Mestrado Integrado em Engenharia Química

Influence of Cord Design on Mechanical Properties of Tire Cords

Master's Thesis

by

Andreia Daniela Ferreira da Cruz

Performed at

Continental AG -
Body Compound & Reinforcement Technology

Supervisor from FEUP: Prof. Adélio Mendes

Supervisors from Continental: Dr. Günter Wahl & Mr. Ricardo Silva

FEUP

Departamento de Engenharia Química

February, 2014

Acknowledgements

This Master Thesis was much more than a work, it was completely a BIG life experience! For me, it was not only a challenge but especially, it was the best road that I could have crossed to grow up as a person and as a future professional.

In so many ways I had lucky in having an amount of people that supported and encouraged me in crucial moments. Regarding to that, I properly express my deepest gratitude to:

Professor Adélio Mendes, for his availability, support, constant encouragement and humor that always transmitted to me;

Dr. Günter Wahl, Mr. Eduardo Diniz and Mr. Manuel Pinheiro for the opportunity to work at Continental R&D in Hannover and to visit Indústria Têxtil do Ave (ITA) in Lousado; to Dr. Günter Wahl I have a special gratitude for his supervision, but specially for his precious time teaching me and telling me how to manage the scientific life;

Mr. Ricardo Silva, for his head-front knowledge, constructive criticism, endless patience and friendly words that were crucial in several times;

Dr. Thomas Kramer, Mr. Thomas Felten and Mr. Juergen Tschimmel, for giving the vision of experts to the presented questions;

Mr. Andreas Maibohm, Mr. Jose Fernandez and all people from Reinforcement Testing Laboratory, for the support and assistance during the lab work;

Body Compound & Reinforcement Technology department for all friendly partnership;

Mr. Alexandre Gomes, for the guided tour at ITA that allowed a better understand of the industrial context;

Ms. Aurora Madureira, Ms. Diana Pinto, Mr. Nuno Drumond, Ms. Ana Martins and Ms. Rute Pacheco, for the entire commitment that they had with material provision and specially for the good spirit and partnership that all they showed during my stay at ITA;

“Badi 9”, for being such a special, funny and sociable WG that always supported and encouraged me, making me feel all time on my own home;

My parents for their love and trust and Paulinho for his support while I was far away from home;

At last but not least, to João Cravo for all love, friendship and dedication that gives to me and especially for the positive side that He always has and makes me see.

Thanks to all my friends for everything!

Abstract

Day after day the industrial world proves to be increasingly competitive and demanding, seeking new challenges and improving and develop new products and processes. One of the most prestigious industries worldwide is the automotive, where Continental AG stands out through its constant technological innovation and evolution in the tire industry.

A tire is composed of a series of rubber compounds, metal and textiles reinforcements that provide a decisive role in its structure and performance. Concerning to textile reinforcements, they are determined by the usage of textile fibers such as nylon, polyester, aramid and rayon. This thesis is precisely focused on deeper characterization of the mechanical properties of reinforcement materials.

This thesis was driven by a partnership between Continental AG, Indústria Têxtil do Ave (ITA) and Faculdade de Engenharia da Universidade do Porto (FEUP). The main goal was the characterization of new cords constructions, highlighting the use of thinner fibers compared to those which are currently used. The study is divided into two main parts: pure cords and hybrid cords. Regarding to pure cords the analysis was restricted to nylon and polyester and concerning the hybrids aramid – polyester materials were considered. Afterwards, the analysis was based on the influence of textile fiber type, twist level and decitex in the cords constructions. At the end, a comparison was made of these new constructions to the currently used in tires, in order to evaluate possible future replacements.

Key words: tire, textile reinforcements, cord constructions, thin cords

Resumo

Dia após dia o mundo industrial demonstra ser cada vez mais competitivo e exigente, visando sempre a procura de novos desafios e o desenvolvimento melhorado e eficaz de novos produtos e processos. A indústria automóvel é atualmente uma das mais prestigiadas e a Continental AG afirma-se pela sua constante evolução tecnológica e inovadora, essencialmente direcionada para a área do pneu.

O pneu tem na sua constituição uma série de compostos de borracha e reforços metálicos e têxteis que proporcionam um papel determinante na sua estruturação e performance. Relativamente aos reforços têxteis, estes são determinados pelo uso de fibras têxteis como o nylon, polyester, aramida e rayon. Esta tese foca-se precisamente na caracterização mais profunda das propriedades mecânicas dos reforços têxteis.

Esta tese foi impulsionada por uma parceria estabelecida entre a Continental AG, a Indústria Têxtil do Ave (ITA) e a Faculdade de Engenharia da Universidade do Porto (FEUP). O principal objetivo definido foi a caracterização de novas construções de cordas, destacando-se o uso de fibras mais finas comparativamente às atualmente usadas. O estudo foi dividido em duas grandes categorias: cordas puras e cordas híbridas. Relativamente às cordas puras a análise restringiu-se ao nylon e ao polyester e as cordas híbridas estudadas foram aramida-polyester. A posterior análise baseou-se essencialmente na influência do tipo de fibra e das especificações escolhidas (como o nível de torcedura) nas construções das cordas. Por fim foi feita uma aproximação destas novas construções às atualmente utilizadas de forma a serem avaliadas futuras possíveis substituições.

Palavras-chave: pneu, reforços têxteis, construções de cordas, cordas finas

Official Statement

I declare, under honor commitment, that the present work is original and that every non-original contribution was properly referred, by identifying its source.

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Glossary

List of acronyms

AG	Automotive Group
ITA	Indústria Têxtil do Ave
FEUP	Faculdade de Engenharia da Universidade do Porto
PA6.6	Polyhexamethylene-dipamide
PET	Polyethylenetherephthalate
ASTM	American Society for Testing and Materials
TP	Tuning parameters
TL	Twist level
E@B	Elongation at Break
LASE	Load at Specific Elongation
L@3.5%	Load at 3.5 % of Elongation
C-ITA	Continental - Indústria Têxtil do Ave

1 Introduction

1.1 Continental AG & Project presentation

The present Master Thesis report was developed at Continental AG with collaboration of Indústria Têxtil do Ave (ITA) and Faculdade de Engenharia da Universidade do Porto (FEUP).

Continental was founded in Hanover in 1871 as a stock corporation "Continental-Caoutchouc und Gutta-Percha Compagnie", producing soft rubber products, rubberized fabrics and solid tires for carriages and bicycles. In 1898 began the development and manufacture of automobile pneumatic tires with a plain tread and in 1904 Continental became the first company worldwide to develop grooved tires for automobiles. Nowadays, the company ranks among the top 5 automotive suppliers worldwide of brake systems, components for power trains and chassis, instrumentation, vehicle electronics and tires. A constant concern regarding to the driving safety and global climate is also an important characteristic to be mentioned. Continental is also a competent partner in networked automobile communication with around 170 000 employees in 46 countries. [1] ITA belongs to Continental Group since 1987 and it is one of two producers of textile for Continental tires, being the other in USA.

By many measures the tire industry must be considered mature, but technical changes in tires promise to continue at a rapid rate and at the heart of many of these changes are tire cords. The prime or basic challenge to tire cord engineers is to develop a deep understanding of tire cord materials and how they work in a tire. Reinforcement materials of a tire — tire cord as textile and steel cord as bead wire — are the predominant load carrying members of the cord rubber composite. They provide strength and stability to the sidewall and tread as well as contain and withstand the inflated air pressure, which means that reinforcement textiles have a significant role in the performance of a tire. The most used polymer based textile materials in tire industry are nylon, polyester, aramid and rayon. [2]

The developments in tire technology were primarily focused towards higher speed, safety, fuel efficiency and comfort. As a consequence of higher speed, heat generation (or rolling resistance) also increases, which has an adverse impact on performance and durability of tires. Besides the rolling resistance, there are other major characteristics related to the tire performance such as endurance and handling.

Reinforcement polymers as textiles for tire applications is an area of continuous research and thus, there is a great need to develop materials and cord constructions with better specifications than actual standard textile cords. This Master Thesis works precisely as a first step in the investigation of new construction of cords, focusing on alternative and ultrathin materials.

1.2 Project Motivation and Contribution

The main motivation for research new constructions of cords remains in the fact that reinforcement materials by its different properties and characteristics dominate the tire performance. This means that with a systematic and deep evaluation of each type of construction, it is possible to determine which those provide higher stability and advantages for future tire development.

In this Master Thesis was characterized pure cords of nylon and polyester and also hybrid cords composed with aramid and polyester. The linear density which is described as “decitex” of the yarns ranged between high and small values in order to evaluate that influence in the cords. The characterization started with mechanical and thermal tests such as force-elongation, shrinkage and shrink force, relaxation, creep and hysteresis. However, during the laboratory work it was necessary to discuss the capability and sensitivity of test methods and corresponding testing equipment, towards to new thinner constructions.

The investigation and characterization of the cords response, regarding to modifications in design construction, is the main contribution of this work. A comparison of these new cord constructions versus to the standard ones used in tire building was also made, in order to evaluate potential future replacements.

1.3 Thesis organization

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

Chapter 1. Introduction gives an initial approach to Continental AG role on global tire market and reinforcement materials importance.

Chapter 2. State of the Art describes all the knowledge known so far about tires, textile fibers, reinforcement materials, hybrid cords and cords characterization.

Chapter 3. Technical Description explains the cords properties, methodology and all procedures used for the characterization of the new cord constructions.

Chapter 4. Results and discussion refers all results and its analysis/discussion.

Chapter 5. Conclusions indicate all main conclusions of the work performed.

Chapter 6. Project Assessment synthesizes the accomplished objectives and provides information for future development.

Chapter 7. Bibliography is a complete list of all the references used throughout this work.

2 State of Art

2.1 Tire

A tire is regarded as “just a black wheel” by the majority of people, but the modern tire technology blends a unique mix of chemistry, physics and engineering that give to consumers a high degree of comfort, performance, efficiency, reliability and safety.

The tire production facilities require a massive amount of machinery and the processing technology involved to achieve the final product could surprise anyone that never had an opportunity to visit a plant. Tires are highly engineered structural composites whose performance can be designed to meet the vehicle manufacturers’ ride, handling and traction criteria, plus the quality, safety and performance expectations of the customer. [2]

There are two types of tires regarding the cord layer direction within the carcass casing (tire body) below the tread and belt: diagonal bias tires and radial tires. The radial tires are by far the majority of the passenger car tire volume on the market and compared with the other types of tires, they support radial body cords that deflect more easily under load, thus they generate less heat, give lower rolling resistance and better high-speed performance and endurance performance. [2]

As shown in Figure 1, a radial tire comprises several parts and each one represents an essential role in the proper functioning of the tire.

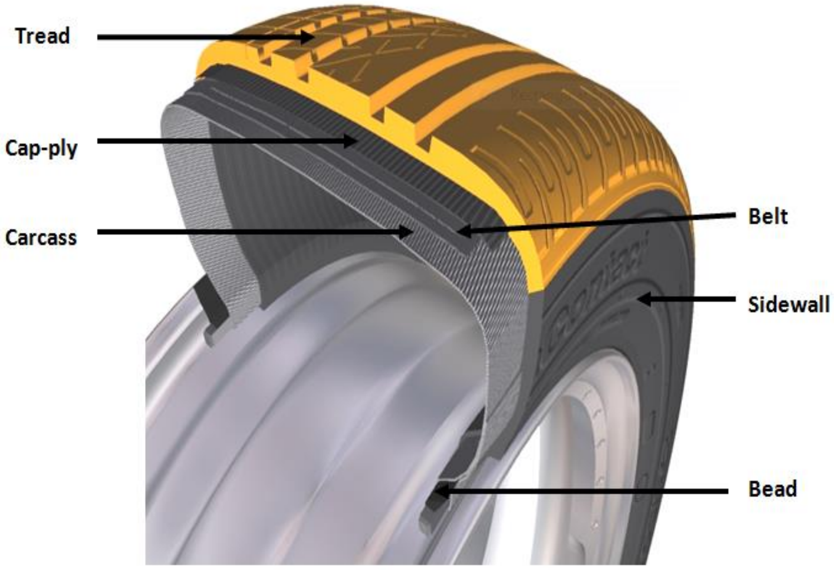

Figure 1 - Radial tire cross-section (adapted from [3])

The cap-ply and the carcass, which can be designated body plies, are made by rubberized fiber polymers (textile reinforcement materials) placed in circumference and radial direction, respectively. The carcass acts to withstand air pressure and vertical load, while cap-ply protects the tire from the centrifugal forces resulting from high speed inducted belt growth and provides stability and endurance of the tire. Steel based reinforcements are located in angled direction as belt, on top of the carcass and below the cap-ply. This part protects and shapes the tire contour during driving service. The tread is specially formulated to provide a balance between wear, traction, handling and rolling resistance. The sidewall protects the body plies from abrasion and impact. This two last constitutes of a tire are made only of rubber compounds. The bead anchors the inflated tire to the wheel rim and ensures sufficient rim seating of the tire. [2][4]

2.2 Reinforcement Materials

Actually the most textile materials used in the tire industry are polyamide, polyester, aramid and rayon. Polyamids were among the first synthetic polymers used for fiber applications and they can be classified into aromatic polyamides and aliphatic polyamides. This last group can be designated as either PA-*x* or PA-*x.y* where *x* and *y* represent the number of carbon atoms between nitrogen atoms. PA6.6 is the most used in tire industry and is produced from hexamethylene diamine and adipic acid while PA6 is synthesized by ring-opening polymerization of ε-caprolactam. PA6.6 is a high-elongation, low-modulus, high fatigue resistant and good adhering synthetic yarn. Regarding to these characteristics in addition to its typical hot shrinkage behavior, it has the major contribution in cap-ply. [5][6][7]

Polyesters comprise the largest amount of totally synthetic polymer produced in the world and the majority is polyethyleneterephthalate, which is made from terephthalic acid and ethylene glycol. The most common usage is in radial body plies as carcass and the advantages of PET as tire cord are high strength, good durability and high modulus combined with moderate to low hot shrinkage. [6]

The p-Aramid, also known as poly-p-phenylene terephthalamide is derived from 1,4-phenylenediamine and terephthalic acid. It has significant higher breaking strength of high-tenacity nylon and polyester, but its most outstanding physical property is high tensile stiffness. This property has lead to high-volume usage of the fiber as reinforcement in composite materials such as belts and cap-ply in radial tires. [2]

Regarding to rayon, a purified cellulose is chemically converted into a soluble compound. A solution of this compound is passed through the spinneret to form soft filaments that are then converted or regenerated into almost pure cellulose. Because of the reconversion of the soluble compound to cellulose, rayon is referred to as a regenerated cellulose fiber. The principle characteristics of this fiber are lower shrinkage, higher modulus and good adhesion properties. However, it requires big costs to the tire production and from the economic point of view, this act as a huge disadvantage. [2][8]

2.3 Cord design – nomenclature

In the tire industry exists multiple constructions and material concepts. Regarding to cord design, it is first required to define some important and useful terminology, which is represented on Table 1. [2][9][10]

Table 1 – Nomenclature of Cord Design

Terminology	Description
Filament/fiber	Single part with high ratio of length/cross sectional area
Yarn/ply	Assembly of filaments plied together
Cord	Two or more yarns plied and twisted together
Fabric	A structure used in tire manufacture, comprising a sheet of warp cords or yarns bounded together by widely spaced weft yarns
Greige Cord	Cord before dipping and heat setting process
Dipped Cord	Cord after chemical treatment
Pure Cord	Cord composed with same polymer
Hybrid Cord	Cord composed with different polymers
Titer	Unit for linear density, mass in grams per length tex = g / 1000 m , dtex = g / 10000 m
End Count	Number of warp or weft yarns / cords per dm in a fabric (epdm)
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
Breaking Force	Maximum force to break a cord. Expressed in Newton
Elongation at Break	Maximum elongation of the cord when it breaks. Expressed in percentage
Tenacity	Specific breaking strength per titer. Could be expressed in cN/dtex
EASL	Elongation at Specific Load. Can be visualized on the Force-Elongation curve and it is expressed in percentage
LASE	Load at Specific Elongation. Can be visualized on the Force-Elongation curve and it is expressed in Newton
Modulus	Slope between the initial linear portion of the Force-Elongation curve. It is based on Young's Modulus

2.4 Manufacture of textile reinforcements

All the textiles used in tires are specially prepared and processed in order to build up structures designated as fabrics. The manufacture of these structures is based on several transformations, which can be summarized [10][11]:

Spinning process: the fiber is transformed into yarn. This process can be performed in 5 different ways: using wet, dry, melt, gel or dispersion method and this choice depends of the characteristics of the material;

Twisting process: two or more yarns are twisted individually in the "Z" direction and afterwards, they are twisted together in the "S" direction. From here results a greige cord. The yarn's twist increases cohesion between the fibers by increasing the lateral pressure in the yarn, thus giving enough strength to it;

Weaving process: a greige cord is transformed into greige fabric. In this method occurs an interception between the warp (cord that runs lengthwise to the machine) and the weft (cord that runs in right angle to warp);

Dipping process: the final greige fabric is emerged in a Dip solution and afterwards is exposed to a heat treatment. The final results should be a fabric with perfect conditions that allows good adhesion with the rubber and provides the necessary tensile requirements and thermal properties.

In the case of manufacture of a cord and not a fabric, the weaving process does not exist, passing the greige cord directly to the dipping process.

2.5 Hybrid Cords

The concept of hybrid cords is established in tire industry. A combination of two or more different types of yarns twisted together has been proved as an innovation and meanwhile many studies are being done in order to obtain a deeply evaluation of this types of constructions. The most used hybrid cord is made by aramid with PA6.6. Aramid is a high tenacity, high modulus, low elongation and a thermally stable (non-shrinking) yarn material, while PA6.6 is a high elongation, low modulus and it is high fatigue resistant. In conclusion, the combination of these two different synthetic yarns results in a diversified range of mechanical properties that may fits perfectly in a certain type of requirements and even better, they can lead to a similar performance of a conventional cord but with lower cost [12][13][14].

2.6 Cords Characterization

As mentioned before on Chapter 2.1, tire cords are contributing by their anisotropic modulus and strength within the rubber composite of tires. As such, they must provide the tire with axial and lateral rigidity for forces due to acceleration, braking, cornering and dimensional stability for uniformity, handling and ride [2], and to achieve this kind of conditions it is necessary, first of all, to do a specific characterization of the material. In Table 2 are described some mechanical and thermal tests that can be performed on the Reinforcement Testing Laboratory.

Table 2 - Description of tests performed on reinforcement materials [10][15][16]

Test	Description
Force Elongation	Measures the relation between tensile force and elongation
Thermal Shrinkage	Measures the percentage of cord length that shrinks when subjected to a determinate heat (temperature) for a certain period of time
Thermal Shrink force	Measures the force which occurs as a result of heat (temperature), time and pre-tension with a constantly fixed length
Creep	Measure the increasing deformation while load is constant
Relaxation	Measure the decreasing in load while deformation is constant
Adhesion to rubber	Measure the adhesion of textiles that are bonded to rubber compounds
Disc Fatigue	Measure the phenomenon leading to filament fracture under repeated tension/compression stress
Hysteresis	Measure the energy loss of the cord during loading and unloading conditions. The work loss is obtained by subtracting the relaxation area from the tension area. This loss could be represented by tan delta ($\tan\theta$), which represents the relative degree of material damping.

With an increasing demand for the longer lasting high performance products, continues improvement regarding the above mentioned characteristics is required for tire reinforcing materials. However, the future improvement needs to be focus too in the expansion and evolution of new mechanisms and methods to perform a proper evaluation of the material.

2.7 Dynamic analysis

Polymers are composed of long molecular chains having unique viscoelastic properties. This viscoelasticity reflects the combined viscous and elastic response, under mechanical stress.

Dynamic mechanical analysis (DMA), where a sinusoidal force is applied to a material and the resulting displacement (strain) is measured can be used for characterizing the viscoelasticity of a polymer cord or fiber. The analysis of the dynamic response can be divided into two components, the real component related to the elastic response of the sample, and the imaginary response that combines the elastic response with an accumulation term related to the energy spent in irreversible processes such as polymer molecules slit, burst, etc. [17]
The use of dynamic processes for characterizing cords used in the automotive industry is innovative and has the potential to bring new and relevant information, especially related to the in process aging of the cords.

3 Technical Description

This chapter describes all the methodology and techniques used for develop this project.

3.1 Operating Conditions and Cords properties

The main goal of this project concerns the characterization of new cords constructions, such as cords composed with thinner yarns. The cords used during this project were divided in two main categories: pure cords and hybrid cords. As explained in Chapter 2.3, pure cords are composed with yarns of the same type of material and the hybrid cords are composed by a combination of different types of materials. Reinforcement Prototype Center ITA supplied all materials used in this project.

This project regards the cords behavior as a whole, taking into account not only the difference of total decitex between the cords but also the influence of the twist level that each cord construction has. Concerning to this, the choice fell on two different levels of twist: low (250 tpm) and high (550 tpm). The twist for the ply was fixed in the “Z” direction and for the cord was fixed in the “S” direction, and both had a balanced twist, which means that the twist level for the ply was the same that was used for the cord, and this procedure was used for both categories of constructions mentioned before.

Cords of PA6.6 and PET were chosen for being characterized. In

Table 3 are described the construction characteristics of the pure cords. For these new cords investigated within this Master Thesis, the constructions were fixed on x1x2, and it is worth noting that was added an asymmetric construction combining two yarns with different decitex of PA6.6 in order to see the influence of the individual yarn´s decitex.

Table 3 – Cord Constructions of Pure Cords

Pure Cord	Cord Construction[1]	Twist Level
PA6.6	700 x 1 x 2	250 tpm; 550 tpm
	470 x 1 + 700 x 1	
	470 x 1 x 2	
	235 x 1 x 2	
PET	550 x 1 x 2	

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[1] Polymer decitex x ply number

Regarding the characterization of the hybrid cords, these are composed of one-ply aramid and one-ply polyester twisted together. The idea behind this category is check what is the influence of the decitex of the aramid and polyester in different constructions. Therefore, to achieve a better understanding in this category, two divisions can also be made: in to symmetric hybrid cords and asymmetric hybrid cords. In Table 4 are described the characteristics of the hybrid cords constructions.

Table 4 – Cord Constructions of Hybrid Cords

Hybrid Cord	Cord Construction[2]	Twist Level
Aramid + Polyester (Symmetric)	1100 x 1 + 1100 x 1	250 tpm; 550 tpm
	550 x 1 + 550 x 1	
	220 x 1 + 238 x 1	
Aramid + Polyester *(Asymmetric)*	1100 x 1 + 550 x 1	
	1100 x 1 + 238 x 1	
	550 x 1 + 1100 x 1	
	550 x 1 + 238 x 1	
	220 x 1 + 1100 x 1	
	220 x 1 + 550 x 1	

3.2 Selected Tests

In order to analyze the cords behavior regarding to mechanical and thermal properties, the effects of twist level, temperature, frequency and linear densities (decitex) were investigated. To plan the experiences that should be performed, it was necessary to define the target tire production specifications and tire service conditions which give indication of the force load of cords inside the tire.

It is known that the in-tire cord could be subjected to a maximum strain of 3.5 % and is heated at high temperature during vulcanization and tire service. The engineers responsible for the developments during the design development of tire construction base their decisions on the first part of the Force-Elongation curve, up to 20 % - 30 % of these curves, which represent the “secure level” of the cord. Concerning the rolling service of a tire, the temperature inside depends on many aspects such as the velocity of the rolling and the external environment, but it is possible to say that a tire could reach values between 23°C up to 200°C, being the maximum temperature a completely extreme condition for a tire. In general, a tire works at high frequencies, such as 10 Hz (which corresponds to travel at 100 km.h^{-1}) or more.

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[2] Aramid decitex x ply number + Polyester decitex x ply number

Considering this information and the functionality of the equipment, the next step is designing the tests and the parameters that should be performed to best characterize these materials:

- **Force Elongation**

It is normally always the first test to be made in order to obtain the most important information about the cords: the maximum force and elongation that the cord stands. Two temperatures were considered, room temperature (RT) and 80°C to delineate the first specifications of the material and to observe the influence of the temperature on the tensile properties;

- **Shrinkage**

The tests were performed at 180°C during 2 minutes. The linear retraction along the cord axis in the presence of heat and pre-tension is particularly important for the processing of tire in the molds;

- **Shrink force**

The tests were performed at 180°C during 2 minutes in order to evaluate the force that is applied in the cord when the holding time, during the heat treatment;

- **Relaxation**

The tests were performed at RT and at 80°C with a fixed elongation of 3.5 %, during 20 minutes. This test is important because give us a perception of force loss when a specific tension (such as elongation) is fixed.

- **Static Creep**

At the beginning, the test was performed at RT and 100°C with a fixed stress of 20 % of the breaking force of the specific and individual cord construction and kept for 2 hours statically. However, the equipment and the test method used were not properly verified as reliable method. The initial behavior of the obtained curve was observed completely irregular (for further information see Appendix A.1) due to some device tools were not working sufficient. Regarding to this situation, it was made a second attempt in another machine during 20 min (at this time the behavior was considered stable) but only at RT. The creep test is also an important characterization of material since measures the cord growth when a force is being applied.

- **Dynamic Creep**

The tests were performed at RT during 2 hours with a frequency of 10 Hz, using a fixed stress of 20 % of the breaking force of each cord construction. An elongation amplitude was selected and corresponds to 10 % of the applied stress (meaning 10 % of the applied basis force which by itself relates to 20 % of cord specific breaking force). The main concept behind the dynamic and static creep tests is the same; however, the dynamic test gives access to the static resistance but also to the dynamic resistance. Beside the dynamic creep results, the machine used for this test also gives the *tan delta*, however the resolution of the available load cell is too low (it is around 1 kN) for testing thin materials with low force levels at corresponding elongation, leading to a work loss very close to zero and in some cases below zero, which does not make any physical sense.

- **Hysteresis**

Regarding to previous descriptions about *tan delta*, a second approach was done in a different machine with a load cell with higher resolution (500 N). The tests were performed with a stress control of 20 % of breaking force, an elongation amplitude corresponding to 10 % of the applied stress and a frequency of 0.5 Hz. However, the results showed nonuniformity in the cycles, leading one more time to work loss values of approximately or below zero (for further information see Appendix A.2). So regarding to the hysteresis analyses, further tests including test method development should be done in order to reach the best parameters for investigations.

In general, relaxation, creep and hysteresis tests are important to evaluate the cord constructions with higher detail, because the standard tests that already exist are not sufficient enough to characterize efficiently and deeply the all kinds of cord constructions.

3.3 Testing procedures

The force elongation tests were performed by using a tensile testing machine (Zwick Z010) according to standard ASTM D885 [15]. Averages of at least five specimens were reported for each type of cord. In this test it was necessary to apply a pre-tension to the cord in order to confer it an initial linearity, and this parameter is set directly in the controlling software.

The thermal shrinkage and the thermal shrink force were measured using a shrinkage testing machine (Lenzing TST10) and the average of three samples was recorded, according to standards ASTM D885 and ASTM D4974 [15][16]. As can be seen in Figure 2 and Figure 3, in this test it was also necessary to apply a pre-tension on the material. Thought there are standard pre-tensioning weights, for these thin cords they cannot be applied and new weights were proposed.

Figure 2 – Established pre-tension (minimum 10 cN)

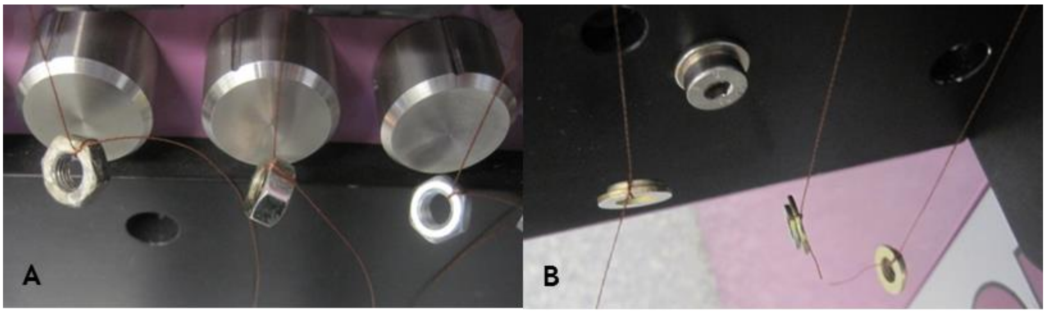

Figure 3 - Proposed pre-tensions for thinner material: A (5 cN), B (2.5 cN)

The relaxation test was performed using the same machine that was used for shrinkage because the equipment has a lever that allows inputting an elongation in a range of 0 % - 3.5 %, as can be seen in Figure 4. The cord is fixed in the first clamps and a pre-tension is applied. Afterwards, the program starts, the lever is pushed until reach the 3.5 % and the second clamps are fixed. The average of three samples was recorded.

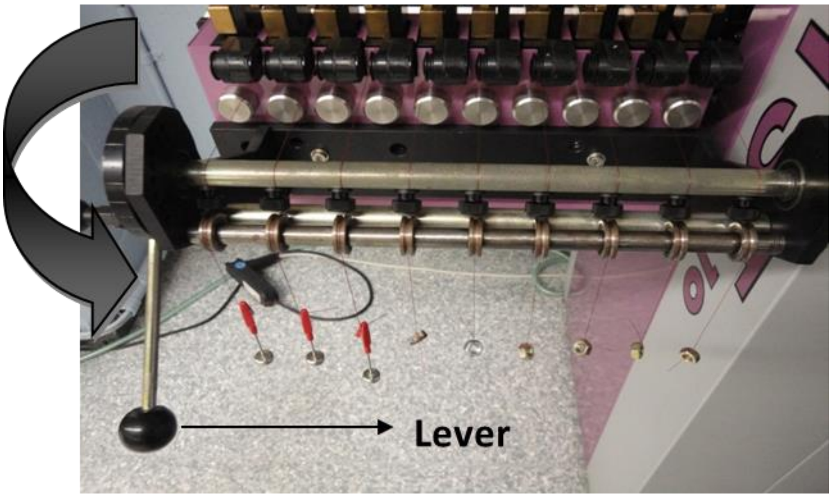

Figure 4 – Preview of Relaxation test

Regarding to creep, the same number of samples was taken into account and the tests were performed on equipment MTS Landmark 200 Hz Elastomeric Test System, which was configured specifically for characterizing the dynamic properties of elastomeric materials and components. The system is optimized for frequencies up to 200 Hz and available with maximum force capacities of 1 kN, as mentioned before in Chapter 3.2. This machine was not in the same laboratory as the others, so it was necessary carried the material from one side to the other, which could provoked a loss on the properties of the material regarding to temperature and humidity. For this reason it was established at the beginning of each test, a waiting time of at least 1 minute in order to conditionate the material.

The only difference between the static and dynamic tests is the application of a frequency and amplitude, which does not exist in the static test. The first step was fixed a cord in the clamps and put directly in the software the testing parameters. To improved sinusoidal signals during the test, it was necessary to optimize the so-called Tuning Parameters (TP), parameters concerning the operation of the testing machine. During the tests was possible to observe in the oscilloscope the sinusoidal signals, which allow us to check if the test is running with the right parameters (for further information see Appendix B).

This project was the first work with this equipment, so during the experiments and during the data analysis, many questions were raised, regarding for example to the influence of the resolution of the load cell, the choice of the TP values and the influence of the increase/decrease frequency and amplitude. It is for sure a challenging new world to explore.

3.4 Data analysis – Relaxation & Creep

As explained before in Chapter 3.2, the relaxation and creep tests are two important approaches to characterize cords constructions. The difference between these testing methods is that relaxation is based on strain control while creep is based on stress control. Although, it is possible to say that the first step of both tests is similar regarding to the fact that an initial condition is applied in both cases. So what is important to study with these tests, in order to characterize the material, is not the entire force history but force history from the point and setting force is reached. Figures 5 and 6 show the first 30 seconds of relaxation and creep results from ARA1100x1 + PET1100x1, respectively.

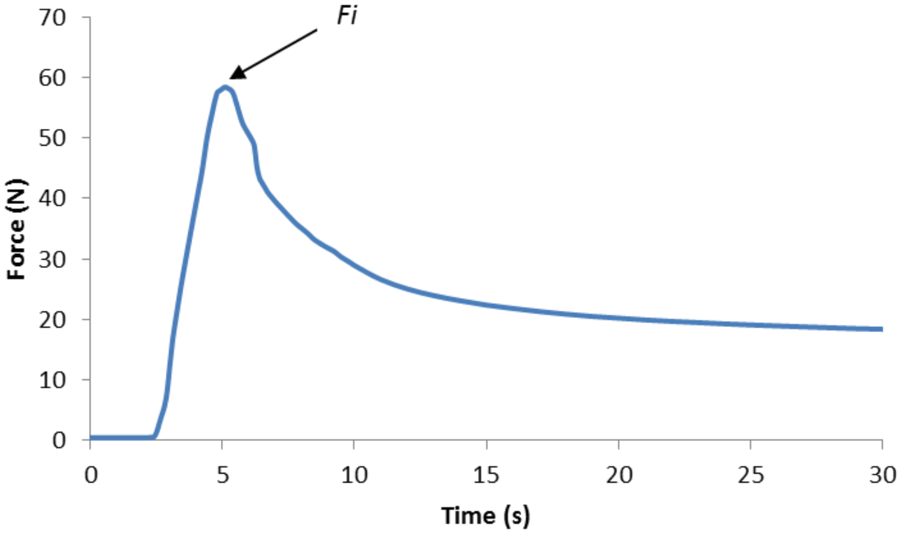

Figure 5 - First 30 seconds of Relaxation test at RT on ARA1100x1+PET1100x1

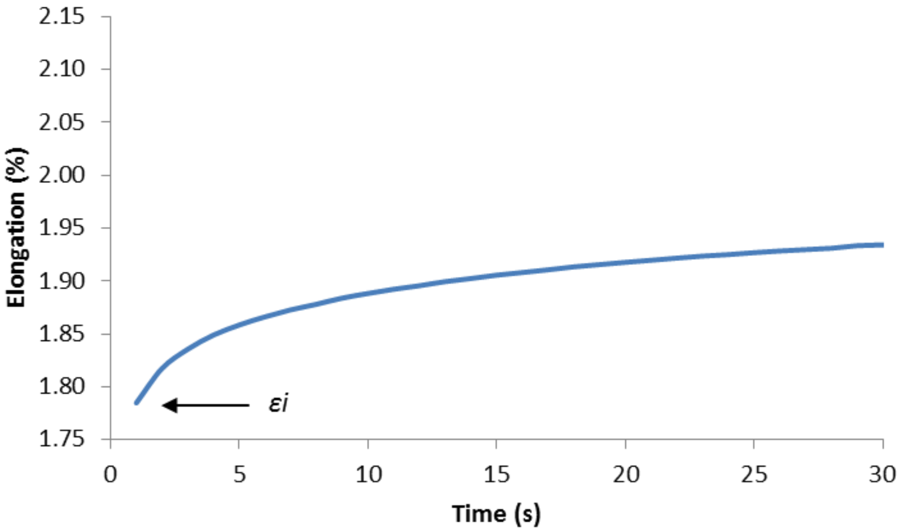

Figure 6 - First 30 seconds of Static Creep test at RT on ARA1100x1+PET1100x1

The first point taking into account in the relaxation plot is marked as Fi (cf. Figure 5) and regarding to static and dynamic creep results, the software only records force values from the precisely moment when the first condition is already obeyed.

The relaxation values are obtained from Equation 1:

$$Relaxation\ (\%) = \frac{Ff(N) - Fi(N)}{Fi(N)} \times 100 \qquad \text{(Equation 1)}$$

where Ff represents the final force reached during the test. The final result represents the force drop that each cord construction has during the experimental time.

Regarding the creep test, the relevant values are obtained accordingly to Equation 2:

$$Creep\ (\%) = \varepsilon f(\%) - \varepsilon i(\%) \qquad \text{(Equation 2)}$$

where εi and εf represent the initial and final elongation, respectively. In this case the final result gives already the cord growth in percentage.

4 Results and discussion

4.1 Design of Pure Cords

In this sub-chapter, the main goal is to study the influence of cord designs regarding to the specific breaking strength, load at specific elongation (LASE), elongation at break (E@B), shrinkage, shrink force, relaxation and creep for all new pure cords constructions. In Figure 7, it is possible to observe a general diagram of the pure cords that will be evaluated in this section, when each line represents a cord construction.

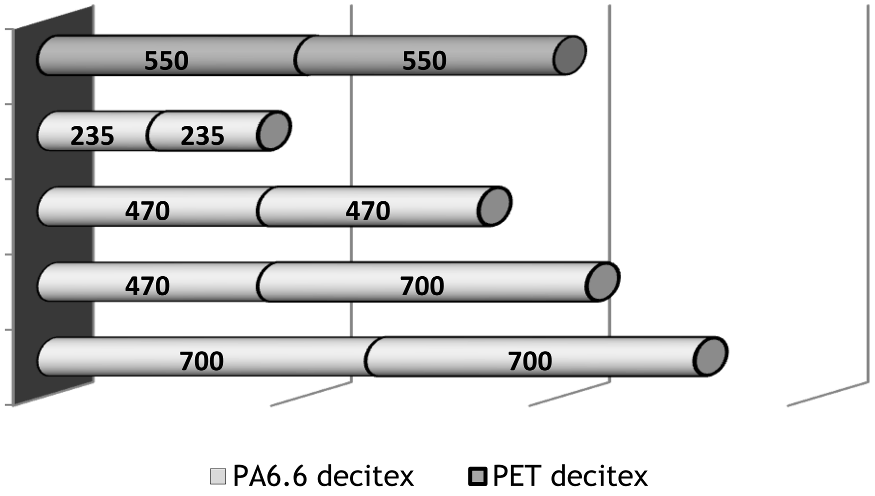

Figure 7 - Diagram of Pure Cords constructions

4.1.1 Influence on Tenacity, LASE and Elongation at Break

In order to get a first evaluation of pure cords, the first step was to analyze the basic data obtained by their Force-Elongation curves. As the cord constructions have different titers, it is necessary to normalize them first, by dividing the force by the cord titer. This way, one can compare the materials behavior, regardless of their titer. It is generally expressed in Tenacity (cN/dtex) as function of Elongation (%). In Figure 8, it is possible to compare the given materials, twisted with 250 tpm and tested at RT.

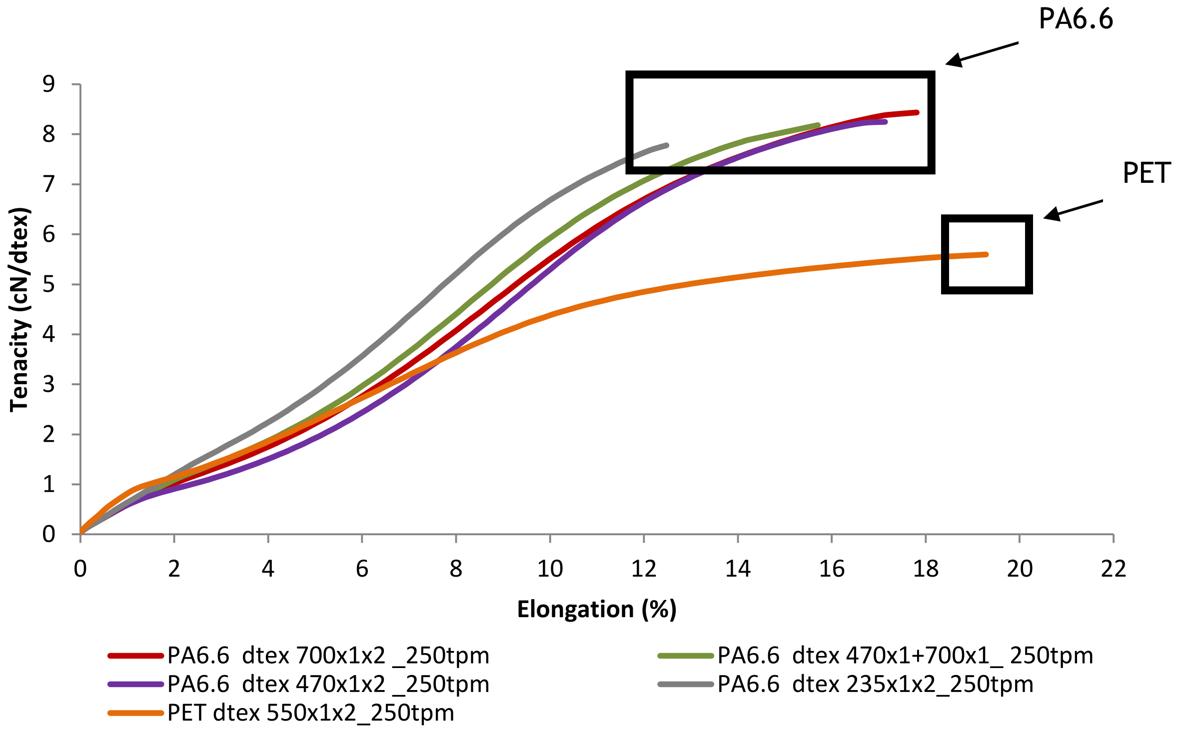

Figure 8 - Tenacity-Elongation curve of Pure Cords (250 tpm) at RT

Regarding to PA6.6, all cords independently of decitex, have approximately the same specific breaking strength (around 8 cN/dtex) but concerning to elongation at break, it is clear that it is really dependent of material titer. As titer increases, the cord´s elongation at break also increases, even with the same construction. It is also important that the combination of yarns with different decitex provokes a decrease on E@B comparatively with the cords composed with symmetric yarns. However, this observation is only possible at 250 tpm, as can be seen afterwards.

Regarding to PET, it is possible to observe that comparing with PA6.6, it has less tenacity (around 6 cN/dtex) but elongates approximately 1 % more than PA6.6 dtex 700x1x2.

As described in Chapter 3.1, a twist level of 550 tpm was also used to evaluate the influence of this parameter in cords behavior. This evaluation was done by normalizing the absolute values at 250 tpm and 550 tpm, using Equations 3 and 4, respectively, where X corresponds to an absolute value of a certain property:

$$Normalized\ Value_{@250tpm} = \frac{X_{250tpm}}{X_{250tpm}} = 1 \qquad \text{(Equation 3)}$$

$$Normalized\ Value_{@550tpm} = \frac{X_{550tpm}}{X_{250tpm}} \qquad \text{(Equation 4)}$$

Taking into account this mathematical evaluation, the final results were represented in a radar chart, or also called as spider web chart, as can be seen in Figure 9. It is important to remember that the analysis regarding to tenacity and LASE were made in cN/dtex and the E@B was always treated as percentage. The study regarding to LASE was done at 3.5% of elongation because the relaxation test was made with this fixed value. An attempt was made to check if the values of load at specific 3.5 % elongation (L@3.5%) and *Fi* (initial force reached during relaxation test) matched with each other, which in general it was possible to confirm.

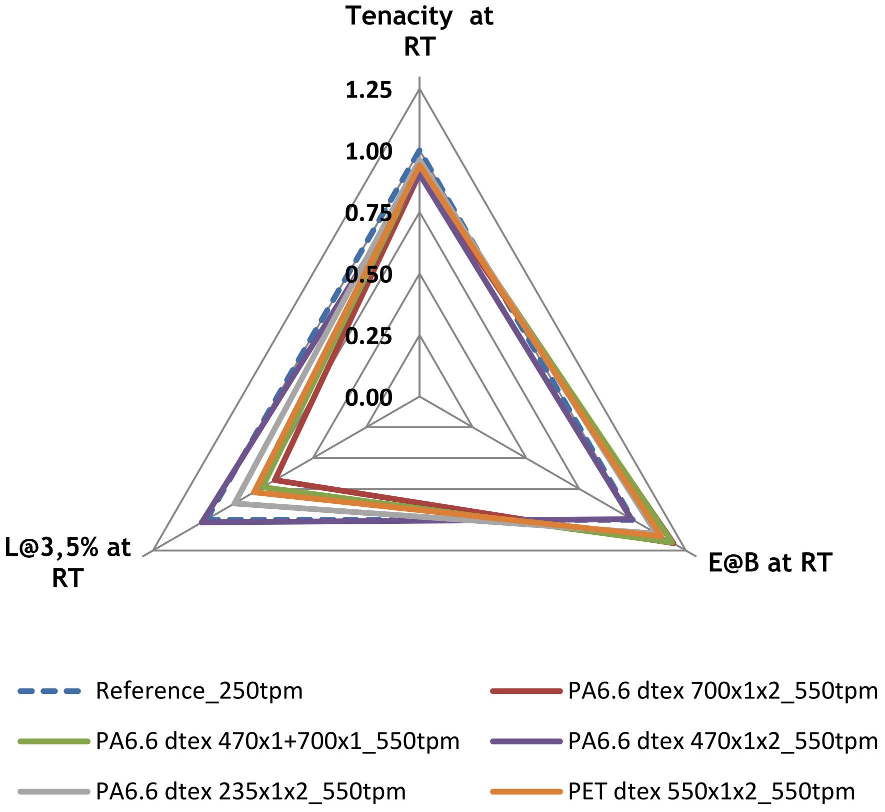

Figure 9 - Influence of twist level at RT on Tenacity, L@3,5% and E@B of Pure Cords

Observing the chart above, it is possible to say that tenacity suffers a decrease around 10 % with the increase of twist level, which means that a twist of 550 tpm on these pure cords has not a big influence on the specific breaking strength. This is remarkable because gives us the perception that either PA6.6 or PET do not suffer a big decrease on tenacity doubling the value of twist level. Concerning yet to asymmetric pure cord, it is possible to observe that PA6.6 dtex 470x1x2 almost does not suffer any changes on the E@B with the increase of twist level, which turns the evaluation of the asymmetric cord more difficult regarding to E@B.

In general, as the twist level increases, L@3.5% decreases and E@B increases. This happen because, at higher twist levels, the cords have a kind of "spring effect", as can be seen in Figure 10, which allows responding easily to light inputs (therefore the lower L@3.5%), and also increases the overall elongation of the materials when subjected to a load. The twisting imparts on cords constructions a more packing structure of the yarns, and each twist step acts as a mechanical interlocking of the yarns. This packaging effect applies extra tension on both yarns, increasing the helix angle between the cord and yarn axis.

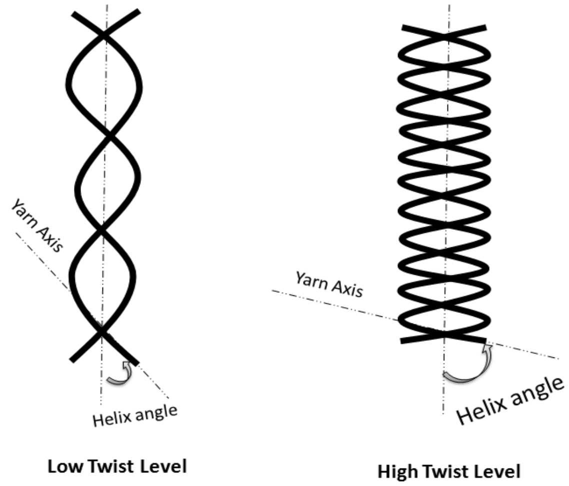

Figure 10 - Influence of twist level on helix angle

This spring effect can also be connected to a simple equation used to design cord constructions: the twist factor (α). This factor was calculated using Equation 5 and the results are represented in Table 5.

$$\alpha = Twist\ level\ .\sqrt{\frac{Total\ cord\ dtex}{10000}} \qquad \text{(Equation 5)}$$

Table 5 - Twist factors of Pure Cords

Polymer	Cord Construction[3]	Twist Factor (α)		$\Delta\alpha$[4]
		TL = 250 tpm	TL = 550 tpm	
PA 6.6	700 x 1 x 2	94	206	112
	470 x 1 + 700 x 1	86	188	102
	470 x 1 x 2	77	169	92
	235 x 1 x 2	54	119	65
PET	550 x 1 x 2	83	182	99

---

[3] Polymer decitex x ply number

[4] $\alpha_{550\ tpm} - \alpha_{250\ tpm}$

As it can be seen, a high twist level corresponds to a higher twist factor, which proves that at high twist and with a higher total cord decitex, the plies have higher geometrical packaging. It is also possible to say that with thinner cords, the difference of twist factor ($\Delta\alpha$) is lower compared to the thicker cords, which can result in a lower influence of twist level in the studied properties. This effect can also be observed directly on the cords.

In Figure 11 and Figure 12, it is possible to observe microscopic pictures of a thinner and a thicker pure cord (for further information see Appendix E.1), respectively, and the packaging effect that a twist level provokes in a cord structure.

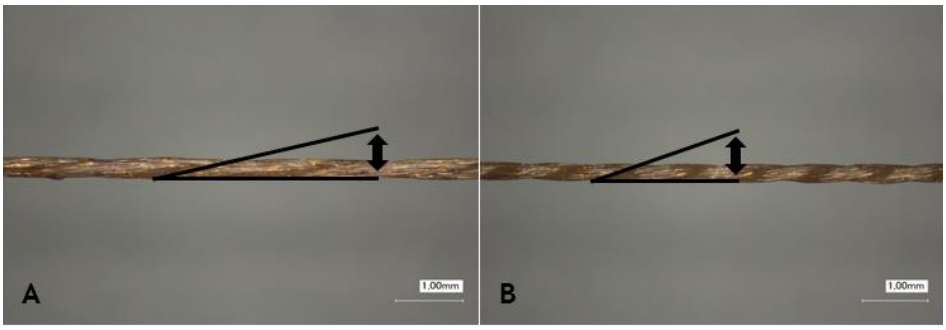

Figure 11 - Microscopic view of PA6.6 235x1x2: A (250 tpm) and B (550 tpm)

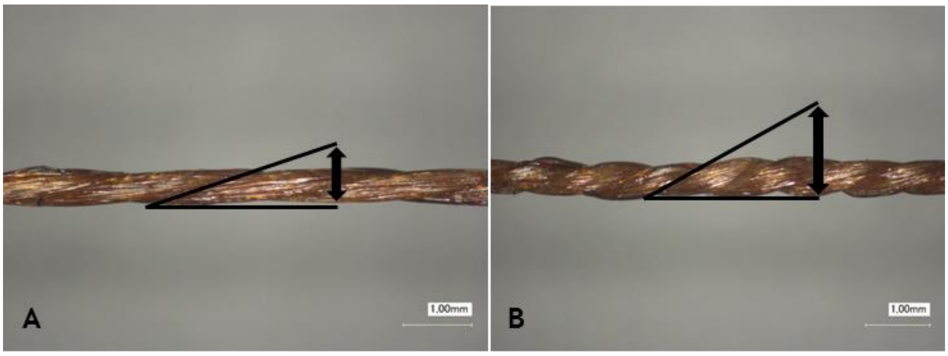

Figure 12 - Microscopic view of PA6.6 700x1x2: A (250tpm) and B (550tpm)

It is true that thicker cord presents a structure much more condensed and nonlinear than thinner cord, which means that the helix angle will be even higher when a comparison it is done at the same twist level. The increase of twist level promotes also an increase of the number of sharing points per cord unit length.

At 80 °C, the only important change is that tenacity of PA6.6 decreases around 1 cN/dtex while PET remains practically with the same tenacity. Regarding to E@B, at this temperature all PA6.6 cords present higher values while PET remains practically with the same result. This fact could be explained taking into account the glass transition temperature of each polymer. It is known that for PA6.6 it is 55 °C and for PET it is 80 °C [2]. This means that when the material is subjected to a temperature of 80 °C, PA6.6 will be already softer than PET, ending with less tenacity and higher E@B. Regarding to the influence of twist level in the actual properties in study, it was possible observed that at 80 °C does not exist a big general difference relatively to RT. However, the most important remark that can be enhanced is that at 80 °C the influence of twist level on tenacity is higher on the asymmetric PA6.6 cord (almost 20 %), which means that the asymmetry of the yarns in pure cords may brings some issue regarding to loss of strength at high temperatures (for further information see Appendix C.1).

4.1.2 Influence on Shrinkage and Shrink force

In Figure 13 and Figure 14, it is possible to observe the shrinkage and shrink force results of the pure cords in study, respectively.

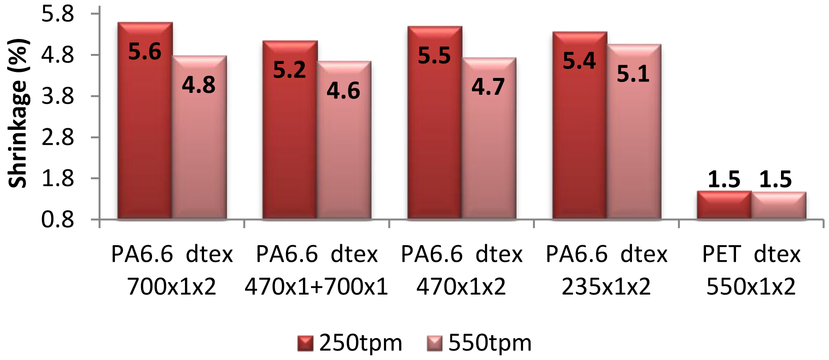

Figure 13 - Shrinkage of Pure Cords

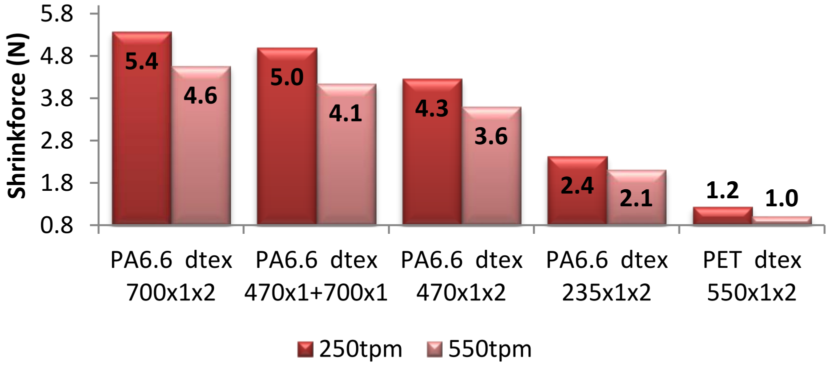

Figure 14 - Shrink force of Pure Cords

In general, it is possible to allege that the increase of twist causes a decrease on the shrinkage and shrink force values. Regarding to know-how about the shrinkage test itself, the linear retraction of the cord is measured only along the horizontal axis, but the cord itself is not exactly a line and can be visualized taking into account a vertical (or transversal) and a horizontal axis, as can be seen in Figure 15.

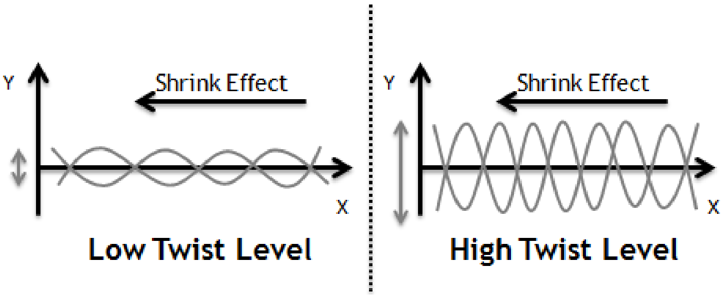

Figure 15 - Influence of twist level on Shrink Effect

This means that when a cord has low twist, the contribution of both yarns for the vertical axis is lower than at high twist level, making the final shrinkage values smaller at high twist level.

Concerning to the absolute shrinkage values, PA6.6 cords present a range between 4.8 % and 5.8 % while PET cords shrinkage varied between 1 % and 1.3 %. This fact is explained taking into account the crystalline phase of this polymers. Thermoplastic fibers, such as nylon and polyester, are considered to be composed of a mixture of crystallites and amorphous domains, as can be seen in Figure 16.

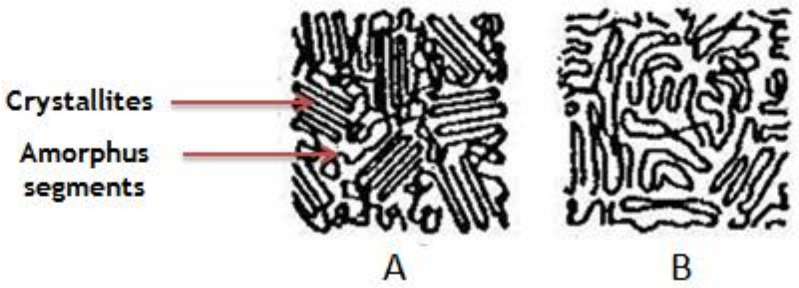

Figure 16 – Higher crystalline structure (A) and lower crystalline structure (B)

It is known that shrinkage is proportional to the volume fraction of amorphous material and to the orientation in amorphous segments [10], which is higher in PA6.6 than PET. This ends up with lowest shrinkage values for PET.

About shrink force and making an evaluation on PA6.6, it is possible to observe that as the total cord decitex decreases, the shrink force values also decreases. This happen because the thicker the cord is, with more forced it will react to the shrink effect.

Despite of PET 550x1x2 has higher total cord decitex comparatively with PA6.6 235x1x2, it is important to mention that shrink force is dependent not only of cord decitex but also of shrinkage itself. As PET do not suffer so much shrinkage as PA6.6, the shrink force for PET ends to be also lower.

4.1.3 Influence on Relaxation and Creep

As can be seen in Figure 17, it is clear that relaxation decreases with increase of twist level.

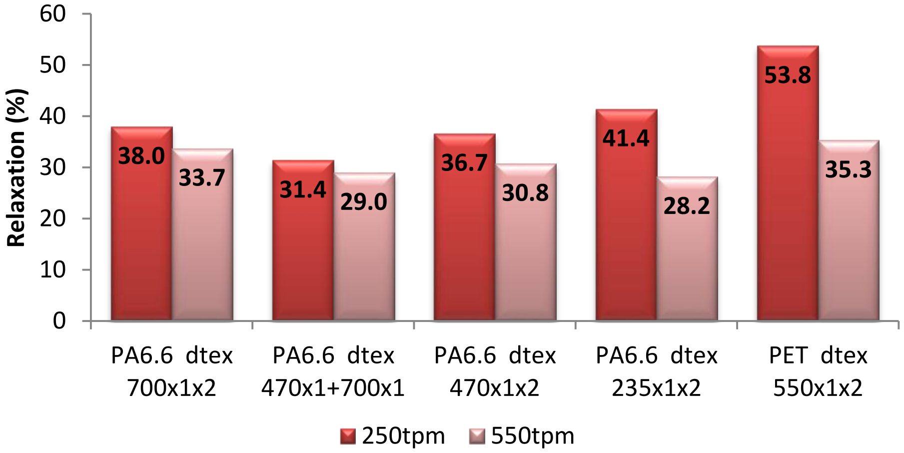

Figure 17 - Relaxation at RT of Pure Cords

This happen because the cord with high twist level always suffer more structural elongation than a cord with low twist, which means that the cord has less relaxation when is suffering only a structural alteration than when is already suffering changes in material itself. Regarding to the differences between PA6.6 and PET, it is also possible to observe that PET suffers more relaxation than PA6.6 (looking only to one twist level individually). A hypothetical explanation could be the fact that PET suffers an easily reorganization of the amorphous part when a tension is applied (in this case was 3.5 % of elongation) comparatively to PA6.6, which in the end leads to higher relaxation values for PET.

At 80 °C it is expected that relaxation values for PA6.6 should be lower because at 80°C, as explained before, the polymer was already subjected to the glass transition temperature, which makes the polymer softer over the time. In addition to this, it is also possible to say that as PA6.6 suffers more shrinkage effect than PET, and shrink force that it will suffer at 80 °C, even being low, will balance the relaxation, making the final value of the relaxation lower. Regarding to PET, increasing the temperature from RT to 80 °C should make almost any difference because the shrink force that this cord suffers is lower than PA6.6 and besides that, the glass transition on PET occurs around this temperature (for further information see Appendix D.1).

Regarding to Creep and analyzing Figure 18, it is possible to observe an opposite behavior comparing with relaxation. In other words, the increase of twist level increases the growth of the cord, as expected, because the cords with high torsion elongate more.

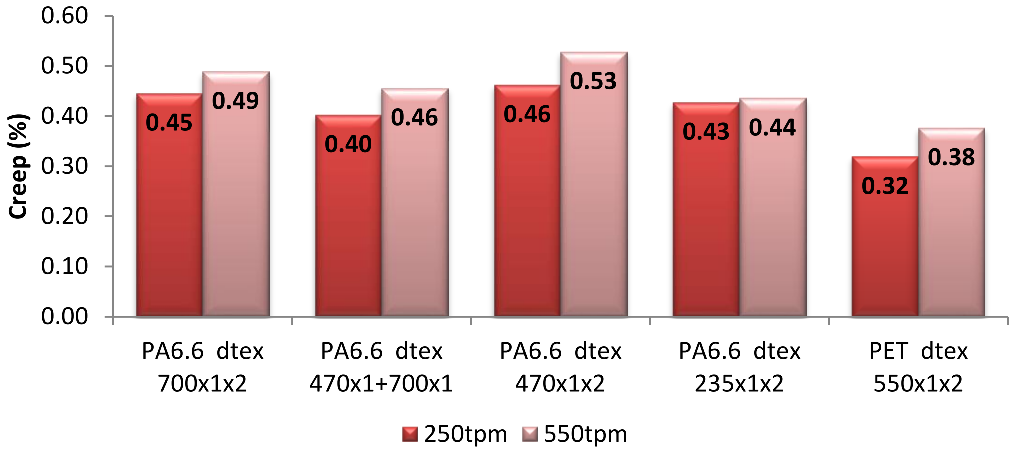

Figure 18 - Static Creep at RT of Pure Cords

In case of pure cords, it is possible to say that PET dtex 550x1x2 is the cord that suffers the less creep effect. This happen because as explained before, the crystalline fraction and the orientation in the crystalline zone is higher on PET, which makes that when a force is applied in this polymer, it will not grow so much as PA6.6.

Regarding to dynamic creep, it was observed the same qualitative evaluation as in static creep, being the creep values around 0.1 % higher for all categories of cord constructions in this thesis. This means that a frequency of 10 Hz practically did not change the qualitative behavior and the absolute growth of the cords. However, it is not possible to say that a dynamic input do not have at all any influence on the behavior of the cords because during this Master Thesis only was tested one frequency and the creep loads such as the amplitudes were normalized for all cords, as explained in Chapter 3.2. Concerning to this topic, it is really important and very interesting to do future analysis in order to evaluate the influence of testing parameters such as frequency, creep load and amplitude. To be able to analyze the dynamic outcome, it is suggested to observe also the influence of different test specifications like temperature, humidity or time on creep effect.

4.2 Design of Symmetric Hybrid Cords

In this sub-chapter, the main goal is to study the influence of hybrid cord designs on the same properties before. In Figure 19, it is possible to observe a general diagram of the symmetric hybrid cords that will be evaluated in this section, when each line represents a cord construction.

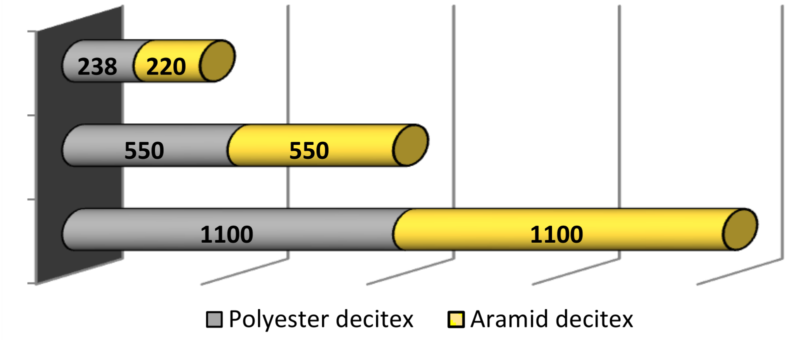

Figure 19 - Diagram of Symmetric Hybrid Cords constructions

4.2.1 Influence on Tenacity, LASE and Elongation at Break

In Figure 20, it is possible to observe the Tenacity-Elongation curve of the symmetric hybrids in study, with a fixed twist level of 250 tpm.

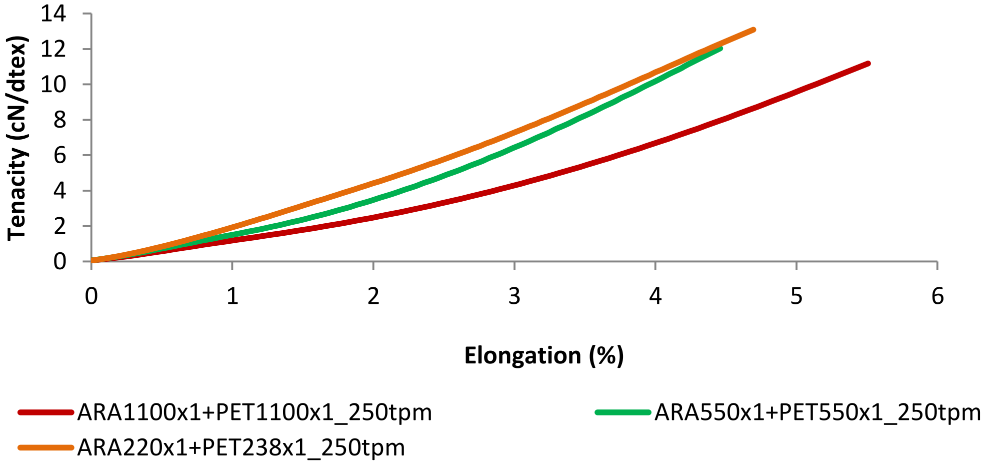

Figure 20 - Tenacity-Elongation curve of Pure Cords (250 tpm) at RT

It is possible to observe that the thinner cords present higher modulus and higher tenacity comparatively to the other symmetric hybrids, which it is expected taking into account the information from the suppliers regarding to the spinning process of the filaments. The most significant difference it is on ARA1100x1+PET1100x1 cord which loses modulus and has the highest E@B.

In order to establish an explanation for this fact, the twist factors were also calculated in this category of cords and the results are represented in Table 6.

Table 6 - Twist factors of Symmetric Hybrid Cords

Hybrid Cord	Cord Construction[5]	Twist Factor (α)		$\Delta\alpha$[6]
		TL = 250 tpm	TL = 550 tpm	
Aramid + Polyester	1100 x 1 + 1100 x 1	117	258	141
	550 x 1 + 550 x 1	83	182	99
	220 x 1 + 238 x 1	54	118	64

The first observation that it is possible to be made is that thicker cord presents the highest twist factors. This important remark works as the first sign for this cord has a bigger different behavior comparatively to the remaining cords.

As observed before for pure cords, it was proved that material thickness and twist level have a big influence on the helix angle of the cords and in the Tenacity-Elongation properties of the cords. As can be seen in Figure 21, it is possible to observe that the helix angle on ARA1100x1+PET1100x1 is more pronounced in comparison with other cords, which leads to a higher structural elongation. This fact provokes a decrease on cord modulus and an increase on E@B.

However, the thinner cord presents a slightly increase of E@B comparatively to ARA550x1+PET550x1, which at first sight it is not so expected because this last cord has more structural elongation than the first one. This observation could be explained taking into account the suppliers of each aramid yarn. The supplier of the thinner aramid 220 dtex (as called “Supplier A”) was not the same for aramid 500 dtex and 1100 dtex (as called “Supplier B”). In previous studies already done in the company, it was stated that the same material from different suppliers can behave differently. Regarding to aramid specifically, it was proved for the same yarn decitex that while the yarn from Supplier A appeared to have higher E@B, the one from Supplier B presented higher modulus. However, both presented the same equivalent breaking tenacity.

Figure 21 - Microscopic view of Symmetric Hybrids Cords at 250 tpm: ARA220x1+PET238x1 (A), ARA550x1+PET550x1 (B), ARA1100x1+PET1100x1 (C)

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[5] Aramid decitex x ply number + Polyester decitex x ply number

[6] $\alpha_{550\ \mathrm{tpm}}$- $\alpha_{250\ \mathrm{tpm}}$

Taking into account the evaluation made until now regarding to the lower twist level, it turns interesting to observe the Tenacity-Elongation curves with 550 tpm, which are dotted in Figure 22.

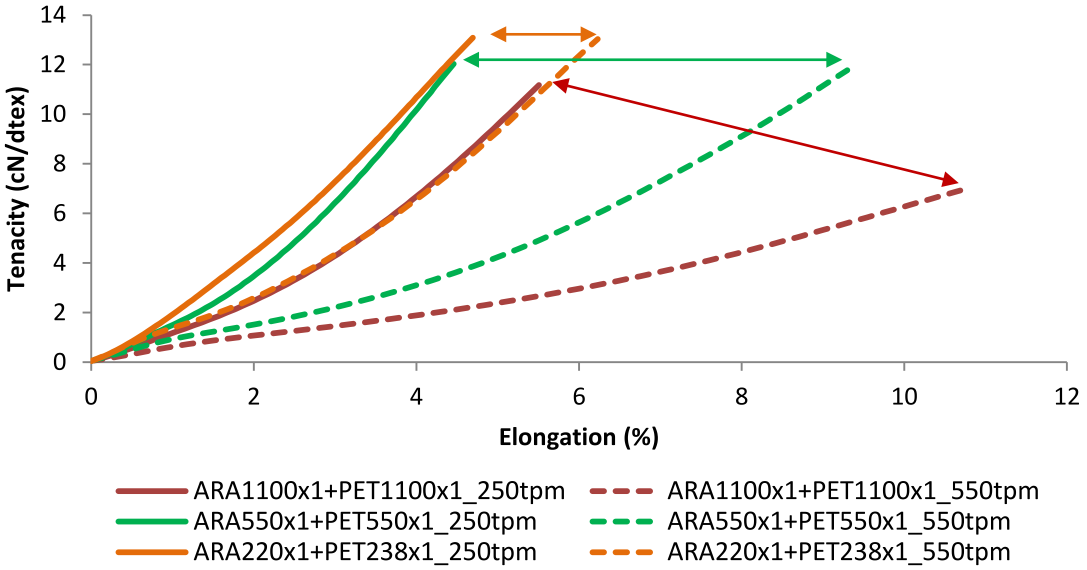

Figure 22 - Tenacity-Elongation curve of Symmetric Hybrids Cords with both twist levels at RT

It is possible to observe that the curves are completely different at high twist level. It was already observed in Table 6 that the twist factors for this twist level were higher comparing with 250 tpm, which indicates from the beginning that the behavior of the cords at high twist level will present significant differences. Besides this, it is also possible to observe that the helix angles of the symmetric hybrids cords at high twist level shows to be even more intensified, as can be seen in Figure 23. All these facts lead to a lower significant influence on material suppliers.

Figure 23 - Microscopic view of Symmetric Hybrids Cords at 550 tpm: ARA220x1+PET238x1 (A), ARA550x1+PET550x1 (B), ARA1100x1+PET1100x1 (C)

Regarding to tenacity itself, it is possible to observe that at 250 tpm all symmetric hybrids present a tenacity around 12 cN/dtex, while at 550 tpm the thicker cord suffers a bigger decrease (around almost 40 % comparatively to the same cord construction at low twist level).

At first sight, the cause for this extreme drop in tenacity from one twist to another in ARA1100x1+PET1100x1 could remain in this difference on high twist factor that starts to damage the aramid yarn, leading to a weaker material and a higher decrease on the breaking force of the global cord.

However, in order to get a deeply explanation for this fact, it was done a second attempt, analyzing the greige cords with the highest content of aramid because some dip-formulas or the dipping process could cause damages in the cords. However, the results showed that the greige cords have approximately the same behavior as the dipped cords, showing an influence of twist level around 40 % on tenacity, which means that the dipping process is not the main cause.

Regarding to this observation, a greige yarn of aramid 1100 dtex was tested and the results proved exactly this theory: the yarn with high twist level suffered a decrease on tenacity around 40 %. This means that exist an evident relation between the properties of individual yarns with the cord properties. In case of the global hybrids in study, it is possible to say that the aramid with higher linear density is much more sensitive concerning to the influence of twist level.

Regarding to the influence of twist level on L@3.5%, it will not be so high in ARA1100x1+PET1100x1 comparing with ARA550x1+PET550x1 because at 550 tpm the cord behaves as if it had already saturated, and the modulus cannot decrease more.

At 80°C, all cords at 250 tpm suffered a decrease on tenacity (around 1 cN/dtex) because PET is passing the glass transition phase, which could make it softer during elongation and the global breaking tenacity of the cord decreases. However, it is unknown the influence of temperature over the time in the aramid yarn/cord, so it turns uncertain the reasons for this drop in tenacity on aramid-polyester hybrids. The influence of twist level at 80°C showed to be inconclusive taking into account that thinner cord with 550 tpm suffered a big decrease on tenacity and the elongation at break did not changed at all comparing with 250 tpm, and the tenacity of the ARA550x1+PET550x1 also suffered a decrease at 550 tpm comparatively to 250 tpm. So regarding to this topic, it is recommended to do further tests in order to evaluate the influence of temperature on these hybrids cords (for further information see Appendix C.2).

4.2.2 Influence on Shrinkage and Shrink force

In Figure 24 and Figure 25 it is possible to observe the results from shrinkage and shrink force regarding to the hybrid cords actually in study.

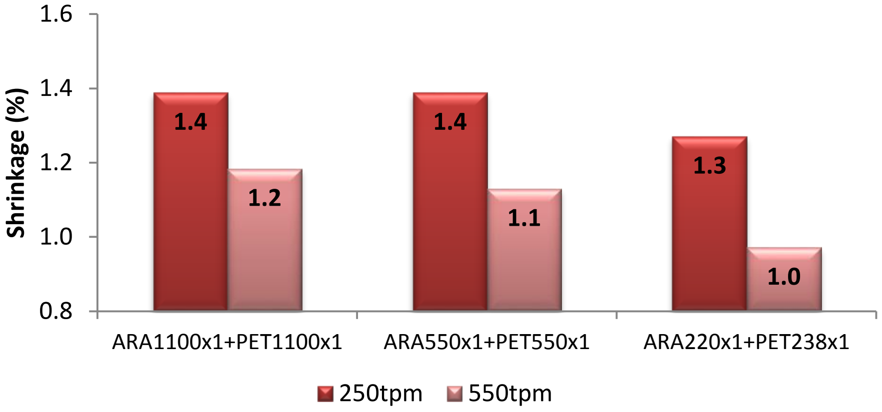

Figure 24 - Shrinkage of Symmetric Hybrid Cords

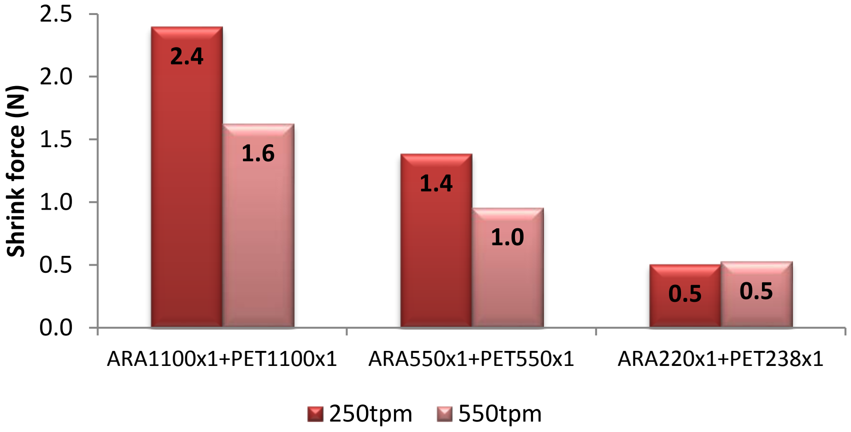

Figure 25 - Shrink force of Symmetric Hybrid Cords

An important fact that should be mentioned in the first place is that during fiber manufacturing process, polymeric fibers passed a series of thermal and mechanical processes and a high crystalline phase is also obtained. The flexibility of polymer molecules such as polyester or even nylon is higher than aramid, which ends up in two orientation structures phases (crystalline and amorphous) for polyester while for aramid exists only the crystalline phase. As shrinkage is proportional to volume fraction of amorphous material and to the orientation in amorphous segments, this leads to shrinkage values for aramid nearly zero. Taking into account all this information, it is observed that polyester controls the shrinkage effect of the cord. The values obtained in these cord constructions are around 1.2 % and 1.4 % which combines with the values showed before on Chapter 4.1.2 for PET.

The first expectation regarding to the influence of twist level is based on the same theoretical explanation took before for pure cords, regarding to the shrinkage measurement. As at high twist level the contribution for the vertical axis is higher, the cords end with lower shrinkage values. Besides that, at high twist level the cord itself do not have so much space to shrink taking into account the higher helix angle characteristic for the higher twist levels.

Regarding to shrink force, as total cord decitex decreases, shrink force also decreases as expected, because it is dependent of the modulus and decitex of the cord or in this case, of polyester decitex.

4.2.3 Influence on Relaxation and Creep

In Figure 26 it is possible to observe the relaxation values obtained for symmetric hybrid cords at RT. Concerning to this characterization, it is a fact that the increase of twist level provokes a decrease on relaxation and does not exist almost any difference from RT to 80°C (for further information see Appendix D.2).

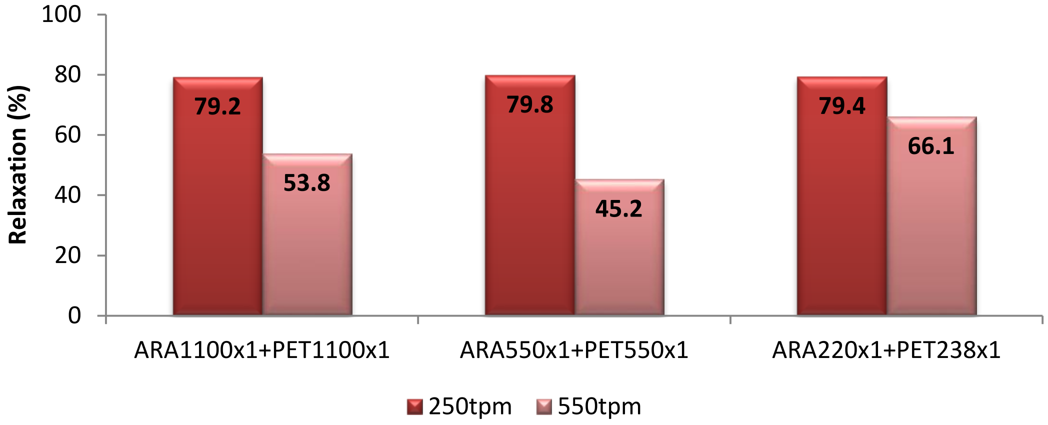

Figure 26 - Relaxation of Symmetric Hybrid Cords at RT

Regarding to specific relaxation values, all symmetric hybrid cords presents the same relaxation (around 80 %) at 250 tpm. The explanation for at low twist all cords present the same relaxation is that at 3.5 % of elongation all cords are suffering already material elongation, which leads to the conclusion that relaxation is linked with material itself.

Taking into account the analysis already done for shrinkage, it is known that aramid presents a morphology much stiffer than PET. This means that the intermolecular chains inside the polymer are practically all oriented and when the aramid is subjected to an external tension, such as 3.5 % of elongation, the effect will be less elastic and the material response will be more critical. This leads to higher relaxation values for these hybrid cords comparatively to relaxation values observed before for PET.

Concerning to the influence of twist level, what should be expected is a low relaxation value for ARA1100x1+PET1100x1 at 550 tpm, due to a high structural elongation. However, the value is not so low because this cord is already damaged as proved before, and the applied tension is by now too high for this cord, which means that it does not recover.

Regarding to static creep, it is possible to observe in Figure 27 the growth effect on the symmetric hybrid cords at both twist levels.

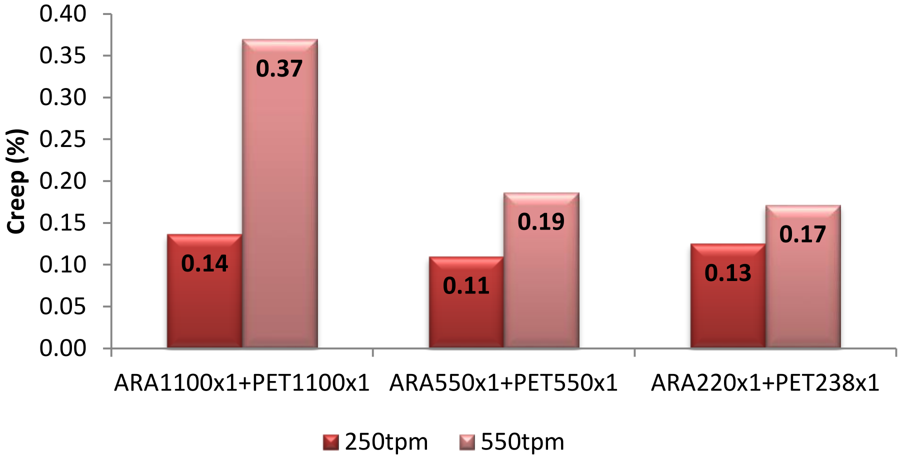

Figure 27 - Static Creep of Symmetric Hybrid Cords at RT

Taking into account that aramid has a higher crystalline phase than PET, it is decisive that aramid dominates the growth effect on these symmetric hybrid cords. However, the difference between creep is more evident on the thicker cord at 550 tpm. The load that was chosen for all cord constructions was determined taking into account 20 % of the breaking force. However, this cord is "damaged" and the force that was applied did not functioned as if the cord was in a good state, which leads to higher creep.

Like pure cords, a frequency of 10 Hz showed the same qualitative response on creep as the experiment without any dynamic contribution.

4.3 Design of Asymmetric Hybrid Cords

In this sub-chapter the main goal is to study the influence of cord design regarding the same properties that was done for the two previous categories. In Figure 28, it is possible to observe a general diagram of the asymmetric hybrids cords that will be evaluated in this section, when each line represents one cord construction.

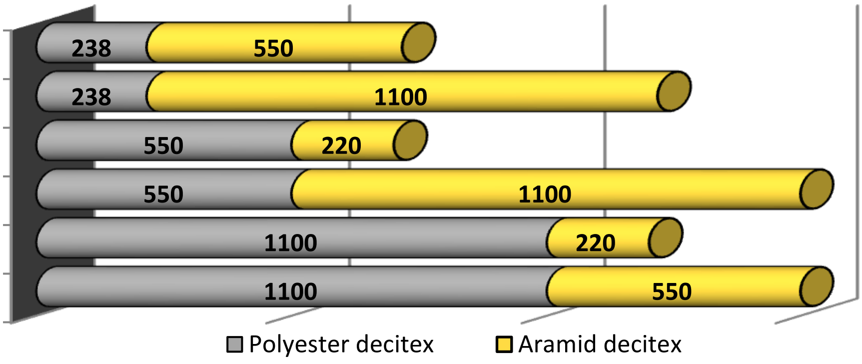

Figure 28 - Diagram of Asymmetric Hybrid Cords constructions

4.3.1 Influence on Tenacity, LASE and Elongation at Break

In order to obtain a better understanding of the possible behavior of the asymmetric hybrids, the first step was to do a theoretical attempt taking into account all the know-how about the polymers behavior and force elongation test. It is known that the most noticeable properties of aramid are high modulus and low elongation at break, while for polyester is low modulus and high elongation at break. It is also known that during the force elongation test, the cords suffer in the first place a structural elongation and then a material elongation. Concerning all this information, it was possible to achieve a general theory about the behavior of this group of cords, which becomes truthful as will be seen afterwards. In Figure 29, it is possible to observe an expected Tenacity-Elongation curve for the asymmetric hybrids in study.

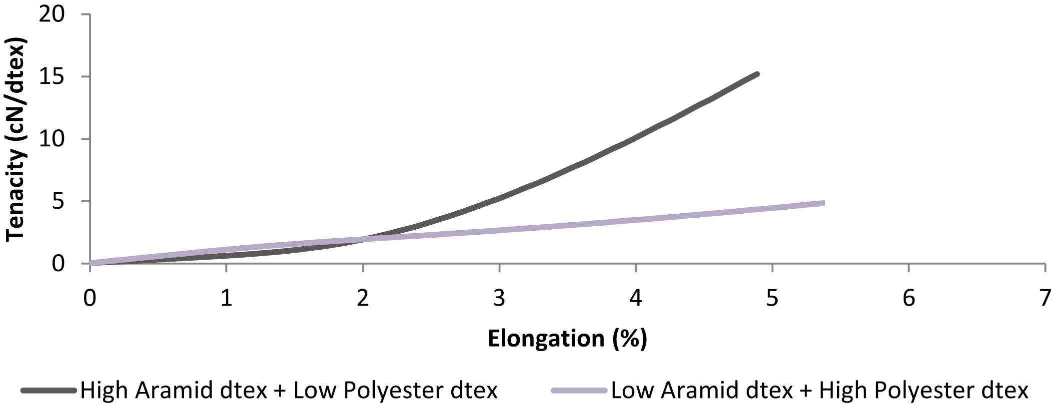

Figure 29 - Theoretical Tenacity-Elongation curve of Asymmetric Hybrids Cords

When the proportion of aramid is higher than PET´s, at the beginning of the test it is PET that suffers material elongation while aramid suffer structural elongation. Then, when the structural elongation of aramid is finished, the modulus of the cord increases substantially because of the strength and material elongation of aramid, but PET continues to suffer material elongation. However, the elongation of PET will not be so high because aramid is dominating. When the proportion of aramid in the cord is low, the material elongation of aramid basically starts in the beginning of the force elongation test and then is basically only polyester that elongates, which ends up in a low modulus curve and should end in a higher elongation at break.

As can be seen in Figure 30, this theory works when a comparison is made between:

1. ARA1100x1+PET238x1 and ARA220x1+PET1100x1
2. ARA550x1+PET238x1 and ARA220x1+PET550x1

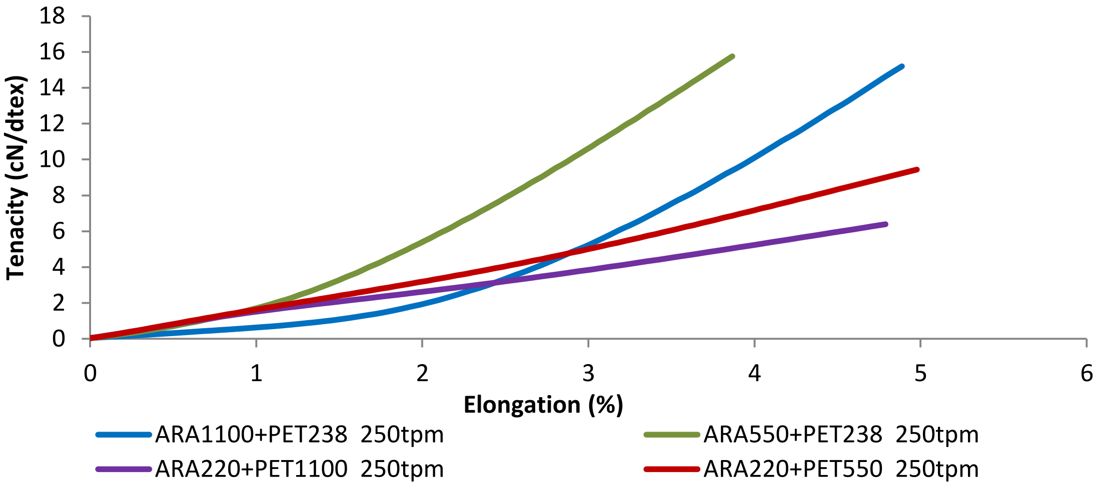

Figure 30 - Tenacity-elongation curve of ARA1100x1+PET238x1 and ARA550x1+PET238x1 with the Asymmetric Hybrids correspondents, at 250 tpm

Regarding to comparison 1, during the force elongation test it was possible to observe that concerning to ARA1100x1+PET238x1 both yarns broke at the same time, while in ARA220x1+PET1100x1 aramid started to break gradually first and then the entire cord broke. Because of this aramid behavior, the entire cord will lose stability and have less elongation at break than expected.

Regarding to comparison 2, it was possible to observe that in ARA550x1+PET238x1 both yarns broke at the same time while in ARA220x1+PET550x1 aramid broke first but polyester continued to elongate, so ended with highest elongation at break. However, with this last cord, it was not easy to observe when the entire cord breaks because in a lot of specimens the test stopped and polyester still not had broken. This happened because when a drop of about 80 % of the maximum force occurs, the test is automatically stopped.

It is also possible observe that ARA1100x1+PET238x1 suffers more structural elongation than ARA550x1+PET238x1 because of the structure of each cord itself, which is more linear in this last cord (for further information see Appendix E.2).

However, and as can be seen in Figure 31, with the third possible comparison (ARA1100x1+PET550x1 with ARA550x1+PET1100x1), the general theory was not observed.

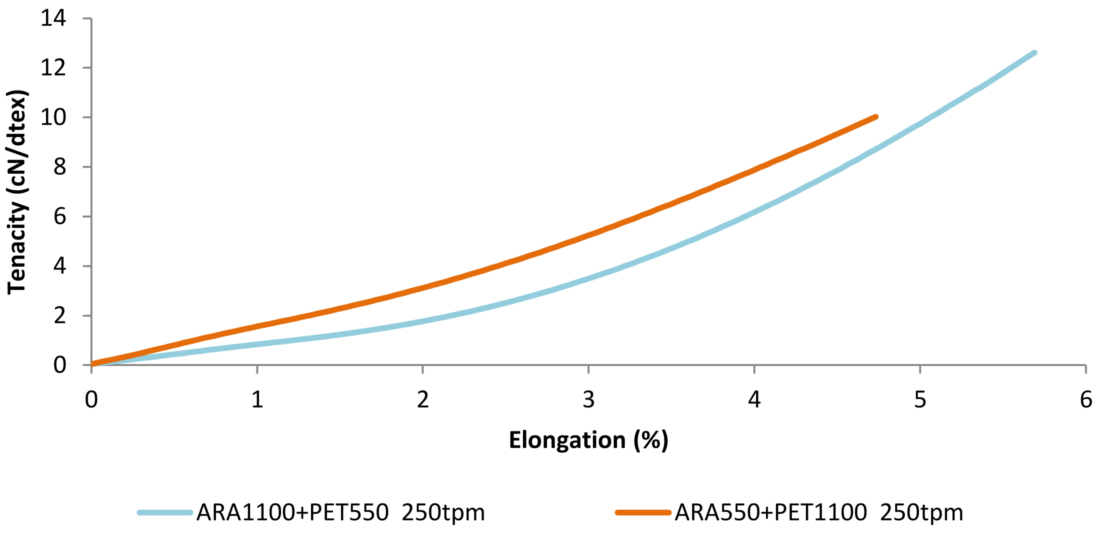

Figure 31 - Tenacity-elongation curve of ARA1100x1+PET550x1 with the Asymmetric Hybrid correspondent, at 250 tpm

During the force elongation test, it was observed that in ARA1100x1+PET550x1 the entire cord broke at the same time but with ARA550x1+PET1100x1, aramid broke first and several times the test stopped before polyester broke completely.

The first step in order to evaluate a possible explanation for this fact was to calculate the twist factors, which are represented in Table 7.

Table 7 - Twist factors of Asymmetric Hybrid Cords

Hybrid Cord	Cord Construction[7]	Twist Factor (α)		$\Delta\alpha$[8]
		TL = 250 tpm	TL = 550 tpm	
Aramid + Polyester	1100 x 1 + 550 x 1	102	223	121
	1100 x 1 + 238 x 1	91	201	110
	550 x 1 + 1100 x 1	102	223	121
	550 x 1 + 238 x 1	70	154	84
	220 x 1 + 1100 x 1	91	200	109
	220 x 1 + 550 x 1	69	153	84

It is possible to observe that inside of each comparison described before, all cords constructions present the same twist factor, as expected.

Opposite to what was seen in symmetric hybrids, in this category the evaluation depends not only of the total cord decitex but mainly in the proportion of each polymer in

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[7] Aramid decitex x ply number + Polyester decitex x ply number

[8] $\alpha_{550\ tpm} - \alpha_{250\ tpm}$

each cord construction. Besides this, in this cord design, it is much more difficult to evaluate the helix angle because of the yarns´s asymmetry. Besides the fact observed in Table 7 that is this third comparison that shows the higher twist factors, in Figure 32 it is possible to observe that ARA1100x1+PET550x1 presents more waviness comparatively to ARA550x1+PET1100x1, which is an indicator for the first cord ended with lower modulus and higher E@B.

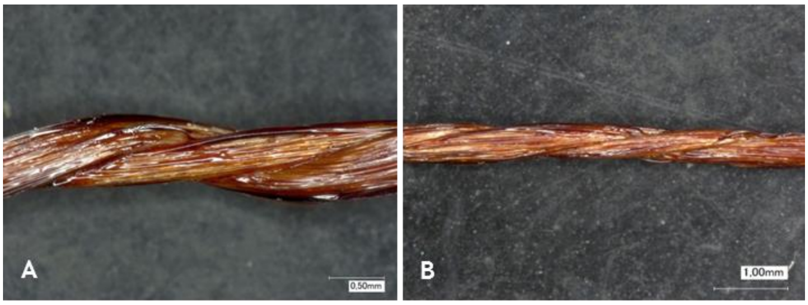

Figure 32 - Microscopic view of ARA1100x1+PET550x1 (A) and ARA550x1+PET1100x1 (B) at 250 tpm

One possible reason for this is the fact that during twisting, the tension of both plies is similar. In case of cord A, the tension necessary to twist and pull the PET yarn is not enough to create tension on the thicker aramid yarn, so they end unbalanced. In case of cord B, this behavior is the opposite. The tension level necessary for the thick PET yarn seems to be similar to the one needed by the thin aramid, so this cord is better balanced.

In order to evaluate the influence of twist level in the asymmetric hybrids, it was used the same normalized method explained before on Chapter 4.1.1 and it is represented in Figure 33.

It is possible to observe that the cords which suffer the higher influence on twist level regarding tenacity are not the thicker cords but the ones with the highest proportion of aramid. In general, the cords composed with aramid 1100 dtex suffer a decrease of almost 50 % by increasing the twist level, when the other cords present a decrease of about 10 %.

In Chapter 4.2.1, it was explained already that the main cause for this intensive decrease in tenacity remains in the thickest aramid yarn. This ends up to be a really important observation because it can motivate future investigations regarding to the influence of twist level in the yarns and their influence afterwards in cords behavior and properties.

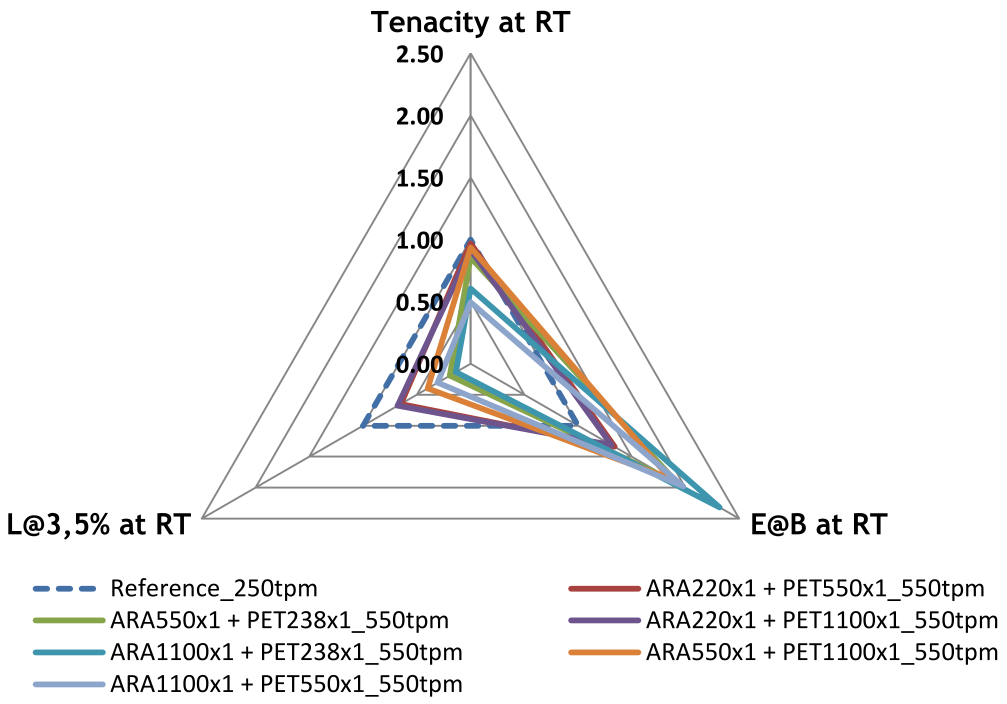

Figure 33 - Influence of LT at RT on Asymmetric Hybrid Cords regarding to Tenacity, L@3,5% and E@B

Regarding to L@3,5% and E@B, it is clear that the influence of twist level is higher in the asymmetric hybrids with higher proportion of aramid. This happen because thicker aramid is much more sensitive to the increase of twist, so this condition ends up in higher properties differences when a twist of 550 tpm is applied.

At 80 °C, all cords suffered a decrease on tenacity around 1 cN/dtex because PET is passing through the glass transition so it can become softer during elongation and the global breaking tenacity of the cord decreases. However, as explained before, the influence of temperature in aramid is unknown so further investigations should be done regarding to this topic. Concerning to the influence of twist level at 80 °C, ARA220x1+PET550x1 showed an unexpected behavior looking to the loss of tenacity at 550 tpm and to the E@B that did not suffer any change. This fact only reinforces the need of the exploration of the influence of temperature on aramid yarns/cords (for further information see Appendix C.3).

4.3.2 Influence on Shrinkage and Shrink force

In Figure 34, it is possible to observe, for the asymmetric hybrid cords in study, the shrinkage results obtained after the experimental work.

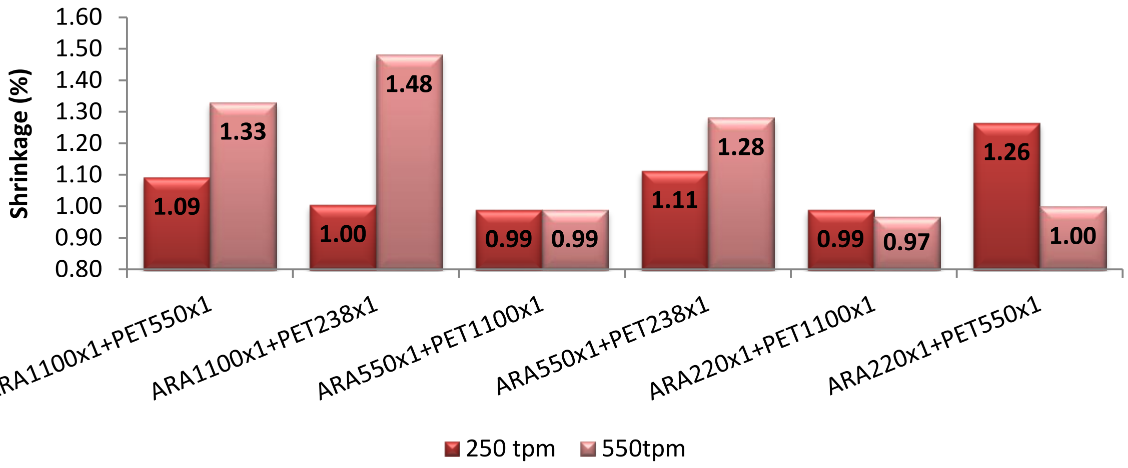

Figure 34 - Shrinkage of Asymmetric Hybrid Cords

It is observed that asymmetric hybrids cords do not show the same behavior as symmetric hybrids.

Normally and in the same way that was observed before, the increase of twist level provokes a decrease on shrinkage. However, this is not observed in these three cases:

- ARA1100x1 + PET550x1
- ARA1100x1 + PET238x1
- ARA550x1 + PET238x1

One fact is already known: aramid does not shrink. Regarding to know-how about the shrinkage test itself, the linear retraction of the cord is measured only along the horizontal axis, but the cord itself is not exactly a line and can be visualized taking into account a vertical (or transversal) and a horizontal axis, as explained before in Chapter 4.1.2. In Figure 35, it is possible to observe a theoretical representation of the asymmetric cords during shrinkage test.

It is possible to say that when a thicker aramid surrounds polyester at high twist level, the yarn of polyester will have more free space to shrink (the residual force in the sharing points between the yarns will be really low), while at low twist it will not have so much space because the contribution of aramid to the horizontal axes will be higher. As PET yarn is the only yarn that shrinks, this ends up in higher shrinkage values for high twist level in this type of cord constructions. It is also possible to affirm that the influence of twist level on shrinkage decrease as the ratio between aramid and PET decreases.

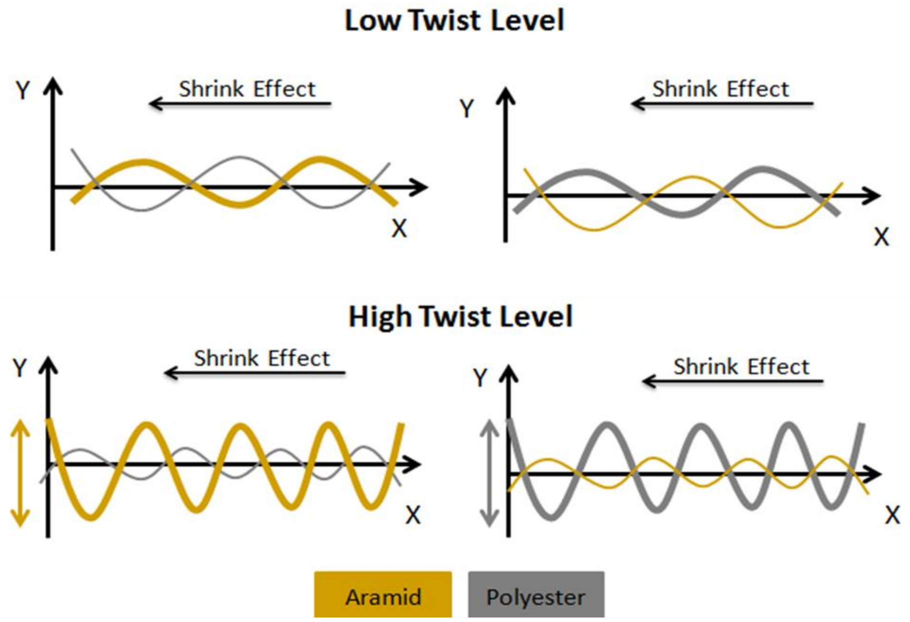

Figure 35 - Theoretical representation of Asymmetric Hybrids Cords during shrinkage test

When the opposite happens, or in other words, when PET´s yarn has the highest titer in the cord, this means that it will have more contribution to the vertical axes. As shrinkage measures in the horizontal axis cord, the results ends up with small values at higher twist, because with higher torsion the contribution to horizontal axis of polyester is lower. However, the influence of twist level is lower in the cords with PET 1100 dtex because the residual forces in the shared points between the yarns are lower and from one twist to the other remains practically the same. However, the shrinkage for ARA220x1+PET550x1 at low twist level is higher because this cord has also the lowest twist factor comparatively to ARA550x1+PET1100x1 and ARA220x1+PET1100x1, which leads to a higher shrink effect.

Regarding to shrink force, it is possible to observe in Figure 36 that as general rule, the shrink force increases when the proportion of polyester in the asymmetric hybrids increases. This is explained with the fact that it is always polyester that suffers the shrink effect and it puts a lot of force to shrink the entire “package”. As shrink force depends of the decitex of the cord, in this case it will depend only of the polyester yarns decitex.

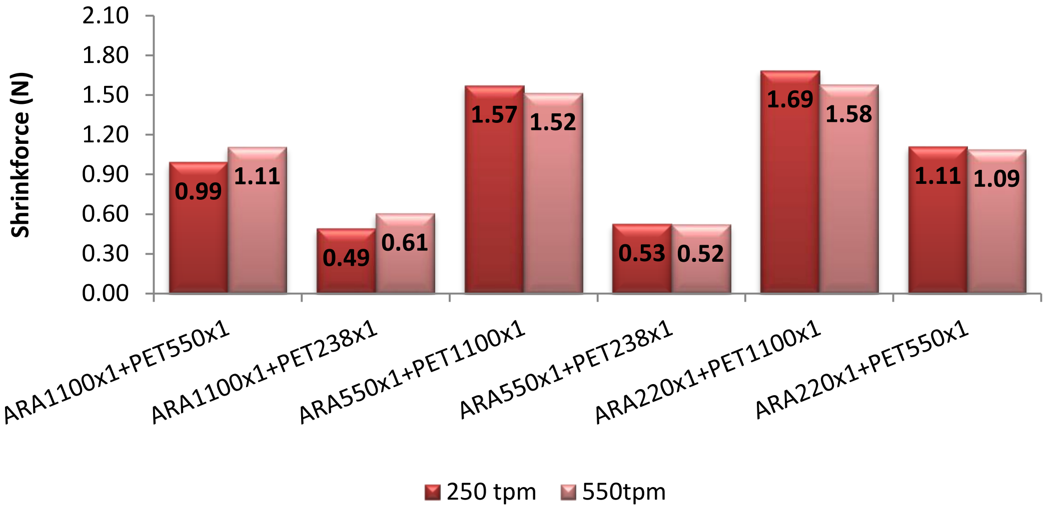

Figure 36 - Shrink force of Asymmetric Hybrid cords

4.3.3 Influence on Relaxation and Creep

In order to evaluate the influence of twist level regarding relaxation, all results obtained were represented in a column chart, as can be seen in Figure 37. The relaxation is only represented at RT because at 80 °C the influence of twist level shows precisely the same effect and the absolute values at high temperature are approximately the same (for further information see Appendix D.3).

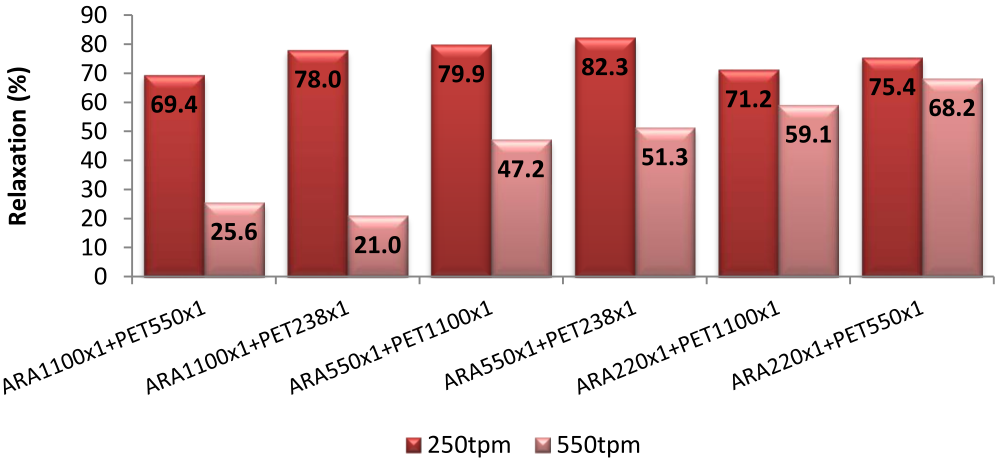

Figure 37 - Relaxation of Asymmetric Hybrids Cords at RT

It is possible to observe that all asymmetric hybrids at low twist level have a relaxation in a range of about 70 % - 83 %. This happen because at low twist level, does not exist such a higher structural influence as at high twist level, which means that practically all cords are suffering in the same way an influence on the material itself.

However, at higher twist level the hybrids with less proportion of aramid suffer more relaxation. This is absolutely predictable and happens because the cords with highest proportion of aramid at higher twist level, during the relaxation test are suffering a structural elongation, which ends up in a small relaxation values for this type of cords. The cords with lowest proportion of aramid start to suffer sooner material elongation, leading to higher relaxation results.

Regarding to creep test it is possible to observe in Figure 38 the static creep results obtained for the asymmetric hybrids in study.

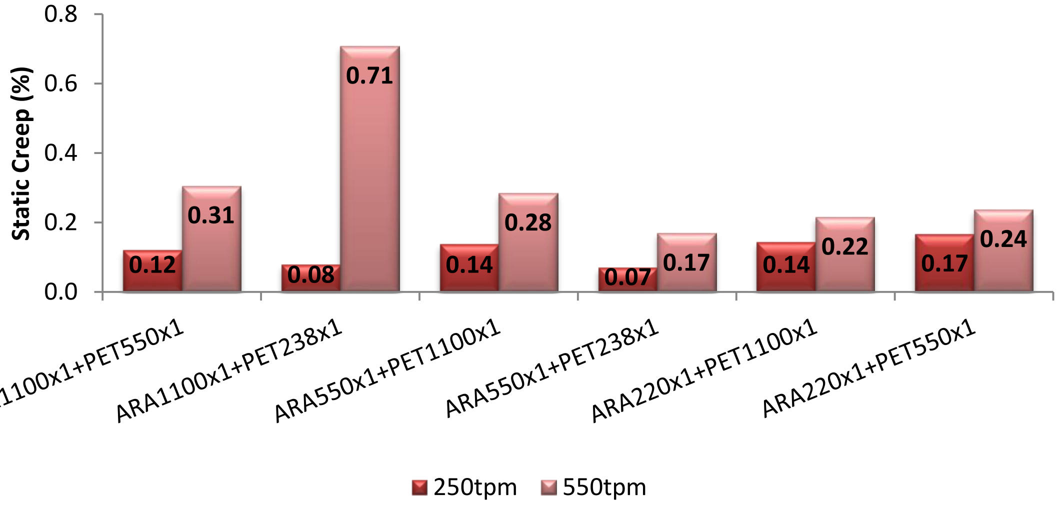

Figure 38 - Static Creep of Asymmetric Hybrids Cords at RT

It is possible to affirm that as aramid is stiffer than PET, it ends up controlling the creep effect because it will works as the obstacle for material growth. As the load applied during the experiment at low twist level was normalized (20 % of the breaking force), all cords ends to show practically the same creep. However, the creep load applied to cord constructions with highest proportion of aramid was the same for low and high twist level. This means that as both cords at high twist level suffered a big decrease on tenacity, during the creep test they were subjected to a higher stress, which leads to a highest split between the yarns and the cord grows more.

4.4 Potential replacements

As characterization of the different cord constructions is already done, it becomes interesting to do a comparison between these new cords and standard cords that are used nowadays in tire design, having in mind the substitution for thin materials. These substitutions can bring advantages regarding to rolling resistance because the entire amount of reinforcement/rubber package may be reduced. An amount of comparisons was done between the pure cords, symmetric hybrids and asymmetric hybrids cords, and the cords which showed more potential are described below.

It is known that for cap-ply what is important to evaluate is cord modulus and shrinkage, which means that a substitution of PA6.6 by PET does not bring advantages because with high speeds the tire suffer a huge increase of temperature and if the material is not capable to shrink (as PET), the cap-ply is not stable enough and the tire might fail. By adjusting the end count values for each cord, it was possible to do an evaluation between PA6.6 dtex 1400x1 at 100 tpm and 110 epdm and new pure cords. However, in a fabric design it is important to evaluate the maximum end count that it can have, taking into account the diameter of each cord and the packing factor, which is fixed as 85 % as the maximum value in tire production. Regarding to this, it is possible to calculate the maximum end count for each cord using Equation 6:

$$Packing\ [\%] = \emptyset \times \frac{Maximum\ End\ Count}{100} \qquad \text{(Equation 6)}$$

where Ø represents the diameter of each cord in mm.

As can be seen in Table 8, the required end counts that were reached, making an approximation between the Force-Elongation curves of PA6.6 dtex 1400x1 and the pure cords, are below of the maximum values, which proves that it is possible to make substitutions with these cords.

Table 8 - End Counts of Pure Cords

Polymer	Cord Construction[9]	Maximum End Count		Required End Count	
		TL = 250 tpm	TL = 550 tpm	TL = 250 tpm	TL= 550 tpm
PA 6.6	700 x 1 x 2	185	167	105	160
	470 x 1 + 700 x 1	193	173	130	170
	470 x 1 x 2	213	189	180	180

In Figure 39, it is possible to observe the adjusted Force-Elongation curves of these cords and to confirm that with the required end counts reached, it is achievable the same initial modulus between all cords.

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[9] Polymer decitex x ply number

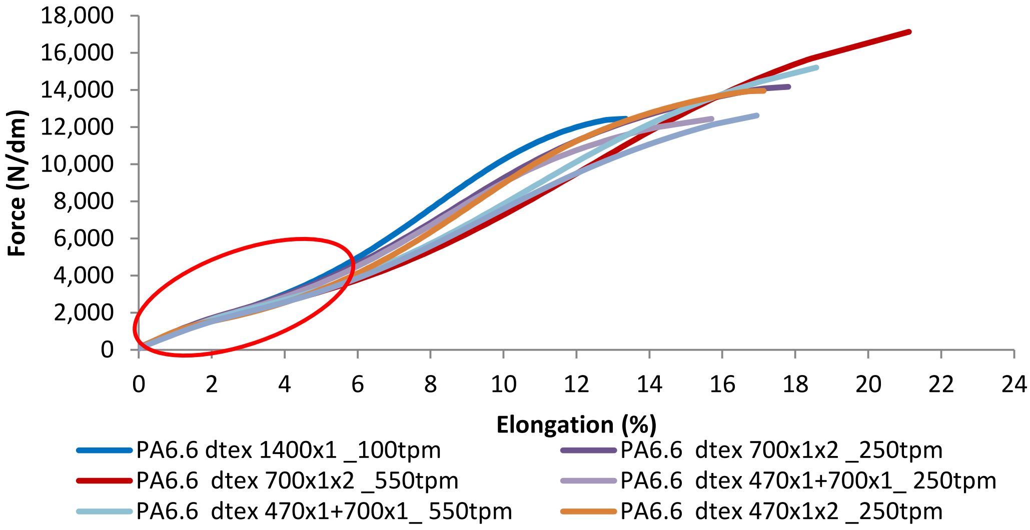

Figure 39 - End count analysis between standard PA6.6 dtex 1400x1 and thinner PA6.6 cords

An additional information to this topic is that PA6.6 dtex 1400x1 suffers a relaxation around 57 % which comparatively with these pure cords brings even more advantages, taking into account the previous information that thin pure cords of PA6.6 suffers a relaxation in a range of 30 % - 40 %. This is important because of the vulcanization process and after this process, because the 3.5 % of strain applied remains in the tire, which means that the relaxation values gives the perception of how much strength the cord will lose after this procedure and tire service.

Regarding to potential substitutions between PA6.6 dtex 1400x1 (110 epdm) and aramid-polyester hybrid cords, the best matches that were possible to achieve were ARA550x1+PET550x1 with 90 epdm and ARA550x1+PET238x1 with 130 epdm, both with twist level of 550 tpm, as can be seen in Figure 40.

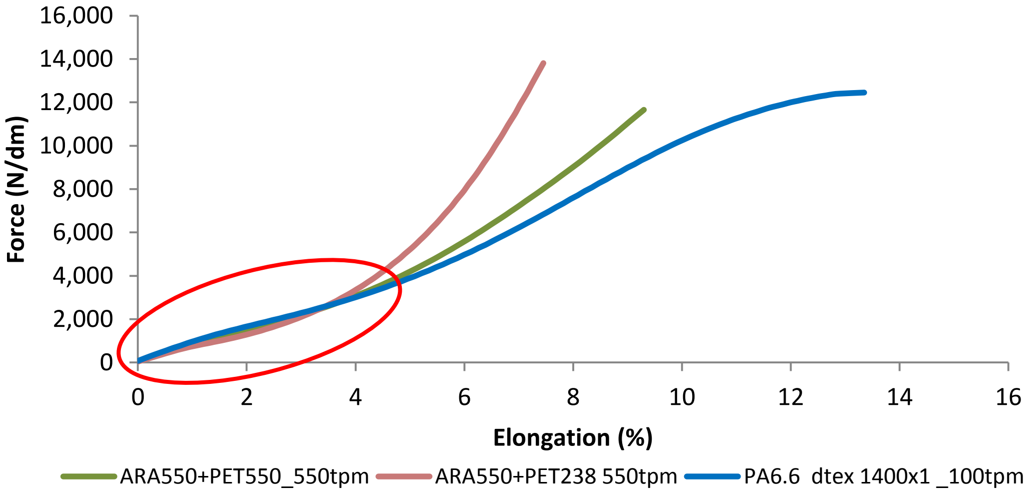

Figure 40 - End count analysis between standard PA6.6 dtex 1400x1 and hybrid cords

It was possible to confirm, taking into account the cords diameters, that these end counts required for these cords are within its limits. However, it is known that despite of these hybrid cords are thinner and have the same initial modulus, they do not suffer almost any shrinkage, which becomes a disadvantage regarding to performance of cap-ply.

Regarding to carcass, what is important to evaluate is the maximum forces of the cords, which is related to the maximum pressure that the tire can hold. Taking into account this parameter and the standard cords that are actually in use on carcass (PET dtex 1100x1x2 at 410 tpm with 105 epdm and PET dtex 1440x1x2 at 310 tpm with 95 epdm), it was possible to achieve a promising relation with ARA550x1+PET550x1 with a twist level of 550 tpm and 100 epdm. Making use of this cord diameter, it was possible to calculate the maximum end count for the cord, which is around 197 epdm. In Figure 41 it is possible to observe the Force-Elongation curves of these cords.

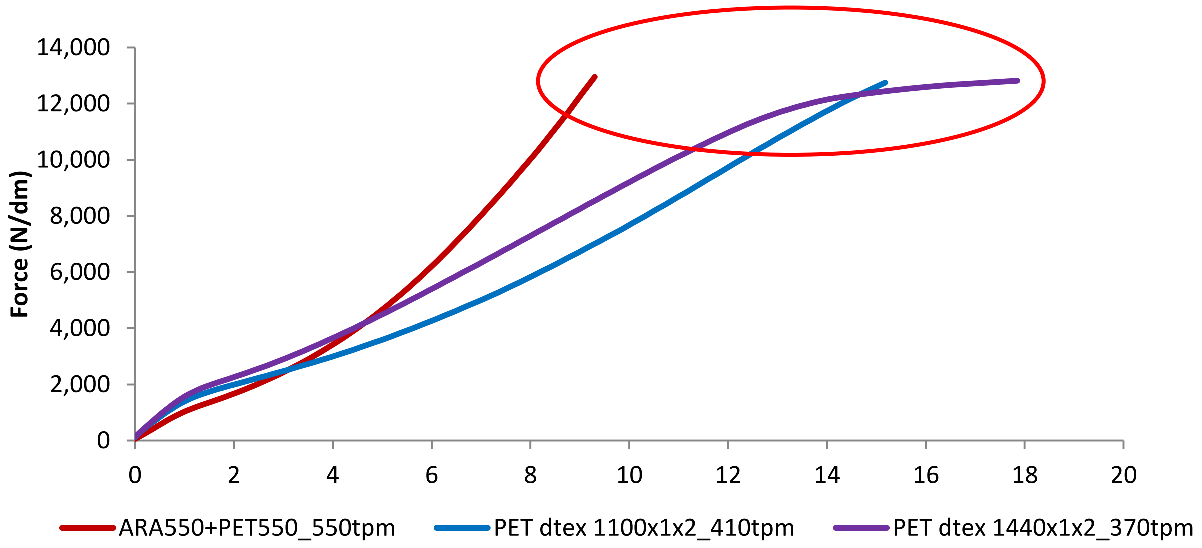

Figure 41 - End count analysis between PET dtex 1100x1x2, PET dtex 1440x1x2 and ARA550x1+PET550x1

As can be seen, this aramid-polyester hybrid cord shows some potential taking into account the maximum load that carries and the fact that is a cord much more thinner than standards ones. Besides these facts, this hybrid cord presents a lower creep (around 0.2 %) comparatively to PET dtex 1100x1x2 which presents a creep around 0.46 % and PET dtex 1440x1x2 which has a creep around 0.33 %. The creep property is an important factor to be analyzed on carcass because it influences sidewall indentation, which is an issue in tire appearance. However, the elongation at break is considerably lower, which means that further analysis should be done in order to check the properties of this cord construction in terms of impact damages.

5 Conclusions

The first group of cords that was evaluated was pure cords, where the highlighted polymers were PA6.6 and PET. It was possible to observe that tenacity of PET is lower than PA6.6. Regarding to this last polymer it is possible to say that tenacity is independent of total cord decitex but regarding to elongation at break this is not true because is lower in thin cords. Concerning to the increase of twist level, it was also possible to realize that tenacity did not suffered a big change.

It was proved that PA6.6 shrinks more than PET, which was expected taking into account the morphology of the polymers. Regarding to relaxation and creep, it was possible to conclude that PET loses more strength when a fixed tension is applied but suffers a lower cord growth compared with PA6.6. These conclusions confirm the usage of PA6.6 in cap-ply and PET in carcass.

Concerning the aramid-polyester cords, it was possible to conclude that comparing with the analyzed pure cords, the hybrid cord has higher tenacity and modulus and lower elongation at break than pure cords because of aramid. The influence of twist level was really big in all hybrids with aramid 1100 dtex, concluding that 550 tpm for this yarn leads to specific breaking strength loss.

In the asymmetric hybrids it was possible to observe that the proportion of each polymer in each cord construction and the entire cords design leads to completely different properties. It was concluded that tenacity is dependent of the proportion of aramid (higher proportion of aramid leads to higher tenacity) but the elongation at break is not dependent of the proportion of polyester.

Regarding to shrinkage, it was possible to observe that for all hybrids, the increase of twist level leads to lower shrinkage values, however in the asymmetric hybrids with higher proportion of aramid is the opposite that happens, taking into account that aramid with high torsion has not almost any contribution for the cord length that shrinks. The shrink force in all cases is dominated by PET titer: the higher the PET decitex, the higher the shrink force.

Regarding to relaxation and creep, it was possible to conclude that the hybrid cords suffers more relaxation and less creep compared with pure cords because of aramid presence. It was also possible to conclude that the influence of twist level regarding to these two properties is dependent not only of cord modulus but also of material morphology.

At higher temperature (80 °C), the evaluation was not enough to reach with precision the influence of temperature in cords behavior. However, it was possible to observe that the thin aramid yarn (220 dtex) at high twist level seems to be more sensitive to the increase of temperature, taking into account the specific breaking strength and elongation at break of the cords composed with this yarn.

A dynamic input on creep test did not show different results compared with the ones obtained by static creep, taking into account the chosen test parameters and the specifications of the machine.

Regarding to future replacements on standard cords that are actually use in tire production, such as PA6.6 dtex 940x1 on cap-ply, PET dtex 1100x1x2 and PET dtex 1440x1x2 on carcass, it was possible to arrive to an interesting approach with the thinner pure cords tested in this thesis and the symmetric hybrid ARA550x1+PET550x1 at high twist level. However, the information obtained in this thesis is not enough to say that these replacements brings with absolutely certain more advantages to tire performance.

6 Project Assessment

6.1 Accomplished Objectives

The main goal of this project was to study and characterize new cords constructions to fulfill new demands for tire performance and to reach a deeply evaluation of the reinforcement materials regarding to mechanical properties. Force-Elongation, shrinkage and shrink force tests are not the only tests that gives all the information about textile reinforcements, and day by day it is necessary to create and improve new mechanisms in order to reach a better evaluation of the materials. In this thesis, it was made a new attempt to the relaxation and creep evaluation, which became interesting in the end because it gave the perception that the cords behavior is not dependent only of cord design but also of the polymers morphology itself. This fact can open doors for future investigations in order to evaluate in a deeply way what exactly is the influence of polymer morphology in cords performance, which turns out afterwards in tire service.

During this project, it was also possible to find out that a certain testing machine was not the most suitable for evaluate creep property. This fact worked as important information for future lab experiments.

In this thesis was also made a first attempt to study the dynamic properties of the new cord constructions planned in this project, however the results became inconclusive.

In contribution to the objectives of the project, it was done a comparison of the studied cords constructions with the standard constructions, in order to evaluate promising future replacements, where in case of standard PA6.6 dtex 1400x1, PET dtex 1100x1x2 and PET dtex 1440x1x2 was possible to achieve an interesting approach.

6.2 Limitations and Future Work

The major limitation in this project was, without any doubts, the time. A characterization of these new cord constructions was accomplished but it could be possible to do more, especially regarding to dynamic characterization and influence of external specifications such as temperature, if the project had more time. As the thesis was developed at Continental AG in Germany and the material provision was made by C-ITA in Portugal, the practical work started with delay and adding to this, the availability of the Reinforcement Testing Laboratory was very limited because a lot of projects were running at the same time and not always the necessary machines for this project were free. Besides that, the language was also a limitation, especially during the laboratory work because all software was in German and most employees in the lab do not speak English, which sometimes caused long delays in solving technical problems. As this project functioned as the first experience in the dynamic machine, all results and technical problems were also very difficult to answer because it is a completely new machine and nobody worked/tested any material with it before.

As future work, it is recommended:

- a deeply evaluation of static relaxation and creep test methods, as also the realization of these tests in all different available machines, in order to estimate the reliability of the equipment for each test;
- the evaluation of the influence of the new dynamic machine specifications, in order to achieve more effectiveness afterwards;
- a strongly study of yarns with different titers and twist levels;
- to do a characterization in all used cords constructions in this thesis, making use of higher temperatures than 80°C, in order to reach an higher information of these cords response;
- a specific study of aramid's yarns/cords, concerning to the influence of temperature;
- a deeply investigation of the morphology of polymers taking into account the connection existent with relaxation and creep behavior.

6.3 Final Assessment

Even with all challenges and delays that happened, this thesis was without any doubts a Huge and significant step for me, as a student and as a person, which I will never forget. The idea of work with complete new cord constructions, to characterize them with new tests and machines and to figure that out what could be the explanations for all results was the most interesting part of the project, absolutely. The motivation in the professional and even in the personal life passes to find out solutions for new problems, which should be called as new challenges. During this thesis this was not an exception and numerous future improvements and developments were launched, and several paths can be taken in order to achieve it.

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[16] ASTM D4974 - 04: "Standard Test Method for Hot Air Thermal Shrinkage of Yarn and Cord using a Thermal Shrinkage Oven". 2011: Annual Book of ASTM Standards

[17] Ferry, J.D., Viscoelastic properties of polymers, 3th Edition, 1980, Wiley

Appendix A - Irregular Tests

A.1 Creep result from Lenzing TST10 machine

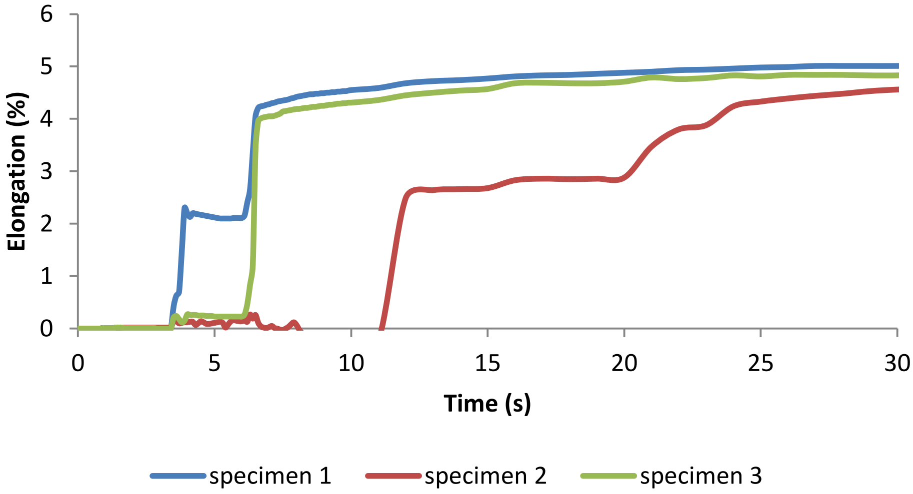


Figure 42 - Creep chart obtained on Lenzing TST10 for ARA1100x1+PET1100x1 (250 tpm)

As can be seen, it is impossible to define and trust, with precision, in the *εi* value.

A.2 Hysteresis test

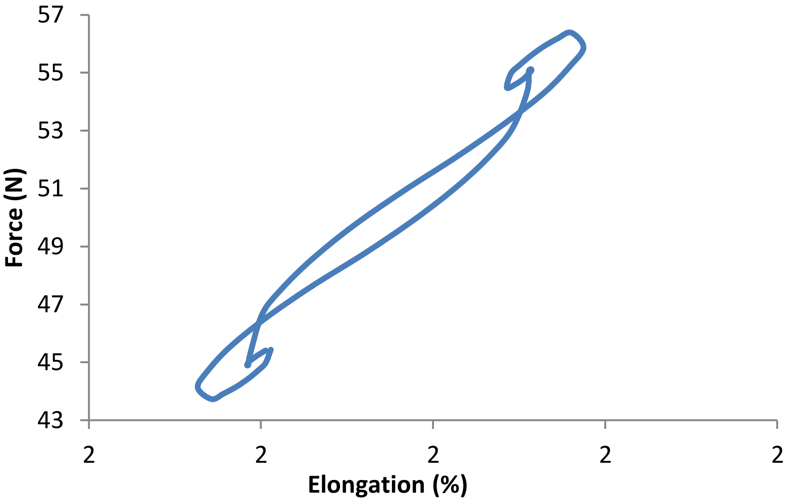
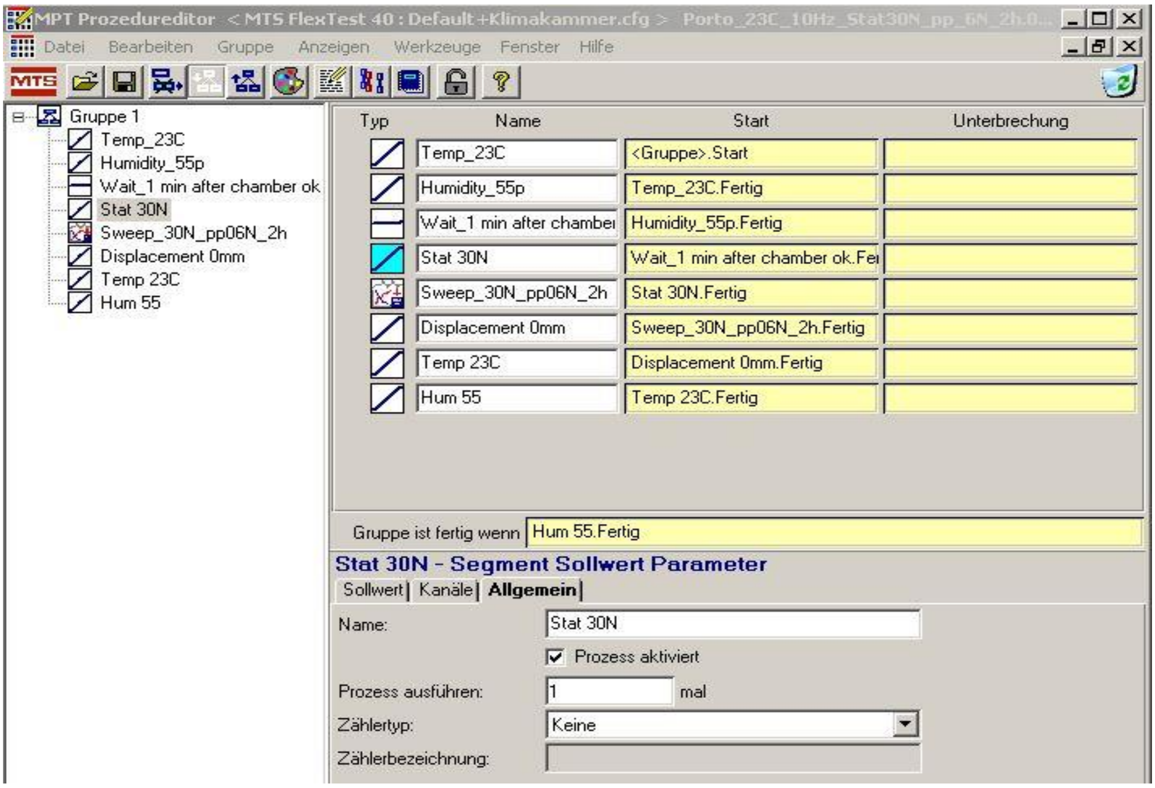


Figure 43- Last cycle of one Hysteresis test for ARA1100x1+PET1100x1 (250 tpm)

The cycle is not uniform because the machines cannot detect precisely the limits of the test conditions. As work loss is calculated taking into account the area inside the relaxation and tension area, the final results are around zero or below zero.

Appendix B - Screenshots of MTS Landmark



Typ	Name	Start	Unterbrechung
／	Temp_23C	<Gruppe>.Start	
／	Humidity_55p	Temp_23C.Fertig	
—	Wait_1 min after chambe	Humidity_55p.Fertig	
／	Stat 30N	Wait_1 min after chamber ok.Fe	
	Sweep_30N_pp06N_2h	Stat 30N.Fertig	
／	Displacement 0mm	Sweep_30N_pp06N_2h.Fertig	
／	Temp 23C	Displacement 0mm.Fertig	
／	Hum 55	Temp 23C.Fertig	

Gruppe ist fertig wenn: Hum 55.Fertig

Stat 30N - Segment Sollwert Parameter

Sollwert | Kanäle | **Allgemein**

Name: Stat 30N

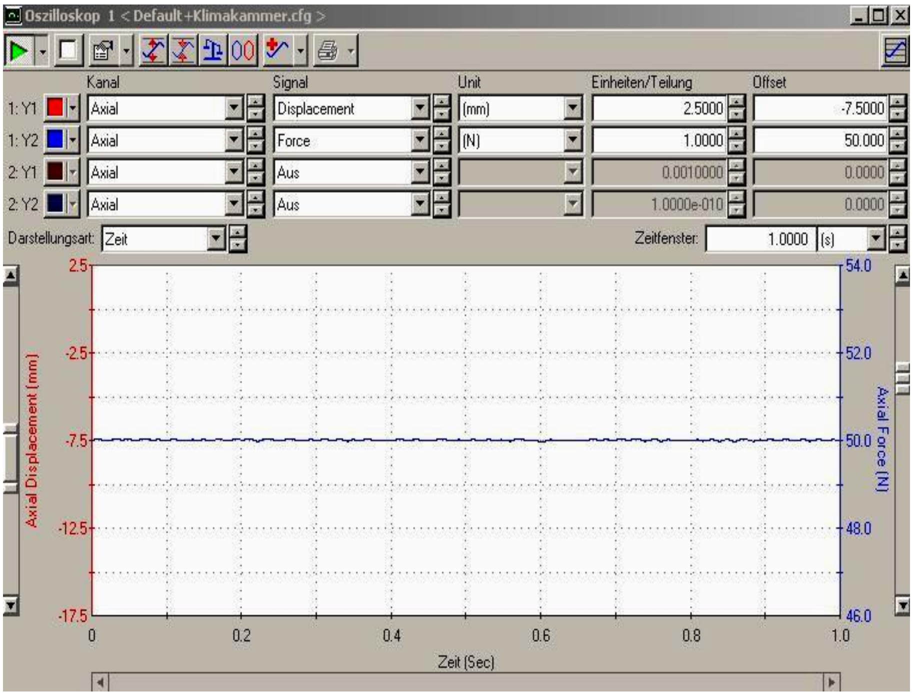
☑ Prozess aktiviert

Prozess ausführen: 1 mal

Zählertyp: Keine

Zählerbezeichnung:

Figure 44 – Layout of dynamic creep experiment (F = 30N ± 3N)

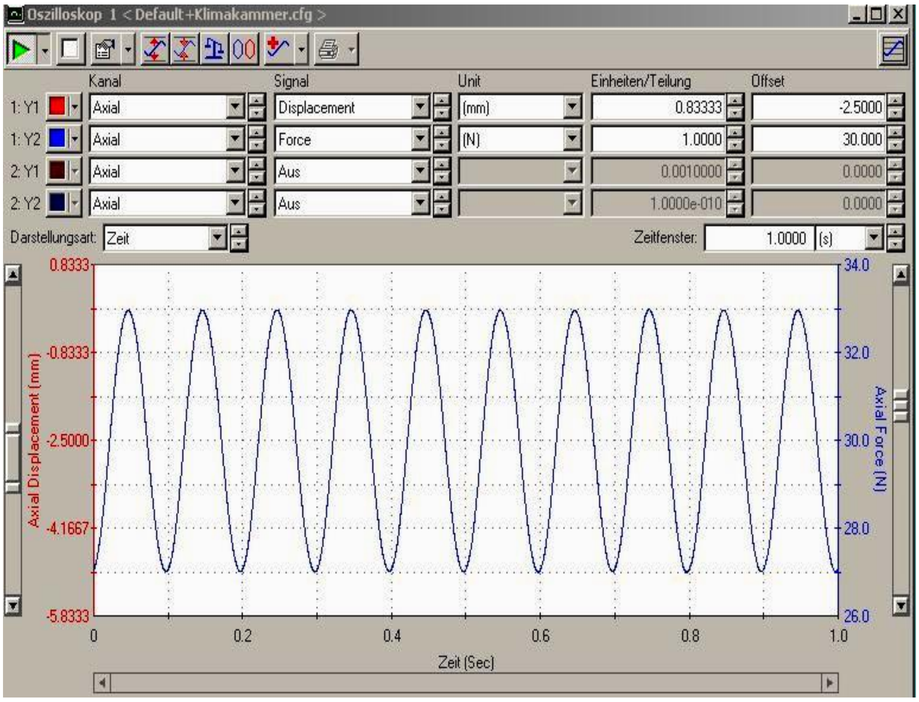


	Kanal	Signal	Unit	Einheiten/Teilung	Offset
1: Y1	Axial	Displacement	(mm)	2.5000	-7.5000
1: Y2	Axial	Force	(N)	1.0000	50.000
2: Y1	Axial	Aus		0.0010000	0.0000
2: Y2	Axial	Aus		1.0000e-010	0.0000

Darstellungsart: Zeit

Zeitfenster: 1.0000 (s)

Figure 45 – Static Creep plot (F = 50N)



Oszilloskop 1 < Default+Klimakammer.cfg >

	Kanal	Signal	Unit	Einheiten/Teilung	Offset
1: Y1	Axial	Displacement	(mm)	0.83333	-2.5000
1: Y2	Axial	Force	(N)	1.0000	30.000
2: Y1	Axial	Aus		0.0010000	0.0000
2: Y2	Axial	Aus		1.0000e-010	0.0000

Darstellungsart: Zeit

Zeitfenster: 1.0000 (s)

Figure 46 - Dynamic Creep plot (F = 30N ± 3N)

Appendix C - Influence of TL on Tenacity, LASE and Elongation at break at 80°C

C.1 Pure Cords

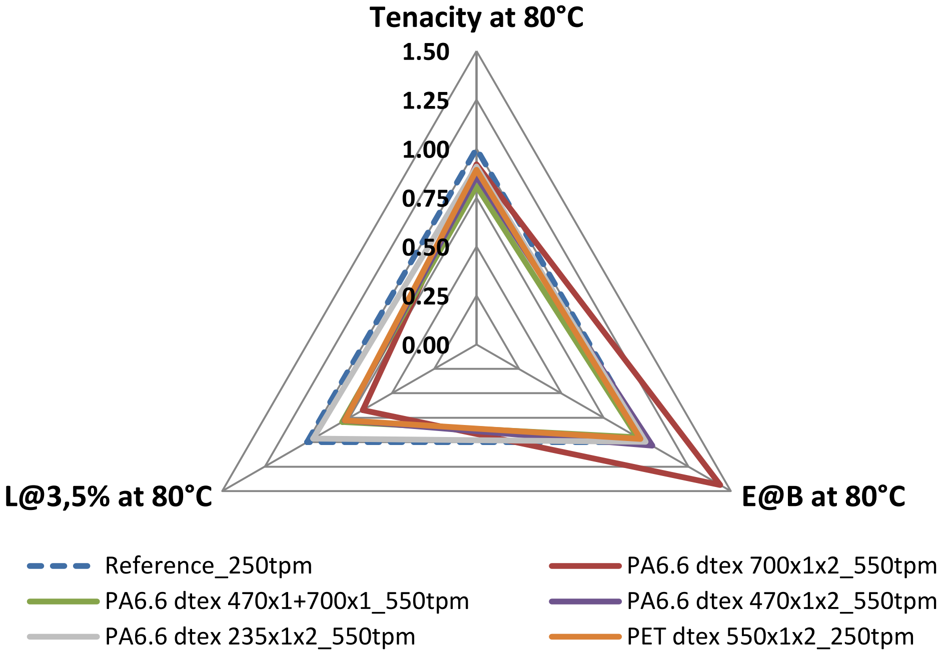


Figure 47 - Influence of TL at 80°C on Tenacity, L@3,5% and E@B of Pure Cords

It is possible to observe that PA6.6 dtex 700x1x2 suffers an influence of twist level around 50 % on elongation at break, which is a very different behavior comparatively to the others pure cords. A hypothetical theory for this fact is that at high temperature the polymer became softer and as at high twist level exist a higher sharing points effect, the waviness inside this points at high temperature becomes also softer, ending with a big elongation at break. However, further analysis should be done in order to evaluate the influence of temperature in these pure cords.

C.2 Symmetric Hybrid Cords

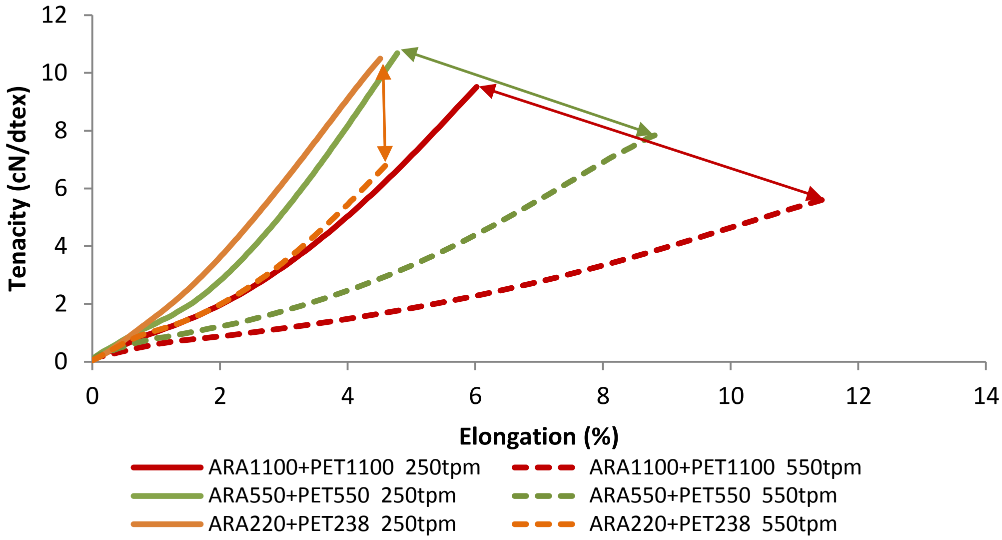


Figure 48 - Influence of TL at 80°C on Tenacity, L@3,5% and E@B of Symmetric Hybrid Cords

The tenacity drop in ARA1100x1+PET1100x1 was already expected taking account the twist factors of this cord, as explained in Chapter 4.2.1. However, the intensive decrease on tenacity on ARA550x1+PET550x1 and ARA220x1+PET238x1 and the E@B of ARA220x1+PET238x1 are results that are completely unexpected. The sensitivity of aramid yarn should be tested afterwards in order to reach more conclusions about these cords behavior.

C.3 Asymmetric Hybrid Cords

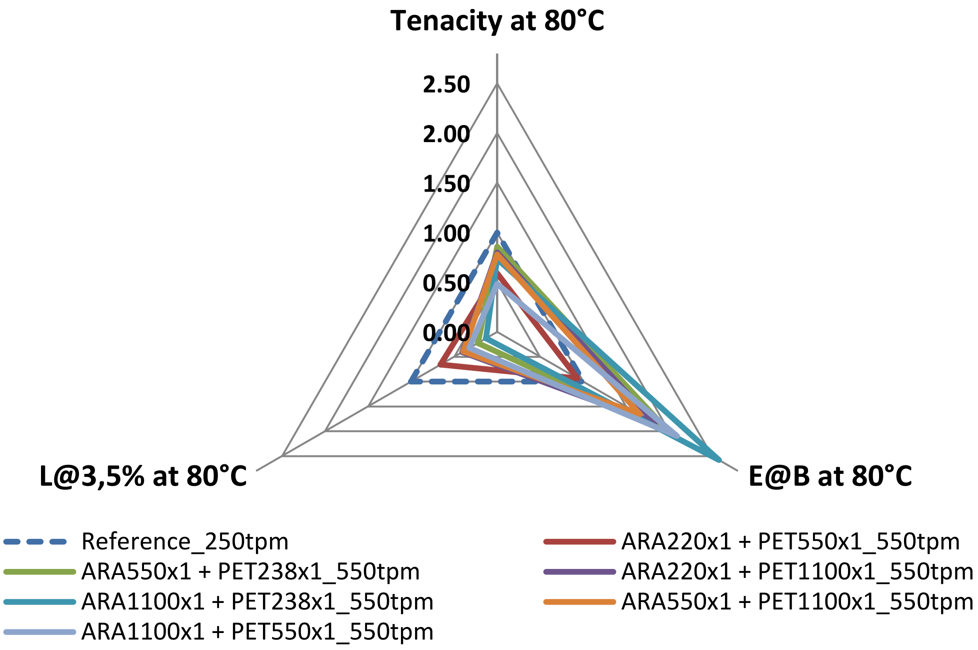


Figure 49 - Influence of TL at 80°C on Tenacity, L@3,5% and E@B of Asymmetric Hybrid Cords

It is possible to observe that ARA220x1+PET550x1 at 80°C suffers a big decrease on tenacity (around 50%) comparing with 250 tpm, which is not seen in ARA220x1+PET1100x1, probably because polyester somehow compensates in this last cord.

Appendix D - Relaxation at 80 °C

D.1 Pure Cords

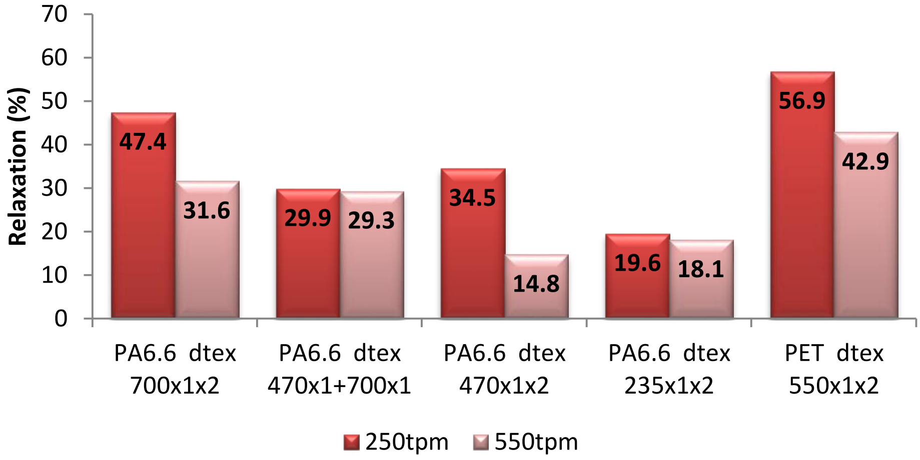


Figure 50 - Relaxation of Pure Cords at 80 °C

However, it is possible to observe that the relaxation values for PA6.6 dtex 700x1x2 at 250 tpm and for PET are higher than expected. A possible explanation at least for PET is that during the relaxation test the material did not become soften enough (the glass transition was not completely finished) and the relaxation did not became lower comparatively to room temperature.

D.2 Symmetric Hybrid Cords

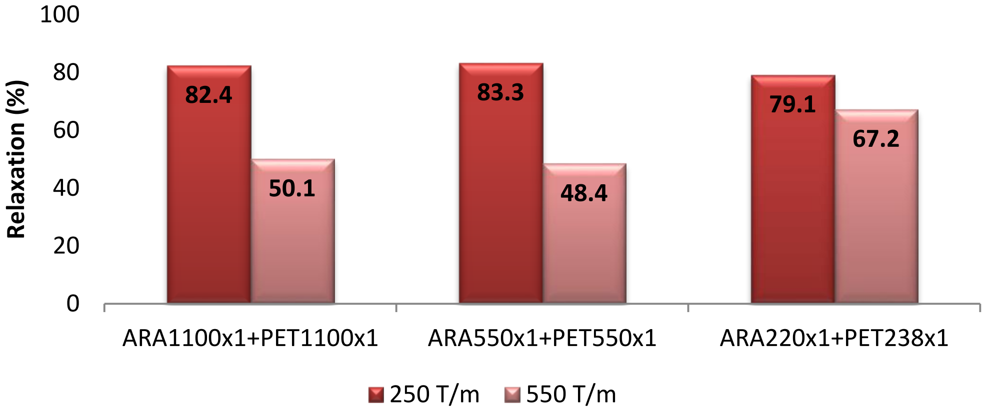


Figure 51 - Relaxation of Symmetric Hybrid Cords at 80 °C

D.3 Asymmetric Hybrid Cords

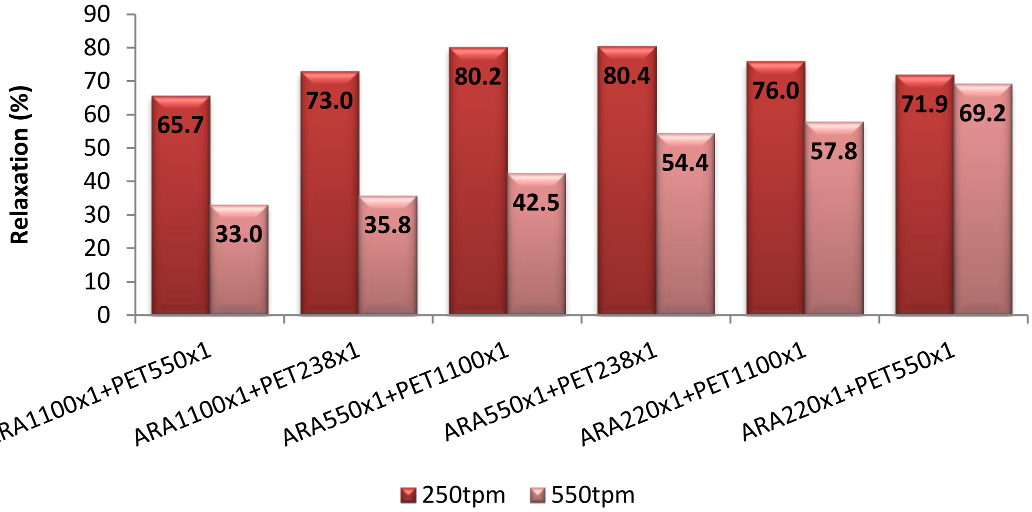


Figure 52 - Relaxation of Asymmetric Hybrid Cords at 80°C

Appendix E - Microscopic pictures of cord constructions

E.1 Pure Cords

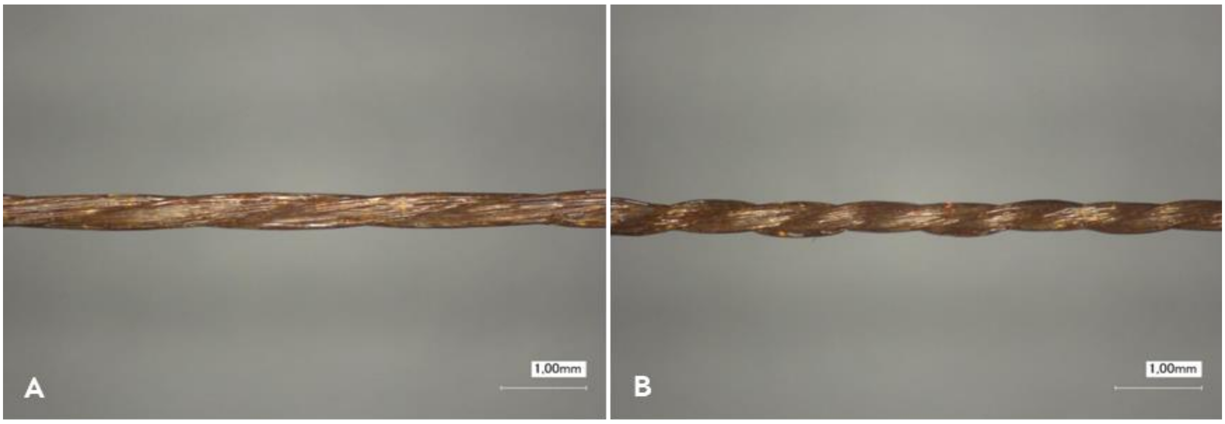


Figure 53 - PA6.6 dtex 470x1x2: A(250 tpm) and B(550 tpm)

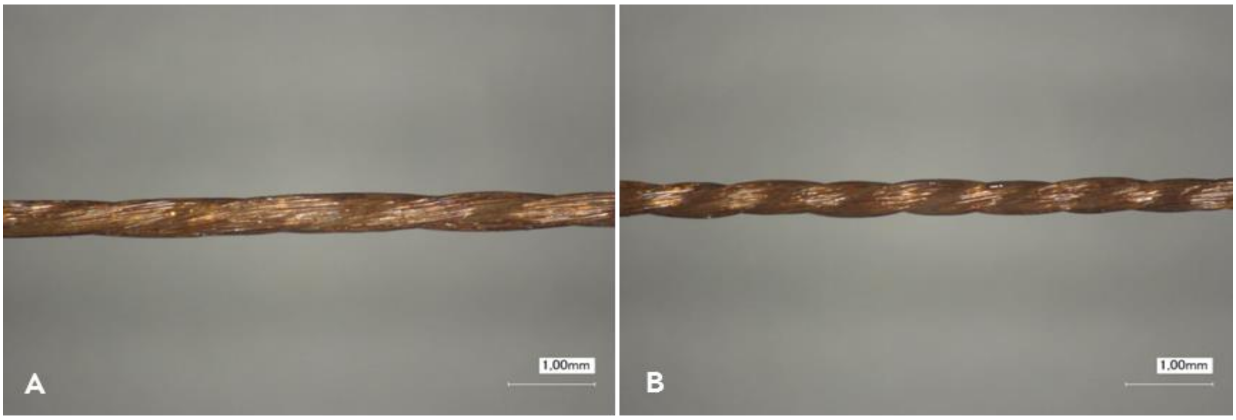


Figure 54 - PA6.6 dtex 470x1 + 700x1 : A(250 tpm) and B(550 tpm)

E.2 Asymmetric Hybrid Cords

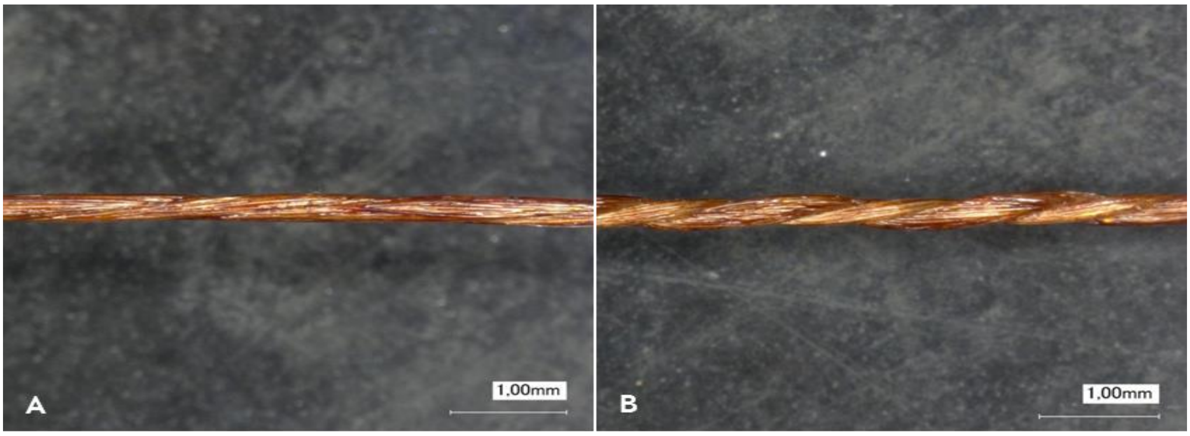


Figure 55 - ARA220x1 + PET550x1 : A(250 tpm) and B(550 tpm)

Figure 56 - ARA220x1 + PET1100x1 : A(250 tpm) and B(550 tpm)

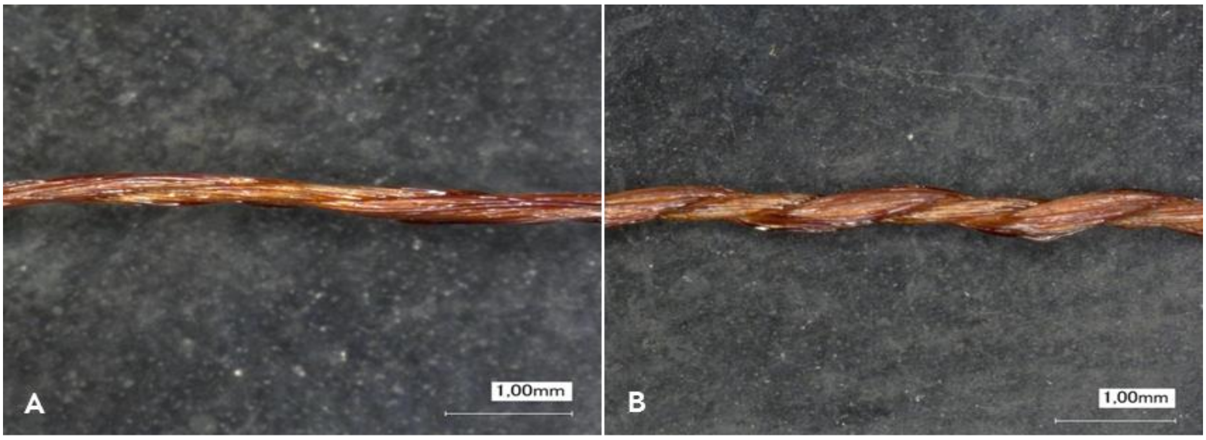


Figure 57 - ARA550x1 + PET238x1 : A(250 tpm) and B(550 tpm)

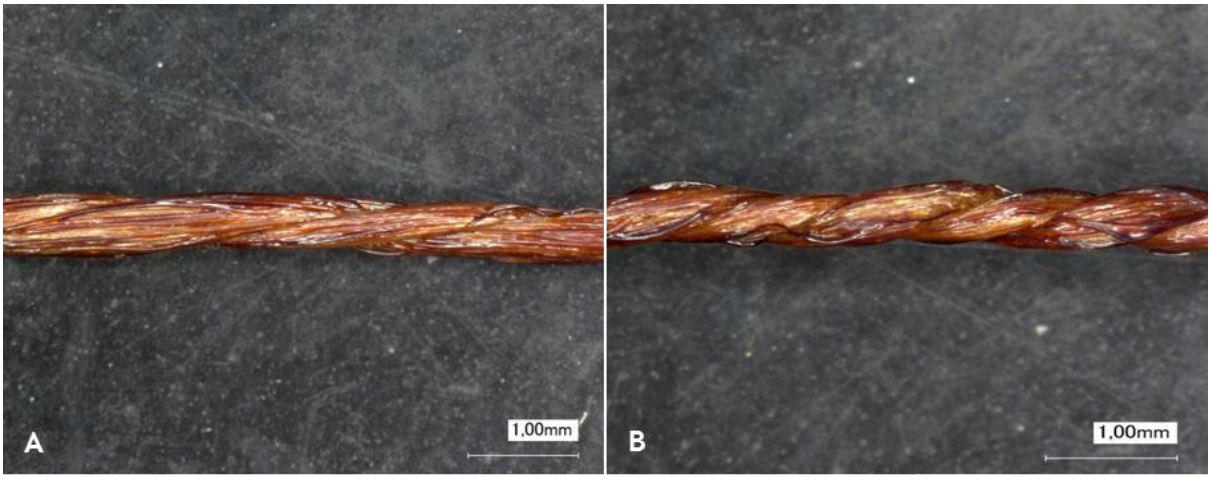


Figure 58 - ARA550x1 + PET1100x1 : A(250 tpm) and B(550 tpm)

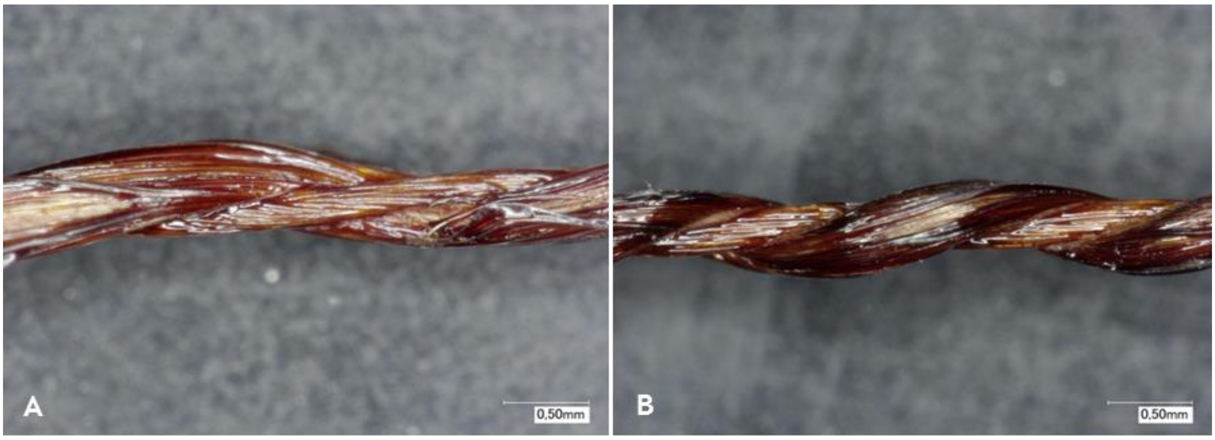


Figure 59 - ARA1100x1 + PET238x1 : A(250 tpm) and B(550 tpm)

Figure 60 - ARA1100x1 + PET550x1 : A(250 tpm) and B(550 tpm)