

CHARACTERIZATION OF TIRE REINFORCEMENT POLYMERS FOCUSING ON TEMPERATURE, LINEAR DENSITY AND HYDROPHILICITY

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***Characterization of Tire Reinforcement Polymers focusing on
Temperature, Linear Density and Hydrophilicity***

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held in

**Continental Reifen Deutschland GmbH / Body Compound & Reinforcement Technology
Department**



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Abstract

Textile reinforcements are key materials in current passenger car tires. In order to ensure tire integrity for the whole tire life, the textiles are chemically bound to the surrounding rubber matrix. With this master thesis, test methods to assess the performance of textiles under dynamic conditions were developed. This is meant to mimic a rolling tire. With society's current path towards a more eco-friendly planet, reducing carbon dioxide emissions becomes crucial, and with that taken into account tires can be a part of this change due to the fact that there is significant impact of tire rolling resistance, which is the mechanical loss of energy as heat by the tire, on fuel economy of cars.

This dissertation was then separated into three areas of research. Firstly, in order to perceive the effect of linear density and temperature on PET and rayon cords, stepwise relaxation tests were performed. Secondly, in order to obtain data to plot nylon's water sorption isotherms thermogravimetric analysis (TGA) was used to measure the water mass uptake of nylon 1440x2, relating to the fact that this is a hygroscopic material due to the presence of amide functional groups, at different atmospheric conditions of temperature and relative humidity. Lastly, static and dynamic tests with temperature and humidity control were done to rayon and nylon cords in order to thoroughly comprehend the data gathered from the TGA and to carry out the characterization of the cords.

In summary, the results obtained from the understanding of linear density and temperature effect were key in correlating the behavior of two different machines, Zwick / Roell and MTS-Acumen™ 3 and also that with the increase of temperature there is a stabilization on the behavior of standard PET, 2200x2 and 3340x2, at 4 % of difference. The first psychrometric chart with constant moisture lines, with the data collected from the TGA, was constructed for nylon and determined the BET specific surface area values for nylon and rayon for different temperatures. Despite the mechanical properties of nylon not following the constant moisture lines, when the temperature is fixed, the effect of water uptake in its tensile behavior is noticeable and thus proving the importance of temperature and relative humidity control when testing nylon.

Overall, this study granted a better understanding of three textiles reinforcements, which are PET, rayon and nylon, and provided valuable information concerning the behavior of rayon and nylon, under static and dynamic conditions, which is going to be used for the prediction of the tire's rolling resistance, which will be pivotal in its optimization in regard to the fuel consumption.

Keywords : nylon cords, rayon cords, hydrophilicity, BET specific surface area, dynamic mechanical analysis

Resumo

Os reforços têxtil são materiais-chave nos pneus dos veículos de passageiros atuais. De forma a assegurar a integridade da sua vida útil, estes têxteis são quimicamente confinados na matriz de borracha envolvente. Com esta tese de mestrado, foram desenvolvidos métodos de teste para avaliar a performance dos reforços têxtil sobre condições dinâmicas. Estes testes têm como objetivo simular um pneu em movimento. Com a sociedade a caminhar para um planeta mais ecológico, é crucial reduzir as emissões de dióxido de carbono, e tendo isso em consideração os pneus podem fazer parte desta mudança pelo facto de haver um impacto significativo por parte da resistência ao rolamento, que é a perda mecânica de energia do pneu sob a forma de calor, na economia de combustível dos veículos automóveis,

Esta dissertação foi então separada em três áreas de pesquisa. Primeiramente, de forma a compreender o efeito da densidade linear e da temperatura nas cordas de PET e raiom, foram efetuados testes de relaxamento com incremento. Segundamente, para obter dados visando a representação das isotérmicas de adsorção de vapor de água, foi utilizada a análise termogravimétrica (TGA) com o intuito de medir a quantidade de água captada por parte do nylon 1440x2, pelo facto de este ser um material higroscópico pela presença de grupos funcionais amida, a diferentes condições de temperatura e humidade relativa. Por fim, testes estáticos e dinâmicos com controlo de temperatura e humidade relativa foram executados para o raiom e o nylon de forma a compreender profundamente os dados recolhidos no TGA e com o objetivo de levar a cabo a caracterização das cordas.

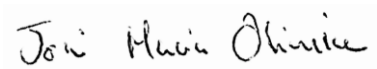
Em suma, os resultados obtidos a partir da compreensão do efeito da densidade linear e da temperatura foram fundamentais na correlação do comportamento de dois equipamentos, Zwick / Roell e MTS-AcumenTM 3 e também que com o aumento da temperatura o comportamento das cordas padrão de PET, 2200x2 e 3340x2, tende a estabilizar em 4 % de diferença. Com os dados recolhidos do TGA, foi construído o primeiro gráfico psicrométrico com linhas de humidade constante para o nylon e foram determinadas as áreas superficiais específicas BET para o nylon e para o raiom a diferentes temperaturas. Apesar de as propriedades mecânicas do nylon não seguirem as linhas de humidade constante, quando a temperatura é fixada, é notório o efeito da captura de água nas mesmas propriedades e portanto comprova a importância do controlo da temperatura e da humidade relativa aquando do uso do nylon para testes.

Em geral, este estudo provisionou um melhor entendimento de três reforços textéis, sendo estes o PET, raiom e o nylon, e providenciou informação valiosa tendo em conta o comportamento do raiom e do nylon em condições estáticas e dinâmicas, que será utilizada para a previsão da resistência ao rolamento por parte do pneu, que será fundamental na sua optimização tendo em vista o consumo de combustível

Palavras-chave : cordas de nylon, cordas de raiom, hidrofilicidade, BET área superficial específica, análise dinâmico-mecânica

Declaration

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

A handwritten signature in black ink, reading "José Maria Oliveira". The signature is written in a cursive style with a light blue rectangular background.

José Maria Oliveira

Hannover, Germany, June of 2020

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Notation and Glossary

A_{cs}	Adsorbate Cross-Sectional Area	nm^2
C	BET constant	
DPU	Dip pick-up	%
E'	Elastic modulus	$\text{N}\cdot\text{mm}^{-2}$
E''	Viscous modulus	$\text{N}\cdot\text{mm}^{-2}$
F	Force	N
l_0	Original length	mm
l_f	Final length	mm
MC	Moisture content	%
M	Molecular weight	$\text{g}\cdot\text{mol}^{-1}$
MD	Mass of dip	mg
MDC	Mass of dried dipped cord	mg
N	Avogadro constant	mol^{-1}
P	Actual pressure	atm
P_0	Total pressure	atm
P_s	Vapor saturation pressure	atm
RH	Relative humidity	%
St	Total surface area	m
S	Specific surface area	$\text{m}\cdot\text{g}^{-1}$
T	Temperature	$^{\circ}\text{C}$
t	Time	s
$\tan \delta$	Damping coefficient	
w	Weigh of the sample	g
W	Weight of water	mg
W_m	Adsorbate monolayer weight	mg

Greek Letters

ω	Frequency	$\text{rad}\cdot\text{s}^{-1}$
δ	Phase Shift	$^{\circ}$
ε	Strain	%
σ	Stress	$\text{N}\cdot\text{mm}^{-2}$

List of Acronyms

BET	Brunauer-Emmett-Teller
DMA	Dynamic Mechanical Analysis
FFT	Fast Fourier Transform
IUPAC	International Union of Pure and Applied Chemistry
MHG	Modular Humidity Generator
MPE	Multi Purpose Elite
MPT	Multi Purpose Testware
PET	Polyethylene terephthalate
R&D	Research and Development
TGA	Thermal Gravimetrical Analysis
2D	Two-Dimensional
3D	Three-Dimensional

1 Introduction

1.1 Framing and presentation of the work

Today's society is progressing towards a green planet, reducing the greenhouse gases emissions throughout the world. Tires can have an important role concerning the reduction of these emissions because they are directly connected with the fuel consumption. Tire performance is intrinsically tied to rolling resistance, which is a parameter specified during the product design. Due to the rolling resistance being defined as the mechanic energy loss by the tires, the rolling resistance is related to the fuel consumption of the vehicle. Understanding and characterizing the constituent materials of a tire will provide more information regarding them and will enable to decrease the rolling resistance, thus reducing the fuel consumption, which plays a big role in diminishing greenhouse gases emissions.

This study emphasis the understanding of the effect of linear density and temperature on PET and rayon cords and also provides fundamental data on the characterization of rayon and nylon cords. These textiles are widely utilized in the tire industry and are key in the assembly of every tire. As a launching platform for this thesis, other studies were taken into consideration, and so, for a better understanding of the topics presented in this thesis it is advised to read the following master thesis, developed within Continental : ‘‘Hysteresis in Tire Textile Reinforcements focusing on PET material’’ by Cardoso. A. and ‘‘Iso-moisture: a new concept to predict moisture content in rayon cords and its influence on tire performance’’ by Silva. L.

The main focus of the study is related to nylon's and rayon hydrophilicity. Both rayon and nylon are hygroscopic polymers, which means that they achieve an equilibrium with the environment regarding water uptake. The moisture uptake by the cords brings alterations concerning the mechanical response of them and thus it is key to understanding the influence of this variable.

1.2 Presentation of the company

Continental-Caoutchouc- und Gutta-Percha Compagnie was founded in Hannover on October 8, 1871 as a joint stock company. Manufacturing at the main factory in Hannover included soft rubber products, rubberized fabrics and solid tires for carriages and bicycles. [1]

Around the world, some 243,000 employees contribute to the company's success each day. Currently operating over 544 locations in 60 countries and markets. [2]

The Continental Corporation is divided into the Automotive Group and the Rubber Group, and consists of five divisions: Chassis & Safety, Powertrain, Interior, Tires and ContiTech. [3]

Today, as a supplier and developer of brake systems, systems and components for powertrains and chassis, instrumentation, infotainment solutions, vehicle electronics, tires and technical elastomers, Continental contributes to enhanced driving safety and global climate protection. Continental is also a competent partner in networked automobile communication. [3]

The Continental Reifen Deutschland GmbH, the place in which this thesis was written, can be seen in Figure 1.



Figure 1 - Display of the Continental Reifen Deutschland GmbH [4]

1.3 Contribution of the author to the work

Textile reinforcements are widely used in the tire industry. These reinforcements contribute to the performance of a tire and their mastery and characterization is of great importance. From these textile reinforcements, three are highlighted in this thesis, PET, rayon and nylon.

Nylon and rayon are both hygroscopic materials, which means that they will quickly uptake water from the environment. This behavior influences their mechanical properties and thus it is daring to perform experimental testing on either.

This thesis is set apart from others performed in Continental due to the fact that it provided insights into the response of viscoelastic materials to static tests, these being them PET and rayon. It is the first study to provide a deeper understanding of nylon's hydrophilicity and also in expanding the knowledge concerning rayon and its hygroscopicity.

Therefore, with this master dissertation, some key accomplishments were achieved:

- Providing a new overview of the effect of temperature in PET and rayon cords;
- Correlating a static test response in one equipment to a physical phenomenon;
- Drawing the adsorption isotherms for nylon cords;
- Construction of a psychrometric chart with constant moisture lines for nylon;
- Determining the specific surface area for nylon and rayon;

→ Proof the moisture content is not a dominant factor when comparing different atmospheres (temperature and relative humidity) but is extremely important when comparing the response for the same temperature for nylon;

→ Characterization of rayon and nylon cords under dynamic conditions for fixed moisture content value.

The achievements within this thesis, which grant new and distinct information regarding the polymers mentioned above, are set to have an important impact on different sectors at Continental.

1.4 Organization of the thesis

This Master Thesis is composed of 8 sections in which there are 6 main chapters and they are briefly described as follows:

1. The **Introduction** offers initial insights into the work performed during the tenure at the company. Furthermore, it provides an overview of the company itself while exposing the main contributions made for the project.
2. **Context and State of the Art** presents the theoretical knowledge used during this master thesis. It starts with an overview of the modern tire and its components, the different textile reinforcements utilized for tires, an insight on rolling resistance and hysteresis. The water molecules adsorption on polymer's surface was also addressed as well as the effect of the temperature and relative humidity on the moisture content and the relationship between temperature and relative humidity.
3. The **Material and Methods** chapter describes not only the materials but also the methodology employed and the equipment that was used to put the methodology into work. This section is divided into three parts, the materials, the tensile relaxation tests and the thermal gravimetric analysis.
4. **Results and Discussion** provide and display of the results and an accurate and deep understanding of them.
5. The **Conclusion** chapter presents a brief review of the main outcomes of this study and its contribution to Continental.
6. In the **Assessment of the Work Done** a critical analysis of the work developed is given, a mention of the accomplishments made and proposals for the continuation of the same study.

References catalogue all the sources referred throughout the thesis.

Annex include complementary information important for the work, and this information was obtained during this study.

Appendix include complementary information related to the work, and this information was authored only by the author of this master thesis.

2 Context and State of the art

2.1 The Tire

Tires are not among the first things on the mind when purchasing a vehicle, but they probably should be. While tires do tend to get overlooked, they are arguably one of the most important components of the vehicle. After all, tires are what allow the vehicle to roll down the road. [5]

Tires are known for maximizing safety through short braking distances and excellent grip as well as reducing fuel consumption by minimizing rolling resistance, and they are also the vehicle's only link with the road. [6]

The main functions of a vehicle's tires include supporting the vehicle load, transmitting traction and braking forces to the road surface, absorbing road shocks, as well as changing and maintaining the direction of travel. To ensure these functions are being adequately met, there several aspects of a vehicle's tire should be inspected regularly, such as the tread depth of your tires, the wear, the air pressure, and any damage or signs of deterioration. [5]

2.1.1 Tire Components

Modern passenger car tires have a complex structure and their components can be grouped into two main structural elements: The tread/belt assembly and the casing/carcass [7]. In Figure 2 it is possible to see the tire and where the different tire components are, which are specified in table 1.



Table 1 – Tire components referring to Figure 1

1	Tread
2	Jointless cap plies
3	Steel cord belt plies
4	Textile cord ply
5	Inner liner
6	Sidewall
7	Bead reinforcement
8	Bead apex
9	Bead core

Figure 2- Tire components scheme [7]

Tread/Belt assembly:

→ The tread is made of synthetic and natural rubber, this textured surface ensures high mileage, good grip on the road and water expulsion. Tire tread connects with the road and the sidewall, and has three areas:

- Cap: The part of the tire which is most in contact with the road, providing grip on all road surfaces, wear-resistance and directional stability. [7]
- Base: Underneath the cap, the base reduces rolling resistance and damage to the tire's internal structure – the casing. [7]
- Shoulder: At the outer edges of the tread, this area forms an optimal transition from the tread to the sidewall of the tire. [7]

→ Jointless cap plies are a layer which sits directly below the tread and enables traveling at high speeds. They consist of a single, strong cord of nylon, embedded in rubber. This cord spirals around the circumference of the tire, from one side to the other, without overlapping. [7]

→ The steel cord belt plies are strong steel cords which provide the tire with rigidity in this layer, thus enhancing shape retention and directional stability, reducing rolling resistance and increasing the tire's mileage performance. [7]

Casing/Carcass:

→ A textile cord ply is a layer of textile, namely rubberized rayon or polyester that controls the internal pressure of the tire and maintains its shape. [7]

→ Inner liner is an airtight layer of butyl rubber that seals the air-filled inner chamber, controlling tire pressure and acts as an inner tube in today's modern, tubeless car tires. [7]

→ The sidewall is the exterior wall of your tire – connected to the tread by the tread shoulder. Made of natural rubber, the sidewall protects the casing from external damage and atmospheric conditions. [7]

→ Bead reinforcement, which is made of nylon or aramid, a type of strong, heat-resistant, synthetic fiber. This fine cabling enhances directional stability and facilitates precise steering response. [7]

→ Bead apex is a stabilizing wedge of synthetic rubber. The bead apex performs the same tasks as the bead reinforcement while also providing additional steering comfort. [7]

→ The bead core is the heart of the bead made up of steel wire embedded in rubber. The core ensures that the tire sits firmly on the wheel rim. [7]

2.2 Textile Reinforcements

The tire's reinforcing materials, tire cord and bead wire, are the predominant load carrying members of the cord-rubber composite. They provide strength and stability to the sidewall and tread as well as contain the air pressure. [8]

As mentioned, the reinforcing materials can have different natures. The different reinforcements used within this study are elaborated upon this subchapter. Those were Polyethylene terephthalate (PET), rayon and nylon.

2.2.1 Polyethylene terephthalate (PET)

Polyethylene terephthalate or more commonly known as PET is produced by the polycondensation of ethylene glycol and terephthalic acid. Ethylene glycol is a colorless liquid obtained from ethylene, and terephthalic acid is a crystalline solid obtained from xylene. When heated together under the influence of chemical catalysts, ethylene glycol and terephthalic acid produce PET in the form of a molten, viscous mass that can be spun directly into fibers or solidified for later processing as a plastic. In chemical terms, ethylene glycol is a diol, an alcohol with a molecular structure that contains two hydroxyl (OH) groups, and terephthalic acid is a dicarboxylic aromatic acid, an acid with a molecular structure that contains a large, six-sided carbon (or aromatic) ring and two carboxyl (COOH) groups. Under the influence of heat and catalysts, the hydroxyl and carboxyl groups react to form ester (CO-OC) groups, which serve as the chemical links joining multiple PET units together into long-chain polymers. Water is also produced as a by-product. The overall reaction can be represented as follows on Figure 3. [9]

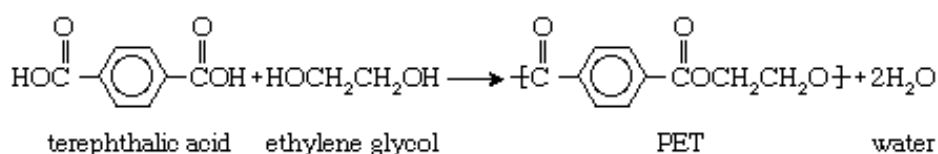


Figure 3 - Molecular structure of Polyethylene terephthalate [9]

Among the industrial applications of PET are automobile tire yarns, conveyor belts and drive belts, seat belts (an application in which it has largely replaced nylon). PET is the most important of the man-made fibers in the quantity produced and in value. [9]

2.2.2 Rayon

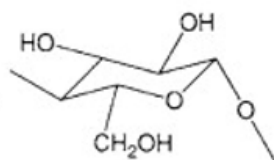
Regenerated Cellulose or rayon is made from purified cellulose, primarily from wood pulp, which is chemically converted into cellulose acetate to make the fiber soluble in solvents. It is the oldest manmade fiber. Because rayon is manufactured from naturally occurring polymers, it is sometimes called a semi-synthetic fiber. [10]

Cellulose is initially treated with sodium hydroxide to form an alkali cellulose. It is then shredded and allowed to age in air, where it is oxidized and undergoes molecular weight reduction to enable subsequent spinning operations. Treatment with carbon disulfide produces cellulose xanthate, which is then dissolved in sodium hydroxide to form viscose. The material undergoes further hydrolysis and is then fed into spinnerets to produce the fiber. This fiber is passed through a bath of sulfuric acid and sodium sulfate, where the viscose fibers are further coagulated. [11]

Rayon fibers have outstanding strength, low elongation and good water absorbency and find many industrial uses where these three properties are required. [10]

Rayon fibers find many industrial applications. Major uses include apparel, upholstery, tire cords, hoses, surgical materials, feminine hygiene products, and linings for a variety of products. [10]

Rayon's molecular structure can be seen in Figure 4.



Regenerated cellulose

Figure 4 - Molecular structure of rayon [11]

2.2.3 Nylon

Nylon is a generic name for a family of synthetic polymers, more specifically, aliphatic or semi-aromatic polyamides in which at least 85 % by weight of the amide-linkages (-CO-NH-) are attached directly to two aliphatic groups. They can be melt-processed into fibers, films or any other shape. [12]

Nylon 6 and Nylon 66, shown in Figure 5, are two of the most popular polymers used in the plastics, automotive and textile industries. Though Nylon 6 and Nylon 66 share some physical properties, their chemical structures are different. Nylon 6 is made from a single type of monomer, called caprolactam, and Nylon 66 is made up of two monomers, adipoyl chloride and hexamethylene diamine. Nylon's semi-crystalline structure is due to the intermolecular hydrogen bonds, which are established throughout. [13]

Nylon fibers are exceptionally strong and elastic as well as stronger than polyester fibers. The fibers have excellent toughness, abrasion resistance, and are easy to wash, and dye in a wide range of colors. The filament yarns provide a smooth, soft, and lightweight fabric of high resilience. [12]

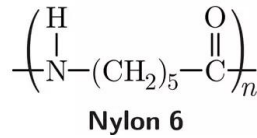
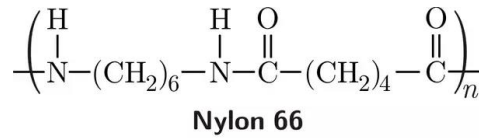


Figure 5 - Molecular structure of Nylon 66 and Nylon 6, respectively [14]

Nylon is hygroscopic, meaning it adsorbs moisture out of the air surrounding the material. The higher the humidity, the faster it will absorb moisture. [15]

2.3 Cord design

The terminology used for defining tire cords comes from the textile industry. To have a better understanding of the cords design and it's characteristics, the following concepts are presented:

- Filament: the smallest continuous element of a tire cord; [16]
- Yarn: an assembly of filaments; [16]
- Cord: a twisted or formed structure composed of two or more yarns; [16]
- Warp: an assembly of cords that run in a lengthwise direction along the fiber axis; [16]
- Decitex: the linear density in SI units, defined as the weight in grams of a length of 10,000 meters; [16]
- Twist: the number of 360° turns per unit length of a yarn or cord, e.g. 10 twists per inch or 40 twists per 10 cm; [16]
- Twist direction: twist direction is termed "S" if the spiral turns clockwise from top to bottom for a vertically held cord and "Z" for a similar counterclockwise turning; [16]
- Twist Level: the number of turns per unit length of a yarn or a cord, typically in turns per meter (tpm); [16]
- Strength: the tensile load required to rupture a cord at a given rate of extension; [16]
- Cord construction: Specified as the polymer linear density in SI units followed by the number of yarns, for example, PET 2200x2, being the linear density of a single yarn 2200 and the number of yarns present being 2; [16]

Moreover, there are three steps which stand out and are of importance for this study, these are:

→ Twisting, in yarn and rope production, is a process which binds fibers or yarns together in a continuous strand. The direction of the twist may be to the right, described as Z twist, or to the left, described as S twist, as previously mentioned. [17]

→ Dipping: a treatment of the textile, typically using a resorcinol formaldehyde latex (RFL) based coating; this process creates an interface that allows the bonding between the cord and the rubber, improving the adhesion; often, an epoxy coating is used in order to increase the compatibility between the cord surface and the RFL coating. [18]

→ Calendaring: is the technique in which the textile is embedded in the rubber, it is also known as rubberization.

The first two steps mentioned affect the properties of the cord and can be correlated with equations.

The Twist Factor (TF) correlates the twist level and the linear density of the cord, which is the linear density of a single cord multiplied by the total number of yarns present, as follows in equation 1. [19]

$$Twist\ Factor = Twist\ Level \times \sqrt{\frac{Total\ cord\ dtex}{10000}} \quad (1)$$

The dip pick up, *DPU*, is characterized as the content of dip in the cord and is measured in percentage. It can be obtained by the following equation in which the MD is the mass of the dip MDC is the mass of the dried dipped cord, as shown in equation 2. [19]

$$DPU = \frac{MD}{MDC} \times 100 \quad (2)$$

2.4 Rolling Resistance in Tires

The force that resists the motion of a body rolling on a surface is called the rolling resistance or the rolling friction. [20]

Rolling resistance is a result of energy loss in the tire, which can be traced back to the deformation of the area of tire contact and the damping properties of the rubber. These lead to the transformation of mechanical into thermal energy, contributing to the warming of the tire. [21]

The rolling resistance is defined as being the ratio between the energy consumed per distance unit by a tire. [22]

With society's current path, which focuses on sustainable long-term solutions, it is key to reduce the rolling resistance while being able to use sustainable materials in order to achieve a reduction on the fuel consumption.

In general, the rolling resistance occurrence is undesirable to both the vehicle performance as well as environmental protection. It is found to be one of the main factors opposing the vehicle's mobility, particularly at higher velocities, and leads to energy losses. Additionally, the vehicle consumes more fuel to maintain its mobility and produces more CO₂ exhaust emissions in the process, contributing to increasing the air-pollution and the global warming. [22]

According to the current literature, the tire's rolling-resistance is caused by three mechanisms that take place in the tire's environment:

→ The tire's cyclic deformation, which causes some losses in its internal mechanical energy (i.e. strain energy loss). This is due to several occurrences such as the reinforcements' friction and the rubber viscoelastic (hysteresis) property. Among those occurrences, hysteresis damping holds the dominant impact on rolling-resistance making the other occurrences insignificant in contrast (i.e. about 80 % to 95 % of the total tire's rolling-resistance). [22]

→ The aerodynamic drag due to the tire cutting through the surrounding air as it rotates, which opposes tire movement and promotes heat transfer between the air and the tire. Such phenomena can account for 0 % to 15 % of the total tire rolling-resistance depending on the tire speed. [22]

→ The frictional slip that takes place when the tire comes into contact with the wheel rim and with the road surface during its rotation, which leads to heat build-up. This is the least important factor of the rolling-resistance since it accounts for only about 5 % of the total tire rolling-resistance. [22]

Regardless, the rolling-resistance is not entirely undesirable as its existence, to some degree, is necessary to achieve other essential functions such as good tire-grip, under proper operational temperature, for traction, cornering and braking. As mentioned, hysteresis is also largely responsible for the tire/road adhesion and hence, the energy loss related to the rolling resistance is given by the hysteresis loop of the material stress-strain curve. The stress, strain and hysteresis concepts are explained in more depth in the following section. [22,23]

2.5 Stress-strain hysteresis

Before the hysteresis subject can be explained, there are three terms which need to be overviewed. They are essential in the understanding of polymers and have great impact on their behavior. They are elasticity, viscosity and viscoelasticity. [24]

Elasticity is the tendency of solid materials to return to their original shape after forces are applied on them. When the forces are removed, the object will return to its initial shape and size if the material is elastic.

Viscosity is a measurement of a fluid's resistance to flow. A fluid with large viscosity resists motion. A fluid with low viscosity flows. For example, water flows more easily than syrup because it has a lower viscosity. Viscous materials are thick or sticky or adhesive, but they can change their behavior with an increase of temperature, which reduces viscosity. [24]

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Synthetic polymers, wood, and human tissue, as well as metals at high temperature, display significant viscoelastic effects. In some applications, even a small viscoelastic response can be significant. [24]

Once an external tensile loading is applied on a specimen, elastic and plastic deformations will be anticipated. Initially, an elastic deformation will occur to the material resulting in a linear relationship of load and extension as it can be seen in Figure 6 corresponding to the elastic strain. The plastic deformation, which corresponds to the plastic strain in Figure 6, is permanent and is not recovered when the load is removed, even though a small portion of elastic part in the deformation is recovered. Calculation of the stress and strain will be done using these equations, 3 and 4 as follows, where σ is the stress, in $\text{N}\cdot\text{mm}^{-2}$, ε is the strain, in %, F is the external axial tensile load, in N, A_{cs} is the cross-sectional area of the specimen, in mm^2 , L_0 is the original length of the specimen. L_f is the final length of the specimen. [25]

$$\sigma = F \cdot A_{cs}^{-1} \quad (3)$$

$$\varepsilon = \frac{L_0 - L_f}{L_0} \cdot 100 \quad (4)$$

Stress-strain curves show the response of a material to an applied (usually tensile) stress. They allow important information such as a material's elastic modulus and yield stress to be determined. In Figure 6 is possible to see a common stress-strain curve of a polymer material.

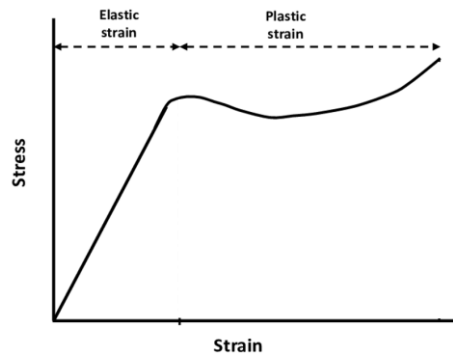


Figure 6 - Typical Stress-Strain curve response of a polymer material [26], adapted

Polymer stress-strain curves are produced by stretching a sample at a constant rate through the application of a tensile force. By using a constant rate of testing the strain-rate dependency of polymer

behavior is not allowed to dominate. However, it should be appreciated that polymers have a marked inherent time-dependence in their response to deformation, which sets their behavior apart from other classes of material. [27]

The procedure of a stepwise relaxation test is shown in Figure 7, which will be explained further in Subsection 3.2., with the constant strain in time, and with the change in the stress along the time.

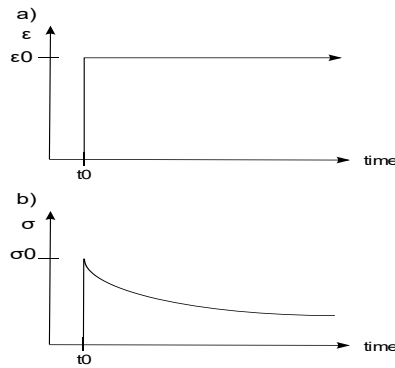


Figure 7 - Constant strain through time and Stress response over time [28]

In the elastic region, stress is proportional to strain and the deformation is completely reversible; Hooke's law is obeyed. The gradient of the straight-line section of the curve gives the elastic modulus of the material, also called Young's modulus. [27]

Some materials, such as polymers show a time-dependent elastic behavior. Although, in the elastic regime, the strain is recoverable, the stress-strain curve is not the same for loading and unloading. Such materials instead exhibit viscoelasticity, involving both elastic and viscous components, which at normal loading and unloading rates leads to hysteresis. A typical hysteresis curve is shown below, and the energy adsorbed during one loading-unloading cycle is given by the area within the loop. The shape of the loop depends on the rates of loading and unloading (unlike normal time-independent elasticity). The so-called hysteresis loop is shown in figure 8. [29]

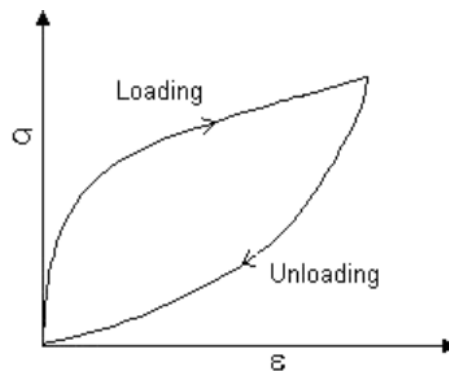


Figure 8 - Hysteresis loop [29]

2.6 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) is a technique where a small deformation is applied to a sample in a cyclic manner. This is widely used to characterize a material's properties as a function of temperature, time, frequency, stress, atmosphere or a combination of these parameters. [30]

In order to characterize the viscoelastic behavior of a material, it is sinusoidally deformed, and the resulting stress is recorded. For an ideal elastic material, the stress and strain are in phase, and the phase shift, δ , is 0° , and for a purely viscous material, the phase shift is 90° . As pointed out before, a viscoelastic behavior is a combination of an ideal elastic response and an ideal viscous response, so the phase shift will be in between 0° and 90° . The DMA technique is used to study the viscoelastic behavior of a material when it is subjected to an oscillatory strain with frequency, ω . Figure 9 shows a viscoelastic response of material with time lag between stress and strain. [31]

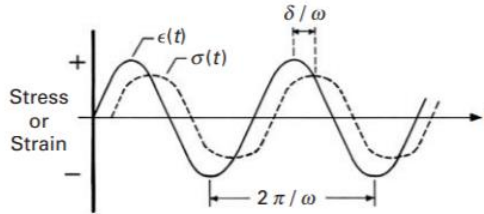


Figure 9 - Typical viscoelastic response to stress and strain

With the content of this Figure it is possible to write the materials stress and strain expressions over time, which is given by the following equations, 5 and 6, respectively. [31]

$$\sigma(t) = \sigma_0 \cdot \sin(\omega t + \delta) \quad (5)$$

$$\varepsilon(t) = \varepsilon_0 \cdot \sin(\omega t) \quad (6)$$

From these expressions, two moduli can be defined, the elastic modulus (or storage modulus), E' , which is the storage modulus and is a measure of the recoverable stored strain, and the viscous modulus (or loss modulus), E'' , which is a measure of the energy loss, generally as a heat form. They are shown in the equations 7 and 8, respectively. [31]

$$E' = \left(\frac{\sigma_0}{\varepsilon_0} \right) \cos \delta \quad (7)$$

$$E'' = \left(\frac{\sigma_0}{\varepsilon_0} \right) \sin \delta \quad (8)$$

A term called loss tangent (or loss factor or damping coefficient) is now defined, as follows in equation 9. [31]

$$\text{Loss tangent} = \text{Loss Factor} = \tan \delta = \frac{\text{energy loss}}{\text{energy stored}} = \frac{E''}{E'} \quad (9)$$

The evaluation of these variables will be rather important to describe the viscoelastic behavior of the reinforcement materials.

2.7 Sorption

Sorption is the common term used for both absorption and adsorption. The major difference between adsorption and absorption is that the first is a surface process and the latter a bulk process. Adsorption takes place on the surface of a substrate and absorption occurs when one substance enters the bulk, or volume, of another substance. [32]

As mentioned above, water molecules adhere onto the surface of nylon due to its hydrophilic behavior correlating with the presence of amide groups, and therefore it is possible to say that the process corresponds to adsorption.

2.7.1 Hydrophilic Behavior by Nylon Cords

Nylon is hygroscopic, meaning that it absorbs moisture right out of the air surrounding the material as previously mentioned on Subsection 2.2.3. The higher the humidity, the faster it will adsorb moisture. However, it only adsorbs moisture until it is saturated. At that point an increase in humidity will not correspond to an increase of the moisture adsorption. [15]

This hygroscopic behavior is given by the presence of multiple amide functional group. Nylon adsorbs moisture easily in comparison to most thermoplastics. Moisture can cause bubbles, silver streaks, and material aging on the product if the polyamide molds with it. Thus, sufficient pre-dehumidification and drying is required. [33]

Polyamide properties vary depending on moisture adsorption as the material naturally adsorbs water. When the polyamide adsorbs more moisture, tensile strength, tensile modulus and hardness decrease. Conversely, elongation and impact strength increase. Thus, the understanding of its behavior among different operating conditions is very important. [33]

The moisture in nylon acts as a plasticizer that reduces the entanglement and bonding between molecules, therefore increasing their volume and mobility. The increase in moisture may cause profound changes in a material's behavior underload; it reduces strength and stiffness while increasing ductility in the material. [34]

Despite the nylon cords hygroscopic behavior there is still to determine whether this behavior remains while protected by a rubber matrix as well as how its presented in the tire.

2.7.2 Nylon behavior when embedded in a rubber matrix

The nylon cords, while inside the tire, are not in direct contact with the surrounding atmosphere. Between the air and the nylon cords there is a rubber matrix. Owing to the solution-diffusion process, the

water vapor molecules go through the rubber matrix and that is why the relationship between air and the nylon cord explained before is still valid. [35]

When the interaction between a surface and an adsorbate is relatively weak, only physisorption takes place. However, surface atoms often possess electrons or electron pairs which are available for chemical bond formation. This irreversible adsorption, or chemisorption, is characterized by large interaction potentials which lead to high heats of adsorption. As is true for most chemical reactions, chemisorption is usually associated with an activation energy, which means that adsorbate molecules attracted to a surface must go through an energy barrier before they become strongly bonded to the surface. [35]

In a rubber matrix there is intermolecular space which is called free volume. This can be referred to as “holes”. This free volume thermally forms and disappears with the movement of the polymer chains. Gases are soluble in rubberlike substance and when rubber is exposed to a gas, solution occurs at the surface and the dissolved gas molecules diffuse into the interior. The diffusion of gas molecules in the rubber membrane is a process in which the gas molecules migrate from “hole” (free volume) to “hole” (free volume). The permeation of gas through a rubber membrane involves its solution on one side and diffusion through the membrane to the other side. Due to this gas permeation throughout the rubber membrane, the gas will reach the nylon cord and affect its mechanical properties. [36]

The car's tires, while on the road, achieve different temperatures by its constant movement. This will bring an effect of temperature on permeability on the rubber. Firstly, and taking into account the silicone rubber, the free volume depends on temperature. Lower temperature results in less free volume and consequently lower permeability. Meanwhile, the mobility of polymer chain of silicone rubber is low at lower temperature. Low mobility of the polymer chains restricts the diffusion of gas molecules. If the ambient temperature is lower than the crystallization temperature or glass transition temperature of the polymer, permeability is significantly reduced. Secondly, the mobility of gas molecules significantly depends on temperature. Having lower temperatures means slower gas mobility, which subsequently results in lower gas diffusivity and permeability. [36]

This manner of describing the gas molecules permeation is called the solution-diffusion model and is presented in Figure 10. [36]

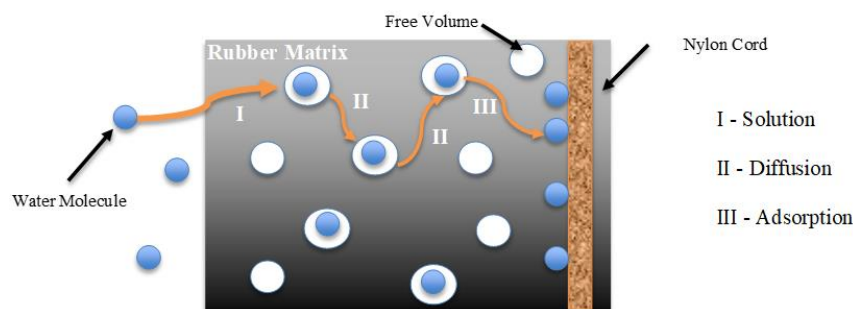


Figure 10 - Solution-Diffusion model through a rubber matrix [37]

2.7.3 Adsorption Isotherms

adsorption can be

characterized by determining what amount of the ions or molecules are adsorbed to the surface. This amount can be determined experimentally by the construction of an adsorption isotherm. [38]

Adsorption equilibrium is essential for the design, sizing and modeling of adsorptive processes. In Figure 11 it is possible to see the physical process of either adsorption, which is an exothermal process, and desorption, which is an endothermal mechanism. [39]

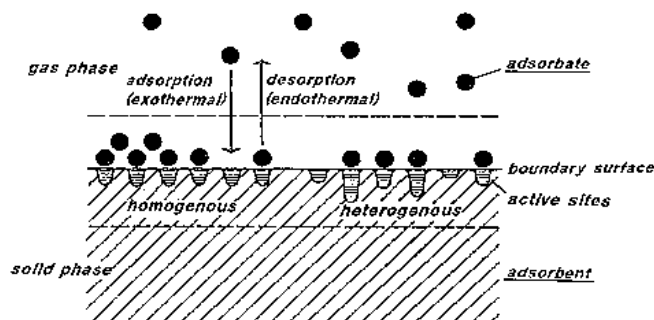


Figure 11 - Sorption equilibrium mechanisms [39]

The adsorption isotherm is a curve which expresses the variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature. They can have many shapes and forms, depending on the behavior of the material. It can also be said that an adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the gas with which it is in contact. [40] That is why according to IUPAC (International Union of Pure and Applied Chemistry), the isotherms are classified into six characteristic types, and shown in Figure 12.

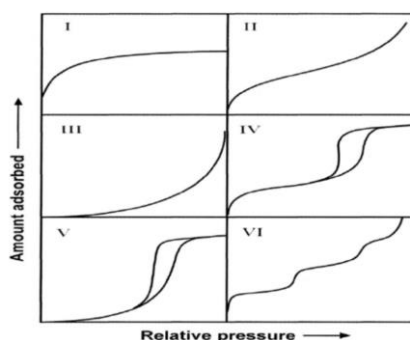


Figure 12 – IUPAC types of sorption isotherms [41]

The x-axis of the isotherm is in this case given as relative pressure, but it can also be represented as concentration or gas pressure. The y-axis is representing the amount of substance on the solid phase, referred as amount absorbed in this picture. [42]

They are called then, and according to Figure 12, microporous solids, Langmuir (I), non-porous or macroporous solids, BET (II), weak interactions (III), Mesoporous solids (IV), (III+IV) (V) and in steps isotherm (VI). [42]

Sorption isotherms describe the relation between the equilibrium moisture content of a material and the ambient relative humidity. Most materials exhibit sorption hysteresis, that is, desorption give higher equilibrium moisture contents than adsorption at equal ambient climate conditions. Nylon, as a polymer, is

not an exception and presents also sorption hysteresis. Sorption Hysteresis is commonly evaluated by determination of an adsorption isotherm followed by desorption starting from the highest relative humidity used in the adsorption measurement. [43]

To obtain the moisture content or, in other terms the mass fraction, equation 10 was utilized for those calculations, further down the use of this equation will be put into context.

$$\text{Moisture Content (\%)} = \frac{\text{mass of the sample} - \text{mass of dried sample}}{\text{mass of dried sample}} \times 100\% \quad (10)$$

2.7.4 Thermogravimetical Analysis

The moisture content, or in other terms, the mass uptake of water by the nylon cords was needed. One of the prime methods used for this is thermogravimetry, which was the method chosen for this study.

Thermogravimetry (TG) is the technique in which the mass of a sample is monitored against time or temperature and is performed with a Thermogravimetical Analyzer (TGA). [44]

A TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust. [45]

The abscissa (x-axis) can be displayed as time or temperature and the ordinate (y-axis) can be displayed as weight (mg) or weight percent (%).

Since it is not possible to vary the humidity with a TGA, a Moisture Humidity Generator (MHG) was attached to the TGA. This enabled the possibility of increasing the humidity as well as keeping a stable heated environment while still analyzing the weight of the sample. This process is explained in Subsection 3.2.

2.7.5 Brunauer-Emmett-Teller Isotherms

There is evidence that surface characteristics of textile fibers have some effect on their properties. Examples of such evidence of surface properties are apparent in the phenomenon of water repellency, in the loss of light-reflectance and in the difference in moisture-sorption capacities of fabrics after various treatments. If one assumes that the adsorption is a multilayer phenomenon, one may calculate the surface area accessible to the first layer. [46]

In order to obtain reliable surface area measurements of textile materials it is necessary to measure the surface area under controlled conditions ensuring true physical adsorption. Knowledge of the molecular area or surface area is believed necessary in order to evaluate properties such as the work of adhesion between the liquid and the solid phase. It seemed, therefore, highly recommendable that the surface areas of the textile fibers, viscose rayon and nylon, be measured. [46,47]

The type II isotherm is well connected with this. In fact, according to the literature, the most common method used to describe specific surface area correlates to the Brunauer-Emmett-Teller (BET) theory, that can be seen from the BET equation, equation 11, where W is the weight of gas adsorbed in mg, W_m the weight of the adsorbate as monolayer in mg, P is the actual vapor pressure, in Pa, P_0 the saturation vapor pressure, in Pa and C is the BET constant. [48]

The determination of specific surface area by means of the BET theory is based upon the phenomenon of physical adsorption of gases on the external and internal surfaces of a porous material. Such a material that is surrounded by and in equilibrium with a certain gas which has a certain temperature and relative vapor pressure physically adsorbs a certain amount of gas. [49]

$$\frac{1}{W \cdot ((P_0/P)^{-1})} = \frac{1}{W_m \cdot C} + \frac{C-1}{W_m \cdot C} \cdot \left(\frac{P}{P_0}\right) \quad (11)$$

By plotting $\left(\frac{P}{P_0}\right)$ vs $\frac{1}{W \cdot ((P_0/P)^{-1})}$, it is possible to retrieve the weight of the monolayer, which is then used, along with the Avogadro constant, N in mol^{-1} , the adsorbate cross-sectional area, A_{cs} in nm^2 and the molecular weight of the adsorbate, M in $\text{mg} \cdot \text{mol}^{-1}$, to calculate the S_t , surface total area. The surface total area can be converted to S , specific surface area, the ratio between the surface total area and the mass of the sample, seen in equations 12 and 13, respectively, which can then be compared with values from the literature. [48]

$$S_t = \frac{W_m \cdot N \cdot A_{cs}}{M} \quad (12)$$

$$S = \frac{S_t}{w} \quad (13)$$

These values show the area in which it is possible for water adsorption to occur. The specific surface area can be defined as the portion of the total surface area that is available for adsorption.[50] The area available for adsorption increases with the increase of temperature. Increasing the temperature increases the free volume, or in other terms, the intermolecular spaces generated by the chains' vibrations. Due to that fact it is expected that the surface total area and the specific surface area values increase with the increase of temperature.

According to the literature, the specific total area of nylon and rayon are $45 \text{ m}^2 \cdot \text{g}^{-1}$ and $204 \text{ m}^2 \cdot \text{g}^{-1}$ at 25°C , respectively. [46]

3 Materials and Methods

3.1 Materials

Throughout this study, many different materials were used. All of which were polymers that are utilized as textile reinforcements for tires. The characterization of these materials is fundamental in order to contribute to the predictions of the material's behavior and to optimize the industrial processes in which they are inserted. In table 2 there are the different polymers utilized during this thesis and their constructions as explained in Subsection 2.3

Table 2 - Materials specifications

Material	Construction	Mass density / $\text{kg}\cdot\text{m}^{-3}$	Diameter / mm
Polyethylene Terephthalate	630x2	1.38×10^3	0.420
Polyethylene Terephthalate	1100x2	1.38×10^3	0.560
Polyethylene Terephthalate	2200x2	1.38×10^3	0.750
Polyethylene Terephthalate	3340x2	1.38×10^3	0.930
Viscous Rayon	1840x2	1.52×10^3	0.527
Viscous Rayon	2440x2	1.52×10^3	0.650
Nylon 66	940x2	1.14×10^3	0.478
Nylon 66	1440x2	1.14×10^3	0.574

These materials were employed in the tests done along this thesis. All the different constructions of PET mentioned and also both of the rayon's mentioned were required for the stepwise relaxation tests. For the Thermogravimetric Analysis (TGA) the tests were done with nylon 1440x2. The data treatment for the BET specific surface area used nylon 1440x2 and rayon 1840x2. The static and dynamic tests with controlled atmospheres were performed for both of the rayon mentioned and for both of the nylon mentioned

3.2 Stepwise Relaxation Test

For testing under static conditions, a Zwick / Roell machine was used, represented in Figure 13. With this equipment the stepwise relaxation tests are possible to perform, which consist of applying a strain while keeping it constant and evaluating the tension response. There was also an increment in the strain, done in steps of 2.5 %



Figure 13 - Zwick / Roell static testing machine

The aim was to get the relaxation state of the polymer for different temperatures, The Zwick Roell software acquires various data concerning the force, displacement and strain suffered by the cord. For the temperature control, a climate chamber was used. This climate chamber provides a homogenous environment around the cord tested thus enabling the evaluation of the temperature effect.

In this study, two different materials were evaluated, PET and rayon, each with different constructions. For rayon, the temperatures in which the test occurred were 23 °C, 40 °C, 45 °C, 50 °C, 60 °C, 80 °C, 90 °C and 100 °C, and for polyester the test was done for 23 °C, 40 °C, 80 °C, 110 °C and 160 °C. The stress-strain, force-strain or force-elongation curve response of the tested materials provides valuable information about the materials' characteristics.

The climate chamber's response was not immediate, and for that the test could only start when the temperature had a steady behavior, which meant that for low temperatures (< 60 °C), the temperature could be reached after 30 minutes, and for high temperatures (> 60 °C) the temperature could achieve a steady plateau after 60 minutes. Thus, before starting the relaxation for 23 °C, 40 °C and 60 °C the waiting period was 30 minutes and for 80 °C, 110 °C and 160 °C the waiting period was 60 minutes. After the waiting period, the sample was clamped, and then the test was started.

The test required inputs on some parameters. The required preload was given in the specifications of the cord, and the remaining inputs and operating conditions are shown in table 3.

Table 3 - Stepwise Relaxation Test software inputs

Material	PET	PET	PET	PET	Rayon	Rayon
Construction	630x2	1100x2	2200x2	3400x2	1840x2	2440x2
Preload / N	0.63	1.10	2.20	3.40	1.84	2.44
Strain rate / mm·min⁻¹	120					
Relaxation strain range / %	2.5 to 12.5					
Relaxation strain increment steps / %	2.5					
Temperature / °C	23, 40, 80, 110, 160				23, 40, 60, 80	
Type of cords	High modulus	High modulus	Standard	Standard	Standard	Standard
Holding time / min	10					
Type of clamps	Radial or Snail					
Clamping pressure / bar	6					
Gauge length / mm	250					

When the test began, to overcome the temperature variation due to the opening of the chamber for the clamping, a 5 minutes step was implemented so that the temperature could be achieved again. After the 5 minutes the sample would then begin to be loaded in order to achieve the deformations and then hold for 10 minutes so it would reach a fully relaxed state. This step was repeated for every load. In Figure 14 a stepwise relaxation test is shown.

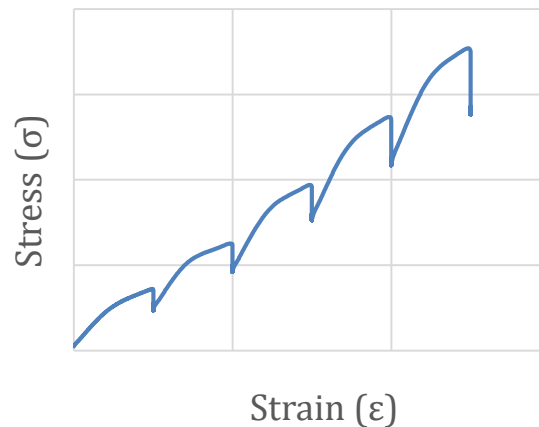


Figure 14 - Typical Stepwise Relaxation Test stress-strain curve response

For each polymer three samples per defined temperature were utilized to replicate the results. An additional sample was tested for a defined temperature on a different day to ensure the reproducibility of the results.

For rayon, due to its hydrophilic behavior, the tests ran with and without a pre-drying step. The experiments with the pre-drying consisted of a drying step inside the chamber at the temperature in which the test would occur before the measurements began.

3.3 Psychrometric Chart for Nylon with constant moisture lines

In this section the methodology used to plot a somewhat psychrometric chart for nylon is described. The diagram can be shown as a three-dimensional (3D) or as a two-dimensional (2D) representation of the effect of Temperature and Relative Humidity on the moisture adsorption by the cord, which means to have a Temperature vs Relative Humidity chart in which each curve is displayed as a contour line of equal moisture content of nylon, the temperature is in the x-axis and the relative humidity in the y-axis. The data required to do this plot was obtained by experimental tests using the thermogravimetric analyzer (TGA).

3.3.1 Thermogravimetric Analysis

This method was performed to investigate if there was any increase of the mass of the sample, due to water vapor molecules adsorption, when the operating conditions had a fixed temperature and a fixed relative humidity. The tests were made on the TGA/DSC 2 from METTLER TOLEDO (TGA) which had a Modular Humidity Generator (MHG) attached in order to control the humidity in the chamber, which can be seen in Figure 15.

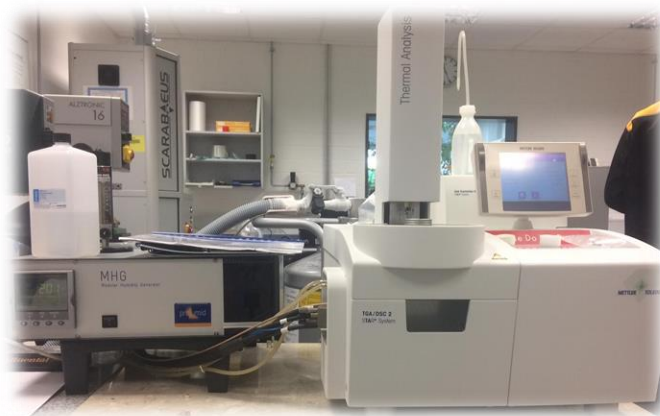


Figure 15 - TGA/DS2 (right) attached with a MHG (left)

For the monitorization of the mass, while the sample was exposed to different conditions of both relative humidity and temperature, nylon 1440x2 was used.

To perform this task, it was required to submit the procedure as an input. For each sample, the temperature was fixed, and the relative humidity was increased in steps. In the beginning, to prevent the effect of not reaching a stable plateau, each step took 3 hours. Furthermore, in conjunction with the previous results, this step was reduced to 2 hours. There was a first step in every test, consisting of 3 hours, which

was meant to dry the sample, due to the laboratory conditions in which the samples were constantly exposed, and therefore, in the procedure there is a first step which consists of a 0 % of relative humidity. In order to minimize the effect of the temperature's variation, both the drying step and the remainder of the experiment were carried out using the same temperature. In that way the cord was always in an isothermal environment, which was done for all the samples. After the procedure was made for the TGA and another one for the MHG, because despite being complementary to each other, they have different software. They were submitted and then the samples were prepared and placed in the autosampler to be analyzed.

3.3.2 Testing Conditions

The study was a continuity of the Ph.D. dissertation done at Continental by Hongying Zhao. In his dissertation, Hongying Zhao studied the mass uptake of nylon cords over time using the same TGA. His study consisted of analyzing the effect of temperature and relative humidity on the mass of the sample nylon cord.

For this the temperature is fixed and the relative humidity is increased in steps and in between each humidity adjustments, there is a drying step. The time used on Hongying's experiments varied, but the goal was always to obtain a steady plateau. Hongying's raw data for Nylon was then treated. In Figure 16 there is an example of the results at 30 °C.

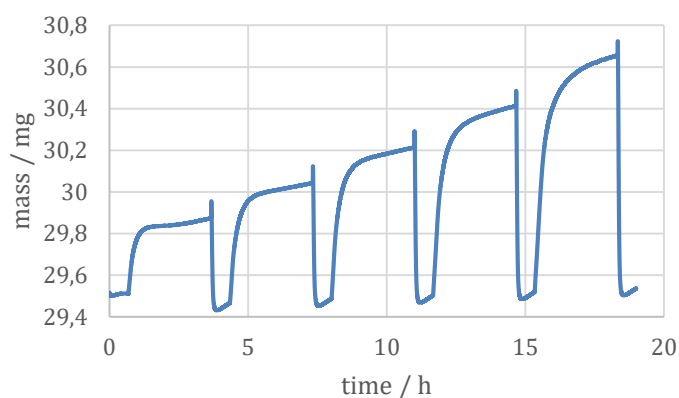


Figure 16 - Data acquired from TGA measurements

The data provided only contemplated three temperatures, 23 °C, 30 °C and 40 °C. For 23 °C there were results from 30 % to 90 % of relative humidity, for 30 °C there were results from 30 % to 70 % of relative humidity and for 40 °C there were results from 30 % to 50 % of relative humidity. These tests were performed with a 10 % step increase. In order to obtain the plot desired, those points were not sufficient. Therefore, new temperatures and relative humidities were tested in order to obtain more moisture content results.

The new data, obtained during this study, was meant to help on the plotting of the psychrometric chart with constant moisture lines. For that to happen, it was decided to measure the mass uptake of nylon at 23 °C, 30 °C, 40 °C and 50 °C from 10 % to 20 % of relative humidity with 5 % increasing step. It was not possible to perform the tests at higher temperatures or even at higher values of relative humidity due to the fact that the dew point would have been achieved which meant, in practical terms, that it would start to rain inside the machine.

The setup conditions used by Hongying Zhao are shown in grey in table 4, while the new setup conditions, performed within this thesis, are shown in blue. Both results are complementary and were used for plotting the psychrometric chart. The data acquired had to be in accordance with the Figure 40 from Annex A due to some machine damaging conditions, which would lead to condensation inside the machine. That data setting is shown in table 4 as well.

The configuration of the test's procedure was conducted by three software, two of which are related to the same equipment. The STARe Software from Mettler Toledo which set the temperature in the chamber over time, and the MHG Method Editor and MHG Control from proUmid that could provide the relative humidity wanted inside the chamber over time.

Table 4 - TGA measurements

	T / °C			
RH / %	23	30	40	50
10				
15				
20				
30				
40				
50				
60				
70				
80				
90				

3.3.3 Data analysis for the psychrometric chart drawing

Both the TGA and the MHG provide important information, and, due to being two different software, their data comes in two different files. The TGA file provides information regarding the mass as can be seen on Figure 16, set temperature and the temperature measure throughout the test while the MHG file contains the set relative humidity and the measured relative humidity over time.

For Hongying's data, which contained a drying step phase in between every humidity increase step, the mass used as mass of dry sample (X) was the last mass recorded in the pre-drying step.

For the data collected in this master thesis, the drying step in between was removed, the mass used as mass of dry sample (X) was the last mass recorded on the first and only drying step.

The mass was converted in weight percentage or moisture content with equation 10 in order to construct a graphic representation which provided clear information on the adsorption of water molecules by the nylon cord. This meant the dried sample had 0 % of water weight percentage and the increase was the amount of water in the sample. When a plateau is reached in the experiment, it means that there is a steady behavior and the sample reached the saturation point and can no longer adsorb more water molecules in those specific conditions.

This section has the objective of providing a three-dimensional (3D) and a two-dimensional (2D) representation of the effect of Temperature and Relative Humidity on the moisture adsorption for Nylon . That can only be done, if for each temperature the value of the moisture content is the saturation moisture content, which can only occur in infinite time. To overcome that, with the plotting of the moisture content vs relative humidity on excel, the data was extrapolated using the forecast tool with a 99 % degree of certainty. This forecast provided the best way to predict the behavior of the data because it accounted for the whole plot. In Figure 17 the forecasting tool of ExcelTM is shown.

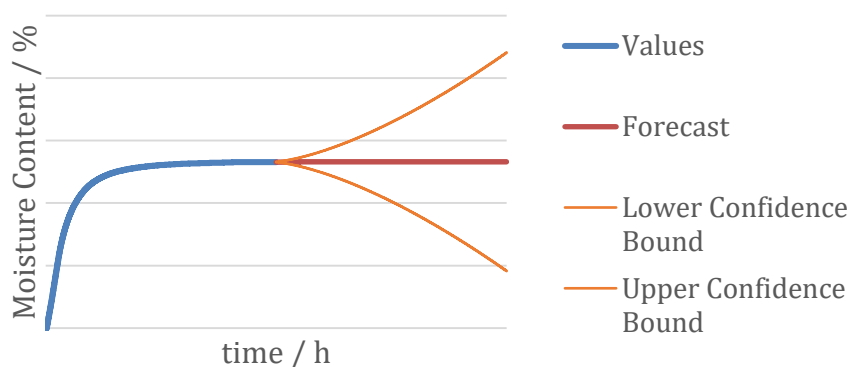


Figure 17 - Example of the use of the forecasting tool from Excel

The procedure mentioned above was done for all the testing conditions, which resulted then in the saturation moisture content value of each sample. This data was then used to obtain the nylon isotherms, the three-dimensional (3D) $MC \times T \times RH$ for nylon and the psychrometric chart lines for nylon.

The data obtained was also used to achieve the specific surface area of nylon 1440x2 at 23 °C, 30 °C and 40 °C. The specific surface area was also calculated for rayon 1840x2 with values gathered from the work of Livia Coutinho, a former master's student performing her master thesis in Continental.

3.4 Static and Dynamic response in a controlled environment

The MTS Acumen™ 3 Test System, which can be seen in Figure 18, connected to the MTS Flextest 40 Controller was used to perform static (low frequency) and dynamic (high frequency) tests for rayon, 1840x2 and 2440x2, and utilized to carry out static tests for nylon, 1440x2 and 940x2. Inside the equipment, the clamping system was composed of pneumatic parallel clamps. To control the temperature and the humidity during these experiments, the Mytron KPK 27 KH Climate Chamber was used. The software MultiPurpose Testware (MPT) and the MultiPurpose Elite (MPE) were used for the test procedure creation and for the data acquisition throughout the test. This setup provided the conditions to perform the tests.



Figure 18 - Representation of the MTS Acumen™ 3 Test System equipment [37]

3.4.1 Static response for constant moisture content values

Throughout Section 4.1, it was perceived that the moisture content affects the tensile strength of rayon. With that in mind, tensile-strength tests for rayon were performed. These tests consisted in a step-wise relaxation tests, as performed in the Zwick / Roell, only differing with humidity and temperature control. The temperature control is more accurate in the MTS Acumen™ 3 due to the chamber being completely closed.

Rayon's psychrometric chart with constant moisture lines can be seen in Figure 41 from Annex B, and those conditions were taken into account in the preparation of these experiments.

The tests embodied two steps, the conditioning of the sample, and then the evaluation of the force as a consequence of an applied strain. The conditioning phase consisted of controlling the relative humidity and the temperature throughout the test. It was only applied strain, two hours after the test had begun, meaning that the samples would stay in a controlled environment two hours before any distension was applied. After that, the temperature and the relative humidity were kept constant and the test ran in the same way as was done for the Zwick / Roell, as presented in Subsection 3.2.

Primarily, rayon 1440x2 was used to perform the evaluation. For this evaluation, three different moisture content values were utilized. These values are 12.1 %, 6.69 % and 5.00 %. For the moisture content of 12.1 %, the chamber needed to be conditioned, for example, at 23.0 °C and 55.0 % of RH or at 34.5 °C and 48.5 % of RH. For the moisture content of 6.69% the conditions inside the chamber needed to be, for instance, 23.0 °C and 25.0 % of RH and 40.0 °C and 21.0 % of RH. For the moisture content of 5.00%, the conditioning of the equipment was done at 23.0 °C and 15.0 % of RH and at 60.0 °C and 9.70% of RH. Note that these conditions follow the moisture content value, and thus, they were obtained by analyzing the psychrometric chart of rayon, which can be seen in Figure 41 in Annex B. The conditions mentioned above can be seen in table 5.

In order to confirm whether different constructions respected the psychrometric chart for rayon, which was built with rayon 1840x2, the same test was also performed, following the line of 5.00 % of moisture content, for rayon 2440x2.

When comparing the results from the Zwick / Roell with the results from the MTS-Acumen™ 3, with the first ones being presented in Subsection 4.1.1. and the latter ones in Subsection 4.3.1., it was possible to see differences regarding the force values and thus it was needed to understand what was making the gap between them. In order to solve this problem two possible solutions were identified and thus they were tested. First there was the need of obtaining confirmation regarding the moisture content of the cords inside the Zwick / Roell resorting to an infrared balance. Secondly, a changing in clamps was performed for both of the machines and new tensile-strength tests with the same conditions were carried out. The Zwick / Roell which was operating with radial clamps, went on to operating with mechanic parallel clamps, and the MTS-Acumen™ 3, which was using pneumatic parallel clamps, also went on to using mechanic parallel clamps. These different clamps can be seen in Figure 59 from Appendix D.

To understand how the mechanical properties of nylon were affected by the moisture uptake, a tensile-strength test for nylon 1440x2 was performed, following two moisture content lines, 1.60 % and 3.00 %. The test for nylon differed from the latter one and instead of being applied strains with 2.5 % steps, only applied one strain of 12.5 % was applied. For the moisture content of 1.60 % the chamber was conditioned at 23.0 °C and 30.3 % of RH, at 30.0 °C and 25.2 % of RH and at 40 °C and 21.1 % of RH. For the moisture content of 3.00 % the conditions inside the chamber were 23.0 °C and 55.0 % of RH and 37.0 °C and 53.0 % of RH. Similar to the process carried out for rayon the conditions for the nylon cords associated with a fixed moisture content were obtained by analyzing the psychrometric chart for nylon, presented in Figure 30. The conditions mentioned above can be seen in table 5.

Table 5 - MTS-AcumenTM 3 chamber conditions according to the respective psychrometric charts

Material	Moisture Content / %	Temperature / °C	Relative Humidity / %
Rayon	12.1	23.0	55.0
	12,1	34.5	48.5
	6.69	40.0	21.0
	6.69	23.0	25.0
	5.00	23.0	15.0
	5.00	60.0	9.70
Nylon	3.00	23.0	55.0
	3.00	53.0	53.0

The same procedure was completed for nylon 940x2 in order to analyze if the psychrometric chart for nylon, which was done with nylon 1440x2, was also valid for nylon 940x2.

From the results obtained in Subsection 4.4.1 regarding nylon further testing was conducted in order to get a clearer view on its tensile response in relation with the moisture content.

For that more tensile-strength tests were performed, equal to the ones in Subsection above for nylon, but instead of fixing the moisture content, the temperature was fixed and the relative humidity varied, thus varying by consequence the moisture content. The tests referred consisted, then, of maintaining firstly the temperature at 23.0 °C and varying the relative humidity, having the values of 10.0 %, 30.0 %, 55.0 %, 70.0 % and 90.0 %, thus giving the values of moisture content of 0.616 %, 1.59 %, 3.00 %, 3.51 % and 5.21 %, respectively, this setup was called FTEMP23. Secondly, for the FTEMP40, the temperature was fixed at 40 °C and the relative humidity varied from 20 % to 50 % with increase in steps of 10 %, thus providing the moisture content values of 1.56 %,1.90 %, 2.56 % and 2.85 %, respectively, This procedure can be better understood with Figure 19, being the orange dots following FTEMP23 and the blue dots in accordance with FTEMP40.

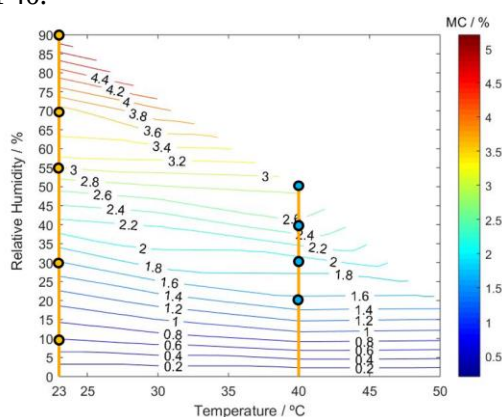


Figure 19 - Fixing a temperature and varying the moisture content for nylon

3.4.2 Dynamic mechanical analysis

There is significant importance in the characterization of rayon and nylon. In order to obtain that information, a dynamic mechanical analysis test was performed in the MTS-Acumen™ 3 Test System. This test was done for two different constructions of rayon, 1840x2 and 2440x2 and for two different constructions of nylon, 940x2 and 1440x2.

Before starting the respective tests, it was necessary to calibrate the machine with the respective characteristics of each cord, and thus in the MPE the calibration was conducted. Since for rayon 1840x2, the calibration had already been done in the company it was only required to do it for rayon 2440x2, nylon 940x2 and nylon 1440x2.

The cords were kept in an environment of 23 °C and 55 % of RH before being tested. These conditions correspond to the laboratory's atmosphere, before being tested. The test began by clamping the sample in the pneumatic clamps and applying a preload for the construction. Each cord, since it has a different construction, will have a different preload. Upon applying that pre-tension, there was a step of sample conditioning consisting of ten cycles of sinusoidal strain ranging between 1 % and 5 %, at 120 mm·min⁻¹, with the objective of pre-damaging the sample and thus excluding this effect from the dynamic response.

With this step concluded, the analysis began. This consisted of applying a sinusoidal strain, ranging from 4 % to 6 %, at 20 Hz for one hour. Following this step lower frequencies were applied to the sample, being them 10, 5, 2, 1, 0.3, 0.1 Hz, respectively. This procedure was applied to different temperatures depending on the objective, which is explained in the following paragraph.

For both rayon 1840x2 and 2440x2 these steps were utilized. The main objective was to follow the moisture content value of 5.00 %. The conditions in which the chamber was climatized were set in order to obtain the 5.00 % value of moisture uptake, which can be obtained from either Figure 41 or 42 from the Annex B. With that in mind the conditions of the chamber to which the test was done were 20.0 °C and 15.0 % of RH, 30.0 °C and 12.4 % of RH, 40.0 °C and 12.1 % of RH, 50.0 °C and 11.0 % of RH and finally 60.0 °C and 9.7 % of RH.

For nylon 940x2 and nylon 1440x2 the same procedure was carried out, with differences in the chamber conditions. The conditions used regarding nylon were set in order to obtain the 2.00 % value of moisture uptake, which can be obtained from either Figure 29 or 30. With that taken into consideration the conditions of the chamber were 23.0 °C and 37.8 % of RH, 30.0 °C and 33.5 % of RH, 35.0 °C and 33.5 % of RH, 40.0 °C and 31.7 % of RH and finally 45.0 °C and 29.2 % of RH.

4 Results and discussion

4.1 Stepwise Relaxation Tests

The stepwise relaxation tests consist, as already mentioned in Subsection 3.2, in the increase of the strain of the cord, and consequently evaluation of the tension or force required for that elongation.

The tests were performed at different temperatures and for different polymers, PET and rayon. For PET the temperatures used were 23 °C, 40 °C, 80 °C, 110 °C and 160 °C and for rayon, 23 °C, 40 °C, 60 °C and 80 °C. In both materials, the strains tested were 2.5 %, 5 %, 7.5 %, 10 % and 12.5 %

4.1.1 Effect of Linear Density and Temperature

Since the stress is nothing but the ratio between force and the cross-sectional area of the specific polymer, the force-curves were plotted to discuss the results. The force-strain curves are a common way of representing this stepwise relaxation test, and with that taken into account, the results for the different PET constructions at 23 °C were plotted in the following representation, Figure 20, with the stress coming in Newton, N, and the strain in percentage, %.

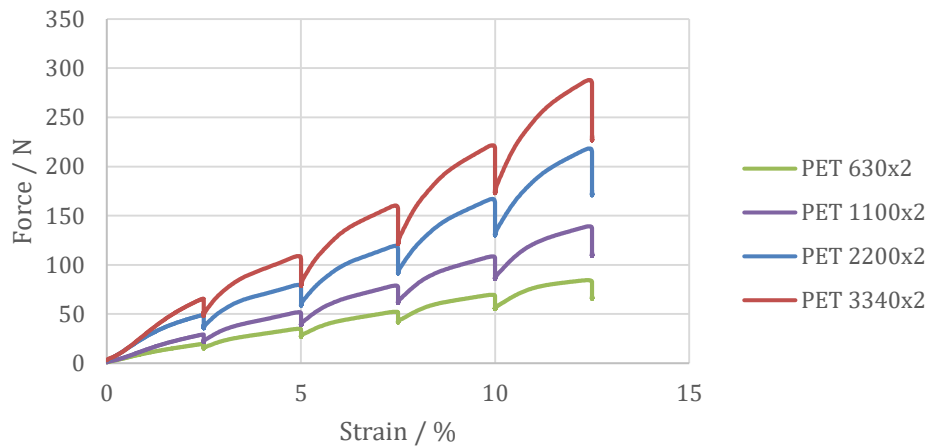


Figure 20 - Force-Strain curves at 23 °C

From what can be observed in Figure 20, the higher the linear density, the more tension is required to achieve the same strain. Figure 21 shows how the force varies with the increase of temperature for the same cords. The force-strain curves for 80 °C and 110 °C can be seen in Figure 45 from Appendix A.

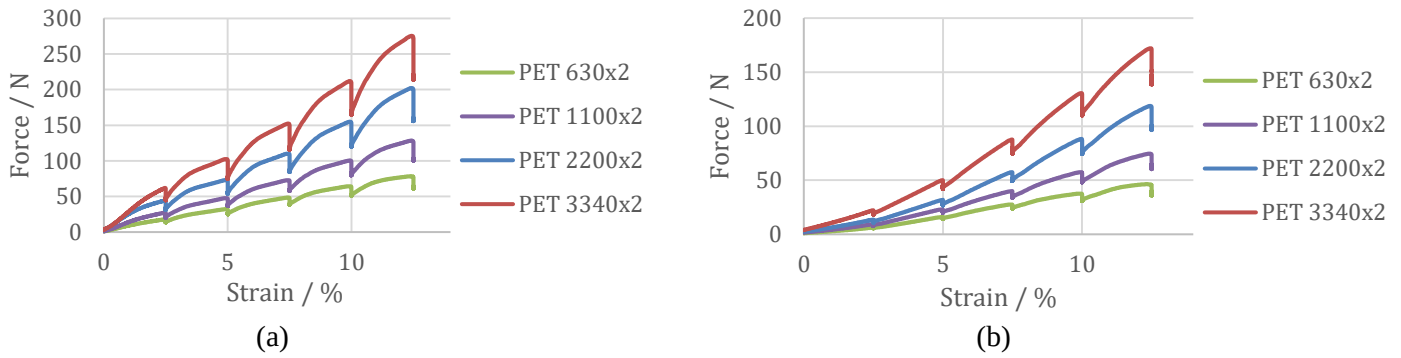


Figure 21 – Force-Strain curves for PET at 40 °C (a) and 160 °C (b)

From Figure 21 it is possible to infer that the temperature affects the force. With the increase of temperature, the force necessary to achieve the same strain is reduced. This is connected to the loss of stiffness by the cord which occurs with the temperature's increase.

The force-strain curves for rayon are shown in Figure 22. For rayon, the tests were done with and without a drying step, which showed no significant difference in the results obtained

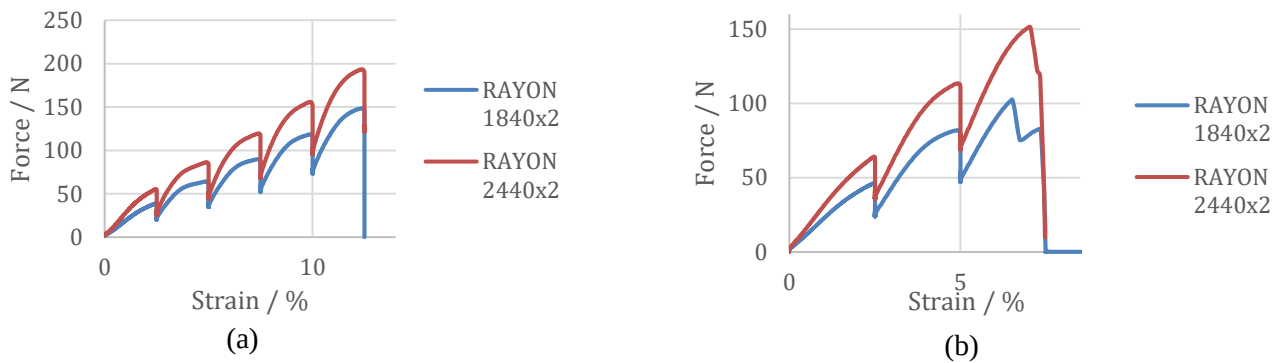


Figure 22 - Force-Strain curves for rayon at 23 °C (a) and at 80 °C

Rayon's behavior for these relaxation tests was not as expected. As shown by Figure 22, the force increases with the increase of temperature. This can be correlated to rayon's ability of capturing water molecules from the air at the laboratory's ambient conditions, which leads the cords to decrease their stiffness. The chamber is not completely closed, and thus the water molecules are still able to influence the cords while being inside the chamber. Due to the increase in the temperature, the relative humidity is reduced in the chamber, leading to stiffer cords because of the reduction in the moisture content. This increase in the stiffness with the increase of the temperature makes the cords break before expected. It shows that for higher temperatures the cords break with less strain.

The laboratory in which the tests were performed had a fixed atmosphere of 23 °C and 55 % of RH. With the equation 14 from Annex C and with the values presented in table 13 from Annex C, which are corresponding to the saturation pressure values for the different temperatures, it is possible to obtain the value of the actual vapor pressure in the laboratory, which will be the same inside the chamber. The temperatures inside the chamber change, and with a fixed actual vapor pressure, the Relative Humidity also

changes. Due to rayon's hydrophilicity, the effect of the temperature and relative humidity highly affect its moisture uptake. The moisture content on the rayon cord can be followed with the Figure 41 on Annex B, and thus conducting to the table 6, in which the different conditions inside the Zwick / Roell are correlated to a moisture content value.

Table 6 - Zwick/Roell chamber behavior prediction

Temperature / °C	23	40	60	80
Relative Humidity / %	55	21	7.8	3.3
Moisture Content / %	12.1	6.69	4.28	$\cong 2$

From the content displayed in table 6 the Zwick / Roell atmospheric conditions towards the relation with the rayon cord behavior can be better. It is then possible to infer that the behavior of temperature is not the same for rayon and for PET, with this equipment. For PET, which is a hydrophobic polymer, the increase of temperature decreases the stiffness of the cord, while for rayon, the increase temperature influences the moisture content of the cord, and thus with the reduction of moisture content there is an increase in the stiffness of the cord.

4.1.2 Removal of the Linear Density effect

The force-strain curves are a usual way of showing information related to the stepwise relaxation test, found all over the literature. One way of representing it, which is also widely used, is by force-elongation, with the force coming in Newton, N, and the elongation in millimeters, mm.

Figures 20 to 22 showed the behavior of the linear density for different temperatures. One thought that might occur is that when the force of the cords is normalized, which means removing the effect of linear density by dividing the force by the corresponding dtex, the behavior of the cords should be the same as they are all the same material. In Figure 23 that same behavior is shown for PET, including the temperature's effect. The temperatures utilized were the same as in previous results for PET.

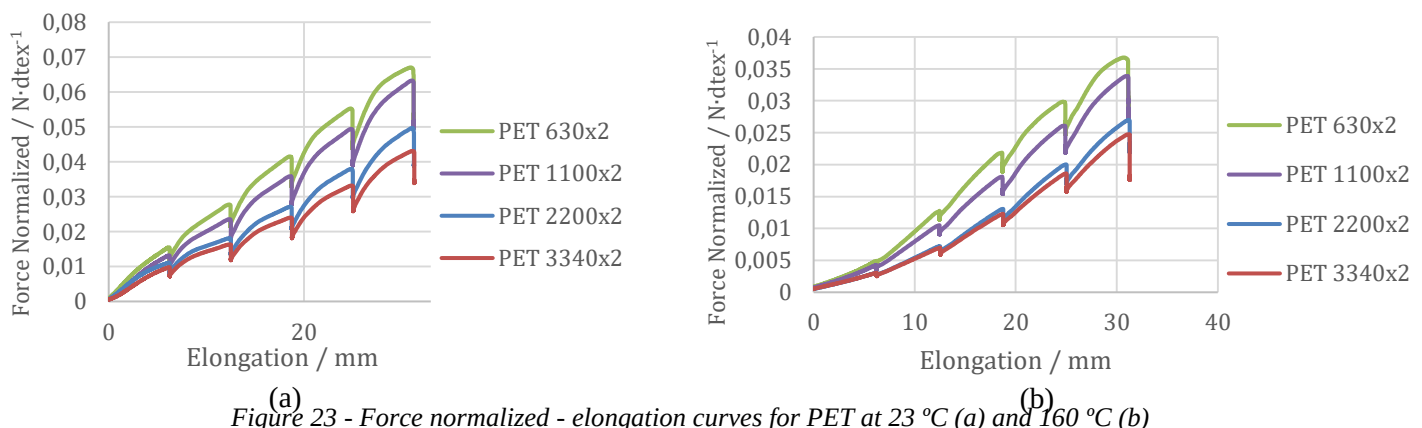


Figure 23 - Force normalized - elongation curves for PET at 23 °C (a) and 160 °C (b)

With the Figure 23 it is possible to see that the behavior has changed greatly from the previous results without normalization. Nonetheless, if we consider the information in Subsection 3.1., the results seem to corroborate that information. Both the PET 2200x2 and 3440x2 are standard cords, which means they should have the same behavior. There is a tendency for their behavior to be identical with the increase of the temperature. The PET 630x2 is a high modulus cord, which means that it was designed to sustain more stress for lower linear density, somewhat like PET 1100x2, despite the latter not being able to sustain as much. Unlike the standard cords (PET 2200x2 and 3440x2) their behavior when normalized is not affected by the temperature. This can be seen in the following representation, Figure 24.

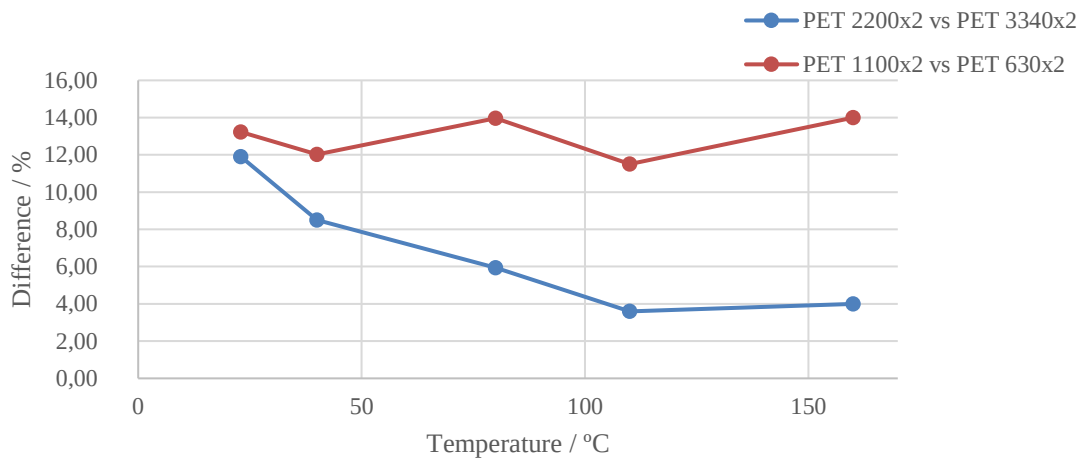


Figure 24 - Difference between high modulus cords and standard cords

For the standard PET, 2200x2 and 3340x2, the difference between the two decreases with the increase of temperature, stabilizing at 4 %, conducting to the understanding that the behavior of the standard cords, when the linear density factor is removed, tends to get similar with the increase of the temperature, whilst for PET 630x2 and PET 1100x2 the difference is constant with the increase of temperature, ranging from 12-14 %.

The removal of the linear density was also done for rayon, as follows in Figure 25.

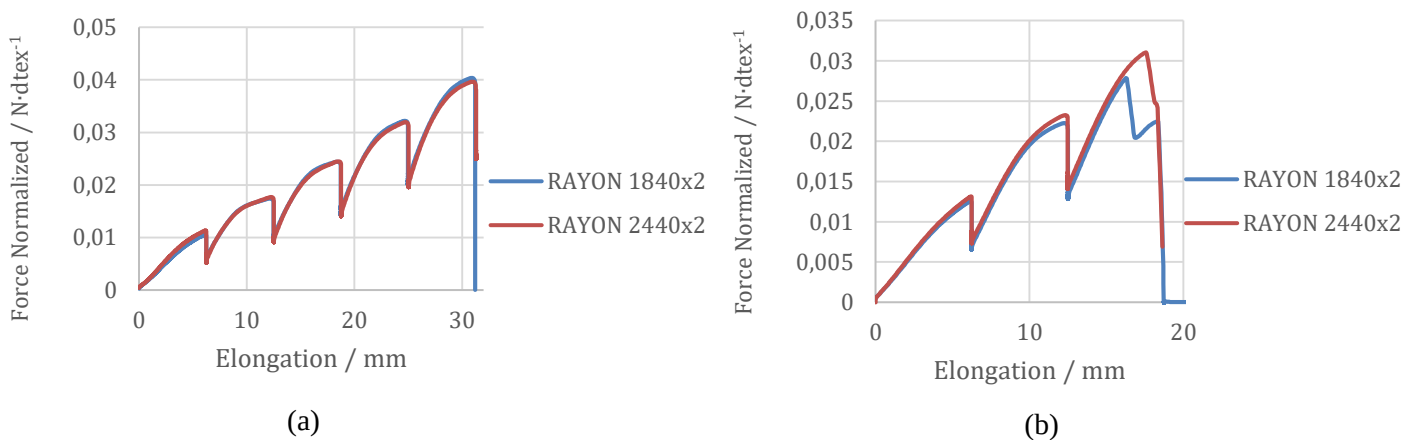


Figure 25 - Force normalized - elongation curves for rayon at 23 °C (a) and at 80 °C (b)

Both rayon 1840x2 and 2440x2 are standard rayon, and such can be proven by their behavior when normalized, which shows no difference, apart from some experimental errors.

Differently from PET, rayon is highly hygroscopic, which means that it has a great capacity for adsorbing water molecules. The atmosphere in which the rayon cord surrounded greatly affects its behavior, not only the temperature but also the relative humidity of the environment. Rayon will be studied further in this thesis with respect to its hygroscopic behavior.

Apart from the results for rayon, as already explained that they were consistent with the decrease of moisture content, when the temperature is increased for the same strain, the force decreases, which proves the decrease in the stiffness of the cords, which can also be seen when the tension values are normalized

4.2 Constant Moisture Lines in a Psychrometric Chart

4.2.1 Thermogravimetric analysis

As shown by the literature, multiple factors such as temperature and relative humidity affect the water uptake by nylon cords. It is key to understand the water uptake behavior for different temperatures and relative humidity conditions, which can be relevant when interpreting mechanical properties of the cord.

During the performance of a car, the tire is subjected to different conditions throughout. The tire will behave differently for different atmospheric conditions. The tires used in the desert and in a formula 1 race are not the same, and these different atmospheric conditions associated will also affect the mechanical properties of nylon. They influence nylon's force-strain curve response which is related to the tensile strength.

The thermogravimetric analysis was used to discover the point in which, at a defined temperature and relative humidity, the cord would reach its saturation point of water adsorption, or in other terms, at which point the cord would achieve an equilibrium with the surrounding environment regarding water adsorption.

The testing conditions used for this thesis, already mentioned in table 4, are presented in Figures 26 and 27. Figure 26 depicts the water uptake over time for 10 %, 15 % and 20 % of RH for 40 °C and 50 °C. In Figure 27 the variation of the water's mass for 30 %, 40 % for 23 °C and 40 °C, respectively, is presented.

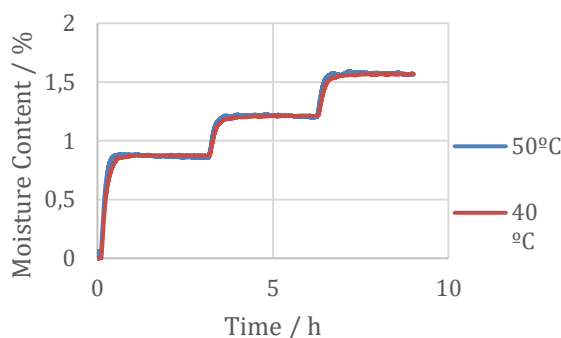


Figure 26 - Water uptake at 10 %, 15 % and 20 % of RH

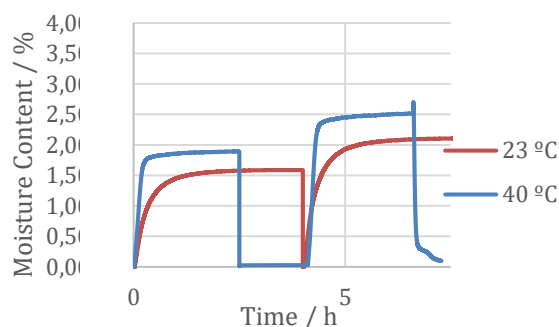


Figure 27 – Water uptake at 30 % and 40 % of RH

These results are shown in different representations due to a procedure's optimization. The results done for the testing setup presented in this study, Figure 26, in which the duration had the objective of ensuring a stable plateau, show that for lower values of relative humidity the moisture content does not increase with the increase of temperature. In Figure 27 the results with Hongying's testing setups are presented. It can be perceived that even in Hongying's testing setups, Figure 27, there were optimizations due to the testing procedures being very time consuming.

From Figure 27, two main observations are noticed. Firstly, an increase of relative humidity, for a fixed temperature, increases the water uptake by the nylon cord. This effect can be explained by the fact that for higher relative humidity values, there are more water molecules available in the air to be adsorbed by the sample. Since nylon is a semi-crystalline polyamide, more water molecules will be attached to the amide groups with the increase of relative humidity, which correspond to the accessibility of water molecules to the amide groups through the amorphous region of the polymer. For smaller values of relative humidity this behavior does not happen, as can be seen from Figure 26, in which the values of the moisture content by the nylon's cord tend to be similar.

The other observation is that, for a fixed relative humidity, with the increase of temperature there is also an increase on the moisture content values. The explanation for this is related to the thermodynamics of the air moisture, which provides information regarding the fact that the saturation vapor pressure of water increases with the increase of temperature, which means that there will be more capacity for the air to hold the water molecules in absolute terms for the same relative humidity value. This means that there will be more water available in the air to be adsorbed.

4.2.2 Forecasting the saturation moisture content of nylon cords

The thermogravimetric analysis for a wide range of temperature and relative humidity values provided the moisture content for the nylon cord. The main objective was to obtain the saturation moisture content, which is when the water vapor within the nylon cord reaches an equilibrium with the water vapor presented in the environment regarding the amount the cord can uptake. The values registered by this analysis were not corresponding to the saturation values, which can be seen by the fact that the plateau is not

yet completely stable, and thus it was required to find a tool which would reveal this value, or at least which could, with the behavior of the actual curve, predict a value for a very long time.

For that, as mentioned on Subsection 3.3.3., the ExcelTM tool Forecast was chosen. This tool provided the continuation of the plateau taking in account the whole curve. The extrapolated results, which correspond to the saturation moisture content, are presented in Table 7. As stated in Subsection 3.3.2, the values in blue correspond to the values gathered within this thesis and the values in grey were obtained through the testing of Hongying Zhao.

Table 7 - Saturation moisture content values for nylon cords

RH / %	T / °C			
	23	30	40	50
10	0.6164	0.7130	0.8773	0.8476
15	0.8326	1.000	1.225	1.197
20	1.064	1.291	1.563	1.552
30	1.587	1.886	1.895	
40	2.123	2.218	2.564	
50	2.661	2.783	2.850	
60	3.348	3.372		
70	3.508	3.942		
80	4.310			
90	5.207			

4.2.3 Adsorption isotherms for nylon

With the data gathered from the thermogravimetric analysis and with the forecasting tool, which provided information concerning the saturation amount of water uptook by the nylon cord, it is then possible, with the use of equation 10, to obtain the adsorption isotherms for 23 °C, 30 °C, 40 °C and 50 °C. Nylon's moisture adsorption isotherms are displayed in the following representation, Figure 28.

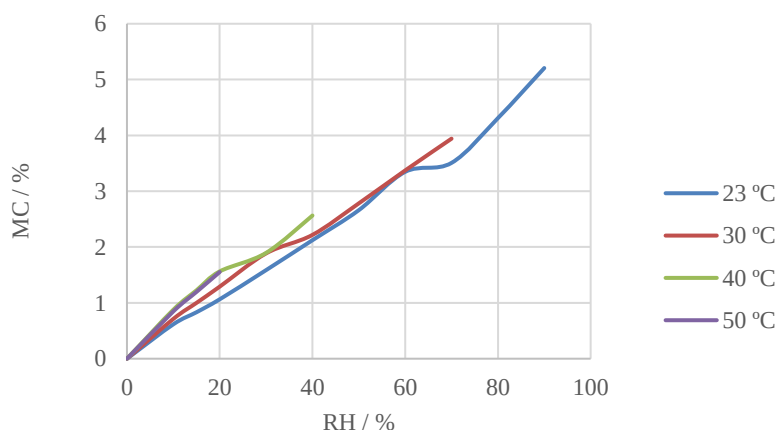


Figure 28 - Adsorption isotherms of nylon

These isotherms' shape can be related to the type II or BET isotherm from the IUPAC classification as can be seen in Subsection 2.7.3, and with this consideration the specific surface areas for nylon and rayon were determined.

In Figure 50 from Appendix B the individual isotherms for a specific temperature, for a better understanding of its shape, are depicted.

4.2.4 Psychrometric Chart with constant moisture lines

As it had already been carried out by a Continental project regarding rayon, for this thesis was proposed to do the same for nylon, or in other terms, to observe whether or not there was an effect of temperature and relative humidity on the moisture content regarding the nylon cords. One of the ways of perceiving this effect is with a three-dimensional (3D) diagram. This diagram relates all of the variables mentioned above, the temperature (x-axis), the relative humidity (y-axis) and the moisture content (z-axis) and is called $M \times T \times RH$. The referred diagram was plotted in MATLAB using the data from Table X, which can also be seen as black dots in Figure 29.

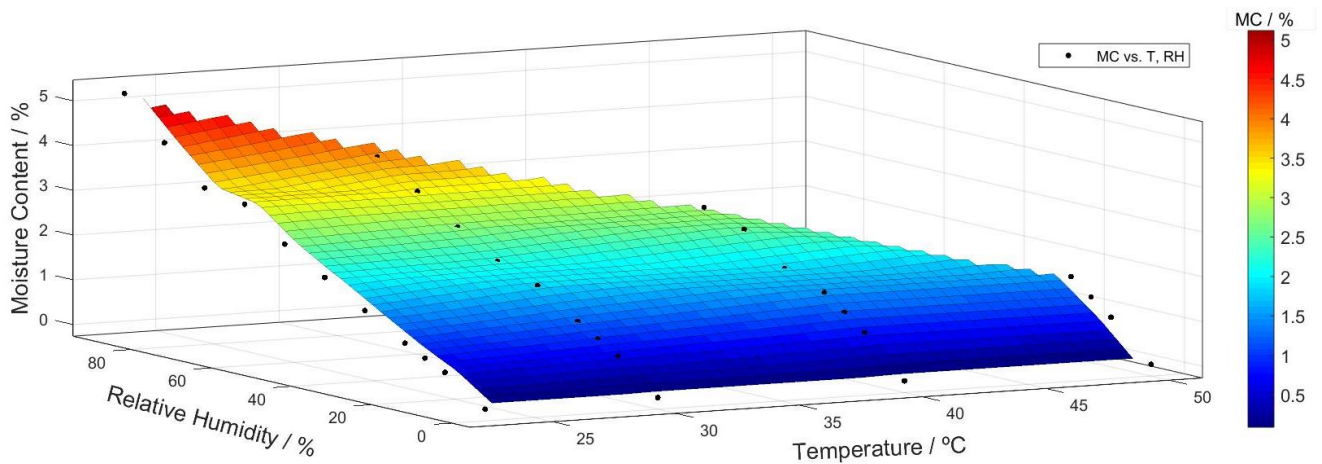


Figure 29 - Three-dimensional (3D) representation of the moisture content behavior for nylon

Still taking into account the same previous project regarding rayon, it was also required to plot a psychrometric chart with constant moisture lines. As the name mentions, it is a typical two-dimensional (2D) plot correlating the temperature (x-axis) with the relative humidity (y-axis) with the constant moisture lines. With this plot, it becomes easy for the user to understand in which position they are, simply by following the lines. By following the lines one can easily understand the moisture content for different atmospheric conditions for the nylon cord. This psychrometric chart can be observed in Figure 30. In order to have a better understanding of nylon's behavior, and with Figure 44 from Annex E, which provides information regarding the effect of nylon's 66 moisture content on the glass-transition temperature, the points from Figure 44 were put in Figure 30 and connected by a black line.

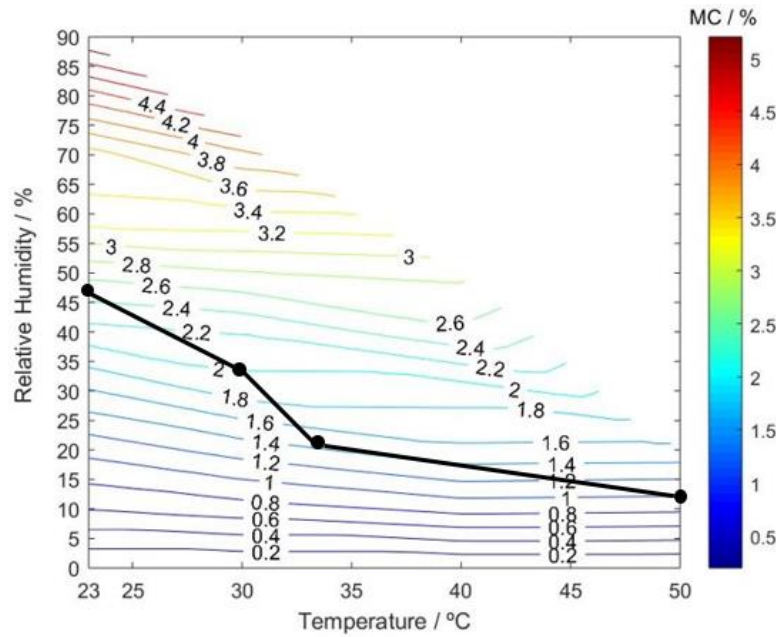


Figure 30 - Psychrometric chart with constant moisture lines for nylon with the relation between glass-transition and moisture content being highlighted with a black line

The use of both the $M \times T \times RH$ and the psychrometric chart with constant moisture lines, provides valid information and excludes the influence of the change in MC , which becomes fundamental to the tests reliability and leads to better results. The three-dimensional and the two-dimensional representations can be used in any laboratory in the world, provided that the conditions, such as temperature and relative humidity, are known. This provides a great help to understating some behaviors that would not be possible to understand without these plots, such as already shown for rayon in Subsection 4.1.1.

From the psychrometric chart it is possible to understand how the temperature and relative humidity correlate with the moisture content. For instance, for a fixed relative humidity, the increase in temperature leads to an increase in the moisture content and for a fixed temperature, the increase in the relative humidity also leads to the increase of the moisture content.

Both of the Figures shown in this Subsection are fundamental in the characterization of nylon and will be used in order to understand the behavior of the cords in tensile-strength tests and also when performing a dynamic mechanical analysis to the nylon cords. These tests are mentioned in Subsection 3.4. and the results are shown in Subsection 4.4. Nylon should exhibit a behavior similar to rayon, meaning that the tensile-strength tests for a constant value of moisture content should overlap, despite having different temperature and relative humidity. [37] This is studied in Subsection 4.4.1.

4.3 Brunauer-Emmett-Teller specific surface area

The extrapolated values for the nylon's moisture saturation content were used in order to obtain the total surface area and the specific surface area. For that the BET equation was utilized.

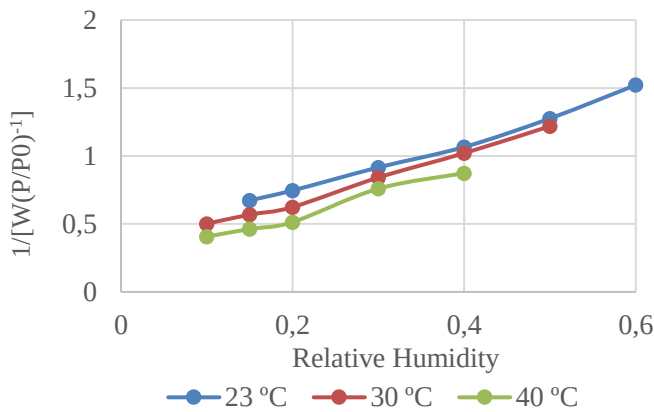
This required to know the mass of water that was adsorbed, W in mg. This mass was collected from the data with help from the saturation moisture content table. With the equation 11, it was possible to obtain the $\frac{1}{W \cdot ((P_0/P) - 1)}$ corresponding values, as shown in table 8 for nylon and in table 9 for rayon. With that, the values were plotted as $\left(\frac{P}{P_0}\right)$ vs $\frac{1}{W \cdot ((P_0/P) - 1)}$, as it can be seen in Figure 31, for nylon (a) and rayon (b).

Table 8 - BET equation values for nylon

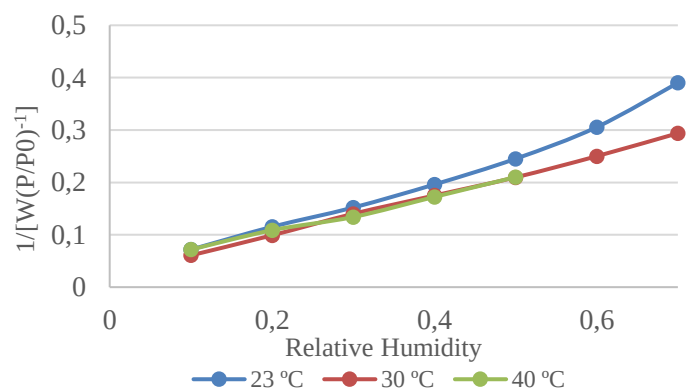
RH / %	RH	1/[W(P/P0) ⁻¹]		
		23 °C	30 °C	40 °C
10	0.1		0.5019	0.4069
15	0.15	0.6733	0.5684	0.4626
20	0.2	0.7463	0.6241	0.5137
30	0.3	0.9158	0.7319	0.7595
40	0.4	1.066	1.020	0.8729
50	0.5	1.276	1.219	
60	0.6	1.522	1.508	

Table 9 - BET equation values for rayon

RH / %	RH	1/[W(P/P0) ⁻¹]		
		23 °C	30 °C	40 °C
10	0.1	0.07168	0.06067	0.07168
15	0.2	0.1152	0.09894	0.1087
20	0.3	0.1520	0.1401	0.1339
30	0.4	0.1961	0.1750	0.1723
40	0.5	0.2451	0.2096	0.2101
50	0.6	0.3055	0.2500	
60	0.7	0.3902	0.2939	



(a)



(b)

Figure 31 - BET equation for nylon (a) and for rayon (b)

With the corresponding curve equation, which can be seen in table 15 from Appendix E, and with equations 11, 12 and 13 the values of the specific surface area were obtained. The values of the slope, y-intercept, R^2 , monolayer weight (Wm) and the BET constant (C) can also be seen in table 15 from Appendix E while the surface total area (St) and specific surface area (S) values are shown in Table 10 and 11, for nylon and rayon respectively. The values of the specific surface areas for both nylon and rayon at the different temperatures were plotted in Figure 32, with the x-axis being the specific surface area, in $m^2 \cdot g^{-1}$, and the y-axis being the temperature in $^{\circ}C$.

Table 10- Surface total area and specific surface area values for nylon

	23 °C	30 °C	40 °C
St / m^2	1.63	1.70	1.92
$S / m^2 \cdot g^{-1}$	52.5	54.9	61.9

Table 11 - Surface total area and specific surface area values for rayon

	20 °C	30 °C	40 °C
St / m^2	6.98	8.91	9.56
$S / m^2 \cdot g^{-1}$	199	254	273

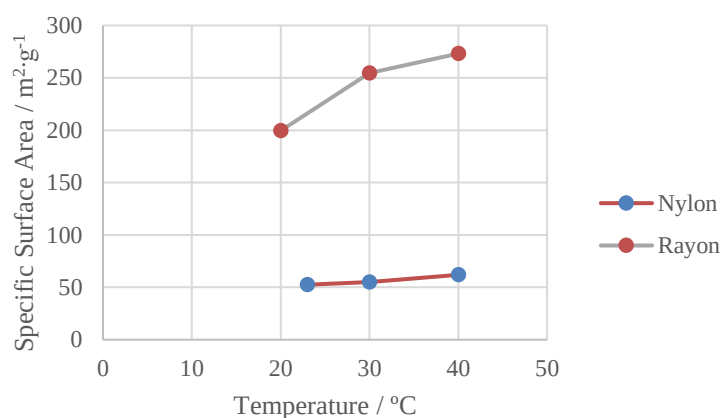


Figure 32 - Temperature effect in the specific surface area

From Figure 32, it becomes clear that, with the increase of temperature there is also an increase in the specific surface area. That also corroborates the explanation given in subsection 2.7.5.

The values of the specific surface area obtained in this study were also compared to values found in the literature, as can be seen in section 2.7.5. They are $45 m^2 \cdot g^{-1}$ and $204 m^2 \cdot g^{-1}$ for nylon and rayon, respectively. [46] Comparing the values for nylon and rayon with the ones gathered from the literature, despite a difference in the temperature of, for nylon 2 °C and for rayon 5 °C, the values are in the same order of greatness. Another conclusion that can be retrieved from this comparison is that, despite employing different methods, the results of the specific surface area values are similar.

The total surface area and the specific surface area provide information regarding the temperature effect on the polymer. With the increase of temperature, the area available for the water uptake increases, which means that the increase of temperature will lead to an increase in the moisture content value. Such behavior is supported by the psychrometric chart for both nylon and rayon, which can be seen in Figure 30 and in Figure 41 from Annex B, respectively.

4.4 Static and Dynamic response of rayon and nylon cords

4.4.1 Static response for constant moisture content values

As seen throughout this study, rayon has a highly hygroscopic behavior, which affects its mechanical properties. Due to that some tensile-strength tests were performed, as mentioned in Subsection 3.4.1. and the results associated with the procedures mentioned for rayon 1840x2 and 2440x2 are shown in Figures 33 and 34. In Figure 33 (a) the response following a moisture content value of 12.1 % is shown for rayon 1840x2 and in Figure 33 (b) and 34 the same representation as the latter but for a moisture content value of 5.00 % is presented for rayon 1840x2 and 2440x2, respectively.

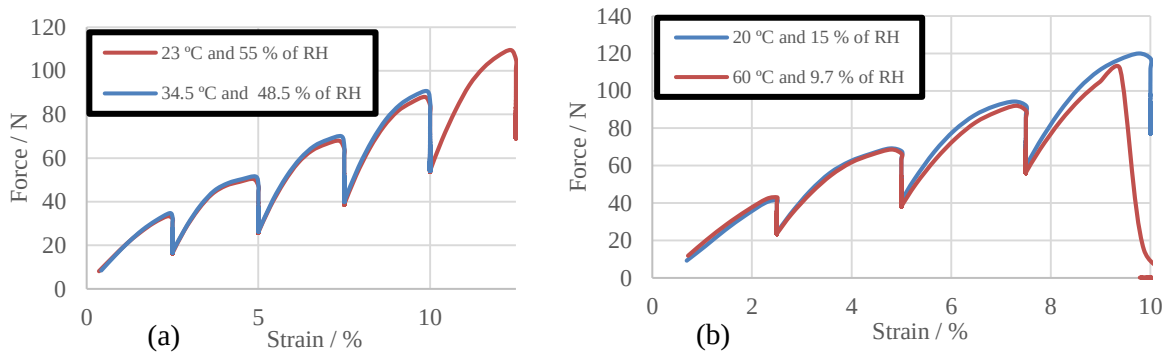


Figure 33 - Force-strain response for rayon 1840x2 at 12.1 % (a) and at 5.00 % (b) of MC

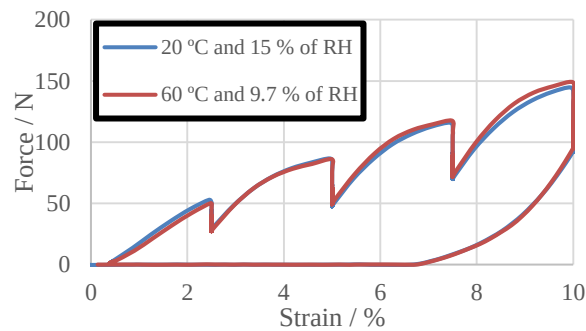


Figure 34 - Force-strain response for rayon 2440x2 at 5.00 % of MC

For rayon, at a fixed value of moisture content, with different atmospheres associated, the tensile-strength test shows the same response, for a wide range of values, meaning that the behavior of both of those constructions of rayon can be pursued correctly taking into account the psychrometric chart with constant moisture lines for rayon presented in Figure 41 from Annex B.

Comparing Figure 33 (a) with 22 (a), the latter being the one for rayon 1840x2 in the Zwick / Roell, some differences can be noticed. It is possible to see that the results for the Zwick / Roell show higher values of force for the same strain. One first thought was that perhaps the conditions in the Zwick / Roell were not the ones predicted and thus there was the need to perform this confirmation. The cords were then left in the environment for 3 hours, as was done for the thermogravimetric analysis in which that time was sufficient to achieve an equilibrium concerning the water uptaken. The values measured can be seen in table 12.

Table 12 - Moisture content comparison for rayon

Moisture Content / % (Prediction)	12.1	6.66	4.28
Moisture Content / % (Measured)	11.8	6.24	4.06
Difference / %	2.48	6.73	5.14

As shown by the content in table 12, there is not a noteworthy difference between the results, or at least one that would be significant to provide the differences which can be seen when comparing Figure 22 (a) with 33 (a). With that in mind, the assumption that the issues could originate from using different clamping systems was then proposed, the one used on the Zwick / Roell being radial, while the one used in the MTS-AcumenTM 3 is pneumatic parallel.

Both of the clamping systems were switched for mechanic parallel clamping systems. The pneumatic parallel clamps were compared with the mechanic parallel clamps for PET, as it can be seen in Figure 49 from Appendix A, and they did not show any difference. In Figure 35 we can see the results for two environment conditions, 23.0 °C and 55.0 % of RH and 40.0 °C and 21.0 % of RH, which supposedly provide different moisture content values, 12.1 % and 6.69 %, respectively, with the different clamping systems for both machines associated.

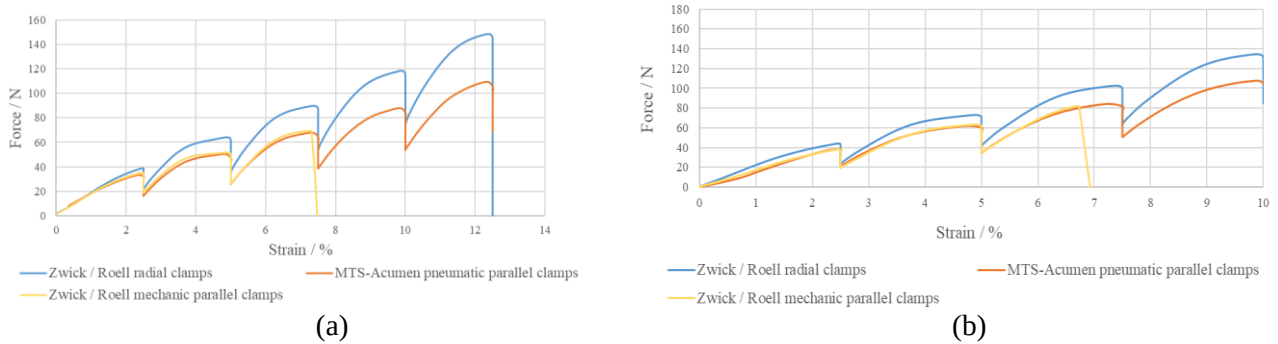


Figure 35 - Force-strain response of rayon 1840x2 at 23 °C and 55 % of RH (a) and at 40 °C and 21 % of RH (b) with different clamping systems

In Figure 35, it is possible to observe that different machines, with the same clamping system have similar results for what was thought to be the same conditions. Because the results overlap, that means that the conditions in the Zwick / Roell are the same as in the MTS-AcumenTM 3. Since the conditions were identical this proves that the predictions made in Subsection 4.1.1, which can be seen in table 6, are now confirmed.

As also mentioned in Subsection 3.4.1. the same moisture content comparison was done for nylon. Within the same construction it was compared the same moisture content but with different atmospheric conditions. In Figure 36 (a) the response for 3.00 % of moisture content for nylon 940x2 and in Figure 36 (b) the response for 3.00 % of moisture content for nylon 1440x2 can be seen.

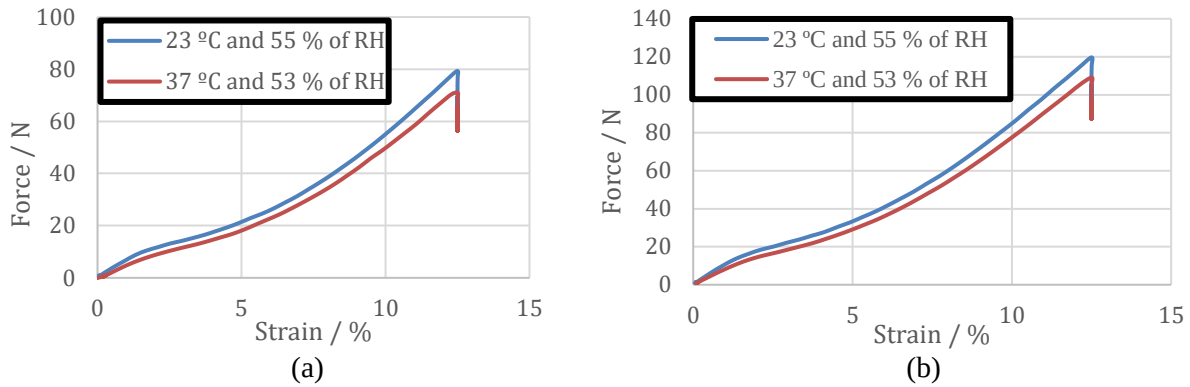


Figure 36 - Force-strain response for nylon 940x2 (a) and for nylon 1440x2 (b) at 3 % of MC

For nylon, at a fixed value of moisture content, with different atmospheres associated, the tensile-strength test shows different responses meaning that the behavior of both of those constructions of nylon cannot be simply pursued taking the psychrometric chart with constant moisture lines for nylon into account. In the response it can be seen that the temperature is the dominant factor when comparing the same moisture content value. That can be followed by Figure 30, in which, for the conditions mentioned, the values are above the line of the glass-transition temperature.

Even though the moisture content does not represent the main force affecting the nylon cords' behavior, it was still pivotal to understand how the water uptaken by the cord affected its tensile-strength. Tensile-strength tests for nylon 1440x2 were performed fixing the temperature and varying the relative humidity, which meant varying the moisture content by consequence. In Figure 37 the response for 23.0 °C and for 40.0 °C can be observed.

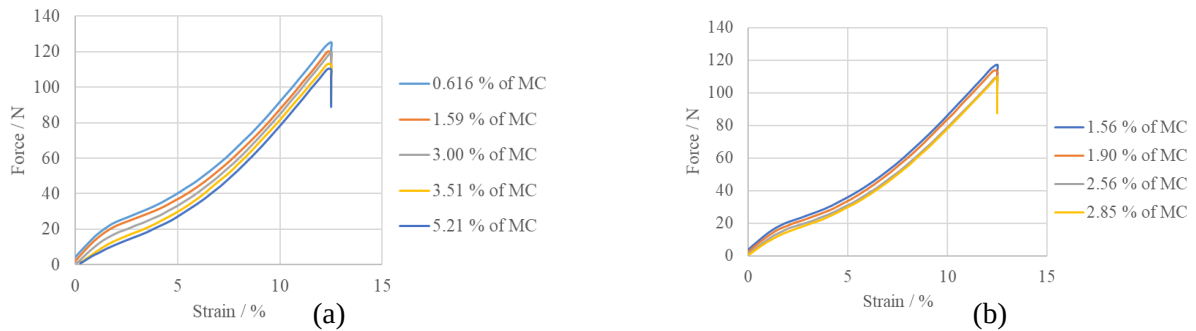


Figure 37 - Force-strain curve of nylon 1440x2 at 23 °C (a) and at 40 °C (b)

As it is possible to see from Figure 37 there is an impact on the force, resulting in its decrease with the increase of moisture content. This brings confirmation to the importance of moisture control for nylon.

4.4.2 Dynamic mechanical analysis

As mentioned in Subsection 3.4.2 the dynamic mechanical analysis was performed for rayon 1840x2 and rayon 2440x2.

To characterize the rayon cords the DMA was performed at different frequencies and different conditions of temperature and relative humidity. The latter two are in correlation with the moisture content value and it was crucial that the combination of the two provided a moisture content value of 5.00%. The

characterization of the nylon cords was done for a moisture content of 2.00%. Figure 38 corresponds to the response for rayon, 1840x2 and 2440x2, respectively, and Figures 39 to nylon 940x2 and 1440x2, respectively.

With this test it was possible then to proceed to the characterization of viscoelastic behavior of the cords. The elastic modulus (E') over frequency for iso-moisture conditions, which is shown from Figure 38 and 39 was derived from the Fast Fourier Transform (FFT) and the response derived directly from the results could be shown, but since the hysteresis loop from the FFT overlaps with the hysteresis loop from the experimental data, as can be seen in Figures 52, 54, 56 and 58 from Appendix C, for the constructions tested, the results from the FFT become validated. The remainder parameters, E'' and $\tan \delta$ were calculated from the FFT and are shown in Figures 52, 54, 56 and 58 to Y from Appendix C.

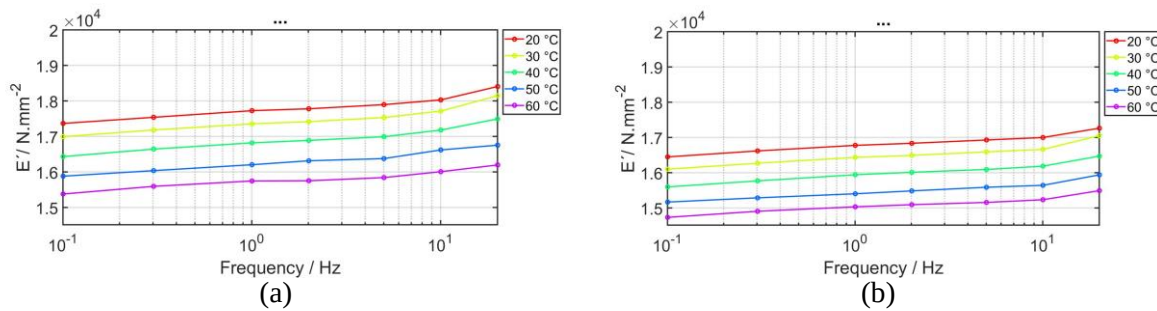


Figure 38 - Elastic modulus of rayon 1840x2 (a) and of rayon 2440x2 (b) over frequency

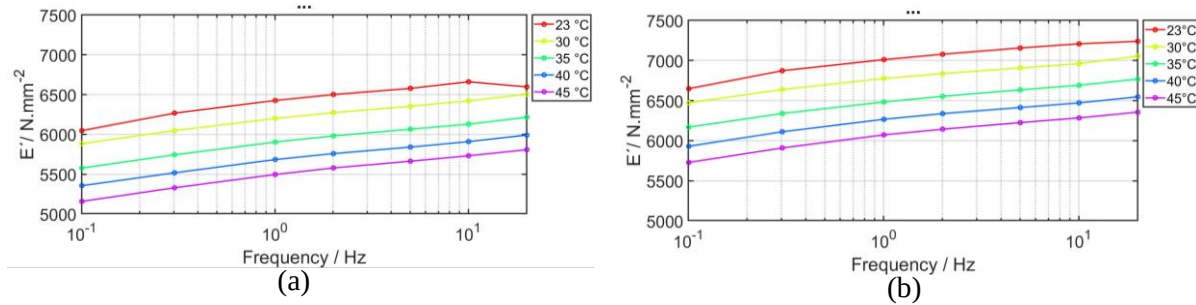


Figure 39 - Elastic modulus of nylon 940x2 (a) and of nylon 1440x2 (b) over frequency

From Figures 38 and 39, it is possible to perceive that the elastic modulus (E') decreases with the increase of temperature. This behavior can be seen for both of the rayon and nylon constructions. By comparison, the elastic modulus values for the rayon 1840x2 construction are higher than the ones from the 2440x2 construction. For nylon 940x2 the elastic modulus values are higher than the ones shown for nylon 1440x2. The elastic modulus was expected to be same for both of the constructions of rayon and for both of the constructions of nylon. These differences could be related to the fact that only one trial was made for each sample, which means more tests are needed to ensure replicability and reproducibility. It could be related to deviations in the crystallinity associated with the cords' manufacturing, which cannot be corroborated by any work done in this study.

With that taken into account, there is need for amelioration of the procedure to prevent the nylon cords from buckling, which can lead to better results that can be utilized for the prediction of the tire's rolling resistance.

5 Conclusion

This master thesis grants new knowledge in regard to the linear density effect and temperature effect on the mechanical behavior of PET, rayon and also the effect of rayon's and nylon's hydrophilicity in their mechanical responses. With this taken into account, three distinct insights can be gathered from the results shown in Section 4, which are described as follows.

Firstly, for PET 2200x2 and 3340x2, the standard cords, when the effect of linear density is removed, the increase of temperature tends to approximate them in terms of mechanical response, starting with a difference of 12 % for 23 °C and stabilizing at 4 % for higher temperatures. For rayon, the results were not the expected ones, having higher force values for higher temperatures, in contrast to previous findings, an increase in temperature did not result in an increase of the cord's stiffness. Since rayon is a hygroscopic polymer, the temperature is not the only factor affecting the response. This brought a new understanding of the climatization inside the Zwick / Roell testing machine chamber's, thus showing that with the increase of temperature, there is a decrease in the relative humidity, due to the chamber not being completely isolated and being in contact with the laboratory's atmosphere, which affects the water uptake by the cords thus affecting its mechanical response. The response was compared to the response obtained in the MTS-Acumen™ 3, which has temperature and humidity control, and after optimizing the procedure, the results overlap, proving that the prediction of the atmosphere inside the Zwick / Roell chamber is confirmed and validated.

The second research laid in collecting data to draw the sorption isotherms of nylon cords at 23 °C, 30 °C, 40 °C and 50 °C. With this data a three-dimensional representation, $M \times T \times RH$, which can be used to predict the saturation moisture content of nylon for any condition was drawn. The moisture content contour lines of this $M \times T \times RH$ were plotted, which corresponds to the psychrometric chart with constant moisture lines for nylon. With the data used for the latter plots and taking into account the shape of the adsorption isotherms, type II (BET), the specific surface areas for nylon and rayon were determined. For nylon the specific surface area values, determined for 23 °C, 30 °C and 40 °C, are $52.5 \text{ m}^2 \cdot \text{g}^{-1}$, $54.9 \text{ m}^2 \cdot \text{g}^{-1}$ and $61.9 \text{ m}^2 \cdot \text{g}^{-1}$, respectively. For rayon the specific surface area values, determined for 20 °C, 30 °C and 40 °C, are $199 \text{ m}^2 \cdot \text{g}^{-1}$, $254 \text{ m}^2 \cdot \text{g}^{-1}$ and $273 \text{ m}^2 \cdot \text{g}^{-1}$, respectively.

Lastly, despite nylon cords not having the same mechanical response within the same moisture content value, at different atmospheric conditions, proving that is not a crucial condition when comparing different atmospheres, the effect of the moisture content on the nylon cords is still noticeable when comparing the behavior for a fixed temperature. This proves that there is in fact the need to have climate control when employing the cords in either programming simulations or industrial processes and signifies the importance of the psychrometric chart with constant moisture lines for nylon. Both, the static and dynamic tests with the temperature and humidity control performed for rayon and nylon concede information regarding the cords characterization which can be used in the prediction of the tire's rolling resistance.

6 Assessment of the work done

6.1 Objectives Achieved and future work

The main intents of this dissertation were achieved. For PET, was optimized a procedure for step-wise relaxation tests, which was already at work and allowed for a better understanding of the temperature dependency and linear density of different constructions, 630x2, 1100x2, 2200x2 and 3340x2. For rayon the effect of temperature and linear density in its mechanical response was also evaluated, utilizing the same procedure mentioned above which provided comprehension concerning rayon 1840x2 and 2440x2. The effect of its hydrophilicity for static tests and dynamic tests was also assessed due to the fact that rayon is a hygroscopic polymer and thus the control of temperature and relative humidity in its characterization is key. For nylon, the first in-depth study regarding its hydrophilicity was carried out, or in other terms, nylon's ability to uptake water from the environment, which as for rayon, changes the tensile behavior. With this in mind the first psychrometric chart with constant moisture lines for nylon was created and knowledge was collected on how the moisture content affects its tensile response, for two different constructions, 940x2 and 1440x2, when used in static and dynamic tests in order to characterize the polymer.

It is imperative that these textile reinforcements continue to be studied in order to improve the current rolling resistance predictions and for that some suggestions are left. One suggestion is to perform static tests with controlled atmospheres for nylon regarding lower moisture content values, which might simulate the conditions more accurately inside a real functional tire. Another suggestion is to obtain the information on how long it takes for the rayon cords and the nylon cords to achieve an equilibrium with the surrounding atmosphere concerning the water uptake in order to have a better understanding on how time affects the mechanical response of the cords. Lastly, to overcome the water uptake issue, it would be key to integrate superhydrophobic coatings, which would protect the cords from any water adsorption, and perceive how it reacts with the cords and how it would later on adhere onto the rubber matrix.

6.2 Final Assessment

I can only be thankful to have been handed the opportunity to do my master thesis in Continental. The current situation in the world, with the covid-19 pandemic, made this master thesis a great challenge but with the help and support from the team, those challenges were overcome. Throughout the project, it was possible to combine knowledge obtained from the courses within the university in order to perceive and to solve the real problems which kept appearing. It was also really beneficial to have the insight of the daily routine of an international company and how a R&D department functions. Overall the experience had a positive effect in my life not only in a professional or academic level but also in a personal level.

7 References

- [1] - Continental Reifen Deutschland GmbH, “Our History”, Available at <https://www.continental.com/en/company/history> (Accessed February 2020).
- [2] - Continental Reifen Deutschland GmbH, “Employee key figures and structure”, Available at <https://www.continental.com/en/sustainability/employees/employee-key-figures-and-structure-6336> (Accessed February 2020).
- [3] - Continental Reifen Deutschland GmbH, “Facts and Figures”, Available at <https://www.continental-tires.com/specialty/company/aboutcontinental/corporate> (Accessed February 2020).
- [4] - Schulze & Partner, “WETTBEWERB: CONTINENTAL R&D CAMPUS HANNOVER-STÖCKEN”, Available at <https://www.schulze-architektur.com/projekte/2011/wettbewerbe/continental-r-d-campus/index.php> (Accessed February 2020).
- [5] - Bluestar, “The importance of your vehicles tires”, Available at https://www.bluestar.com/get_informed/article/the-importance-of-your-vehicles-tires/ (Accessed February 2020).
- [6] - Continental Reifen Deutschland GmbH, “Products & Innovations”, Available at <https://www.continental.com/en-us/products-innovation/overview/tires> (Accessed February 2020).
- [7] - Continental Reifen Deutschland GmbH, “Tire knowledge”, Available at <https://www.continental-tires.com/car/tire-knowledge/tire-basics/tire-components> (Accessed February 2020).
- [8] - E. T. McDonel, “Tire Cord and Cord-to-Rubber Bonding”, Ch. 1. in The Pneumatic Tire, 2006.
- [9] - The Editors of Encyclopaedia Britannica, “Polyethylene Terephthalate”, Available at <https://www.britannica.com/science/polyethylene-terephthalate> (Accessed February 2020).
- [10] - Polymers Properties Database, “Regenerated Cellulose Fibers (Viscose Rayon)”, Available at <https://polymerdatabase.com/Fibers/Rayon.html> (Accessed February 2020).
- [11] - Brendan Rodgers, Walter Waddell, in The Science and Technology of Rubber (Fourth Edition), 2013.
- [12] - Polymers Properties Database, “Polyamide Fibers (Nylon)”, Available at <https://polymerdatabase.com/Fibers/Nylon.html> (Accessed February 2020).
- [13] - Campo, E. Alfredo, The Complete Part Design Handbook, Hanser, 2006.
- [14] - Quora, “Nylon Fabric”, Available at <https://www.quora.com/Why-are-Nylon-6-Nylon-6-6-and-Nylon-6-10-called-that> (Accessed February 2020).
- [15] - Rajindar Singh, in Membrane Technology and Engineering for Water Purification (Second Edition), 2015.
- [16] - E. T. McDonel, “Tire Cord and Cord-to-Rubber Bonding”, Ch. 3. in The Pneumatic Tire, 2006.

- [17] - The Editors of Encyclopaedia Britannica, “Twisting – Textile Process”, Available at <https://www.britannica.com/technology/twisting> (Accessed May 2020).
- [18] - M.Gomes, “Hysteresis in Tyre Textile Reinforcements”, 2018.
- [19] - 09_chapter3, “Materials, Methods and Characterization”, Available at https://shodhganga.inflibnet.ac.in/bitstream/10603/163630/9/09_chapter%203.pdf (Accessed March 2020).
- [20] - The Engineering Toolbox, “Rolling Resistance”, Available at https://www.engineeringtoolbox.com/rolling-friction-resistance-d_1303.html (Accessed March 2020).
- [21] - Jörnßen Reimpell Prof.Dipl.-Ing., ... Jürgen W. Betzler Prof.Dr.-Ing., in The Automotive Chassis (Second Edition), 2001.
- [22] - H. S. Aldhufairi and O. A. Olatunbosun, “Developments in tyre design for lower rolling resistance: a state of the art review” Proceeding of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering, 2017.
- [23] - Rosato, D.V., “Design Parameters”, Plastics Engineered Product Design, 2003.
- [24] - Sorbothane, “The Difference Between Elastic Materials and Viscoelastic Materials”, Available at <https://www.sorbothane.com/the-difference-between-elastic-materials-and-viscoelastic-materials.aspx> (Accessed at March 2020).
- [25] - Iman Faridmehr, Mohd Hanim Osman, Azlan Bin Adnan, Ali Farokhi Nejad, Reza Hodjati, and Mohammad Amin Azimi, “Correlation between Engineering Stress-Strain and True Stress-Strain Curve” American Journal of Civil Engineering and Architecture, 2014.
- [26] - Campbell, John & Petta, Nicole & Stein, Ori & Liu, Ying & Lu, Y. & Jiang, L. J., Three-dimensional printing and deformation behavior of low-density target structures by two-photon polymerization, 2017.
- [27] - University of Cambridge, “Polymer stress-strain curve”, Available at <https://www.doitpoms.ac.uk/tlplib/polymers/stress-strain.php> (Accessed March 2020).
- [28] - Wikipedia the Free Encyclopedia, “Stress Relaxation”, Available at https://en.wikipedia.org/wiki/Stress_relaxation (Accessed March 2020).
- [29] - University of Cambridge, “Viscoelasticity and hysteresis”, Available at <https://www.doitpoms.ac.uk/tlplib/bioelasticity/viscoelasticity-hysteresis.php> (Accessed March 2020).
- [30] – Perkin Elmer, “Dynamic Mechanical Analysis (DMA) – A Beginner’s Guide”.
- [31] – M. A. Meyers and K. K. Chawla, Mechanical Behavior of Materials, 2nd ed., Cambridge University Press, 2009.
- [32] – Chromatography Today, “ Adsorption, Absorption and Desorption - What's the Difference?”, Available at <https://www.chromatographytoday.com/news/hplc-uhplc/31/breaking-news/adsorption-absorption-and-desorption-what39s-the-difference/31397> (Accessed April 2020).

- [33] - Tech Center, Korea Engineering Plastics Co., Ltd, “Polyamide absorption characteristics”.
- [34] - Jia, Nanying & Kagan, “Mechanical Performance of Polyamides with Influence of Moisture and Temperature – Accurate Evaluation and Better Understanding”, 2001.
- [35] - Trunschke, A., “Surface Area and Pore Size Determination”, Modern Methods in Heterogeneous Catalysis Research, 2013.
- [36] - Zhang, H., “The Permeability Characteristics of Silicone Rubber”, 2006.
- [37] – Silva, L., “Iso-moisture: a new concept to predict moisture content in rayon cords and its influence of tire performance”, 2020.
- [38] - H.J. Butt; K. Graf & M. Kappl, “Adsorption”. Physics and Chemistry of Interfaces, 2nd ed., 2006.
- [39] - A.M. Ribeiro, J.C. Santos, A.E. Rodrigues, “Adsorption equilibrium and kinetic data measurement”.
- [40] - Faculty of Washington, “Adsorption Equilibria”, Available at <http://mimoza.maramara.edu.tr/~zehra.can/ENVE401/3.%20Adsorption%20Equilibria.pdf> (Accessed April 2020).
- [41] - Alothman, Zeid, “A Review: Fundamental Aspects of Silicate Mesoporous Materials”, 2012.
- [42] - Loureiro, J.M., “Adsorption Isotherms”, Apontamentos de Processos de Separação II, 2019.
- [43] - Fredriksson, M., Thybring, E.E., “Scanning or desorption isotherms? Characterising sorption hysteresis of wood”, 2018.
- [44] – Groenewoud, W.M., in Characterisation of Polymers by Thermal Analysis, 2001.
- [45] – Perkin Elmer, “A Beginners Guide Thermogravimetric Analysis”.
- [46] - John W. Rowen and R. 1. Blaine, “Sorption of Nitrogen and Water Vapor on Textile Fibers”, 1947.
- [47] - W. D. Harkins; “Surface chemistry”, AAAS publication No. 21, 55 (Science Press Printing Co. 1943).
- [48] - Neal Leddy, CMA Analytical Workshop, “Surface Area and Porosity”, 2012.
- [49] - G. Fagerlund, “Determination of specific surface by the BET method”, 1973.
- [50] – U. Kuila, M. Prasad, “Specific surface area and pore-size distribution in clays and shales”, 2013.
- [51] – R. Vieweg, A. Müller, “Polyamide. Aufbau, Verarbeitung, Eigenschaften und Anwendung. Herausgeg”, Kunststoff—Handbuch, 1966.
- [52] – The Engineering Toolbox, “Water – Saturation Pressure”, Available at https://www.engineeringtoolbox.com/water-vapor-saturation-pressure-d_599.html (Accessed May 2020).

Annex A - TGA/DSC 2 working range

The TGA/DSC 2 from METTLER TOLEDO has a specific working range in order for the equipment to not achieve the dew point, which could mean damage for the machine. That working range is shown in the Figure 40, shown below.

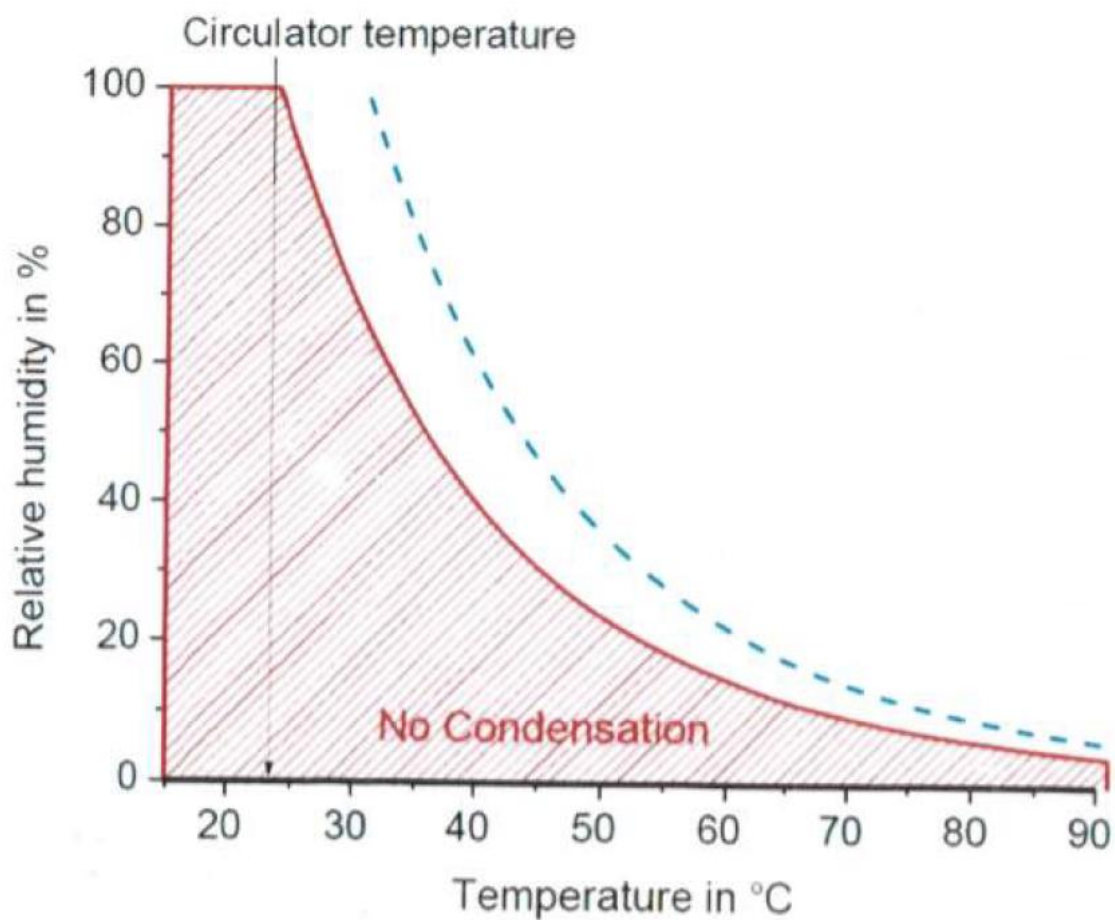


Figure 40 - Working conditions for the thermogravimetical analysis [37]

Annex B - Psychrometric chart for rayon with constant moisture lines

There was one internal study at Continental done by Livia Silva in which it was plotted a two-dimensional (2D) and a three-dimensional (3D) representation of the psychrometric chart for rayon with constant moisture lines. It was intended for these charts to correlate the temperature and the relative humidity with the moisture uptake by the nylon cords. These charts for rayon were one of the great motivations to also perform the same for nylon. In Figure 41 and 42 it can be seen both of those representations for rayon.

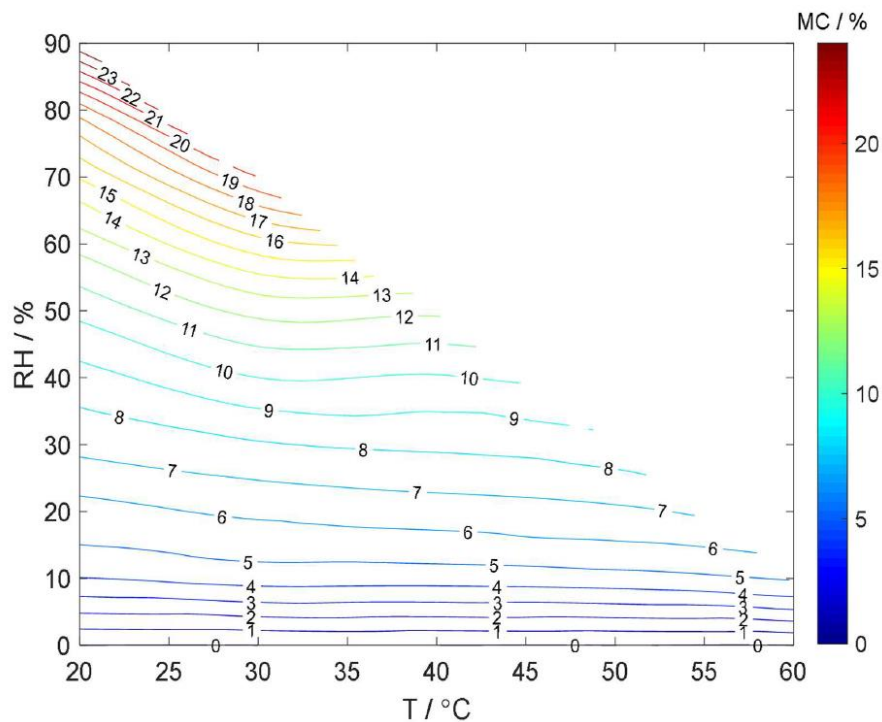


Figure 41 - Psychrometric chart with constant moisture lines for rayon cords [37]

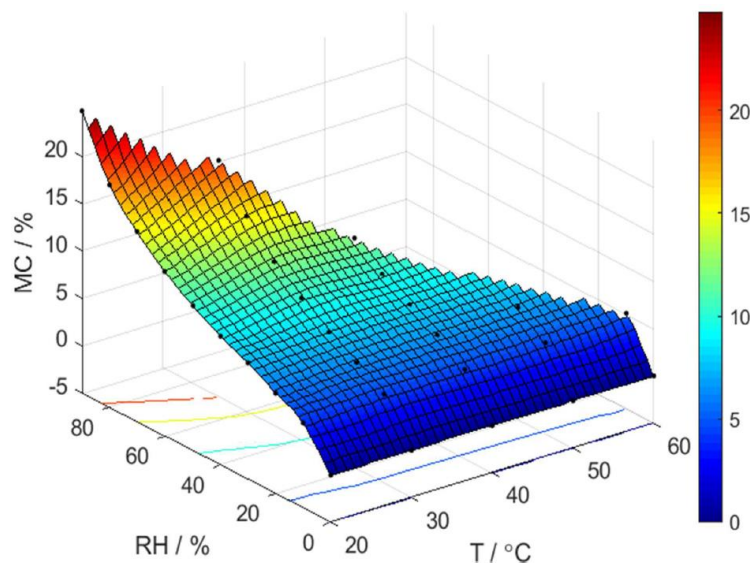


Figure 42 - Three-dimensional (3D) representation of the moisture content behavior for rayon [37]

Annex C - Water vapor saturation pressure

As seen in Subsection 4.1.1. the environment conditions, more concretely, the relative humidity inside the Zwick / Roell chamber changes with the changing in temperature, which then affects gravely the rayon cords. Therefore, that behavior was predicted with the use of know values of water saturation vapor pressure for different temperatures. Those values are shown in table 13.

Table 13 - Water saturation values [52]

Temperature	Water saturation pressure		
[°C]	[kPa], [100*bar]	[atm]	[psi]
0.01	0.61165	0.0060	0.088712
2	0.70599	0.0070	0.10240
4	0.81355	0.0080	0.11800
10	1.2282	0.0121	0.17814
14	1.5990	0.0158	0.23192
18	2.0647	0.0204	0.29946
20	2.3393	0.0231	0.33929
25	3.1699	0.0313	0.45976
30	4.2470	0.0419	0.61598
34	5.3251	0.0526	0.77234
40	7.3849	0.0729	1.0711
44	9.1124	0.0899	1.3216
50	12.352	0.122	1.7915
54	15.022	0.148	2.1788
60	19.946	0.197	2.8929
70	31.201	0.308	4.5253
80	47.414	0.468	6.8768
90	70.182	0.693	10.179
96	87.771	0.866	12.730
100	101.42	1.001	14.710

The relative humidity for a determined temperature can be calculated using the actual vapor pressure, P , and the saturated vapor pressure, P_s , which is dependent of the temperature. Thus, it is calculated using the following equation. [37]

$$Relative\ Humidity\ (\%) = \frac{P}{P_s} \times 100 \quad (14)$$

Annex D - Rayon's water adsorption isotherms

In order to determine the specific surface area of rayon, as was done for nylon, the adsorption isotherms for rayon, which can be seen in Figure 43, were needed as well as the data through which the following representation was obtained.

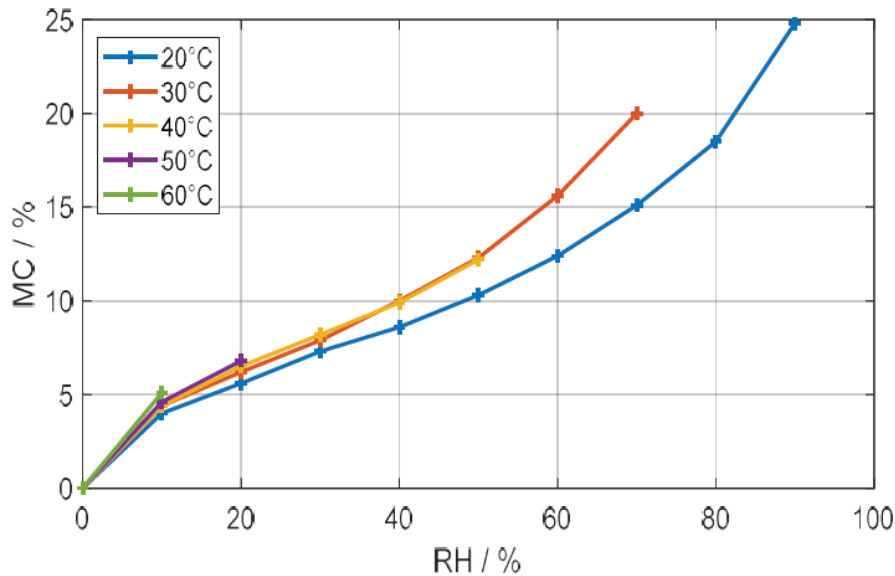


Figure 43 - Rayon's water adsorption isotherms [37]

As it can be seen from Figure 43, the shape of adsorption isotherms resembles the IUPAC type II isotherm or the BET isotherm. For that matter, it can be used to determine rayon's BET specific surface area.

Annex E - Effect of the moisture content on glass-transition temperature for polyamides

The glass-transition temperature of polyamides is greatly affected by the moisture content, and that can be seen from Figure 44. [51]

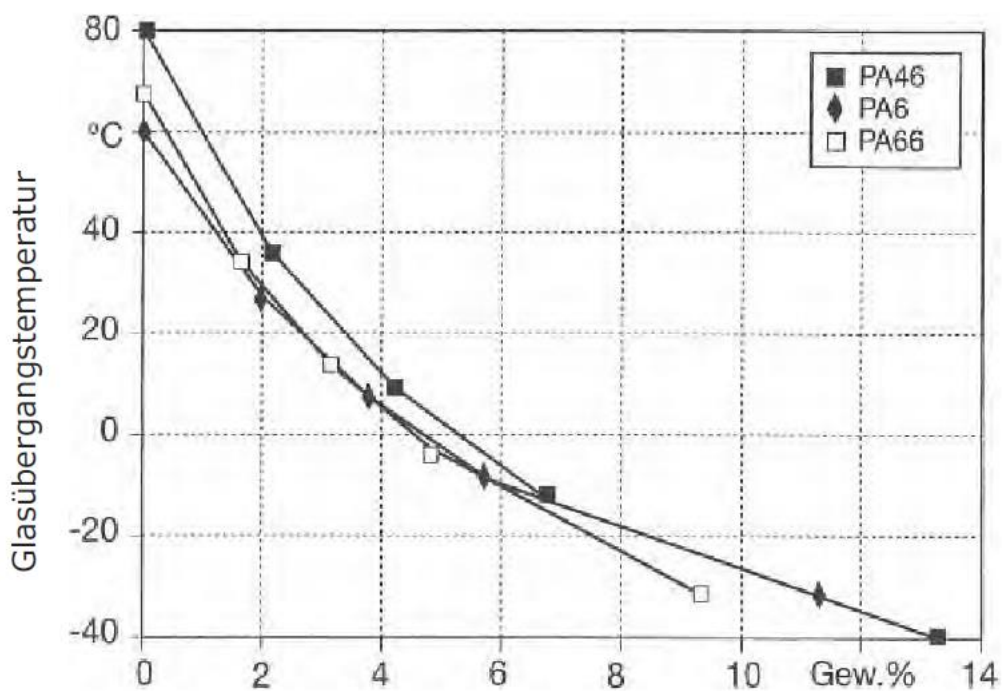


Figure 44 – Glass-transition temperature as a function of water content of polyamide 46, 6 and 66 [51]

Appendix A - Tensile-strength test results

The temperature and linear density affect the tensile-strength as shown in subsection 4.1.1., and the results of the tests performed for different temperatures are shown in Figures 45 and 47 for PET and in Figures 46 and 48 for rayon. In section A3., the results with different clamping systems for PET at different equipments are shown.

A1. Force-strain curves

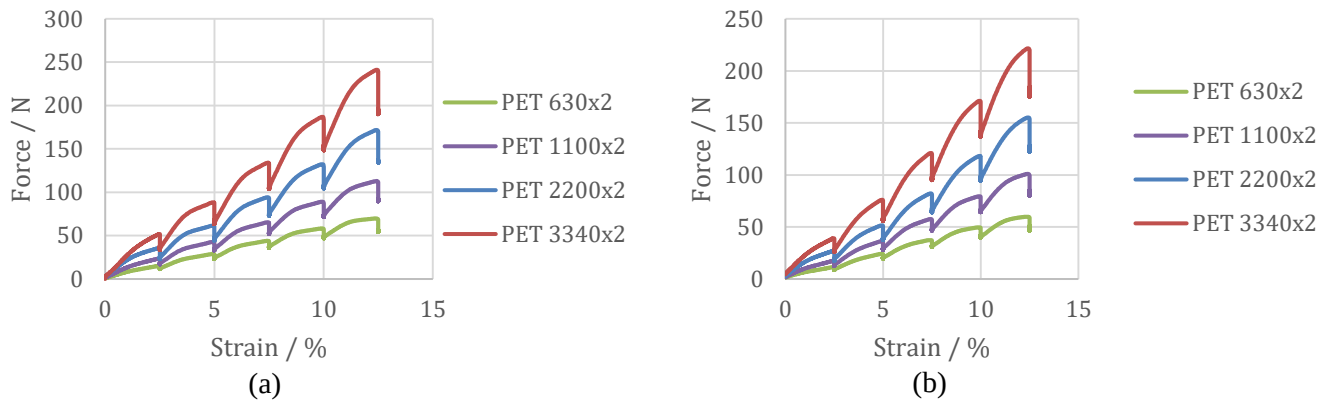


Figure 45 - Force-strain curves for PET at 80 °C (a) and at 110 °C (b)

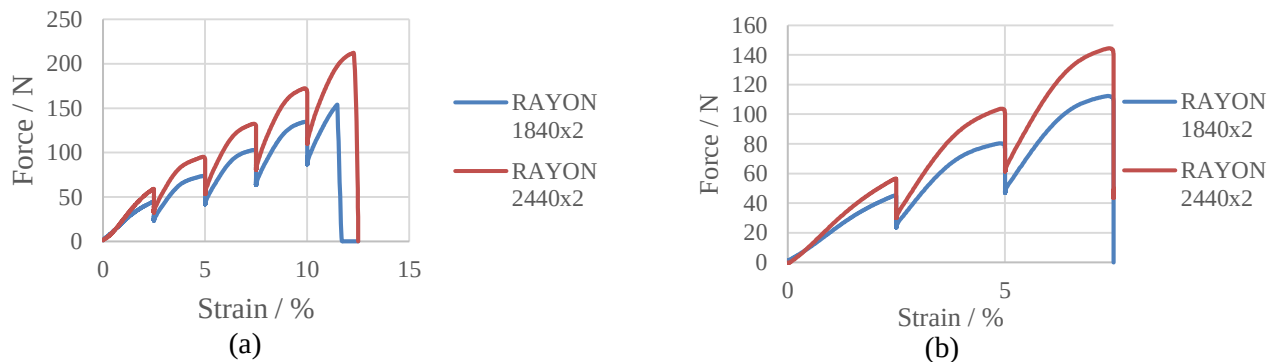
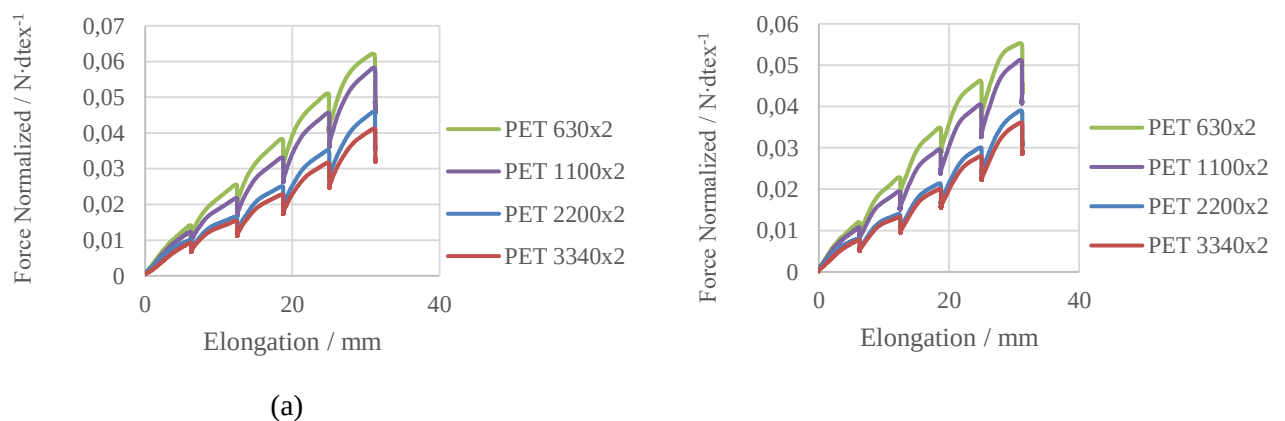


Figure 46 - Force-strain curves for rayon at 40 °C (a) and at 60 °C (b)

A2. Force normalized-elongation curves



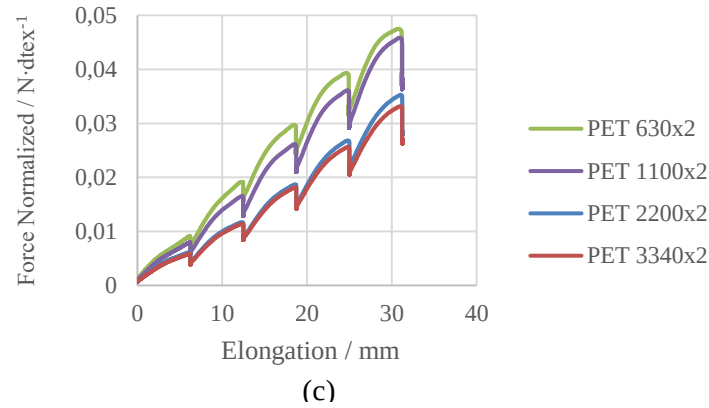


Figure 47 - Force normalized - elongation curves for PET at 40 °C (a), at 80 °C (b) and at 110 °C (c)

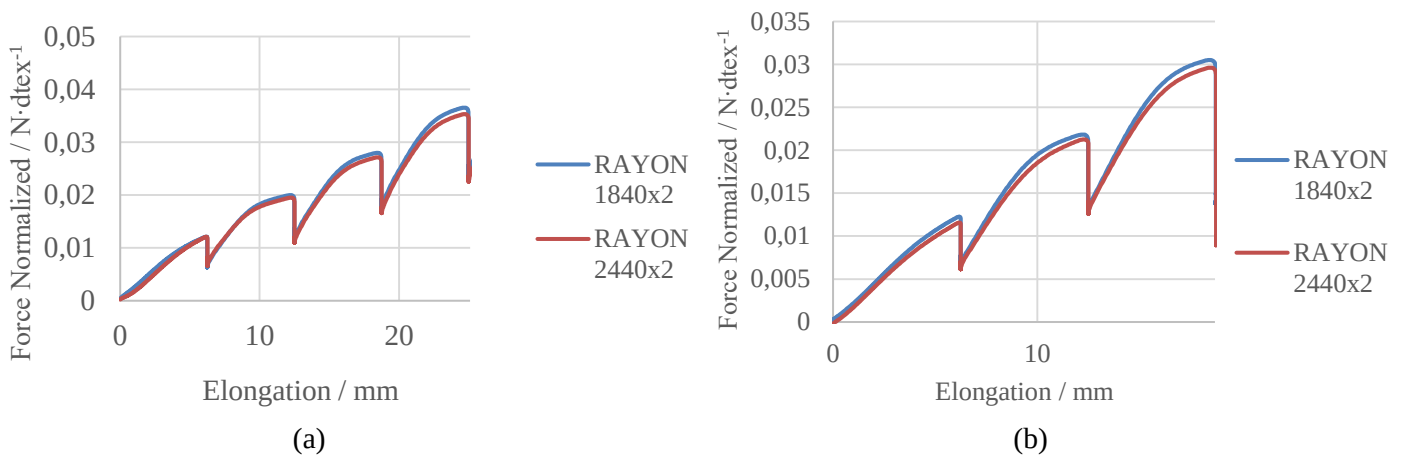


Figure 48 - Force normalized - elongation curves for rayon at 40 °C (a) and 60 °C (b)

A3. Force-strain curves with different clamping systems for the Zwick / Roell and MTS-Acumen™ 3

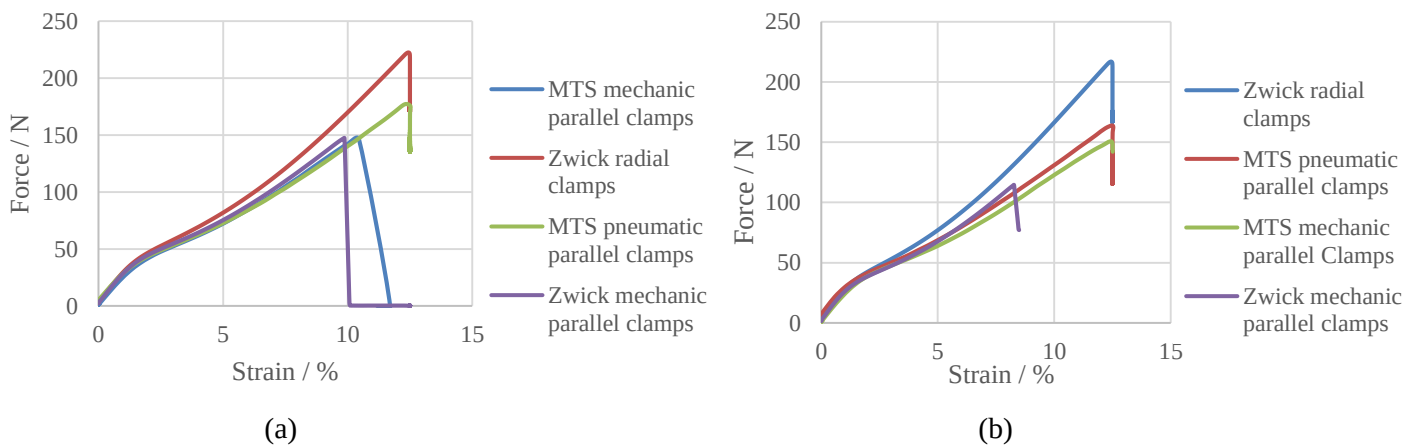


Figure 49 - Force-strain curves for PET at 23 °C and 55 % of RH (a) and at 40 °C and 21 % of RH (b)

Appendix B - Nylon's water adsorption isotherms

In order to have a better understanding of Subsection 4.2.3 and 4.3, the water adsorption isotherms for nylon, which are all adjoined in Figure 28, are shown in the in Figure 50 (a), (b), (c) and (d), for 23 °C, 30 °C, 40 °C and 50 °C, respectively.

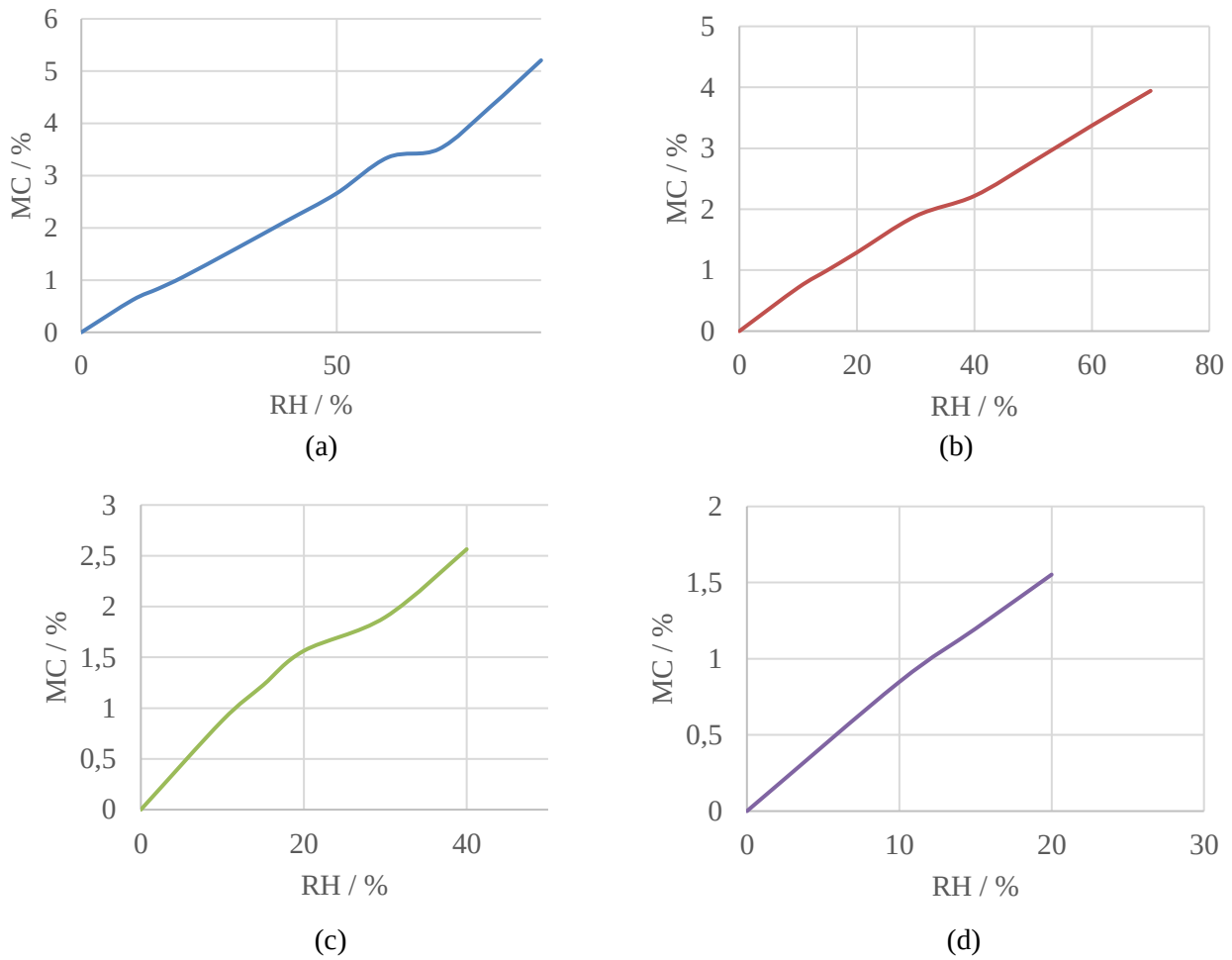


Figure 50 - Nylon's water adsorption isotherm at 23 °C (a), 30 °C (b), 40 °C (c) and at 50 °C (d)

Appendix C - Dynamic Mechanical Analysis (DMA)

In this appendix the remainder of the results from the dynamic mechanical analysis under controlled conditions are shown for the different polymers utilized. The results shown from Figure 51 to 58 are mentioned in Subsection 4.4.2

C1. Rayon 1840x2

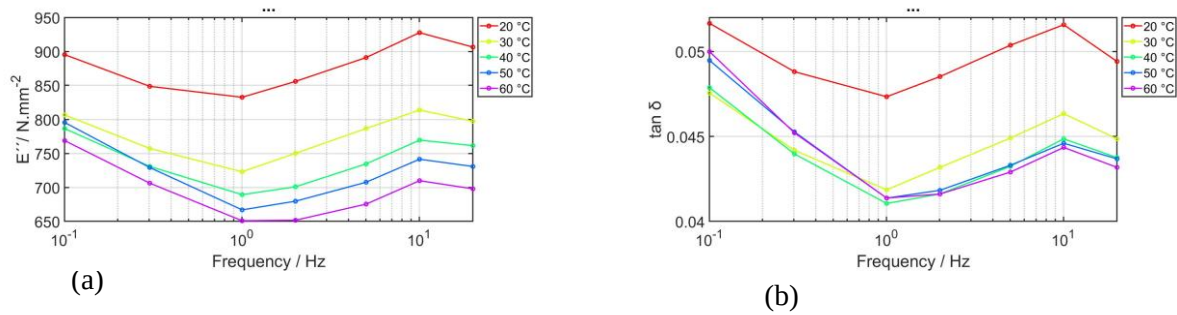


Figure 51 - Viscous modulus (a) and damping coefficient (b) of rayon 1840x2 over frequency

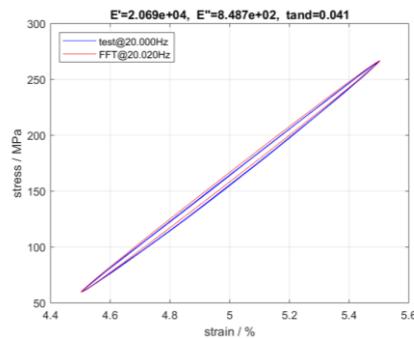


Figure 52 - Example of a hysteresis loop for rayon 1840x2 from raw test data and from FFT evaluation

C2. Rayon 2440x2

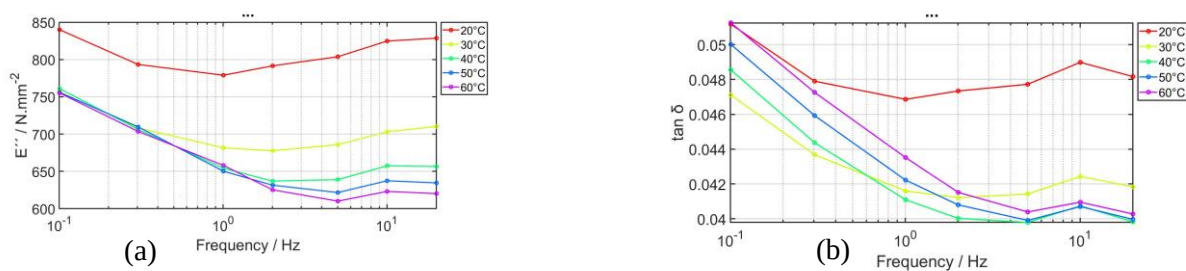


Figure 53 - Viscous modulus (a) and damping coefficient (b) of rayon 2440x2 over frequency

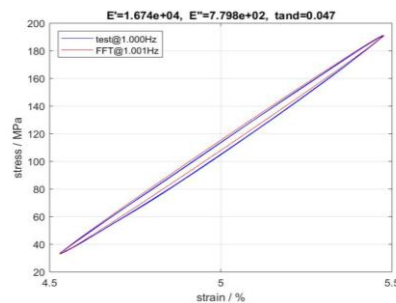


Figure 54 - Example of hysteresis loop for rayon 2440x2 from raw test data and from FFT

C3. Nylon 940x2

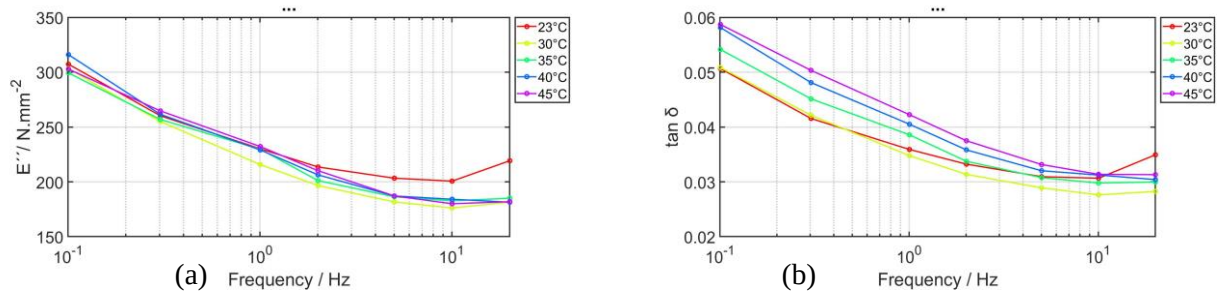


Figure 55 – Viscous modulus (a) and damping coefficient (b) of nylon 940x2 over frequency

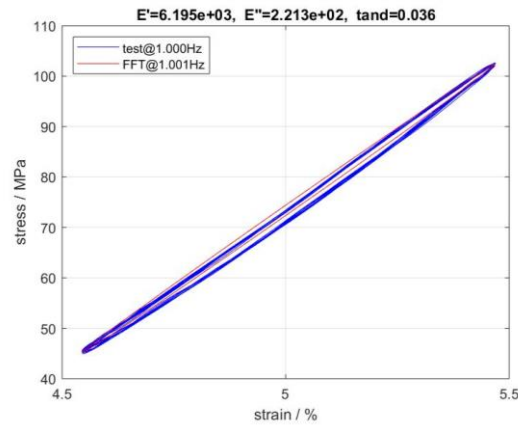


Figure 56 -Example of hysteresis loop for nylon 940x2 from raw test data and from FFT evaluation

C4. Nylon 1440x2

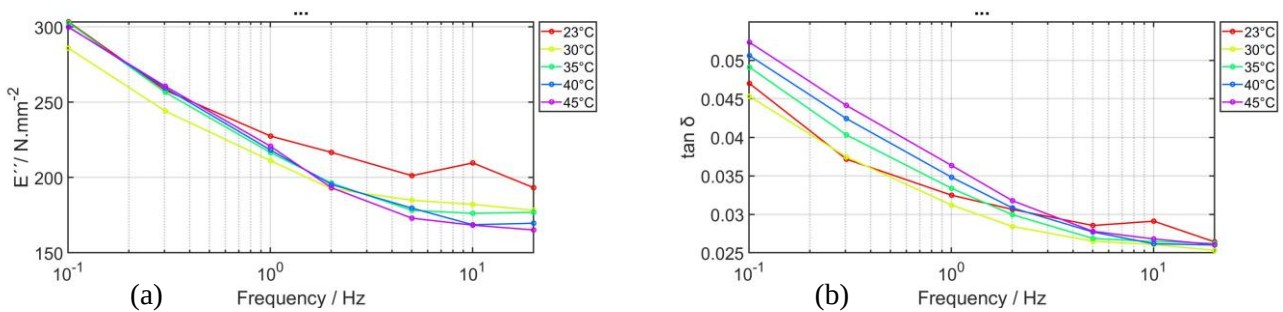


Figure 57 - Viscous modulus (a) and damping coefficient (b) of nylon 1440x2 over frequency

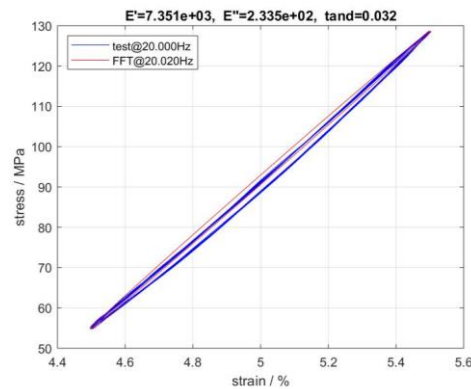


Figure 58 – Example of hysteresis loop for nylon 1440x2 from raw test data and from FFT evaluation

Appendix D - Types of clamps

Throughout this study for the Zwick / Roell and the MTS-Acumen™ 3, three different clamping systems were used, these systems can be seen in Figure 59.

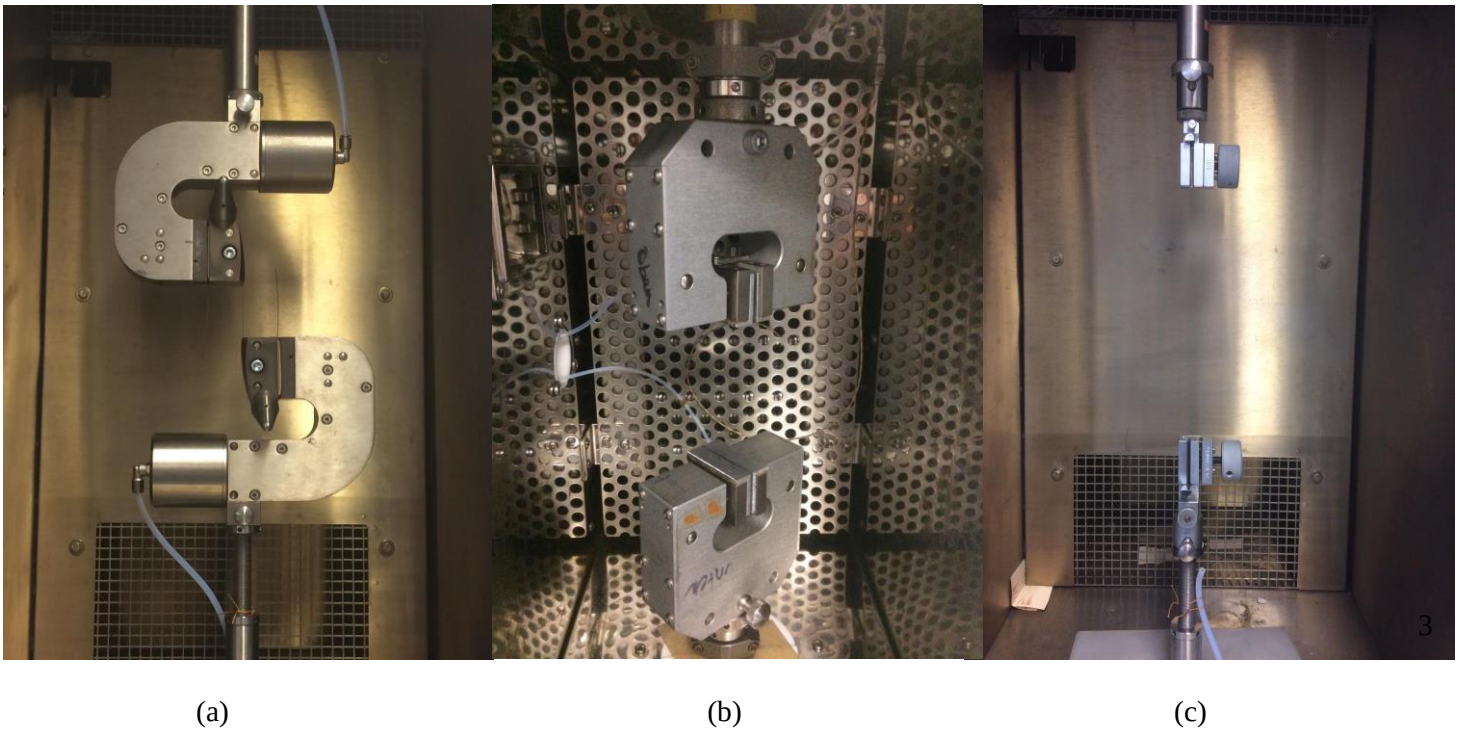


Figure 59 - Clamping systems: Radial (a), pneumatic parallel (b), mechanic parallel (c)

Appendix E - Brunauer-Emmett-Teller equations

In section the values of the retrieved from the BET equations are presented. They can be seen in table 14 for nylon and rayon.

These values were fundamental to the determination of the surface total areas and specific surface areas or nylon and rayon.

Table 14 - Brunauer-Emmett-Teller equation values

	Nylon			Rayon		
	23 °C	30 °C	40 °C	20 °C	30 °C	40 °C
Slope	1.85	1.83	1.66	0.511	0.383	0.340
Y-interception	0.371	0.293	0.221	0.00660	0.0224	0.0372
R²	0.993	0.910	0.977	0.979	0.965	0.999
W_m / mg	0.451	0.471	0.532	1.93	2.47	2.65
C	5.98	7.24	8.50	78.3	18.1	10.2