

**MECHANICAL CHARACTERIZATION OF POLYPROPYLENE:
INDENTATION, TENSILE AND FATIGUE ANALYSIS**

KAROLINE SALES DE OLIVEIRA GUSMÃO

**DISSERTAÇÃO DE MESTRADO EM CIÊNCIAS MECÂNICAS
DEPARTAMENTO DE ENGENHARIA MECÂNICA**

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Resumo

Este estudo tem como objetivo investigar as propriedades mecânicas do polipropileno (PP) em diversas condições de carga. O PP é escolhido devido à sua estabilidade e boa resistência mecânica, embora o entendimento atual do seu comportamento mecânico ainda seja limitado. O estudo inclui testes mecânicos, incluindo carga monotônica e cíclica em tensão, bem como testes de indentação para análise de compressão, a fim de avaliar propriedades importantes, como módulo de elasticidade, limite de resistência à tração, resistência à fadiga, entre outras. Além disso, são investigados os efeitos da temperatura e da taxa de deslocamento.

Testes de dureza foram conduzidos em uma faixa de cargas de 100 N a 400 N, utilizando um indentador esférico de 5 mm de diâmetro, e de 500 N a 2 kN, com um indentador esférico de 15mm de diâmetro, para avaliar as propriedades elásticas do material sob compressão. É observada uma tensão de escoamento de aproximadamente 40 MPa nos ensaios de compressão e um comportamento dependente da taxa de carregamento nos ensaios de tração. Esses resultados destacam a importância de considerar as taxas de carregamento ao avaliar o desempenho e o comportamento do material. Além disso, nos ensaios de tração, a tensão de escoamento, σ_y , e o limite de resistência a tração, σ_u e o módulo de elasticidade, E, observados são 21.03 ± 0.50 MPa e 33.7 ± 0.8 MPa, 2094.0 ± 0.5 MPa para 2 mm/min e 2060.0 ± 0.5 MPa para 6 mm/min respectivamente, por meio de ensaios monotônicos em diferentes taxas de deformação (2 mm/min e 6 mm/min), revelando a dependência em relação a taxa de deslocamento para o módulo de elasticidade e para o limite de resistência a tração.

Ao realizar testes de fadiga em diferentes temperaturas (24 ± 2 °C e 30 ± 2 °C a 1 Hz), foi observado, um aumento da vida em fadiga com a diminuição da temperatura. Sendo também observado proximidade em números de ciclos até a fratura entre os valores extremos de carregamento utilizados, em diferentes temperaturas, mostrando que a vida em fadiga se assemelhou para as cargas de 13,68 MPa a 30 ± 2 °C e 16,29 MPa a 24 ± 2 °C, sendo de 300,309 e 468,183 ciclos, respectivamente.

Abstract

This study aims to investigate the mechanical properties of polypropylene (PP) under different load conditions. PP is chosen due to its stability and good mechanical strength, although the current understanding of its mechanical behavior is still limited. The study includes mechanical tests, including monotonic and cyclic tension loads, as well as indentation tests for compression analysis, to evaluate important properties such as elastic modulus, tensile stress, and fatigue strength, among others. Additionally, the effects of temperature and loading rate are investigated.

Hardness tests were conducted in a load range from 100 N to 400 N using a spherical indenter with a diameter of 5 mm, and from 500 N to 2 kN using a spherical indenter with a diameter of 15 mm to evaluate the elastic properties of the material under compression. A yield stress of approximately 40 MPa is observed in compression tests, and a rate-dependent behavior is observed in tension tests. These results highlight the importance of considering loading rates when assessing the performance and behavior of the material. Furthermore, in the tension tests, the yield stress, σ_y , the ultimate tensile stress, σ_u , and the elastic modulus, E , are found to be 21.03 ± 0.50 MPa, 33.7 ± 0.8 MPa, and 2094.0 ± 0.5 MPa at a deformation rate of 2 mm/min, and 2060.0 ± 0.5 MPa at a deformation rate of 6 mm/min, respectively. This reveals the dependence on the displacement rate for the elastic modulus and the ultimate tensile stress.

When conducting fatigue tests at different temperatures (24 ± 2 °C and 30 ± 2 °C at 1 Hz), an increase in fatigue life is observed with decreasing temperature. It is also observed that the number of cycles until the fracture is close for extreme loading values used at different temperatures, showing that the fatigue life was similar for loads of 13.68 MPa at 30 ± 2 °C and 16.29 MPa at 24 ± 2 °C, with 300,309 and 468,183 cycles, respectively.

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LIST OF SYMBOLS

τ_{max}	Principal shear stress
ε	Strain
ε_t	True Strain
E^*	Combined Elastic modulus
F	Applied load
L_0	Original length
r	Radius of the measured pressure
R' and R''	Principal curvature radii of the surfaces at the origin of the coordinate system
R_e	Equivalent radius
T_g	Glass transition temperature
z	Position from the point of contact along the z-axis
σ	Stress
σ_3, σ_z	Normal stresses
σ_t	True stress
σ_u	Ultimate tensile stress
σ_y	Yield stress
δ	Displacement of each point on the surface
p_m	Mean contact pressure
a	Contact area radius for contact between revolution solids
h	Distance between the surfaces
A	Cross-sectional Area

ASTM	American Society for Testing and Materials
D	Diameter of indenter
d	Diameter of indentation
DSPI	Digital Speckle Pattern Interferometry
E	Modulus of elasticity or Young's Modulus
FTIR	Fourier-Transform Infrared Spectroscopy
G	Gauge Length
HDPE	High Density Polyethylene
HWB	Brinell Hardness
ISO	International Organization for Standardization
J	Joule
k	Contact Stiffness
KBr	Potassium Bromide
kgf	kilograms-force
L	Instantaneous Length
LDPE	Low Density Polyethylene
LO	Total length
MWCNT	Multi-walled carbon nanotube
N	Newton
nu	Poisson ratio
Pa	Pascal
PC	Polycarbonate
PE	Polyethylene
PEEK	Polyether ether ketone
PMMA	Polymethyl Methacrylate
POM	Polyoxymethylene
PP	Polypropylene

PS	Polystyrene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
SI	International System of Units
T	Gauge Thickness
W	Gauge Width

Chapter 1

Introduction

This chapter is organized into three sections, which provide a concise contextualization of the topic under study and motivations related to the research gap. Additionally, it includes a description of the objectives and a preview of the upcoming chapters.

1.1 Motivation and the State-of-the-Art

Thermoplastic polymers have gained significant attention in recent years due to their unique properties and versatility for various applications [1]. A thermoplastic polymer can be melted and remolded multiple times without any significant degradation in its properties. This feature makes them an ideal choice for various industrial applications, including packaging, automotive, medical, and civil engineering [2].

Furthermore, the use of thermoplastic polymers in composites has also been studied extensively [2–4]. The addition of thermoplastic polymers to composite materials can enhance their mechanical properties, reduce their weight and improve their durability. This has led to the development of new composite materials for various applications, including aerospace and automotive industries.

The viscoelasticity of a thermoplastic polymer is defined as the phenomenon whereby there is a viscous behavior as a liquid superimposed on an elastic behavior as a solid [5]. The elastic fraction of deformation occurs due to variations in the angle and distance of bonds between atoms, both in the main chain and in the side groups. The plastic fraction occurs due to friction between the main polymeric chains and side groups [5].

Polypropylene (PP) is a polymer widely known and used for many applications. It shows interesting mechanical properties in novel areas where it has been introduced. Other than that, polypropylene is a thermoplastic, semi-crystalline polymer commonly used due to its high specific performance, low cost and easy recycling process [3, 6, 7].

Nevertheless, its widespread use has been restricted due to an incomplete understanding

of their mechanical behavior [1]. The mechanical behavior or the performance is of key importance for many engineering applications [3]. The performance of most polymers is often affected by crystallinity, molecular weight, environmental conditions (temperature and humidity), and loading conditions (strain rate for monotonic loading or hold time and load frequency for cyclic loading) [8].

Therefore, for one to have a broad understanding of the mechanical behavior of any polymeric material, thorough mechanical testing, both at monotonic and cyclic loading conditions, in tensile and compression modes, is required. To study the mechanical properties, it is important to consider some relevant properties, such as Young's Modulus, Ultimate Tensile Stress, Hardness, Shear, Poisson's ratio, Yield stress and Fatigue life.

To better understand the behavior of these materials in compression, in this work, the behaviors of this thermoplastic polymer were analyzed with the aid of the indentation test, this test commonly analyses the hardness of material in different types of scales, it is a common technique used to evaluate the mechanical properties of polymers. In this method, a small indenter is pressed into the surface of the material, and the resulting deformation is measured [9]. Indentation tests provide important information on the mechanical behavior of polymers, including their hardness, elastic modulus and viscoelastic properties [10].

Previous studies have focused on the development and application of indentation testing for polymers. For example, researchers have used nanoindentation to study the mechanical behavior of thin polymer films and coatings [11, 12]. This technique allows for precise measurements of mechanical properties at small scales and can provide valuable insights into the structure-property relationships of polymers [13].

Studies investigated using indentation testing and phenomenological modeling, the viscoelastic behavior of PP/multi-walled carbon nanotube (MWCNT) nanocomposites was examined [4]. Conclusions of the experiment suggested that the micro-mechanical characteristics of PP/MWCNT nanocomposites are improved by the incorporation of nanotubes into the polypropylene. With increasing MWCNT loading, indentation hardness and elastic modulus both considerably increased [4].

The coefficient of proportionality between stress and strain is the Modulus of Elasticity or Young's modulus. It is related to the energy required to deform the angles and the distance and bonds between the atoms of the polymeric chain [9]. In addition to the influence of temperature, the loading rate also has a major influence on tensile tests on polymers. The lower the applied loading rate, the greater the observed plasticity due to the time the polymer chains have to organize themselves, and this is also related to viscosity [5].

A relatively easy way to investigate the properties of polymers is through interferometry techniques. Young's Modulus and Poisson's Ratio of Polypropylene using Digital Speckle Pattern Interferometry (DSPI) is reported in [14]. Furthermore, as the degree of crystallinity grows, the modulus of elasticity, yield strength and hardness increase, this effect can be seen by comparing the stress-strain behavior of Polyethylene (PE) of different densities [10]. As

for Polypropylene, in the same way as for PE, the modulus of elasticity increases linearly with the increase in density and crystallinity of the material. Therefore, any variation in the procedure for its preparation and processing or post-treatment, such as slow cooling or subsequent heat treatment, which provides an increase in density and crystallinity, will also increase the modulus of elasticity and rigidity [8, 11, 12].

Li, et al. [15] investigated the mechanical properties of isostatic polypropylene with different crystallinities at room and elevated temperatures. In this study, the results showed that Young's modulus of polypropylene was sensitive to the service temperature and the crystallinity. There is a decrease in the first one with the increase in temperature and a decrease in crystallinity [15].

Some studies have been using polypropylene reinforced with concrete matrices or as the matrix itself [3, 16, 17], but the study of the mechanical properties of pure polypropylene has not been so present in literature. The use of continuous fiber-reinforced polymer matrix composites in structural applications has increased due to their important mechanical characteristics. However, in reliable applications of composite materials in the structural element, it is difficult to assess its service life, additionally, it is important to know the mechanical characteristics of the pure material, whether it is used as reinforcement or as a matrix [1, 3, 7, 18].

Composite materials have significant fatigue strength. However, although the failure of metallic materials can be studied from the perspective of start and growth for cracks, especially micro-cracks, composite materials show more complex damage mechanisms. Several destruction mechanisms started, developed and interacted to modify the state of the material, for example, geometry, load and environmental conditions. The failure mechanism of composite materials depends on the characteristic fiber and matrix layer, interface strength and load condition. These mechanisms include fiber breakage, fiber-matrix debonding, matrix cracking, and stratified [3, 7, 16].

Tesfay et al. [19] studied the mechanical properties of polypropylene reinforced with sisal fiber using a tensile test which was made at the strain rate of 10 mm per minute and 50 mm gauge length was maintained and can be seen that PP composites exhibit ultimate tensile stress and elastic modulus improvement compared to pure PP. Bourmaud and Baley [20] proposed that, although PP/hemp and PP/sisal composites provided an important strength enhancement compared with pure PP, recycling will not cause any significant change in ultimate tensile stress's value of PP/hemp composites, but there is a significant PP/sisal composite material decreases after 7 cycles. Similarly, Rowell et al. [21] studied the recyclability of polypropylene using jute-reinforced composite materials and observed that tensile and bending strength are not significantly affected in nine reprocessing attempts.

It is also of major importance to consider another characteristic of this behavior: the viscoelastic response. Polymers are touchy to weak breaks coming about because of cyclic stacking. Also, the bending nature of the plastics increases during their wear because of the hotness consumed by them during testing, particularly at high frequencies [7].

Besides evaluating a polymer's mechanical properties, understanding how it fails under different loading conditions is also of extreme importance. For instance, fatigue, which is a failure mechanism related to cyclic loading, is caused by the degradation of a material due to loss of strain energy, development of cracks, and eventually fracture [22, 23]. A detailed study of PP fatigue behavior is yet to be found. Indeed, a few fatigue studies using PP either as a matrix or reinforcement have been published [3, 16]. However, the pure material is not fully addressed. Some researchers have been studying the fatigue behavior for a range of thermoplastic polymers or composite materials, as was reported in [24]. However, the influence of temperature and loading frequency is not considered by the authors.

The fatigue behavior of layered HDPE used in vehicle gasoline tanks was examined in [17]. Between 50 °C and 80 °C, tension-tension loads were used for the fatigue testing. The chosen R ratios varied, and the test frequencies ranged from 0.01 to 0.1 Hz. It was shown that an increase in frequency induces heating, which, in turn, causes failure. Also, as the ambient temperature rises, the fatigue life decreases dramatically. Additionally, as frequency increased, the fatigue life decreased under cyclic load. It concluded as a result that the maximum stress effectively determines the fatigue life and that the influence on the minimum stress is low as long as the stress ratio is less than 0.8.

Amjadi et al [25] investigated creep and fatigue behaviors of HDPE under different temperatures and loading conditions, and in addition, it was observed that manufacturing techniques and it was observed that the self-heating can significantly affect the fatigue life of the thermoplastic polymer. In conjunction with that, the injection molding processing technique resulted in significantly higher fatigue life than either blow molding or compression molding processing techniques, thought to be due to the higher crystallinity and molecular orientation induced in injection molding. Furthermore, the fatigue strength significantly reduces with increasing temperature due to higher micro-structural mobility in both amorphous and crystalline phases.

In this work, to understand the mechanical behavior of pure polypropylene, an attempt was made to carry out an analysis that permeates from the fundamentals of contact mechanics and the resistance of materials, analyzing the behavior of the material in terms of traction, compression and fatigue. Tests are carried out using standard specimens carefully controlled for dimension and surface finish. Monotonic tests are executed at two strain rates (2 mm/min and 6 mm/min) and their results are used for the identification of the material's ultimate tensile stress. Preliminary tests were used for the proposition of a fatigue test matrix for the evaluation of the PP life curve [26]. The fatigue tests were performed at two different temperatures and a low frequency was adopted to prevent thermal effects.

1.2 Objectives

This work aims to bring a significant contribution to the literature regarding the mechanical behavior of pure polypropylene. Due to the fact that this subject in these aspects has been little addressed and that it is hard to be found given the great use of this material in the packaging industry. For this, some points will be addressed:

- As for the characterization of the specimens, analyzing spectra obtained in Fourier-Transform Infrared Spectroscopy- FTIR analysis, to identify and compare the obtained polypropylene spectra with those available in the literature.
- Compression behavior, analyzing the indentation test results and the load versus depth of the mark.
- Tensile behavior, analyzing the elastic and plastic properties of the material when subjected to monotonic axial loading, through the stress versus strain ratio obtained in the tensile tests in two displacements rates, 2 mm/min and 6 mm/min.
- Fatigue behavior, observed at a load ratio $R = 0.1$, referring to a variation of 10% in a nominal engineering load, despite being the most common loading condition used in fatigue tests, results for it are not available in the literature. Moreover, two temperatures are analyzed (24°C and 30°C).

1.3 Outline

This work consists of six chapters described below:

Chapter 2 - In this section, a comprehensive analysis of the pertinent theories related to this study is provided. Given their importance for the contextualization and complete understanding of the theme.

Chapter 3 - This section describes the materials and methodologies employed to achieve the objectives of this work. Specifically, it describes the mechanical tests performed to obtain crucial data, along with the tests performed for each specimen and the microscopy analysis when indentations were performed.

Chapter 4 - A full presentation of experimental test results is provided in this section, accompanied by discussions based on data analysis.

Chapter 5 - The final segment of this paper presents a concise summary of the main conclusions derived from the data analysis in the previous section. In addition, recommendations for future studies on the same subject are provided.

Chapter 2

Concepts

This chapter provides an overview of relevant concepts for the present study. It covers contact mechanics, including Hertzian formulae and the nonlinear behavior of solids. Mechanical compression concepts, indentation testing, and hardness in polymeric materials are also reviewed. Considerations on tensile tests and fatigue testing under tensile loading are discussed. The chapter then focuses on thermoplastic polymers, particularly polypropylene, the material studied in this work. Details about the polymer used are provided. Finally, the chapter concludes with a brief review of characterizing polymeric materials using Fourier transform infrared (FTIR).

2.1 Contact Mechanics

This area of study is crucial in understanding physical phenomena related to adhesion, wear, friction, plastic deformation, fatigue, viscoelasticity and lubrication [27]. The study of contact mechanics helps in predicting and analyzing the behavior of materials when they interact or come into contact with each other, optimize manufacturing processes, develop novel materials, improve the performance and durability of mechanical systems. Contact mechanics investigates the response and behavior of materials under the influence of external forces during contact. It examines how materials deform, interact and transfer loads when they come into contact. This includes studying the mechanical properties, such as elasticity, plasticity and viscoelasticity, of the materials involved. When materials come into contact, the interaction takes place at the surface level. Surface roughness, topography and chemical composition make a significant role in determining the nature and force of contact between materials. Surface properties influence adhesion, friction and wear behavior, thus affecting the overall performance and reliability of contact systems.

One essential aspect of the mechanics of contact is the analysis of the contact area, contact pressure, and pressure distribution along the contact surface. The contact area is the region where the two bodies come into contact, while the contact pressure is the normal

force per unit area in that contact region. The pressure distribution along the contact surface is impacted by the geometry of the bodies and the properties of the materials in contact. Furthermore, within the mechanics of contact, there are conformal and non-conformal contact patterns. In conformal contact, the contact surfaces fit perfectly with one another, resulting in a well-defined and uniform contact area. Bearings and gears are examples of such contacts. In contrast, non-conformal contacts do not fit perfectly and they result in an irregular contact area. Welded joints and interfaces between mechanical components are instances of non-conformal contacts.

Non-conformal contact patterns often cause a non-uniform pressure distribution in the contact area, resulting in issues like fatigue, wear and fracture. Analyzing non-conformal contact patterns is complex and requires taking into account several factors like bodies' geometry, material properties and applied forces. There are several geometries used but the most common are pyramidal or spherical, the geometry chosen in this work is spherical and will be addressed in detail.

2.1.1 Contact between solids and Hertz Theory

The Sphere-to-Flat Hertzian solution is an important aspect of the mechanics of contact in materials science and engineering. It is a theoretical model that describes the contact between a sphere and a flat surface and is used to calculate the contact pressure and the size of the contact area. It is based on the assumptions of elastic deformation and a linear relationship between the contact force and the deformation.

It has important applications in many areas of engineering, such as the design of bearings, gears, and other mechanical components. By calculating the contact pressure and the size of the contact area, engineers can predict the wear and fatigue of these components and design them to withstand the required loads. It is also useful in the study of biological systems, such as the contact between teeth and food, or the contact between bones in joints.

This solution is derived from the Hertzian formulae, which describes the contact between two elastic bodies of any shape. The Hertzian solution is a powerful theoretical tool that can be used to study a wide range of contact problems, including the contact between two spheres, the contact between a cylinder and a flat surface, and the contact between a sphere and an ellipsoid.

Based on a set of differential equations that describe the deformation of the elastic bodies under contact, these equations can be solved analytically for the case of a sphere and a flat surface, and the resulting solution provides an accurate description of the contact behavior of these two bodies. The solution is characterized by several parameters, including the contact pressure, the size of the contact area, and the maximum deformation.

Considering the contact between two non-conforming surfaces, as the surfaces approach each other, an area of contact starts to form. Initially, it appears as a point, but as the contact

progresses, it takes on an elliptical shape [27]. In other words, can be assumed that the separation distance between the surfaces is represented by h and the principal curvature radii of the surfaces at the origin of the coordinate system are denoted by R' and R'' . These radii correspond to the maximum and minimum values of the curvature radius among all possible cross-sections of the profile. It can be demonstrated that the relationship between h and the coordinates x and y takes the form:

$$h = \frac{1}{2R'}x^2 + \frac{1}{2R''}y^2 \quad (2.1)$$

To determine the stress distribution can be considered a cross section of the contact between the surfaces, as shown in Fig. 2.1. Upon applying a compressing load P , the surfaces undergo deformation. If the surfaces did not deform, their profiles would overlap, as indicated by the dotted lines. However, due to the contact pressure, certain points such as T_1 and T_2 move parallel to the z -axis by distances δ_1 and δ_2 , respectively. Additionally, the surface of each body experiences displacement parallel to the z -axis by amounts u_{z1} and u_{z2} concerning T_1 and T_2 , respectively. Consequently, the shape of the contact area changes, potentially forming a circle, a line, or other configurations. Through simple geometric considerations, Johnson demonstrates how to obtain pressure distributions and elastic displacements for different contact configurations. By performing dimensional analysis, one can derive the mean contact pressure p_m , which satisfies the aforementioned geometric assumptions for two contacting surfaces composed of materials with principal radii R_1 and R_2 and elastic moduli E_1 and E_2 . The results show that, for a given material and geometry, the contact pressure and associated stresses increase proportionally with the linear dimension of the contact area [27].

while the Equivalent radius, R_e , is given by,

$$\frac{1}{R_e} = \frac{1}{R_1} + \frac{1}{R_2} \quad (2.3)$$

It is worth noting that there is an equivalence between sphere-on-flat contact and crossed-cylinder contacts in specific cases. For example, when two cylinders with radii R' and R'' are placed perpendicular to each other, the resulting contact contours perfectly match the shape given by Eq. (2.1), in other words, identical contact areas and pressure distributions can be achieved for completely different configurations by selecting appropriate equivalent radii. of Hertz [28] and can be illustrated in Fig. 2.3.

The solution to the problem illustrated in Fig. 2.2 goes back to the classical work of Hertz [28], although he studied the generalized problem of a sphere contact area. Hertz also made use of potential theory. For a small contact radius a compared to the radius of the sphere R , the profile shape in the contact can be characterized by the parabola:

$$f(r) = \frac{r^2}{2R}$$

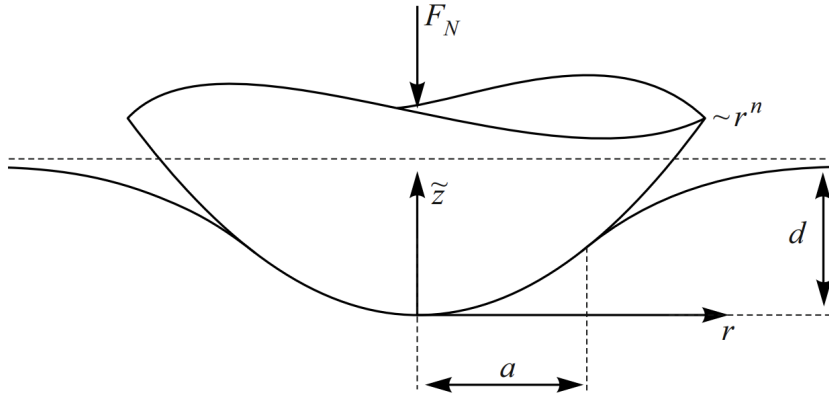


Figure 2.2: Sphere to flat contact relationship [29].

The value of a can be obtained:

$$a = \sqrt{d \cdot R_e} \quad (2.4)$$

The summary of this is that the pressure distribution proposed by Hertz is:

$$p = p_0 \left(1 - \left(\frac{r}{a} \right)^2 \right)^{\frac{1}{2}} \quad (2.5)$$

where r is the radius of the measured pressure and p_0 is the maximum pressure of contact between two solids. This relation, with the geometry determined for the contact of a sphere to flat, results in the radius of the area of contact as:

$$a = \left(\frac{3FR_e}{4E^*} \right)^{\frac{1}{3}} \quad (2.6)$$

and the mutual approach of points in the solids as:

$$\delta = \frac{a^2}{R_e} = \left(\frac{9F^2}{16R_e E^{*2}} \right)^{\frac{1}{3}} \quad (2.7)$$

The total load is related to the pressure by:

$$F = \int_0^a p(r) 2\pi r dr = \frac{2}{3} p_0 \pi a^2 \quad (2.8)$$

Given that the applied load is typically known, the maximum pressure can be determined by solving for it.

$$p_0 = \frac{3F}{2\pi a^2} = \left(\frac{6FE^{*2}}{\pi R_e^2} \right)^{\frac{1}{3}} \quad (2.9)$$

Under the given conditions, the normal stresses can be determined.

$$\sigma_3 = \sigma_z = -p_0 \left(1 + z^2/a^2 \right)^{-1} \quad (2.10)$$

where z is the position from the point of contact along the z-axis. At the point of contact, $z = 0$, so the maximum pressure is the maximum stress at contact.

To provide an illustrative comparison, Fig. (2.3) presents the stress distributions caused by uniform pressure and those calculated using Hertz's theory.

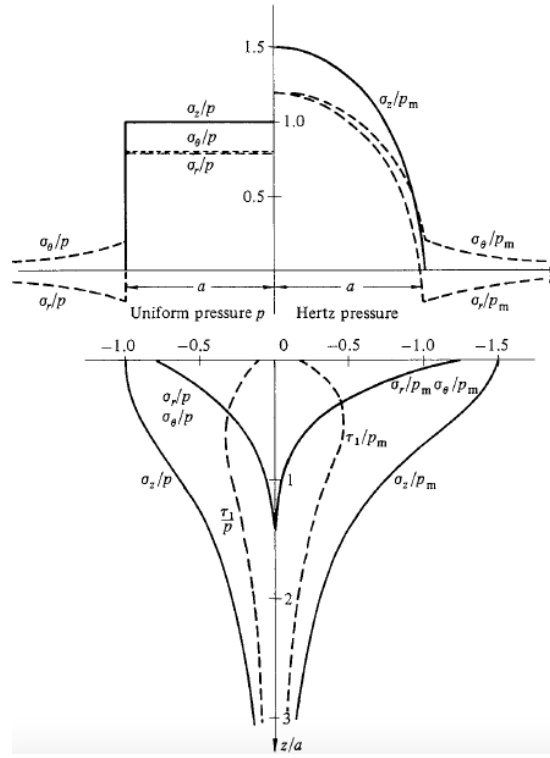


Figure 2.3: Comparison between stress distributions at the contact surface and along the z-axis: a) Caused by uniform pressure; b) Caused by Hertz pressure [27].

In terms of stress analysis, the principal stresses along the z-axis are denoted as σ_r , σ_z , and σ_θ . It is noteworthy that the principal shear stress τ_{max} does not occur on the surface itself but beneath it, at a certain distance from the radius a . Hence, a crucial observation can be made that plastic yielding is expected to initiate below the surface rather than on the surface. Furthermore, all stresses are compressive, except at the edges of the contact area where they exhibit tensile characteristics, with a maximum value of $(1 - 2\nu)\frac{p_0}{3}$. This particular stress is responsible for the formation of annular cracks in brittle materials.

However, it is important to emphasize that Hertz's theory applies only to elastic materials operating within their elastic limits. These equations can be utilized to predict the behavior of the contact until the point where plastic deformation occurs.

2.2 Mechanical compression

Mechanical compression is a force that acts on an object to reduce its size, typically by compressing its volume. The resistance to this compression force is known as compression resistance. This is a vital concept in the mechanics of materials, which studies the behavior of materials when they are subjected to forces such as compression, tension, bending, and torsion.

Compression resistance is a crucial property in the design of structural components and materials. It refers to a material's ability to withstand compressive forces without experi-

encing permanent deformation or failure. This property is important in many engineering applications, such as designing buildings, bridges, and vehicles, where compressive forces are commonly present.

The compressive strength of a material is an important parameter that indicates its resistance to compression. It is typically measured by applying a compressive force to a sample until it fails. The compressive strength of a material depends on factors such as its microstructure, porosity, and composition.

Understanding the mechanics of compression is critical in designing robust and reliable structures and materials that can withstand compressive forces. Compression resistance is the ability of a material to withstand compressive forces without yielding, and compressive strength is a parameter that measures this ability.

There is a relationship between mechanical compression and the mechanics of contact. When a compressive force is applied to an object, it creates a contact area between the object and the surface it is resting on. The contact pressure distribution along this area is affected by the shape and properties of the contacting surfaces, as well as the magnitude and direction of the compressive force.

In the mechanics of contact, the analysis of the contact area, contact pressure, and pressure distribution are crucial in understanding the behavior of materials in contact, including their ability to withstand compressive forces. The contact area and pressure distribution are affected by the geometry and properties of the contacting surfaces, which can affect the material's compressive strength.

Moreover, non-conformal contact patterns, where the surfaces of the two objects do not fit perfectly, can lead to non-uniform contact pressure distributions, which can cause stress concentrations and result in failure under compression. Thus, understanding the mechanics of contact is essential when analyzing the behavior of materials under compressive forces.

2.3 Indentation tests

In materials science and engineering, the testing of mechanical properties is a fundamental aspect of understanding the behavior of materials and their suitability for specific applications. One of the most commonly used testing techniques for measuring mechanical properties is indentation testing.

Indentation testing is a non-destructive technique that involves applying a compressive force to a material using a small indenter, typically made of a hard and sharp material such as a diamond. The indenter is pressed into the material surface, creating an indentation whose size and shape can be measured using various techniques such as microscopy or profilometry. From the dimensions of the indentation, several mechanical properties of the material can be determined, including its hardness, modulus of elasticity and yield strength.

It is widely used in various applications, including material characterization, quality control, and failure analysis. It is particularly useful for evaluating the mechanical properties of materials that are difficult to test using conventional methods, such as thin films or coatings. Moreover, indentation testing provides valuable information about the mechanical properties of a material at the microscale.

The mechanics of contact play a critical role in indentation testing. The indenter creates a contact area with the material surface, and the contact pressure and distribution affect the size and shape of the resulting indentation. Therefore, understanding the mechanics of contact is crucial in interpreting the results of the test and understanding the material's behavior under compressive forces.

Furthermore, the resistance to compression of a material is closely related to its hardness, which is often measured using indentation testing. Hardness is a measure of a material's ability to resist plastic deformation under compressive forces. Thus, a high hardness value indicates a material that is more resistant to compression, while a low hardness value indicates a material that is more prone to plastic deformation under compression.

2.4 Hardness

Hardness testing is a technique used to determine a material's resistance to permanent indentation. The concept of hardness is essential in materials science and engineering, particularly in the selection and design of materials for specific applications. Hardness tests are non-destructive and can be performed quickly and easily, making them popular for quality control and research purposes.

There are several methods of hardness testing, including Brinell, Rockwell and Vickers tests, each with its advantages and limitations. These tests measure the depth or size of an indentation made by a standard indenter under a known load and the hardness is calculated based on the indentation size. The hardness of a material can indicate its strength, wear resistance, and toughness which are crucial factors in determining the material's suitability for a particular application.

The relationship between hardness testing and the mechanics of contact is based on the principles of indentation and the mechanics of elastic and plastic deformation. Indentation testing can provide information about a material's elastic and plastic properties, such as its modulus of elasticity, yield strength and ductility. This is also related to its resistance to compression, which is essential in designing materials for applications where compressive loads are present. Moreover, in quality control, hardness testing helps ensure consistent material performance and identifies any deviations from specifications.

Hertzian contact theory, developed by [28], is a fundamental theory in contact mechanics that helps explain the elastic deformation that occurs when two solid bodies come into

contact under a compressive load. This theory provides a mathematical framework for calculating the contact stresses and contact areas in indentation testing, enabling the analysis of indentation phenomena. Hertzian contact theory assumes elastic deformation and is applicable when the materials involved are linearly elastic and the contact area is relatively small compared to the size of the bodies.

The contact stiffness is a crucial parameter in understanding a material's elastic behavior during indentation testing. It quantifies the relationship between the applied load and the resulting indentation depth. The contact stiffness can be approximated by analyzing the initial slope of the load-depth curve obtained from indentation tests. By measuring the change in load divided by the corresponding change in indentation depth, an estimation of the contact stiffness can be obtained. The contact stiffness provides valuable insights into the material's elastic properties, such as its Young's modulus and its ability to resist deformation under load.

In addition to the contact stiffness, the indentation modulus is another important parameter in indentation testing. The indentation modulus characterizes a material's resistance to elastic deformation during indentation. It takes into account the contact stiffness and the contact area between the indenter and the material surface. The indentation modulus can be calculated using various methods, such as the Oliver and Pharr method [30], which involves analyzing the unloading portion of the load-depth curve. The indentation modulus provides information about the material's ability to withstand elastic deformation and relates to properties such as its elastic modulus and Poisson's ratio.

By analyzing the load-depth curve obtained from indentation testing and utilizing the theories and calculations mentioned above, a comprehensive understanding of the mechanical properties of the polypropylene material can be achieved. The Hardness Brinell (HBW), contact stiffness and indentation modulus are key parameters that allow the assessment of the material's resistance to indentation, its elastic behavior, and its resistance to elastic deformation, respectively. Based on this information, can perform some analysis and calculations:

1. Hardness Calculation:

Hardness is typically determined using the load and the diameter of the indenter ball along with the measured mean diameter of the indentation. In the case of the Brinell hardness test, can calculate the hardness using the following formula according to ASTM E10-18 [31]:

$$Hardness(HBW) = \frac{2 \cdot F}{\pi \cdot D \cdot \left(D - \sqrt{D^2 - d^2} \right)} \quad (2.11)$$

Where: F is the test force in kgf because at the time the Brinell hardness test was developed, the force levels were specified in units of kilograms-force (kgf). Although the standard specifies the unit of force in the International System of Units (SI) as the Newton (N), because of historical precedent and continued common usage of kgf unit,

force values in kgf unit is adopted. D is the diameter of the indentation ball in mm and d is the measured mean diameter of indentation in mm. This formula considers the load applied and the geometric properties of the indenter and the indentation mark.

2. Contact Stiffness:

The contact stiffness provides information about the elastic behavior of the material. It can be determined by analyzing the initial slope of the load-depth curve. By calculating the change in load divided by the change in depth, can obtain an approximation of the contact stiffness. The formula is given as follows:

$$k = \frac{\Delta \text{Load}}{\Delta \text{Depth}}, \quad (2.12)$$

Where ΔLoad is the change in load and ΔDepth is the change in depth over a certain range.

2.5 Tensile Tests

Tensile testing is a fundamental experimental technique used to assess the mechanical properties of materials under axial loading. This method involves subjecting a specimen to an increasing uniaxial force until a fracture occurs. The resulting stress-strain curve provides valuable insights into the material's response to applied loads, including its elastic and plastic behavior.

In the case of metallic materials, tensile testing reveals distinct regions on the stress-strain curve. The elastic region follows Hooke's law, displaying linear behavior. The yield point marks the transition from elastic to plastic deformation, where the material undergoes permanent deformation without an increase in stress. The subsequent strain hardening region shows an increasing stress requirement for further plastic deformation. The ultimate tensile stress represents the maximum stress the material can sustain before fracture, while the elongation and reduction in the area reflect the material's ductility [32].

Polymers are part of the group of materials that exhibit time-dependent behavior. These materials are known as viscoelastic or viscoplastic materials. The difference between the two classes is that, after the removal of the applied force, the material in the viscoelastic regime will recover all deformation, but not instantaneously, rather over time, which is dependent on the macromolecular structure of the polymer. The viscoplastic regime, on the other hand, is defined by the presence of a permanent deformation component that will not be recovered even over time after the force is removed.

Thus, understanding some aspects such as elastic, plastic, and viscous deformation is initially observed for the study of viscoelastic and viscoplastic theories. The viscous behavior is comprehended when the stress does not occur instantaneously but rather over some time.

An illustrative example to grasp this behavior is through a creep test, where the material undergoes instantaneous tensile loading, followed by a constant stress maintained for a specific duration, and then an instantaneous stress removal. The resulting deformation behavior from the aforementioned loading results in an increase in strain during the instant t_1 when the load is relieved, while the stress remains constant ($t < t_1$), and at time t_1 , a portion of the strain is instantly recovered, representing the elastic component, while the remaining portion is recovered gradually over time.

The temporal dependency in the mechanical behavior of polymers is linked to the viscous deformation component and can be elucidated through molecular aspects. When a polymer is subjected to tensile loading, the macromolecular chains undergo structural modifications caused by molecular rotation or chain elongation. The separation between lamellae in the crystalline structure, particularly in semicrystalline polymers, can lead to sample whitening during tensile testing due to the formation of cavities or microvoids [33–36]. After stress relief, some of the deformed chains promptly recover from the strain, while others experience relaxation, signifying the chains' tendency to revert to their initial state, albeit gradually over time rather than instantaneously.

Consequently, two distinct behaviors become evident after a certain period (t_∞) where the strain rate becomes constant. One behavior corresponds to complete strain recovery at (t_∞), indicating that the initial strain applied to the material did not surpass the elastic limit. This behavior is commonly referred to as viscoelastic. The other behavior is characterized by the presence of plastic deformation, suggesting that the initially applied strain exceeded the material's elastic limit. In this scenario, three regimes can be observed: elastic, viscous, and plastic. Thus, this type of behavior is widely recognized as viscoplastic.

Even under small strains, numerous polymers exhibit viscoplastic behavior [35, 37, 38]. Hence, when it comes to engineering applications involving these materials, understanding the viscoplastic regime becomes imperative for accurately determining the constants that govern the mechanical behavior of the polymer. A typical stress-strain curve for polymers can be seen in Fig. 2.4.

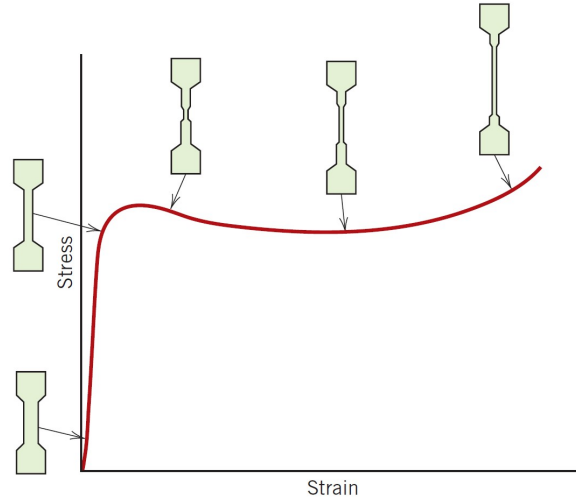


Figure 2.4: Classic stress-strain curve for a semi-crystalline polymer [39].

Polymers exhibit time-dependent mechanical behavior and are widely referred to in the literature as "time-dependent materials". Therefore, the constitutive theories used to represent the mechanical behavior of these materials must encompass not only elastic and plastic effects but also viscous effects. This combination can be achieved by employing rheological elements to represent each behavior. The elastic effect is represented by a spring, the viscous effect by a damper, and the plastic effect by a friction element. However, this topic will not be extensively addressed in this study.

Tensile testing of polymers typically reveals a gradual transition from elastic to plastic deformation. The stress-strain curve is influenced by factors such as strain rate, temperature and humidity. Parameters such as yield strength, ultimate tensile stress, and elongation at break are crucial for characterizing the mechanical properties of polymers.

The tensile test involves several fundamental equations and concepts that will be presented below:

Stress (σ)

The stress (σ) in a material under tensile load is defined as the force (F) applied per unit cross-sectional area (A) of the specimen.

$$\sigma = \frac{F}{A} \quad (2.13)$$

Strain (ε)

The strain (ε) is the ratio of the change in length (ΔL) of the specimen to its original length (L_0).

$$\varepsilon = \frac{\Delta L}{L_0} \quad (2.14)$$

Young's Modulus (E)

Young's modulus (E) is a measure of a material's stiffness and is defined as the ratio of stress (σ) to strain (ε).

$$E = \frac{\sigma}{\varepsilon} \quad (2.15)$$

Engineering Stress-Strain Curve

The engineering stress-strain curve represents the relationship between stress (σ) and strain (ε) for material under tensile loading, where stress is plotted on the y-axis and strain is plotted on the x-axis.

$$\sigma = f(\varepsilon) \quad (2.16)$$

True Stress (σ_t)

The true stress (σ_t) takes into account the actual cross-sectional area (A_t) of the specimen at any given point during deformation.

$$\sigma_t = \frac{F}{A_t} \quad (2.17)$$

True Strain (ε_t)

The true strain (ε_t) represents the logarithmic ratio of the instantaneous length (L) to the original length (L_0) of the specimen.

$$\varepsilon_t = \ln \left(\frac{L}{L_0} \right) \quad (2.18)$$

True Stress-Strain Curve

The true stress-strain curve plots the relationship between true stress (σ_t) and true strain (ε_t), where true stress is shown on the y-axis and true strain is shown on the x-axis.

$$\sigma_t = f(\varepsilon_t) \quad (2.19)$$

2.6 Viscoelasticity

Viscoelasticity is a fundamental property that arises in many materials, including polymers. Understanding their time-dependent behavior is crucial for predicting their response to different loading conditions [40]. Two widely adopted viscoelastic models are the Maxwell-Voigt and Mulliken-Boyce models, which are distinguished by their underlying assumptions and mathematical formulations. These models are extensively employed to characterize the time-dependent behavior of materials in various engineering applications.

The Maxwell-Voigt model is a linear viscoelastic model that combines a Hookean spring (elastic component) and a Newtonian dashpot (viscous component) in series, as shown in

Fig. 2.5. The parallel configuration of the spring and dashpot in this model results in the manifestation of the primary creep phenomenon, as they cannot expand independently. As a consequence, the model does not exhibit steady-state creep and steady-state stress relaxation. Upon stress release, the spring cannot instantaneously return to its original position but instead applies a force on the dashpot, leading to compressive creep under external stress. Over time, all creep strain will eventually recover due to a phenomenon known as viscoelastic contraction, which holds significance in real viscoelastic materials [41].

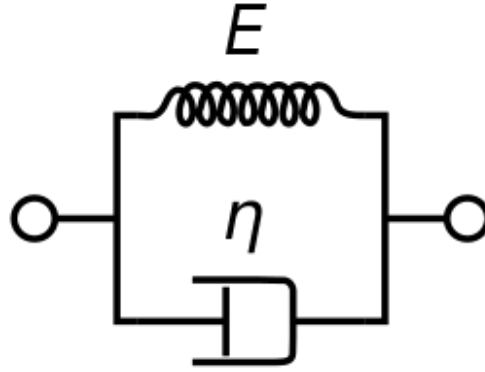


Figure 2.5: One-dimensional rheological representation - Maxwell-Voigt model [41].

The constitutive equation for the Maxwell-Voigt model is given as follows:

$$\sigma(t) = E\varepsilon(t) + \eta \frac{d\varepsilon(t)}{dt} \quad (2.20)$$

Where:

- $\sigma(t)$ is the stress at time t ,
- E is the elastic modulus,
- $\varepsilon(t)$ is the strain at time t ,
- η is the viscosity of the material.

The model predicts that the response of the material to applied stress is a combination of instantaneous elastic deformation and delayed viscous deformation.

The paper presented by Mulliken and Boyce [42] provides a comprehensive overview of the Mulliken-Boyce model. This model was applied to characterize the behavior of PC and PPMA, encompassing their rate-dependent elastic-plastic deformation across a wide range of strain rates. In this model, a new approach is employed where two viscoplastic networks run in parallel, driven by activated molecular processes. Each network has its own set of elastic and viscoplastic properties, as illustrated in Fig. 2.6.

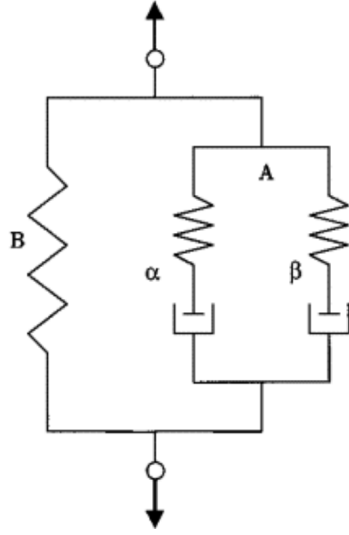


Figure 2.6: One-dimensional rheological representation - Mulliken-Boyce model [42].

The Mulliken-Boyce model is a nonlinear viscoelastic model that extends the Maxwell-Voigt model by introducing a strain-dependent viscosity term. This model is particularly useful in capturing the strain-rate dependency of viscoelastic materials. The constitutive equation for the Mulliken-Boyce model is given as follows:

$$\sigma(t) = E\varepsilon(t) + \eta_0 \exp\left(\beta\varepsilon^2(t)\right) \frac{d\varepsilon(t)}{dt} \quad (2.21)$$

Where:

- $\sigma(t)$ is the stress at time t ,
- E is the elastic modulus,
- $\varepsilon(t)$ is the strain at time t ,
- η_0 is the initial viscosity,
- β is a material-specific constant.

The Mulliken-Boyce model introduces a strain-hardening effect, where the viscosity of the material increases with strain, resulting in a more accurate representation of viscoelastic behavior under large deformation. Both the Maxwell-Voigt and Mulliken-Boyce models have been widely used in various applications, including the design and analysis of viscoelastic materials in engineering and biomedical fields. However, they do have some limitations:

- Maxwell-Voigt model: While it provides a simple and linear representation of viscoelasticity, it may not adequately capture the strain-rate dependency of some materials. Additionally, it does not account for strain-hardening effects.

- Mulliken-Boyce model: While more comprehensive than the Maxwell-Voigt model, the Mulliken-Boyce model's strain-dependent viscosity term can lead to numerical challenges in simulations and may require complex parameter fitting.

2.7 Nonlinear Material Behavior

Nonlinear material behavior is characterized by the behavior of a material that does not follow a linear relationship between stress and strain, and it can be observed across various phases of a material's deformation. The phases of non-linear material behavior are classified based on the stress-strain curve, which shows the relationship between stress and strain during deformation.

The initial phase of non-linear behavior is characterized by the material's elastic deformation, where the stress-strain relationship follows Hooke's law. In this phase, the material behaves elastically, and upon the removal of the load, it returns to its original shape and size. However, if the load exceeds the material's yield strength, it undergoes plastic deformation, leading to a transition to the next phase.

The second phase of non-linear behavior is characterized by the material's plastic deformation, where the stress-strain curve shows a plateau, indicating a constant stress level despite increasing strain. This phase is also known as the yield point and is associated with the material's permanent deformation. The plastic deformation phase can further be classified into strain hardening and strain softening phases based on the material's response to increasing strain.

In the strain hardening phase, the material's resistance to further deformation increases as it undergoes plastic deformation, increasing its strength and toughness. In contrast, in the strain-softening phase, the material's strength and stiffness decrease with increasing strain, resulting in a reduction in its load-bearing capacity. The strain softening phase can lead to material failure, particularly in geotechnical and rock mechanics applications.

The final phase of non-linear behavior is characterized by the material's failure, where the stress-strain curve shows a sharp drop in stress despite increasing strain. The failure phase can be due to various factors, such as excessive stress, fatigue, or environmental factors, such as temperature, humidity and corrosion.

2.8 Fatigue

The fatigue process is characterized by changes in material properties due to repeated application of forces, which can lead to material failure. Fatigue can occur even when the loads are below the tensile or yield stress limits because the plastic deformation generated at the crack tip does not have time to relax during the periods it is subjected to force. This

accelerates the onset of failure [43].

Fatigue failure does not occur suddenly but goes through various stages before resulting in catastrophic fractures. These stages include nucleation due to substructural and microstructural changes, formation of microscopic cracks, growth of microcracks that can become macroscopic cracks, stable crack propagation, and finally, catastrophic fracture. This process occurs at relatively low stresses and frequencies and results in extended fatigue life. However, at higher stresses and frequencies, hysteresis heating of the polymer and the inability to dissipate the heat generated during mechanical fatigue affect the physical and mechanical properties of the material [44].

The microcracks that form within the material usually originate from intrinsic imperfections resulting from the manufacturing process or inadequate processing conditions. These small defects act as stress concentrators when subjected to loads, propagating and leading to component failure in less time than predicted. Several factors can contribute to the occurrence of fatigue in polymers, such as chemical degradation or oxidation, nature of the loading, viscoelastic nature of the material, types of applied stresses, low thermal conductivity, and high material hysteresis, resulting in increased temperature during the fatigue process and failure due to material softening [43].

Therefore, there are two types of fatigue failure: mechanical failure and thermal failure. Frequency also plays a role in thermal fatigue occurrence in plastics, along with the material's thermal and damping characteristics [43]. The study of fatigue is necessary because most failures are related to it. According to [45], fatigue failures account for 50% to 90% of total failures. Fatigue is a type of mechanical failure caused by cyclic loading.

Fatigue is a mechanical phenomenon that occurs when a material fails under cyclic loading. It is a common form of failure in structural components and can have serious consequences if not properly considered during the design and operation of materials and structures [46].

Several theories seek to explain the fatigue failure mechanism. One of the most widely accepted theories is the surface discontinuity theory, proposed by August Wöhler in the mid-19th century [47]. According to this theory, fatigue occurs due to the propagation of microcracks from discontinuities on the material's surface. These discontinuities can be originated from inclusions, pre-existing cracks, corrosion, among other factors.

The load ratio, represented by the letter R , is defined as the ratio between the minimum and maximum stresses applied to the material during a loading cycle. In the context of fatigue, the load ratio is important because it affects the material's response to cyclic loading. When $R = -1$, the load is completely reversed, meaning that the material is subjected to equal magnitude tensile and compressive stresses during each cycle. The load ratio $R = 0.1$ is a stress amplitude where the minimum applied stress corresponds to 10% of the maximum stress. This loading condition is considered severe for assessing the fatigue strength of materials.

When $R = 0.1$, the mean stress during cyclic loading is close to zero, implying a symmetric load. This type of loading is considered critical because it generates high-stress gradients in the material's surface region, where microcracks initiate their propagation. Therefore, the load ratio $R = 0.1$ is often used to assess the fatigue life of materials and components as it represents a severe condition that can lead to early failure.

It is important to note that fatigue is a complex phenomenon, dependent not only on the applied stress level but also on other factors such as loading rate, presence of corrosion, temperature, and material microstructure, among others. Therefore, in addition to the mentioned equations, there are also advanced models and methods to predict and assess the fatigue life of materials and components [45].

The automotive industry is increasingly using thermoplastic polymers and polymer composite materials to reduce the cost and weight of vehicles to meet environmental requirements. However, the fatigue behavior of these materials is less understood than metallic materials, especially the effect of mean stress. It is well known that the fatigue life of metals is significantly influenced by mean stress. The fatigue behavior of PP is shown in Fig. 2.7.

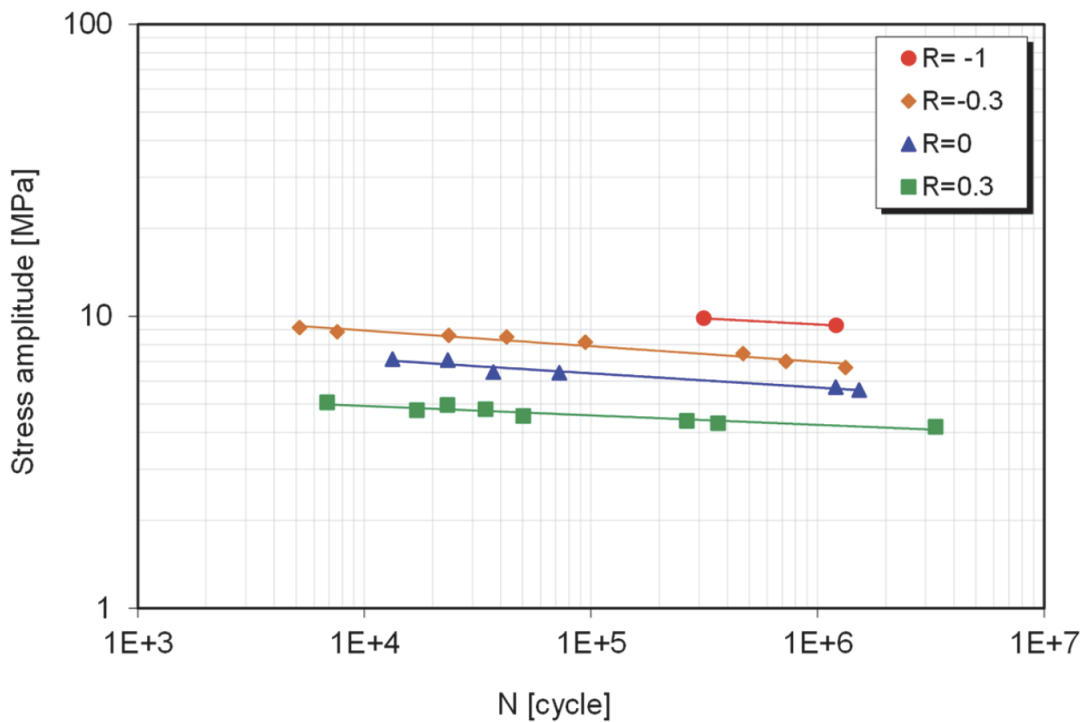


Figure 2.7: Fatigue behaviour of PP [24].

Lu et al [24] studied to examine the effect of a mean stress, seven materials were tested under constant load amplitude at a range of stress ratios under room temperature. The materials tested included four thermoplastic polymers and three short glass fiber-reinforced polymer composites. Various mean stress correction equations were evaluated and was shown that mean stress had a significant influence on the fatigue life and the fatigue behaviour can be described by the Basquin Equation for all the materials within the investigated life regime.

2.9 Thermoplastic polymers and polypropylene

Polymers are materials composed of macromolecules. These macromolecules consist of chains formed by the repetition of a basic unit, called a monomer. Hence the name: poly (many) + mer. Polymers are a type of material composed of long-chain molecules that contain carbon-to-carbon bonds. Examples of polymers include plastics, natural and synthetic fibers, rubbers, cellulose and lignin in wood. Polymers used as engineering materials can be categorized into three groups: thermoplastics, thermosetting plastics and elastomers [39,48]:

- Thermoplastics, commercially known as plastics, are recyclable polymers that can be melted multiple times and exhibit variable mechanical properties, being malleable, rigid, or brittle.
- Thermosetting plastics are polymers that exhibit stability with temperature variations. They are rigid and often brittle. They have a significant disadvantage of not being recyclable, taking hundreds of years to decompose.
- Elastomers, also known as rubbers, exhibit excellent elasticity but are also non-recyclable due to their inability to be melted.

Polymers have been used by the population for many years. According to [49], since ancient times, humans have used natural polymers such as starch, cellulose, and silk, among others. However, starting from the first half of the 20th century, when the German chemist Hermann Staudinger (1881-1963) discovered the polymerization process, polymer synthesis ceased to be merely a natural phenomenon. After the discovery of the polymerization process, the everyday use of polymers has only increased. This is due to their characteristics such as low density, high elasticity, high impact resistance, high corrosion resistance, low processing temperature, as well as thermal and electrical insulation properties. These characteristics allow polymers to replace metals and ceramics in various situations [49].

Polymeric materials are high-molecular-weight organic components, products of addition or condensation polymerization reactions of different basic components [39]. A polymer can be amorphous or crystalline. Crystalline polymers are those in which atoms or molecules are aligned in relatively defined and ordered positions. Amorphous polymers are those in which atoms do not have any geometric arrangement [5].

Thermoplastic materials soften with heating and eventually melt, returning to a solid state upon cooling. Thermoplastic materials present favorable characteristics for their use and production, such as low production cost, high fracture toughness, good impact resistance, good resistance to microcrack propagation, easy quality control, and the possibility of raw material recycling [50].

Thermoplastic polymers can be categorized as either crystalline or amorphous, depending on how their chain molecules are arranged. Crystalline polymers, such as PE, PP, PTFE,

nylon, Kevlar, POM, and PEEK, have an ordered crystalline structure, while amorphous polymers, such as PVC, PMMA, and PC, have a random arrangement [39]. However, some polymers, like polystyrene (PS), can have both crystalline and amorphous forms, depending on the location of their benzene ring substitution. Syndiotactic polymers have a regular alternation of side groups, resulting in a crystalline structure [5].

Amorphous polymers have a glass transition temperature (T_g) below which they behave glassy and brittle [5]. They are limited in their load-bearing applications due to the rapid decrease in modulus above T_g and pronounced time-dependent deformation effects. On the other hand, crystalline polymers tend to be less brittle and retain their stiffness and strength even beyond T_g , making them more versatile in their applications [5]. Crystalline polymers are generally opaque to light, while amorphous polymers are transparent.

The molecular structure of a polymer is affected by the chemical synthesis process, including temperature, pressure, reaction time, catalysts and cooling rate, which can be manipulated to produce polymers with varying properties. Molecular structures that inhibit sliding between chain molecules tend to increase stiffness and strength. These structures can be the branches, or the positions thereof, this includes longer chains, more branches in amorphous polymers, greater crystallinity and crosslinking in normally thermoplastic polymers. These effects are shown above the T_g .

Polypropylene is a downstream product of the petrochemical industry, originating from the olefin monomer known as propylene Fig. (2.8). The manufacturing process involves addition polymerization, where heat, high-energy radiation, and either an initiator or a catalyst are used to connect the monomers, resulting in the formation of extensive polymer chains. Four distinct methods can be employed to enhance the polymerization of any polymer: solution polymerization, suspension polymerization, bulk polymerization, and gas-phase polymerization [51].

Nevertheless, the properties of polypropylene vary depending on the process conditions, the presence of copolymer components, as well as the molecular weight and distribution. Polypropylene can be described as a vinyl polymer, wherein each carbon atom is bonded to a methyl group, and its structure can be represented as illustrated below:

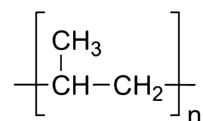


Figure 2.8: Molecular structure of PP [39].

Polypropylene exhibits a crystalline arrangement, rendering it notably rigid and boasting a considerably elevated melting point when contrasted with other thermoplastics available in the market. The stiffness arises from the presence of methyl groups within its molecular chain structure, contributing to its hardness [51].

It is polymerized through a polyaddition reaction process, and its molar mass ranges from

80,000 to 500,000. It is a semi-crystalline polymer with an approximate density of 0.90 - 0.91 g/cm³ and a refractive index of 1.45. The glass transition temperature and melting temperature are around -18°C and 165°C, respectively. It is a highly crystalline polymer, around 60 to 70%, which accounts for its relatively good mechanical strength and hardness. The material's elastic modulus varies between 1.14 - 1.55 GPa. Tensile stress ranges from 31.0 - 41.4 MPa. Yield strength has values in the order of 31.0 - 37.2 MPa. The elongation varies between 100 - 600% [39, 52]. The low cost of the material, combined with its versatility, makes propylene a polymer of interest for industry and science [53].

Nevertheless, polypropylene demonstrates limitations in its usability under temperatures lower than 0°C [54]. Empirical investigations have confirmed that polypropylene exhibits outstanding and favorable physical, mechanical, and thermal characteristics in applications at room temperature. It possesses considerable stiffness, a high melting point, low density, and reasonably robust resistance to impacts [51].

Polypropylene stands out as the most significant material within the polyolefin group for several compelling reasons. Firstly, its remarkable attributes such as low density, high melting temperature, and chemical inertness make it an ideal choice for long-lasting applications, all at a cost-effective price point. Secondly, polypropylene exhibits remarkable versatility, enabling a wide range of structural designs and mechanical properties to be achieved. Thirdly, by incorporating fillers, reinforcing agents, and blending with other polymers, various morphological structures of polypropylene can be obtained, leading to the development of superior characteristics. Some examples of these specialized and reinforced polypropylene grades include elastomer-modified PP, elastomer-modified filled PP, glass fiber-reinforced PP, filled PP, esthetic filled PP, flame-retardant PP, and thermoplastic elastomers [51, 54].

2.9.1 Tacticity and Isomerism in PP

PP is a vinyl polymer derived from propylene monomers, resulting in a linear polymer chain with a backbone of carbon atoms. The arrangement of methyl groups on the carbon atoms leads to different configurations known as tacticity isomers. The three main tacticity isomers found in PP are isotactic, syndiotactic, and atactic.

- **Isotactic PP:** In isotactic PP, the methyl groups are all situated on the same side of the polymer backbone. This regular and orderly arrangement results in a highly crystalline structure, contributing to superior mechanical properties such as high tensile strength, stiffness, and thermal stability.
- **Syndiotactic PP:** In syndiotactic PP, the methyl groups alternate their positions on opposite sides of the polymer chain. This configuration introduces irregularities in the polymer structure, leading to reduced crystallinity and lower mechanical strength

compared to isotactic PP. However, syndiotactic PP exhibits enhanced processability and may possess improved transparency.

- Atactic PP: In atactic PP, the methyl groups are randomly distributed along the polymer chain. This lack of spatial order prevents the formation of a crystalline structure, resulting in an amorphous material with low mechanical strength and softness. Atactic PP is typically used in applications requiring flexibility and elastomeric properties.

The unique arrangement of methyl groups in different tacticity isomers significantly impacts various properties of PP. Isotactic PP demonstrates excellent rigidity, chemical resistance, and dimensional stability, making it suitable for a wide range of engineering applications, including automotive components and household appliances. Syndiotactic PP's amorphous nature provides opportunities for applications in optically clear materials and adhesive formulations. Atactic PP, with its elastomeric properties, finds utility in sealants, gaskets and other flexible products.

Chapter 3

Methodology

In this study, the methodology employed for the analysis of the PP samples is divided into five main steps: evaluation of the specimens and quality control; test setup; indentation test; standard monotonic tensile tests; and standard uniaxial fatigue tests. These steps are described in the following.

3.1 Specimen's evaluation and quality control

The polypropylene pellets, used for the injection molding of the test specimens is the homopolymer H 503 from Braskem. This isotactic polymer (crystallinity of 76%) is indicated for thick-walled parts and has been employed in previous studies [55]. Its main properties are listed in Table 3.1:

Table 3.1: Properties of polypropylene H 503.

Specific Mass [g/cm ³]	Flexural Modulus [GPa]	Tensile Stress [MPa]	Elongation at Break [%]
0.9	1.16	33	11

The granules, after drying in an oven at 80°C for 1 hour, were sent for injection. The injection was performed into molds containing specific cavities for mechanical testing, using the Jasot 300/130 Injection Molding Machine with the programming described in [55].

In this work were used two types of specimens, the first was made with their dimensions are in compliance with the ASTM D638 [56] standards for type I tensile specimens. The second type, used for indentation with an indenter of 15 mm, had square geometry, their cross-section is 25 mm x 25 mm with a thickness of 5.00 ± 0.05 . Both polypropylene specimens were manufactured using an injection molding process.

After production, they have been inspected and verified for total length (LO), gauge length (G), gauge width (W), gauge thickness (T), and size of restraint area (D) using a digital calliper (Mitutoyo 500-144B, with the resolution of 0.01 mm) as shown in Fig. 3.1.

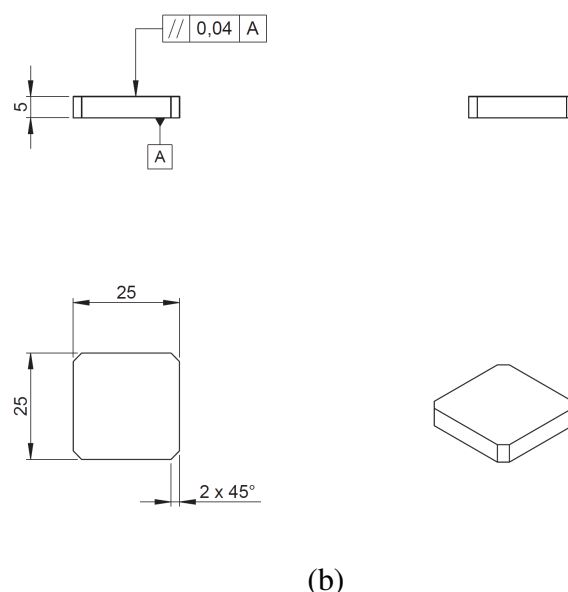
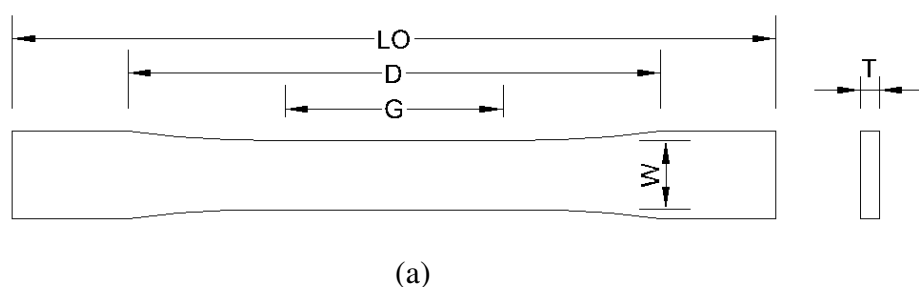


Figure 3.1: Specimen's dimensions: a) Specimen's dimensions according to ASTM D638-14 standard, type I tensile specimens; b) Second type of specimens with square geometry.

In this study, the collection of FTIR spectra was carried out utilizing the Nicolet IS10 spectrometer, a high-quality instrument manufactured by Thermo Scientific, Fig. 3.2. The spectra were obtained over a spectral range spanning from 400 to 4000 cm^{-1} , allowing for comprehensive analysis of the mid-infrared region. A resolution of 4 cm^{-1} was employed, providing detailed spectral information necessary for accurate identification and characterization of molecular vibrations. To enhance the signal-to-noise ratio and obtain reliable data, each spectrum was averaged over 128 individual scans.

The surface finish (tolerance of ± 0.4 mm, XY plane inclination of 1° or lower, ISO grade roughness N12 or lower) has been analyzed using a confocal laser microscope (Olympus LEXT OLS4100) Fig. 3.3.



Figure 3.2: Nicolet IS10 spectrometer [57].



Figure 3.3: Olympus LEXT OLS4100 [58].

This careful control is of great importance to decrease deviation in fatigue results. Nineteen specimens, divided into six groups, have been analyzed and each control measurement has been taken three times.

3.1.1 Indentation setup

To evaluate the compressive strength of polypropylene, indentation tests were performed in two steps. Firstly using a 5 mm tungsten carbide spherical indenter mounted on a universal indentation (ZHU 250) system, Fig. 3.4. The indentation marks were made in the clamping zone of untested tensile specimens.



Figure 3.4: Universal hardness tester [59].

Before the test, the two specimens (each tip was used for a sequence of indentations, from 100 N to 400 N) were polished using a metallographic grinding machine (Pantec POLIPAN-U; wet sandpaper discs, four grit stages: 200, 400, 600 and 800, at 300 rpm and 3 min each) and controlled for a 3.60 ± 0.05 mm thickness.

Results for four loads are reported in this study (100 N, 200 N, 300 N and 400 N), these values were carefully selected after the test. It is noteworthy that immediately after each indentation was made, the marks were inspected under a microscope, as it was possible to observe a rapid elastic recovery of the material at loads below 200 N.

As a second step, to understand the elastic phase in compressive loads, the indentations were made in an MTS 809 axial-torsional testing machine. It has a 25 kN actuator and can perform tests with axial and rotational movement simultaneously. The experimental assembly, with the hemispherical tool and the counterpart inside the holding device, both inserted into the test machine used, was obtained from [60] and is shown in Fig. 3.5 and Fig. 3.6. The applied loads were: 500 N, 1 kN and 2 kN.

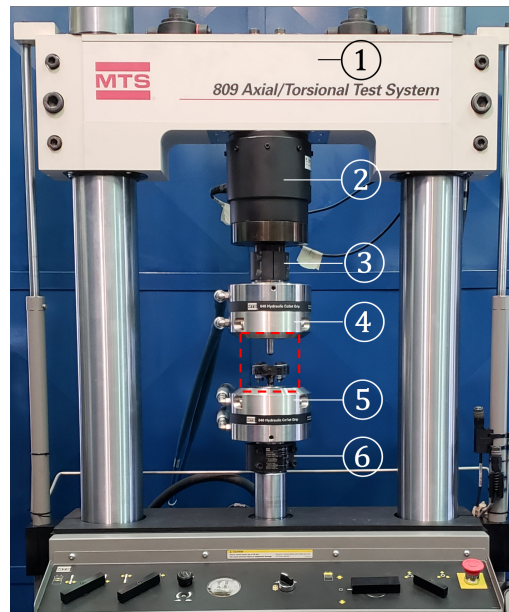


Figure 3.5: Experimental setup for the wear tests. MTS 809 Axial-Torsional. 1) Crosshead, 2) Force transducer, 3) Top cell, 4) Upper grip, 5) Lower grip, 6) Bottom cell [60].

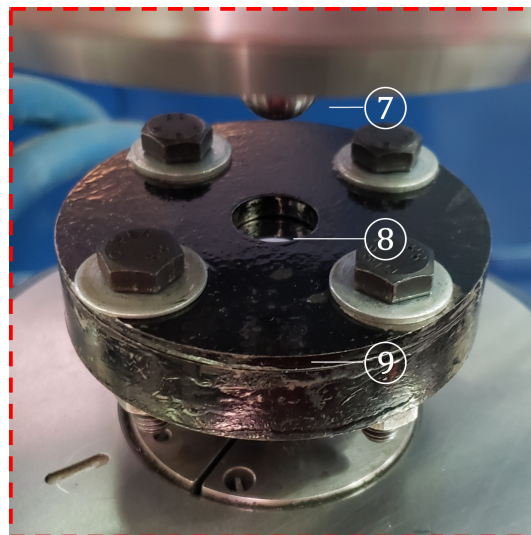


Figure 3.6: Detailed view of the specimens. 7) Hemispherical pad, 8) Flat sample, 9) Holding device [60].

3.1.2 Microscopic inspection

Four indentations (two plus repetition) are made in each one of the specimens to evaluate dispersion with the indenter of 5 mm, with the indenter of 15 mm, were done two indentations (one plus one) for each load. A three-dimensional profile of the mark was created using an Olympus LEXT OLS4100 confocal laser microscope to evaluate the damage caused on a specimen surface after each test, as shown in Fig. 3.7.



Figure 3.7: Olympus LEXT OLS4100 confocal laser microscope [58].

With 20x magnification and 1.0 μm of pitch incremental vertical stages, a stitching technique was completed. Using the microscope companion software, the diameter, depth, and volume of the damage marks were measured, as shown in Fig. 3.8. The intensity, color, or height spectra recorded by the microscope were utilized to gauge the marking's diameters depending on the material's composition.

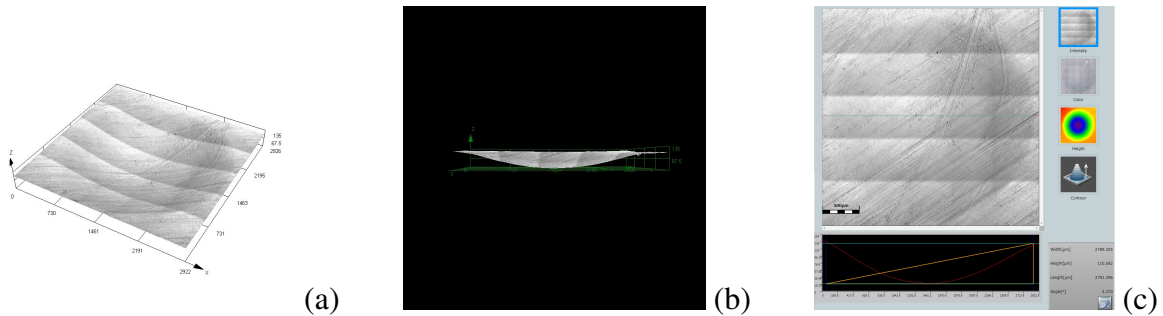


Figure 3.8: Microscope analysis. a) 3D profile of the indentation; b) Alternative representation of the indentation's 3D profile from a different perspective; c) Depth measurement.

3.1.3 Tensile and Fatigue-Mounting setup

The tests are conducted in a servo-hydraulic system (MTS 810 Landmark, load-cell capacity of 5 kN), as shown in Fig. 3.9. The specimens are mounted in a flat clamp system embossed with diamond-shaped grooves for optimal restraining. The contact pressure is set to 1 MPa (with a resolution of 0.5 MPa) and the distance between clamps was controlled at 106 mm (with a resolution of 1 mm) in all tests, to maintain the same usable section in all specimens. The room's temperature was monitored with a thermometer (Fig. 3.9 b), and the specimen's temperature was monitored using a thermal infrared camera (FLIR C5-C8940, 160×120 pixels. Thermal sensitivity/ NETD: less than 70 mK).

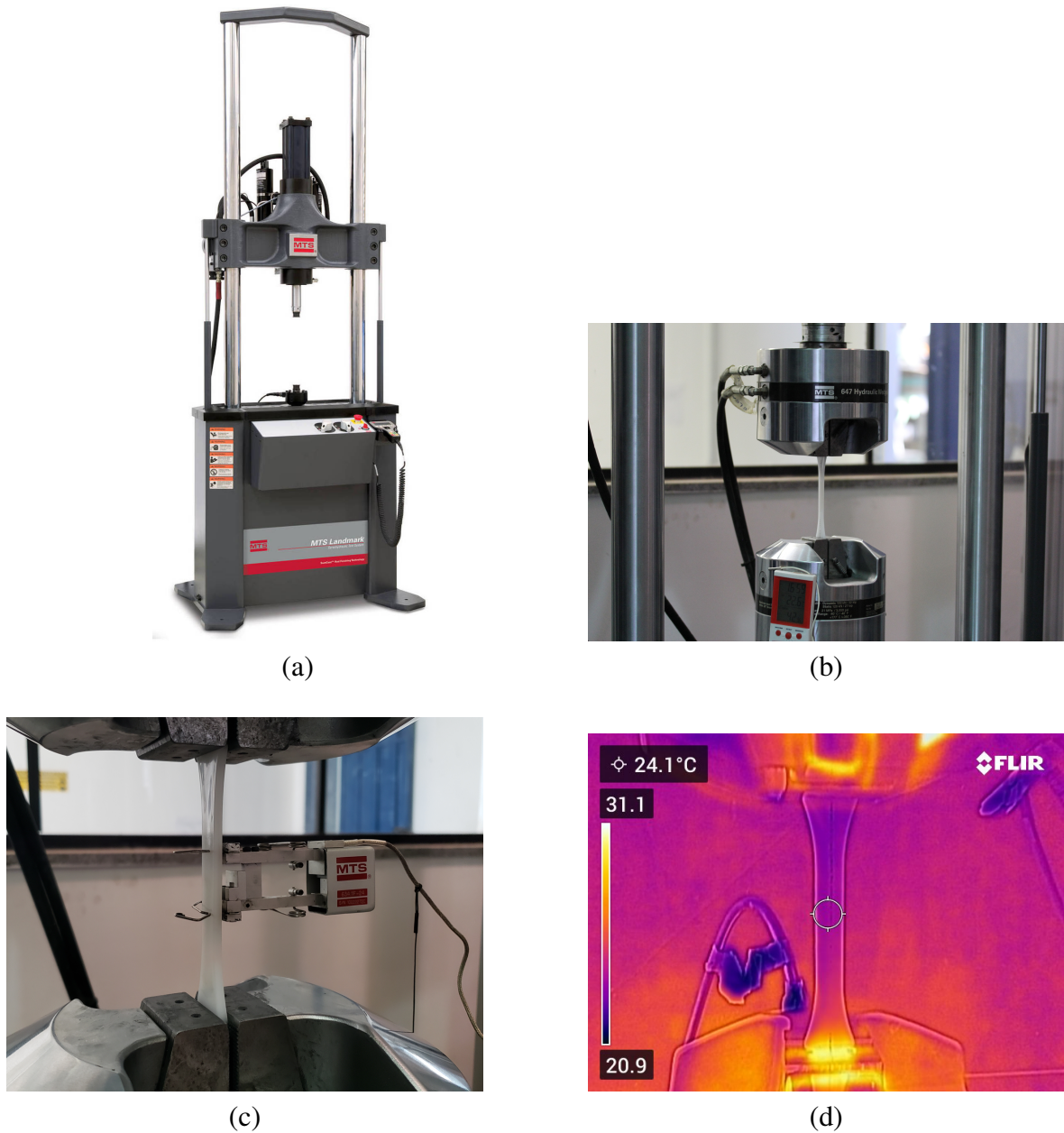


Figure 3.9: Setup experimental: a) Servo-hydraulic MTS 810 Landmark Testing System; b) ASTM 638 test specimen mounted with temperature and humidity control; c) ASTM 638 test specimen mounted with a clip gauge extensometer; d) Specimen's Thermal control with a FLIR [61].

3.1.4 Monotonic tensile tests

Four monotonic tensile tests were performed in displacement control mode to evaluate the force-displacement and stress-strain behavior. Two displacement rates were adopted: 2 mm/min and 6 mm/min. The reason for choosing these two displacement rates is due to the fact that, according to the standard, the tensile test must not exceed 5 minutes. Therefore, when conducted at rates below 2 mm/min, the test exceeded this time limit. On the other hand, when using the 6 mm/min rate, fracture was observed in the specimens. Two tests

were performed for each displacement rate used. A clip gauge extensometer (20 % strain limit) is used for additional information up to 10 % strain, at which point it was separated from the sample. The test continued up to 30 % strain. This choice was due to the loss of stiffness observed in the material after 30 % of deformation without its rupture. The output data for the tests were axial displacement, axial force, axial deformation and time. The data acquisition frequency was 1 Hz.

3.1.5 Uniaxial Fatigue Tests

The specimens, group A to E (Table 3.2), were tested for uniaxial fatigue in accordance with ASTM D7791-17 [62]. An essay (set of preliminary tests) was performed to identify the optimal load ranges for the fatigue testing campaign. The selected stress levels are 13,68 MPa to 16,29 MPa. Each test was repeated once. It is important to remark that the fatigue test campaign lasted a total of 8 months of continuous machine running time. The test conditions are listed in Table 3.2.

The tests were carried out in force control mode and the loads were applied in a sinusoidal waveform. The load frequency was set to 1 Hz. Tests were performed at two different temperatures: 30 ± 2 °C and 24 ± 2 °C.

Table 3.2: Dimensions of specimens used for each test.

Sample	Total length, LO [mm]				Gauge width - W [mm]				Gauge thickness - T [mm]				Test			
	M1	M2	M3	Average	STD	M1	M2	M3	Average	STD	M1	M2		M3	Average	STD
T1.1	164.00	164.00	164.10	164.03	0.05	13.42	13.35	13.37	13.38	0.03	3.79	3.77	3.83	3.80	0.02	Monotonic tensile tests - 2 mm/min
T1.2	164.50	164.60	164.60	164.57	0.05	13.51	13.38	13.42	13.44	0.05	3.80	3.76	3.82	3.79	0.02	Monotonic tensile tests - 2 mm/min
T2.1	163.20	163.20	163.20	163.20	0.00	13.45	13.54	13.38	13.46	0.07	3.81	3.78	3.82	3.80	0.02	Monotonic tensile tests - 6 mm/min
T2.2	165.00	164.80	165.00	164.93	0.09	13.40	13.60	13.20	13.40	0.16	3.75	3.80	3.88	3.81	0.05	Monotonic tensile tests - 6 mm/min
A1	158.00	158.20	158.20	158.13	0.09	13.47	13.42	13.51	13.47	0.04	3.82	3.88	3.77	3.82	0.04	Fatigue test - 13.68 MPa - 30 ±2 °C
A2	157.50	157.40	157.50	157.47	0.05	13.32	13.35	13.31	13.33	0.02	3.64	3.63	3.65	3.64	0.01	Fatigue test - 13.68 MPa- 30 ±2 °C
A3	158.00	158.10	158.00	158.03	0.05	13.38	13.40	13.37	13.38	0.01	3.63	3.63	3.64	3.63	0.00	Fatigue test - 15.39 MPa - 30 ±2 °C
B1	161.10	161.10	161.00	161.07	0.05	13.19	13.24	13.25	13.23	0.03	3.62	3.60	3.60	3.61	0.01	Fatigue test - 15.39 MPa - 30 ±2 °C
B2	158.00	158.20	158.00	158.07	0.09	13.25	13.18	13.22	13.22	0.03	3.57	3.58	3.62	3.59	0.02	Fatigue test - 14.53 MPa - 30 ±2 °C
B3	153.50	153.50	153.40	153.47	0.05	13.23	13.18	13.23	13.21	0.02	3.60	3.62	3.63	3.62	0.01	Fatigue test - 14.53 MPa - 30 ±2 °C
C1	162.00	161.90	161.90	161.93	0.05	13.21	13.18	13.22	13.20	0.02	3.61	3.64	3.64	3.63	0.01	Fatigue test - 14.53 MPa - 24 ±2 °C
C2	162.00	162.00	162.00	162.00	0.00	13.21	13.20	13.22	13.21	0.01	3.62	3.63	3.62	3.62	0.00	Indentation test
C3	159.20	159.00	159.10	159.10	0.08	12.98	13.08	13.02	13.03	0.04	3.70	3.66	3.72	3.69	0.02	Indentation test
D1	161.60	161.60	161.50	161.57	0.05	13.18	13.17	13.20	13.18	0.01	3.59	3.63	3.64	3.62	0.02	Fatigue test - 15.39 MPa - 24 ±2 °C
D2	162.00	162.00	161.90	161.97	0.05	13.26	13.22	13.24	13.24	0.02	3.60	3.60	3.61	3.60	0.00	Fatigue test - 14.53 MPa - 24 ±2 °C
D3	161.50	161.50	161.60	161.53	0.05	13.27	13.28	13.24	13.26	0.02	3.57	3.61	3.59	3.59	0.02	Fatigue test - 15.39 MPa - 24 ±2 °C
E1	162.50	162.40	162.40	162.43	0.05	13.19	13.23	13.25	13.22	0.02	3.61	3.60	3.62	3.61	0.01	Fatigue test - 16.29 MPa - 24 ±2 °C
E2	161.70	161.80	161.80	161.77	0.05	13.26	13.18	13.22	13.22	0.03	3.62	3.58	3.61	3.60	0.02	Fatigue test - 16.29 MPa - 24 ±2 °C
E3	157.00	157.20	157.10	157.10	0.08	12.97	12.96	13.00	12.98	0.02	3.68	3.70	3.70	3.69	0.01	Fatigue test - 15.39 MPa - 24 ±2 °C

Chapter 4

Results and Discussion

Based on the concepts and methodologies presented in chapters 2 and 3, the results of this study are presented in four sections. The first section contains an analysis of the material constitution, including a presentation of the main functional groups found in the FTIR spectrum. The second section deals with the results obtained in tensile tests, analyzing the elastic, transition and inelastic zones. The third section brings an analysis of the material's Brinell hardness (HBW), in addition to the relationship between the indentation depth and the applied force, with an analysis of the force-displacement curves, with the material's compression stiffness, as well as exposing the analytical results. obtained using Hertzian formulas, providing an estimate of the elastic and inelastic behavior of the material. Finally, the fourth part analyzes the behavior of the material under cyclic loading.

4.1 Fourier transform infrared-FTIR

For the analysis of the functional groups present in the samples, the Fourier Transform Infrared Spectroscopy (FTIR) technique was employed, aiming primarily to ensure that the material under study was Polypropylene.

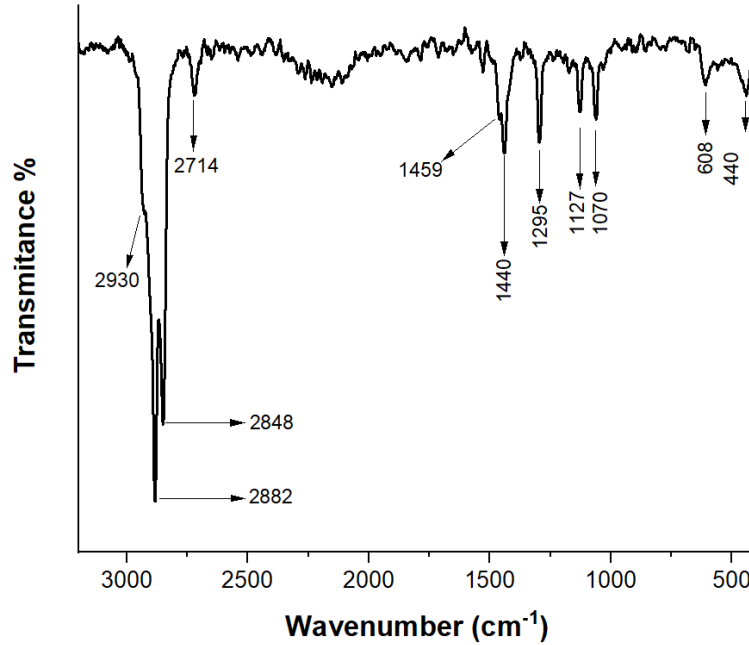


Figure 4.1: Polypropylene FTIR spectrum.

Fig. 4.1 presents the infrared spectrum that confirms that it is a polypropylene (PP) within the 600–3200 cm^{-1} range. The absorption peak at 840 cm^{-1} corresponds to the stretching vibration of the C–CH₃ bond. Additionally, absorption peaks at 1070, 1127, and 1295 cm^{-1} are assigned to the rocking vibrations of the –CH₃ group. The symmetric bending vibration mode of the –CH₃ group is detected at 1440 cm^{-1} . Furthermore, the absorption peak observed at 2930 cm^{-1} is associated with the asymmetric stretching vibration of the –CH₃ group. These absorption peaks collectively indicate the presence of methyl groups in the polypropylene structure. Moreover, the peaks at 1440, 2848, and 2714 cm^{-1} can be attributed to the symmetric bending, symmetric stretching, and asymmetric stretching of the –CH₂– group, respectively.

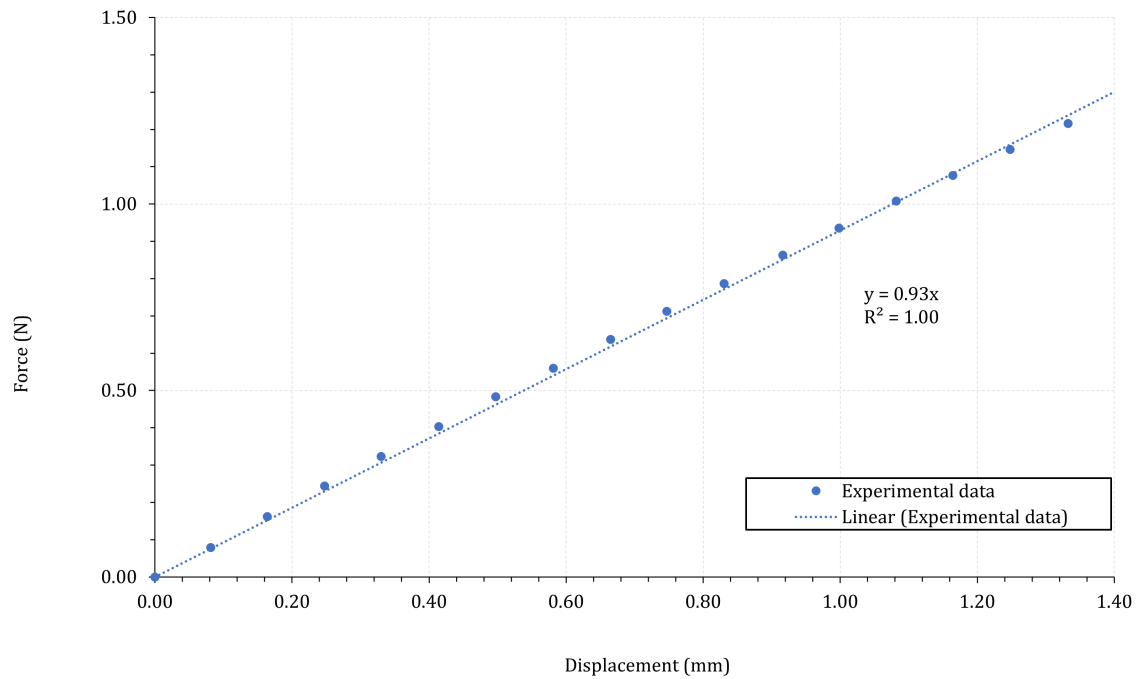
Overall, the obtained infrared spectrum provides valuable insights into the molecular composition and structural features of polypropylene, particularly regarding the presence and behavior of methyl and methylene groups as was reported in [52, 63, 64].

4.2 Tensile tests

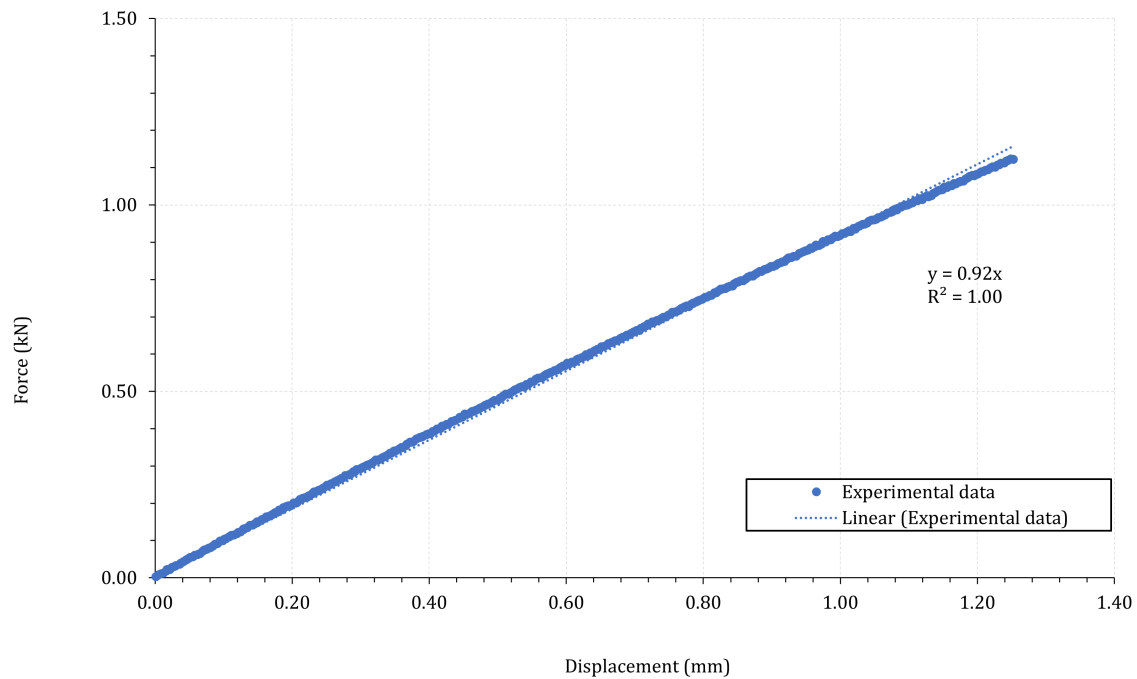
4.2.1 Load-Displacement curves

The force versus displacement curves obtained from four tensile tests on polypropylene, two for each displacement rate, have their average value for each rate shown in Fig 4.2.

The first test was performed at a displacement rate of 2 mm/min, while the second test was performed at a displacement rate of 6 mm/min.



(a)



(b)

Figure 4.2: PP force versus displacement curves:(a) Displacement rate of 2 mm/min;(b) Displacement rate of 6 mm/min.

In both cases, the slope of the curves exhibited a similar trend, indicating comparable mechanical behavior of the material under different deformation rates.

The results revealed that the polypropylene specimens displayed a consistent ratio between force and displacement during the elastic phase of the tensile tests, averaging around 0.9 N/m. This indicates a linear relationship between applied force and deformation within the elastic regime. This linear approximation approached 1.00 due to the uniform choice of the number of significant digits being two. Such behavior is indicative of the material's stiffness and its ability to resist deformation under low-stress conditions.

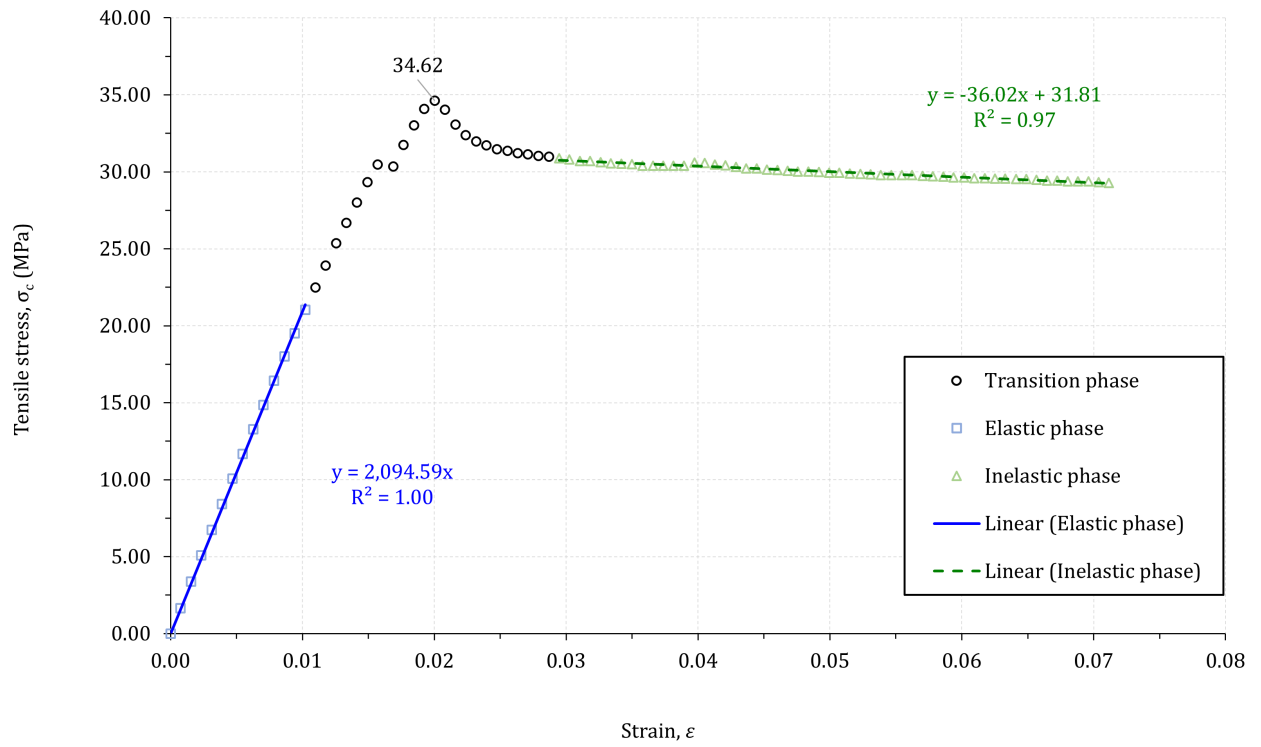
It is worth noting that the similarity in the slope of the force versus displacement curves suggests that the deformation rate had a minimal influence on the mechanical response of the polypropylene samples within the range tested.

The observed consistency in the force versus displacement curves across the different deformation rates signifies the material's stable mechanical response, indicating a reliable and predictable behavior under tensile loading.

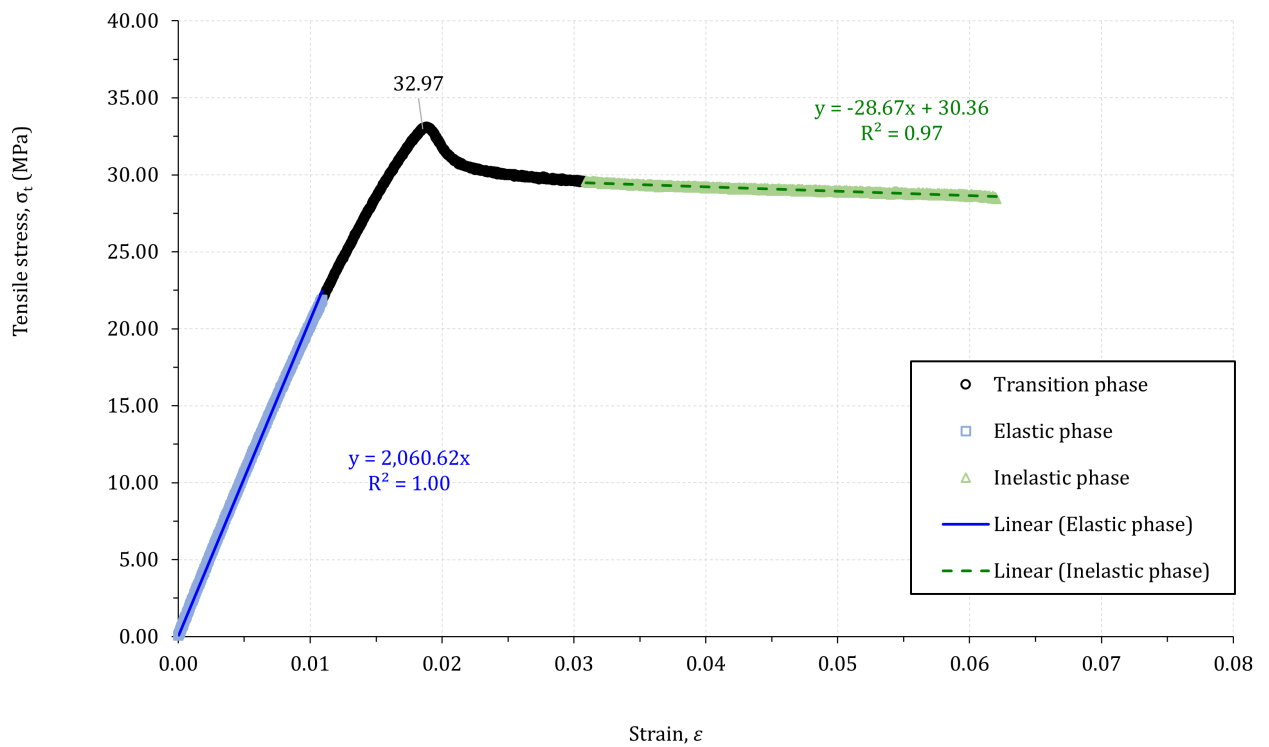
4.2.2 Stress - Strain behavior

Fig. 4.3 shows representative stress-strain curves, performed by averaging the two tests performed for each chosen displacement rate. The tensile tests revealed a dependence of the elastic modulus, E , on the displacement rate, being 2094.0 ± 0.5 MPa for 2 mm/min and 2060.0 ± 0.5 MPa for 6 mm/min, despite the percentage difference found being 1.6%, it was observed that both the modulus of elasticity and the ultimate tensile stress, with a percentage difference of 4.8%, showed a dependence on the displacement rate. Regardless of the chosen displacement rate, the stiffness of the material was calculated and found as k equal to 0.9 N/m. However, a decrease in the modulus of elasticity was observed with the increase in the displacement rate from 2 to 6 mm/min, with this decrease being approximately 34 MPa. It is worth noting that the exact dependence of the modulus of elasticity on the rate of displacement and temperature can vary depending on the specific polypropylene formulation, as well as the test conditions used to measure these properties. In addition, other factors such as molecular weight, molecular weight distribution and degree of crystallinity can also affect the elastic modulus of polypropylene, as shown in [15].

The other relevant parameters (e.g. maximum elongation and inelastic strain coefficient) did not show any correlation to the displacement rate. It is possible for the maximum elongation, and inelastic strain coefficient to not show a significant correlation with displacement rate in certain materials or testing conditions. This is because these parameters are influenced by a variety of other factors in addition to displacement rate, such as the molecular structure, morphology and processing conditions of the material.



(a)



(b)

Figure 4.3: PP stress-strain curves: a) Displacement rate of 2 mm/min; b) Displacement rate of 6 mm/min.

The obtained values of the elastic modulus for a displacement rate of 6 mm/min are higher than 1000 MPa, exceeding the value reported by [65]. Similarly, the maximum stress values are significantly higher than expected ($\sigma_u = 27.0 \pm 1.0$ MPa [65]). The failure mechanism presented in this test was elongation followed by fracture. It was possible to observe that at lower rates, equal to 1 mm/min, the specimen failed due to maximum elongation after the loss of rigidity, at 2 mm/min, elongation and fracture, and at rates equal to or greater than 6 mm/min, fracture.

The viscoelastic behavior of polypropylene combines characteristics of viscous and elastic materials, resulting in a mechanical response that depends both on time, future works, and on the strain rate applied as observed in Fig. 4.3. Viscoelasticity refers to the intermediate mechanical behavior between total elasticity and total viscosity, it is exhibited by some polymeric materials [39]. The deformation behavior of these materials can be described using the concept of viscosity, which measures the resistance of a material to flow under shear force, which was not calculated in the present work.

In the transition zone of the stress-strain curve of polypropylene, significant changes in the mechanical behavior of the material occur, being in the region of $\varepsilon = 0.01$, where the deformation stops being elastic and $\varepsilon = 0.03$, where the deformation starts to be plastic. In this region, deformation increases more rapidly relative to the applied load, resulting in an accelerated increase in polypropylene's deformation. The stress also continues to increase but at a slower rate compared to deformation.

The transition zone is characterized by a shift from elastic to plastic behavior in the polypropylene material. This means that the material starts to undergo permanent deformation even after the removal of the applied load. In this region, the polymer chains of polypropylene begin to slide and rearrange, leading to an increase in plastic deformation.

As plastic deformation increases, the stress reaches its maximum value known as the yield stress, $\sigma_y = 21.03 \pm 0.50$ MPa for 2 mm/min and $\sigma_y = 21.06 \pm 0.50$ MPa for 6 mm/min. Beyond this point, the stress gradually decreases while the deformation continues to increase. This indicates that polypropylene is flowing and undergoing more pronounced deformation.

The transition zone is important for understanding the behavior of polymeric materials such as polypropylene as it signifies the point at which a shift occurs from predominantly elastic to plastic behavior. This has significant implications for the design and application of products made from PP, particularly in situations where permanent deformation and fracture resistance are critical considerations.

In the inelastic zone of PP, also known as the plastic deformation region, the material undergoes permanent or irreversible deformation. This means that the PP experiences a significant change in shape or size without returning to its original state when the applied stress is removed.

During the inelastic zone, the PP molecules undergo rearrangements and slip past each other, leading to the material's ability to sustain plastic deformation. This deformation occurs

due to the movement of dislocations, the creation of new dislocations and the breaking and reforming of intermolecular bonds. The energy required for these processes results in the material exhibiting permanent deformation.

The inelastic zone typically occurs after the material has surpassed its elastic limit or yield point. At this point, the polypropylene has exceeded its ability to elastically deform and enters a regime where the deformation is predominantly plastic. The extent of the inelastic zone depends on various factors, including the applied stress, strain rate, temperature, and molecular structure of the polypropylene.

4.3 Indentation tests

The indentation test data consists of an indentation performed on a polypropylene material using a tungsten carbide indenter with a 5 mm and 15 mm radius. The contact relationship is considered a sphere-plane contact. The data obtained includes the load applied (in Newtons), the depth of the indentation mark (in micrometers), the average of the x and y diameters (in micrometers) and the hardness of the material.

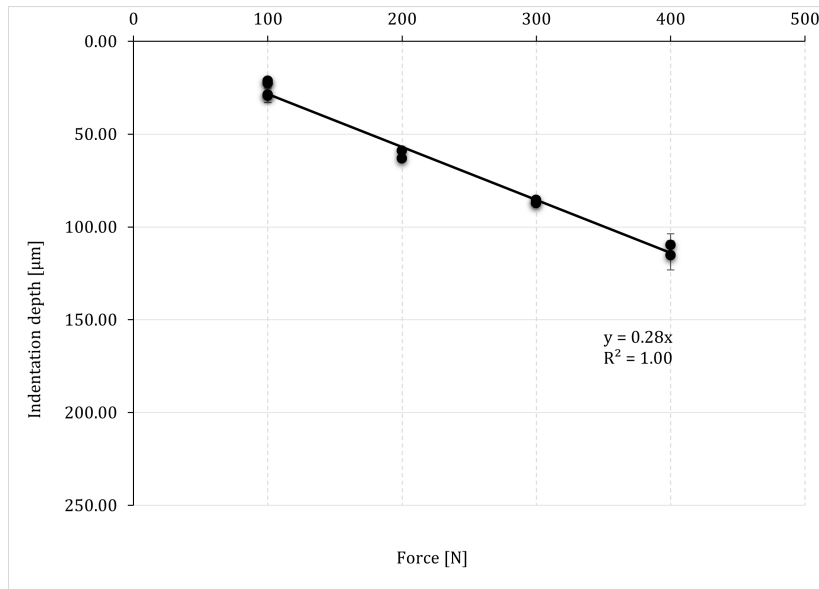
It was observed, in Fig. 4.4 a, that increasing the load from 100 N to 200 N resulted in twice the indentation depth. However, this rate of increase gradually decreases beyond 200 N. This linear approximation approached 1.00 due to the uniform choice of the number of significant digits being two.

The increase in indentation depth in polypropylene can be attributed to several factors. As the load increases, the indenter applies a greater force on the material, causing a higher level of plastic deformation. This plastic deformation results in a larger and deeper indentation, as observed in the table. However, it is important to note that the relationship between load and indentation depth is not strictly linear in polypropylene. Beyond a certain load threshold, the material may exhibit non-linear behavior due to factors such as strain hardening or strain rate effects. These factors can lead to a reduced rate of increase in indentation depth with further load increases, as observed in the graph.

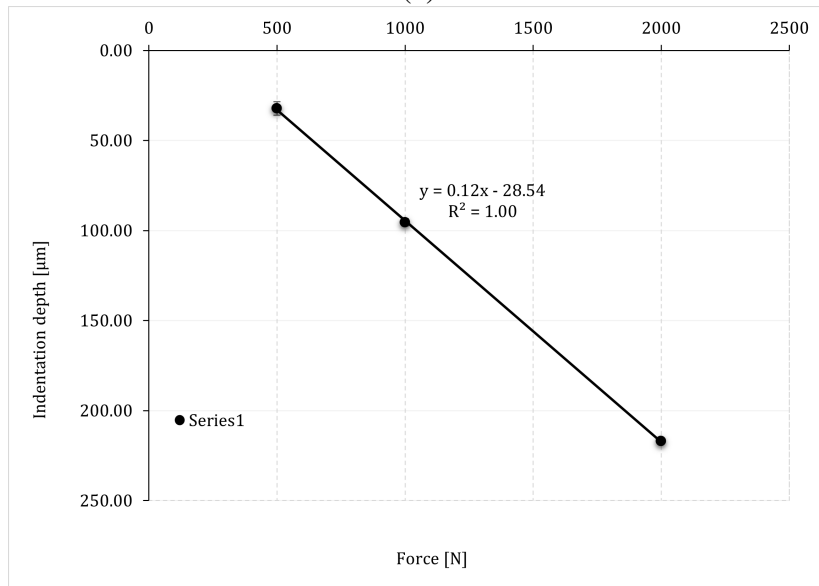
Additionally, polypropylene is a viscoelastic material, meaning it exhibits both viscous and elastic behavior under loading. The time-dependent response of the material can also influence the measured indentation depth. The material's viscoelastic properties, such as its relaxation time or creep behavior, can affect the rate at which the indentation depth increases with load.

However, when higher loads were applied using the 15 mm diameter indenter, Fig. 4.4 b, a linear relationship was observed in the increase of the measured depths.

The increase in indentation depth in polypropylene with the larger 15 mm diameter indenter can be attributed to the following factors: First, the larger indenter applies a higher total force on the material, resulting in a greater amount of plastic deformation and conse-



(a)



(b)

Figure 4.4: Indentation depth versus applied load: a) 5 mm spherical indenter and 3.8 mm thick samples (100 N - 400 N); b) 15 mm spherical indenter and 5.0 mm thick samples (500 N, 1 kN, and 2 kN).

quently deeper indentations. The larger contact area between the indenter and the material also allows for a more efficient transfer of force, leading to increased penetration.

Furthermore, the linear relationship observed between the applied load and the measured depths suggests that the material's response to indentation becomes more predictable and consistent at higher loads. This behavior can be attributed to the material undergoing more pronounced plastic deformation, potentially reaching a stage where the deformation mechanisms are primarily governed by the intrinsic properties of the material rather than external factors.

It is important to note that the linear relationship observed may not hold for all load

ranges or indenter sizes in polypropylene. The material's mechanical properties, including its viscoelastic behavior, molecular structure, and processing conditions, can influence the indentation response and lead to variations in the observed relationship.

By analyzing the load-depth curve and using the above calculations, can gain insights into the mechanical properties of the polypropylene material, including its hardness (Brinell), elastic behavior (contact stiffness), and resistance to elastic deformation (indentation modulus).

In terms of the Brinell hardness of the material, only the tests performed on the Universal Hardness Tester were taken into account. Loadings ranging from 100 N to 400 N were applied, and a variation in measured hardness was observed, ranging from 4.68 HBW at the lowest load to 5.97 Brinell Hardness of Polypropylene when the highest load was applied, as shown in Table 4.1.

Table 4.1: Variation in Brinell Hardness of Polypropylene.

Applied Load (N)	Measured Hardness
100	4.68
200	5.13
300	5.46
400	5.97

The observed variation in Brinell hardness in polypropylene can be attributed to several factors. First and foremost, the applied load plays a significant role in determining the hardness value. As the load increases, the indenter penetrates deeper into the material, resulting in a larger indentation diameter. This increased indentation size leads to a higher hardness value since hardness is calculated based on the ratio of the applied load to the surface area of the indentation.

Furthermore, polypropylene is a viscoelastic material, meaning it exhibits both viscous and elastic behavior under loading. The time-dependent response of the material can influence the measured hardness values. During the indentation process, the polypropylene undergoes a combination of elastic and plastic deformation. The elastic component allows the material to recover partially once the load is removed, while the plastic component results in permanent deformation.

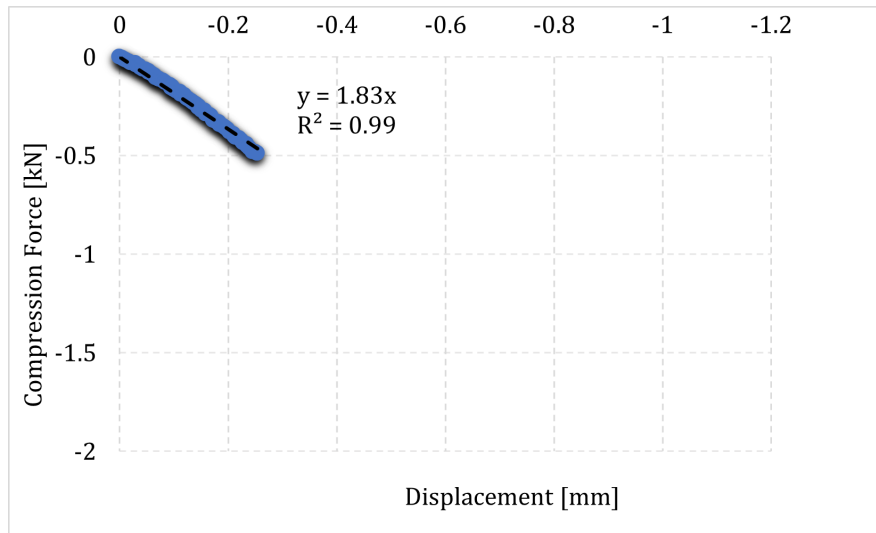
Moreover, polypropylene can exhibit variations in its microstructure, molecular weight, and crystallinity, which can affect its hardness properties. Differences in processing conditions and thermal history can also contribute to variations in hardness. For example, variations in cooling rates during the polymer's solidification process can lead to differences in crystalline structures, which, in turn, can influence the material's hardness.

It is important to note that the measured hardness values are specific to the test conditions and the specific polypropylene sample tested. The inherent heterogeneity of polypropylene and the influence of various factors highlight the need for careful interpretation of hardness

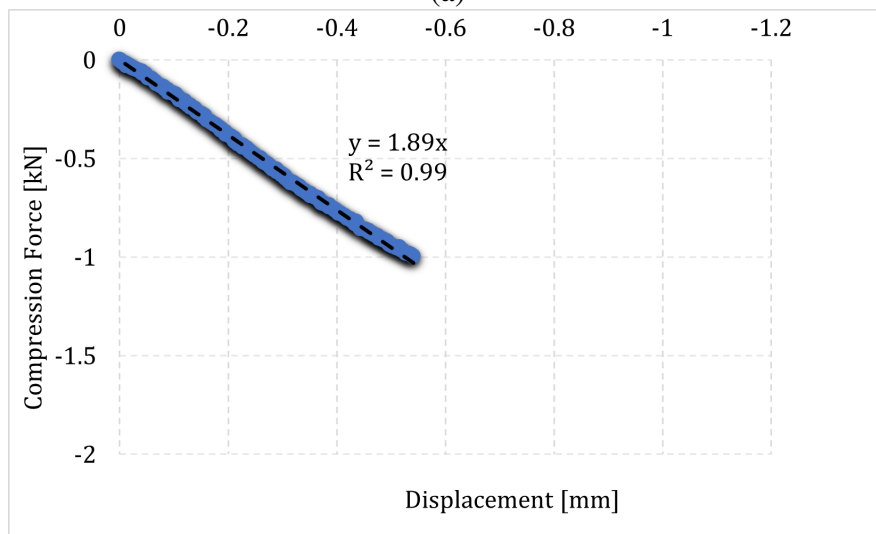
results and consideration of the specific test parameters and material characteristics.

4.3.1 Load-Displacement curves

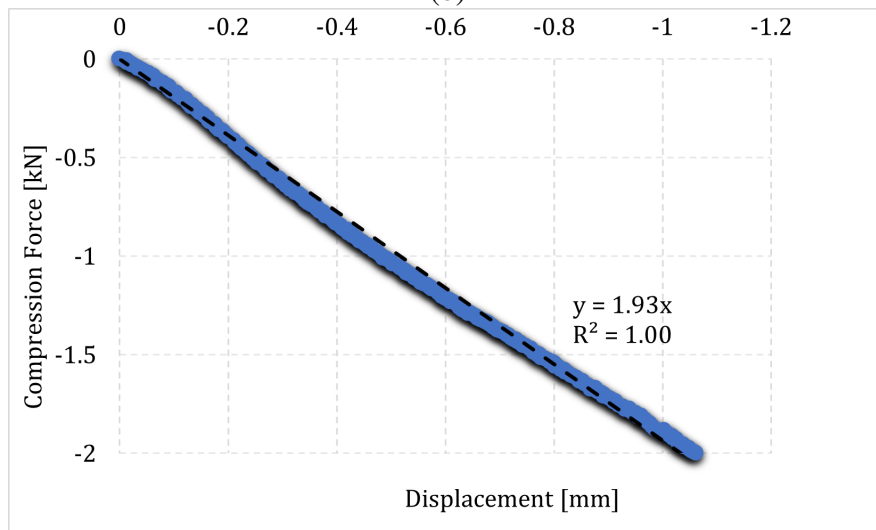
The graphs were generated using processed data, excluding points with fluctuations in the applied load values, and are presented in Fig. 4.5.



(a)



(b)



(c)

Figure 4.5: Load-displacement curves collected during indentation tests for three loads. The loads used: a) 500 N; b) 1 kN; c) 2 kN.

The obtained curves for PP under different conditions, as shown in Fig. 4.5 a, Fig 4.5 b, Fig. 4.5 c, exhibit distinct inclinations. The first curve appears to be linear, while the second and third curves tend to display nonlinear behavior. The selection of these specific load values in this indentation test was motivated by the aim of capturing different material responses. A low load was chosen to represent the elastic regime of the material, an intermediate load was selected to encompass both the elastic and plastic regions, and a third and final load was employed to examine the material's plastic behavior exclusively.

In the elastic regime, the curve shows a linear relationship between the applied load and the displacement a , shown in Fig. 4.5 a, indicating elastic deformation of the material. The slope of this linear region corresponds to the material's elastic modulus.

As the applied load increases, the load-displacement curve may deviate from linearity, indicating the onset of plastic deformation, Fig. 4.5 c. This nonlinearity is often observed as a gradual increase in the slope of the curve, suggesting the material's transition from elastic to plastic behavior. The extent of this nonlinear region provides insights into the material's plastic properties, such as its yield strength and strain hardening behavior.

4.3.2 Stress- Strain behavior

As mentioned previously, the objective of this part of the study was to examine the relationship between indentations and two types of indenters. In both cases, the stress-strain behavior of polypropylene under compression was observed, with lower loads ranging from 100 N to 400 N implemented using a 5 mm diameter indenter, Fig. 4.6, in black and higher loads of 500 N, 1 kN, and 2 kN applied using a 15 mm diameter indenter, in orange. These experimental conditions allowed for the identification of unique characteristics indicative of the material's viscoelastic nature in the plastic phase.

To begin this analysis, with the data obtained from the measurements made in the confocal microscope, the stress and strain values were calculated. For the stress, the maximum stress calculation was used the Eq. (4.1):

$$p_0 = \frac{3F}{2\pi a^2} = \left(\frac{6FE^{*2}}{\pi R_e^2} \right)^{\frac{1}{3}} \quad (4.1)$$

This non-dimensional strain can be expressed mathematically using Eq. (4.2).

$$\epsilon_{ind} = \frac{a}{R_i} \quad (4.2)$$

The non-dimensional strain in Johnson's expression is determined using Tabor's classical equation for the indentation strain, Eq. (4.2). In a more recent study, Bhat et al. [66] proposed

a new definition for the indentation strain, given by:

$$\epsilon_{\text{ind}} = \frac{4}{3\pi} \frac{h_t}{a} \approx \frac{h_t}{2.36a} \quad (4.3)$$

where h_t represents the total depth of indentation and a is the contact radius. This novel definition bears similarity to the classical and intuitive definition of strain, which is the ratio of the change in length (ΔL) to the original length (L). Eq. (4.3) can be visualized as the reduction in the height of a cylindrical region of material with a radius a and an initial height of $2.36a$ (L), caused by an indentation depth of h_t (ΔL). In other words, $\Delta L/L = h_t/(2.36a)$.

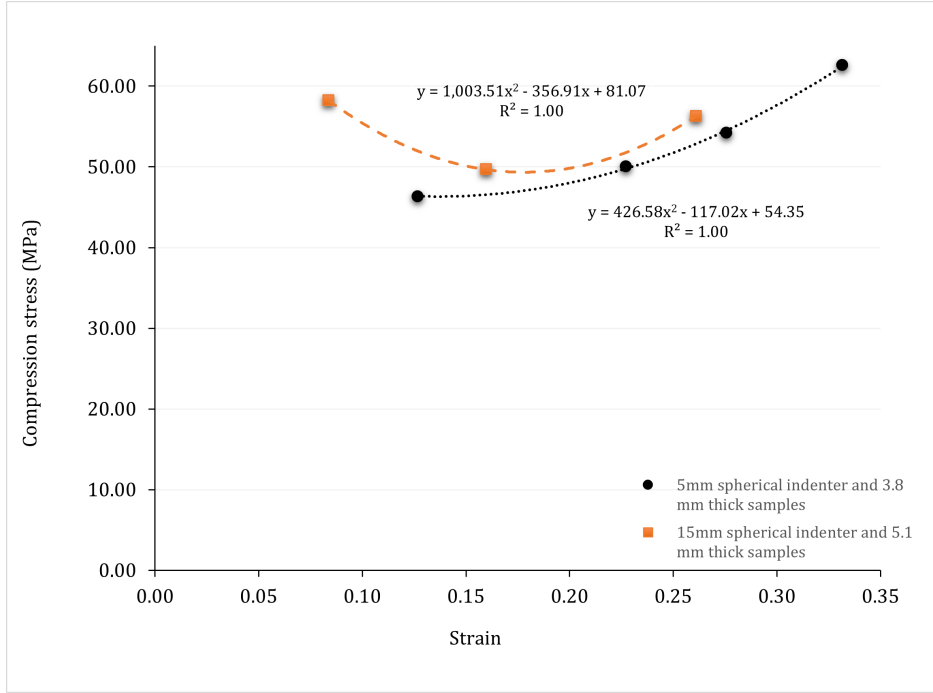


Figure 4.6: The relationship between compressive stress and strain for both types of indenters: 5 mm spherical indenter and 3.8 mm thick samples and 15 mm spherical indenter and 5.0 mm thick samples.

Upon surpassing the yield limit, which signifies the point at which plastic deformation occurs, it was only possible to estimate this limit based on the acquired data. The stress-strain relationship exhibited a quadratic behavior, with values ranging between 50 and 60 MPa. This behavior is a distinctive attribute of the material's viscoelastic properties.

In this study, two distinct materials were utilized, and the contact between the bodies followed a sphere-to-plane configuration. Specifically, the contact involved an offshore steel tool graded as R3 and a PP plate with a radius of $R_1 = 15$ mm, along with polypropylene with an infinite radius ($R_2 = \infty$ mm). The material properties employed were as follows:

Table 4.2: Properties of Steel R3 and Polypropylene [39, 60].

	Steel R3	Polypropylene
Young's Modulus [GPa]	207	E_2
Ultimate Tensile Stress [MPa]	690	33
Yielding Stress [MPa]	410	53.8
Poisson's ratio	0.34	0.40

It is important to emphasize that one of the focuses of this work is to obtain the elastic properties of the material, both in tension and in compression and, as seen in the table above, the aim is to determine the modulus of elasticity of the PP. To start the calculation, the value of a was determined from the force versus displacement data obtained from the 4.5 curves, and from Eq. (4.4).

$$a = \sqrt{d \cdot R_e} \quad (4.4)$$

With this values for a , from Eq. (2.6)

$$E^* = \frac{3P_0 R_e}{4a^3} \quad (4.5)$$

With the values obtained from Eq. (4.5) and using the Eq. (4.6):

$$E^* = \left(\frac{1 - \nu_i^2}{E_1} + \frac{1 - \nu_s^2}{E_2} \right)^{-1} \quad (4.6)$$

In this scenario, with a range of loads from 0 to 20 Newtons ($F = 0 - 20$ N), obtained from the force versus displacement curves, an average modulus of elasticity $E_2 = 1266$ MPa and stiffness of the material was around $k = 0.97$ N/m.

Thus, the stress-strain curve, built analytically, for the elastic regime of polypropylene (PP) is presented below, together with the data referring to the inelastic regime, obtained experimentally, as previously described in Fig. 4.7.

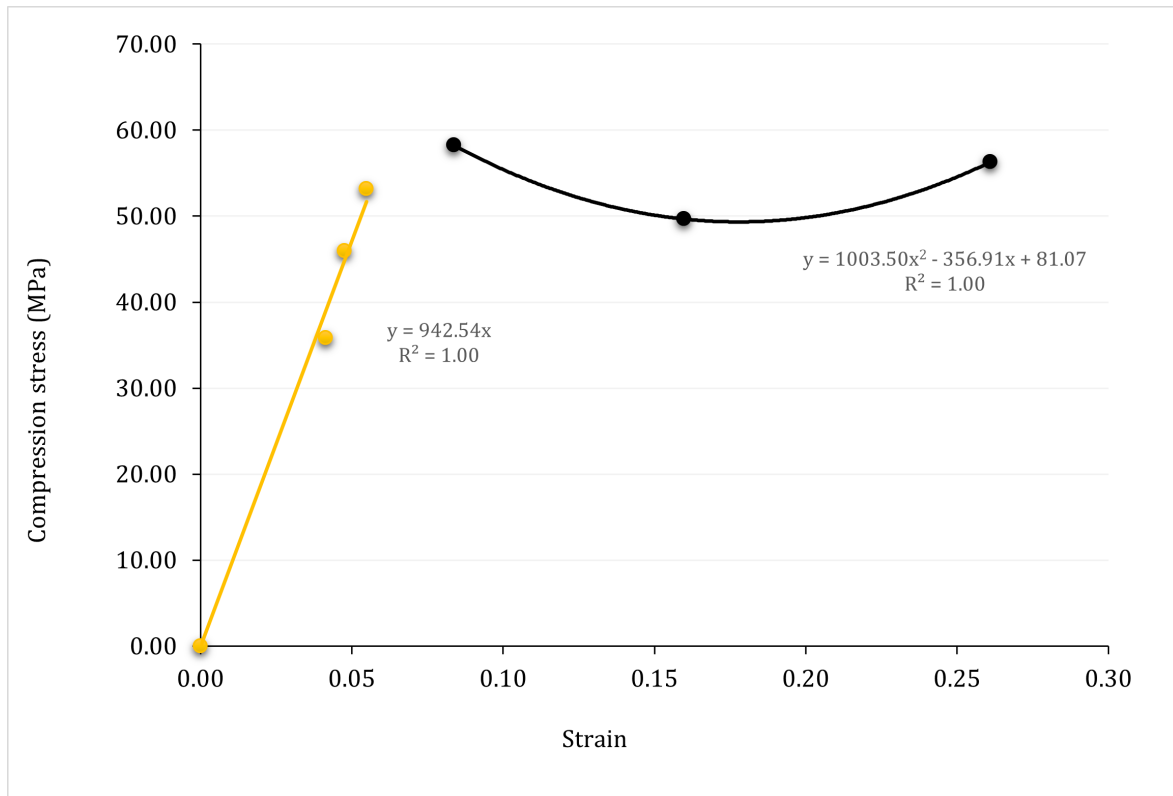


Figure 4.7: Spherical indenter (15 mm of diameter) and 5.0 mm thick samples.

The obtained data reveal significant information about the mechanical properties of the material under different loading conditions. In compression tests, the yield stress denoted as σ_y , was found to be approximately 30 MPa, in line with what was found by [67], while the modulus of elasticity in compression, measured at a rate of 0.5 mm/min, was determined to be 1266 MPa. Comparatively, tensile tests conducted at different loading rates demonstrated variations in the material's behavior. At a rate of 2 mm/min, the modulus of elasticity was approximately 2094.59 MPa, and the yield stress (σ_y) was approximately 21.03 MPa. However, when the loading rate was increased to 6 mm/min, the modulus of elasticity decreased to 2060.62 MPa and the yield stress (σ_y) rose to approximately 21.60 MPa. These findings highlight the rate-dependent nature of the material's mechanical response and emphasize the importance of considering the rate of loading when evaluating its performance and behavior under different conditions.

4.4 Fatigue tests

Fatigue tests were performed ($R = \sigma_{max}/\sigma_{min} = 0.1$) in two different temperatures. The results of the fatigue tests on polypropylene under different loading conditions provide valuable insights into the material's fatigue behavior. In all specimens tested in fatigue, the type of failure observed was by small elongation followed by fracture, being ductile fatigue fracture, Fig. 4.8. The focus of this study was on two specific loading conditions: $R = 0.1$ at

$30 \pm 2^\circ\text{C}$ and $R = 0.1$ at $24 \pm 2^\circ\text{C}$, both tested at a frequency of 1Hz. The temperature was checked about six times a day and was maintained at this interval with the help of fans and the air conditioning system.

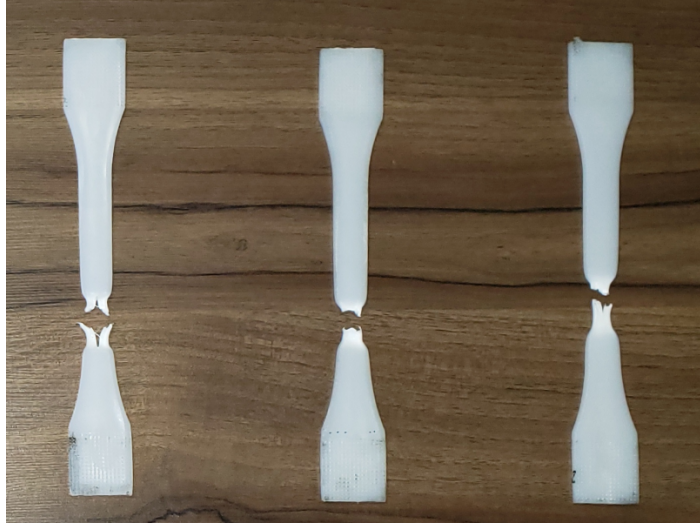


Figure 4.8: Failure mechanism in all fatigue tests: Ductile fatigue fracture.

The fatigue behavior of material within the investigated life regime can be described by the Basquin Eq. (4.7) [32]. Mean stress does have a significant influence on the fatigue life.

$$S_a = A \cdot (N_f)^b \quad (4.7)$$

where S_a is the stress amplitude, N_f is the cycles to failure, A is the intercept at $N_f = 1$, and b is the slope of the fitted curve.

Under the $R = 0.1$ loading condition at $30 \pm 2^\circ\text{C}$, the stress amplitudes ranged from 13.68 to 15.39 MPa. The number of cycles to failure varied between 110,664 and 300,309 cycles. These results indicate that as the stress amplitude decreases, the fatigue life of polypropylene increases. This is in line with the expected behavior of materials subjected to cyclic loading, where higher stress amplitudes lead to shorter fatigue lives.

Similarly, under the $R = 0.1$ loading condition at $24 \pm 2^\circ\text{C}$, the stress amplitudes ranged from 14.53 to 16.29 MPa. The number of cycles to failure varied between 56,466 and 5,300,000 cycles. Notably, the specimens tested at $24 \pm 2^\circ\text{C}$ exhibited higher stress amplitudes compared to those tested at $30 \pm 2^\circ\text{C}$. This suggests that higher temperatures can significantly influence the fatigue behavior of polypropylene, leading to reduced fatigue life and increased vulnerability to failure.

The observed trends in the fatigue behavior of polypropylene can be attributed to various factors. Fatigue failure occurs due to the accumulation of microstructural damage caused by cyclic stress. Higher stress amplitudes result in more rapid damage accumulation, leading to shorter fatigue lives. Additionally, higher temperatures may affect the material's resistance

to crack initiation and propagation, accelerating fatigue degradation.

The specimens tested at $24 \pm 2^\circ\text{C}$ exhibited longer fatigue lives compared to those tested at $30 \pm 2^\circ\text{C}$. For the specimens tested at the highest temperature, the fatigue life reduction was 458062 and 259049 cycles for a 16,29 MPa load condition, which corresponds to a reduction of approximately 98% in this load. Regarding the load of 15,39 MPa, the reduction of fatigue life is 975433 and 1188892 cycles, corresponding to 81% and 83% respectively and finally, when a load of 14,53 MPa is applied, a reduction of 4939207 cycles was observed, about 94% in fatigue life. This indicates that lower temperatures can improve the fatigue performance of polypropylene, allowing it to survive more cycles before failure.

Understanding the fatigue behavior of polypropylene is crucial for its reliable and safe utilization in engineering applications. By considering the stress amplitudes, maximum stresses, and number of cycles to failure, can be make informed decisions regarding the design and service life of polypropylene components. The findings of this study highlight the importance of accounting for loading conditions, including temperature and frequency effects, when assessing the fatigue performance of polypropylene.

Given what is described in the literature regarding the influence of ambient temperature on fatigue tests of thermoplastic polymers, analyzing what had been carried out by Lu et al [24], in this work, the sequence of tests at two different temperatures and with the frequency of loading at 1 Hz, those tests revealed the possible failure limits of the PP stress-life (SN) curve, the fatigue strength and the S-N fatigue behavior of the PP at pure tensile fatigue loads in different temperatures as shown in Fig. 4.9.

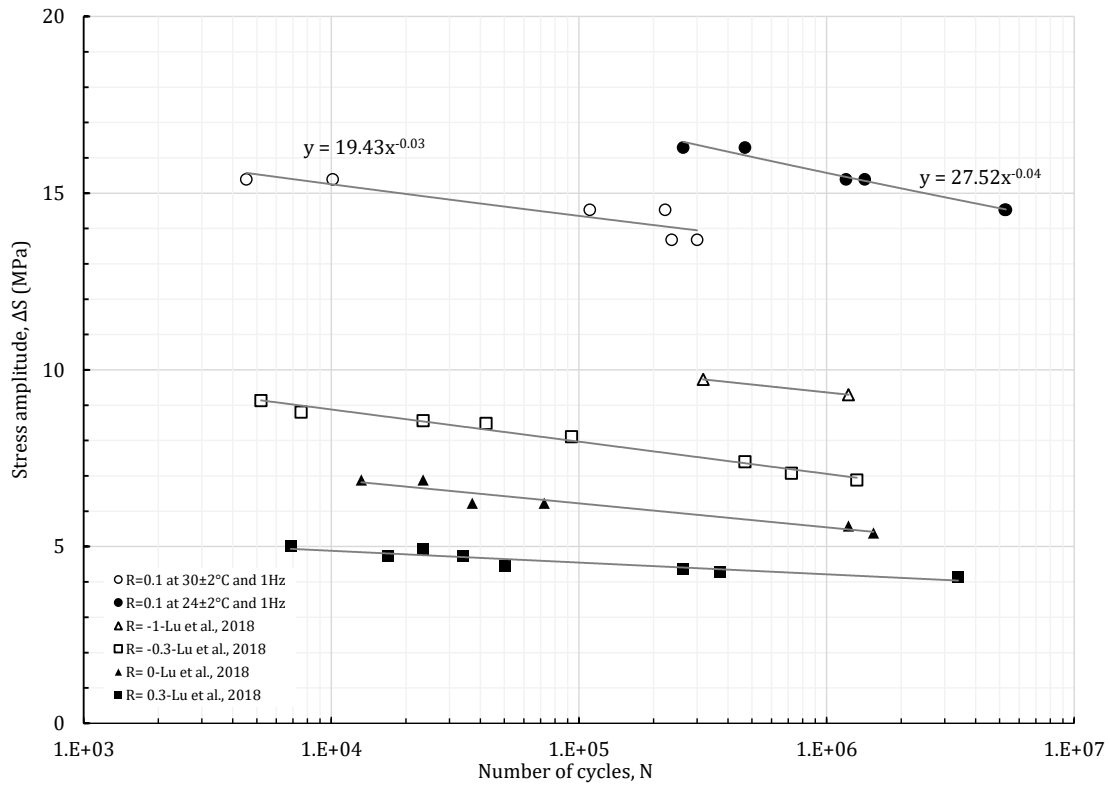


Figure 4.9: Polypropylene stress-life curve at different load ratios.

Along with the available literature for this type of test in polypropylene, the S-N curve was plotted. It was possible to observe that the values in the life in fatigue found in the present work are consistent with those described by [24], Fig. 4.9, which corresponds to a combination of the data obtained by Lu et al [24], in different stress ratios and those obtained in this work with $R = 0.1$, in which frequency and temperature were taken into account. Thus, it was possible to observe, as previously mentioned, that the decrease in temperature caused a significant increase in the number of cycles experienced from loading at 13.68 to 16.29 MPa. This behavior can be explained by the fact already discussed and referred to in previous studies [3, 7], that the increase in the frequency of fatigue tests in polymers causes a heating of the reference length zone.

Chapter 5

Conclusion

This chapter is divided into two sections. The first section addresses the main conclusions obtained in this study, as well as all the elastic properties of polypropylene that could be extracted from the results. The second section presents suggestions for future works.

5.1 Overview

Indentation tests performed on polypropylene revealed important findings about its mechanical behavior. Increasing load resulted in a corresponding increase in indentation depth, indicating elastic deformation followed by plastic deformation. However, the relationship between load and depth was not linear beyond a certain limit, probably due to strain hardening or strain rate effects. Furthermore, the use of a larger indenter showed a relationship similar to that found for the smaller indenter, in the relation between load and depth, suggesting only a scale variation, but the same behavior. The tests also provided information about the hardness of the material, with values ranging from 4.68 to 5.96 on the Brinell scale.

The indentation tests carried out on polypropylene resulted in curves with different inclinations, representing different responses of the material, however, consistent with each other. The first curve exhibited a linear relationship between load and displacement with a lower slope rate, indicating elastic deformation at load values up to approximately 125 N. The second and third curves continued to show linearity up to approximately the same load value, suggesting the onset of plastic deformation from then on. By selecting specific load values, the tests exclusively captured the elastic (through the analytical resolution of Hertz formulas) and plastic behavior of the material (experimentally found). The linear region provided information about the elastic modulus of the material, while the non-linear regions indicated plastic deformation and provided information about the material's plastic properties, including yield strength and strain hardening behavior. It was also possible to observe, when comparing the values of displacement of the indenter and depth of indentation measured in the confocal microscope, that the elastic recovery of this material is between 80 and

90%, an expected value for a polymer.

Tensile tests confirmed the expected relationship between elastic modulus, ultimate tensile stress and displacement rate. As the displacement rate is increased from 2 to 6 mm/min, a percentage decrease of 1.6% in the modulus of elasticity is observed, while for the ultimate tensile stress limit, there is a reduction of 4,8%. However, the other relevant parameters such as maximum elongation and coefficient of inelastic deformation did not show a correlation with the displacement rate.

The values obtained in the compression and tension tests provide crucial information about the mechanical behavior of the material. In compression, the material exhibited a compressive modulus of elasticity of 1266 MPa and yield stress of approximately 39.8 MPa. On the other hand, in tensile tests performed at different loading rates, the material showed a tensile modulus of elasticity of 2094.6 MPa and a yield stress of approximately 21 MPa at a loading rate of 2 mm/min, while at a loading rate of 6 mm/min, the tensile modulus decreased to 2060.6 MPa and the yield stress rose to approximately 21.6 MPa. These findings emphasize the importance of considering compressive and tensile properties for a comprehensive understanding of material performance in various applications.

Concerning material fatigue, these tests proved to be consistent with the available literature, being a complement to what is available regarding pure polypropylene [24]. In addition, it was possible to observe that the failure mechanism in all fatigue tests remained the same, being initiated by a small elongation, followed by fracture. Due to the cost and excessive time required in the tests, it was not possible to perform other load ratios, however, it was possible to observe that the decrease in temperature increases the fatigue life.

There is a considerable scatter (or variability) in the results of the fatigue tests conducted at the two temperatures ($30 \pm 2^\circ\text{C}$ and $24 \pm 2^\circ\text{C}$) under the same loading ratio ($R = 0.1$) and frequency (1 Hz). The stress amplitudes and the corresponding number of cycles to failure show a wide range of values for both temperature conditions.

At 30°C , the stress amplitudes range from 13.68 % to 16.29 % of the maximum stress, and the number of cycles to failure varies from 10,121 to 300,309 cycles. This significant variation in the number of cycles to failure suggests a considerable scatter in the fatigue behavior of the material at this temperature.

On the other hand, at 24°C , the stress amplitudes also range from 13.68 % to 16.29 % of the maximum stress, but the number of cycles to failure shows a much larger variation, ranging from 263,586 to an impressive 5,300,000 cycles. This wide range of cycle numbers indicates a more pronounced scatter in the fatigue performance of the material at 24°C .

The observed scatter in the fatigue test results can be attributed to several factors, including inherent material variations, microstructural heterogeneity, and the sensitivity of the material to temperature changes. These variations can influence the initiation and propagation of fatigue cracks, leading to different fatigue lives under seemingly identical test conditions. A summary of the values of the properties found in this work is shown in Table 5.1:

Table 5.1: Elastic Properties of Polypropylene in Traction and Compression.

Property	Symbol	Value [Unit]
Elastic Modulus (2mm/min)	E	2094.6 ± 0.5 [MPa]
Elastic Modulus (6mm/min)	E	2060.6 ± 0.5 [MPa]
Yield Strength (2mm/min)	σ_y	21.0 ± 0.5 [MPa]
Yield Strength (6mm/min)	σ_y	21.1 ± 0.5 [MPa]
Ultimate Tensile Strength	σ_u	33.7 ± 0.8 [MPa]
Poisson's Ratio	ν	0.33
Hardness	H	5.02 ± 0.4 [HBW]
Tensile Stiffness	k_t	0.90 ± 0.50 [N/m]
Compression Stiffness	k_c	0.97 ± 0.50 [N/m]

5.2 Future works

Based on the results of the indentation and tensile tests on polypropylene, there are several avenues for future research. First, investigating the underlying mechanisms responsible for the observed non-linear behavior in the load-depth relationship during indentation may provide a better understanding of the material's behavior. This may involve studying the effects of strain rate, temperature, and molecular structure on the inelastic response of polypropylene. Additionally, analyzing the material's creep behavior, given its viscoelastic nature, could be explored.

Furthermore, it would be valuable to explore the relationship between measured mechanical properties, such as hardness and modulus of elasticity, and the microstructural properties of polypropylene. This may involve techniques such as microscopy and spectroscopy to analyze the internal structure of the material and its influence on mechanical behavior.

Furthermore, performing additional fatigue tests on polypropylene under different loading conditions and frequencies would provide information on the long-term durability of the material. Understanding the fatigue behavior of polypropylene is crucial to assess its suitability for applications involving cyclic loadings, such as automotive components and structural elements.

In addition, extending the study to other types of polypropylene or variations in processing conditions would allow a broader understanding of the material's behavior, as well as other forms of production, such as additive manufacturing. Comparing the mechanical properties and creep characteristics of different grades of polypropylene or the incorporation of additives can provide information on how to optimize the material for specific applications.

Finally, considering the environmental aspects of polypropylene, it would be relevant to investigate its behavior in different environmental conditions, such as exposure to ultraviolet radiation or humidity. Understanding the material's response to environmental factors is crucial to assessing its long-term performance and suitability for outdoor applications.

Overall, these suggested future research directions would contribute to advancing the understanding of the mechanical behavior of polypropylene and allow the optimization of its properties for a wide range of industrial applications.

REFERENCES

- [1] M. Al-Maadeed, Y. M. Shabana, P. N. Khanam, Processing, characterization and modeling of recycled polypropylene/glass fibre/wood flour composites, *Materials & Design* 58 (2014) 374–380.
- [2] M. Van den Oever, T. Peijs, Continuous-glass-fibre-reinforced polypropylene composites ii. influence of maleic-anhydride modified polypropylene on fatigue behaviour, *Composites Part A: Applied Science and Manufacturing* 29 (3) (1998) 227–239.
- [3] A. M. Abdelhaleem, M. Megahed, D. Saber, Fatigue behavior of pure polypropylene and recycled polypropylene reinforced with short glass fiber, *Journal of Composite Materials* 52 (12) (2018) 1633–1640.
- [4] F. Stan, A.-M. Turcanu, C. Fetecau, Analysis of viscoelastic behavior of polypropylene/carbon nanotube nanocomposites by instrumented indentation, *Polymers* 12 (11) (2020) 2535.
- [5] S. V. Canevarolo, *Ciência dos polímeros*, Vol. 24, Artiber editora, São Paulo, 2002.
- [6] H. Namazi, *Polymers in our daily life*, *BioImpacts: BI* 7 (2) (2017) 73.
- [7] G. Papanicolaou, S. Zaoutsos, Viscoelastic constitutive modeling of creep and stress relaxation in polymers and polymer matrix composites, in: *Creep and fatigue in polymer matrix composites*, Elsevier, 2019, pp. 3–59.
- [8] J. Li, Z. Zhu, T. Li, X. Peng, S. Jiang, L.-S. Turng, Quantification of the young's modulus for polypropylene: Influence of initial crystallinity and service temperature, *Journal of Applied Polymer Science* 137 (16) (2020) 48581.
- [9] J. R. Rocha, K. Z. Yang, T. Hilbig, W. Brostow, R. Simoes, Polymer indentation with mesoscopic molecular dynamics, *Journal of Materials Research* 28 (21) (2013) 3043–3052.
- [10] E. Amitay-Sadovsky, H. D. Wagner, Evaluation of young's modulus of polymers from knoop microindentation tests, *Polymer* 39 (11) (1998) 2387–2390.

- [11] S. Canevarolo, F. De Candia, R. Russo, Stereoblock polypropylene/isotactic polypropylene blends. ii. mechanical behavior, *Journal of applied polymer science* 55 (3) (1995) 387–392.
- [12] R. Strapasson, S. Amico, M. Pereira, T. Sydenstricker, Tensile and impact behavior of polypropylene/low density polyethylene blends, *Polymer testing* 24 (4) (2005) 468–473.
- [13] R. H. Alasfar, S. Ahzi, N. Barth, V. Kochkodan, M. Khraisheh, M. Koç, A review on the modeling of the elastic modulus and yield stress of polymers and polymer nanocomposites: effect of temperature, loading rate and porosity, *Polymers* 14 (3) (2022) 360.
- [14] K.-t. Ma, H. Shu, P. Smedley, D. L'Hostis, A. Duggal, A historical review on integrity issues of permanent mooring systems, *Offshore technology conference* (2013) 24025.
- [15] J. Li, Z. Zhu, T. Li, X. Peng, S. Jiang, L.-S. Turng, Quantification of the young's modulus for polypropylene: Influence of initial crystallinity and service temperature, *Journal of Applied Polymer Science* 137 (16) (2020) 48581.
- [16] J. Vina, A. Argüelles, A. Canteli, Influence of temperature on the fatigue behaviour of glass fibre reinforced polypropylene, *Strain* 47 (3) (2011) 222–226.
- [17] M. Amjadi, A. Fatemi, Tensile behavior of high-density polyethylene including the effects of processing technique, thickness, temperature, and strain rate, *Polymers* 12 (9) (2020) 1857.
- [18] Q. Fu, D. Niu, J. Zhang, D. Huang, Y. Wang, M. Hong, L. Zhang, Dynamic compressive mechanical behaviour and modelling of basalt–polypropylene fibre-reinforced concrete, *Archives of Civil and Mechanical Engineering* 18 (3) (2018) 914–927.
- [19] D. Tesfay, S. Balakrishnan, F. Ashine, P. Sivaprakasam, Sisal fibre/polypropylene composites properties by plunger injection moulding, *Materials Today: Proceedings* 62 (2022) 448–453.
- [20] A. Bourmaud, C. Baley, Investigations on the recycling of hemp and sisal fibre reinforced polypropylene composites, *Polymer Degradation and Stability* 92 (6) (2007) 1034–1045.
- [21] R. M. Rowell, H. P. Stout, *Jute and kenaf*, Fiber Chemistry (1998).
- [22] S. Suresh, *Fatigue of materials*, Cambridge university press, 1998.
- [23] A. Van der Wal, J. Mulder, R. Gaymans, Fracture of polypropylene: The effect of crystallinity, *Polymer* 39 (22) (1998) 5477–5481.
- [24] Z. Lu, B. Feng, C. Loh, Fatigue behaviour and mean stress effect of thermoplastic polymers and composites, *Frattura ed Integrità Strutturale* 12 (46) (2018) 150–157.

- [25] M. Amjadi, A. Fatemi, Creep and fatigue behaviors of high-density polyethylene (hdpe): Effects of temperature, mean stress, frequency, and processing technique, *International Journal of Fatigue* 141 (2020) 105871.
- [26] H. S. Kim, S–n curve and fatigue damage for practicality, in: *Creep and Fatigue in Polymer Matrix Composites*, Elsevier, 2019, pp. 439–463.
- [27] K. L. Johnson, K. L. Johnson, *Contact mechanics*, Cambridge university press, 1987.
- [28] H. Hertz, *Ueber die berührung fester elastischer körper.*, Walter de Gruyter, Berlin/New York Berlin, New York (1882).
- [29] V. L. Popov, M. Heß, E. Willert, *Handbook of contact mechanics: exact solutions of axisymmetric contact problems*, Springer Nature, 2019.
- [30] W. C. Oliver, G. M. Pharr, Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology, *Journal of materials research* 19 (1) (2004) 3–20.
- [31] A. S. of Testing, Materials, ASTM e10-18: Standard test method for brinell hardness of metallic materials, *Book of Standards Volume 03.01* (2018).
- [32] N. E. Dowling, S. L. Kampe, M. V. Kral, *Mechanical behavior of materials: engineering methods for deformation, fracture, and fatigue*, Pearson Education, 1999.
- [33] C. G'Sell, J. Hiver, A. Dahoun, A. Souahi, Video-controlled tensile testing of polymers and metals beyond the necking point, *Journal of materials science* 27 (1992) 5031–5039.
- [34] C. G'Sell, A. Dahoun, F. Royer, M. Philippe, The influence of the amorphous matrix on the plastic hardening at large strain of semicrystalline polymers, *Modelling and Simulation in Materials Science and Engineering* 7 (5) (1999) 817.
- [35] M. Kitagawa, T. Onoda, K. Mizutani, Stress-strain behaviour at finite strains for various strain paths in polyethylene, *Journal of materials science* 27 (1992) 13–23.
- [36] H. Kausch, C. Plummer, The role of individual chains in polymer deformation, *Polymer* 35 (18) (1994) 3848–3857.
- [37] C. Popelar, C. Popelar, V. Kenner, Viscoelastic material characterization and modeling for polyethylene, *Polymer Engineering & Science* 30 (10) (1990) 577–586.
- [38] C. Zhang, I. D. Moore, Nonlinear mechanical response of high density polyethylene. part ii: Uniaxial constitutive modeling, *Polymer Engineering & Science* 37 (2) (1997) 414–420.
- [39] W. D. Callister, D. G. Rethwisch, et al., *Materials science and engineering: an introduction*, Vol. 7, John wiley & sons New York, 2007.

- [40] W. Flügge, *Viscoelastic Models*, Springer Berlin Heidelberg, 1975.
- [41] J. Epaarachchi, 17 - the effect of viscoelasticity on fatigue behaviour of polymer matrix composites, in: R. M. Guedes (Ed.), *Creep and Fatigue in Polymer Matrix Composites*, Woodhead Publishing Series in Composites Science and Engineering, Woodhead Publishing, 2011, pp. 492–513.
doi:<https://doi.org/10.1533/9780857090430.3.492>.
URL <https://www.sciencedirect.com/science/article/pii/B9781845696566500178>
- [42] A. D. Mulliken, M. C. Boyce, Mechanics of the rate-dependent elastic–plastic deformation of glassy polymers from low to high strain rates, *International journal of solids and structures* 43 (5) (2006) 1331–1356.
- [43] M. C. A. d. Cruz, *Correlações entre propriedades dinâmico-mecânicas e durabilidade sob fadiga mecânica em compósitos de polipropileno/polipropileno maleificado/fibra de vidro*, Ph.D. thesis, Universidade Federal de São Carlos (2006).
- [44] H. F. Mark, *Encyclopedia of polymer science and technology.*, Vol. 14, Wiley New York, NY, USA:, 2014.
- [45] E. ROSA, *Análise de resistência mecânica: mecânica da fratura e fadiga*, Santa Catarina RS: Grante (2002).
- [46] J. E. Shigley, L. D. Mitchell, H. Saunders, *Mechanical engineering design*, McGraw-Hill Science/Engineering/Math, 1985.
- [47] B. J. Goodno, J. M. Gere, *Mechanics of materials*, Cengage learning, 2020.
- [48] A. A. Gorni, *Introdução aos plásticos*, *Revista plástico industrial* 10 (09) (2003).
- [49] L. Marques, *O que são polímeros e porque são interessantes*, *Jornal" Diário do Sul* (2009).
- [50] J. Ferreira, J. Costa, P. Reis, Static and fatigue behaviour of glass-fibre-reinforced polypropylene composites, *Theoretical and Applied Fracture Mechanics* 31 (1) (1999) 67–74.
- [51] H. A. Maddah, Polypropylene as a promising plastic: A review, *Am. J. Polym. Sci* 6 (1) (2016) 1–11.
- [52] J. Karger-Kocsis, *Polypropylene: An A-Z Reference*, Polymer Science and Technology Series, Springer Netherlands, 1998.
URL <https://books.google.com.br/books?id=ZQ5HAAAAYAAJ>

- [53] G. Machado, Estudo da morfologia e cristalinidade em polipropileno isotático submetido a deformação uniaxial em temperatura ambiente, Ph.D. thesis, Universidade Federal do Rio Grande do Sul. Instituto de Química. Programa de Pós-Graduação em Ciências de Materiais. (2002).
- [54] M. Shibata, Z. Xiaochuan, R. Yosomiya, Impact properties of the polymer blend of polypropylene and thermoplastic elastomer, *Journal of Macromolecular Science—Pure and Applied Chemistry* 35 (7) (1998) 1207–1215.
- [55] S. Luz, Estudo das propriedades mecânicas, interface e morfologia de compósitos de polipropileno reforçados com fibras de bagaço e palha de cana. 2008. 153f, Ph.D. thesis, Tese (Doutorado em Biotecnologia Industrial)—Escola de Engenharia de Lorena ... (2008).
- [56] A. S. of Testing, Materials, ASTM d638-14: Standard test methods for tensile properties of plastics, *Book of Standards Volume 08.01* (2014).
- [57] Thermo Scientific Nicolet iS20 FTIR Spectrometer, <https://www.thermofisher.com/order/catalog/product/br/en/IQLAADGAAGFAHDMAPC> (2023).
- [58] Olympus 3D Laser Measuring Solution, <https://www.olympus-ims.com/pt/metrology/ols4000/> (2023).
- [59] Universal Hardness Tester, <https://www.zwickroell.com/products/hardness-testing-machines/universal-hardness-testing-machines> (2023).
- [60] T. Pandim, T. Doca, A. Figueiredo, F. A. Pires, Torsional fretting wear experimental analysis of a r3 offshore steel against a pc/abs blend, *Tribology International* 143 (2020) 106090.
- [61] MTS Landmark Testing Solutions, <https://www.mts.com/br/products/materials/dynamic-materials-test-systems/landmark-servo-hydraulic> (2023).
- [62] A. S. of Testing, Materials, ASTM d7791-17: Standard test methods for uniaxial fatigue properties of plastics, *Book of Standards Volume 08.03* (2017).
- [63] P. Larkin, *Infrared and Raman spectroscopy: principles and spectral interpretation*, Elsevier, 2017.
- [64] J. Luongo, Infrared study of polypropylene, *Journal of Applied Polymer Science* 3 (9) (1960) 302–309.

- [65] S. M. d. Luz, S. M. d. Costa, A. R. Gonçalves, A. P. Del'Arco Junior, S. A. d. Costa, Polypropylene composites reinforced with biodegraded sugarcane bagasse fibers: static and dynamic mechanical properties, *Materials Research* 19 (2016) 75–83.
- [66] A. Bhat, R. W. Neu, An improved methodology for extracting uniaxial stress–strain curves from spherical indentation data, *Mechanics of Materials* 174 (2022) 104459.
- [67] A. H. Awad, R. El Gamasy, A. Abd El Wahab, M. H. Abdellatif, Mechanical and physical properties of pp and hdpe, *Eng. Sci* 4 (2019) 34–42.