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HEAT INDUCED SHRINKAGE BEHAVIOUR OF TEXTILE TIRE REINFORCEMENTS

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Body Compound & Reinforcement Technology



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Abstract

The portfolio of Continental is a broad range of products that satisfy vehicle manufacturers as well as end-consumer needs for optimum performance under a variety of service conditions. This performance relies to a great extent on the properties of the textile tire reinforcements. Polyester and nylon cords make up the majority of synthetic fibers used as reinforcements, and one of the most critical characteristics is their dimensional stability at high temperatures. Throughout the various stages of reinforcement and tire manufacturing, and the remainder of their useful lives on the road, tire cords must resist the effects of heat.

Circumscribed in this context, the main goal of this project was the thorough analysis of thermally induced axial shrinkage to obtain a proper understanding of all potential impact factors. In order to determine the thermal shrinkage and shrinkage force brought on by heating the materials with a specified pre-load and defined temperature for a specified period of time in an oven, all trials were performed on Lenzing Instruments Thermal Shrinkage Tester 510/250.

To evaluate the influence of stress, oven exposure time and temperature in the shrinkage force behaviour, the three levels full factorial response methodology was employed for dipped PET and PA 6.6 cords, with constructions of 1100 dtex x2 and 1400 dtex x2, respectively. The results demonstrated that temperature and pre-load exhibited significant interactions on the response. In addition, the rate-of-creep equation, originally derived by Tobolsky and Eyring, has been revised to describe the influence of these parameters on shrinkage of these oriented polymers.

Moreover, the examination of the shrinkage force allowed a more sensitive analysis of all the phenomena that occur during the heating of the cords in which it was possible to associate with entropy, structural and modulus fluctuations. On the other hand, distinct experiments were performed to scrutinise the impact of moisture, twist factor, greige and calendered material.

To complement the results obtained, measurements were also performed using differential scanning calorimetry. This method allowed the observation of glass transition temperatures as well as fusion and crystallization events. The crystallinity of all standard dipped samples was around 30%, regardless of their construction, proving their semi-crystalline nature. In addition, it has been experimentally proven that crystallinity rises with increasing twist factor.

In the end, this project was able to provide an analysis of all the phenomena that occur during the heating of the textile reinforcements and how the shrinkage fluctuates along the cord manufacture. This knowledge should serve as a basis for future preventive actions.

Keywords:

Textile reinforcements; Thermal shrinkage; Thermal properties; Design of experiments

Resumo

O portfólio da Continental compromete uma vasta gama de produtos que satisfazem os fabricantes de veículos, bem como as necessidades dos consumidores finais para um desempenho ótimo sob uma variedade de condições de serviço. Este desempenho depende, em grande medida, das propriedades dos reforços têxteis dos pneus. As cordas de poliéster e nylon constituem a maioria das fibras sintéticas utilizadas como reforço e uma das características mais críticas é a sua estabilidade dimensional a altas temperaturas.

Circunscrito neste contexto, o tema principal deste projeto foi a análise minuciosa da contração axial induzida termicamente para obter uma compreensão adequada de todos os potenciais fatores de impacto. A fim de determinar a contração térmica e a força de contração provocada pelo aquecimento dos materiais com uma pré-carga especificada e temperatura definida durante um determinado período de tempo, todos os ensaios foram realizados no equipamento Lenzing Instruments Thermal Shrinkage Tester 510/250.

Para avaliar a influência da pré-carga, tempo de exposição ao forno e temperatura no comportamento da força de contração, foi utilizada a metodologia de resposta fatorial completa a três níveis para cordas de PET e PA 6.6 impregnados, com construções de 1100 dtex x2 e 1400 dtex x2, respetivamente. Os resultados demonstraram que a temperatura e a pré-carga exibiram interações significativas na resposta e uma equação de taxa de fluência, originalmente derivada por Tobolsky e Eyring, foi revista para descrever a influência destes parâmetros na contração térmica destes polímeros.

Além disso, o exame da força de contração permitiu realizar uma análise mais sensível de todos os fenómenos que ocorrem durante o aquecimento das cordas, no qual foi possível associar a diferenças de entropia, variação no módulo de elasticidade e mudanças estruturais. Por outro lado, foram realizadas experiências para examinar o impacto da humidade, do nível de torção, do material em verde e do material calandrado.

Para complementar os resultados, foram também realizados ensaios de calorimetria diferencial. Este método permitiu a observação de temperaturas de transição vítrea, bem como os eventos de fusão e cristalização. A cristalinidade de todas as amostras testadas foi de cerca de 30 %, independentemente da sua construção, provando a natureza semi-cristalina destes materiais. Para além disso, foi provado experimentalmente que a cristalinidade aumenta com o aumento do fator de torção.

Em suma, este projeto foi capaz de fornecer uma análise de todos os fenómenos que ocorrem durante o aquecimento dos reforços têxteis e de como a contração varia ao longo do fabrico das cordas. Estes conhecimentos deverão servir de base para futuras ações preventivas.

Palavras-chave:

Reforço Têxtil; Contração Térmica; Propriedades térmicas; Design of experiments

Zusammenfassung

Das Portfolio der bei Continental produzierten Produkte hat sich aufgrund der Entwicklung der Automobilindustrie in bislang unbekannten Märkten ausgebreitet, die Kunden mit hohen Erwartungen an die Reifenleistung bereithalten. Die wesentlichen Funktionen eines Reifens beruhen weitgehend auf den Eigenschaften der Textilverstärkung. Polyester- und Nylon-Fasern bilden den Großteil der als Verstärkungen verwendeten Kunstfasern und eines der kritischsten Merkmale dieser orientierten Kunstfasern ist ihre Formstabilität bei hohen Temperaturen.

In diesem Zusammenhang beschrieben, war das Hauptthema dieses Projekts die gründliche Analyse der thermisch induzierten axialen Schrumpfung, um ein angemessenes Verständnis der möglichen Einflussfaktoren zu erhalten. Um die thermische Schrumpfung und Schrumpfkraft zu bestimmen, die durch Erhitzen der Materialien mit einer vorgegebenen Vorlast und Temperatur für einen vorgegebenen Zeitraum in einem Ofen erzeugt wird, wurden alle Versuche mit dem Lenzing Instruments Thermal Shrinkage Tester 510/250 durchgeführt.

Um den Einfluss von Spannung, Erwärmungszeit und Temperatur auf das Schrumpfkraftverhalten zu bewerten, wurde die dreistufige voll faktorielle Ansprechmethodik für getauchte PET- und PA 6.6-Fasern mit Konstruktionen von 1100 dtex x2 bzw. 1400 dtex x2 angewendet. Die Ergebnisse zeigen, dass Temperatur und Vorspannung einen signifikanten Einfluss auf das Verhalten haben. Außerdem wurde eine ursprünglich von Tobolsky und Eyring hergeleitete Gleichung für die Kriechrate wurde überarbeitet, um den Einfluss dieser Parameter auf die thermische Schrumpfung dieser orientierten Polymere zu beschreiben.

Darüber hinaus erlaubt die Untersuchung der Schrumpfkraft eine sensitivere Analyse aller Phänomene, die beim Erwärmen der Fasern auftreten, sodass es möglich war Entropie-, Struktur- und Modulschwankungen zu verknüpfen. Auf der anderen Seite wurden verschiedene Experimente durchgeführt, um den Einfluss von Feuchtigkeit, Verdrillungsgrad, grünem und kalandriertem Material zu untersuchen.

Ergänzend zu den Ergebnissen der thermischen Schrumpfung wurden auch Versuche zur dynamischen Differenzkalorimetrie durchgeführt. Diese Methode erlaubt die Beobachtung von Glasübergangstemperaturen sowie von Fusions- und Kristallisationsereignissen. Die Kristallinität aller untersuchten Proben lag, unabhängig von ihrer Konstruktion, bei etwa 30 %, was die semikristalline Natur dieser Materialien belegt. Darüber hinaus wurde experimentell nachgewiesen, dass die Kristallinität mit zunehmendem Verdrillungsfaktor steigt.

Letztendlich konnte dieses Projekt eine Analyse aller Phänomene liefern, die während der Erwärmung der textilen Verstärkungen auftreten und wie die Schrumpfung während der Herstellung der Schnüre schwankt.

Schlüsselwörter:

Textilverstärkung; Thermische Schrumpfung; Thermische Eigenschaften; Design of experiments

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions are indicated and due reference is given to the author and source

João Pedro Silva Costa

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Notation and Glossary

b	parameter proportional to the reciprocal stress	
C	fraction of the unreacted reactant	
E^*	complex modulus	cN/dtex
E'	storage modulus	N/mm ²
E''	loss modulus	N/mm ²
ΔE_a	activation energy	kcal/mole
f	stress (tension or compression)	N/mm ²
h	Planck constant	J·s
h_l	yarn length	mm
ΔH_c	heat of cold crystallization	J/g
ΔH_m	heat of fusion calculated from melting endothermic peak	J/g
ΔH_m^0	heat of fusion for pure polymer crystals	J/g
k	Boltzmann constant	J/K
k_n	series of rate constant	
l	fiber length	mm
L	length of the specimen during heating	mm
L_0	initial length of the specimen before heating	mm
L_∞	final length of the specimen after heating	mm
L'	length of fully extended chain	mm
P	Pressure	Pa
r	distance of yarn element from center	mm
r'	end-to-end distance	mm
R	yarn radius	mm
S	thermal shrinkage	%
s_n	series of strains	%
t	Time	s
T	absolute temperature	K
T_g	glass-transition temperature	°C
T_m	melting temperature	°C
T_r	reference temperature	°C
T_s	sample temperature	°C
X_{cr}	crystallinity	%

Greek Letters

α	yarn twist angle	°
α_L	coefficient of linear thermal expansion	
α_V	coefficient of volumetric thermal expansion	
δ	displacement volume	mm ³
δ	phase shift	°
$\tan \delta$	loss factor	
ε	Stress	N/mm ²
θ	helix angle	°
σ	Strain	%
τ_n	relaxation times	s
ω	Frequency	Hz

List of Acronyms

AG	Aktiengesellschaft
ASTM	American Society for Testing and Materials
AR	Aramid
DOE	Design of Experiments
DIN	Deutsches Institut für Normung
DSC	Differential Scanning Calorimetry
FEUP	Faculty of Engineering of the University of Porto
ITA	Indústria Têxtil do Ave
PA 6	Polycaprolactam
PA 6.6	Polyhexamethylene-dipamide
PET	Polyethylene terephthalate
R&D	Research and Development
RMSE	Root Mean Square Error
RFL	Resorcinol Formaldehyde Latex
SEC	Single End Cord
TF	Twist Factor
TST	Thermal Shrinkage Tester

1 Introduction

The present dissertation was submitted in conformity with the requirements for the Master's degree in Chemical Engineering conferred to the Faculty of Engineering of the University of Porto (FEUP). The thesis was written in cooperation with Continental Aktiengesellschaft (AG) at the facility for Body Compound & Reinforcement Technology.

As an overall introduction to this study, this chapter describes the motivation for this thesis. Subsequently, it is given a brief description of the company and an overview of the working environment. The chapter finishes with a synopsis of the thesis' further structure.

1.1 Framing and presentation of the work

Fibers are used as reinforcing material in most of the industrial and consumer rubber products, which plays a crucial role in the structural load of automobiles and should possess outstanding tensile, dimensional stability, strength and fatigue properties. One of the important aims of modern polymer research and development is to achieve a proper understanding of the spatial arrangement and the molecular chain conformation of the polymer molecules in the solid state (Deopura and Padaki, 2015). Besides the intrinsic properties, the external configuration of the fibers also has a significant impact on the overall mechanical and thermal properties.

Circumscribed in this context, structural reinforcements of tires, such as polyester and nylon cords, which are the most abundantly used synthetic fibers in rubber products, have been studied in several projects to objectively define the intrinsic properties of each material, which are determined by its crystallinity, crystal structure, the degree of orientation, rigidity of molecular chain, intermolecular forces and the stress-strain relations between the filaments.

Moreover, one of the most critical characteristics of oriented synthetic fibers is their dimensional stability at high temperatures. Tire cords must survive the effects of heat at different periods in their progress through tire manufacture and during their subsequent useful life on the road. Within these heat-induced processes, it is possible to highlight, *e.g.*, the dipping of the textile components, which aims to confer dimensional stability through thermal treatment (ovens). In addition, a measure of heating also occurs when the rubber is calendered onto the fabric sheet and during the vulcanization process.

Along these lines, it is expected that cords have more than one aspect of heat resistance. According to Wood *et al.* (1959), the materials must not suffer permanent degradation from exposure to prolonged periods at elevated temperatures, should resist as far as possible the reversible loss in strength, which occurs with most textiles, and it must have maximum dimensional stability to minimize total tire failure. Hence, the overall performance of a tire

gets affected following its processing and operating conditions and adversely affects the dimensional stability of thermoplastic cords as they undergo thermal shrinkage, along with creep, stiffness variation and temperature dependency.

The investigation of shrinkage forces generated in oriented polymers, kept constrained at elevated temperatures, has recently attracted intense interest with the purpose of being used as a tool in examining the behaviour of oriented samples. Comprehensive studies, performed by Ribnick (1969), on thermal shrinkage of oriented semi-crystalline polymers, were conveniently demonstrated by measuring the free thermal shrinkage (unconstrained measurement) at different temperatures and the shrinkage force, *i.e.*, the tension developed in the specimen when it is held at a constant length and heated. These empirical investigations, on nylon 66 and polyethylene terephthalate (PET), revealed that thermal shrinkage is time, temperature and stress-dependent. The author, based on experimental results, also introduces thermal shrinkage laws which describe the process accurately under isothermal and constant stress conditions.

Further investigations, on the role of oriented molecular chain motion, have shown that thermal shrinkage is directly interrelated with amorphous orientations. When an oriented textile polymeric fiber is heated to a temperature above its glass-transition temperature (T_g), amorphous polymer chain segments will gain mobility and, subsequently, this disorientation would be responsible for the fiber length change due to entropic force (Trznadel *et al.*, 1992).

Regarding these concerns, the key objective addressed in this thesis is the extensive analysis of thermal-induced axial shrinkage to achieve a proper understanding of all possible impact factors that may affect the results, such as, cord construction, number of yarns, twist level, temperature, oven exposure time, pre-tension applied and among other aspects. For this purpose, dipped material of polyamides (PA 6.6 and PA 6), polyester (PET), aramid (AR) and hybrid cords, present in Continental's portfolio, were selected to perform the experimental work. In the end, the results were also compared with greige and calendered material.

Furthermore, since measurements of thermal shrinkage involve dimensional changes, it is necessary to discuss the possibility of an overlapping of the shrinkage effects and the thermal expansion of the material with structural changes. Therefore, it is essential to adopt stress-strain constitutive models, already present in the literature, considering the influence of the thermal, chemical and mechanical effects of all the interacting phenomena.

In this study, an experimental investigation of the processing parameters is conducted using Design of Experiments (DOE). This process of planning the experiments grants an appropriate collection of data that can be analysed by statistical methods to obtain valid and objective conclusions and determine cause-and-effect relationships.

1.2 About Continental AG and working environment

The portfolio of products produced at Continental AG has been expanding into hitherto unknown markets, largely due to the development of the automotive industry that presents increasingly demanding customers with high expectations in relation to vehicle performance. Currently, Continental is the leader in the tire industry in Germany, it is the second largest tire producer in Europe and the fourth largest worldwide, which makes this Group a highly recognized multinational with the cooperation of 49 countries (Tire Business, 2021).

Well known for its pioneering technologies and services for sustainable and connected mobility of people and their goods, Continental is divided into five distinct groups: Chassis & Safety, Powertrain, Interiors, Tires and ContiTech. Due to the multitude and growing of market and customer requirements, each group is supported by research and development (R&D) activities that focus on developing innovative and sustainable products, systems and services for customers in a wide variety of industries (Continental, 2022).

Continental Tire R&D centre in Hanover-Stöcken, in which this present project took place, has around 1 400 employees working on the development of up to 9 000 different tires to fulfil various requirements regarding tire performance, e.g., speed rating approvals, rolling resistance optimization, reinforcement materials development, inch dimensions, legal considerations, application purposes and among others (Continental, 2022).

The product development process is a multistage plan that involves taking a tire from initial concept to final market launch and lasts between three and five years, involving a host of indoor and outdoor tests. Continental owns various laboratories for an in-depth insight into tire development which keeps pace with the rapid advancement in technology. All the applied sciences laboratories have state-of-the-art infrastructure.

The empirical results in this thesis were obtained from tests conducted at Physical Reinforcement Testing Laboratory. The main task, of all parties involved in this laboratory, is to perform an evaluation and quality management of steel and textile cords. Furthermore, it supports material development for emerging new reinforcement materials and skim compounds. Presently, Continental has a close cooperation with two internal reinforcement converters, one in the United States of America (Aldora Mills) and the other in Portugal (*Indústria Têxtil do Ave*, ITA).

The majority of the samples used in this project were provided by ITA, which is an integrated part of the Continental group since 1993. Various types of fibers arrive at this plant from different suppliers and ITA is responsible for the transformation of twisted greige cords into high-value dipped cords and fabric, to improve adhesion between cords and the rubber compound to grant the tire important mechanical properties.

1.3 Contribution of the author to the work

Based on the current state-of-the-art, although there were many studies published on the thermal effects of different polymeric materials with thermal analysis testing devices, there have not been many studies conducted in the field of tire cords. This dissertation contributes to a proper comprehensive understanding of heat induced shrinkage on textile tire reinforcements to study the effect of selectively chosen factors and evaluate the influence of the raw material and supplier on the existing variation of the thermal shrinkage and the shrinkage force at different temperatures.

Thereby, the author conceived and planned the presented idea of an experimental investigation of the processing parameters using a DOE approach. The preparation of all the samples and their respective analysis was executed in the Physical Reinforcement Testing Laboratory according to the American Society of Test Methodology (ASTM) procedures.

Since this was the first approach to this project, numerous obstacles emerged which were later overcome with the contribution of the supervisors in interpreting the results and providing critical feedback and aided shape the research, analysis and manuscript.

From an overall perspective, this project was able to provide a more sensitive analysis of all the phenomena that occur during the heating of the cords.

1.4 Organization of the dissertation

For the preparation of this manuscript, it was adopted the structure that was considered the most appropriate for the presentation and understanding of the different themes involved in this study. The purpose of each one of these chapters is described as follows:

1. **Introduction:** frames and briefly describes the objectives of the project and its main goals. In addition, it presents some of the Continental Corporation R&D activities.
 2. **Context and State of the art:** details the background knowledge necessary for a thorough read of the present dissertation. Further, it explores related projects and state-of-the-art approaches relevant to this investigation.
 3. **Materials and Methods:** describes the methodological approach and reviews the experimental work procedures including materials and test methods.
 4. **Results and Discussion:** presents an extensive analysis of the outcome results.
 5. **Conclusions:** draws concluding remarks and summarizes the results.
 6. **Assessment of the work done:** evaluates the accomplished work and presents proposals for future work, considering the results obtained and limitations of the project.
 7. **References:** lists all references that were used throughout this thesis.
- Annexes and Appendices:** provides supplementary information.

2 Context and State of the art

This chapter aims to present core concepts of tire engineering and to demonstrate the unique properties of textile reinforcements which are crucial components of tires, providing various purposes, such as, tire stability and good driving experience. Furthermore, all theoretical background of thermal effects in tire cord materials and some accurate models of the physical phenomena involved are outlined.

2.1 Global Tire Industry

Tire engineering is a complex combination of mathematics, materials science and structural engineering. The history of pneumatic tires started in the late 1800s, in Great Britain, as an upgrade of solid rubber tires for bicycles, characterized by small cross-sections and high pressures. As time passed, the industrialization in Europe and North America, alongside with the discovery of vulcanization of rubber by Charles Goodyear, allowed the tire to evolve from a rubberized canvas covering a rubber tube to a wide variety of chemicals, elastomeric composites, fabrics, and types of steel, rendering it the most complex composite in mass production (Rodgers and Waddell, 2013; Rodgers, 2020).

Currently, the global tire industry is showing remarkable growth, reflecting the advance of the global economy and the corresponding improvement in living standards. Excluding the pandemic impact of COVID-19, global tire production was expected to exceed 3 billion in 2020 (STTC, 2020). Although there is substantial variation in researchers' estimations for previous and future production, tire industry growth is nearly linear over time, regardless of the source.

Geographically, most of the future industrial growth will occur in East and Southeast Asia, and despite car-sharing and other urban demographic trends, there is always the desire to own a vehicle. Secondly, transportation growth and increased efficiency will continue to drive demand for the truck industry and its associated truck and bus tires. In addition, national economic policies will influence future investment in new capacities, which makes tire manufacturing labour and capital intensive, requiring highly skilled workers to support government employment policies (Rodgers and Waddell, 2013).

Furthermore, given the nature of different markets, the portfolio of tires can be quite large, covering products from, *e.g.*, racing, passenger car and light truck tires to farm, heavy-duty off-road and aircraft tires. However, regardless of their application, tires are undoubtedly the most critical safety component on a vehicle and there are still many evaluation factors in tire technology in common, such as, tire design, construction, materials technology, manufacturing and final product performance.

2.2 Tire Technology

The dampening characteristics, elasticity properties of rubber, unique deformability and recovery properties combined, turn tires into advanced structural composites. Its performance can be tailored to the manufacturer's ride quality, handling and traction standards, combined with customer insights, safety, and performance expectations.

According to Rodgers (2021), regardless of the tire structure or application, all tires need to perform a basic set of functions. Among these purposes, a tire must provide load-carrying capacity of a vehicle, via inflation with air volume under specific pressure. The load range is also a term used to define the load-carrying capability of a tire and it is usually specified by the European Tire and Rim Technical Organization. Furthermore, it should transmit acceleration forces and braking torque (longitudinal direction) and provide cornering forces in curves and during lane changes (lateral direction). Moreover, for smooth operation at full potential, tires must support chassis damping and cushioning of uneven road conditions (vertical direction).

Resource conservation and fuel economy are also amongst the focus points of new tire innovations, that are geared towards safer and more environmentally sound options, exploring also safer and even more comfortable driving experiences. Usually, the industry proactively addresses the potential improvements associated with the tires' life cycle. Along these lines, Table 1 summarizes fundamental areas of research allowing tire optimization for future mobility of Passenger & Light Truck Tires (PLT) (Sousa, 2018).

Table 1 - Optimization areas of a typical PLT tire (adapted from Sousa, 2018).

Economy › Tread wear › Rolling resistance › Price	Environmental Aspects › Noise › Legal material requirements › Life expectancy before disposal
Comfort › Damping of uneven road conditions › Noise › Comfortable vehicle handling › Uniformity	Driving Safety › Breaking distance › Traction › Lateral/side forces › Endurance

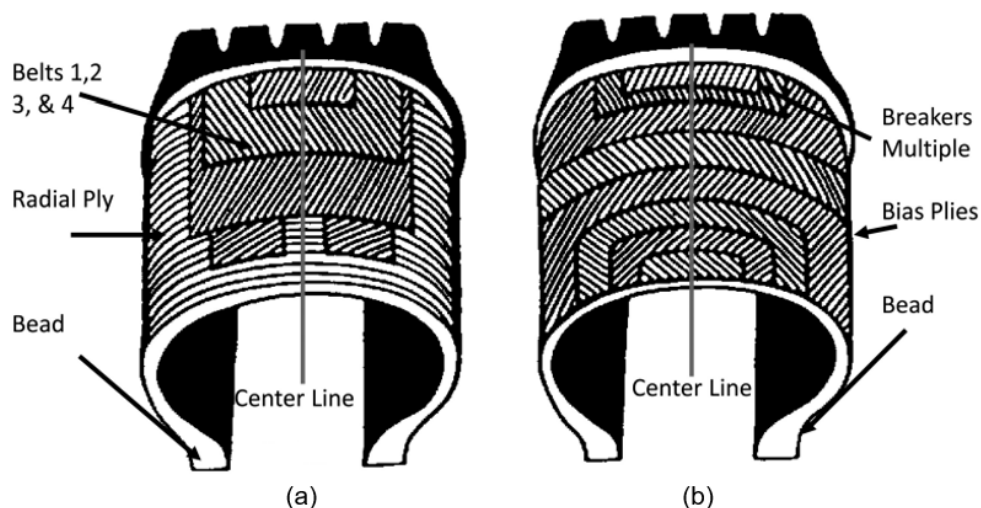
Nevertheless, the implementation of a truly sustainable mobility and circular economy model requires a long-term vision based on three key pillars: sustainable use of resources, innovation and economic growth. From this perspective, the major tire industries are expanding the use

of renewable material resources, developing innovative solutions and investing in breakthrough technologies to integrate more recyclable and renewable components (Araujo-Morera *et al.*, 2021). This mindset is at the centre of the strategic plans of the biggest tire corporations.

2.2.1 Tire Construction

Within the tire, there are some specialized components which serve to ensure that the product meets the intended design and performance requirements. Today's modern tires, found on the global market, fall into one of two types: bias-ply construction or radial-ply tires, as illustrated in Figure 1. There are other design derivatives, such as, when the belt is applied to the construction of a bias tire, sometimes referred to as a bias-belted construction, though none were ultimately successful. Presently, most tires display a radial-ply construction, since this arrangement has the advantage of granting an easier deflection under load and, therefore, it reduces the generation of heat, diminishes the rolling resistance and improves high-speed performance. However, radial tires are the most difficult and expensive to produce due to their complex construction which increases material and manufacturing costs (Rodgers, 2020). More information concerning the structure of a modern radial car tire can be found in Annex A.

The main concerns when designing tires are the belt extent, bead area, and belt and ply cord tension. Radial tires contain multiple belts, so these layups should be considered as a package. The stiffness of the tire is a function of belt wire angle, wire gauge, belt gauge, and composite stiffness and, as an empirical guide, numerous developers believe that an increase in the stiffness of the belt package, while maintaining belt width, improves tread wear performance.



1. Bias tire plies made from nylon or polyester
2. Radial tire ply is steel
3. Bias truck, farm, and aircraft market still strong
4. Bias passenger tire market still present in some Asian regions

Figure 1 - Cross-sectional view of a typical (a) Bias and (b) Radial tire constructions. Belt 1, in the radial construction, is the first above the ply. (adapted from Rodgers, 2021).

2.3 Tire Textile Reinforcements

Textile cords have been used as reinforcement materials since the first pneumatic tires were designed (the usual terminologies, regarding this topic, can be found in Annex B). The use of textile reinforcements has been increasing in recent decades and the continuous sophistication of the physical properties has led to the adoption of lighter, tougher and more accurately engineered yarns. From natural fibers, such as cotton, to synthetic fibers, e.g., rayon and polyamide, a high variety of reinforcements to enhance tire strength, dimensional stability and wear resistance, are being currently employed (Wilson, 2016).

Compared to steel cords, textile reinforcements or textile and steel cord combinations have the advantage of being lightweight and environmentally friendly and occupy an important role in tire performance. For instance, textile cords must yield durability to the tire against bruises and impact, serve as a support to the inertial load, confine the inflating gas, provide rigidity to accelerating, cornering and braking provide dimensional stability for uniformity, ride and handling. Table 2 summarizes the effects of reinforcements on tire performance.

Table 2 - Reinforcement and Tire Properties (adapted from Kumar, 2016)

Tire Performance Parameter	Effects of Reinforcement
Burst strength	Cord tensile strength
Bruise and cut resistance	Increase hot tensile strength and rigidity
Durability	Fatigue resistance, adhesion
Power loss	Hysteresis, density
Tire dimensional stability	Modulus, creep, stress relaxation
Uniformity; Flat spotting	Glass transition temperature, creep, modulus
Tread Wear	Modulus
Noise	Creep
Spring rate	Modulus

The global textile market size for tire cords was estimated to be US \$ 5.5 billion in 2019. From 2020 to 2027, it is expected to grow at a Compound Annual Growth Rate of 3.4 %. For instance, polyamide tire cords, with a 56.3% revenue share, are the largest segment in the global market. Geographically, the Asia Pacific region is the largest market for textile tire cords in 2019, with a 47% market share. The main reasons are the local availability of important raw materials such as natural rubber, increased capacity and the dramatic increase in demand for automobiles in Asia over the last decade. In addition, the fundamental trends of major corporations, driven by market segmentation, focus on individual areas, e.g., new products such as aramids and hybrid cords, growth to meet quality requirements (tonnage) and supply safety of the global tire industry and the integration to control supply and cost (Wilson, 2016; Zhao, 2020).

2.3.1 Fabric Tire Cords

There are five main types of fibers used in the manufacture of tire reinforcements: cotton, rayon, nylon, polyester and aramid. Cotton was the first reinforcing material, but it is increasingly being replaced by other synthetic fibers.

High molecular weight polyamides and commonly known as nylon, were also one of the first synthetic polymers used in textile applications and can be divided into aromatic and aliphatic polyamides. This last group can be represented as either PA-x or PA-x.y, where x and y correspond to the number of carbon atoms between nitrogen atoms. There are several types of nylon polymers available but only two have found application in tires, particularly for medium/heavy-duty truck and off-road tires: PA 6.6 (Poly[imino(1,6-dioxohexamethylene) iminohexamethylene] and PA 6 (polycaprolactam) (Cruz, 2014).

PA 6.6 is the most used in the tire industry and is produced from hexamethylene diamine and adipic acid. Figure 2 shows PA 6.6 molecular structure. On the other hand, PA 6 is synthesized by ring-opening polymerization of ϵ -caprolactam. Both materials have similar properties, but PA 6.6 has a weakness in cost. However, this last one shows higher resistance to moisture uptake and improved moisture tensile strength (Deopura and Padaki, 2015).

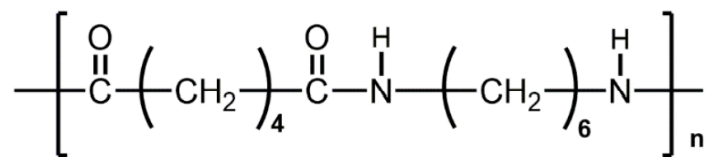


Figure 2 - PA 6.6's molecular structure (Zhao, 2020).

The morphological structure of high-strength nylon comprises microfibril regions and inter-microfibril regions. The microfibril region is composed of crystalline and amorphous regions, whereas the inter-microfibril region is made of oriented molecular chains (Figure 3).

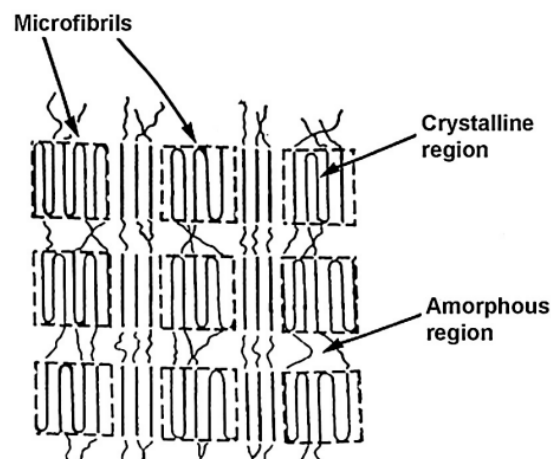


Figure 3 - Microstructure of highly orientated polyamide fibers (Deopura et al., 2015).

In the early 1960s, polyester cords were introduced by the Goodyear Tire Company to reinforce passenger car tires (Takeyama and Matsui, 1969). Polyester is a category of synthetic long-chain polymer that contain ester functional groups in the backbone. This generally is referred as polyethylene terephthalate (PET) which is a condensation polymerization product from ethylene glycol and dimethyl terephthalate or terephthalic acid (Deopura and Padaki, 2015). Figure 4 illustrates PET's molecular structure. Nowadays, it is the most used fiber worldwide in tires and it is applied on the carcass of radial tires for passenger cars or light trucks.

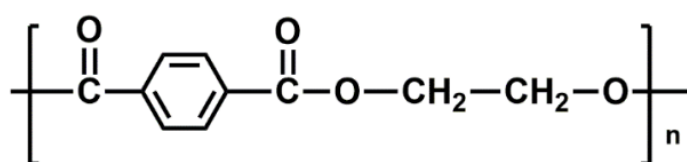


Figure 4 - PET's molecular structure (Zhao, 2020).

In its natural state, PET is a semi-crystalline resin and similar to polyamide fibres, polyester fibres are composed of a partially oriented and partially crystalline structure.

As these structural characteristics affect a wide range of properties, from optical to mechanical, reproducible control of the crystallinity and morphology of PET and PA 6.6 semi-crystalline polymers is essential for their usability in many applications. However, the morphology is dependent on processing techniques and conditions. Since semi-crystalline polymers have multiscale structures ranging from crystal unit cells to lamellae crystal to spherulites, it is difficult to find connections between the processing-microstructure-mechanical properties (Ye *et al.*, 2017). The processing conditions, such as the temperature, which regulates both the nucleation rate and the crystal growth rate to impact the size and crystallinity of spherulite, influence multiple length scales.

On the other hand, the high crystalline polymer poly p-phenylene terephthalamide, more known as aramid is a wholly synthetic aromatic polyamide. Para-aramids are synthesized by a poly-condensation reaction between p-phenylene diamine with terephthaloyl dichloride in an n-methyl pyrrolidone solvent (Pereborova *et al.*, 2019). Figure 5 illustrates para-aramid's molecular structure.

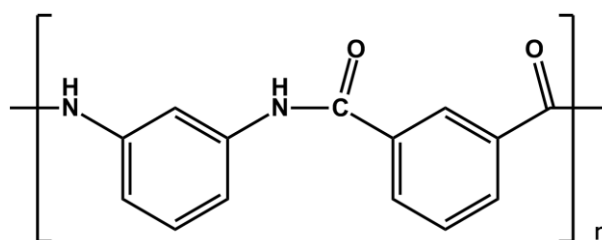


Figure 5 - Para-aramid's molecular structure (Zhao, 2020).

In the case of para-aramid, the presence of amide bonds in the polymer chain favours an extended chain structure that supports the formation of liquid crystals. Therefore, the resulting para-aramid fiber structure is composed of fully elongated chains with a very high degree of crystallinity and orientation (Deopura and Padaki, 2015). The relatively high cost has delayed its application as a common radial belt material for which steel cords work well. Thus, aramid is especially useful when weight is important, such as belts for radial aircraft tires or overlay layers for premium high-speed tires (Rodgers, 2020).

Though its use is now very restricted, due to its high cost, limited supply and environmental concerns, rayon is also an excellent choice for passenger car tires. This material is regenerated cellulose produced as a continuous filament and spun into yarn (Cordenka, *n.d.*).

Along these lines, textile reinforcements confer well-known and specific properties according to their application. ITA, at the moment, uses the four different fibers mentioned above as raw materials. Annex C presents some additional properties of these textile reinforcements.

Nevertheless, there can always be enhancements, and finding new materials with unmatched characteristics is always an objective. One way of obtaining this is through hybrid cords, which are the combination of two or more different types of yarns twisted together. Using the example of the aramid-nylon cord, this structure has better properties than the aramid-aramid structure, since it improves fatigue resistance, increases elongation, lowers raw material costs and reduces shrinkage. Compared to the nylon-nylon construction, the hybrid cord has less shrinkage and improved handling and cornering stability, speed performance and rolling resistance.

2.3.2 Manufacturing

All textiles used for tires are specially prepared and processed to build a structure called fabric or single-end cords (SEC). To obtain them, a series of processes of spinning, twisting, weaving and dipping is required.

First, the filament yarns are picked up and each filament runs the entire length of the yarn. The spinning process allows the polymer to be converted into a variety of denier and twisted continuous thread yarns and it usually includes numerous steps. The polymer is produced first (*e.g.*, polymerization and chemical modification). Afterwards, the spinning solution (molten polymer) is then extruded through the spinneret. This is followed by a stretching process which increases the molecular orientation of the filament and improves fiber tenacity, modulus, and elongation. Finally, the filament is heat treated and converted into a yarn. There are different types of spinning such as dry, wet, gel and melt spinning that is applied to each fiber depending on physical and chemical properties. Some of the spinning processes also include cord construction (Kramer, 2013; Cardoso, 2014; Cruz, 2014).

The next step is the twisting process. At this stage, untreated material, called greige yarns, is twisted to improve the elasticity and fatigue resistance of the fabric and other types of deterioration associated with tensions by refining the strength, flexibility and weight. The twisting process can be completed in one or two steps, either by twisting the cords directly or by first twisting the yarn and then twisting the cords. If the cable can be obtained in one step, the direct cabling method is adopted and the yarns are twisted together in a single operation without introducing twists to form individual yarns. If the cord is manufactured in two stages, the processes used can be flying spinning, ring spinning or two-for-one twisting and it is conceivable to obtain a cord with different twists on plies and cord. In addition, a cord or yarn can be twisted in the “Z” (clockwise) and “S” (counter-clockwise) directions (Couto, 2015). Annex D presents in more detail information about twisting and cord construction.

Applying a twist in the yarn causes the fibres to follow a helical path along its axis. The geometry of yarn can be described by the helix angle and the pitch length or the yarn diameter. Figure 6 exhibits the ideal filament path and the geometry of a helical filament where the cylindrical yarn geometry is unfolded (Hearle, Grosberg and Backer, 1969). At a particular radius r , and for a length of one turn of twist h_l , the helix angle θ , is given by Equation 1. In addition, α represents the value of θ at the surface of the yarn.

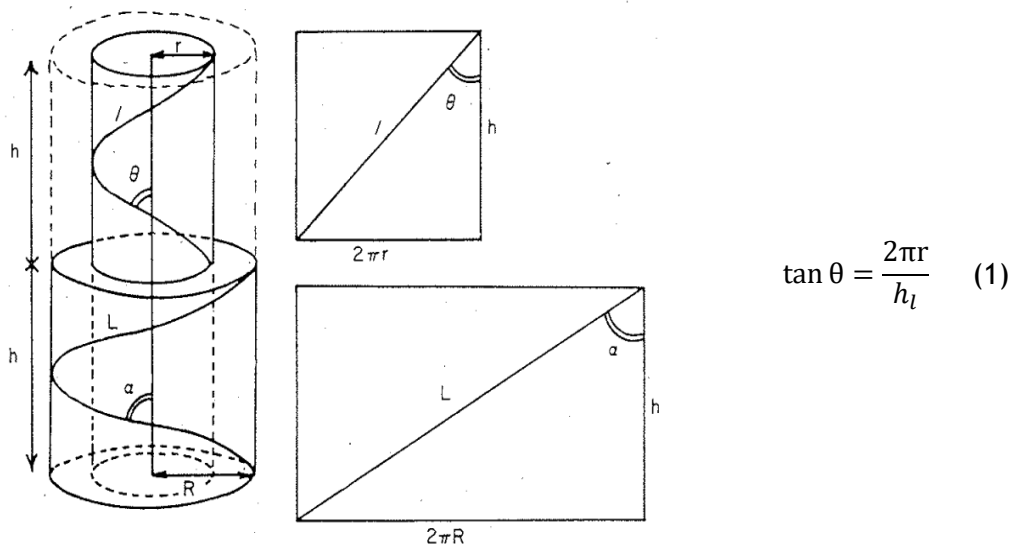


Figure 6 - Geometry of an idealized twisted yarn (adapted from Hearle et al. 1969).

As the twist of the cord increases, the helix angle upsurges and the tensile stress, perpendicular to the cord axis, results in greater-force parting filaments. The reason for the decrease in strength can also be confirmed in Figure 7, whereupon the force, in the yarn axis direction, increases and the overall breaking strength decreases. Furthermore, according to Gafurov *et al.* (2015), the stiffness of fibers located in the helical line generally increases to a certain level and then begins to decrease by increasing the predisposition of the helix angle. As a result, the irregularity of the microstructure of the yarn and range of characteristics for yarn deformation

(such as breaking load) and the simultaneous interaction of a great number of complex physical phenomena can provide difficult assessments in terms of its modelling and precise measurement.

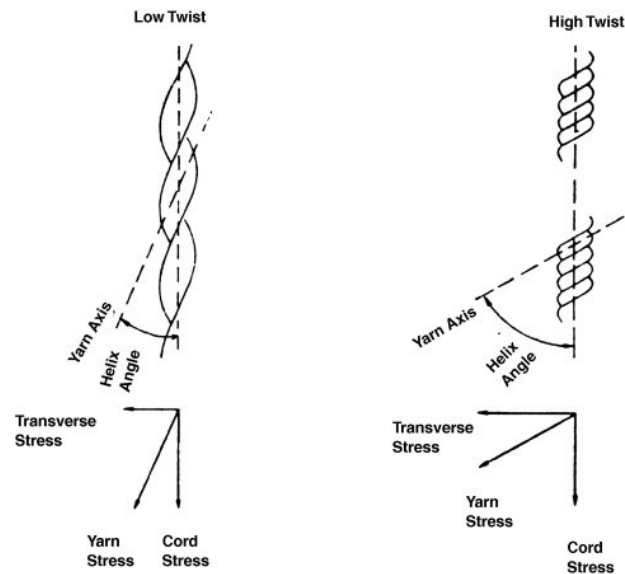


Figure 7 - Cord geometry and stresses for low and high twist levels (Rodgers, 2020).

Along these lines, since twisting is a determining factor in the mechanical properties of cords, it is commonly used the numerical value of the twist factor, which represents the measurement of the spiralling orientation of the fibers in a spun yarn (Kramer, 2013). It correlates together the linear density and the twist level, as represented in Equation 2.

$$TF = \text{Twist level} \sqrt{\frac{\text{Total cord dtex}}{10\,000}} \quad (2)$$

After twisting, the fabric greige cord is produced through the weaving process. This can be done under different conditions depending on the function of the fabric. A certain number of cords are arranged in a longitudinal direction (end of the warp) and interwoven with the weft of the loom (transverse direction) (Cardoso, 2014). As a result, the outcome is an organized arrangement of reinforcement cords that can be transferred to further operations.

The dipping procedure is the last step in the manufacturing process of textile reinforcements. The cords or fabric are dipped into a solution of Resorcinol, Formaldehyde and Latex (RFL) and then stretched, through drying, in the ovens at the optimum conditions to achieve the requisite adhesion and appropriate mechanical qualities. In some exceptional situations, such as with most PET and some aramid fibers, the cords are first dipped in a pre-dip solution made primarily of isocyanates and polyepoxy (Pacheco, 2014). Afterwards, the rubber is calendered onto the fabric sheet at 100 °C. Annex E and Annex F illustrate the schematic layout of the dipping process and the calendaring unit for textile reinforcing. Further details regarding these steps can also be found in these annexes.

2.4 Thermal Effects in Tire Cord Reinforcements

The velocity and spatial range of molecular motion are highly temperature dependent and define the number of thermal transitions observed in the polymer. The two most important thermal transitions are the glass-to-rubber transition characterized by temperature T_g , and the melting of crystalline elements characterized by temperature T_m (for semi-crystalline polymers). Below T_g , the material is in its hard glassy state, and molecular motions are limited to side chains since the molecules cannot overcome the energy barriers due to intramolecular repulsion. However, there could be some short-range conformational movements within the amorphous phase. In this region, some irreversible shrinkage may also be possible if solvent or water evaporates from the fiber and introduce free volume in the polymer (Magalhães, n.d.; Trznadel and Kryszewski, 1992).

Furthermore, at temperatures lower than T_g the sample exhibits reversible thermal expansion. In this expansion area, one of the most common techniques is to measure the linear isobaric expansivity, also called the coefficient of linear thermal expansion (CLTE, α_L) with respect to temperature at constant pressure P , according to equation 3 (Menczel and Prime, 2008).

$$\alpha_L = \frac{1}{L_0} \left(\frac{\Delta L}{\Delta T} \right)_P \quad (3)$$

Isotropic surfaces (Figure 8, a) have the same topography independent of measuring direction, and therefore, the coefficient of linear thermal expansion is identical along all three axes. However, anisotropic (Figure 8, b) materials have clear directionality and differ considerably in roughness and the properties of the materials are not the same at all points or directions which provides difficult assessments in terms of determining the CLTE (Kramer, 2013). In semi-crystalline polymers, such as PET, PA 6.6 and PA 6, both areas are coexisting.

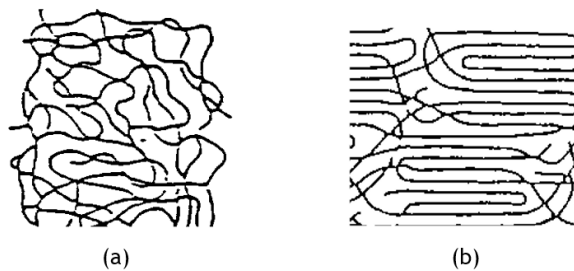


Figure 8 - Isotropic (a) and Anisotropic (b) materials (adapted from Kramer, 2013).

The following paragraph describes a typical shrinkage curve for a drawn, partially crystalline fiber. For a better understanding of the concepts mentioned below, Figure 9 provides a schematic illustration of a typical shrinkage thermogram at zero load for a drawn partially crystalline fiber, with the respective trace of the first derivative of the shrinkage dS/dT .

Regarding the glass transition region, the fiber exhibits a quick, irreversible shrinking at T_g as a result of the relaxation of oriented amorphous chains (the corresponding peak observed in

the dS/dT trace corresponds to the temperature of the maximum rate of this relaxation). Reorganization and recrystallization may occur in the temperature range between T_g and T_m . Furthermore, at high temperatures above T_g , which is the start of the backbone chain mobility in the amorphous region, the material becomes soft and rubbery and increased segment mobility allows for certain structural transformations, such as increased chain packing and crystallite growth. Above T_m , the crystallites melt and all materials are in a highly viscous liquid state (Magalhães, n.d.; Menczel and Prime, 2008). Variations and overlaps in the regions mentioned can be anticipated, depending on the process's characteristics and structure.

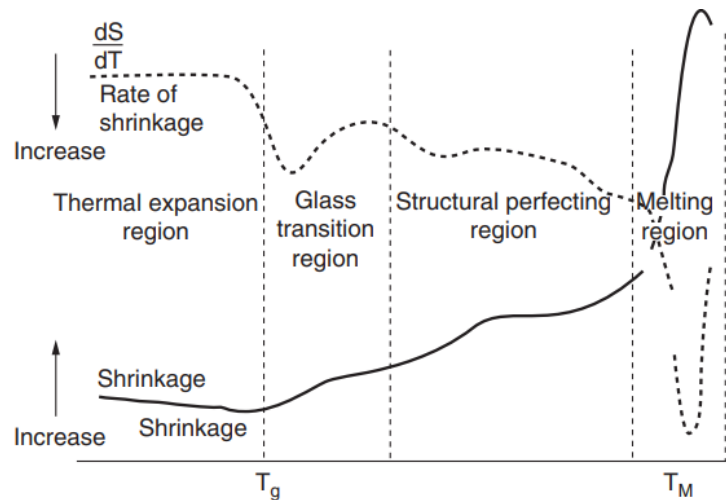


Figure 9 - Thermogram of a drawn, partially crystalline fiber, with the representation of shrinkage and differential shrinkage (Menczel and Prime, 2008).

Furthermore, when considering the placement of polymers in reinforcement materials, special attention should be paid to the mutual orientation of the chain elements. In oriented materials, there is a specific direction in which the chain segments are aligned, as opposed to anisotropic or isotropic ones that do not have macroscopic order. In fact, the presence of macromolecular crystalline structure means macromolecular orientation, but only at the local microscopic level, which is limited to the volume of a single microcrystal. However, in unoriented polymers, the crystalline domains are distributed in a non-oriented manner, forming a macroscopically isotropic material with randomly arranged amorphous phase chains. Therefore, the changes in mechanical properties and shrinkage behaviour are correlated with the change in crystal structure and fiber orientation, *i.e.*, an increase in crystallinity will spatially fix the oriented amorphous regions through their partial immobilization, and thus will reduce shrinkage.

During the manufacturing of the tire cord reinforcements at Continental, through a series of thermomechanical operations, high draw ratio molecular structures with orientated chains in the fiber direction are created from polymeric fibers. The amorphous zones are frequently organized by this heat setting under load, which also alters the existing crystalline sections. It is possible that crystallites will undergo some modification, including a change in their size and

shape. Additionally, larger crystallites may become more perfect during heat setting by eliminating flaws from the crystals. As a result, a compact packing of molecules is the product of orientation.

Even though polymeric fibers are strongly orientated and crystallized, amorphous zones still exist in the yarns and have a substantial impact on the material characteristics of cords. According to Kramer (2012), the shrinkage is proportional to the volume fraction of amorphous material and to the orientation in amorphous segments. Therefore, when exposed to high temperatures, thermoplastic cords, such as nylon and PET, which are a mixture of crystallites and amorphous domains, exhibit some tendency to shrink. Further investigations, performed by Cruz (2014), have shown that it is expected lowest shrinkage values for PET.

On the other hand, it is noteworthy to mention that the free energy of an ideal polymer chain is derived from its conformational entropy. At any given temperature, macromolecules tend to assume the most favourable conformations and to increase chain packing, reaching thermodynamic equilibrium. The difference between the energy and entropy components of the macromolecules that make up a polymer system often represents the thermodynamic potential. With the extension of the chains, the entropy (measure of how many ways the desired arrangement can be realized) decreases. If this decrease is not accompanied by a substantial drop in internal energy, the value of the thermodynamic potential increases, shifting the system further from equilibrium (Trznadel and Kryszewski, 1992; Rath, Chaki and Khastgir, 2012). Therefore, the stability of orientation depends on the changes in internal energy which are determined by the interactions between the neighbouring elements of polymer chains.

Along these lines, numerous monographs have discussed the presence of entropic forces acting at the ends of the chain segments. Due to the micro-Brownian movements of thermally vibrating molecules, the chain changes its conformation. If the chain ends are fixed, a force operating along the line connecting the ends is applied to them (Figure 10). This force originates only from entropy and is brought about by the chain's propensity to acquire the most coiled shape. This force can be determined by equation 4, where T is the absolute temperature, k is the Boltzmann constant, a is the length of the chain link, r' is the end-to-end distance, and L' is the length of the fully extended chain (Trznadel and Kryszewski, 1992).

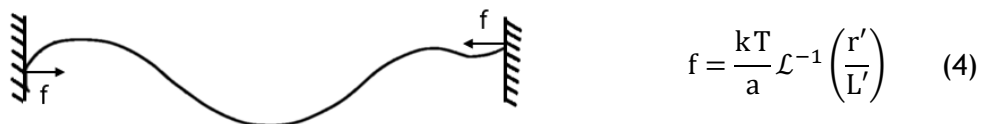


Figure 10 - Schematic representation of a force acting on the restrictions of a single, freely rotating chain that is maintained at a fixed length.

3 Materials and Methods

As an overall introduction to the experiments performed to assess the proposed methodology, this chapter describes all the techniques and procedures used in this project. Section 3.1 presents the experimental setup used to obtain the results and the planning of experiments, that allowed the extensive analysis of thermal-induced axial shrinkage, is presented in section 3.2.

3.1 Thermal Analyses

Thermal analysis setups refer to a group of measurement methods that share a common feature: they gauge how a material reacts to heat or cold (or, in some cases, held isothermally). The objective is to establish a relationship between temperature and particular material attributes. The most widely used methods, in the tire reinforcement industry, are those that are the subject of this thesis, namely thermomechanical analysis (TMA) and differential scanning calorimetry (DSC).

3.1.1 Thermal Shrinkage Tester

Thermomechanical analysis is a highly beneficial thermal-analysis method with several practical applications. While the sample is being treated to a controlled temperature program, TMA monitors the dimensions changes. Additionally, it can quantify the forces that are shaped in the sample when dimensions change in relation to temperature.

The applied load, atmosphere and time-temperature are the three main influencing factors in TMA measurements. The fact that the parameters measured by TMA (length change, stress, and time/temperature) are the same as the key factors affecting fiber processing, gives it a significant edge in the field of fiber research (Menczel and Prime, 2008).

Determination of end-use properties such as shrinkage, shrinkage force and CLTE is the major TMA application in fiber research. As previously mentioned, the main focus of this project lies in the investigation of parameters that may influence shrinkage. Several methods can be used to determine the shrinkage of multifilament yarns. The methods mainly differ in heat medium in which boiling water, hot air (oven) and steam are commonly used. The Lenzing Instruments Thermal Shrinkage Tester (TST) 510/250, used in this project, makes efficient quality control simple by testing up to 10 samples at once in the same test run to determine the thermal shrinkage and/or shrinkage force brought on by heating the materials at a pre-set and defined temperature for a specified period of time in an oven (static conditions) (Lenzing Instruments, *n.d.*). Additionally, TST 510/250 provides the option of dynamic tests, where the behaviour of

the yarn is assessed while it is exposed to a temperature ramp at a constant rate of temperature increase. However, no tests have been performed under these last conditions.

Together with the high-resolution length measuring sensors and load cells, the specifically developed oven-type heater safeguards the measurement from any external ambient influences. In addition, TST 510/250 ensures stable testing conditions, the utmost level of accuracy and results that are repeatable. On the linked computer, a graphic representation of the heated yarn's whole shrinkage or shrinkage force behaviour is shown throughout the test.

All trials should be performed according to ASTM D5591, ASTM D4974 and DIN 53866. The schematic representation of the experimental setup TST 510/250 is illustrated in Figure 11. Temperature variations throughout these testing procedures shouldn't exceed 2°C and the samples are placed on the measurement instrument and pre-tensioned. According to the standards and in order to have a taut cord, the prescribed pre-tensioning mass should be applied to the free end of the specimen with the right mass (see Annex H) outside the right-hand post. The samples are then subjected to 180 °C for 2 minutes and cooled down for another 2 minutes at room temperature. For each cord construction, an average of three measurements should be taken to confirm the reproducibility of the data.

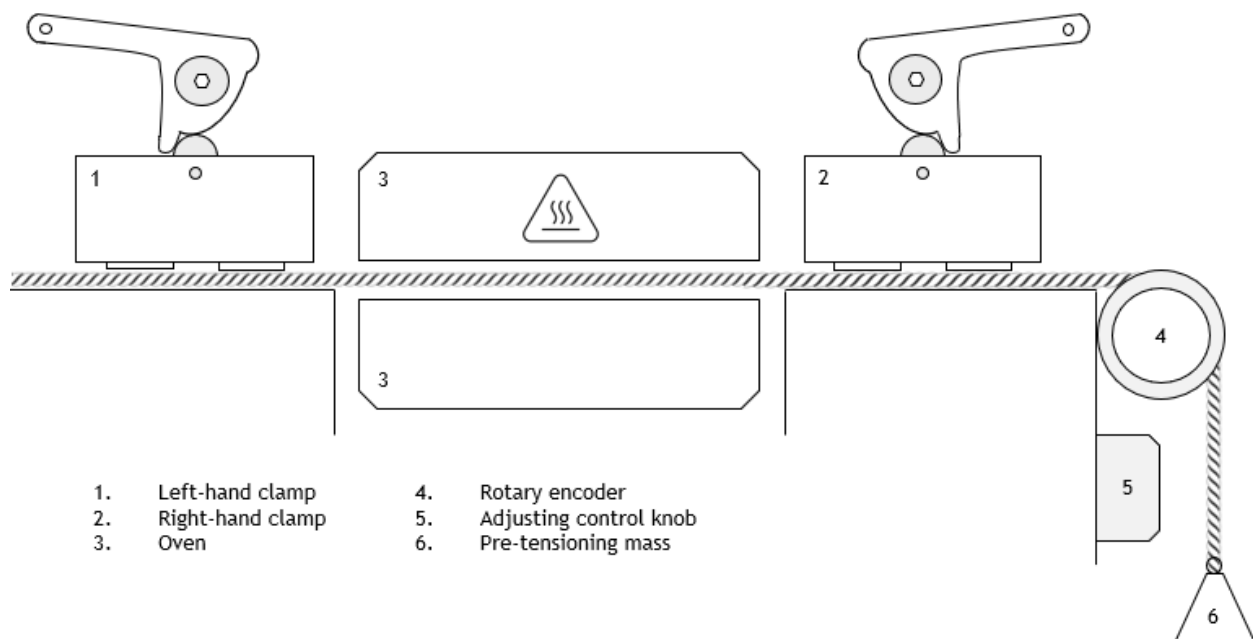
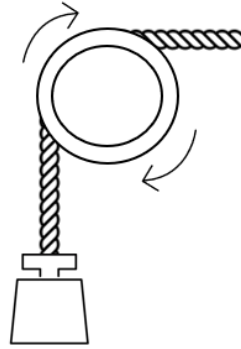


Figure 11 - Schematic representation of the TST 510/250.

For the thermal shrinkage measurement, clamp 1 should be closed and clamp 2 fully open so that it does not affect the rotational sensor (4). An encoder wheel attached to an encoder's shaft is what makes up a measuring wheel or follower-wheel encoder. The wheel interfaces directly with the surface of the material being measured and, as the material moves relative to the encoder, the wheel turns, rotating the encoder code disc and generating a signal, *i.e.*, as the cord moves, the transducer produces an electrical signal that is proportional to the

cord's linear extension or contraction (Figure 12). To calculate the length travelled, it is used the output from an incremental encoder and the thermal shrinkage can be calculated by Equation 5. Here, L_0 represents the initial length of the sample before thermal application and L is the length, between the same data lines, after subjecting to the thermal application. Positive values indicate thermal shrinkage and negative values indicate thermal expansion.



$$\% \text{ Shrinkage} = \frac{(L_0 - L)}{L_0} \cdot 100 \quad (5)$$

Figure 12 - Schematic representation of the operating principle of the rotary encoder for the shrinkage measurement.

On the other hand, the strain gauge underneath clamp 1 allows the measurement of shrinkage force, converting mechanical strains into resistance change. When the shear force is applied on the upper surface of the sensor, the upper layer moves with respect to the lower layer in the direction of the applied shear force. This relative movement between the layers results in a change in the distance between the upper and lower electrodes. As a result, the current flowing between the upper electrode and the lower electrode increases or decreases, according to whether the cord is contracting or expanding, respectively. The x-axis shear force sensor's working principle is depicted schematically in Figure 13.

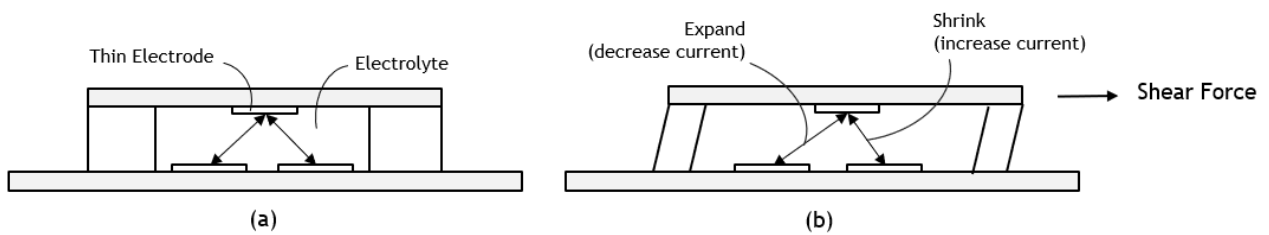


Figure 13 - Schematic representation of the operating principle of the shear force sensor for the shrinkage force measurement. Resting-state (a) and shear force-imposed state (b).

Furthermore, it is noteworthy to mention that there are numerous error sources when measuring strain. Among these measurement deviations, it stands out the fact that there is an uncertainty of the gauge factor (typically 1 %), non-linearity of the Wheatstone bridge circuit, load application, external influences (e.g., temperature gradient, humidity and electromagnetic interference), among others. Therefore, it is essential to perform calibration periodically to assure the accuracy and linearity of the instrument itself. More often, calibration

is frequently required to scale the instrument's sensitivity (by altering the gauge factor) such that the recorded output corresponds easily and correctly to some specified input.

3.1.2 Differential Scanning Calorimetry

The ASTM standard E473 defines DSC as a method in which the sample is submitted to a controlled temperature program while the heat flow rate differential, between the substance and a reference is measured as a function of temperature. The sample and reference are separated from direct contact with the sensor and encapsulated in a pan, constructed of a high-thermal-conductivity material, such as high-purity-aluminium (Menczel and Prime, 2008).

For this project, the equipment used was the DSC 1 Mettler Toledo which uses a grouping of thermocouples called a thermopile, as illustrated in Figure 14. The thermocouples are linked in series using a symmetric zigzag design. The difference between the heat fluxes to the sample and reference is proportional to the difference between the sample and reference thermopiles.

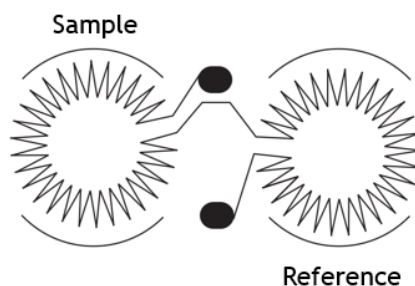


Figure 14 - Schematic representation of a thermopile used in a DSC 1 Mettler Toledo (adapted from Menczel and Prime, 2008).

The DSC studies were performed under a nitrogen atmosphere at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$. Noteworthy to mention that the DSC curves' shape and the conclusions drawn from them are both influenced by the heating rate. At fast heating rates, the temperature resolution drastically decreases because of the large temperature gradients within the sample and hence a dramatic increase in the thermal lag¹. The substantial temperature gradients in the sample will also cause wider transitions with reduced resolution and increased thermal latency when the sample mass is too large. As a result, lower heating rates (and small sample masses) are preferred for high resolution, however, this reduces the instrument's sensitivity and necessitates longer DSC runs durations.

Numerous distinguishing qualities of a sample can be measured using differential scanning calorimetry. This method allows the observation of glass transition temperatures as well as

¹ **Thermal lag** | Difference between the average sample temperature and the sensor temperature and is caused by so-called thermal resistance, which characterizes the ability of the material to hinder the flow of heat.

fusion and crystallization events. As the temperature of the amorphous solid rises, glass transitions may take place. These changes can be seen as a step in the baseline of the DSC signal that was recorded. No formal phase transition takes place and instead, the sample's heat capacity changes as a result. An amorphous solid will become less viscous as the temperature rises. The molecules might eventually acquire sufficient motional freedom to spontaneously organize themselves into a crystalline structure. This transition from amorphous solid to crystalline solid is an exothermic process and results in a peak in the DSC signal. The sample gradually approaches its melting point as the temperature rises and the signal exhibits an endothermic peak due to the melting process. As an illustration, Figure 15 shows the DSC heating curve of quenched (*i.e.*, cooled at an extremely high rate) PET fibers.

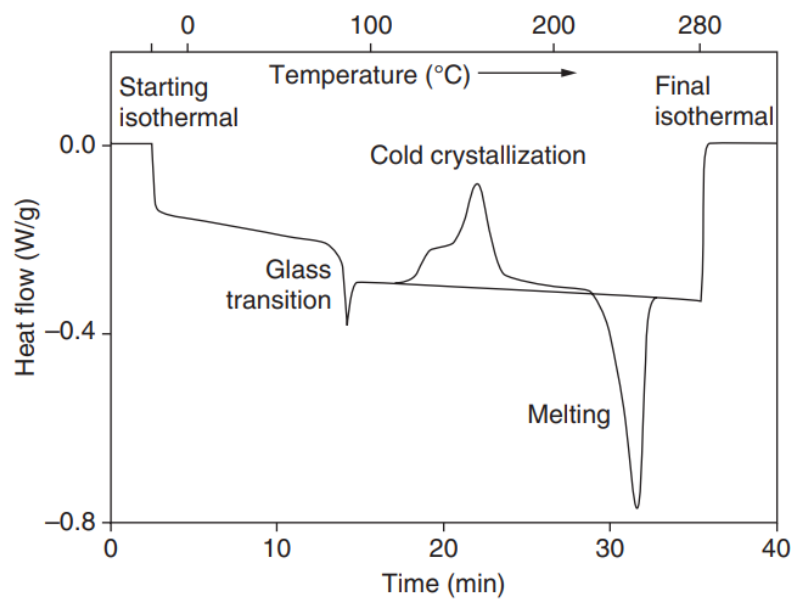


Figure 15 - Typical DSC heating scan of quenched PET fiber (Menczel and Prime, 2008).

Furthermore, the crystallinity can be calculated with Equation 6, in which X_{cr} is the crystallinity, ΔH_m is the heat of fusion calculated from melting endothermic peak, ΔH_c is the heat of cold crystallization and ΔH_m^0 is the heat of fusion for pure polymer crystals (Table 3).

$$X_{cr} = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \quad (6)$$

Table 3 - Polymer Heats of Fusion (Menczel et al., 2008).

Polymer	$\Delta H_m^0 / \text{J} \cdot \text{g}^{-1}$
PET	140.1
PA 6	230
PA 6.6	255.8

3.2 Materials and Design of Experiments

For this project, it is intended to analyze all the textile tire reinforcements available in Continental's portfolio, with the exception of rayon cords. However, an understanding of thermal shrinkage and elucidation of the mechanism responsible for the contraction of oriented semicrystalline polymers, such as PET and Nylon, is the fundamental objective.

Therefore, according to Figure 16, to evaluate the influence of pre-tension, oven exposure time and temperature in the shrinkage force behaviour of these cords, individually, an experimental design for the evaluation of process parameters based upon three levels full factorial response methodology was utilized. The experimental designs were performed using Minitab statistical software. Noteworthy to mention that the chosen temperatures of 180 °C and 100 °C on this DOE, allow the simulation of the processes of calendaring and vulcanization (Annex F and G provide a full description of these processes). The times were chosen as a function of the one used in the standard model and the pre-loads were chosen randomly.

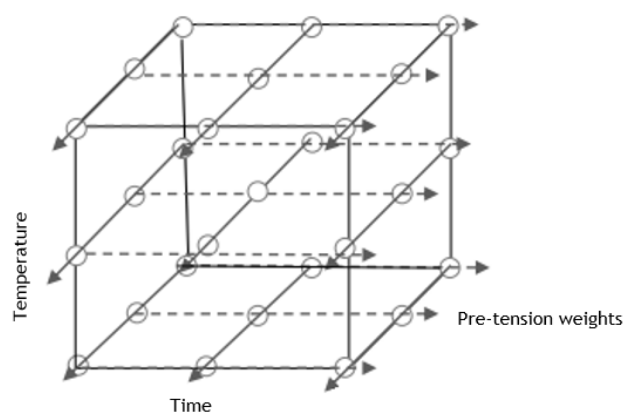


Figure 16 - Schematic representation of the 3^k Factorial Design.

Furthermore, to complement the results and to analyse constrained oriented polymers when subjected to temperatures which are not sufficiently high to bring about immediate shrinkage, tests were also performed at temperatures below T_g . In addition, this project considers the behaviour of the cords, accounting the influence of the twist level that each cord construction has, as well as the variation in total decitex between the cords. Regarding this, it became pertinent to study the effect of different twist levels (keeping in mind that it is desired a similar range of twist factor for thin cords and thick cords, so that the results are comparable) and the state in which the cord is, *i.e.*, it is also relevant to perform an analysis beyond the standard dipped cord, using greige and rubberized cords.

Moreover, textile cords, in particular those composed of natural fibers or derived from cellulose, are referred to as moisture-sensitive products. During production or storage, some polymer fibers may absorb moisture from the surroundings. Therefore, the shrinkage properties of the fiber reinforcement materials can be affected under moisture influence and it is

pertinent to conduct an experimental approach for measuring this effect. However, to avoid high variations in moisture and temperature, since it can affect other mechanical properties of the fibers, the laboratory temperature and humidity are usually conditioned according to ASTM D1776 and ISO 139. The conditioning environment in the laboratory is designed to obtain reproducible results on textile and textile products.

On the other hand, supplier performance needs to be monitored continuously. This performance monitoring is important to be carried out as an evaluation material which can later be used to improve supplier performance or as a consideration to seek alternative suppliers. Therefore, this project was also the target of a supplier evaluation considering different converters and yarn producers.

To sum up, Appendix I, presents all the tests performed, which will be discussed in chapter 4.

Regarding the preparation of the samples, experience has shown that cords when taken from packages (bobbins) and left to relax for a while at room temperature, exhibit a contraction in length (and a resultant increase in linear density). They will, therefore, register larger thermal shrinkage force values if they are tested without being given enough time to relax because the relaxation shrinkage will be mistakenly included as the thermal shrinkage force. With this in mind, special care was taken to all samples taken from bobbins, putting them to relax for at least two days.

In addition, when performing shrinkage trials, it is also necessary to consider the mechanism of cord elongation. The cord has two important contributions, the material and the structural component. As such, when the load is applied to the cord, it will first go through a mainly structural elongation, followed by a section that consists mostly of material elongation. In this project, the maximum tension applied was 10 N and according to Gomes (2018), there is only reversible structural elongation at this uttermost range. Along these lines, some trials were performed on TST 510/250 to verify if the standard procedure for measuring shrinkage (ASTM D4974) is being appropriately employed, *i.e.*, if it is correct to start the test immediately after placing the pre-loads. The methodology used as well as the results obtained can be found in Appendix J.

The same premise is applied to the shrinkage force trials, however, for this case, it is not possible to perceive how much the structural elongation impacts the results. Nevertheless, in these measurements, it is necessary to consider the efficiency of the clamping force, which reflects the amount of force applied to the workpiece by closing and locking the clamp. It is generally less than the stated “holding capacity” which refers to the maximum external force that the clamp can safely resist in its locked position without incurring any permanent deformation. Along with these trials, it was also verified that there was some slippage in the clamps. Appendix K presents in more detail information about these clamping trials.

4 Results and discussion

This chapter aims to present the detailed results obtained. For this, firstly, a thorough analysis of the PET and Nylon materials, with the respective 3^k Factorial Design, was performed with a detailed assessment of the effect of time, temperature and stress. Later, to complement the project will be presented results for other materials present in the portfolio as well as other studies and investigations of variables already mentioned in the previous chapter.

4.1 Thermally induced shrinkage of PET

The DOE containing the 27 experimental runs was used to implement a Three-Level Full Factorial Design (Table 4) with the intention to carry out an experimental investigation of the thermally induced axial shrinkage force of PET with 1100 dtex x2 construction. This subchapter, it is intended to carry out a systematic investigation of time dependence of thermal shrinkage, particularly as it is related to temperature and stress. In addition, a comparison will be made with the results obtained for other constructions and with the DSC experimental data.

Table 4 - Design level with the respective factors under study.

	Factor		
	Pre-tensioning force / cN	Temperature / °C	Oven exposure time / s
Level	22	100	120
	147	150	240
	450	180	480

4.1.1 Time Dependence of Thermal Shrinkage

The percentage thermal shrinkage and shrinkage force of PET, with a 1100 dtex x2 construction, at 180 °C and constant load of 147 cN is plotted as a function of time in Figure 17. The tests were performed according to the oven exposure times listed in Table 4 and cooled down for another 2 minutes in a normal conditioning atmosphere.

As it can be observed, the initial rate of shrinkage of polyester yarns is high and more than 50% of the final shrinkage is reached within 30 seconds. The rate of shrinkage decreases significantly (denoting a non-linear time dependence) as the equilibrium is approached, which is attained even before 2 minutes. According to Andrews (1955), this persistent shrinkage equilibrium is reached only if macromolecular segments are frozen at sufficiently low temperatures after or during the orientation process (heat treatment). Such behaviour, together with the occurrence of external forces during constrained shrinkage, proves the existence of a persistent molecular

network which transmits the internal stresses, consistently, throughout the whole volume of the investigated material.

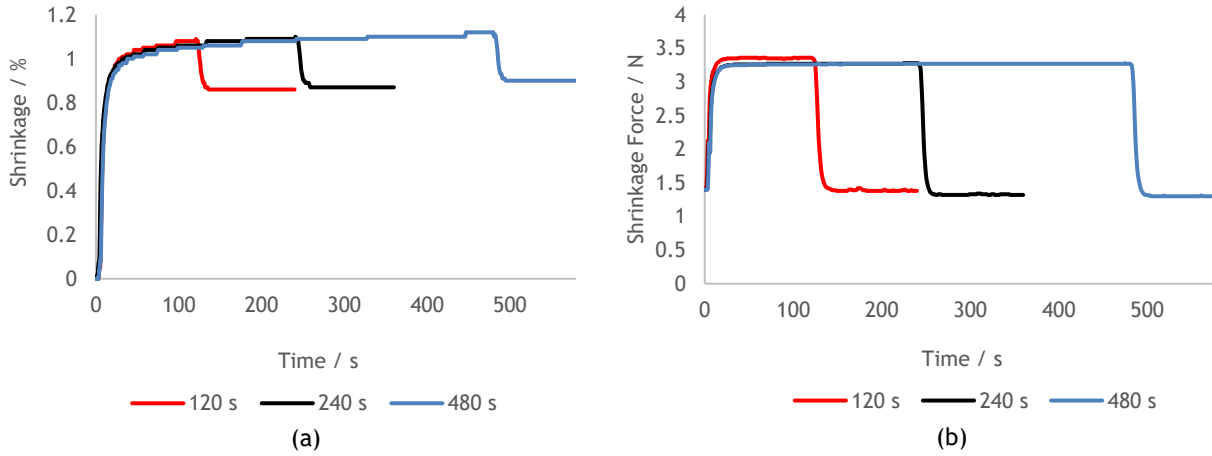


Figure 17 - Shrinkage (a) and Shrinkage force (b) as a function of time, for different periods of time.

Furthermore, the exponential damping behaviour may correctly be correlated with the viscoelastic properties in which several rate processes must be considered (such as creep). Based on experimental results linking thermal shrinkage to time, Ribnick (1969) proposed an expression such as the following Equation 7 to fit the experimental data, where $S(t)$ is the percent shrinkage at time t , s_n are a series of strains (similar to shrinkage) and k_n are a series of rate constants.

$$S(t) = \sum s_n(1 - \exp^{-k_n t}) \quad (7)$$

Noteworthy to mention that the series of rate constants are similar to viscoelastic relaxation times which govern time-dependent, *i.e.*, $k_n = 1/\tau_n$, where τ_n represents the reciprocal relaxation times. Equation 7 can also be achieved by performing an analysis of the kinetics of isothermal shrinkage (consult Appendix L)

Therefore, although thermal shrinkage and creep are independent phenomena, by using a similar analysis, it is possible to provide some physical interpretation to the overall mechanical modelling of thermal shrinkage.

Further investigations performed by Diaz and Youngblood (2016), and still making an analogy to creep, showed that the overall mechanical modelling of thermal shrinkage could be represented by stretched entropic springs, and dashpots, whose length contraction is mediated by force loads and temperature. Two Kelvin-Voigt units (*i.e.*, spring and dashpot in parallel) in series (Equation 8) can describe the increasing shrinkage response, where the first unit describes the rapid initial response and the second damps the response at long times. Although this model is apparently adequate, a dashpot unit should be added to obtain a partially reversible response of shrinkage, after the oven is removed (see Appendix M).

$$S(t) = \sum s_{n1} \left(1 - \exp^{-\frac{t}{\tau_1}} \right) + s_{n2} \left(1 - \exp^{-\frac{t}{\tau_2}} \right) \quad (8)$$

Furthermore, and considering that the residual shrinkage is the remaining change length, after the oven is removed, while the sample remains in the conditioned environment and pre-tension is maintained, it is evident from the shrinkage percentage plot that the contractile process is irreversible, in which only approximately 0.2 % of its initial length was recovered (due to thermal relaxation). Concerning the shrinkage force plot (Figure 17, b), the same conclusions cannot be drawn, since when the oven is removed, the entropic force decreases and, with the applied stress, the cord was able to return to its initial state of force (1.47 N). In addition, it is necessary to discuss the possibility of overlapping the shrinkage effects with dimensional, structural and properties (e.g., complex modulus transient behaviour) changes, which will be further investigated in subchapter 4.1.3.

4.1.2 Temperature Dependence of Thermal Shrinkage

To study the effect of temperature on shrinkage behaviour, experimental assays were conducted in accordance with the temperatures shown in Table 4, at a constant load of 147 cN and with an oven exposure time of 480 s. Along these lines, Figure 18 exhibits the dependence of shrinkage and shrinkage force as a function of time for different temperatures.

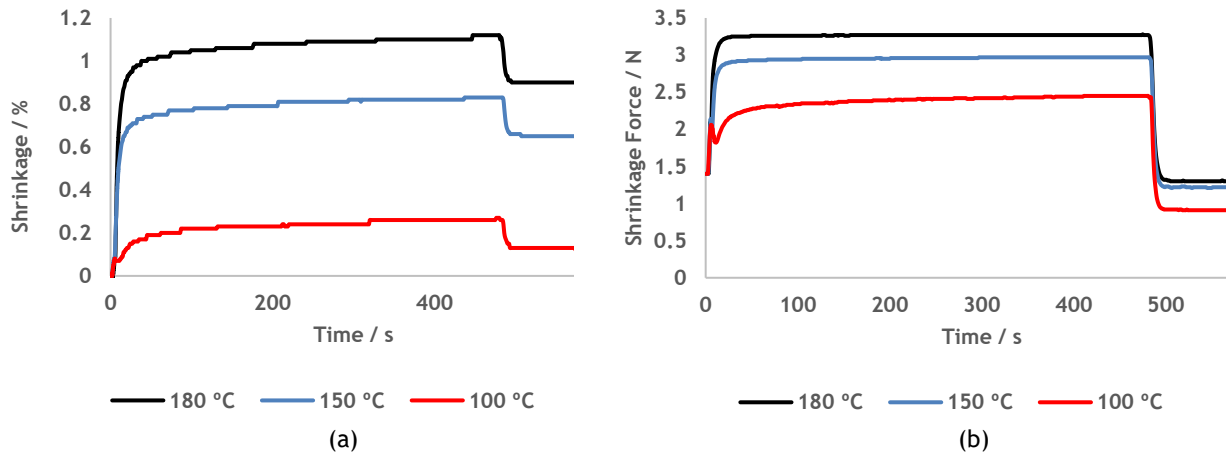


Figure 18 - Shrinkage (a) and shrinkage force (b) as a function of time, for different temperatures.

Once again, as can be seen in Figure 18, the PET yarns' initial rate of shrinkage is swift and the final equilibrium thermal shrinkage is obtained in less than two minutes for all temperatures. Similar to these results, thermal shrinkage has been demonstrated to vary exponentially with temperature, according to studies performed by Ribnick (1969). Equation 9 expresses this functional relationship, where ΔE_a is the activation energy, T is the absolute temperature, k and h are the Boltzmann and Planck's constants, respectively.

$$S(t) = \frac{tkT}{h} \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (9)$$

This relationship was based on Kambe and Kato (1973) who firstly proposed a straightforward, two-state model of the energy levels of a polymer segment to explain the process of the thermal shrinkage of orientated polymers. Tanabe and Kanetsuna (1979) subsequently adjusted the model to describe the shrinking of polystyrene monofilaments. They assumed that each of the polymer's molecular chains is divided into submolecules that can exist in either a contracted or an extended form, which is divided by an energy barrier. Figure 19 illustrates the contour of the energy change that occurs during state transitions, where k_f and k_b denote transition rates between the states and ε represents the energy difference between the states. It is possible to connect the relative contraction of a model macromolecule with the populations of the states by assuming a fixed number of submolecules in the chain (Trznadel *et al.*, 1992).

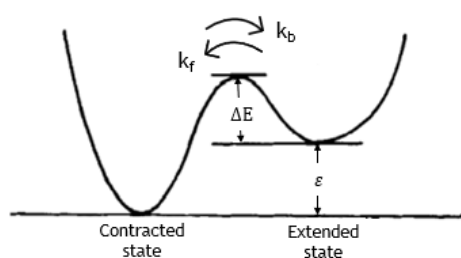


Figure 19 - Contour of the energy changes of a two-state model of thermal shrinkage (adapted from Trznadel, 1992).

This method is theoretically qualitatively well-aligned with experimental data, and quantitative fitting could allow the estimation of the activation energy of thermal contraction. The inverse relationship of Equation 9 is easier to use for this interpretation and may be rewritten:

$$t = \frac{h}{S(t)kT} \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (9)$$

If logarithms are taken of both sides of this equation, the shrinkage data may be plotted as $\log(tT)$ as a function of the inverse of the absolute temperature to determine whether there is adherence to the data and to evaluate the activation energy.

Despite this compliance, it was difficult to fully embrace the proposed conception on this project, which holds that thermal shrinkage solely entails energy changes and makes no mention of the process's actual entropic source, structural changes and external disturbances. As will be possible to analyse in detail in the next subsection, there are numerous factors that influence the results and the curves do not present a perfect exponential behaviour as indicated by this model, making it unreasonable to calculate the activation energy. Besides, the model does not predict the appearance of shrinkage forces at the ends of a sample kept at constant length because its individual subunits are treated as independent and not as interacting with each other and, on the other hand, it does not connect the simultaneous and individual contributions of thermal expansion, temperature dependence of elastic modulus and possible creep extensions resulting from residual stress.

4.1.3 Stress Dependence of Thermal Shrinkage

The influence of stress on the thermal shrinkage of PET cords was investigated at the temperatures mentioned in Table 4 and at temperatures below T_g . Figure 20 exhibits the dependence of shrinkage as a function of time for different pre-tensioning masses. Noteworthy to mention that this plot is for the temperature of 180 °C. The behaviour of the curves for the other temperatures is similar, as already noted in the previous subchapter.

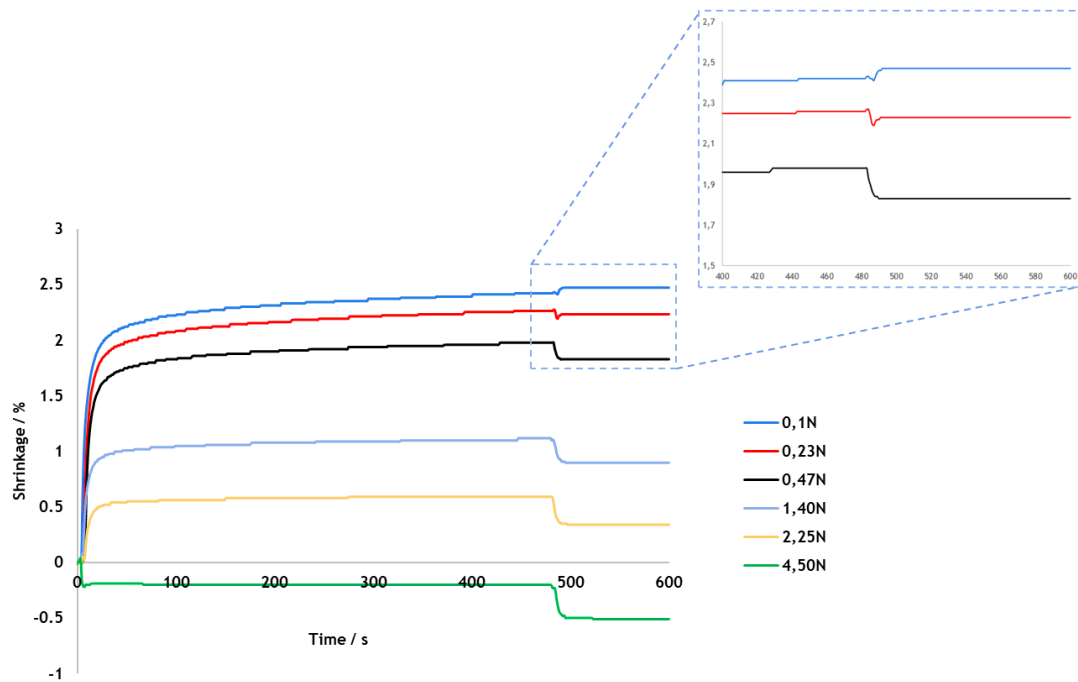


Figure 20 - Shrinkage of PET 1100 dtex x2 as a function of time, for different pre-tensioning weights.

As can be seen in Figure 20, the effect of increasing the load is to decrease the shrinkage quite markedly, as one might expect. The thermal shrinkage falls rapidly with increasing load, indicating that the functional dependency is an exponential one. In order to test this functional relationship between thermal shrinkage and load, Ribnick (1969) proposed Equation 10 as the intended expression to fit the experimental data, where b is a parameter proportional to the reciprocal of the stress f .

$$S(t) = \exp^{-bf} \quad (10)$$

In the stress field of the original absolute-rate theory of creep of polymers as a function of temperature and stress, the displacement volume, δ , is regarded as the molecular volume that has been moved by the motion of the force centres (intermolecular bonds). The displacement volume idea has been kept since it seems to apply to the thermal shrinkage of orientated polymers as a function of stress and temperature. Therefore, Tobolsky and Eyring (1943) subsequently used the notion of absolute reaction rates to construct a similar statement for the creep of polymers as a function of temperature and stress and, according to this analogy,

the parameter b is equal to $\frac{\delta}{2kT}$, where k is the Boltzmann constant and T is the absolute temperature.

Since δ and ΔE_a have theoretically equivalent significances with respect to stress and temperature, it may be useful to first consider how the dependences on stress and temperature for the thermal shrinkage of polyester yarns can be combined into a single mathematical expression. Therefore, the final expression (Equation 11) states that the thermal shrinkage increases exponentially with temperature (as its negative inverse) and decreases exponentially with the stress, the two principal modifying constants being the activation energy and displacement volume.

$$S(t) = \frac{t k T}{h} \exp\left(-\frac{\Delta E_a}{RT}\right) \exp\left(-\frac{\delta f}{2kT}\right) \quad (11)$$

Although this model is apparently quite accurate, it does not consider the fact that textile tire cords are materials with complex geometry and results of thermal shrinkage can be overlapped by structural and thermophysical properties changes such as enthalpy, heat capacity, volume and complex modulus, which behave differently from glassy state to rubbery state. For example, according to experimental tests carried out by Tian *et al.* (2020), during glass transition, the complex modulus², E^* (Equation 12), of thermoplastic tire cords (PET, PA 6 and PA 6.6) decreases rapidly and energy dissipation due to internal friction increases, thus making $\tan \delta^3$ (Equation 13) reach its peak value. However, below T_g , thermoplastic cords exhibit a high and constant dynamic modulus, where the modulus is quite high and the material becomes less soft and less fluid. On the other hand, in accordance with previous research performed by Prevorsek (1977) with the increase in static load applied to specimens, the polyester tire cord exhibited a higher dynamic modulus and a lower $\tan \delta$. This conclusion was later drawn by Tian *et al.* (2020) for the same material tested and presented in this subchapter (PET 1100 dtex x2), as illustrated in Figure 21. Analysing this figure, it is possible to confirm that, low temperatures caused molecular chain segments to become "frozen", and the polyester tire cords displayed a glassy form. With an increase in temperature, the intermolecular force weakened, the mobility of chain segments was activated and conformational changes occurred. These concepts

² **Complex modulus** | Defined as the ratio of the sinusoidal stress to strain: $E^* = \frac{\sigma(t)}{\varepsilon(t)} = \frac{\sigma_0 e^{i(\omega t + \delta)}}{\varepsilon_0 e^{i\omega t}}$ (12)

³ **Tan δ** | Represents the ratio of energy dissipated to energy stored per cycle of deformation: $\tan \delta = \frac{E''}{E'}$ (13)

E' | Storage modulus is a measure of the elastic character or solidlike nature of the material: $E' = \frac{\sigma_0}{\varepsilon_0} \cos(\delta)$ (14)

E'' | Loss modulus is a measure of the viscous character or liquidlike nature of the material: $E'' = \frac{\sigma_0}{\varepsilon_0} \sin(\delta)$ (15)

associated with the complex modulus, significantly affect shrinkage and will allow to understand some physical behaviours.

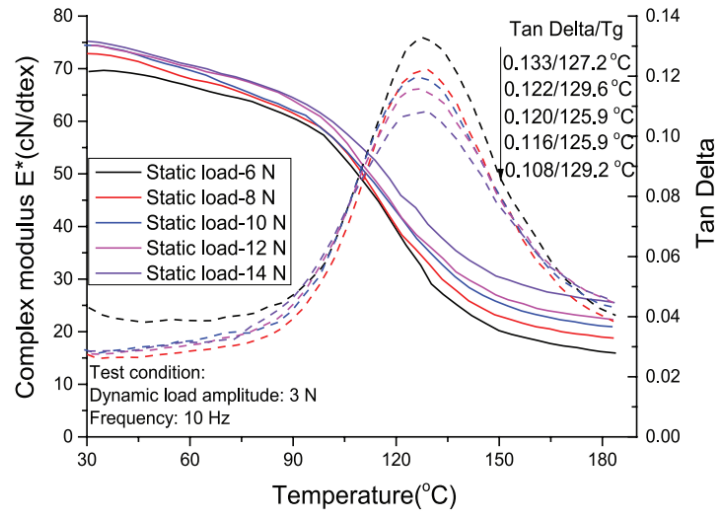


Figure 21 - Impact of temperature and load on dynamic modulus E^* and $\tan \delta$ (Tian et al., 2020).

Moreover, returning to the analysis of Figure 20, after removing the oven, it is possible to verify that for the trial with 0.1 N of pre-load, the shrinkage slightly increases. It would be expected that these values become constant or decrease since the entropic force, associated with the constant heat provided, decreases sharply leading to thermal relaxation. A plausible justification for this behaviour may lie in the fact that, when the oven is removed, the material will contract slightly since there is no longer orientation of the chains, *i.e.*, lower temperature means less free volume and the cord undergoes shrinkage.

This effect is not visible when the tensile loading is higher, since this stress overcomes the entropic force (which decreases with temperature) and thus causes the elongation of the cord. In addition, for the trial performed with 4.50 N of pre-load, it is observed that the force originated only from entropy is not enough to counteract the applied stress and therefore negative values are detected, given the fact that this decrease is due to thermal expansion, reduction of complex modulus and structural changes, until it reached the equilibrium.

On the other hand, the relationship between shrinkage force and time for various pre-tensioning masses is shown in Figure 22, for the temperature of 180 °C. Once again, it is firstly observed that for all the pre-loads used, the shrinkage force reaches an equilibrium after some time, *i.e.*, entropic forces of contracting segments are balanced by the reaction of external constraints. This causes the whole molecular system to be under load and hinders further shrinkage and increases the possibility of relaxation processes through the breakage of physical links leading to intermolecular slippage. In addition, it is observed that cords undergone free thermal shrinkage (pre-tensioning mass approximately 0 N) shows lower residual shrinkage values compared to cords subjected to higher stress since the pre-load is not enough to counteract the entropic force originated.

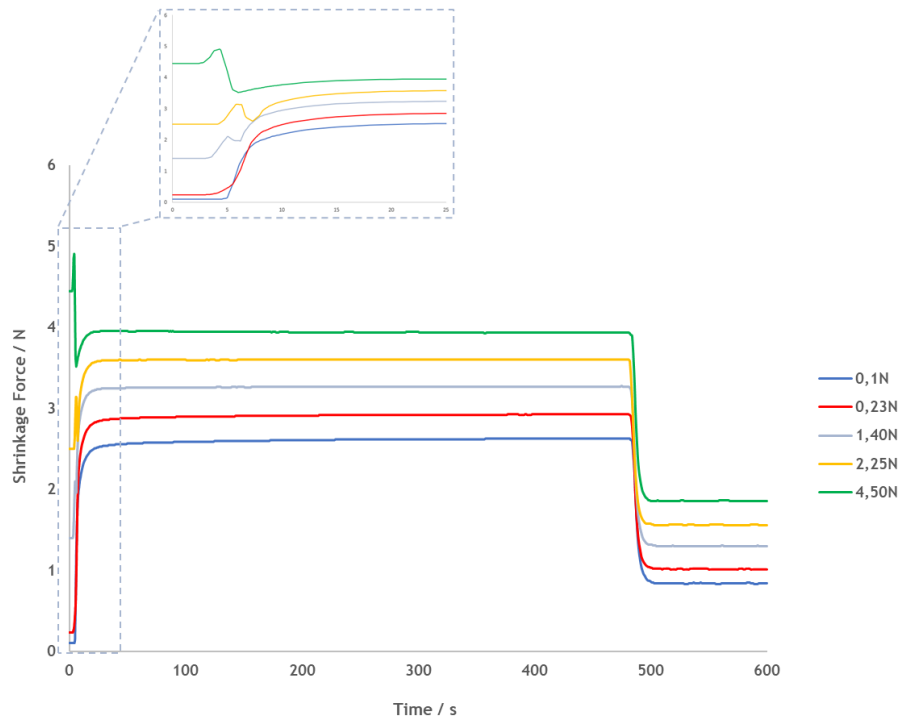


Figure 22 - Shrinkage force of PET 1100 dtex x2 as a function of time, for different pre-loads.

Moreover, analysing in detail Figure 22, when the tensile loading is higher, there is an initial peak in the shrinkage force followed by a decrease (decline of complex modulus and structural elongation) and subsequent force equilibrium. This behaviour can be explained by the fact that with the increase in static load, the polymer chain mobility is more restricted due to the higher orientation of polymer chains, as illustrated in Figure 23. Therefore, the initial entropy state is different for both cases, *i.e.*, for a higher static load (a), the entropy is lower and whenever yarns are subjected to thermal treatment, a tendency will be to go toward the state of higher entropy and, consequently, the entropy difference will be superior as the pre-load increases, attaining a more pronounced peak. Subsequently, up until the shrinkage force reaches equilibrium, the entropic forces of contracting segments are counterbalanced by the response of external restraints.

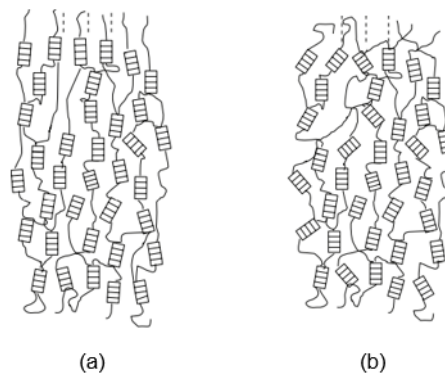


Figure 23 - Hypothesized structure model of loading (a) and unloading (b) of a polymer chain (adapted from Tian *et al.*, 2020).

The stress dependence of thermal shrinkage was also performed for the other temperatures mentioned in Table 4. The normalized shrinkage force results as a function of the pre-load are present in Figure 24.

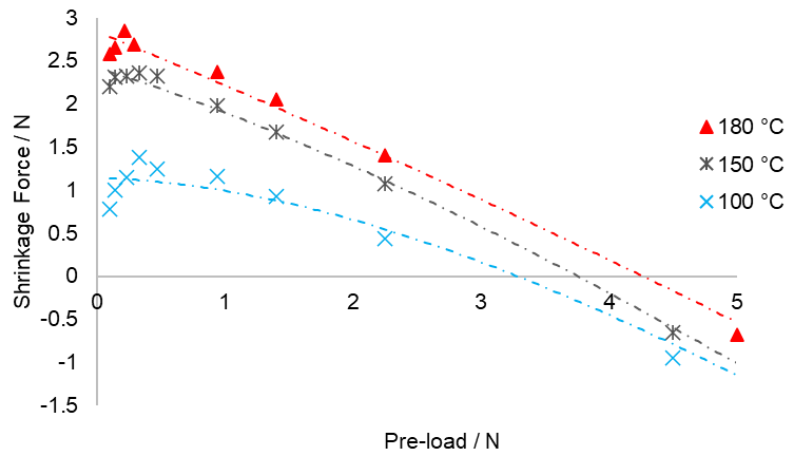


Figure 24 - Shrinkage force of PET 1100 dtex x2 as a function of the tensile holding, for different temperatures, above T_g .

Examining the plot of Figure 24, it is verified that the shrinkage force does not continuously decrease with the increase of the pre-tensioning masses and the tendency is to obtain a maximum of 0.22 N for 180 °C and approximately 0.33 N for the temperatures of 150 °C and 100 °C. On the one hand, this result may go against of what was previously explained, *i.e.*, for a smaller tensile loading, a minor entropy difference develops, since the polymer chain already has a high degree of disorder. However, according to the literature, it would still be expected that for a smaller pre-load, the shrinkage force would be higher, as there is not enough force and orientation to prevent the chains from gaining high mobility.

Fiber mobility is a key structural aspect of yarn, and this might be the main reason why a loss in shrinkage force is observed for smaller pre-loads. In the case of continuous-filament yarn, filaments are adhered together by virtue of their large number and the long inter-filament contact under lateral forces imposed by the outer filaments pressing against the inner ones. When continuous-filament yarns are converted into texturized yarn, a great deal of inter-filament space is created between filaments leading to lower compactness and, therefore, whenever heat is applied to the material, the filaments will become more mobile to settle down, cohere and to follow the same path of minimum energy, filling in the interfiber spaces (thermal structural elongation). This phenomenon is analogous to the structural (helix) elongation, observed in the force-elongation curves, *i.e.*, when a force is applied to the cord, at first the structure elongates due to inter-filament and inter-ply free space, before the material has to, as it is illustrated in Figure 25. Therefore, under low levels of stress, the fiber compactness is lower, and it is likely to result in many behavioural changes in the yarn.

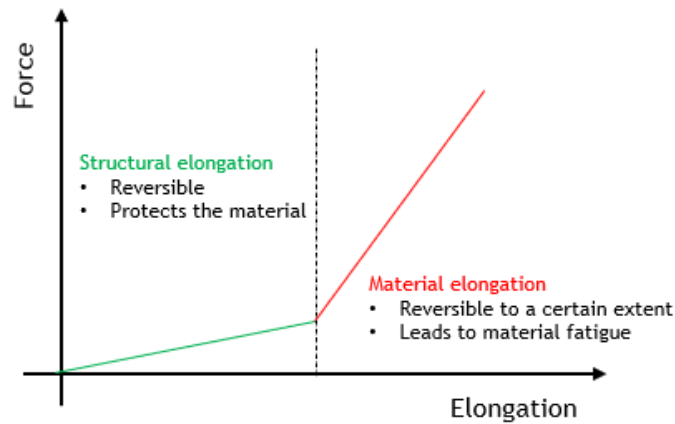


Figure 25 - Schematic representation of a conventional force-elongation curve.

For this reason, according to the standard ASTM D5591 and in order to have a taut cord (with few empty spaces), the prescribed pre-tensioning mass should be applied to the free end of the specimen (Annex H). In the case of PET, with the construction of 1100 dtex x2, 0.22 N of pre-load should be applied and this agrees with the maximum obtained for the temperature of 180 °C. However, for the remaining temperatures, no specifications are given, but according to the results obtained, it appears that the maximum tends to increase, which can be justified by the fact that for lower temperatures, the developed entropic force is lower and more conformational arrangements can occur, since it takes more time to overcome the energy barrier which divides submolecules in a contracted or an extended state.

Furthermore, inherent to the yarn structure, some disturbing features can influence the results obtained, namely, the number of fibers, the fiber arrangement and shape, which is the degree of circularity in the yarn cross-section, that largely indicates the uniformity of packing density in the fibers and the twist factor. All these factors will also affect the shear-induced friction, Figure 26, which plays a major role in energy dissipation. Results from numerous authors demonstrate that shear deformation leads to qualitatively new energy dissipation behaviours including dissipation dynamics associated with internal inter-filament friction and on inter-ply shear associated with external friction at the surface of the yarn.

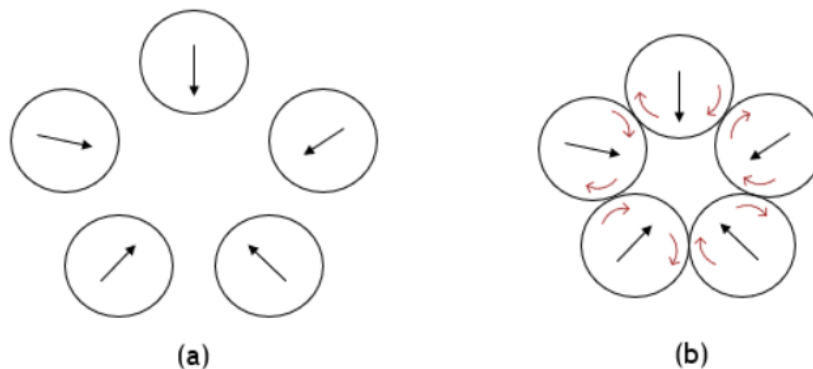


Figure 26 - Schematic representation of thermal compaction (a) and shear-induced friction (b).

To complement the previous results, the stress dependence of thermal shrinkage was also performed at temperatures below T_g . Figure 27 displays the normalized shrinkage force outcomes as a function of the pre-load.

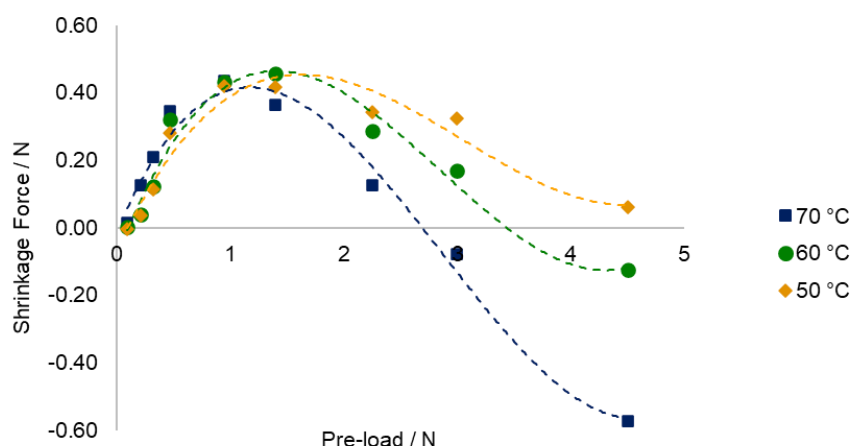


Figure 27 - Shrinkage force of PET 1100 dtex x2 as a function of the tensile holding, for different temperatures, below T_g .

According to the literature, at temperatures below T_g , the sample exhibits reversible thermal expansion and for this reason, it would be expected that the shrinkage force would present negative values. However, the behaviour of the curve, exhibited in Figure 27, is similar to what has been previously observed for temperatures above T_g . At any given temperature, macromolecules constantly tend to adopt the most advantageous conformations and to increase chain packing. This behaviour leads to thermodynamic equilibrium, which is characterized by the minimum value of the suitable thermodynamic potential. The difference between the energy and entropy components of the macromolecules that make up a polymer system often represents this potential, as stated in the context and state of the art. Therefore, when energy (heat) is provided to the material, the entropy associated with a single molecule increases dramatically, due to the large number of different conformations the chain can assume and, for this reason, positive values (associated with this entropic force) are observed, not invalidating the fact that along with the development of this force, there is also thermal expansion and thermal structural elongation. Moreover, cords undergoing almost free thermal shrinkage (≈ 0 N), exhibit a shrinkage force of 0 N and it is possible to draw the same conclusion from Figure 24, in which the entropy difference will be superior as the pre-load increases, to a certain extent.

In addition, it was investigated the possibility of chemical and thermal degradation. According to several researchers, hydrolysis appears to be the main degradation for PET cords at temperatures lower than 70 °C. Water diffuses into the amorphous polymer areas, causing the ester bonds to break (*cf.* Figure 4) and, therefore, these groups are loosened thermally or

dissociated, allowing the chains to move and to assume another configuration. The hydrolysis rate will therefore be highly dependent on the degree of crystallinity of the PET material, as well as on the temperature and humidity. However, regarding the good conditioning environment in the laboratory, this hypothesis becomes almost null. Photolytic degradation and depolymerization were also excluded.

To sum up this subchapter, the DOE was employed to identify significant variables and the interaction effect on responses. Pareto chart was deployed to analyse the significant variables and the effects of possible interactions among the testing parameters on the response of shrinkage force. Results, displayed in Figure 28, demonstrated that temperature and static load exhibited significant interactions on the response. Time variable had any significant effect on the response of shrinkage force in this study.

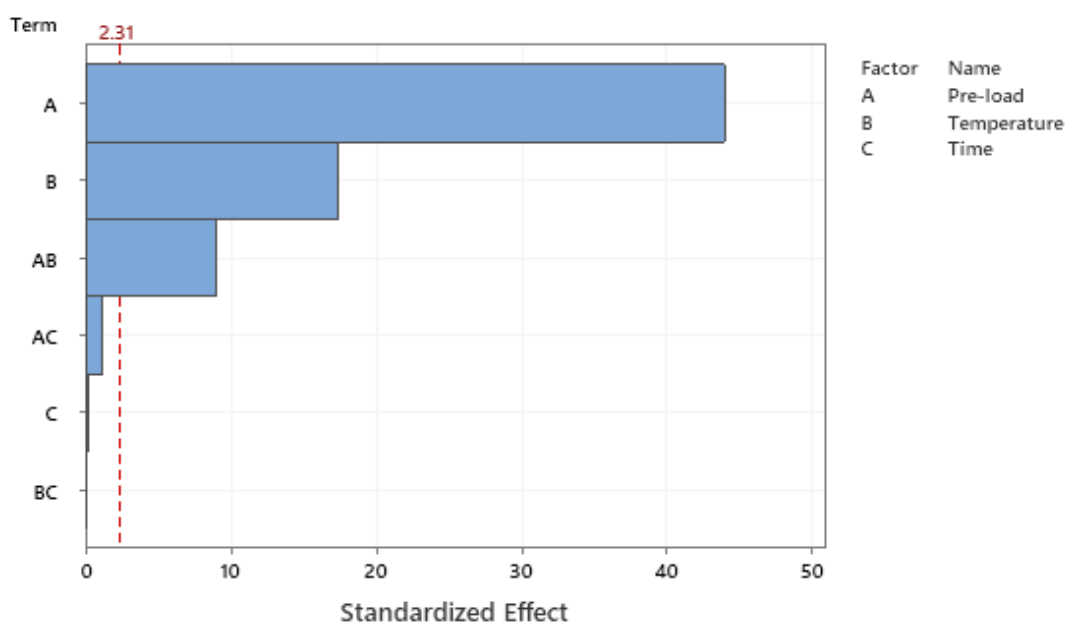


Figure 28 - Pareto chart of selected variables on the response of shrinkage force of PET 1100 dtex x2.

Noteworthy to mention that the standardized effects, present in Figure 28, are t-statistics that test the null hypothesis that the effect is 0. The chart also plots a reference line (2.31) to indicate which effects are statistically significant.

From the residual plots present in Appendix N, it can be concluded that there are not large deviations from the normal distribution. It was also performed an additional Anderson-Darling test and the p-value obtained was 0.294. Therefore, it should not be rejected the null hypothesis that the data is normally distributed, and it is possible to accept that the data is normally distributed. Further details can be consulted Appendix N.

All these results presented previously refer to PET with the construction of 1100 dtex x2. The remaining results, for the other constructions, can be found in Appendix O. In general, it is possible to allege that the increase in the linear density, leads to an intensification in shrinkage

and shrinkage force as expected. Furthermore, the behaviour of the curves is similar, verifying that the effect of the thermal structural elongation intensifies with the increase of the linear density, since there are more filaments and more inter-fiber and inter-ply spaces, which will lead, consequently, to a greater requirement of tensile loading to obtain a taut cord.

4.1.4 DSC spectrums of PET specimens

Figure 29 exhibits the DSC heating curves of dipped PET fibers, for two different constructions. When heated, the drawn fibers with the construction of 3340 dtex x2, apparently exhibit a glass transition at approximately 70 °C, followed by an endothermic peak indicating evaporation of absorbed water. However, some replications were performed and no changes were observed in this region, as it was also perceived with the construction of 1100 dtex x2. A possible justification could be the fact that the cord presents heterogeneity in its polymer chain, in which certain segments present a higher degree of crystallinity than others, *i.e.*, the thermal treatment was not completely homogeneous and imperfect crystallites may have been formed (branching of polyethylene chains). Replications of these assays can be found in Appendix P.

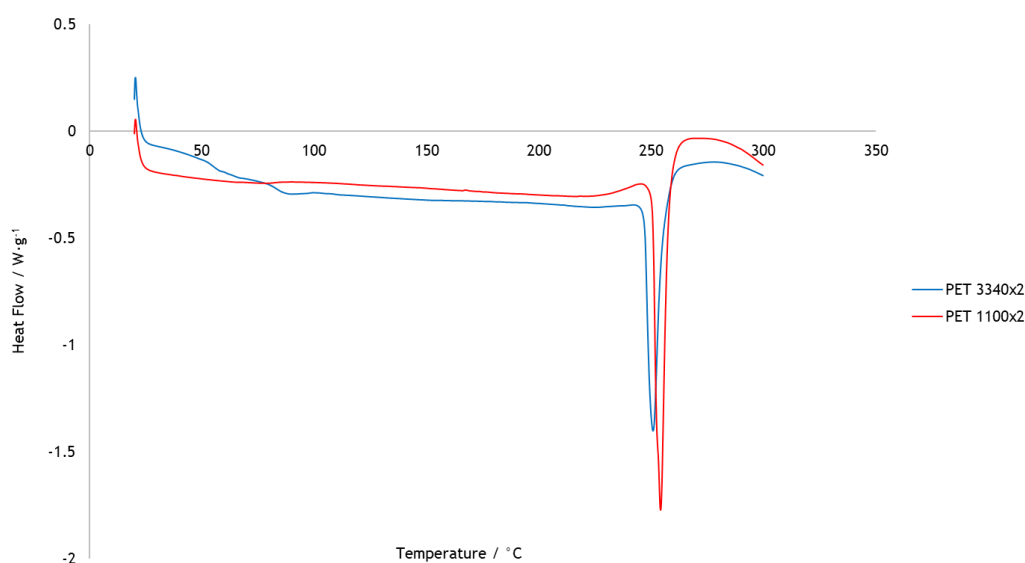


Figure 29 - DSC thermograms of heat-treated PET dipped cords.

Furthermore, comparing these results with those of Figure 15 (quenched PET fiber), it is verified that the analysed samples do not present exothermic peak associated with cold crystallization. It is noteworthy to mention that cold crystallization only takes place when the sample is cooled swiftly and has no time to crystallize during the cooling phase. Therefore, it can be concluded that this effect did not affect the shrinkage results previously presented.

Although the peak of cold crystallization is not observed, it is important to note that, currently, there are many ways to accelerate the crystallization of such polymers, *e.g.*, by an annealing at crystallization temperature for some time. Investigations performed by Zhao et al. (2001) have also shown that annealing at temperatures below and close to the T_g resulted in some

structural change, which made the subsequent cold crystallization easier. Furthermore, the incorporation of nucleating agents promotes nucleation for crystal growth.

On the other hand, the crystallinity of these fibers can be calculated from the heat of fusion as described in Section 3.1.2. Noteworthy to mention that the heat of fusion or heat associated with any other endothermic event, ΔH_m , can be determined by integrating the peak with the appropriate baseline method. The results are presented in Table 5 and it is verified that there is not a significant difference between the two constructions.

Table 5 - Percentage of crystallinity calculated from the DSC analysis, for PET fibers.

Material	Construction / dtex	$\Delta H_m / \text{J} \cdot \text{g}^{-1}$	$\Delta H_c / \text{J} \cdot \text{g}^{-1}$	$\Delta H_m^0 / \text{J} \cdot \text{g}^{-1}$	$X_{cr} / \%$
PET	1100x2	46.5	0	140.1	33.2
	3340x2	49.6			35.4

In addition, analysing Figure 29, there is a shift in the baseline as a result of modifications to the sample's weight, heating rate or specific heat. For example, after a transition, such as melting, the sample frequently experiences a shift in specific heat and during volatilization or breakdown, sample weight frequently fluctuates.

On the other hand, due to the long length of the fiber samples, sample preparation is a significant issue in DSC studies of textile cords. Another problem is that the tested cords are heavily drawn and thus highly orientated and therefore, they typically shrink when heated. As a result, literature proposes two main ways to measure the thermal properties of these fibers, the constrained-state or fixed-length measurement, which measures the glass transition and melting while maintaining the fiber's length throughout the DSC measurement and the "free-to-shrink" or unconstrained measurement, which involves cutting the fiber into small pieces so that the ends are free to shrink during the heating.

In this project, it was only possible to perform the second option, which may have affected the results. When drawn fibers are measured in a confined condition, the melting point is always higher compared to free-to-shrink measurement. Since the macromolecules are stretched in a constrained measurement and will remain partially stretched in the melt, it makes intuitive sense that the entropy gain in a constrained measurement is smaller than in a free-to-shrink measurement. They will lose their orientation in the melt, but that will require some time. Considering that both methods of measurement yield the same amount of fusion heat (which is not always true but can be accepted as a first approximation), the melting point will increase in the constrained-state measurements because of the decrease in the conformational entropy of fusion. In addition, the crystalline portion exhibits reorganization during heating, but the crystallites in the constrained fiber can superheat as well, even at a modest heating rate.

4.2 Thermally induced shrinkage of Nylon

The thermal shrinkage of PA 6.6 and PA 6 has been found to be nonlinear with respect to time, temperature and stress. The rate-of-creep equation (Equation 11), described in the previous subchapter, originally derived by Tobolsky and Eyring (1943) also applies to these materials. In addition, the behaviour of the shrinkage and shrinkage force curves is reportedly identical to those of PET. However, for a larger tensile holding, after the entropy peak, there is a much more pronounced decrease in shrinkage force compared to PET. A plausible justification lies in the fact that PA 6.6 and PA 6 have a much smaller modulus, *i.e.*, they are floppier and the thermal structural elongation ensues straightforwardly. The response of external restrictions then balances the entropic forces of contracting segments until the shrinkage force achieves equilibrium. By way of illustration, Figure 30 displays the results for shrinkage force as a function of time for PA 6.6 with the construction of 1400 dtex x2, at 180 °C.

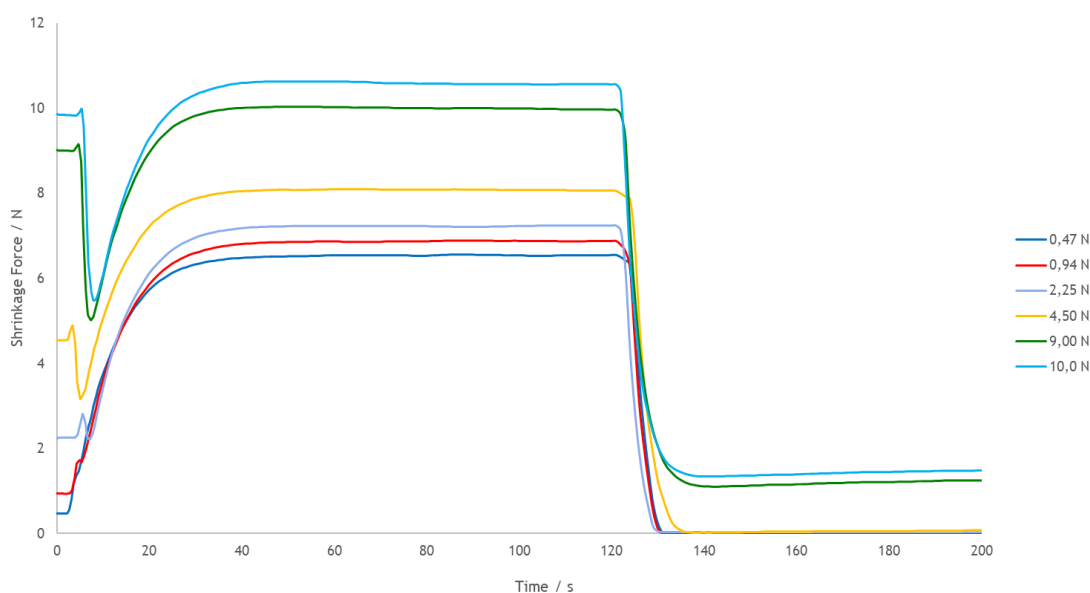


Figure 30 - Shrinkage force of PA 6.6 1400x2 as a function of time, for different tensile holdings.

For the other temperatures, the thermal shrinkage stress dependence test was also conducted. Figure 31 exhibits the normalized shrinkage force outcomes as a function of the pre-load, for PA 6.6 with the construction of 1400 dtex x2. As a first observation, it is possible to verify that, opposing to what was observed with PET, here the shrinkage force decreases linearly as the pre-load increases. Once again, the reason may lie in the modulus difference and making an analogy to the force-elongation curves (Figure C.1 , Annex C) it is possible to easily verify that for a given applied load, nylon elongates effortlessly and this leads to the hypothesis that when applying temperature, there is a lower and residual loss of force until the thermal structural elongation equilibrium is reached and, therefore, the maximums observed in the PET curves are not present. However, this does not mean that the tendency is not to have a loss of force

for smaller pre-loads, *i.e.*, if the logarithmic plot is executed, it turns out that the tendency is to form a maximum.

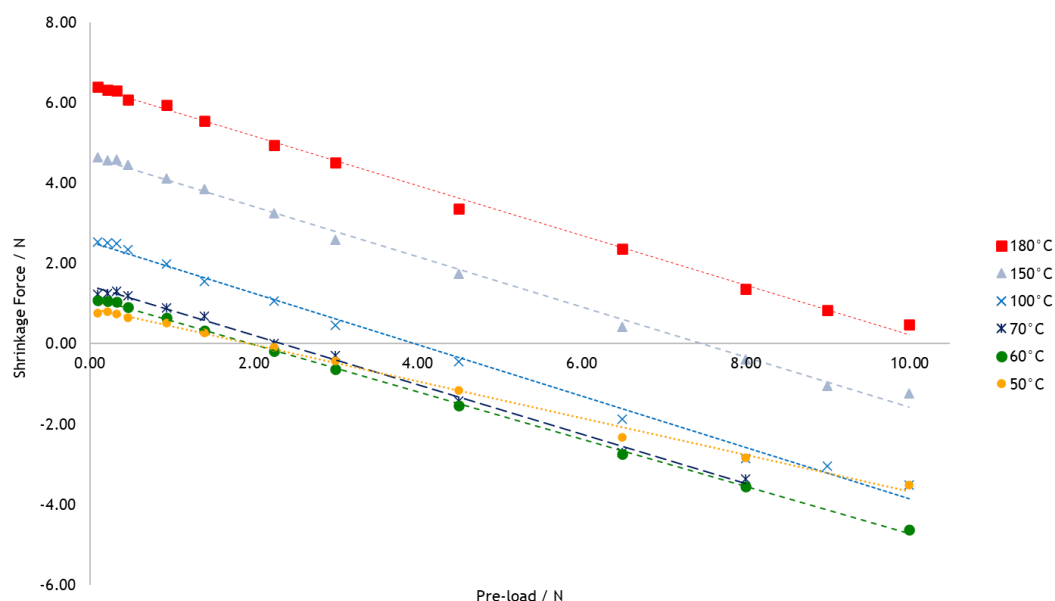


Figure 31 - Shrinkage force of PA 6.6 1400 dtex x2 as a function of the tensile holding, for different temperatures.

Furthermore, tests were performed below the theoretical T_g ($\approx 55^\circ\text{C}$). However, analysing Figure 31, there are no significant differences in the behaviour of the curves concerning the other temperatures. Noteworthy to mention that the glass transition does not occur as a definite sharp transition as would be required by equilibrium thermodynamics, and it must be considered a kinetic transition. Therefore, the ideal procedure would be to perform static tests at a temperature further away from T_g (e.g., 40°C), however, the TST 510/250 oven presents several deviations at this temperature and it was not possible to stabilize it.

The results for the other cords, including the DOE analysis performed as in PET, can be found in Appendix O and Appendix N. The behaviour of the curves is reportedly the same for all constructions (including PA 6), except for one PA 6.6 construction, with experimental specifications (not specified due to confidentiality purposes). The behaviour of this curve is identical to PET, keeping the hypothesis that the thermal structural elongation has a vast effect on the shrinkage of this material. Since PA 6.6 is a hygroscopic material and the water absorption can reach a maximum up to 2.5 % w/w, it was investigated, in subchapter 4.4, the possibility that moisture is influencing the results of this cord.

Regarding the investigation of chemical and thermal degradation, it was concluded that theoretically there could be residual effects. The degradation of nylon is mostly due to the absorption of light in the 270-280 nm and 300-340 nm and the conditioning environment in the laboratory has another wavelength fulfilment. In addition, contrary to PET, nylon is only hydrolysed in aqueous acids, resulting in an increase in the concentration of amine end-groups.

4.2.1 DSC spectrums of PA 6.6 and PA 6 specimens

The DSC heating scans of dipped PA 6.6 and PA 6, for different constructions, are given in Figure 32. In contrast to the PET samples, the temperature at which the glassy state changes to a rubbery state is well defined as it is observed with the endothermic peak at 55 °C. Furthermore, an endothermic peak indicating evaporation of absorbed water is spotted with a peak temperature close to 100 °C.

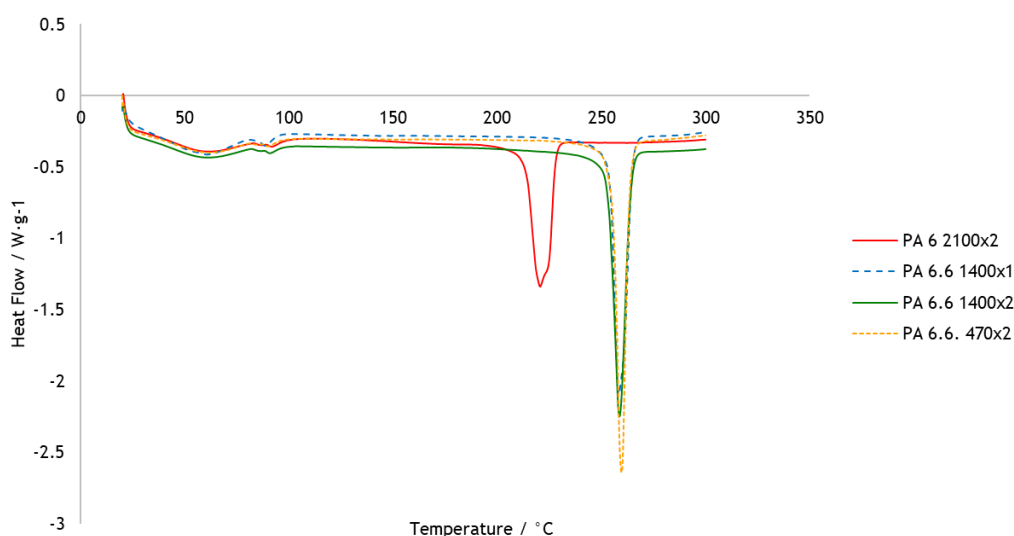


Figure 32 - DSC thermograms of heat-treated PA 6.6 and PA 6 dipped cords.

Moreover, analysing Figure 32, it is confirmed that PA 6 has a lower melting point compared to PA 6.6. A plausible justification lies in the fact that PA 6 has only two sites for hydrogen bonding per repeating unit, and PA 6.6 has four sites per repeat unit and, as a result, less energy is required in PA 6 to break intermolecular interactions. In addition, PA 6.6 is slightly stiffer and more heat resistant than PA 6 due to its more crystalline structure (Menczel and Prime, 2008). This conclusion can also be drawn from Table 6, in which it is found that the degree of crystallinity is lower for PA 6. Furthermore, as far as PA 6.6 is concerned, there are no significant differences in crystallinity between constructions.

Table 6 - Percentage of crystallinity calculated from the DSC analysis, for PA 6.6 fibers.

Material	Construction / dtex	$\Delta H_m / \text{J} \cdot \text{g}^{-1}$	$\Delta H_c / \text{J} \cdot \text{g}^{-1}$	$\Delta H_m^0 / \text{J} \cdot \text{g}^{-1}$	$X_{cr} / \%$
PA 6.6	470x2	82.4	0	255.8	32.2
	940x2	80.2			30.9
	1400x1	81.0			31.7
	1400x2	78.4			30.6
PA 6	2100x2	66.2	0	230.0	28.8

4.3 Thermally induced shrinkage of Aramid

To complement the results previously demonstrated, experimental trials were performed on pure aramid, which is a material with high crystallinity and, theoretically, eliminates any shrinkage, even when exposed to heat. Regarding the thermal shrinkage results, there was no significant difference from the initial length. However, when it comes to shrinkage force there is a substantial alteration, especially for higher tensile loading. Figure 33 displays the results of shrinkage force as a function of time for different pre-loads and temperature of 180 °C.

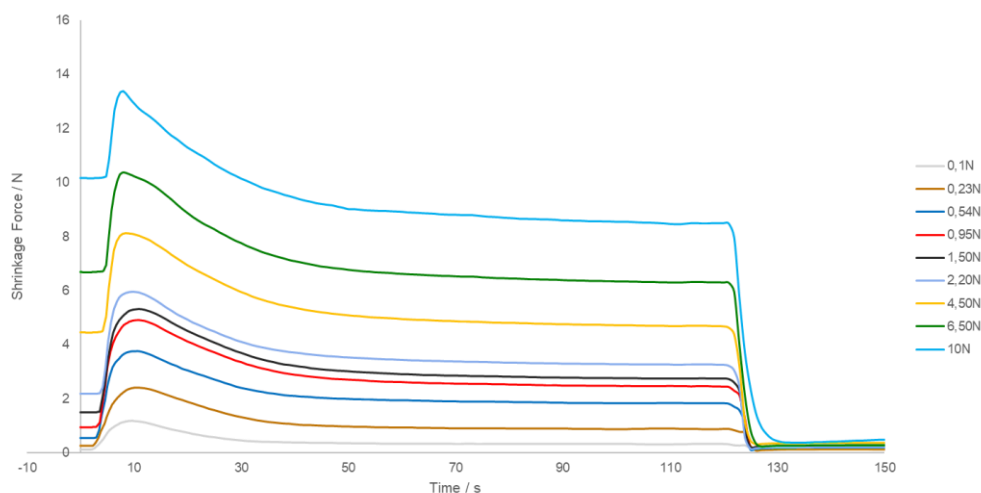


Figure 33 - Shrinkage force of Aramid 1670x2 as a function of time, for different tensile holdings.

As a first observation of Figure 33, it can be realised that for all pre-tensioning masses, the shrinkage force initially increases with sharper peaks for higher tensile loading. This behaviour resembles the results obtained for PET (under T_g) and, therefore, it can be concluded once more that this behaviour is due to the entropy change, accompanied by thermal expansion and structural elongation. However, it is necessary to consider that under normal conditions (at room temperature), macromolecules of aramid yarns are found in the *trans* conformation, *i.e.*, geometrically they are more or less straightened out segments. With an increase in temperature, these macromolecules gradually change their geometric structure, transitioning to the *cis* conformation, which involves segments that are no longer straight but rather it is possible to observe a wavy structure (increasing the shrinkage force). Furthermore, it is noteworthy to mention that the sample tested is quite old and hydrolytic degradation mechanism, involving the scission of the amide N-C linkage, yielding acid and amine functions, could gradually reduce the molar mass of the fiber and, therefore, impacting shrinkage force.

Nowadays, pure aramid is not so much used in cap-ply but hybrid cords combined with PA 6.6 and aramid are being widely used. Experimental trials were performed for these cords (Appendix O) and it was found that the behaviour resembles the PA 6.6 curves. The shrinkage is proportional to volume fraction of amorphous material and to the orientation in amorphous segments and this leads to shrinkage values for aramid nearly zero compared to PA 6.6.

4.4 Impact of moisture on thermal shrinkage

To investigate the influence of moisture on thermal shrinkage, experimental tests were performed on PET 3340 dtex x2 and PA 6.6, with the experimental specifications mentioned before. As it was already examined, even at temperatures below T_g , the entropy of the material is modified and, therefore, a desiccator was used instead of an oven for drying the samples. Regarding PET, it was not possible to remove large water content and the results were reportedly similar to those already obtained. However, PA 6.6 is a hygroscopic material, due to the polar amide groups and it was possible to perform experimental trials with high and low moisture content (2.44 % w/w and 1.05 % w/w, respectively). The results are reported in Figure 34, for the temperatures of 180°C and 100°C.

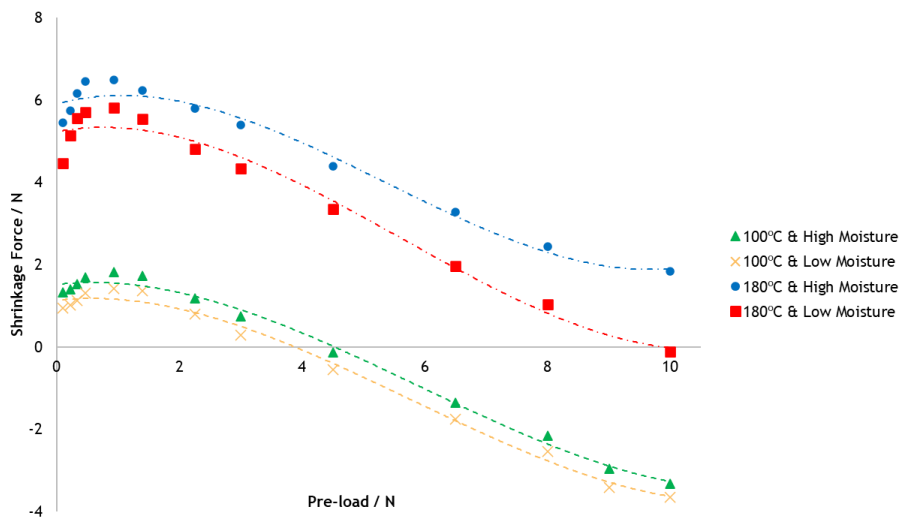


Figure 34 - Shrinkage force of PA 6.6, with experimental specifications, as a function of the tensile holding, under different conditions.

As a first observation of Figure 34, it is possible to verify that the nonlinear behaviour remains the same and it can be concluded that moisture has a residual influence on this and, therefore, the experimental specifications should be revised, since apparently the filament and yarn migration are having a vast impact for this material. Furthermore, it can be noticed that for both temperatures, the shrinkage force is always lower for low moisture content. Water is a potent plasticizer for PA 6.6 and will penetrate the amorphous regions preferentially. It rapidly breaks hydrogen bonds to the amide group and improves molecular chain mobility (dipole-dipole interactions between matrix and fibers become less effective). The usual outcome is a decrease in the tensile modulus, the work to elongate and recover, and a significant reduction of T_g . In addition, the breakdown of intermolecular hydrogen bonds, as a result of water absorption causes PA 6.6 to become more crystalline (Hassan *et al.*, 2011), which improves the packing of the hydrocarbon chain segments and for this reason, it is effectively observed that the shrinkage force is superior for higher moisture content.

4.5 Influence of twist level on thermal shrinkage

A comparison of shrinkage and shrinkage force values of dipped cords PET 1440 dtex x2 and PA 6.6 940 dtex x2, with different twist levels are demonstrated in Figure 35, for 180 °C. The curves reportedly present the same behaviour as the standard dipped cord.

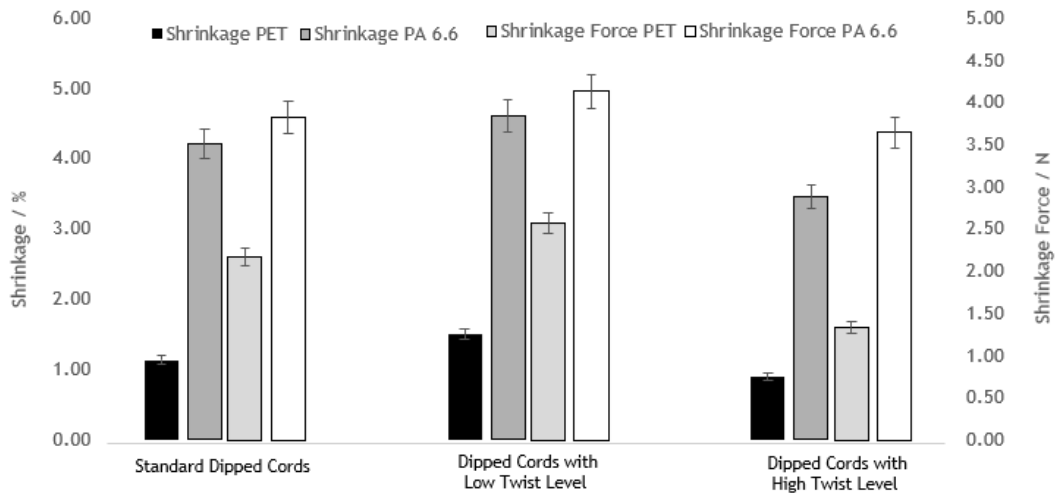


Figure 35 - Shrinkage and shrinkage force of dipped cords, PET 1440 dtex x2 and PA 6.6 940 detx x2, for different twist levels.

As the twist increases, linear density, *i.e.*, the weight of material in unit length increases and, therefore, it was expected that the shrinkage values of PA 6.6 and PET cords would increase with higher twist factors. However, from Figure 35, it is possible to allege that the increase in twist causes a decrease in the shrinkage and shrinkage force values. According to Tian *et al.* (2020), by increasing the twist level, the dynamic modulus decreases and $Tan \delta$ (related to energy dissipation) increases and, for this reason, when heat is applied, the thermal structural elongation (a force that contracts the contraction force) ensues more straightforwardly for higher twist levels and decreasing consequently the shrinkage values. On the other hand, it was found that for lower twist levels, crystallinity decreased (see Appendix P) and for this reason, the shrinkage and shrinkage force will be higher. Furthermore, Cruz (2014) also proposed the premise that the linear shrinkage needs to be analysed at vertical (or transversal) and horizontal axis, as can be seen in Figure 36. This would indicate that the contribution of both yarns to the vertical axis is lower at low twist levels, (which also presents a grater space between yarns and therefore more space to shrink), resulting in smaller shrinkage values at high twist levels.

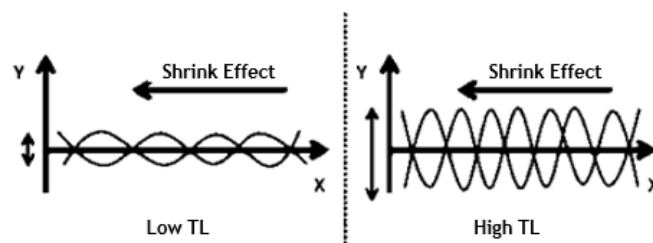


Figure 36 - Influence of twist level on shrinkage effect (adapted from Cruz, 2014).

4.6 Thermally induced shrinkage of greige and calendered material

To complement the results, measurements were performed on greige and calendered fabric to analyse how the shrinkage fluctuates along the cord manufacture. The results concerning the greige cords (PET 1440 dtex x2 and PA 6.6 940 dtex x2) are shown in Figure 37, for 180 °C.

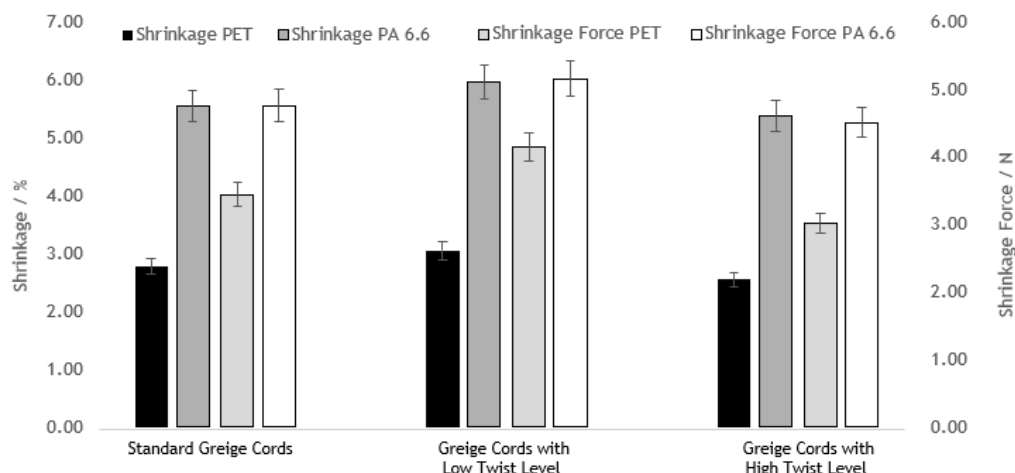


Figure 37 - Shrinkage and shrinkage force of greige cords, PET 1440 dtex x2 and PA 6.6 940 dtex x2, for different twist levels.

An important observation that should be mentioned in the first place is that during fiber manufacturing process, especially in the dipping process, polymeric fibers passed a series of thermal and mechanical processes (e.g., stretching), and a high crystalline phase is also obtained. For this reason, it is effectively verified, in Figure 37, that the shrinkage and shrinkage force is always lower for dipped cords. Furthermore, for the greige material, it was found that for higher twist levels the shrinkage and shrinkage force is continuously lower, corroborating the conclusions that were drawn in the previous subchapter.

Hence, it can be stated that crystallinity is the major impact of these experimental results. However, it is noteworthy to mention that the resin RFL goes through cross-linking reactions during thermosetting composite curing, which could result in a rise in material density and a fall in volume. The process of volume reduction, the so-called chemical shrinkage, together with thermal effects can lead to the development of high locked-in stresses where there is constraint. This effect not only affects the shrinkage values but further restricts the movement of the material. On the other hand, some studies were conducted by Wootton (1982) for PA 6.6. shown that when treatment of cords with RFL resin is done at high temperature, which could allow the penetration of the RFL dope into the nylon cord structure, causes surface swelling disrupting the intramolecular hydrogen bonds and weakening the fibre structure. Wootton agrees that a reaction between the hydroxyl and amide groups may occur, even though he claims there is not a completely good chemical interaction between RFL and cords. Therefore, the fiber's molecular structure is disturbed by this process and the cord stiffens and becomes slightly brittle with more susceptibility to rupture and with lower shrinkage values.

For the calendered material, tests were also carried out for PET and PA 6.6 cords with standard specifications and compared with dipped cords. Under proper tension, the dipped fabric is continually pressed through two steel rollers, and simultaneously the rubber compound is added to the opening area between the rollers. These stresses that are applied to the material are optimized so that, at a temperature of 100 °C, no shrinkage develops and the other physical properties of the material do not change. That said, it was found that for PET, shrinkage and shrinkage force exhibited the same value, with few deviations, as expected. However, for PA 6.6 this is no longer the case, and the results can be observed in Figure 38.

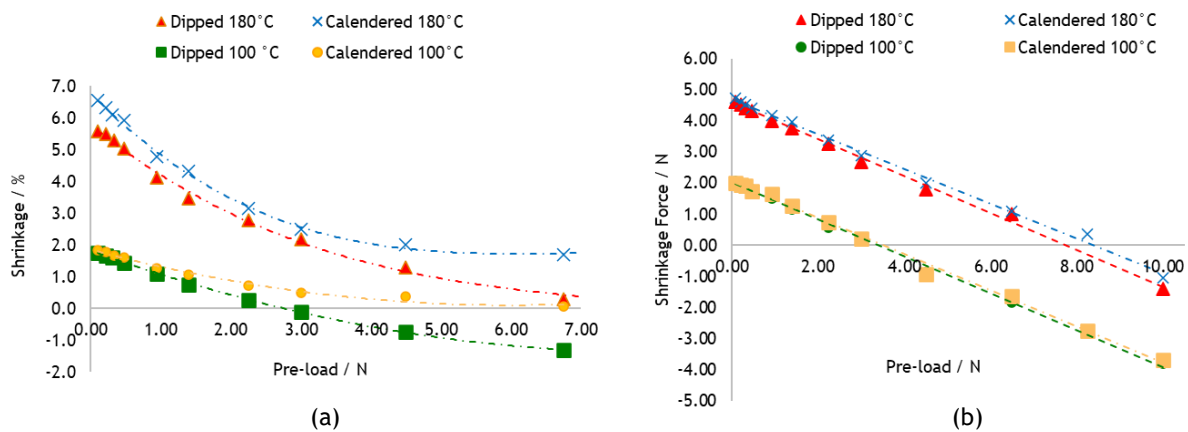


Figure 38 - Shrinkage (a) and shrinkage force (b) of PA 6.6 940 dtex x2 as a function of the tensile holding, under different conditions.

As a first observation of Figure 38, it is verified that the deviations are mainly observed for the percentage of thermal shrinkage. Making an analogy to the results obtained for standard dipped cords, when the material passes through the calender, thermal structural elongation is expected to occur first, even if there is no increase in entropy at the optimized applied stresses. Furthermore, the flow in the calender is highly converging, which means a pressure builds up until it reaches the maximum value closely to the narrowest cross section of the roll gap. In this region close to the surface of the rolls, the material is forced against the pressure gradient providing greater compaction of the material which later, due to the presence of rubber on the surface, will not relax so effortlessly. Hence, when the calendered material is again subjected to high temperatures in the TST, it is expected that there is not much energy loss due to the thermal structural elongation of the cord and the shrinkage will ensue straightforwardly, corroborating the higher values of shrinkage. Regarding the shrinkage force, there are not many deviations for the two temperatures tested. As we have seen throughout this project, the shrinkage force measurement is more sensitive than the shrinkage percentage since, e.g., there may be no difference in sample length, but the movements between the filaments and the yarns will cause fluctuations in the force that will be detected by the strain gauge sensor. That said, it is expected that for dipped cords, there will be a higher elongation loss force, but also a higher development of shrinkage force, due to the lower degree of compaction. On the other

hand, for the calendered material, the elongation loss force is lower but the shrinkage force is also reduced, since the material has retained inner forces after the compaction (calendered) of the material and the presence of residual rubber on the surface, hinders the movement and loss of these forces. Thus, considering that the measured force is the amount of the force lost by elongation and the shrinkage force generated, in the end, it can be concluded that the final force for the two materials will be identical. In addition, it is important to note that, at 180°C, the residual rubber undergoes curing (chemical cross-linking process) by which polymer molecules are bound to each other through the formation of sulphur cross-links, which, analogously to what was explained before for the RFL, will affect the shrinkage values. Further investigation, performed by Wennekes (2008), demonstrated that the accelerator moieties that were added to the rubber compound have a strong affinity for the RFL-dip. The RFL crosslink density, near the RFL-rubber interface, increases due to the high concentration of accelerators, as seen by the nano-indentation studies, and this action further limits the material's ability to move while also affecting the shrinkage values.

4.7 Supplier Evaluation

To complement the results previously presented in this project and to rule out the possibility that the data might be influenced by the distributor of the material, a supplier evaluation was performed. The purpose is to compile a list of the best suppliers available and monitor their performance, in order to mitigate risks and drive improvement. To complete this objective, it was studied dipped cords from the suppliers listed in Table 7 and it was used cross-correlation, which measures the similarity of two series as a function of the displacement of one relative to the other, by calculating the Root Mean Square Error (RMSE) and the Pearson correlation coefficient. According to the values presented in Table 7, quite satisfactory values were obtained for both materials since the RMSE is low, indicating that there is a minimal deviation between the curves, and the coefficient is relatively high, indicating a decent correlation between the tested suppliers.

Table 7 - Supplier evaluation performed for dipped PET 3340 dtex x2 and PA 6.6 940 dtex x2.

Material / dtex	Series	Yarn Producer/ Converter	Shrinkage		Shrinkage Force	
			RMSE	Pearson's r	RMSE	Pearson's r
PET 3340x2	1	Performance Fibers/ ITA	0.014	0.922	0.034	0.914
	2	Hyosung/ Hyosung				
PA 6.6 940x2	1	PHP Fibers/ Kordana	0.079	0.899	0.062	0.911
	2	Dikai/ ITA				

5 Conclusions

The work conducted and presented throughout this thesis was structured in view of accomplishing the several objectives initially drawn. The main topic of this thesis was the thorough analysis of thermally induced axial shrinkage to research the potential impact factors.

The thermal shrinkage of oriented PET, PA 6.6 and PA 6 yarns appeared to be composed of a very fast rate of contraction which is followed by monotonically decreasing rates until the shrinkage growth vanishes with time. Even though shrinkage and creep are distinct processes, a comparable analysis was used to stipulate the mechanical modelling of thermal shrinkage, where rate constants are similar to viscoelastic relaxation times. Moreover, a rate-of-creep equation, originally derived by Tobolsky and Eyring, has been revised to interpret the physical interaction of time, temperature and stress dependency of the shrinkage of these oriented polymers. Furthermore, the 3^k factorial design was employed to identify significant variables and the results demonstrated that temperature and load exhibited significant interactions in the response.

On the other hand, the examination of the shrinkage force allowed a more sensitive analysis of all the phenomena that occur during the heating of the cords. For instance, for a larger tensile holding, the presence of an initial peak of the shrinkage force was observed, due to the increase in entropy, followed by a decrease (decline of complex modulus and structural changes) and subsequent force equilibrium. In contrast, when normalizing the shrinkage force values as a function of stress, it was verified that for the PET samples, it does not decrease linearly, since a portion of the energy provided will assist the thermal structural elongation. The energy required for this elongation is considerably lower for PA 6.6.

Moreover, under T_g , it was proven that alongside thermal expansion and structural elongation, the entropy associated with a single molecule increases which, therefore, increased the shrinkage force values, resembling the results that were also obtained for aramid.

Experimental trials were also performed to analyse the impact of moisture and twist level on shrinkage and shrinkage force. It was detected that the shrinkage force is superior for higher moisture content, and it was also possible to allege that the increase of twist causes a decrease in the shrinkage and shrinkage force values.

At the end of this project, it was also important to scrutinise how the shrinkage fluctuates along the cord manufacture. Regarding the greige cords and considering that this is a product that precedes the heat treatment, it was found that it presented higher values of shrinkage and shrinkage force. As for the calendered material, there were no significant differences in PET, but in PA 6.6 there were some alterations that were justified by the dissimilar states of elongation and compactness of the cords.

6 Assessment of the work done

This chapter presents a summary of the project's final accomplishments and significant setbacks. In addition, it is offered some insights for future work.

6.1 Objectives Achieved

The primary concern raised in this thesis was the thorough examination of thermally induced axial shrinkage in order to fully comprehend all potential influencing variables that might have an impact on the outcomes. With the exception of rayon, it was covered experimental trials for all of Continental's product lines.

Based on the results obtained, it was possible to characterize the impact of stress, oven exposure time and temperature on the thermal shrinkage of oriented polymers. Furthermore, the analysis of the shrinkage force, made it possible to sensitively identify the entropy, structural elongation, and modulus fluctuations as the main phenomena that arise during the heating of textile tire reinforcements.

Moreover, the study of the influence of moisture and twist level allowed to validate and reject some hypotheses that were open until then. In addition, the examination of greige cords and calendered material also provided an overview of how shrinkage and shrinkage force vary throughout the cord manufacturing process.

6.2 Limitations and Future Work

Countless conclusions were drawn based on the literature, so for a more complete and well-founded analysis, other trials should have been carried out to effectively prove the experimental results. These include, *e.g.*, the determination of linear isobaric expansivity and the transient behaviour of the complex modulus for the material tested. On the other hand, it was not possible to reach a reasoned conclusion on the behaviour of PA 6.6 material with experimental specifications compared to the other nylon samples. Therefore, despite the fact that it is a material still under investigation, the properties should be further investigated.

6.3 Final Assessment

With this project, it was possible to clarify some hypotheses and the author believes that with the knowledge acquired, it will be conceivable to apply the concept of preventive actions on textile reinforcements, which should be expressed through the use of risk-based thinking in formulation quality management. From a personal point of view, this work has been a real growth experience, and it was a pleasure to have participated again in a project powered by Continental.

7 References

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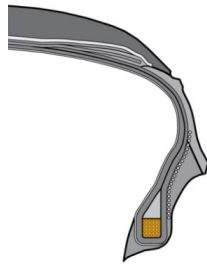
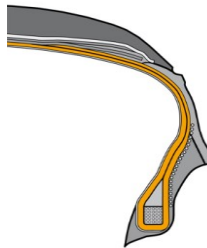
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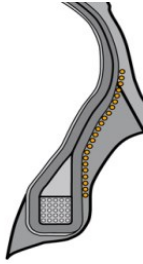
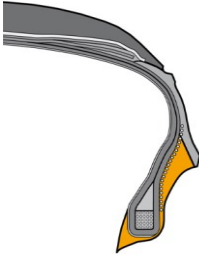
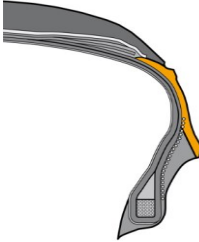
Annexes

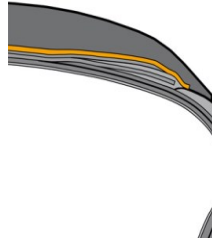
Annex A - Cross section of a radial tire

Annex A is intended to describe the function of each layer that makes up a typical radial passenger car tire. Therefore, Table A.1 provides all the essential information supplemented with a representative illustration of the respective component (cross section perspective).

Table A.1 - Tire structural cross-sectional composition (adapted from Sousa, 2018).

Component & Description	Illustration
<u>Bead Core</u> Material: Steel wire embedded in rubber Function: Ensures a firm connection of the tire with the rim	
<u>Apex</u> Material: Synthetic rubber Function: Improves driving comfort, since it is responsible for enhancing directional stability and steering precision	
<u>Innerliner</u> Material: Rubber blend, containing Halo-butyl and optional platy fillers Functions: Improves air retention by reducing permeation outwards through the tire	
<u>Carcass Ply</u> Material: Layer(s) of rubberized textile cords (Rayon/ Polyester) in radial direction Function: Maintains tires shape controlling internal pressure, providing strength and stability to the sidewall	

Component & Description	Illustration
<u>Bead Reinforcement</u> Material: Layer of rubberized textile / steel cords (Rayon/ Nylon/ PET) Function: Stiffens the lower sidewall/ bead area to promote directional stability and precise steering response	
<u>Rim strip</u> Material: Synthetic rubber Functions: Guarantees the correct seating of the tire on the rim and stiffens the lower bead area particularly with a rim protection rib	
<u>Sidewall</u> Material: Natural rubber Function: Protects the carcass from external damage and atmospheric conditions. In addition, it influences force transmission, withstands high shear strain stresses in very small sidewall heights	
<u>Belt</u> Material: Minimum two layers of calendared steel cord and fabric Function: Stabilizes the crown area of the tire and transmit forces from the contact patch to the carcass allowing the optimization of directional stability and rolling resistance, increasing the tire's mileage performance.	

Component & Description	Illustration
Cap ply Material: Rubberized textile cords (Nylon/ Hybrid/Polyester) Function: Belt package stiffness and hoop force limits are influenced by the choice of cover ply fabric and layup pattern. Controls the static and dynamic contours of the tire. This affects geometric dimensions, high speed functionality, and footprint	
Tread Material: Synthetic and natural rubber with multiple components (cap/ base/ shoulder) Function: Cap - Provides grip on all road surfaces, wear-resistance and influences aquaplaning and noise Base - Diminishes rolling resistance and damage to the casing. Shoulder - Forms an optimal transition from the tread to the sidewall.	

Annex B - Textile reinforcements terminologies

The vocabulary related to textile reinforcement industry, presented in Annex B, provides a specific nomenclature that is crucial to understand further concepts associated with this project. For instance, Table B.1 presents an overview of key terms regarding cord components and portrays some meaningful tire cord properties alongside with physical tests performed with reinforcements.

Table B. 1 - Textile tire reinforcements terminology (adapted from Cruz, 2014).

Fiber	Linear macromolecules oriented along the distance of the fiber axis
Filament	Smallest continuous element of a tire cord
Yarn	Assembly of continuous filaments twisted together
Cord	Twisted structure composed of two or more yarns
Fabric	Sheet of warp cords or yarns with extensively spaced weft yarns, woven in the orthogonal direction. Calender Lines apply fabric reinforcements
Single End Cord	Wires wound on individual spools. Cap strip lines apply single end cords reinforcements
Greige Cord	Twisted cord before dipping and heat setting process
Dipped Cord	Twisted cord after chemical treatment
Hybrid Cord	Cord composed with different polymer materials
Calendered cord	Product obtained from the calendering process
Linear Density	Weight of a specific length of cord or yarn
Twist Level	Number of turns per meter of a twisted cord or yarn
Twist factor	Mathematical correlation between the twist level and linear density.
End Count	Number of warp or weft yarns/cords per dm in a fabric
Breaking Force	Maximum force required to break a cord
Elongation at Break	Maximum elongation achieved of the cord when it breaks
Tenacity	Specific breaking strength normalized by the linear density
Elongation at Specific Load	Load-elongation curve and it is expressed in percentage
Load at Specific Load	Load-elongation curve and it is expressed in Newton
Stiffness	Required force to bend textile cords

Young Modulus	Slope between the initial linear portion of the Load-Elongation curve
Creep	Escalating deformation while load is constant
Relaxation	Decreasing in load while deformation is constant
Disc Fatigue	Phenomenon leading to filament fracture under hysteresis
Peel test	Adhesion of textiles bonded to rubber compounds
Thermal Shrinkage	Shortening of the testing length caused by temperature, time and pre-tension.
Thermal Shrinkage Force	Force which is generated as a result of heat, time and pre-load with a constantly fixed length
Residual Shrinkage	The remaining change in the length after the initial shrinkage test, while the sample remains in the conditioned environment and the pre-tension is maintained

Annex C - Typical properties of fibers

Annex C is intended to present the main characteristics of the textile tire reinforcement materials. Table C.1 presents the strengths and weaknesses of the materials used.

Table C. 1 - Reinforcement fibers: Strengths and Weaknesses (adapted from Kumar, 2008).

Fiber	Strengths	Weaknesses
PA 6 & PA 6.6	Good heat resistance and strength	Heat set occurs during cooling (flat spotting)
	Less sensitive to moisture	Long-term service growth
PET	High strength with low shrinkage	Not as heat resistant as nylon or rayon
	Low heat set	
	Low cost	
Aramid	Very high strength and stiffness	Expensive
	Heat resistant	Processing constraints

The elongation at specific force for diverse types of fibers are present in Figure C.1. This load-elongation curve of may be converted into the engineering stress-strain curve. The conventional, stress is given by dividing the load by the original cross-sectional area of the gauge length, and the strain is as defined above, namely the extension of the gauge length divided by gauge length.

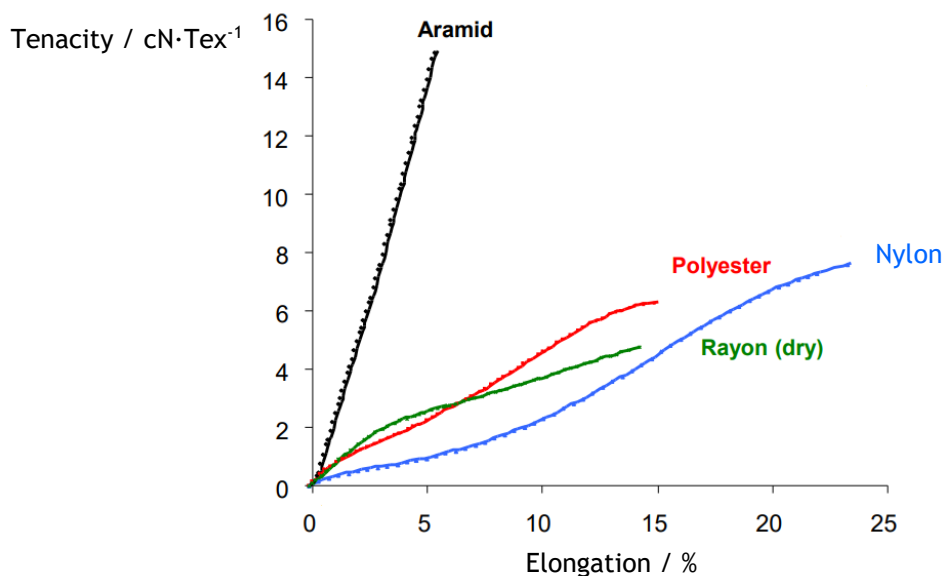


Figure C. 1- Assessment of elongation at specific force for diverse types of fibers (adapted from Couto, 2015).

Further properties of the fibers, analysed in this work, can be found in Table C.2.

Table C. 2 - Typical tire cord fiber characteristics (adapted from Kumar, 2008)

Property	PA 6	PA 6.6	PET	Aramid
Tenacity / cN·Tex ¹	80	85	80	190
Elongation at break / %	19	16	13	4
Modulus / cN·Tex ¹	300	500	850	4000
Shrinkage / % at 150 °C	6.0	5.0	2.0	<0.1
Moisture regain / % at RT ¹	4.5	4.5	0.5	<2.0
Specific gravity	1.14	1.14	1.38	1.44
Melting temperature / °C	225	250	250	>500
Glass transition temperature / °C	55	55	80	-
Heat resistance / °C	180	180	180	250

¹ RT - Room Temperature

Annex D - Tire cord construction

The twist level, the direction of the twist, the type of construction, and the linear density (dtex) describe a tire cord. The linear density, of each yarn that makes up the cord, is added to determine its overall linear density. It should be noted that the contraction factor is not taken into account for this characterisation. Figure D.1 presents a schematic representation of the cord twist direction and cord construction.

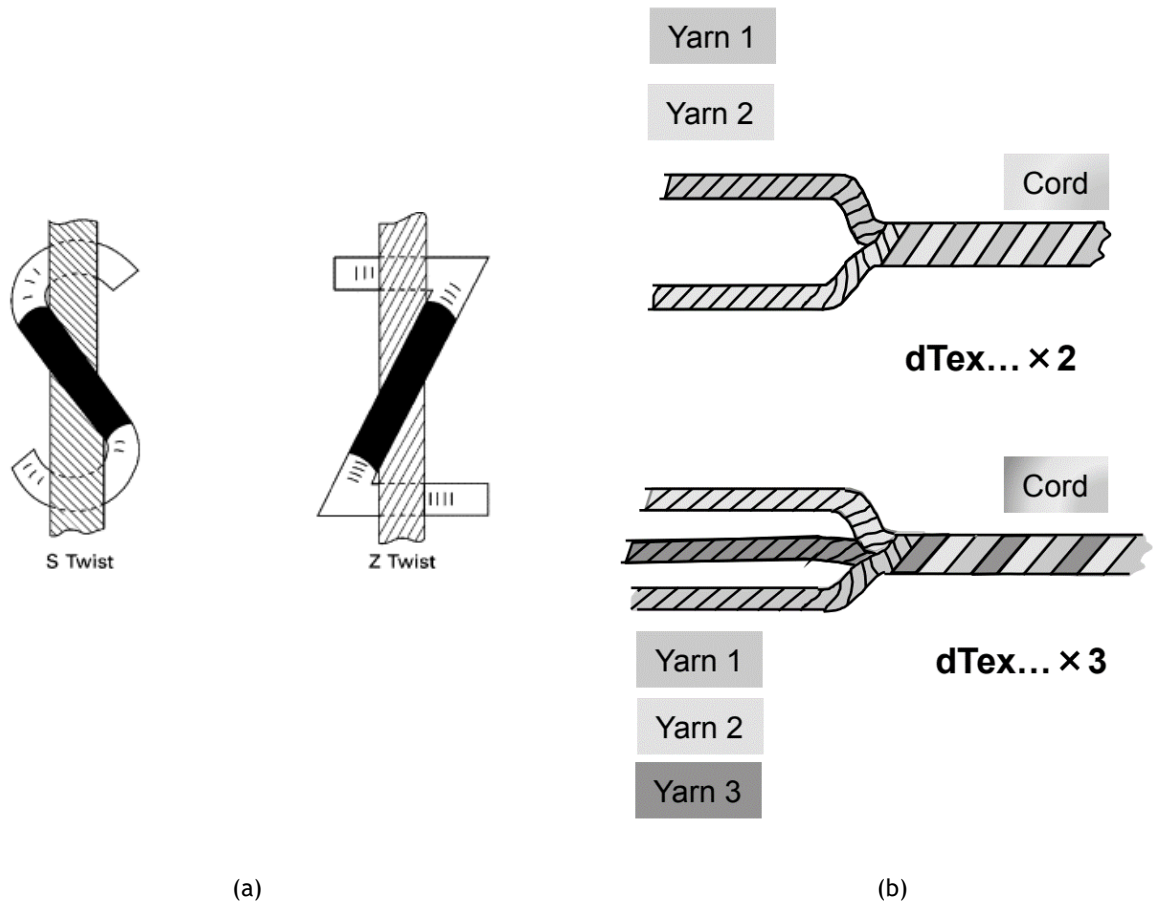


Figure D. 1 - Schematic illustration of the cord twist direction (a) and cord construction (b) (Behery, 2010; Pacheco, 2014).

Annex E - Dipping and heat treatment unit

Within the dipping process unit (Figure E.1), specific temperatures and pressures are set at various exposure times to produce the greatest possible cord qualities, especially, for strength, shrinkage, and modulus. The temperature and tensions determine the ratio of crystalline and amorphous areas. Noteworthy to mention that in this process, the cord shrinking behaviour can be adjusted by stretching the cord in the first heating zone and then relaxing it gradually in the second zone.

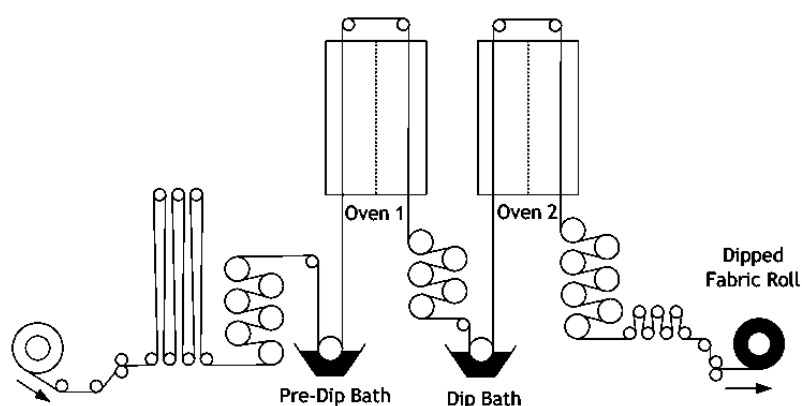


Figure E. 1 - Dipping and Heat treatment process (adapted from Wennekes, 2008).

The RFL impregnating emulsion (dip) (Figure E.2), used in this treatment, is composed of a rubber latex on a solution of resorcinol and formaldehyde in water. Two steps are taken to prepare this emulsion. The preparation of the resorcinol and formaldehyde aqueous solution is the first step, which sodium hydroxide or ammonium hydroxide are also added to this solution. The second stage involves adding a latex and water solution to the first-stage solution. If left alone, latex would interact well with rubber compounds but not with fiber (Pacheco, 2014).

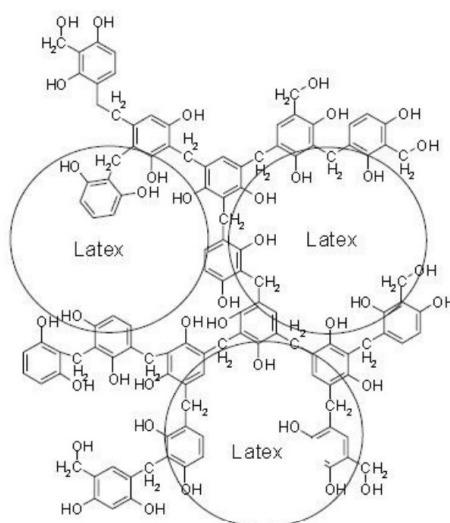


Figure E. 2 - RFL 's chemical structure (Pacheco, 2014).

Annex F - Calendaring unit

Regarding calendaring, it is performed on a calender, at 100 °C consisting of 4 rollers and its objective is to coat the cords of the fabrics with rubber. In addition to this basic equipment, a set of auxiliary systems is required to complement the calendaring process. The rubber compounds used can only be used if they are within their intended limits of use, *e.g.*, expiration date. The impregnated fabric is a textile fiber that has been soaked in a suitable solution at the supplying company, which is one of the raw materials in the calendaring process, and as such should only be used if it is identified with a supplier's label, so that it can be identified in case of problems in the calendaring or subsequent processes.

The calendaring process begins with the mixing of the rubber compound in mixers. Next, the rubber is applied by means of large rotating rollers on both sides of the textile fabric, at which point the final thickness of the material is checked. The calendered fabric then goes through the cooling system and is collected on spools and covered with the polyethylene film so that it does not stick (Ferreira, 2018). Figure F.1 shows a representative scheme of the calendaring mode.

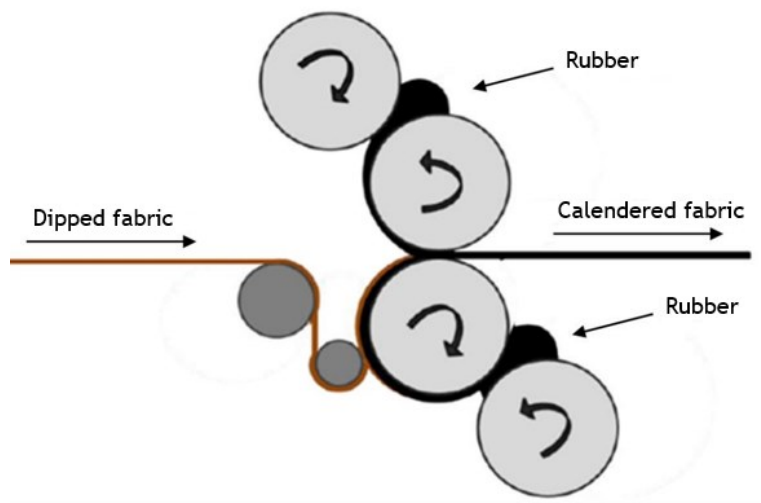


Figure F.1 - Schematic representation of the calender configuration (adapted from Ferreira, 2018).

For single-end cords, it is used a system that is slightly different from calendaring, since the introduction of the rubber into the textile is done through an extrusion process - capstrip. The structure is made up of two spinnerets that introduce the rubber on both sides of the dipped cord. This equipment consists of the creel, being the place where the various coils of the textile cord are located. Finally, it has a winding system, where the single-end cord is wound onto spools.

Annex G - Curing unit

Regarding curing, the tire is placed in the press and the bladder is molded by feeding it with saturated steam. This step is extremely important because it allows the tire to be positioned correctly, which is a necessary condition for closing the press, in which a shaping pressure is created, which will also allow the tire to be removed from the mold more easily later. After this press closure, the mold moves from outside to inside and the bladder is fed with saturated steam in order to reach the internal pressure, allowing to follow the specifications of a predefined vulcanization cycle at 180°C. This pressure is controlled by a pressure transducer, which defines the opening of the internal valve, whose function is to regulate the flow of steam entering the bladder.

Along with the step previously described, a stream of saturated steam circulates in the upper and lower part of the dome, promoting the heating of the mold. The mold that surrounds the tire is made of metallic material, usually steel or aluminum, so it quickly reaches thermal equilibrium with the surrounding fluid, due to its high thermal conductivity. Thus, there is heat transfer internally from the bladder to the tire and externally from the mold to the tire. Throughout the vulcanization cycle, condensate is formed and drained off to ensure that the temperature, during the curing time, follows a certain predefined vulcanization cycle. At the end, the total drainage of the water resulting from the steam condensation is performed. Once the drainage is done, the wet vapor present in the bladder is pumped out, in order to allow the tire to exit. The aspirated vapor condenses due to cooling and is routed through the secondary and primary branches to a reservoir. The reservoir functions as an air/condensate separator, and the condensate is sent to the water treatment plant. Figure G.1 exhibits the various stages of the vulcanization process, described above.

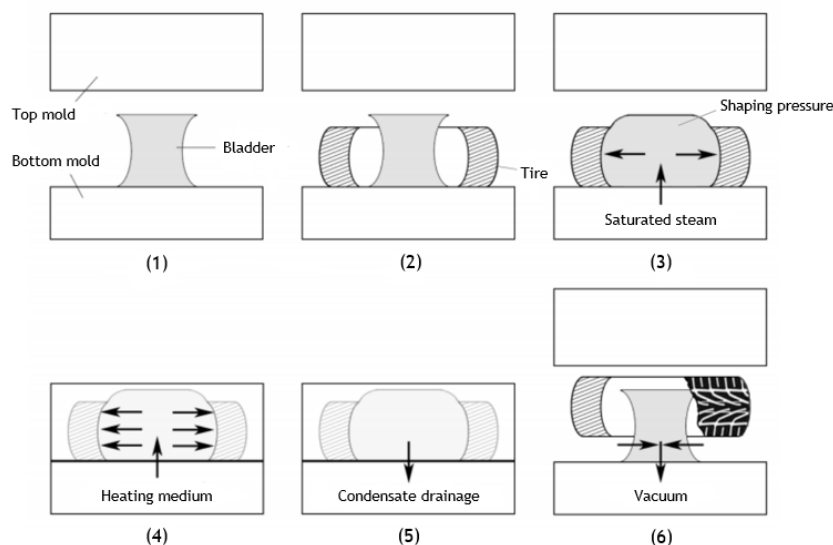


Figure G.1 - Stages and operations underlying a vulcanization cycle.

Annex H - Thermal Shrinkage Tester 510/250

Annex H is intended to present the technical data concerning the operation of the Thermal Shrinkage Tester 510/250. Along these lines, Figure H.1 and Table H.1 display the actual image of the equipment as well as its specifications, provided by Lenzing Instruments, respectively.



Figure H. 1 - Thermal Shrinkage Tester 510/250 (Lenzing Instruments, n.d.).

Table H. 1 - Technical data of Thermal Shrinkage Tester 510/250 (Lenzing Instruments, n. d.).

Testing temperature	From 45 °C to 300 °C
Heater length	250 mm
Temperature distribution	The temperature's distribution over the 10 testing positions within the oventype heater is better than 1 %
Range of shrinkage length	From - 500 % to 99 % Accuracy: ± 0.1 %
Range of shrinkage force	1 - 2000 cN (other ranges on request) Accuracy: < 0.2 % (at 50% of full scale) Calibration: with 10 N weight
Max. sample width	1.3 mm
Pre-tensioning	With pretension weights, from 0 to 500 cN possible (depending on linear density of sample)
Resolution	Force: 1 cN (=0,01N) Temperature (display): 0,1 °C Shrinkage length: 0,1%

The prescribed pre-tensioning mass (for the standard measurements performed in this equipment) to the free end of the specimen is specified by the ASTM D4974 and D 5591 and it can be found in Table H.2.

Table H. 2 - Standard pre-tensioning masses for shrinkage and shrinkage force measurements ^{1,2}.

Material	Construction / dtex	Pre-tensioning force / cN
Polyester (HMLS)	1100x2	22
	1440x2	29
	2200x2	44
	3340x2	67
PA 6 & PA 6.6	470x2	48
	940x2	94
	1400x1	70
	1400x2	140
	2100x2	210
Hybrid	1670x2 AR + 470x1 PA 6.6	24
	1670x1 AR + 1400x1 PA 6.6	70

¹ The pre-tensioning for all materials except polyester (HMLS) is 0.05 cN/dtex and is dependent on the nominal titer.

² For polyester (HMLS), a pre-tensioning of 0.01 cN/dtex applies, which is also dependent on the nominal titer.

Appendices

Appendix I - Planning of experiments

Table I.1 - List of materials used in this project, as well as the studies that were conducted for each one.

Material	Construction / dtex	Twist Level / trn·m ⁻¹	Twist Factor	Non-standard Twist Factor	Fabric/SEC	State of the cord	Yarn Producer	Converter	Measurements/ Analyses
PET	1100x2	420	197.0	-	Fabric	Dipped	-	-	Standard shrinkage and shrinkage force
									3 ^k DOE
									DSC
									Structural elongation
									Clamping force
	1440x2	380	203.9	246.9	Fabric	Dipped	-	-	Standard shrinkage and shrinkage force test
				150.3		Greige			Twist level analysis
						Calendered			
	2200x2	300	199.0	-	Fabric	Dipped	-	-	Standard shrinkage and shrinkage force
	3340x2	250	204.3	-	Fabric	Dipped	PF	ITA	Standard shrinkage and shrinkage force
							Hyosung	Hyosung	DSC
							Hyosung	Hyosung	Structural elongation
							Hyosung	ITA	Moisture analysis
									Supplier evaluation

Material	Construction / dtex	Twist Level / trn·m ⁻¹	Twist Factor	Non-standard Twist Factor	Fabric/SEC	State of the cord	Yarn Producer	Converter	Measurements/ Analyses
PA 6.6	470x2	420	128.8	-	Fabric	Dipped	-	-	Standard shrinkage and shrinkage force
									DSC
									Structural elongation
									Clamping force
	940x2	350	151.8	203.8 230	Fabric	Dipped	Dikai	ITA	Standard shrinkage and shrinkage force
						Greige	PHP	Kordana	Structural elongation
						Calendered	Hyosung	Hyosung	Twist level analysis
									Supplier evaluation
	1400x1	100	37.4	-	Fabric	Dipped	-	-	Standard shrinkage and shrinkage force
									DSC
	1400x2	290	153.5	-	Fabric	Dipped	-	-	3 ^k DOE
									Standard shrinkage and shrinkage force
									Structural Elongation
									Clamping force

Material	Construction / dtex	Twist Level / trn·m ⁻¹	Twist Factor	Non-standard Twist Factor	Fabric/SEC	State of the cord	Yarn Producer	Converter	Measurements/ Analyses
PA 6	2100x2	300	194.4	-	Fabric	Dipped	-	-	Standard shrinkage and shrinkage force DSC Structural Elongation
AR	1670x2	302	200.3	-	Fabric	Dipped	-	-	Standard shrinkage and shrinkage force DSC
Hybrid	1670x2 AR + 470x1 PA 6.6	320	205.3	-	SEC	Dipped	-	-	Standard shrinkage and shrinkage force

Appendix J - Studies of the structural elongation influence

To study the influence of the cord elongation mechanism, an experimental set-up was prepared, similar to the one schematically represented in Figure J.1. As it can be observed, a hydraulic lift table was used, so that the length difference recording, starts only when this table is lowered. It should be noted that these measurements were carried out at room temperature and the objective was to realise if it is correct to start the shrinkage test immediately after placing the pre-loads.

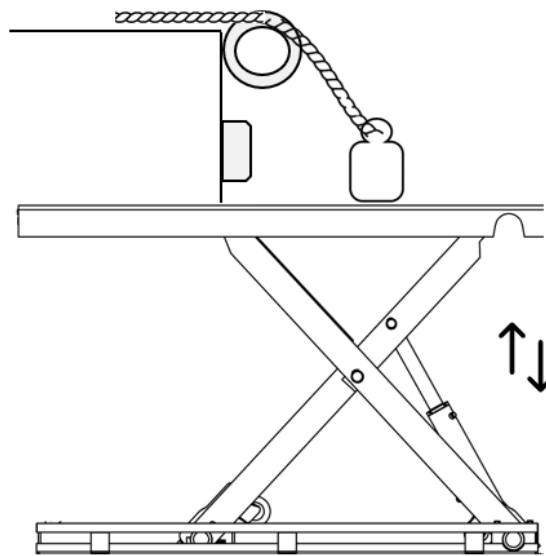


Figure J.1 - Schematic representation of the experimental set-up.

It was experimentally verified that the structural elongation mechanism has no effect for the pre-loads prescribed by the ASTM D4974 and D 5591. However, in this project, for some measurements, a tensile holding much higher than the prescribed one was used. It was proved empirically that for these tests and, in order to obtain results with a smaller margin of error, the measurement should not be started immediately after the pre-load was placed. The normalized results of the elongation as a function of time can be found from Figure J.2 to Figure J.5. As an example, for PET 1100 dtex x 2 (Figure J.2), when a pre-load of 10 N is applied, it takes a long time to complete the structural elongation. However, for the same material, but for a thicker construction, it was found that even for 10 N, the structural elongation mechanism is residual (Figure J.3). On the other hand, for PA 6.6 there are more prominent structural elongation effects, since for a given force, PA 6.6 elongates much more than PET as it is easily observed by the stress-strain curves. For this reason, care was taken to wait at least 2 minutes before starting the shrinkage and shrinkage force tests for PA 6.6.

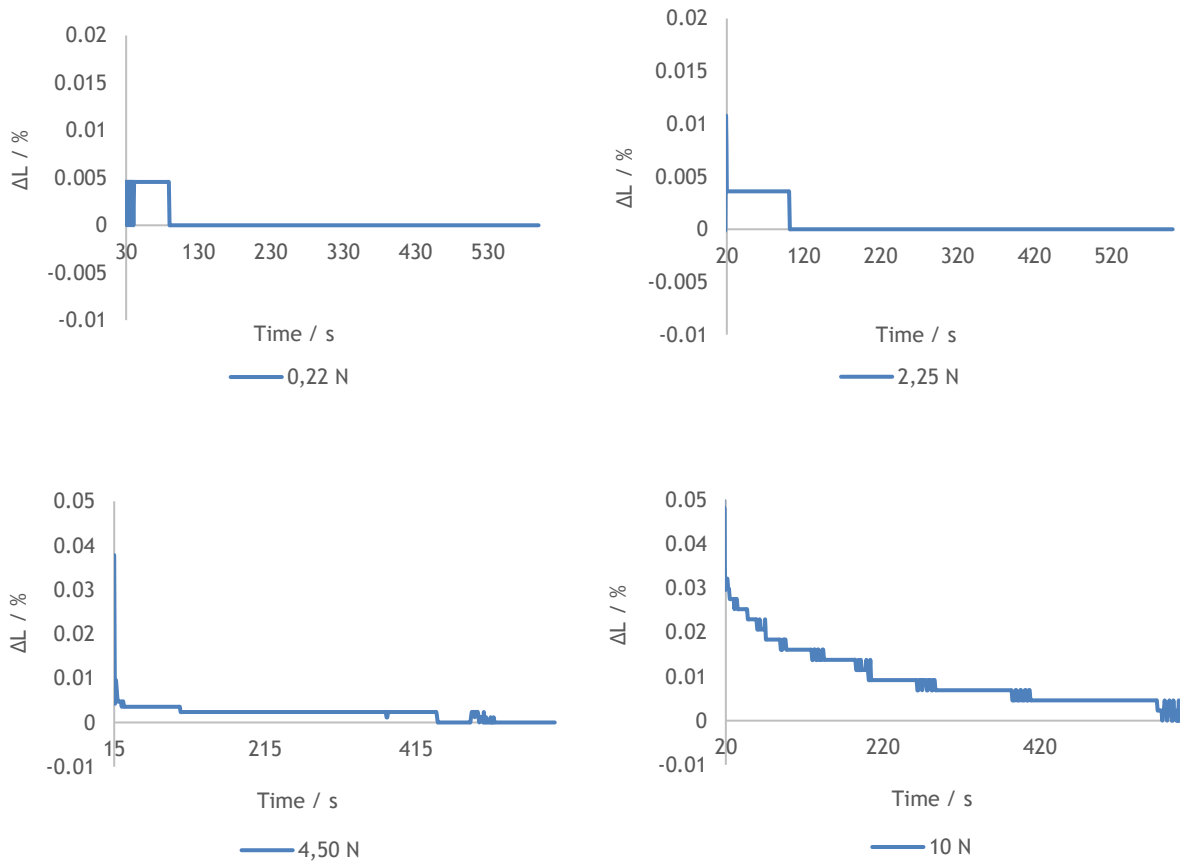


Figure J.2 -Structural elongation as a function of time of PET 1100 dtex x2.

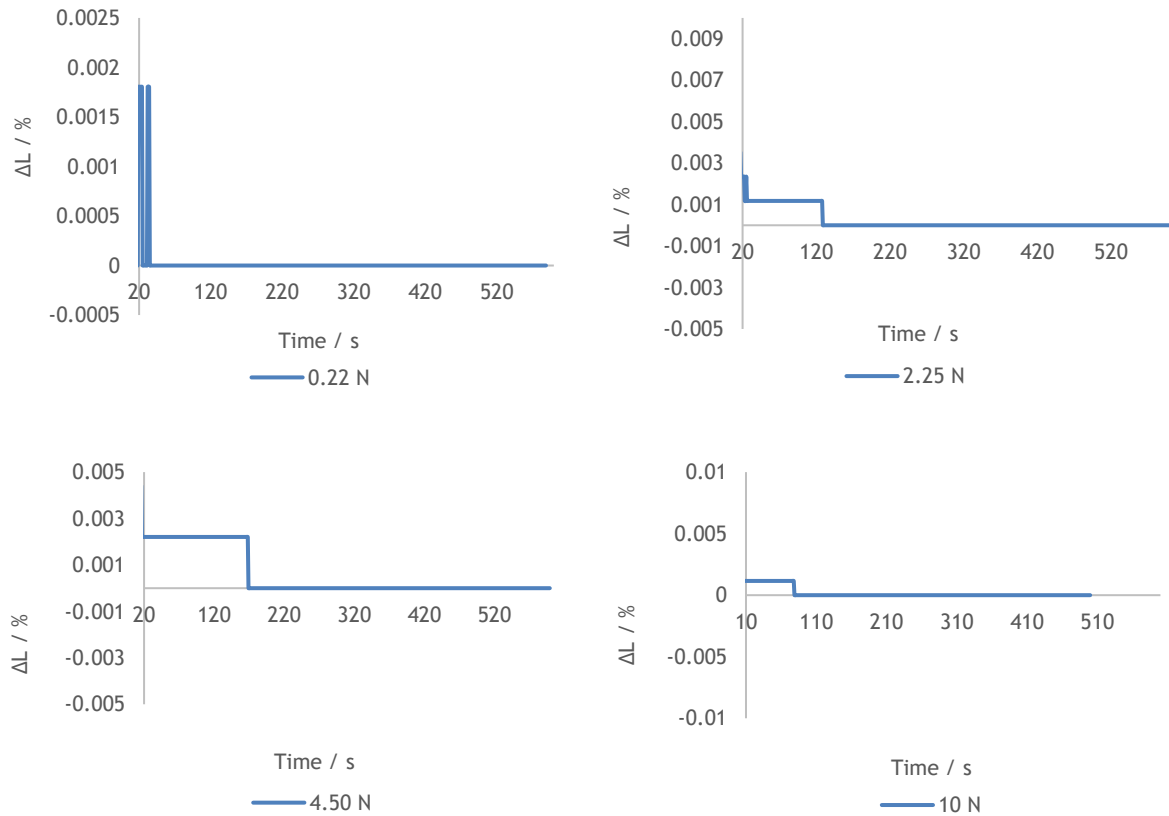


Figure J.3 -Structural elongation as a function of time of PET 3340 dtex x2.

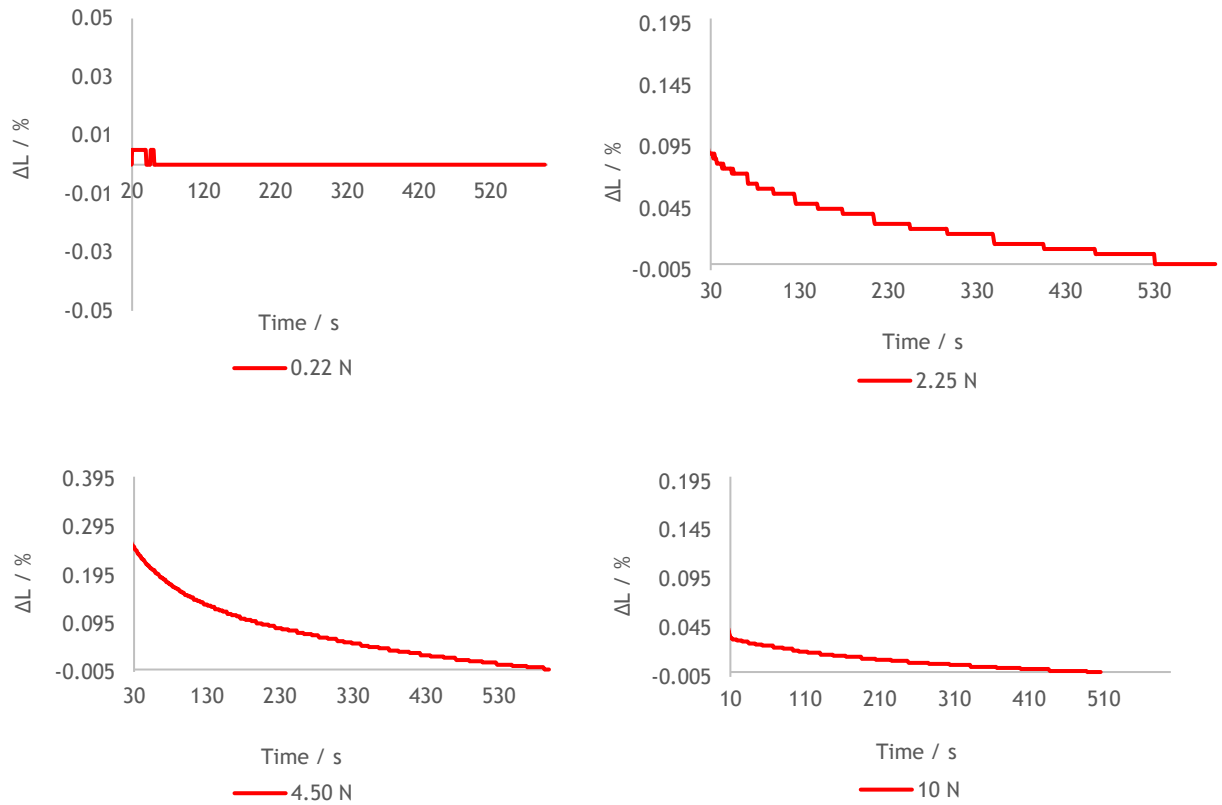


Figure J.4 -Structural elongation as a function of time of PA 6.6 470x2 dtex.

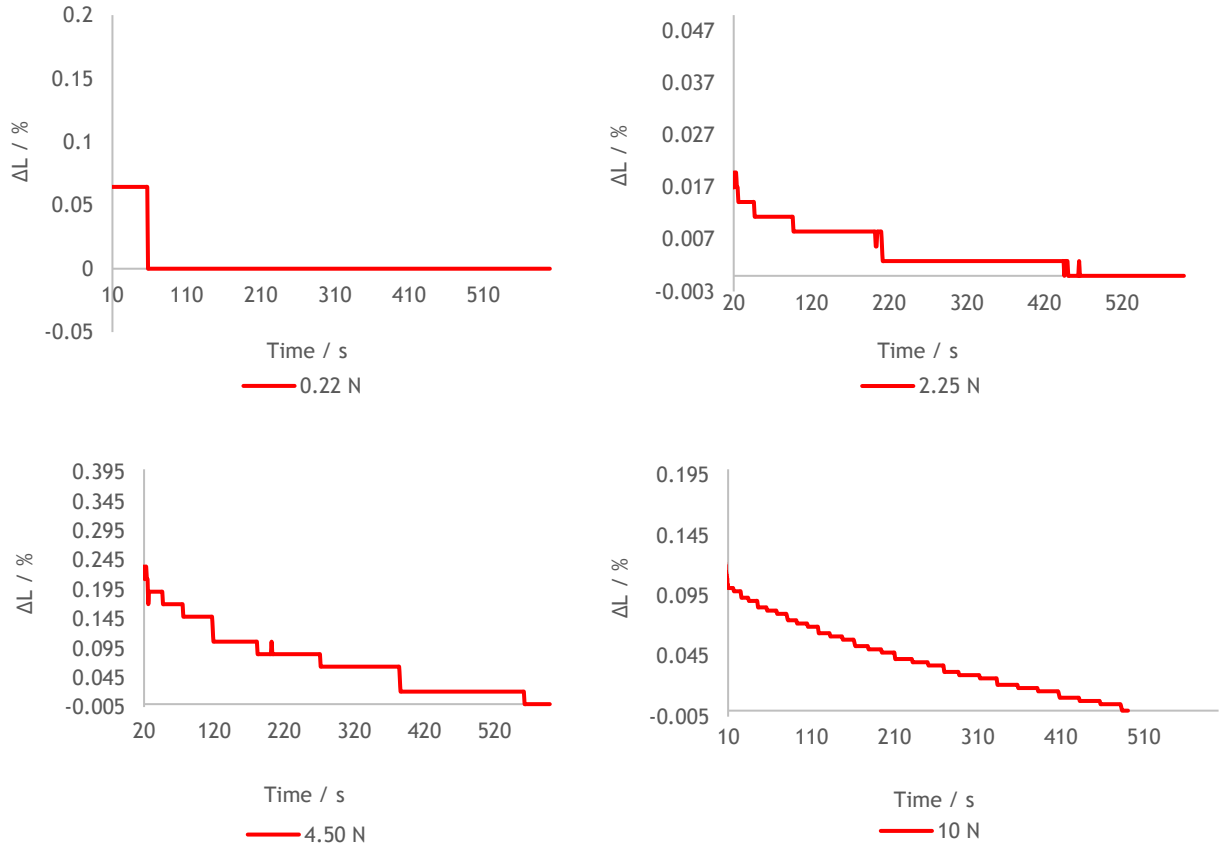


Figure J.5 -Structural elongation as a function of time of PA 6.6 1400 dtex x2.

Appendix K - Studies of the clamps' influence

To every material, there is an appropriated clamp to test it and, more importantly, to correctly grab the cord. Regarding the TST 510/250, these hold action, can be provided by a manual mechanical action, as illustrated in Figure K.1.

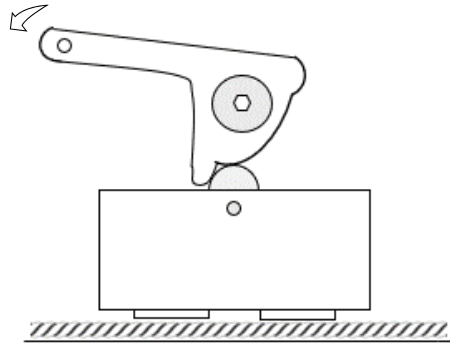


Figure K.1 - Schematic representation of the toggle clamp present in the TST 510/250.

In addition to the manual opening and closing of the clamp, with the aid of the adjusting control knob, it is possible to slide the clamp axially to adjust the pre-tension.

However, in this analysis, in order to examine a possible influence that the clamp may have on the shrinkage force values, it has been taken measurements of the force evolution when the clamp is closed (at room temperature) without the need to adjust the force with the control knob. For that purpose, the knob positions described in Figure K.2 were used. Furthermore, to avoid any disturbance caused by the structural elongation, perceived earlier, it should be waited at least 2 minutes before closing the clamp.

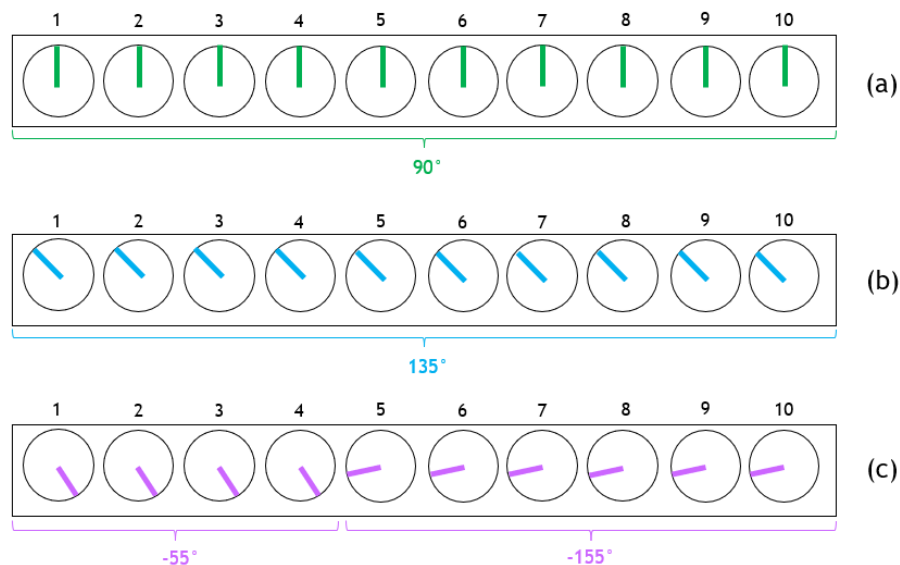


Figure K.2 - Schematic representation of the tested positions of the adjusting control knob.

For these measurements, the thickest and thinnest cord available in the portfolio was chosen for PET and PA 6.6 materials. The results showed that for the PET with the thickest cord, there is no excessive loss of force and with the further assistance of the adjusting control knob it is possible to regulate the desired pre-load. However, when testing the thinner cord, it was found that for a pre-load of 10 N, there is a significant loss of force in most positions (Figure K.3), alongside with some residual slippage. Considering that for this material, the contact area between the clamp and the cord is smaller, the clamping force will then be affected. Having said this, although these results do not influence the measurements performed with the prescribed pre-load defined by ASTM D4974 and D 5591, periodic inspections of the clamps should be carried out and if possible, perform a tool clamping wear examination.

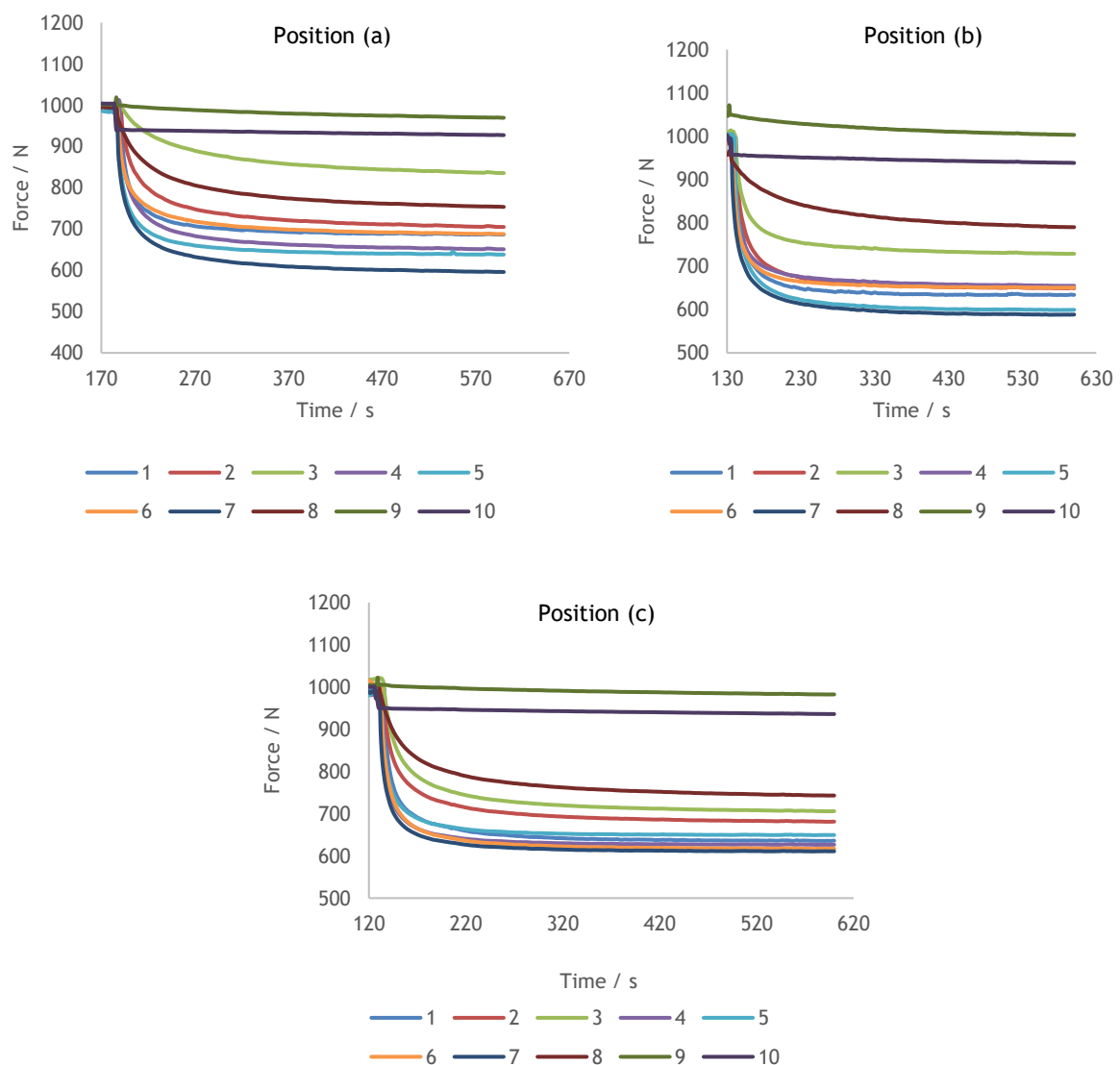


Figure K.3 - Clamp load loss of PET 1100 dtex x2, for different knob positions.

The same procedure was applied to the PA 6.6 constructions and the results were similar to those obtained for PET. However, for this thin cord, the force did not stabilize and may be due to structural elongation observed (Figure K.4) in the previous subchapter, since the 2 minutes

before closing the clamp may not be enough to prevent structural elongation from impacting the results.

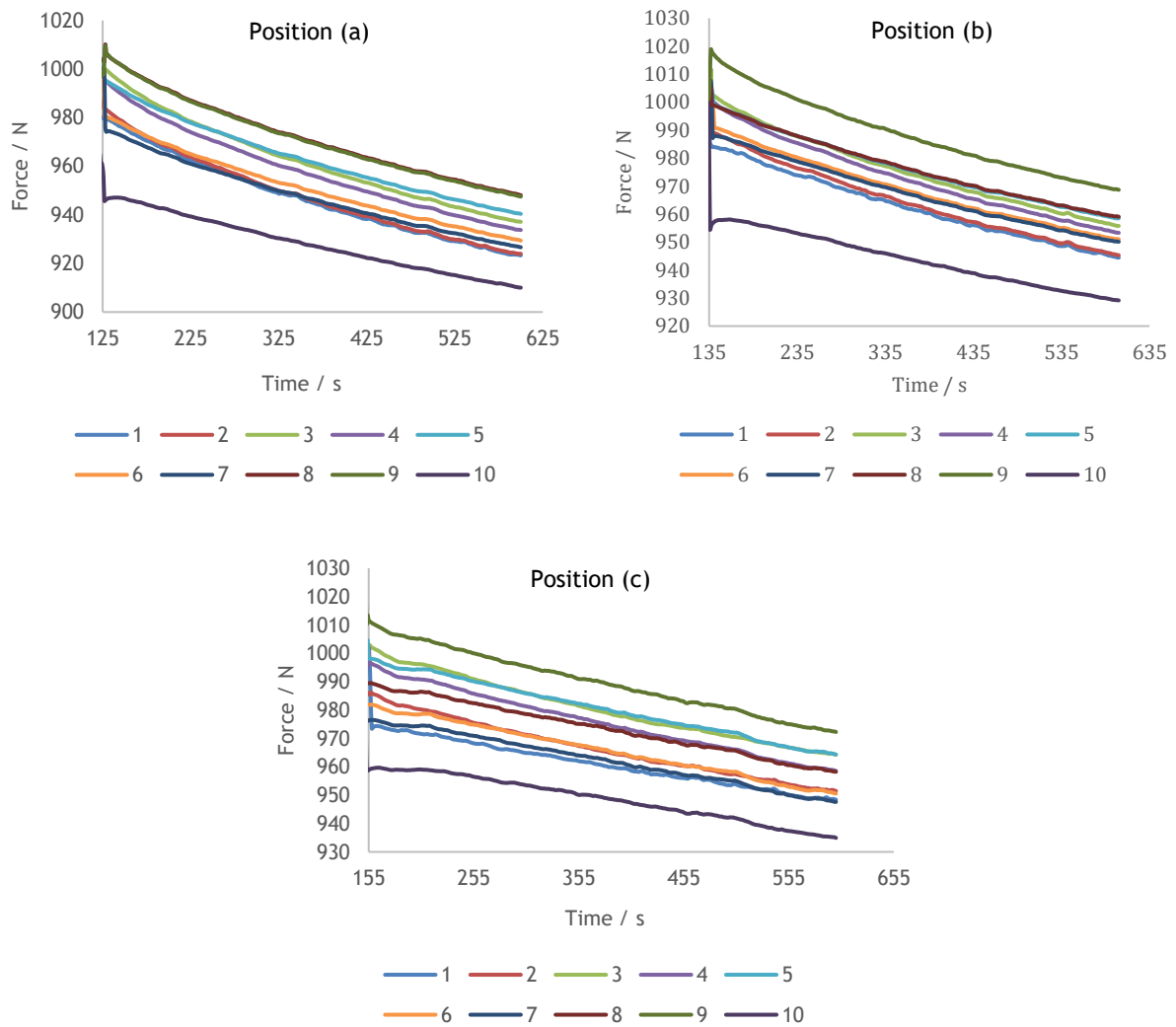


Figure K.4 - Clamp load loss of PA 6.6 1400 dtex x2, for different knob positions.

Appendix L - Kinetics of Isothermal Shrinkage

Assuming that the shrinkage follows the first order reaction. The change (first derivative) of concentration with respect to time, dC/dt , is proportional to the concentration, C , and given by Equation L.1:

$$\frac{dC}{dt} = -kC \quad (\text{L.1})$$

where, C is equivalent to the fraction of the unreacted reactant. Therefore:

$$C = \frac{l - l_{\infty}}{l_0 - l_{\infty}} \quad (\text{L.2})$$

Rearranging Equation L.1 and integrate the equation using the following boundary conditions (BC):

$$\text{BC1: } t=t_0, \quad C=1 \quad (l=l_0)$$

$$\text{BC2: } t=t, \quad C=C$$

Then:

$$\int_1^C \frac{dC'}{C'} = -k \int_{t_0}^t dt' \quad (\text{L.3})$$

Which can be rewritten as:

$$\ln C = -k(t - t_0) \quad (\text{L.4})$$

Or:

$$C = \exp[-k(t - t_0)] \quad (\text{L.5})$$

Substituting the definition for C into Equation L.5:

$$\frac{l - l_{\infty}}{l_0 - l_{\infty}} = \exp[-k(t - t_0)] \quad (\text{L.6})$$

Rearranging Equation L.6:

$$\frac{\frac{l_0 - l_{\infty}}{l_0} - \frac{l_0 - l}{l_0}}{\frac{l_0 - l_{\infty}}{l_0}} = \exp[-k(t - t_0)] \quad (\text{L.7})$$

Making an analogy with the definition of Shrinkage (Equation 5):

$$\frac{s_{\infty} - s}{s_{\infty}} = 1 - \frac{s}{s_{\infty}} = \exp[-k_n(t - t_0)] \quad (\text{L.8})$$

Or:

$$s = s_{\infty} (1 - \exp[-k_n(t - t_0)]) \quad (\text{L.9})$$

Appendix M - Shrinkage Modelling

The full shrinkage response modelling of semi-crystalline can be planned using a simple model, which is a combination of the two Kelvin units (the springs, S_1 and S_2 , and the dashpots, D_1 and S_2 , in parallel), purposed by Diaz and Youngblood (2016), and one dashpot unit in series, as shown in Figure M.1. The shrinkage will not start until the temperature reaches a critical onset temperature, where the spring stress, overcomes the viscous retardation of the dashpot. If the dashpot D_3 is not then attached to the extended Kelvin units, the Kelvin units are not fixed and relaxes freely without constraints. Therefore, with this proposed representation, when the oven is removed, the deformation of dashpot D_3 is not recovered, and the result is a permanent degradation.

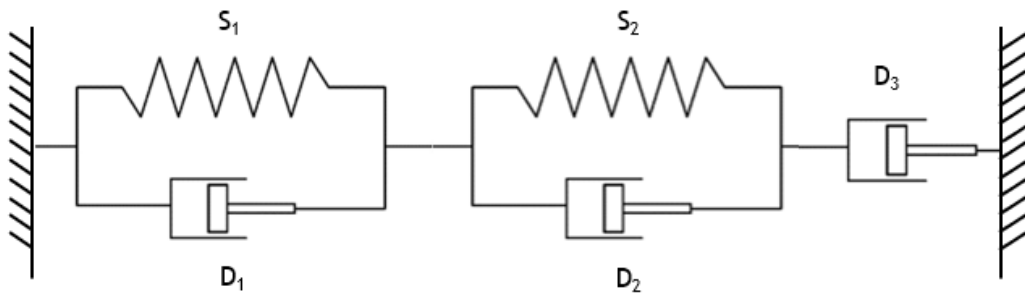


Figure M.1 - Proposed model to describe the shrinkage of uniaxially oriented semi-crystalline polymeric segments.

Appendix N - Design of experiments

Appendix N is intended to present the results of the Design of Experiments carried out for PET 1100 dtex x2 and for PA 6.6 1400 dtex x2, with the aim to determinate which variables are most influential on the response of shrinkage force.

Results, displayed on Figure 28, already demonstrated that for PET 1100 dtex x2, temperature and static load exhibited significant interactions on the response. Time variable had any significant effect on the response of shrinkage force.

The normal probability plot, the residuals as a function of fitted values, the histogram and residuals as a function of order of data can be found in Figure N.1.

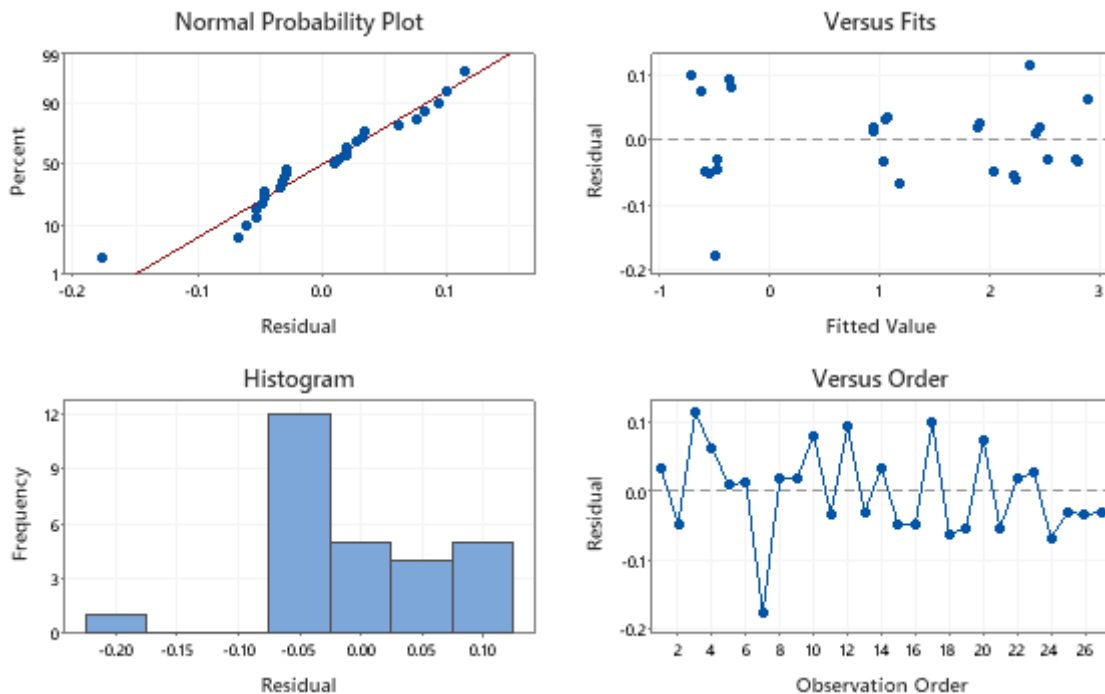


Figure N.1 - Analysis of residuals (DOE analysis of PET 1100 dtex x2).

The normality assumption can be checked by analysing the normal probability plot of the residuals. It can be concluded that there are not large deviations from the normal distribution, thus the residuals form a straight line.

The residual as a function of fitted values displays a random pattern of residuals on both sides of 0. There is no pattern in the residual plot, being in accordance with the constant variance assumption.

The residual as a function of order of data plot corroborates the assumption that the residuals are uncorrelated with each other, as there is no pattern in the results.

Furthermore, the residuals as a function of the parameters studied can be found in Figure N.2.

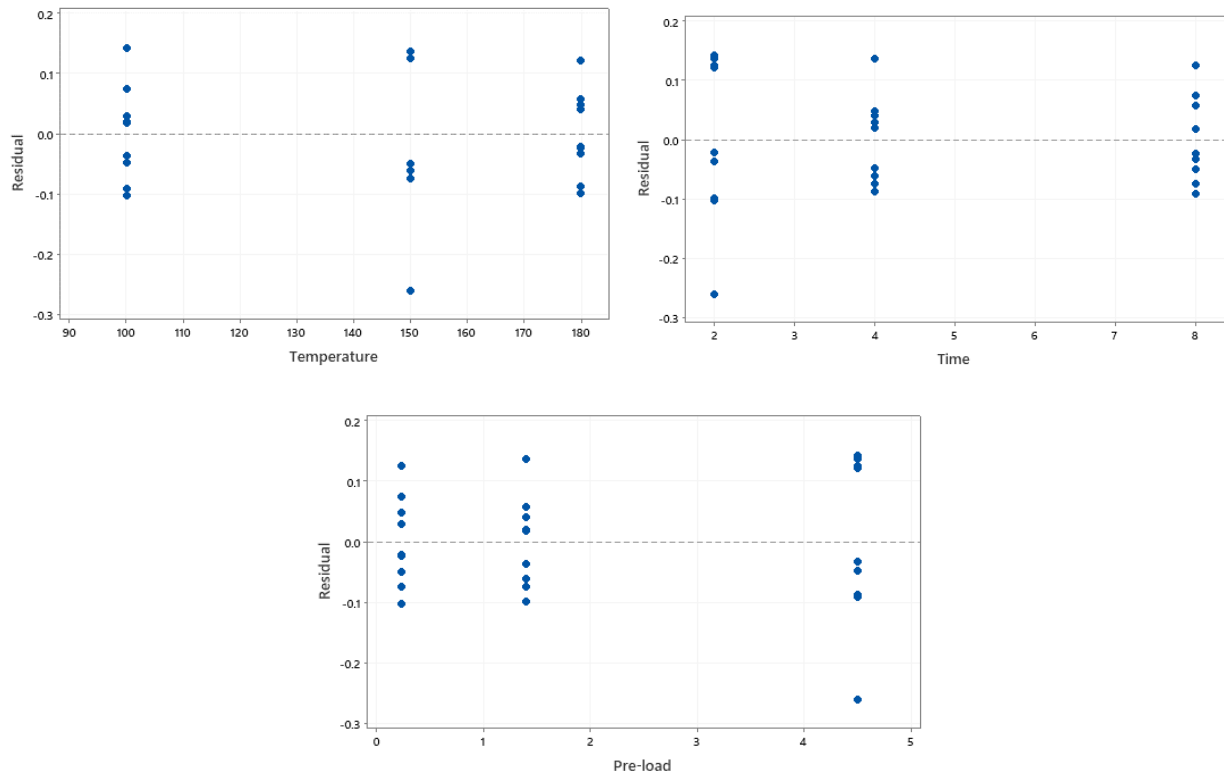


Figure N.2 - Residuals of the factors (DOE analysis of PET 1100 dtex x2).

In addition, it was examined, for the factors of interest, the main effect plot. As it is seen in Figure N.3, pre-load and temperature factors present significance, *i.e.*, the mean response changes across the levels of a factor.

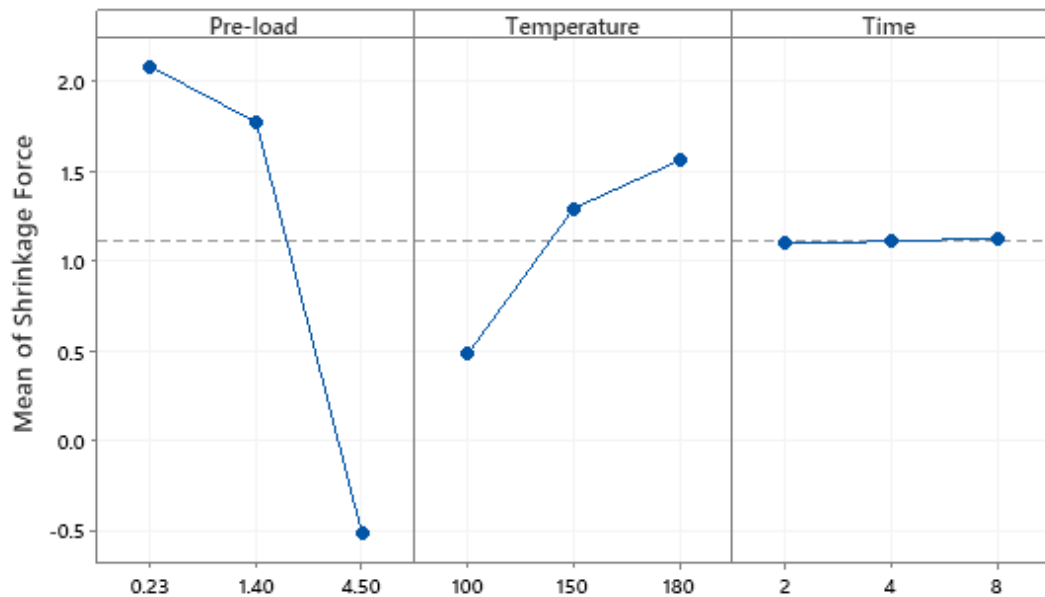


Figure N.3 - Main effect plot (DOE analysis of PET 1100 dtex x2).

Furthermore, the interaction plot graphic supports the interaction effect between pre-load and temperature (Figure N.4). Noteworthy to mention that an interaction between factors occurs when the change in response from the low level to the high level of one factor is not the same

as the change in response at the same two levels of a second factor. That is, the effect of one factor is dependent upon a second factor.

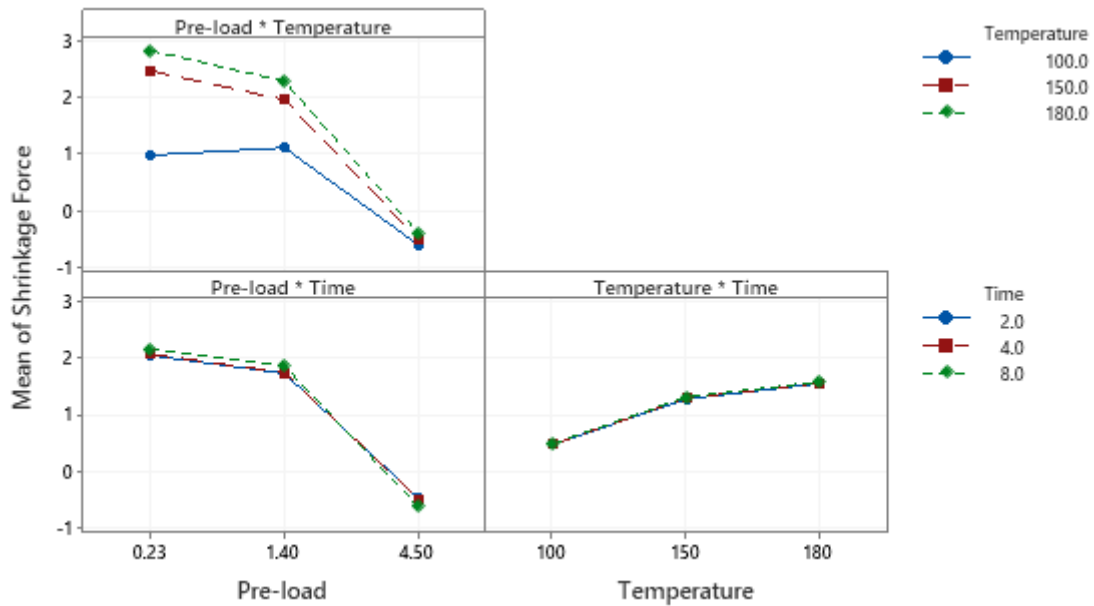


Figure N.4 - Interaction plot (DOE analysis of PET 1100 dtex x2).

Moreover, an analysis of the variance that summarizes the main effects and interactions, can be found in Table N.1. Observing at the p-values it is seen three significant values, *i.e.*, the values are lower than $\alpha = 0.05$.

Table N.1 - Analysis of the variance (DOE analysis of PET 1100 dtex x2).

	F-value	P-value
Pre-load	1339.18	0.000
Temperature	208.54	0.000
Time	0.12	0.884
Pre-load x Temperature	43.72	0.000

Regarding the results obtained for PA 6.6, which was used the same Design Level of Table 4, it was found that once again the temperature and the pre-load have more influence on the response of the shrinkage force. However, it is noteworthy to highlight that for this case, the temperature presents more influence when compared with the pre-load, contrary to what happened with PET. The same analysis and conclusions mentioned above, can serve for the present results from Figure N.5 to Figure N.9 and Table N.10. The p-value obtained was 0.211 by the Anderson-Darling test. Once again, it should not be rejected the null hypothesis that the data is normally distributed, and it is possible to accept that the data is normally distributed.

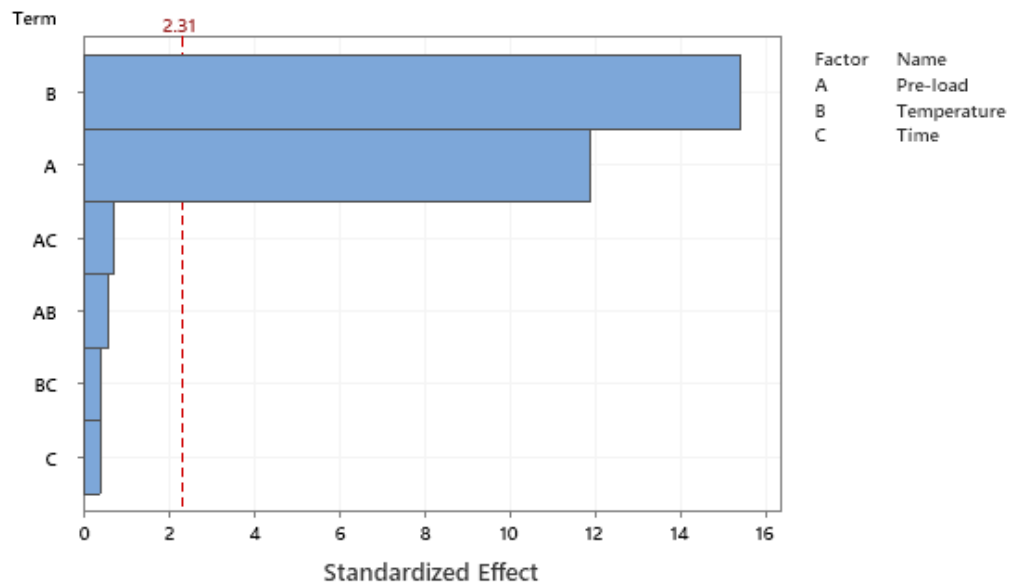


Figure N.5 Pareto chart of selected variables on the response of shrinkage force of PA 6.6 1400x2 dtex.

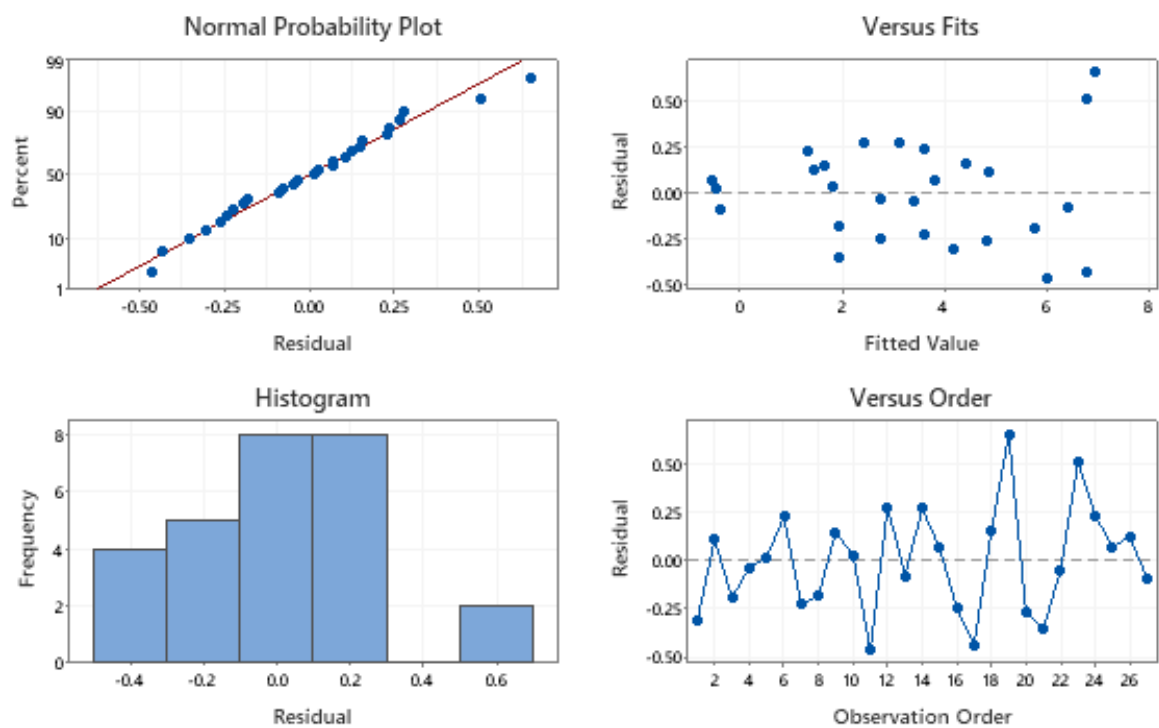


Figure N.6 - Analysis of residuals (DOE analysis of PA 6.6 1400 dtex x2).

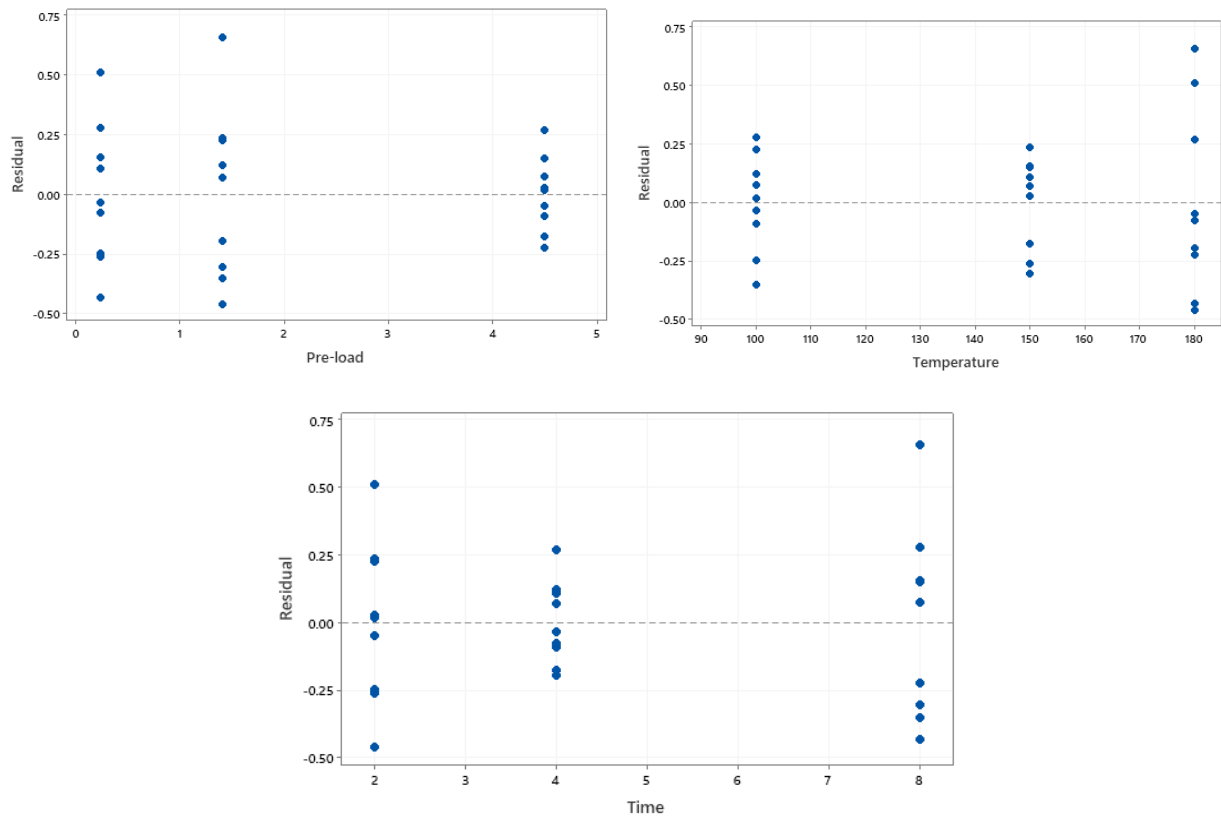


Figure N.7 - Residuals of the factors (DOE analysis of PA 6.6 1400 dtex x2).

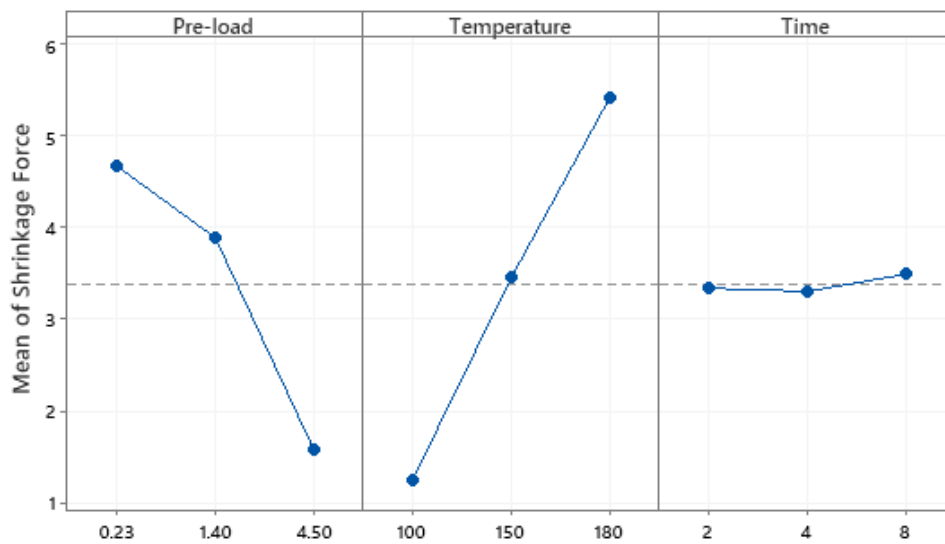


Figure N.8 - Main effect plot (DOE analysis of PA 6.6 1400 dtex x2).

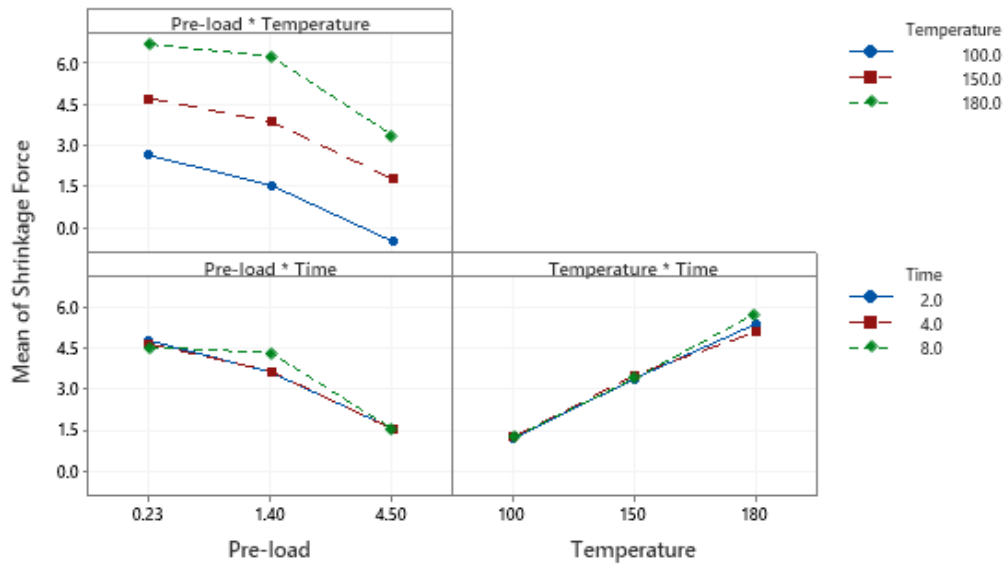


Figure N.9 - Interaction plot (DOE analysis of PA 6.6 1400x2).

Table N.2 - Analysis of the variance (DOE analysis of PET 1100x2).

	F-value	P-value
Pre-load	88.06	0.000
Temperature	98.56	0.000
Time	165.23	0.697
Pre-load x Temperature	0.76	0.582

Appendix O - Shrinkage force curves

Appendix O is intended to present the normalized shrinkage force curves as a function of the pre-tensioning weight for the different materials assessed in this project.

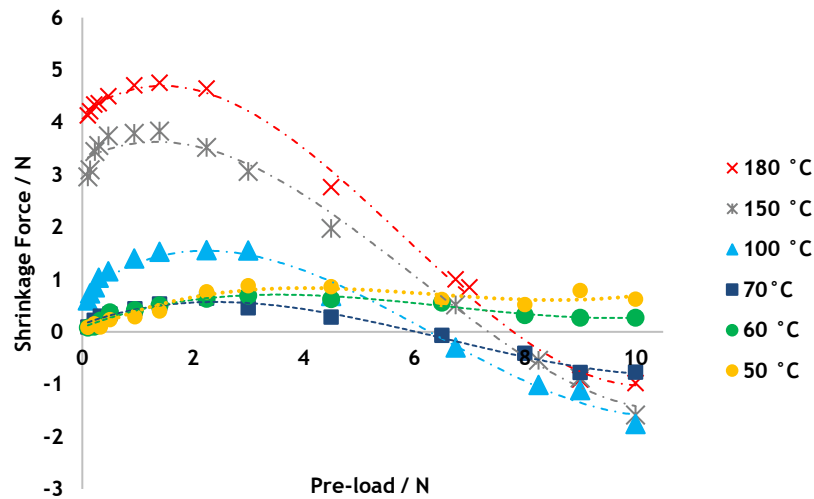


Figure O.1 - Shrinkage force of dipped PET 3340 dtex x2 as a function of the tensile holding, for different temperatures.

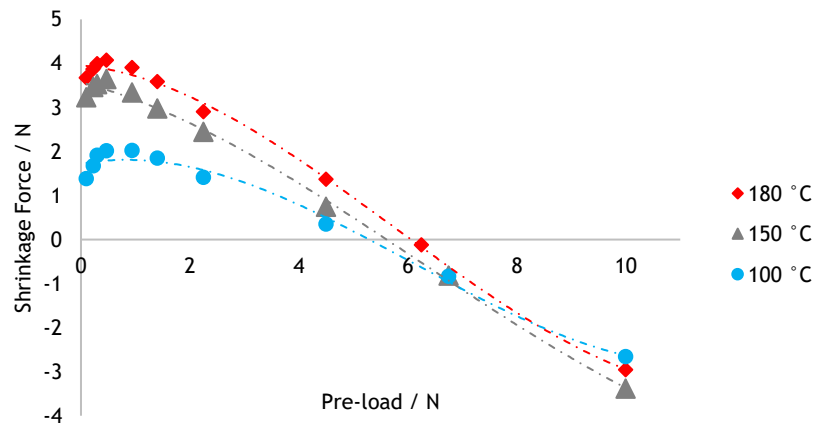


Figure O.2 - Shrinkage force of dipped PET 2200 dtex x2 as a function of the tensile holding, for different temperatures.

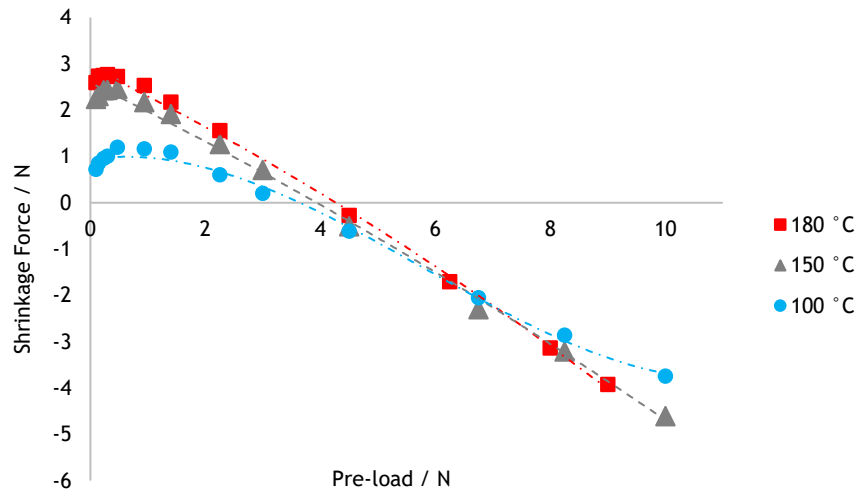


Figure O.3 - Shrinkage force of dipped PET 1440 dtex x2 as a function of the tensile holding, for different temperatures.

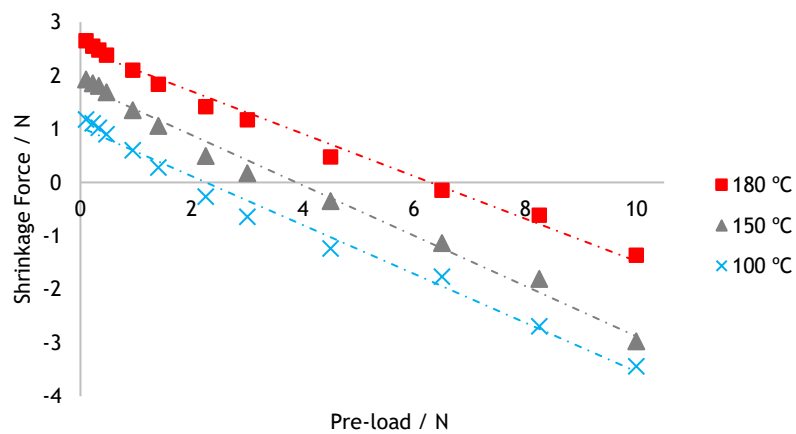


Figure O.4 - Shrinkage force of dipped PA 6.6 470 dtex x2 as a function of the tensile holding, for different temperatures.

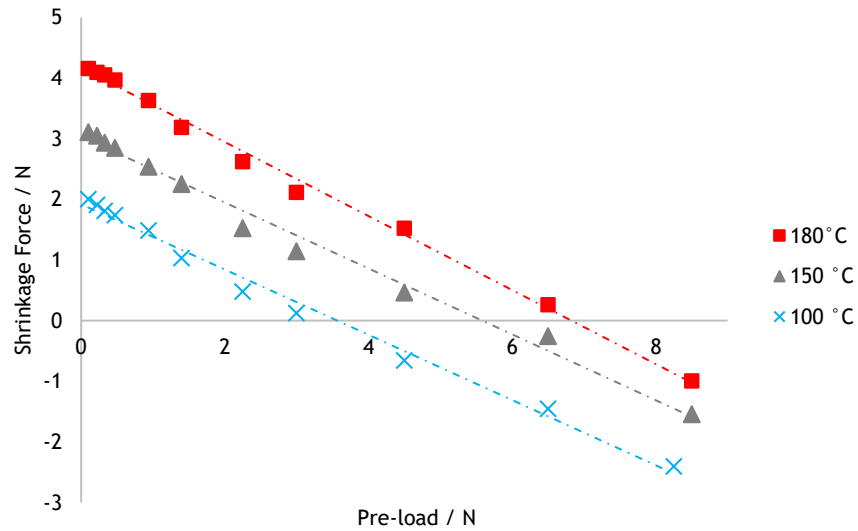


Figure O.5 - Shrinkage force of dipped PA 6.6 1400 dtex x1 as a function of the tensile holding, for different temperatures.

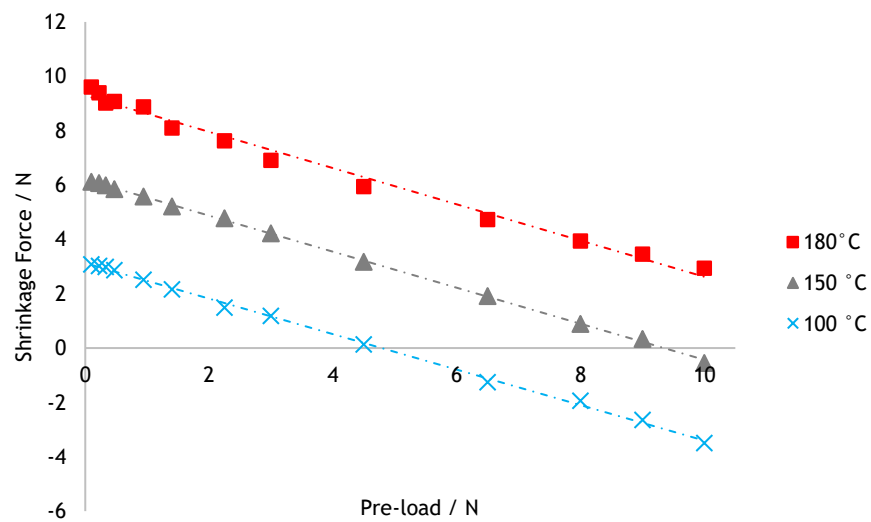


Figure O.6 - Shrinkage force of dipped PA 6 2100 dtex x1 as a function of the tensile holding, for different temperatures.

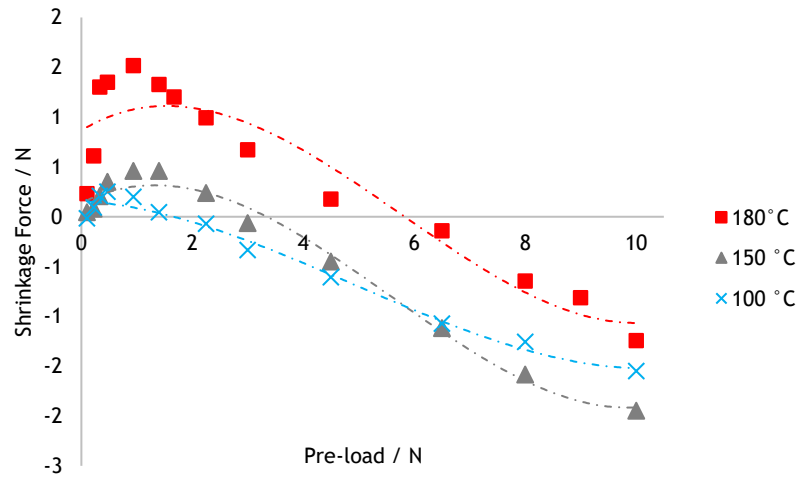


Figure 0.7 - Shrinkage force of dipped Aramid 1670 dtex x2 as a function of the tensile holding, for different temperatures.

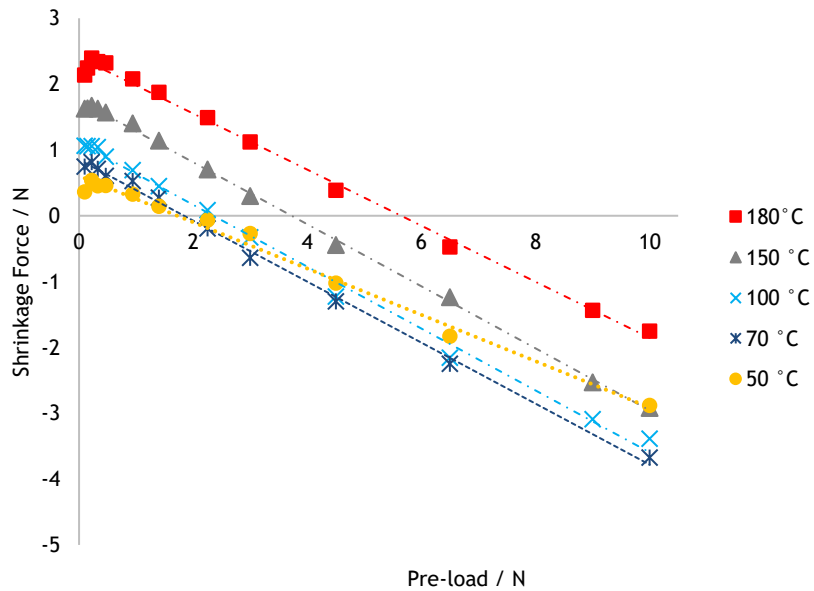


Figure 0.8 - Shrinkage force of dipped Aramid 1680dtex x2 + PA 6.6 470 dtex x1 dtex as a function of the tensile holding, for different temperatures.

Appendix P - DSC thermograms

Appendix P is intended to present the remaining DSC measurements performed in this project. The results for the different PET specimens can be found in Figure P.1 and Table P.1.

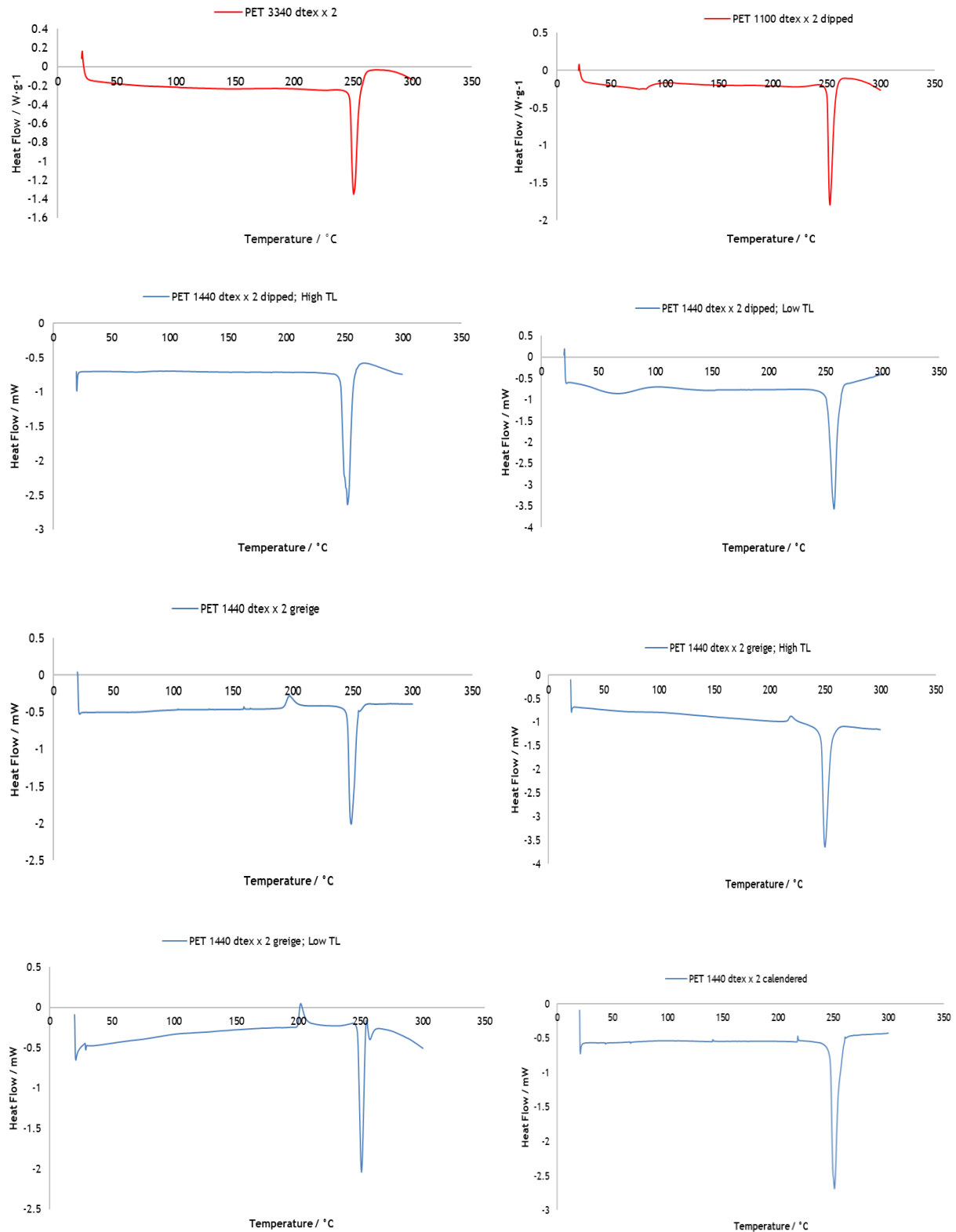


Figure P.1 - DSC thermograms of PET samples.

Table P.1 - Percentage of crystallinity calculated from the DSC analysis of PET specimens.

Material	Construction / dtex	State of the cord	$\Delta H_m / \text{J} \cdot \text{g}^{-1}$	$\Delta H_c / \text{J} \cdot \text{g}^{-1}$	$\Delta H_m^0 / \text{J} \cdot \text{g}^{-1}$	$X_{cr} / \%$
PET	1100x2	Dipped	49.41	0	140.1	35.58
	3340x2	Dipped	48.45	0	140.1	34.58
	1440x2	Dipped/ High TL	48.53	0	140.1	34.64
		Dipped/ Low TL	45.75			32.66
		Greige	40.99	4.41		26.11
		Greige/ High TL	44.85	1.26		31.11
		Greige/ Low TL	32.9	5.86		19.30
		Calendered	52.76	0		37.66

Regarding the results of PA 6.6, these can be found in Figure P.2 and Table P.2.

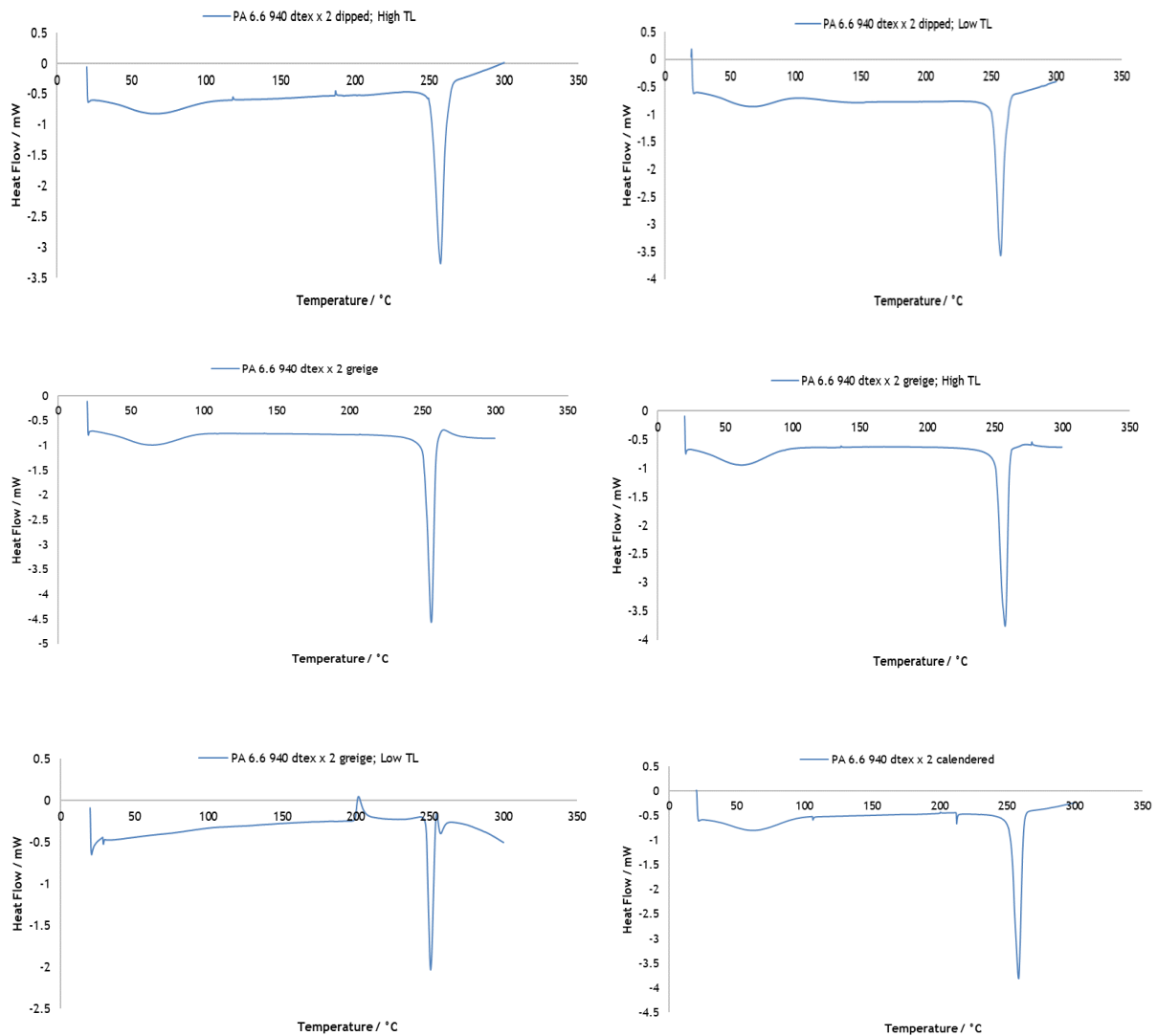
**Figure P.2** - DSC thermograms of PA 6.6 samples.

Table P.2 - Percentage of crystallinity calculated from the DSC analysis of PA 6.6 specimens.

Material	Construction / dtex	State of the cord	$\Delta H_m / \text{J}\cdot\text{g}^{-1}$	$\Delta H_c / \text{J}\cdot\text{g}^{-1}$	$\Delta H_m^0 / \text{J}\cdot\text{g}^{-1}$	$X_{cr} / \%$
PA 6.6	940x2	Dipped/ High TL	77.55	0	255.8	30.32
		Dipped/ Low TL	75.75			29.61
		Greige	64.84			25.35
		Greige/ High TL	68.49	5.86	255.8	26.77
		Greige/ Low TL	32.9			10.57
		Calendered	75.37			29.46