tested. Figure 37 shows the different conditioning states of the material.

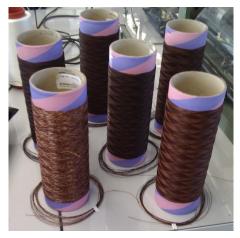
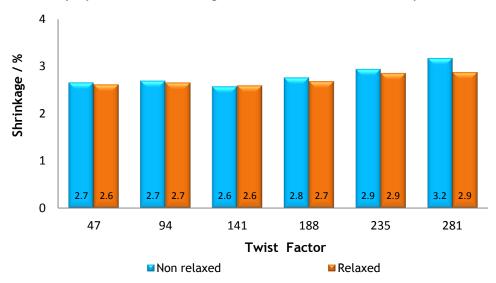


Figure 37 - Different conditioning state of cords.

It is important do not forget that all materials need to be exposed to a standard atmosphere at least the 24 hours that precede the trials. Figures 38, 39 and 40 show the results for polyester cords and Figure 41 shows the results for nylon cords.



 $Figure \ 38 - Shrinkage \ results \ for \ relaxed \ and \ non \ relaxed \ conditioning \ of \ PET1100x1x2 \ cords.$

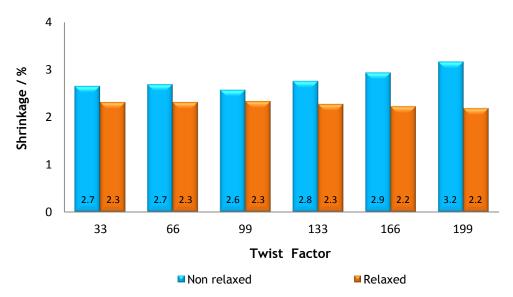


Figure 39 - Shrinkage results for relaxed and non relaxed conditioning of PET550x1x2 cords.

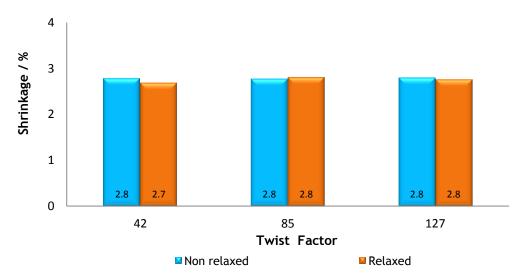


Figure 40 - Shrinkage results for relaxed and non relaxed conditioning of PET225x1x2 cords.

Regarding polyester cords it can be seen that shrinkage increase with twisting, but only for high twist, above a twist factor of 150. That is the reason why it is not possible to see the effect of twist for PET225x1x2 cords construction. Concerning the effect of conditioning it is visible that relaxed cords present lower shrinkage, but once again, only for high twist.

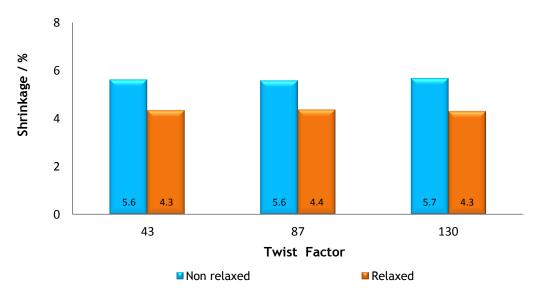


Figure 41 - Shrinkage results for relaxed and non relaxed conditioning of polyamide 6.6 235x1x2 cords.

Regarding nylon cords cannot be seen the effect of twist. This can be related with the twist factor range studied. As explained above, the effect of twist on thin cords is noted only for high twist. Respecting the effect of conditioning is clear that relaxed cords present low shrinkage, regardless the twist. It is even possible to compare the different materials tested. Then can be seen that nylon presents about 2.6 % more shrinkage regarding non relaxed cords and about 1.6 % more shrinkage regarding relaxed cords. In general, nylon cords present higher shrinkage than polyester cords. This can be explained by the benzene rings on polyester fibers, that must stiffen up the amorphous regions.[22] Aramid fibers were not included in this study once that they present a negligible shrink.

4.1.5. Materials comparison

In order to make a comparison between the different materials, it is important to keep in mind that yarns from the same fiber but with different dtex, must be provided by the same supplier. As presented on the previous chapter, when the twist is applied to a textile cord, the breaking strength of the cord increases initially up to an maximum and then decreases.[10] Figures 42 and 43 represent the evolution of tenacity with twist, for all cord constructions at RT and 80 °C.

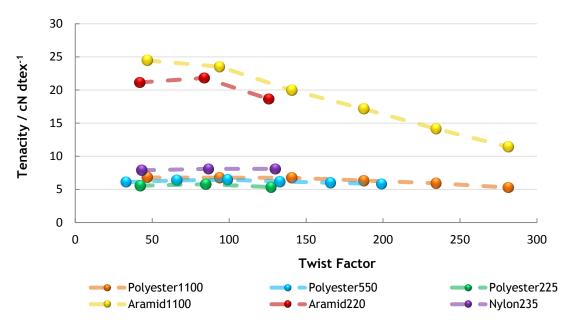


Figure 42 - Tenacity as a function of twist factor of PET1100x1x2, PET550x1x2, PET225x1x2, ARAMID1100x1x2, ARAMID220x1x2 and NYLON235x1x2 cords at RT (lines were added for readability).

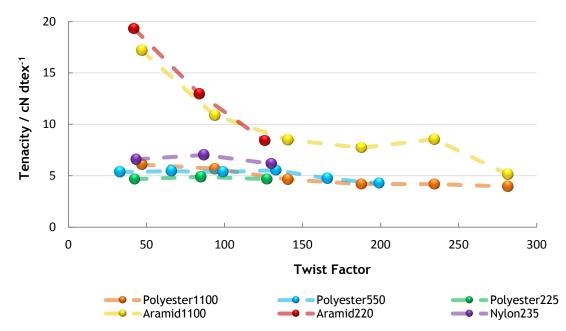


Figure 43 - Tenacity as a function of twist factor of PET1100x1x2, PET550x1x2, PET225x1x2, ARAMID1100x1x2, ARAMID220x1x2 and NYLON235x1x2 cords at 80 $^{\circ}$ C (lines were added for readability).

Regarding tenacity it is clear that aramids present higher tenacity than nylon and polyester. This was an expected result since aramid fibers present a highly oriented rigid molecular structure that provides a strong intermolecular chain bonding; on the other hand polyester and nylon are amorphous materials. As fibers are oriented preferentially along their axial direction, the orientation of segments in amorphous regions is weaker. [23] Figure 44 illustrates this difference in orientation.

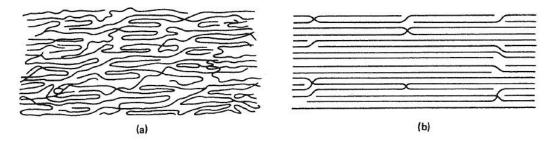


Figure 44 - Polymer chain orientation: (a) Conventional organic fibers; (b) Aramid fiber (adapted from [20]).

It is also clear that aramids are much more sensitive to twist than polyester and nylon. Once again this can be explained by the crystalline configuration of aramids, which makes that they are much more unsettled by twist.

In order to clarify this susceptibility, Figure 45 presents the maximum loss of strength with twist, for all cord constructions.

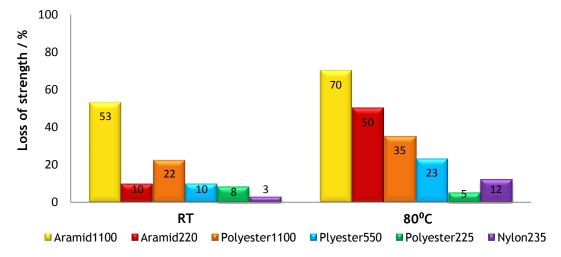


Figure 45 - Maximum loss of strength with twist at RT and 80 $^{\circ}$ C.

It can be noted that temperature enhances the loss of strength.

Figures 46 and 47 present the evolution of elongation with twist for all cords at RT and 80 $^{\circ}$ C.

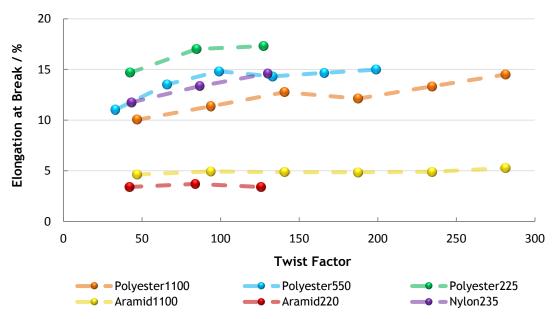


Figure 46 - E@B as a function of twist factor of PET1100x1x2, PET550x1x2, PET225x1x2, ARA1100x1x2, ARA220x1x2 and NYLON235x1x2 cords at RT.

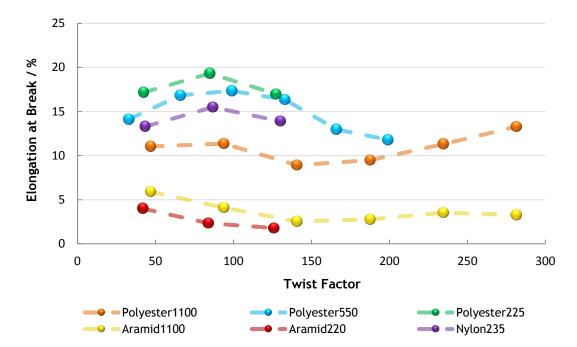


Figure 47 - E@B as a function of twist factor of PET1100x1x2, PET550x1x2, PET225x1x2, ARA1100x1x2, ARA220x1x2 and NYLON235x1x2 cords at 80 $^{\circ}$ C (lines were added for readability).

Through the figures represented above, it can be noted that aramids present lower elongation than polyester and nylon. Unlike to what happened with tenacity, aramid fibers are less affected by twist level in terms of elongation. Besides, it is not possible to increase the structural elongation of aramids. It is also possible to perceive that thin nylon presents higher elongation than thick polyester, regardless the temperature.

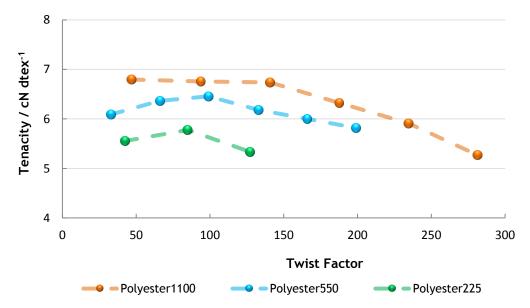


Figure 48 - Tenacity as a function of twist factor of PET1100x1x2, PET550x1x2 and PET225x1x2 cords at RT (lines were added for readability).

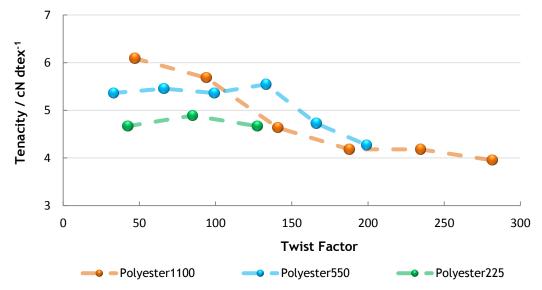


Figure 49 - Tenacity as a function of twist factor of PET1100x1x2, PET550x1x2 and PET225x1x2 cords at 80 °C (lines were added for readability).

Regarding polyester it is possible to retain that tenacity increases with dtex at RT. That means that thick cords present higher tenacity. At 80 °C tenacity depends on dtex and twist. This is a clear example why temperature and twist are so important regarding the performance of tire cords.

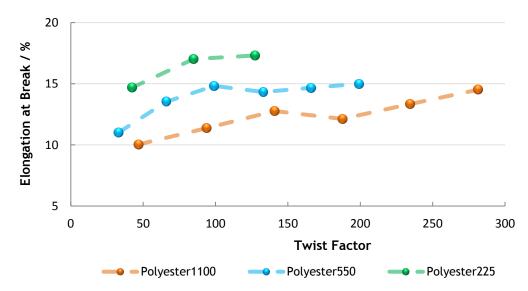


Figure 50 - E@B as a function of twist factor of PET1100x1x2, PET550x1x2 and PET225x1x2 cords at RT (lines were added for readability).

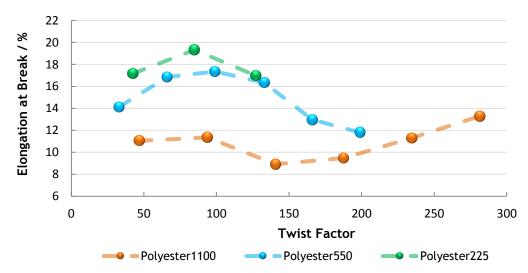


Figure 51 - E@B as a function of twist factor of PET1100x1x2, PET550x1x2 and PET225x1x2 cords at 80 °C (lines were added for readability).

Regarding elongation of polyester cords, it can be retained that elongation decreases with dtex, regardless the temperature. Generically it is possible to increase the structural elongation up to a specific twist factor at RT. It is possible to increase the structural elongation of polyester cords in 3 % at RT up to a twist factor of 140, regardless the dtex. At 80 °C it can be seen that elongation of thin cords starts to decrease above a specific twist factor; on the other hand thick cords can retain their properties at 80 °C and it is possible to increase its structural elongation. One possible reason that can explains this behavior is the fact that high twist destroys some filaments. This destruction affects and leads to loss of material properties.

Figures 52 and 53 illustrate the tenacity of thick and thin cords at 80 $^{\circ}$ C. Thus it is possible to compare the tenacity of different materials at high temperature.

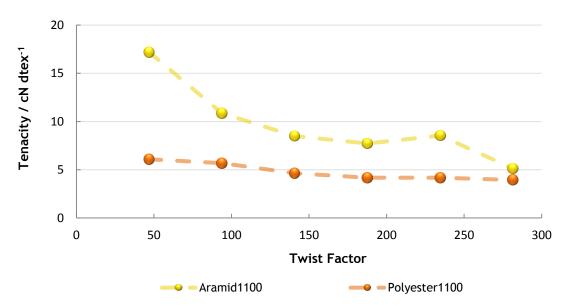


Figure 52 - Tenacity as a function of twist factor of ARAMID220x1x2 and PET1100x1x2 cords at 80 $^{\circ}$ C (lines were added for readability).

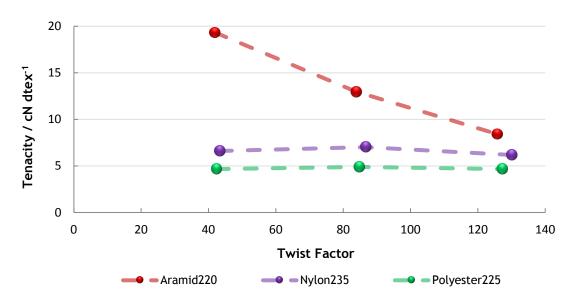


Figure 53 - Tenacity as a function of twist factor of ARAMID220x1x2, NYLON235x1x2 and PET225x1x2 cords at 80 $^{\circ}$ C (lines were added for readability).

Regarding thick polyester and aramid cords, they present similar tenacity for high twist over a twist factor of ca. 281. Regarding thin cords, polyester, nylon and aramid present similar tenacity above a twist factor of ca. 130. This behavior can be explained by the amorphous structure of nylon and polyester that it is not affected so severely by twist as it happens for aramid fibers.

4.2. Aramid fibers comparison

In order to understand the performance of tire cords made from different types of aramid fibers, results regarding tenacity and E@B at RT, $40\,^{\circ}$ C, $80\,^{\circ}$ C, $120\,^{\circ}$ C and $160\,^{\circ}$ C, fatigue resistance, peel adhesion, creep and relaxation were considered.

4.2.1. p-aramid vs m-aramid vs p-m-aramid vs arselon

Figures 54 and 55 illustrate the influence of temperature influence on tenacity and the maximum loss of strength with temperature.

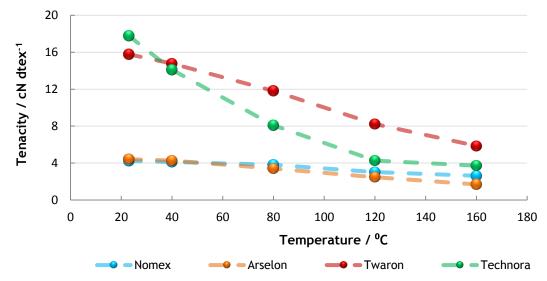


Figure 54 - Tenacity as a function of temperature for each type of aramid fiber (lines were added for readability).

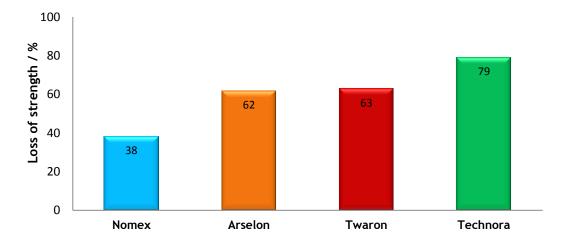


Figure 55 - Maximum loss of strength with temperature for each type of aramid fiber.

From Figure 54 it is clear that Twaron and Technora are high tenacity fibers. There are a several factors related to the molecular structure of these fibers that can explain this behavior. From these factors can be highlighted the presence of aromatic rings instead of aliphatic rings, the strong chemical bonds within a molecular chain and a high degree of symmetry and regularity in the internal structure.[19] From Figure 55 it is important to note that in terms of percentage of loss of strength, Arselon and Twaron present the same loss rate. Although Technora presents a decrease of 218 N while Arselon presents a decrease in tenacity of 53 N, taking into account absolute values of load. Afterwards it is clear that Nomex is the more stable and Technora the less stable regarding temperature.

Figure 56 illustrates the elongation of different aramid fibers as a function of temperature.

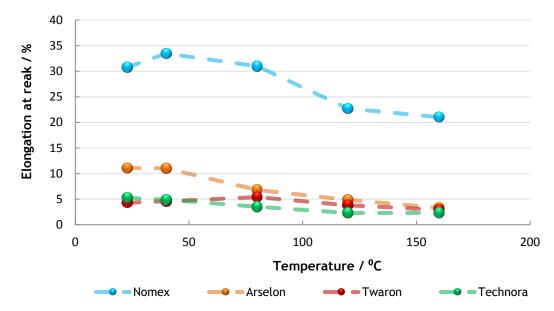


Figure 56 - E@B as a function of temperature for each type of aramid (lines were added for readability).

It can be noted that Nomex presents an untypical elongation, regarding aramid fibers. At the same time every aramid fibers tested present a significant decrease in elongation, where Twaron and Technora fibers are the less affected by temperature. This high elongation is due to the molecular structure of Nomex consisting mainly of meta-linkages, contrary to what happens for Twaron and Technora fibers.

Figures 57, 58 and 59 illustrate the dimensional stability and shrinkage results for the different types of aramid fibers studied.

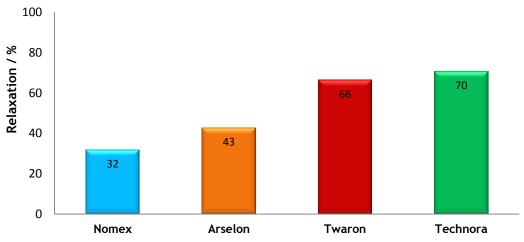


Figure 57 - Relaxation rate of each type of aramid fiber.

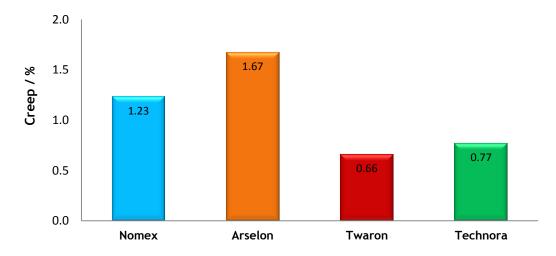


Figure 58 - Creep rate of each type of aramid fiber.

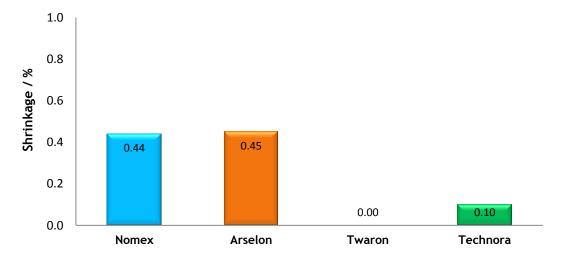


Figure 59 - Shrinkage of each type of aramid fiber.

Regarding the results obtained in terms of creep and relaxation, it can be seen that Twaron fiber presents better performance regarding creep and Nomex fiber presents better performance regarding relaxation. From Figure 59 it is clear that Twaron does not shrink and Technora presents much lower shrinkage than Nomex and Arselon. Once again this can be explained by the para-linkages that comprise the molecular structure of Twaron and technora fibers. Thus these results support that meta-linkages on molecular structure allow higher shrinkage.

Figures 60 and 61 present the fatigue resistance and peel adhesion results. It is important do not forget that these two results represent mandatory requirements for tires.

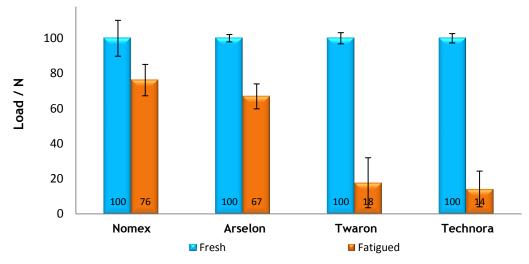


Figure 60 - Residual force of each type of aramid fiber.

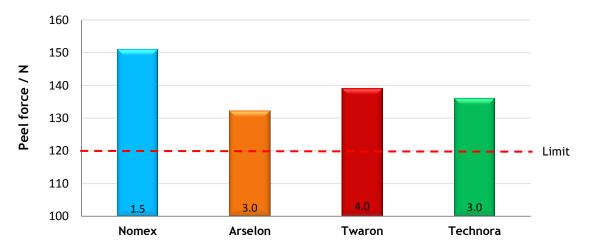


Figure 61 - Peel adhesion results as a function of twist factor of each type of aramid fiber.

Concerning fatigue resistance it is clear that fibers with para-linkages are much more affected by fatigue. This leads to the low fatigue resistance presented by Twaron and Technora fibers. However, Nomex is the unique that presents a truly poor adhesion. This poor coverage of Nomex explains the fact that their specimens present a significant variation between fresh samples.

5 Conclusions

With this project it was studied the effect of twist level on the performance of tire cords targeting to maximizes the tenacity, elongation at break, fatigue resistance, and rubber adhesion of the cords. It was also uncovered the performance differences among the various types of aramid fibers Nomex, Arselon, Twaron, and Technora. For this purpose load/elongation at RT, 40 °C, 80 °C, 120 °C and 160 °C, thermal shrinkage, disc fatigue, peel test, creep and relaxation tests were performed.

Concerning pure cords the proper twist for each cord construction was set taking into account the tire performance requirements. The optimal twist factors are: 210 for PET1100x1x2, 160 for PET550x1x2, 90 for PET225x1x2, 90 for NYLON235x1x2, 200 for ARA1100x1x2 and 60 for ARA220x1x2. Through the twist study it was still possible to understand that the test method used to test the fatigue resistance was not suitable for cords with a dtex below 900.

It was concluded that aramids are more sensitive to twist than nylon and polyester, regardless of temperature and dtex. This sensitivity was characterized by the loss of strength by a maximum of 50% at RT and by a maximum of 70% at high temperature for thick aramid cords. For polyester thick cords a loss of strength was observed up to a maximum of 20% at RT and up to a maximum of 35% at high temperature. For aramid the elongation was observed not to increase with the twist level. On the other hand, it was concluded to be possible to increase the structural elongation of polyester cords in 3% at RT and up to a twist factor of 140. It was also verified that relaxed polyester cords presented lower shrinkage than non-relaxed cords, but only for high twists. The relaxed nylon cords present lower shrinkage even for low twists. When comparing the two materials, nylon presented higher shrinkage than polyester regardless of the state of the cords.

Concerning the different types of aramid fibers, Technora and Twaron showed high tenacity although a very low fatigue resistance. On the other hand Nomex showed the highest stability fiber with respect to temperature and showed better results in terms of relaxation but a truly poor adhesion.

Conclusions 44

6 Project assessment

This chapter provides a final overview over the achieved goals and the major limitations in the course of the project. At the end are still given some insight for future work.

6.1. Accomplished objectives

The main aims of this project began to realize the effect of twist in the performance of tire cords and set the proper twist for each cord construction. It was also performed a studied targeted to perceive the performance of tire cords with different types of aramid fibers. For this purpose a total of 46 textile cords were made and conducted over 1500 trials. Thus, it was possible to obtain all the described results that enabled the achievement of each stated goal.

With the revelation of the proper twist for each pure cord construction it is now possible to develop new hybrid cord constructions with an exact yarn twist. With the disclosure of the performance of different aramid fibers it is now possible to select the most appropriate fiber to the desired final application.

6.2. Limitations and future work

In respect to limitations time was certainly one of them. Another striking limitation in this project was the twist limit presented by the Lab Twisting Unit machine used to make all cords. Thereby it was not possible to explore higher twists in thin cords. In fact, thin cord constructions were the major source of problems in relation to laboratory tests. The reason for that happened is that the set of physical tests performed are directed to materials currently used in production, which are fairly thicker than thick cord constructions used.

As future work it would be interesting and beneficial to realize about the problem that occurred with thin cord constructions in relation to the disc fatigue test. Another noteworthy improvement it would be the optimization of the dipping process parameters in relation to the aramid fibers.

6.3. Final assessment

This thesis was a challenging experience either professionally or personally. As usual it is always difficult to start working with new materials. Nevertheless, supported by a highly motivated team it was always possible to find a way to solve problems and overcome all difficulties. Until the very end of this project the expectation to obtain serious results served as a driving force as well.

Project assessment 45

Despite all, the obtained promising results are the beginning of an exciting project. It is missing a mandatory part in order to be able to achieve the ultimate goal, hybrid cords with an optimized twist.

Project assessment 46

7 References

- 1. Website http://www.continental-corporation.com, accessed on February 2014.
- 2. Website http://www.contitech.de, accessed on February, 2014.
- 3. Mukhopadhyay S. K., Partridge J. F., "Automotive textiles", Textile Progress, 29, 1-125, 1999.
- 4. Gent A. N., Walter J. D., "The pneumatic tire", NHTSA, EUA, 2005.
- 5. Continental, "Tire basics components of a tire", 2009.
- 6. Shingo F., "Effect of material properties on tire performance characteristics", tire science and technology, Part I, TSTCA, 15, 198-206, 1987.
- 7. Sondhelm W. S., "Technical fabric structures Woven fabrics", in "Handbook of technical textiles", H. R. Horrocks & S. C. Anand, 62-94, **2000**.
- 8. Cruz A. D., "Influence of cord design on mechanical properties of tire cords", Master Thesis, FEUP, **2014**.
- 9. Website http://nhseacadets.mainstream.net/marlinspike_training, accessed on March, 2014.
- 10. Aytac A., Yilmaz B., Deniz V., "Effect of twist level on tyre cord performance", Department of Chemical Engineering, Engineering Faculty Kocaeli University, Turkey, 2009.
- 11. Kramer T., "Basics of reinforcements", 2014.
- 12. Škoc M. S., Pezelj E., "Abrasion resistance of high performance fabrics", Abrasion Resistance of Materials, http://www.intechopen.com/books/abrasion-resistance-of-materials/abrasion-resistance-of-high-performancefabrics.
- 13. ASTM D885: "Standard test methods for tire cords, tire cord fabrics and industrial filament yarns made from manufactured organic-base fibers", Annual book of ASTM standards, Vol. 07.
- 14. ASTM D4974: "Standard test method for hot air thermal shrinkage of yarn and cord using a thermal shrinkage oven", Annual book of ASTM standards, Vol. 07.
- 15. ASTM D6588: "Standard test method for fatigue of tire cords", annual book of ASTM standards, Vol. 07.

References 47

- 16. "Standard test method for fatigue of tire cords (disc fatigue test)", Annual book of ASTM standards, Vol. 07.
- 17. ASTM D4393: "Standard test method for strap peel adhesion of reinforcing cords or fabrics to rubber compounds", annual book of ASTM standards, Vol. 07.
- 18. "Long term performance of polymers", from http://www.motovated.co.nz/newsletter/aug13/Long-term-performance-of-polymers.pdf, accessed on March, 2014.
- 19. Website http://www.teijinaramid.com, accessed on March, 2014.
- 20. Chang K. K., "Aramid fibers", E.I. Du Pont de Nemours & Company, Inc.
- 21. Hockenberger A. S., Koral S., "Effect of twist on the performance of tire cord yarns", Indian Journal of Fiber & Textile Research, 29, 19-24, **2004**.
- 22. "Some unsolved problems in the science of nylon and polyester fibres", Indian journal of fibre & textile research, 16, 1-6, 1991.
- 23. Hearle J. W. S., Hollick L., Wilson D. K., "Yarn texturing technology", The Textile Institute, 2001.
- 24. Website http://en.wikipedia.org/wiki/Weaving, accessed on March, 2014.
- 25. Website http://www.zwick.com/br/produtos/software-de-ensaios-testxpert-ii-inteligente-e-seguro/aplicacoes-de-ensaio-avancadas/organizacao-abrangente.html, accessed on March, 2014.

References 48

Annex A - Tire

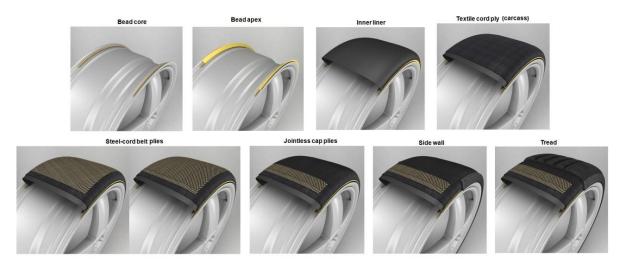


Figure 62 - Passenger car tire parts (extracted from [5]).

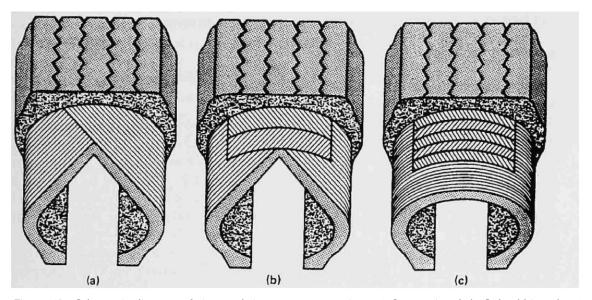


Figure 63 - Schematic diagram of tire cords in passenger car tires; a) Conventional; b) Belted bias-ply; c)
Radial (extracted from [3]).

Annex 49

Annex B - Twist and Fabric

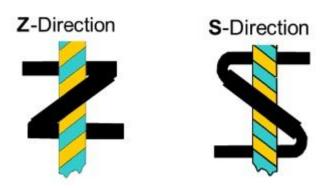


Figure 64 - Twist directions (extracted from [11]).

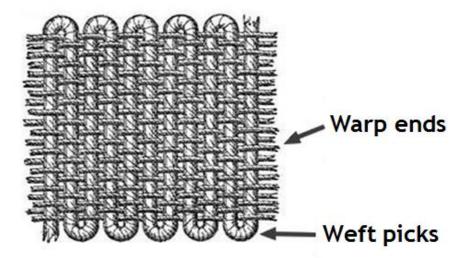


Figure 65 - Woven fabric (adapted from [25]).

Annex 50

Annex C - Test Methods

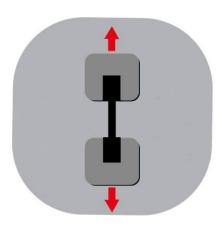


Figure 66 - Force Elongation test (extracted from [26]).

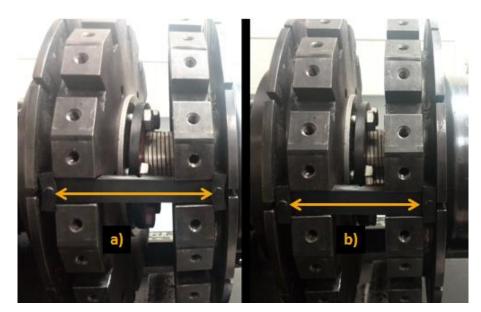


Figure 67 - Rotating discs in two opposite positions: a) extension; b) compression.

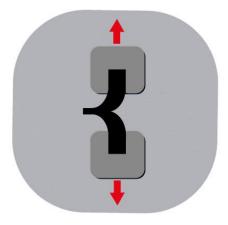


Figure 68 - Peel test (extracted from [26]).

Annex 51