

Wood-biopolymers Composites

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Abstract

This Master's thesis aimed at bringing a new use to sawdust. Sawdust is an inherent residue of the wood industry in its most varied branches, being that, to invest in its recycling is an advantage to be combating the waste of raw material, in other words, looking for sustaining the "Zero Waste" policy, the reuse and reutilization of waste.

As a way of providing a new application to sawdust, two new composite materials were created containing wood in the form of sawdust in its constitution. Besides the addition of sawdust, it was also sought that these composites, of the polymeric matrix, constitute a more environmentally friendly option than the existing options until then. These composites are derived from the polymers polyglycerol citrate and glycerine with corn starch. They were chosen because they use natural products or products from eco-friendly processes.

As the main purpose of this thesis is the use of sawdust, it was also established as an objective of this work the attempt of increasing the mass of wood inserted in the polymer that serves as a matrix to the composite concerning the already existing commercial solutions, namely the ones that use PLA mixed with wood.

An attempt was made to produce filament for FDM 3D printing using the composite glycerine/corn starch/ sawdust in which, in turn, there was also a focus on increasing the mass of wood present in the filament when compared to commercial samples of Polylactic Acid (PLA) mixed with wood.

Finally, mechanical and physical-chemical tests were carried out on the glycerine/corn starch/ sawdust composite.

Keywords: Biopolymers; Biocomposites; Sawdust; Wood; Sustainability

Resumo

Com esta tese de mestrado pretendeu-se dar uma nova utilização ao serrim. O serrim é um resíduo inerente da indústria da madeira nos seus mais variados ramos, sendo que, apostar na sua reciclagem constitui uma vantagem ao se estar a combater o desperdício de matéria-prima, ou seja, procurando sustentar a política do "Zero Waste", a reutilização e reaproveitamento de resíduos.

Como forma dar uma nova utilização ao serrim, criaram-se 2 novos materiais compósitos com madeira na forma de serrim na sua constituição. Além da adição de serrim, procurou-se ainda que estes compósitos, de matriz polimérica, constituíssem uma opção mais amiga do ambiente que as opções até então existentes. Os polímeros utilizados nestes compósitos, poliglicerol citrato e a glicerina com o amido de milho foram escolhidos dado na sua constituição recorrerem a produtos naturais ou provenientes de processos ecologicamente amigos.

Posto que o propósito principal desta tese é a utilização do serrim, estabeleceu-se também como objetivo deste trabalho a tentativa de aumentar a massa de madeira inserida no polímero que serve de matriz ao compósito em relação às soluções comerciais já existentes, nomeadamente as que utilizam PLA misturado com madeira.

Foi realizada uma tentativa de produção de filamento para impressão 3D em FDM utilizando o compósito glicerina/ amido de milho/ serrim em que, por sua vez, existiu também um foco no aumento da quantidade de madeira presente no filamento quando comparado com as amostras comerciais de Poliacido Láctico (PLA) misturado com madeira.

Finalmente, foram feitos testes mecânicos e físico-químicos ao compósito glicerina/ amido de milho/ serrim.

Palavras-chave: Biopolímeros; Biocompósitos; Serrim; Madeira; Sustentabilidade

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Nomenclature

σ : Strength

E : Young Modulus

ε : Extension

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List of Acronyms

ABS	Acrylonitrile Butadiene Styrene
AM	Addictive Manufacturing
ASTM	American Society for Testing and Materials
BSF	Banana Pseudo Stem Fibre
bio-PE	bio-polyethylene
bio-PET	bio-polyethylene terephthalate
bio-PP	bio-propylene
CAD	Computer-Aided Design
CF	Curauá fibres
CNC	Computerized Numerical Control
DDGS	Distillers dried grain
DTG	Differential thermal analysis
FDM	Fused Deposition Modelling
FFF	Fused Filament Fabrication
FGMs	Functionally Graded Materials
GRAS	Generally Recognized As Safe
IUPAC	International Union of Pure and Applied Chemistry
LDI	Lysine Diisocyanate
MAPP	Maleic Anhydride Grafted Polypropylene
MDF	Medium Density Fibreboard
Micro-ct	Micro-computed Tomography
PA-11	Nylon 11 or Polyamide 11
PEEK	Polyether Ether Ketone
PE	Polyethylene
PEF	Polyethylene Furanoate
PEI	Polyethyleneimine
PETG	Polyethylene Terephthalate Glycol-modified
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

PLA	Polylactic acid
PLGA	Poly (lactic-co-glycolic acid)
PLLA	Poly-L-lactide
PDMS	Polydimethylsiloxane
PP	Polypropylene
PVA	Polyvinyl Alcohol
PVC	Polyvinyl Chloride
SEM	Scanning Electron Microscopy
SS	Saccharum spontaneum
TG/TGA	Thermal gravimetric analysis
TPC	Thermoplastic copolyester
TPS	Thermoplastic-sheathed
WF	Wood Flour
WPC	Wood-plastic Composite
XRM	3D X-ray Microscope

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1. Introduction

This work addresses the process of obtaining 2 new composites of biopolymer origin, from its idealization, through its conception, to its characterization using physicochemical and mechanical tests and an attempt to produce filament for 3d printing. The starting point of this work was the search for raw materials from natural sources or eco-friendly manufacturing processes, which could be applied in the development of new composites with wood. From the research originally done, it was not possible to find much information about the polymers used in the development of the composites.

1.1. Motivation

Currently, there is a strong attempt to ensure the preservation of the environment, which has driven industries to use and research more environmentally friendly raw materials (Horta et al., 2017).

Wood is an abundant natural and renewable material present on planet earth (Palser, 2009). The trees, from which the wood is obtained are responsible for balancing the ecosystems. Wood is used for the most diverse industrial purposes (Lippke et al., 2010).

The trees that compose the forests spread throughout the world are great lungs of the earth, as they are responsible for transforming the carbon dioxide produced by the most varied living activities into oxygen, which is necessary for the existence of life (Palser, 2009). Figure 1 also tells us that each cubic metre of the forest can transform, in approximate values, 1 metric tonne of carbon dioxide into 700 kg of oxygen.

Thus, the use of wood and reuse of its surpluses represents a positive activity from the environmental and economic point of view, providing a circular economy and following the zero-waste rule (Long et al., 2010). For the wood industry, the cutting of trees is essential, but if this felling is followed by subsequent reforestation and, consequently, a sustainable renovation of the forest area, we are not only contributing to the preservation of the forests but also to the maintenance of the economy in this area, since the necessary raw material for its correct functioning is guaranteed, with a waste reduction.

For the appropriate functioning of forests, it is also necessary to guarantee a constant forest renewal, in which the oldest trees are successively cyclically replaced by new ones. This not only contributes to an optimised efficiency in the photosynthesis process but also allows the wood from older trees to be used industrially, without jeopardising the air renewal cycle (CEI-Bois, 2009). This process is called forest development on a sustainable basis. It is estimated that 90% of the wood used in Europe for industrial purposes comes from forests developed on a sustainable basis. It is also guaranteed that more trees are planted than are cut down, in a spread equivalent to the area of Cyprus, 806,000 hectares. Analysing the data for the total amount of sawn wood by the amount that is planted in Europe, and knowing that Europe produces annually about 100 million cubic metres of sawn wood, we can conclude that the wood industry plays a very important role in the sustainable development of ecosystems (Palser, 2010).

Industrially, wood and its respective by-products are the main components used in the furniture industry, a commodity found in most buildings used by human beings (Trang et al., 2016). Being this industry considered subtractive (Lucisano et al., 2016), i.e., starting from one or more large pieces and, by processes of material subtraction such as cutting and sanding, obtaining the final product, there is a lot of material that is wasted, and on average only 40% of wood is used (Oliveira et al., 2017).

This solid wood waste constitutes a loss of profitability for the producer in the form of sawdust, wood strips, and waste, which is undesirable both from an economic and environmental point of view, so the aim is to reuse it (Feitosa, 2007).

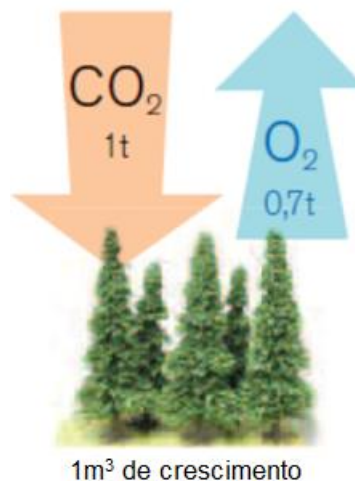


Figure 1 - Representation of photosynthesis, performed by trees (adapted from WOODNA, 2021).

Although there are already ways of reusing wood waste, such as using it to produce biomass, pellets, and wood-based panels like MDF, they represent very high investments for the industrialists of the furniture industry sector, who, due to lack of economic possibilities, cannot invest in equipment to make this reuse, accumulating them in their facilities (EOS/OES, 2019; Fernandes De Abreu, 2005; Scheeper et al., 1995). Moreover, the companies responsible for the production of biomass cannot reach all the factories, and the minimum requirements in terms of contamination of wood waste are not always met, since there are limit values for the existence of contaminants (residues of varnish, inks and other treatments given in the furniture, production of wood panels and by-products) (EPF, 2018).

There is a global increase in plastic consumption, which, not only due to its long residence time in the earth's environment but also to economic factors, leads to a great need to create biodegradable products. Plastic is so globally necessary for everyday use that in 2010, 57 million tonnes of plastic were produced in Europe on its own (Fatimah Kader Sultan & Lutfi Wan Johari, 2017). There is, therefore, a strong necessity to reduce dependence on the consumption of petrochemical feedstocks to reduce environmental pollution (Gonzalez-Gutierrez et al., 2010; Mariano-Torres et al., 2015; Rosentrater & Otieno, 2006).

As 3D printing is a technology in notorious growth at the scientific and industrial level, representing a trend in the future, it is really interesting to relate it with waste reduction and circular economy (Campbell et al., 2011). Unlike most of the industry, 3d printing represents an additive production method to produce the desired product (Perkins & Skitmore, 2015). It is therefore a challenge to combine additive manufacturing with wood, in order to reduce the waste of this raw material during its manufacture, as it can be reused by manufacturers to produce other necessary elements in their activity, reducing costs and contributing to a more sustainable environment.

Although there are already some solutions in this sense, namely using PLA mixed with wood, these solutions do not represent the greenest way to reuse wood (Faludi et al., 2013; Gregorova et al., 2011). According to Zhao et al., considering a closed recycling cycle of the PLA used in 3D printing in its most varied variants, the reprinting process using this material can only be carried out twice without this polymer losing its mechanical and viscosity properties, important for correct printing. It has also been proven that the most effective way to recycle this polymer is incineration, which, despite not only being a polluting process, does not allow the material to be reutilised. For this reason, it is important to create new biopolymers, also compatible with wood, that is truly environmentally friendly.

1.2. Objectives

The objectives of this thesis are the development and study of the physical-chemical and mechanical characteristics of 2 composites, which meet the following requirements:

- The biopolymer matrices of the composites should be bio-based and use raw materials that are products or by-products of low-polluting or eco-friendly processes.
- Promote the use of residues resulting from the wood industry, i. e., sawdust.
- They must be biodegradable biopolymers.
- Have a similar visual appearance to wood.

In this way, besides the development of these new products, it was also sought to study their properties in order to be able to characterise them. They may also be used in 3D printing, in Fused Deposition Modelling (FDM).

Considering all these factors, these materials were sought to be a more ecological and sustainable alternative to the polymeric composites with wood already existing in the market, as well as applicable in an additive printing technology.

1.3. Thesis Outline

Chapter 1, Introduction: in this section, the motivation for this thesis and the reason for its elaboration, its scientific relevance and main objectives are explained.

Chapter 2, State of the Art: an overview of the information present in the literature about the category of polymers and composites that are being studied, as well as the use of its compounds in the production of other polymers.

Chapter 3, Materials & Methods: this chapter describes the materials that will be used to study the two composites that were developed in the thesis, as well as the preparations that were carried out to obtain them. Also, the physical-chemical and mechanical tests that were performed to characterize the materials, as well as an attempt to extrude filament for 3D printing in Fused Deposition Modelling (FDM) are discussed.

Chapter 4, Experimental: the results obtained from the preparation of each of the polymer variants are analysed, comparing the possibilities studied. The mechanical and physical-chemical tests that were carried out are also analysed, as well as the results of the printed filament.

Chapter 5, Results & Discussion: in this chapter, the results obtained in the mechanical tests of this work are more deeply discussed, also looking for the interconnection between all the stages mentioned in the previous chapters.

Chapter 6, Conclusions: summarizes the whole document, exposes the lessons learned, the original contributions, mentions the works to be performed in the future and, also, some final remarks of the work were developed.

2. State of the Art

2.1. Biopolymers

Biopolymers are considered advanced materials, which are materials with ground-breaking features reinforcing new manufacturing technologies and processes, such as FDM printing, and the opportunities to fabricate entirely new technologies and products based on raw materials (Mitchell, 2018). Biomaterials term is usually used to mean biomedical, biological, and bioderived materials (Sayem et al., 2020), where biopolymers can also be considered due to their relations with the two last categories. According to Shahbazi & Jäger, 2021, nowadays biopolymers are the most used materials for 3d printing.

Polymers are synthetic materials composed of long chains of carbon monomers and other substances. If most of the polymers that are used nowadays are fossil-based, history says that the first polymers that were produced were bio-based, namely celluloid (van Wijk & van Wijk, 2015). It is known that polymers, in general, are often used in industry and they have a wide variety of applications as we can see in figures 2 and 3.

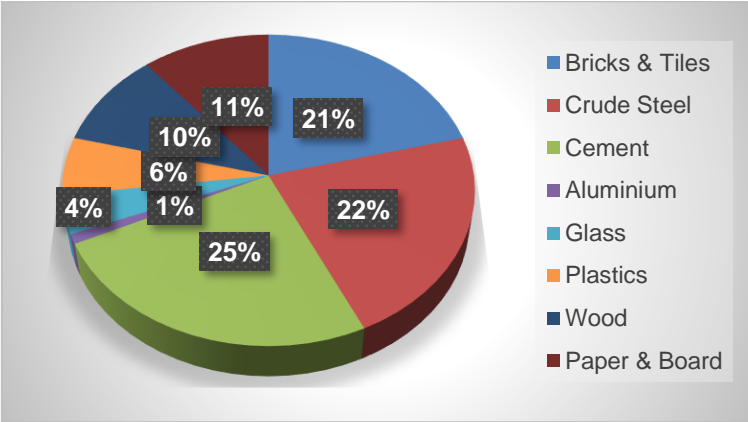


Figure 2 - Market shares of bulk materials (adapted from van Wijk & van Wijk, 2015).

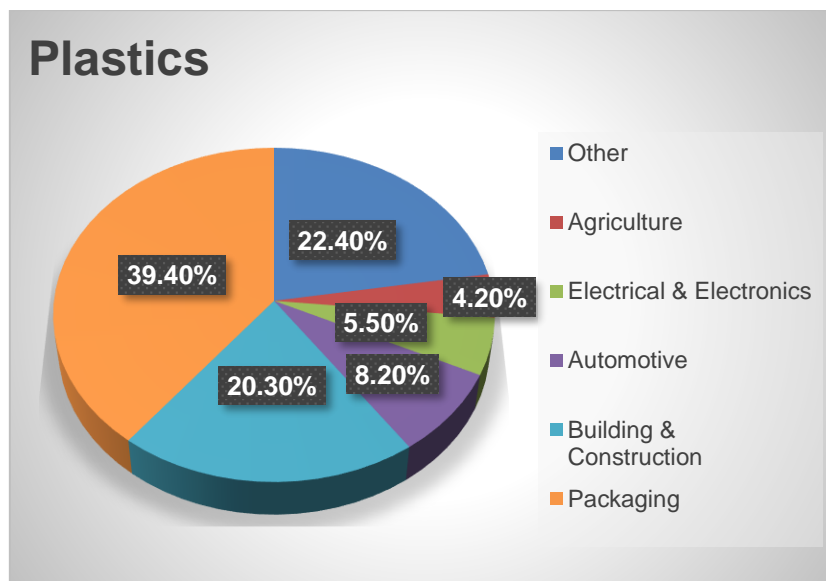


Figure 3 - Polymers applications (adapted from van Wijk & van Wijk, 2015).

Bioplastics or biopolymers, according to European Bioplastics Organization, is a really wide concept. These words include bio-based and biodegradable polymers, which are 2 kinds of materials (Verma & Fortunati, 2018). If bio-based materials are the ones that are bio-products made from living organisms like trees and plants, biodegradable materials are the ones that can be degraded naturally (Yang et al., 2018). To be a biopolymer does not necessarily mean that it is biodegradable, because, according to the official definition of this word, fossil-based polymers are in this category (Verma & Fortunati, 2018). Because of these facts, biopolymers can be divided into 3 distinct groups: biodegradable biobased, biodegradable fossil-based, and nonbiodegradable biobased. These groups are presented in the table 1.

Table 1 - Biopolymer categories and examples (adapted from E. Yang et al., 2018).

Groups of Biopolymers	Examples
Biodegradable Biobased	Polylactic acid, polyhydroxyalkanoates, starch blends (including Mater-Bi®), polybutylene succinate (Adipate) [PBS(A)]
Biodegradable Fossil-based	Polybutylene adipate terephthalate, [PBS(A)], polycaprolactone, polyvinyl alcohol
Nonbiodegradable Biobased	Bio polyethylene terephthalate, bio polyethylene, Polyethylenefuranoate, Bio polypropylene, bio polyamides (Nylon/bioPA), polytrimethylene terephthalate

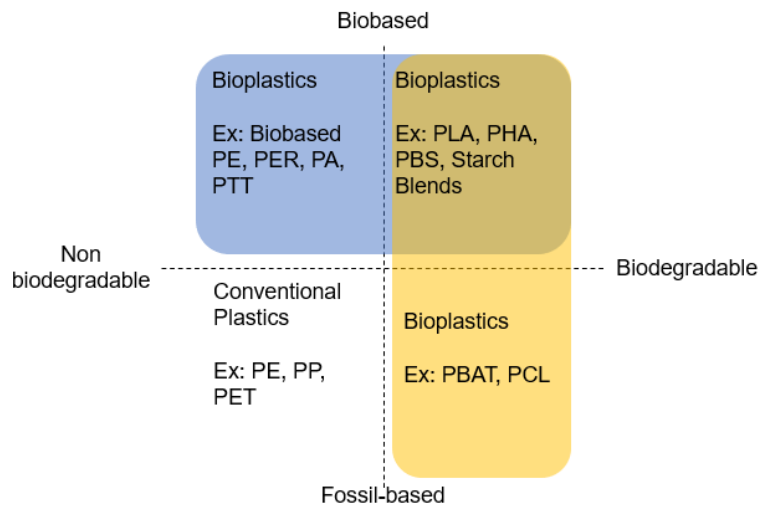


Figure 4 - Type of Polymers related to source and biodegradability (adapted from Gokhale, 2020).

Biodegradability is a fuzzy term since some polymers may degrade very fast in certain conditions but take a lot of time in another. So, one timeframe and environment should be defined to evaluate this subject with scientific meaning (Verma & Fortunati, 2018). In figure 4, a relation between biodegradability and categories of polymers can be seen. Biodegradable plastics are those which degradation is a consequence of the action of naturally occurring microorganisms like bacteria, fungi, and algae (American society for testing and materials, 2019).

IUPAC (International Union of Pure and Applied Chemistry) considers a polymer as bio-based if it is “composed or derived whole or in part of biological products issued from the *biomass* (including plant, animal, and marine or forestry materials)” (Gokhale, 2020; Vert et al., 2012). It is relevant to mention that bio-based does not mean *environmentally friendly* nor *biocompatible* nor *biodegradable* (Vert et al., 2012). Bio-based polymers can be split into drop-in or novel polymers.

A ‘drop-in’ bio-based biopolymer is a kind of “bio-similar” reinterpretation of petrochemical polymers, but it is made from biomass instead of fossil oil. One advantage of ‘drop-in’ bio-based biopolymers is that they can be used industrially almost immediately, without requiring major modifications to the technology or equipment used in fossil-based polymers. Bio-Ethylene, bio-polyethylene (bio-PE), bio-propylene (bio-PP), bio-polyethylene terephthalate (bio-PET) are some examples of ‘drop-in’ bio-based biopolymer (Barrett, 2018).

On the other hand, there are completely novel bio-based polymers with a chemical structure like no other, for example, PLA and PEF (Verma & Fortunati, 2018).

There are a lot of bio-based polymeric materials such as PLA, PLLA (poly-L-lactide), PLGA (poly(lactic-co-glycolic acid)), TPC (thermoplastic copolyester), TPS (thermoplastic-sheathed), PA-11 (nylon 11 or polyamide 11) and PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) (van Wijk & van Wijk, 2015). The most dominant is PLA (The European Plastics Industry, 2013).

Biopolymer's utilization in 3D Printing starts to be common in a large range of industries, such as biomedical, textile, food, aerospace, automotive, and bioindustrial. This fact leads to substantial interest from academics, environmentalists, and society at large. The most widely used biopolymer in AM is PLA, but starch, cellulose, chitosan, lignin, alginate, and polycaprolactone (PCL) are also used to print (Pradhan et al., 2021; Sandanamsamy et al., 2021).

2.2. Corn Starch in biopolymers

Starch represents one of the strongest sources for the development of biopolymers (Fatimah Kader Sultan & Lutfi Wan Johari, 2017). Since that time, corn has been developed and used, and today it is a well-known source of starch and has become one of the largest sources of human food (Fatimah Kader Sultan & Lutfi Wan Johari, 2017). In countries with high farm output, corn starch is abundantly produced and at low prices (Maulida et al., 2016; Ohkita & Lee, 2006). Given the fact that starch in certain regions of the world is produced in abundance and at low prices, it has also become one of the most frequently used raw materials in the manufacture of biopolymers, intending to replace fossil-based polymers (Fakhouri et al., 2013). Thanks to the abundance of corn production, the food industry has no shortage of feedstock caused by its use in the manufacture of biopolymers, thereby maintaining its low price for both sectors. The interest in using corn to produce biopolymers is coincident with the emergence of biopolymers as well, given that as early as the beginning of the 20th century, the well-known Henry Ford started using soybean and corn oil to manufacture the parts for his cars (The Henry Ford, 2021).



Figure 5 - Corn starch and glycerine biopolymer

The polymers produced using starch exhibit several characteristics that make them an interesting object of study, the most relevant of which is their high biodegradability, especially their decomposition in the soil (Nandiyanto et al., 2020). Up to now many research has been carried on the synthesis of biopolymers made from starch, including corn starch in specific, as can be seen in table 2. However, observing the same table, it can be seen that the biodegradability of a biopolymer does not always contribute to its good mechanical properties, as there are polymers based on corn starch that, while presenting good biodegradability, had less favourable mechanical properties. The factor that most

highlights this fact is that there is little information on the properties of pure biopolymers, without any type of reinforcement component, which would be important to have in order to carry out a correct study of their properties (Nandiyanto et al., 2020).

Table 2 a)- Sample of existing reports on the synthesis of biopolymers with corn starch (adapted from Nandiyanto et al., 2020).

Raw Material	Results	Reference
Corn starch, sodium benzoate, dimethyl sulfoxide, and photosensitizer	The best condition was obtained by adding 0.75% of sodium benzoate. The surface morphology is uniform and homogeneous	(Zhou et al., 2008)
Corn starch, glycerol, and sorbitol	Biopolymers by casting method had a lower thickness and had a greater tensile strength compared to that by pressing and blowing method	(Fakhouri et al., 2013)
Corn starch, polylactide, lysine diisocyanate (LDI)	Corn starch decreased the thermal stability of biopolymer. LDI increased the temperature of thermal degradation (compared to biopolymer without LDI) and decreased biodegradability. LDI allowed a homogeneous surface morphology	(Ohkita & Lee, 2006)
Corn starch, potassium hydroxide, formaldehyde, resorcinol, and <i>Saccharum spontaneum</i> L. (SS)	Addition of SS as an amplifier improved mechanical properties and thermal stability. Biopolymer degradation time with the amplifier requires 60 days	(Maiti et al., 2010)
Corn starch, taro starch, glycerol, and distilled water	Taro starch improved mechanical properties and thermal stability	(Dai et al., 2015)

Table 2 b) - Sample of existing reports on the synthesis of biopolymers with corn starch (adapted from Nandiyanto et al., 2020).

<p>Corn starch, banana pseudostem fibre (BSF), and glycerol</p>	<p>10% of BSF increased tensile strength and Young's modulus. The surface morphology of the fill particle in the aggregate biopolymer matrix</p>	<p>(Hermansyah et al., 2014)</p>
<p>Corn starch, polydimethylsiloxane (PDMS), and acetoxypolysiloxane (Acetoxy-PDMS; Elastosil E43)</p>	<p>Biopolymer prepared with PMDS has good elongation and tensile strength compared to that without PMDS. SEM Surface morphology was uniform and homogeneous</p>	<p>(Ceseracciu et al., 2015)</p>
<p>Corn starch, glycerol, white vinegar, titanium dioxide nanoparticles (TiO₂) as reinforcing agents</p>	<p>TiO₂ increased the tensile strength of biopolymers from 3.55 to 3.95 MPa, decreased elongation from 88 to 62%, and increased decomposition temperature. Morphology was a homogeneous surface with fewer cracks</p>	<p>(Amin et al., 2019)</p>
<p>Corn starch, distillers dried grain (DDGS), and phenolic resin</p>	<p>DDGS and phenolic resins improved mechanical properties. 25% of DDGS concentration gave good tensile strength. Up to 75% of DDGS increased biodegradability from 0 to 38% and reduced surface hardness</p>	<p>(Tatara et al., 2009)</p>
<p>Corn starch, polypropylene (PP), calcium carbonate, Maleic anhydride grafted polypropylene (MAPP), curauá fibres (CF), and potassium hydroxide</p>	<p>The addition of CF increased hardness, tensile strength, and Young's modulus, as well as decreased bio composite extension. Biopolymer had a homogeneous surface with the addition of CF and MAPP</p>	<p>(Lenz et al., 2018)</p>

2.3. Glycerine in Biopolymers

Glycerine is a water-soluble polyol. One of the sources of glycerine is as the main by-product resulting from biodiesel production, made through the transesterification of oils and fats (Goyal et al., 2021; Hayyan et al., 2010; Mota et al., 2009). After the reaction is complete, glycerine is separated by centrifugation and then used in a wide range of applications, such as pharmaceuticals, cosmetics, the food industry, lubricants, polymer creation, etc (Vicente et al., 2007). An important feature of products developed using glycerine is that they are generally biocompatible, which makes them suitable for use in the health and cosmetics sectors (Goyal et al., 2021). Focusing on the importance of glycerine in polymer creation, this by-product is an important agent in the plasticisation of polymers, together with water (Halpern et al., 2014; Karande et al., 2020; Mariano-Torres et al., 2015; Rezende et al., 2019). Glycerine is used in plasticisation to improve mechanical properties and water solubility (Karande et al., 2020).

Even though not many studies have been found in the scientific literature, the use of glycerine is becoming increasingly present in research into biopolymers. In particular, Mariano-Torres et al., 2015, when researching an innovative polymer that combines citric acid and glycerine, explored the effect of the relative composition has on the development of polyglycerol citrate. The higher the proportion of glycerine in the mixture, the lower the polymer's viscosity will be, while the efficiency of the reaction will be higher, as will be the amount of saturated citric acid protons. The behaviour resulting from the increasing glycerine content in the polymer is related to the existence of OH- groups, in which in the 1:1 (figure 6) ratio there is less intensity of OH groups at the end of the reaction than in the other ratios, namely 1:3. Thus, the 1:1 polymer initially presented a hard, very inflexible, and fragile behaviour, however, after a few weeks in air, it gains flexibility and hardness due to humidity absorption. A potentially interesting feature of this polymer is its good biodegradability (Mariano-Torres et al., 2015). Identical studies have been developed by other researchers, such as Rezende et al., 2019, in which the conclusions were similar (Rezende et al., 2019).



Figure 6 - Polyglycerol citrate (1:1)

Halpern et al., 2014, also worked with citric acid and glycerine. From their experimental process, carried out by esterification, they concluded that, regardless of the molar ratios, the polymer being studied is a thermoset. For the development of this material, no catalyst is needed, and it is a simple, economic process using biocompatible monomers. They also concluded that the chemical and mechanical properties of the final biopolymer depend on the conditions adopted for the preparation of the polymer such as curing temperature, time and molar ratio (Halpern et al., 2014).

Another example of polymer development using glycerol was done by Forrester et al., 2020. A family of acrylic polymers was designed using a multi-acrylic glycerol monomer, again, through an esterification process. This work sought to respond to the great demand for bio-derived plastics, combined with the large supply of glycerine in the market since it is considered that there is a lack of viable glycerol polymers in the market. The final application of this polymer is to be used as a sustainable wood adhesive (Forrester et al., 2020).

2.4. Wood-Polymer Composites

Wood composites are defined as materials that bond together small pieces of wood, usually waste resulting from wood manufacturing operations, to produce products with specific and definable physical and mechanical qualities. Wood composites are the class of materials most abundantly used in construction at present (Matuana & A. Heiden, 2005).

As a general rule, WPCs (Wood-Polymer Composites) result from the by-products from two different industries, which in itself represents an environmental and economic advantage (Horta et al., 2017). These composites, mainly used in the form of decking boards, pavements and railing systems, are mostly based on polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) (Klyosov, 2007). In smaller quantities, WPCs are also used as cladding, fencing, pallets, roofing tiles, and window frame liners. Other uses such as pilings, railroad ties, marinas, shutters, and noise barriers are rather experimental, not yet marketed, or sold at a very small fraction compared to the main WPC products. Automotive products also often make use of this solution (Klyosov, 2007).

This range of composite products already represents a strong presence on the market, with sales of 220,000 tonnes per year in Europe in 2010. However, the marketing of wood composites begins in 1972, when the "Gruppo Ovattifici Riuniti" (GOR) created the "Woodstock" WPC for the cars of the Italian Fiat. A year later, in 1973, in Sweden, Sonneson AB created PVC-wood fibre floor tiles. Over decades, many research and improvement activities have been carried out in this field, and this sector had its great growth already in the 1990s, mainly between 1997 and 2000 (Spear et al., 2015).

Similarly to the other polymers, WPC composites can be either thermoset or thermoplastic (Rowell, 2012).

The origin of wood-thermosets was at the beginning of the 20th century (Rowell, 2012). Since a thermoset is a polymer that, once cured, cannot be melted again by heating (Almeida Ferreira Gomes, 2018), it is possible to include in this class of polymeric composites cured resins such as epoxy and

phenolic resins. The wood-thermosets are products widely present as wood adhesives in the forest products industry. According to Rowell, 2012, one of the first wood-thermoset to be commercialised was composed of a phenol-formaldehyde (Bakelite®) and sawdust (figure 7) and was used for a gearbox knob of the British Rolls Royce car manufacturer, in 1916.



Figure 7 - Bakelite® + sawdust sheet and rod (adapted from Alexinsulation, 2014).

Unlike thermosets, thermoplastics can be melted, which means they soften when heated and harden when cold. This behaviour of wood-thermoplastics, similarly to thermoplastics in general, is due to their composition of linear molecular chains (Grigore, 2017). Contrary to what happens with wood-thermosets, wood-thermoplastics have had great growth in the last decades on their marketing and research. This means that, due to this growth, thermoplastics have become more important in wood-polymer composites (WPCs) and the terms wood thermoplastic and WPC are often confused (Rowell, 2012). Within the wood-thermoplastics, the most used are PE (polyethylene) (figure 8b) and PP (polypropylene) (figure 8c), however, the use of polylactic acid (PLA) with wood (figure 8a) is being strongly developed, namely in fields such as 3D printing (Csikós et al., 2015; Gregorova et al., 2011; Horta et al., 2017; Rowell, 2012).

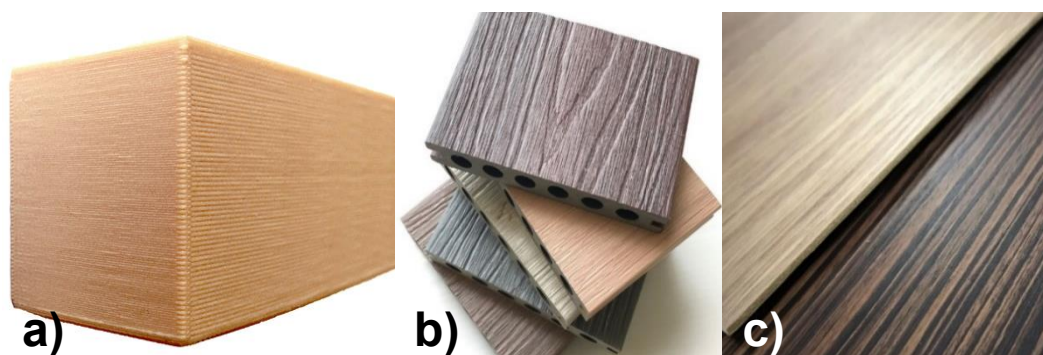


Figure 8 - a) PLA with wood 3d printed (adapted from Imagin Plastics, 2020); b) PE with wood deck (adapted from Hanming Composite, 2020); c) PP with wood boards (adapted from Celadon Technology CO., 2021).

One of the biggest challenges in the development of WPC is related to chemical interactions between the polymer and wood, more precisely its main constituent, cellulose. Cellulose presents low thermal stability, which makes it difficult to obtain polymers and processes compatible with their industrialisation (Correa et al., 2003). One of the great challenges in the manufacture of WPC lies in the fact that there is usually a poor adhesion between wood and the polymeric matrix, i.e., most

polymers studied so far are incapable of establishing chemical bonds with wood, acting only as binders. According to Kim & Pal, 2010, it is notorious that, in general, the density of wood composites is higher than that of natural wood.

Wood-polymer composites are not only used as a way of making use of waste such as sawdust. A striking example that supports the preceding statement is the use of PLA with sawdust which, in addition to the aesthetic factor, the sawdust acts as a reinforcement of the properties of PLA (Faludi et al., 2013). For the improvement of PLA's properties, wood particles of a generous size (more than 100µm) and larger than those normally used as fillers, are used (Faludi et al., 2013). Wood flour (WF) is another expression for sawdust. Some of the advantages of using wood flour (WF) are its abundance, renewability, low cost, low abrasiveness, and low density. WF-enriched composites also have problems, such as higher moisture absorption, lower thermal stability, lower dispersion, and low interfacial compatibility between filler and matrix (Gregorova et al., 2011).

3. Materials & Methods

3.1. Sawdust

Wood samples in powder form, also known as sawdust, result from the cutting processes of this wood. From cutting the tree to its final application, for instance in furniture, the wood undergoes several transformation processes and treatments; from some of them, sawdust is produced. The formation of sawdust is more evident in the wood sawing and sanding processes, which occur, for instance, in the construction of furniture and decoration in carpentries and joinery shops.

The sawdust samples used in this work were collected from two carpentries in the district of Aveiro, Portugal, which are referenced for only using solid wood in their production. The aim was to avoid particles resulting from wood by-products, such as particleboard, as they may contain chemical contamination. The samples collected are mainly of mixed oak (figure 9b) and pine (figure 9a). These two types of wood can be visually distinguished by their colour, where pine has a lighter brown colour than oak.

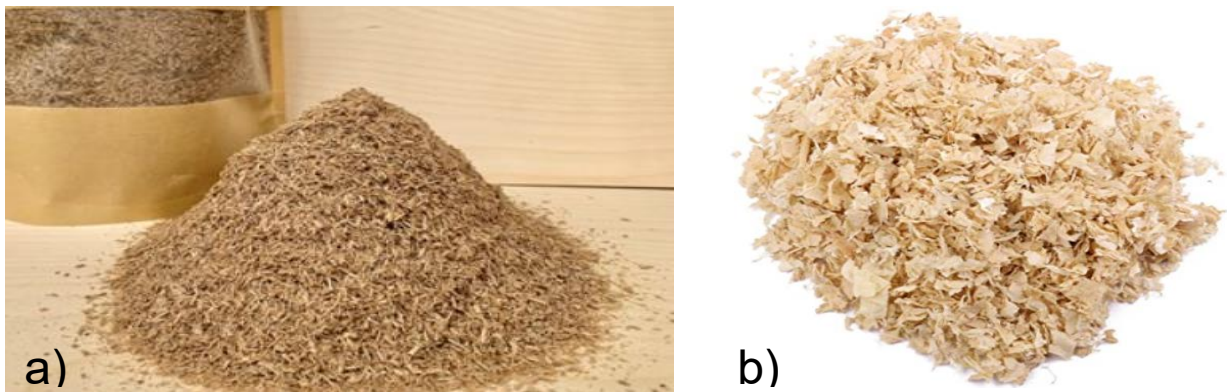


Figure 9 - a) oak sawdust; b) pine sawdust

These particles may show different shapes depending on the process that originated them. One sample was obtained from woodcutting with circular saw blades, in sliding table saws and toothed cutting strips, in band saw blades and the other sample from sanding, in a wide belt sanding machine with a roller-roller configuration. The particles resulting from sanding have a more elongated profile, while those resulting from cutting have a more rounded shape as can be seen in the figure below.

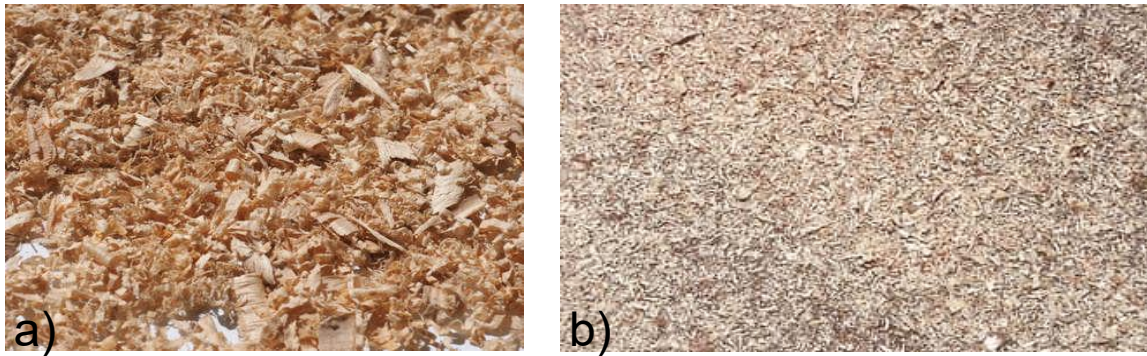


Figure 10 - a) particles resulting from sanding and b) particles resulting from break-in cutting (circular saw blades and band saw blades)

From the sawdust collected in the sawing processes, a sample was taken to be sieved. The sample selected was used to analyse the particle size distribution of the sawdust. All the work presented hereafter was done using the sawdust resulting from the sawing.

The sieving process consists of separating a certain sample of known dry mass into different particle size distributions utilizing a series of sieves with successively smaller apertures (ASTM C136 / C136M-19, 2019).

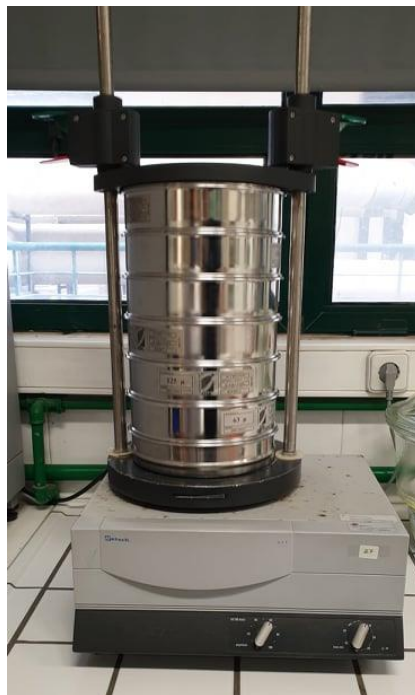


Figure 11 - Sieving process.

A Retsch® sieve shaker, model A200 basic (figure 11), was used to perform the sieving, where the sieves were inserted; the aperture between meshes in the lower sieve was $63\mu\text{m}$ increasing upwards and in the upper sieve was $710\mu\text{m}$. The results of this process are presented in the table 3.

Table 3 - Wood particle size distribution resulting from the cutting processes.

Sieve (μm)	Dp (μm)	Mass (g)	Mass (%)
710	855	39.4	18.8
500	605	40.0	19.1
355	427.5	41.7	19.9
250	302.5	34.4	16.5
125	187.5	39.5	18.9
63	94	9.68	4.6
0	31.5	4.39	2.1
Total:	-	209	-

To do this work, the sawdust with a granulometry of 125-250 μm was used. The choice of this size was due to the fact that not being the coarsest sawdust, it was the one that presented the highest abundance among the smaller sizes. It was decided not to mix the sizes smaller than 125 μm in this work, in order to have a narrower range of wood particle sizes.

3.2. Corn Starch

Starch is a polysaccharide, more precisely a carbohydrate, which has favourable properties arising from physiological safety and biodegradability. Given its abundance, as it is the main reserve substance in plants, starch already has an important commercial role, accounting for 70-80% of the caloric energy consumed worldwide. It is obtained from seeds of corn, wheat, rice, tubers, and roots, particularly potatoes, sweet potatoes, and cassava. Natural and modified starches have various applications from food products to adhesives, binders, and film-formers, in addition to acting as gelling agents, thickeners, moisture retainers, and retarders of retrogradation in some foods (Weber et al., 2009).

The starch chosen for this work is the most abundant commercially in Portugal, as well as the most accessible to the common citizen, corn starch. This starch is extracted from corn kernels and, according to information provided by the manufacturer Espiga®, characteristically dissolves easily in cold liquids (Espiga, n.d.). For this reason, it seemed suitable for the production of the polymer. The sample used in this work is in figure 12.



Figure 12 - Espiga® corn starch used in preparation.

3.3. Glycerine

Glycerine (propane-1,2,3-triol), which is a trade name for glycerol, is a water-soluble polyol (National Center for Biotechnology Information, 2021). Glycerol was first discovered in 1779 by Scheele by heating a mixture of lead oxide and olive oil. Glycerol appears naturally in combined forms, such as triglycerides, in all animal and vegetable fatty oils and is isolated when these oils are saponified with sodium or potassium hydroxide in the soap manufacturing process. Since 1949, glycerol has also been produced commercially by the synthesis of propene. The first stage is a high-temperature chlorination, involving free radicals as intermediates, to form allyl chloride. Then, it reacts with hypochlorous acid (bleach) giving a double addition product (halohydrin). Finally, treatment of the halohydrin with excess base leads to glycerol (Mota et al., 2009).

Purified glycerine, also known as pharmaceutical glycerine, was chosen for the development of this work. Non-purified glycerine is cheaper than pharmaceutical glycerine, however, the impurities in the first one could introduce large variability in the results, so purified glycerine was used. Therefore, pharmaceutical glycerine of LABCHEM® was used, with the certificate of analysis shown in table 4.

Table 4 - LABCHEM® Pharmaceutical Glycerine certificate of analysis

Test	Specification	Unit	Result
Content	>99.5	%	18.8
Colour	≤10	APHA	3
Refractive Index (20°C)	1.470-1.475	20°C	1.4743
Density (20°C)	≥1.260	34.4	1.2628

3.4. Citric Acid

Citric acid or 2-hydroxy-1,2,3-propanetricarboxylic acid, $C_6H_8O_7$, is a chemical commodity produced and consumed worldwide, with high demand due to its low toxicity when compared to other acidulants used mainly in the pharmaceutical, food, beverage, detergent, cosmetics, hygiene products, and other industries. Although it represents one of the oldest industrial fermentations, its worldwide production still reflects a very fast growth. Due to new biotechnological production facilities, the global supply of citric acid over the past two decades has increased from less than 0.5 to more than 2 million tons, making it the major chemical product obtained through biomass fermentation and the most extensively employed organic acid (Berovic & Legisa, 2007; Ciriminna et al., 2017; Soccol et al., 2006). It derives its name from the Latin word "Citrus" and is obtained naturally by metabolic processes carried out in living cells through the tri-carboxylic acid cycle and is also classified as a Generally Recognized As Safe (GRAS) compound (Sawant et al., 2018).

This acid, among other features, can be applied to acidify foods, to control the growth of pathogenic microorganisms, such as Salmonella, serve as a conservative and extending the shelf life of foods (Al-Nabulsi et al., 2014). The citric acid commercial production is roughly made by resorting to submerged fermentation in a medium containing excess sugar (Vandenberghe et al., 2000), however, the higher production of citric acid is directly related to the quantity and quality of the sugar present in the substrate and the metabolic activity of the microorganism strain employed, with saccharose being the most widely used (Magalhães et al., 2019).

For the preparation of the experimental processes used in this work, citric acid from the manufacturer Riedel-de Haën was used, whose technical guarantee analysis can be seen in table 5.

Table 5 - Riedel-de Haën® Citric Acid guarantee analysis

Assay	99.5-101%	Lead (Pb)	Max. 0.0002%
Water (Karl Fischer)	7.5-9.0%	Zink (Zn)	Max. 0.0005%
Sulphated Ash	Max. 0.01%	Chloride (Cl)	Max. 0.0005%
Calcium (Ca)	Max. 0.005%	Oxalate (C₂O₄)	Max. 0.005%
Copper (Cu)	Max. 0.0005%	Phosphate (PO₄)	Max. 0.001%
Iron (Fe)	Max. 0.0003%	Sulphate (SO₄)	Max. 0.002%
C₆H₈O₇*H₂O		M=210.14g/mol	

Lot: 92020

3.5. Corn Starch/ Glycerine

One of the polymers used in this study results from the polymerisation of a mixture of glycerine and corn starch. The glycerine and corn starch that were employed in this study are those previously presented. This preparation was performed only with the two biomaterials previously mentioned. No catalyst or reinforcement elements to the polymer matrix were used for this preparation.

In this experimental procedure for the preparation of the pre-polymer, a hot plate, pharmaceutical glycerine and corn starch, previously presented, and distilled water was used. The cure of the polymer was done in an oven.

3.5.1.Preparation

The first step was to put together 10 g of glycerine and 10 g of corn-starch in a container, that is, the two components in equal mass proportion, 1:1. Once these two elements had been added to the same container, they were stirred to ensure that they were properly mixed, before adding distilled water. Then, after adding 5g of distilled water and stirring the solution, it was placed on the hot plate to start the polymerization. The solution was stirred on the hot plate manually, while adding 5g of distilled water progressively because, given the viscosity of the solution, it was not possible to use a magnetic stirrer. to ensure that the connections were made, not leaving OH- groups unreacted. A temperature range between 55°C and 65°C was used for 30 to 45 minutes, to ensure that the distilled water that was added either reacted or evaporated, leaving the prepolymer with high viscosity (figure 13).

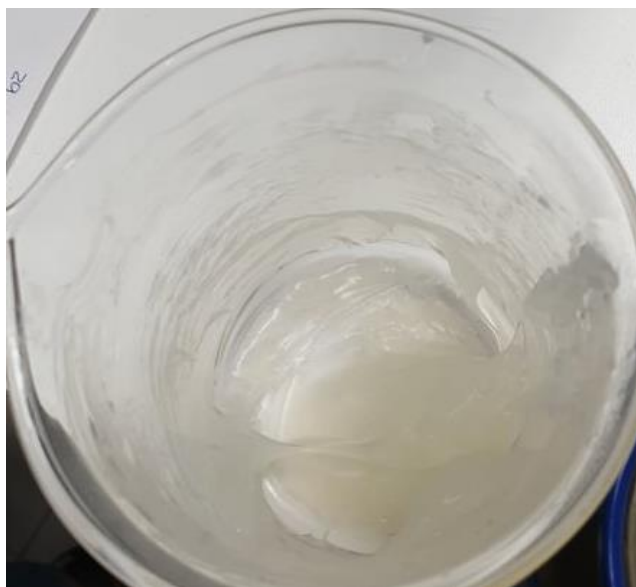


Figure 13 - Pre-polymer obtained with 1:1 proportion.

The solution leaves the hotplate still in the form of a pre-polymer and therefore needs to be cured. To carry out the curing, the polymer was placed in an oven, where a controlled and constant temperature is ensured, so that the polymer finishes polymerising and evaporates the water still present in it. After

an overnight of 8 hours at a temperature of 125°C, the final result was obtained, as it is shown in figure 14.



Figure 14 - Polymer in a 1:1 ratio after curing in the oven.

The same approach was done for samples with higher glycerine concentration, with 5g steps, which means that for the same amount of corn starch, 10g, the amount of glycerine was increased to 15g and 20g. The results are illustrated in figure 15. The sample containing 20g of glycerine showed a viscous performance, which led us to conclude that there was still glycerine to be reacted with corn starch. The 15g sample showed a lower viscosity than the one mentioned above, however, it was not in a so solidified condition as the 10g sample, so it was decided to continue the study with the samples in the proportion 1:1, i.e., 10g of glycerine to 10g of corn starch.



Figure 15 - Comparison of glycerine/ corn starch polymer containing 20g, 15g, 10g glycerine to 10g corn starch, respectively.

3.6. Polyglycerol Citrate

To prepare the polyglycerol citrate, pharmaceutical glycerine and citric acid previously presented were used. We tried not to use any type of catalyst in the reaction, in order to study the characteristics of the polymer in the purest form possible. To perform the pre-polymerization, a hot plate was used, while, to

cure the polymer, two different options were used: cure is done in the oven and a conventional kitchen microwave. The specifications of the microwave can be seen at ELECTROSACAVÉM, 2020.

3.6.1. Preparation

In the preparation of polyglycerol citrate, it was made for the 2:1 and 1:1 stoichiometries, glycerine: citric acid, respectively. The molar masses of 92.0938g/mol and 192.124g/mol were considered for glycerine and citric acid, respectively.

For the 1:1 preparation, the pharmaceutical glycerine, in the amount of 69.07g, was first inserted into a beaker and then placed on the hotplate with a magnetic stirrer to start its heating (figure 16a). When the glycerine, already less viscous, reached 80°C, 144.093g of citric acid was added (figure 16b). After this procedure, the mixture was allowed to reach 100°C and left for about 1 hour at that temperature, until it was observed that the reaction between glycerine and citric acid was apparently completed. The solution had a higher viscosity, maintaining its transparency, as it is possible to see in figure 16c.



Figure 16 - Polymer preparation: a) heating glycerine; b) with citric acid added to the reaction; c) pre-polymer ready to go to be cured.

The polymer was then placed in an oven at a constant temperature of 180°C for 20 hours, where the result shown in figure 17 was obtained.



Figure 17 - Polymer in a 1:1 ratio after oven curing.

The same procedure was repeated, this time using a microwave for curing the polymer, at a power of 700W for 10 minutes, where the result can be seen in figure 18.



Figure 18 - Polymer in 1:1 ratio after microwave curing.

The same procedures, from heating the glycerine to curing the polymer in the oven and microwave, were also repeated for the 2:1 ratio. For this ratio, 29.95g of glycerine and 30.7g of citric acid were used. Figure 19 shows the polyglycerol before and after being placed in an oven at 180°C for 20 hours.

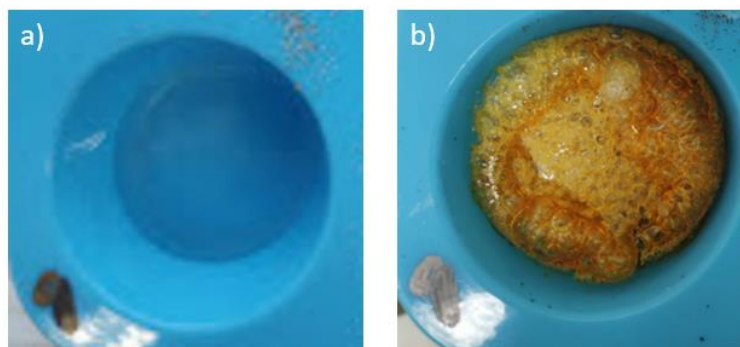


Figure 19 - Pre-polymer 2:1 a) before going to the oven; b) after curing.

3.7. Sawdust/ Polyglycerol Citrate

The polymeric composite binding sawdust with polyglycerol citrate was prepared using the prepolymers already presented in chapter 3.6 and the sawdust described in chapter 3.1. To prepare the polyglycerol citrate was used pharmaceutical glycerine and citric acid previously presented. No type of catalyst was used in the reaction, similarly to what was done in the preparation of the previous polymers, which serve as a polymeric matrix for this composite. To perform the pre-polymerisation, a hot plate was used. After mixing the wood, two different options were used: curing done in the oven and done in the microwave.

3.7.1.Preparation

The preparation of the polyglycerol citrate/ sawdust composite is similar to the preparation of the polymer serving as its matrix (polyglycerol citrate), explained in chapter 3.6. First, the pre-polymer, polyglycerol citrate, was prepared as described in chapter 3.6.1, either with the stoichiometric proportion 1:1 or with 2:1, glycerine and citric acid, respectively. With the pre-polymer already prepared, sawdust was added in different amounts. Figure 20a shows the final appearance resulting from the addition of wood to the polymer in a 2:1 ratio. In the same figure 20, there are four numbered samples. In sample 1 no sawdust was added, presenting only 7g of polymer; in sample 2 there are 7g of polymer and 3g of sawdust (30% wood); in sample 3 there are 7g of polymer and 1g of wood (12.5% wood) and, finally, in sample 4 there are 7g of polymer and 2g of wood (22.2% wood).

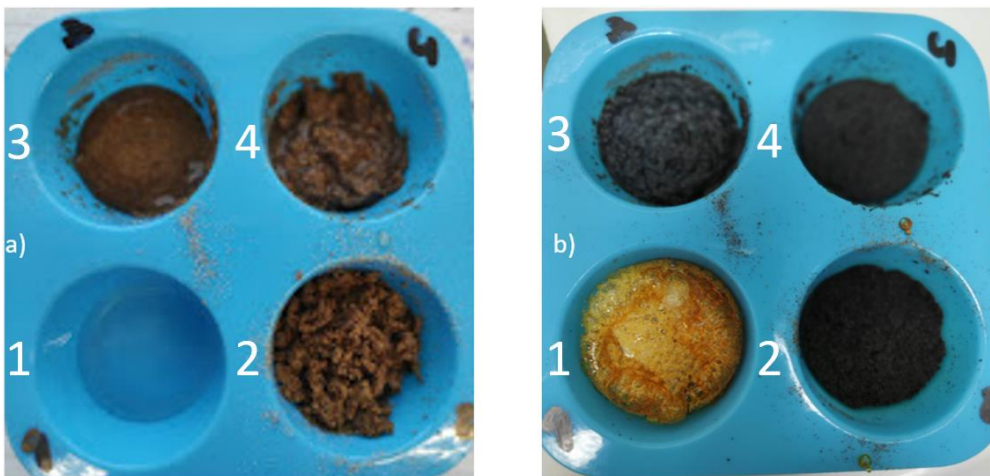


Figure 20 - Polyglycerol Citrate/sawdust a) before curing in the oven; b) after curing in the oven.

The polymer composites were cured in the oven at 180°C for 20 hours. The final result is visible in figure 20b. The procedure was repeated in the same way for the 1:1 ratio.



Figure 21 - 2:1 Polymer with sawdust, microwave cured.

1:1 and 2:1 samples containing 7g prepolymer and 3g sawdust, like the one shown in figure 21, were cured in the microwave at 700W power for 10min.

3.8. Sawdust/ Corn Starch/ Glycerin composites

The wood-polymer composite consisting of sawdust, corn-starch and glycerine was prepared using the components previously presented in Chapters 3.1, 3.2 and 3.3, respectively. No catalyst was used in this reaction, as it happened in the preparation of the polymer that is the matrix of this composite. As a way to ease the chemical bonds, leaving as few free OH- groups as possible, distilled water was added to the mixture. To perform the pre-polymerization, a heating plate was used, and the polymer cure was performed exclusively in the oven.

Similarly to what happened with the polyglycerol citrate/ sawdust, the equipment described in section 3.9.3 was used in the end to check if the composite had a behaviour of a thermoplastic or a thermoset.

3.8.1.Preparation

The preparation of the pre-polymer began with the addition of the three components that form the composite, in a beaker. The corn starch and glycerine were used in equal proportion, being only varied the amount of sawdust. Samples containing 7g, 10g or 15g of wood were made, as a way of progressively increase the amount of wood in the composite. Therefore, for 10 g of corn starch and 10 g of glycerine, the 3 different amounts of wood previously mentioned were used.

Once the components were added in the appropriate amounts, they were mixed until there was some cohesion and homogeneity between them. Distilled water was added in 5 grams amounts until a 55g quantity of water was pre-filled, to make mixing easier.

Afterwards, the solution was placed on the hot plate and, using a stirring rod, the solution was stirred while it was heated. Due to the high viscosity of the solution, even with the addition of distilled water, it was not possible to use the magnetic stirrer. The solution was heated to temperatures between 60°C and 70°C so that the prepolymer could be boiled and the chemical bonds to form the prepolymer could be established; at this point, the excess distilled water in the mixture was evaporated. When the distilled water had evaporated or reacted mainly with the other components and the prepolymer had a viscosity that made stirring difficult, it was removed from the hot plate (figure 22). The operation of creating the prepolymer requires approximately 30 minutes.



Figure 22 - Pre-polymer with wood, before drying in the oven. In the first image, the viscous solution is fresh off the hotplate and in the next one after 1 hour in ambient air.

Once the processes described above were duly concluded, the pre-polymer composite was taken to the oven. It remained there for 12 hours at a temperature of 125°C. When the composite was removed from the oven, the result obtained was the one shown in figure 23.



Figure 23 - Glycerine/ corn starch/ sawdust after curing in the oven.

After shredded, the composite was deposited in the device designed to the type of the polymer and was put in an oven at 360°C for 12 hours.

Nevertheless, as explained in chapter 4.4, the polymer that was later used to create the mechanical test specimens was prepared differently. The glycerine was first heated to reduce its viscosity, at a

temperature between 30 and 40°C, so that there was no great degradation of its chemical properties. While stirring the heated glycerine, corn starch was added. The mass proportion of that components was 1:1. The solution was stirred continuously, its viscosity increasing until it became a solution that could not be further stirred. At this point, sawdust was added to the pre-polymer, in quantities representing 16.67% and 28.57% of the total mass of the composite. After mixing and homogenizing the mixture in a mortar (figure 24), the composite was placed in the oven at 150°C for 12 hours.



Figure 24 - Corn-starch/ glycerine/ sawdust composite prepared in the mortar, before being deposited in the dies.

3.9. Physical-Chemical Characterization

3.9.1. Thermogravimetry

Thermogravimetric analysis can be defined as a method for the characterisation of an element, compound or mixture by measuring the changes in physical-chemical properties at high temperatures as a function of increasing temperature. There are two main methods of performing this analysis: differential thermal analysis (DTG), in which changes in "heat content" are measured as a function of temperature increase; and thermogravimetric analysis (TG), in which differences in mass are measured as a function of temperature increase (Coats & Redfern, 1963). These tests are carried out at a controlled temperature and atmosphere, using a thermobalance. A thermobalance is a device capable of measuring the mass of a given sample as a function of temperature and time. The composition of the thermobalance varies from one instrument to another (Menczel & Prime, 2008).

Samples of glycerine/corn-starch/sawdust were characterized by thermogravimetry (Netzsch® STA 409 PC equipment), under air flow, to evaluate their thermal stability and degradation temperature. The samples were heated from 30°C to 1100°C at 25°C/min using alumina crucibles. The DTG profiles, the weight losses and the degradation temperatures were computed using the equipment software.

3.9.2. Tomography

Tomography is the process of obtaining density distribution through multiple X-ray projections. Computerised tomography is currently used in various fields, from medicine to biology and, as in the case under study, engineering (Herman, 2009). To perform this characterisation, a 3D X-ray microscope (XRM) combined with micro-computed tomography (micro-ct) was used. In figure 25, it is possible to see a sample of glycerine, corn starch and sawdust composite inserted in the instrument that performed the tomography.



Figure 25 - Preparation of tomography to glycerine/corn starch/ sawdust composite

3.9.3. Assessment Thermoplastic/ Thermoset behaviour

At this point, it was necessary to assess if the composite was a thermoplastic or a thermoset. To do this, the device shown in figure 26 was designed.

A device that consists of 1 aluminium cylindrical tank, 1 steel compactor cylinder, 2 steel plates, 1 cylindrical steel ring and 3 screws was created. The cylindrical tank is where the polymer is deposited. In turn, the compacting cylinder, as its name indicates, compacts the polymer deposited in the tank. The pressure applied by the compacting cylinder was the weight of two steel plates of different heights and masses. These plates are connected to the compacting roller by an M6 screw. Three different compacting cylinder configurations are possible, i.e. three different levels of applied forces: cylinder; cylinder + large plate; cylinder + small plate; cylinder + 2 plates. To limit the horizontal mobility of the compacting cylinder, a cylindrical ring was designed to be inserted into the tank, laterally pressed by 2 M3 screws. This ring has also contributed to an increase in the useful volume of the tank.

Due to constraints caused by the size of the muffle used, the following configuration for the compacting cylinder was used: cylinder+ smaller plate.

Using thermal gravimetric analysis (TGA), a physicochemical characterisation technique explained in chapter 3.9.1, it was possible to assess the decomposition temperature of the polymers under study. It is known that a thermoplastic, when heated, first melts and then decomposes, while a thermosetting

maintains its state until it decomposes. So, it was thought that if the shredded composite was heated to a temperature close to its decomposition temperature. If there was no change in the state of composite particles, it would be a thermoset. However, if there was a change in the physical state of the composite and, in turn, in the binding of the powder particles, it would be a thermoplastic.



Figure 26 - The cast used to determine whether the polymers were thermosetting or thermoplastic.

3.10. Mechanical Tests

To mechanically characterize the composites, it is essential to carry on several tests.

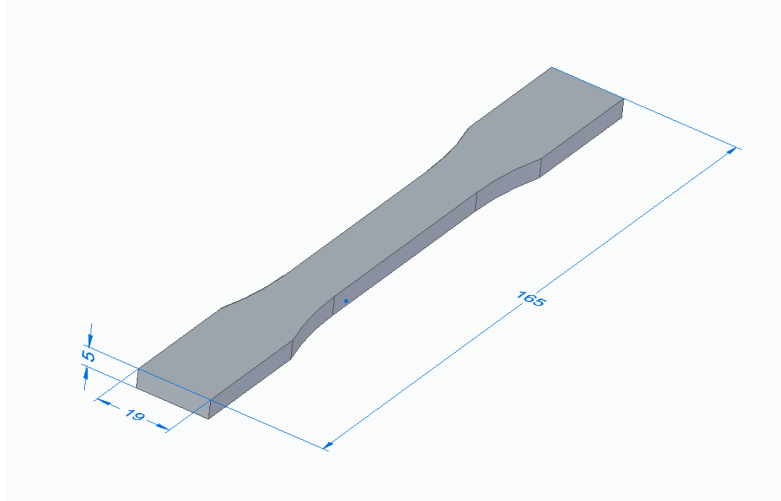
In the composites that are being studied, it is not known, nor is it possible to establish, a pattern for wood fibres orientation. After bibliographical research, it was verified that the standards for tensile and compressive tests of composites with polymer matrix do not include composites with heterogeneous fibre orientation. Therefore, it was considered more correct to use the standard for polymers.

Thus, it was concluded that ASTM D638-14 (ASTM, 2014) for tensile tests, ASTM D695-15 (ASTM D695, 2015) for compression tests.

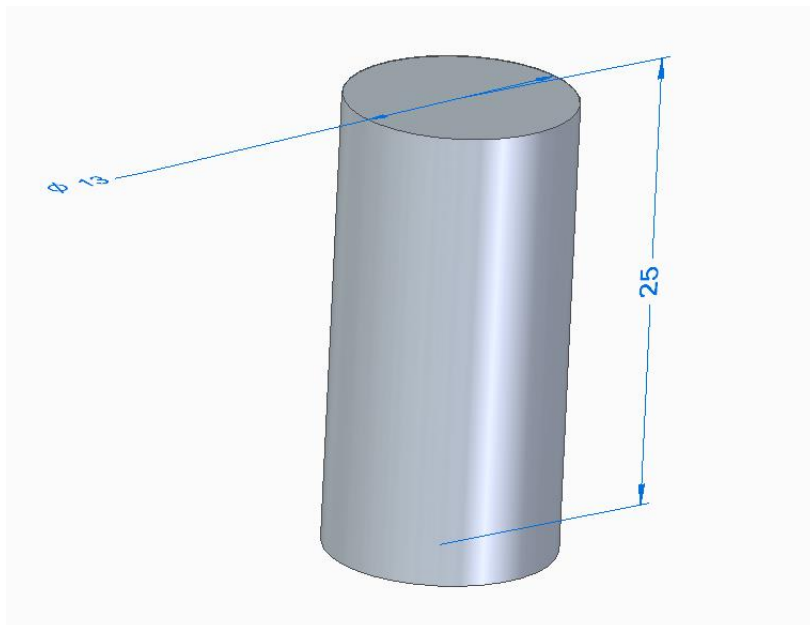
The Instron® 5566 universal testing machine, in figure 27, present in the LEM2 laboratory, was used to perform the mechanical tests, duly equipped with the 500N load cell, as well as the specific ties for each type of test. The technical specifications and user manual of the equipment can be consulted in (Instron, 2005b). The software used for the test and data processing was the Bluehill 2, developed by Instron and its datasheet can be found in (Instron, 2005a).



Figure 27 - The Instron 5566 Universal Testing Machine, used to perform all of the mechanical tests.



(a) Tensile tests specimen



(b) Compressive tests specimen

Figure 28 - Mechanical Tests Specimens 3D CAD

3.10.1. Tensile Tests

As mentioned above, the tensile tests would be performed following the ASTM D638-14 standard. The specimens used for this test were obtained by casting. A modification in specimen sizing was performed, as shown in figure 28a. To reduce the effect caused by surface irregularities, the specimen thickness was increased from 3.2 ± 0.4 mm to 5 ± 0.4 mm. This extra size acted as a guarantee that the specimens could be demoulded without fracture and that any effect caused by surface irregularities from the demoulding would be mitigated in the mechanical characterisation of the material. This fact can be explained by the increase of the area of the specimen that would be under tensile stress, causing that surface stresses would be smaller when compared to the total stresses of the test.

Initially, a mould was dimensioned, which, to facilitate its handling, was intended to have a reduced mass. The mould could be made of steel or aluminium, as both can be easily machined and represent a reasonable cost, but aluminium has a lower density. Since aluminium guaranteed a lower mass for the moulds, combined with an acceptable machinability, it was the material chosen for these moulds. Thus, two aluminium bars with dimensions of (46x30x1000) mm were purchased.

The moulds were designed in 3D CAD (figure 29). The mould of the tensile specimens was divided into 2 parts, a base where the shape of the specimen is machined and a cover, where the pre-polymer injection gites are fitted. To guarantee perfect alignment of the two parts of the mould, they had 2 alignment pins at opposite ends, as well as 2 screws to close the specimen.

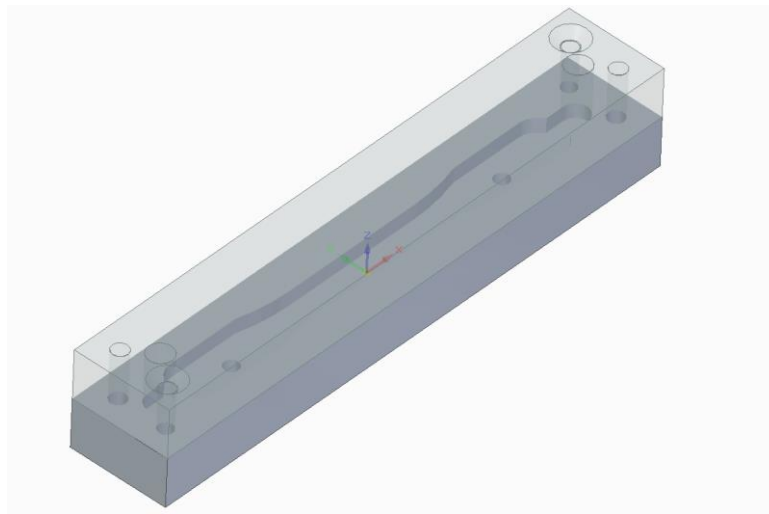


Figure 29 - Tensile specimens cast.

After the design process of the moulds was finished, they were machined. Conventional metalworking machines, such as a lathe, a milling machine and a drilling machine were used. Minor compromises were made within the normal limitations of using manual machining processes, as Computer Numerical Control (CNC) was not available to manufacture the moulds. The final appearance of the mould can be seen in figure 30.

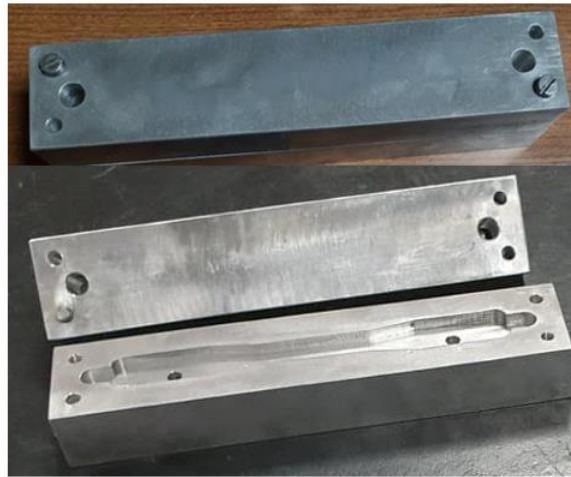


Figure 30 - Tensile specimen dies.

With the dies machined, the corn starch/glycerine/sawdust composite and the polyglycerol citrate were deposited in the space destined for the manufacturing of the specimen, initially using a syringe that injected the polymer and the composite through one of the breathing holes that was in the cover. After changing the composite manufacturing process of the composite (it is explained in detail in chapter 4.4), it was deposited along with the whole extension of the mould until it was filled and properly compressed by its cover. Then, the moulds went to the oven to cure the composite for 8 and 12 hours.

The tensile tests were performed using, as previously mentioned, a 500N load cell. The ties for the tensile tests were installed and properly aligned and calibrated. To measure the strain of the specimens, a video extensometer was used, which, in turn, was also duly calibrated to correctly measure the extension values in each test. The specimens, due to their dark colour, were also marked with white spots representing the test area of each one. In the test program, a test speed of 1.2 mm/min was used. The final appearance of the setup can be seen in figure 31.



Figure 31 - Assembly for tensile tests.

3.10.2. Compressive Tests

As mentioned before, the compressive tests were performed to be respecting the ASTM D695-15 standard, however, due to the unavailability in the workshop of a half-inch drill bit necessary for the manufacture of the die, a drill bit with size as close as possible to this value was used, which was 12mm. Thus, the specimens used in this test have a diameter of 12mm, respecting, however, the other dimensions imposed by the standard.

The specimen used in the polymer compression tests was first designed in 3D CAD, respecting the standard dimensions, as shown in figure 28b. After designing the specimen, the format for the die that would give it shape began to be studied. Several shapes and configurations of these dies were designed, however, the configuration in figure 32 was the one that met the requirements to obtain the most perfect specimens possible. The die consisted of 2 aluminium parts, 2 alignment pins, 2 screws and a punch. The aluminium parts were developed in such a way that the 2 holes from which the specimens were made respected the desirable diameter. However, the length of this space where the pre-polymer resides was increased so that the specimen could then be cut to the desired size. These 2 holes have the same diameter, and one of them is where the material is injected, which, through a connecting channel present, passes to the other hole, from where the specimen will be originated. The 2 alignment pins are inserted in the slots created for this purpose, ensuring that the specimens come out cylindrical, minimising misalignments. The screws are responsible for the tightening of the 2 pieces that constitute the die. The punch has the function of pressing the pre-polymer from one hole to the other.

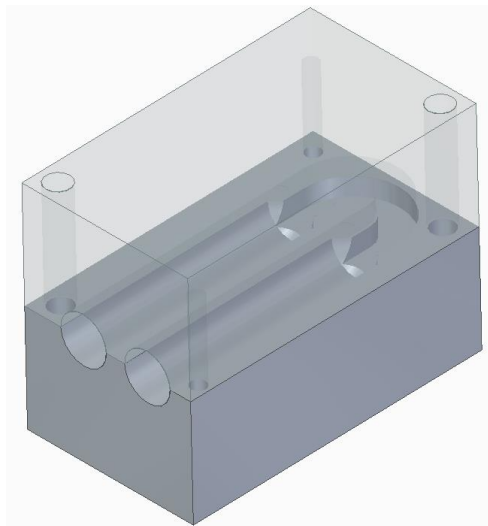


Figure 32 - Compressive specimens cast.

After modelling the die, its production started in the workshop. For this, the drilling machine, the milling machine and the lathe were used. The final result can be seen in figure 33.

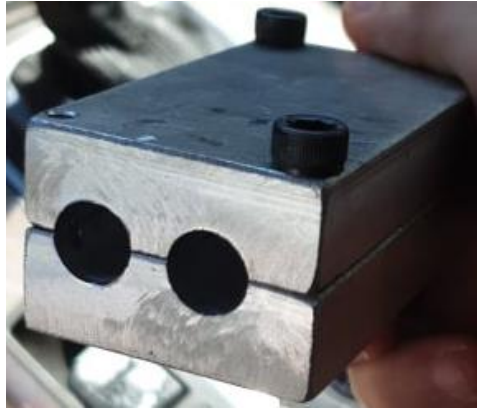


Figure 33 - Dies for compression specimens.

After obtaining the dies, the corn starch/glycerine/sawdust composite was deposited in the holes intended for the manufacture of the specimen, initially using a syringe that injected the polymer through one of the cylindrical spaces and was then pressed by the punch manufactured for that purpose, ensuring that there were no empty spaces. For the second composite manufacturing process

(chapter 3.8), the composite was deposited through the two cylindrical holes, properly compacted by the punch previously mentioned, doubling the rate of specimen production for each time the die was placed in the oven. The moulds were, then, placed in the oven to cure for 8 and 12 hours. For this test, 8 specimens were obtained.

The compressive tests were performed using a load cell of 500N. In this test compression plates were used (figure 34). A test speed of 5 mm/min was used.



Figure 34 - Assembly for compressive tests.

3.11. Filament Extrusion

In this step of the thesis, the previous developed polymer was used to extrude filament with 1.75mm or 2.85mm. For this action, a 3DEVO filament maker, model Precision Series 350 was used, equipped with optional 2- and 3-millimeters nozzles. More information about the equipment can be seen in the 3DEVO document stated in the bibliography (3DEVO, n.d.).

As it can be seen in figure 36, this filament maker is composed of a feed hopper where the composite polymer is deposited after shredded and gradually enters in a heated turning screw. The turning screw speed is adjustable within a range from 2 to 15 rpm, while 4 independent adjustable heaters are responsible for keeping the turning screw hot enough to melt the polymer and perform the extrusion. Each heater can reach a maximum temperature of 350°C which is acceptable for the material that is being studied. The turning screw will progressively push the melted polymer into the extrusion nozzle. Different nozzles, with 2mm, 3mm and 4mm were used (figure 35).



Figure 35 - 2-mm and 3-mm nozzles purchased for the filament extruder.

The best values found for the temperature at each of the control points as well as of the rotation speed of the turning screw resulted from an iteration process.

Initially, a constant temperature profile was worked, changing the rotation speed of the worm gear.

Next, a stair temperature profile was tested, with a drop of 10°C between each of the 4 heating points. This time worm speeds between 6 and 10 rpm were used.

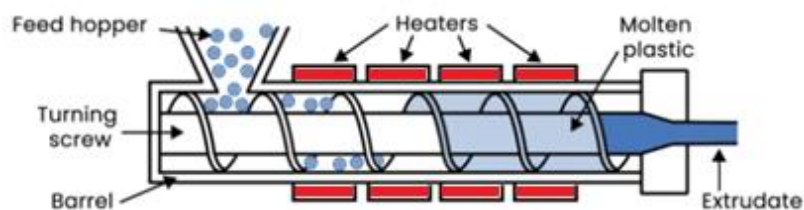


Figure 36 - Filament Maker scheme (adapted from 3DEVO, 2021).

After leaving the extrusion nozzle, in a vertical position, the filament passes through a rapid cooling zone with two fans, angularly adjustable and with an option to adjust the speed (percentage adjustment). Tests were carried out with these fans in various operating modes, including switched off (natural cooling).

Then, an optical sensor (figure 37) analyses the diameter of the filament in a precise way (43micron precision) if it presents values between 0.5 and 3.0 millimetres. This sensor is placed in a position that is considered by the manufacturer to be ideal to guarantee the roundness of the filament, which will then pass through a puller system composed of 2 puller wheels that will adjust the filament extrusion speed so that there is precise control of the filament diameter, guaranteeing the required dimensions.



Figure 37 - Optical sensor responsible for measuring the diameter of the filament being extruded.

Before reaching the winder, the filament, already in its final size, passes through an adjustable filament positioner for a coil up to 120mm wide. Winding takes place automatically.

4. Experimental

4.1. Preparation of Corn Starch/ Glycerine

This polymer was made in more than one batch, varying some conditions in which it was prepared, as described in the past chapter 3.5. The variations that caused more significant differences in the results were the change in the amount of glycerine added to the sample and the stage time in the oven for curing the polymer.

As previously mentioned, samples were made with an equal proportion of corn starch and glycerine (10 g of each) and with an additional 5 and 10 g of glycerine (15 and 20 g of glycerine to 10 g of corn starch, respectively).

First, the behaviour of the mixture before it was placed on the hotplate was evaluated. It was possible to verify that, in the beaker containing 20g of glycerine, this component could be in excess, as areas of glycerine without corn-starch mixed in were observed. This behaviour was not observed in the other two samples. The 15g glycerine solution, on the other hand, was distinguished from the 10g solution by its viscosity and homogeneity, the former showing greater resistance to miscibility than the latter.

In the heating process on the hotplate, differences in behaviour between samples were also noticeable. In the 20g glycerine sample, the viscosity was substantially lower than in the other solutions, presumably due to the existence of an excessive quantity of glycerine. The solution with 15g of glycerine, despite a similar behaviour to the sample with less glycerine, presented less viscous than the latter.

The 3 solutions were taken to the oven at the same time and remained there for 8 hours at 125°C. The final results can be seen in figure 15, previously presented in this text. The solution with 20g of glycerine clearly showed an incomplete polymerization, especially in some areas. The solution with 15g presented a better consistency than the previous one, however, when compared with the 10g solution, it presented a lower stiffness.

Analysing the samples obtained from the polymer with 1:1 proportions from the beginning of its elaboration to the final polymer, it was the solution that presented better polymerisation results. The study was continued with the addition of sawdust in a 1:1 ratio.

4.2. Preparation of Polyglycerol Citrate

The same preparation method was used for the 2:1 and 1:1 stoichiometries. During the whole development cycle of these samples, the behaviours of the prepolymers were similar in terms of solution viscosity, colour and odour.

Both pre-polymers were cured in the oven at 180°C for 20h. After removing the samples from the oven, the polymers appeared to be completely polymerised. The polymer with the 1:1 stoichiometry showed a lighter colour (transparent at certain points of the sample) than the polymer with the 2:1

stoichiometry. The polymer with the 2:1 stoichiometry showed a more yellowish tone. The odour of the 2 samples was similar. Although both samples presented a foam format, it is visible by comparing figures 17 and 19 that the polymer 1:1 presented more air bubbles than the polymer 2:1. Both polymers were quite consistent, hard and difficult to break using human force. In addition, they showed strong adhesion to the various containers in which they were manufactured, even when properly lubricated with a release agent. The 1:1 polymer had thin sharp walls between the air bubbles.

The curing of the polymer in a conventional microwave oven was also tested. 1:1 and 2:1 polymer samples were microwaved for 10 minutes in 2 minutes cycles at 700W power. The polymer showed similar behaviour in the two stoichiometries, however different from that obtained in oven curing. While the samples from the oven were extremely hard, those obtained in the microwave were quite soft and pliable. Another factor that could be observed was that the samples were not polymerised in their interior but were completely polymerised on their surface. As can be seen in figure 38, the microwave-cured polymer also showed air bubbles.



Figure 38 - Polyglycerol citrate 2:1 after curing in the microwave for 10 minutes at 700W, whereby it can be seen that the interior of the preparation was only partially polymerised.

During the production of the specimens for the mechanical tests, moulds were filled with polyglycerol citrate, to observe its performance. The polymer with 1:1 stoichiometry was placed in the oven for 12h at 145°C, and its behaviour during the process is illustrated in figure 39. During the polymerisation process, the polymer started to exit the mould, remaining on the face of the cover. After 8 hours of placing the mould in the oven, neither the material that was still inside the mould nor the one on the cover surface polymerised. It was also verified that the polymer was boiling, justifying its escape through the ventilation channels of the mould. At the end of the experiment, the polymer that was on the cover of the mould polymerised, but what was on the inside was not yet polymerised. Another problem encountered was the difficulty in cleaning the mould, as cleaning with detergents or acetone did not remove the polymer from the mould, whether polymerised or not. Only with boiling water was it possible to wash the mould, which was not an easy procedure. Therefore, the process of developing polyglycerol citrate samples using the designed moulds proved to be impractical.



Figure 39 - Behaviour of polyglycerol citrate in the mould for the specimens for the bending tests after 8h in the oven.

4.3. Preparation of Sawdust/ Polyglycerol Citrate

For the preparation of the polyglycerol citrate/ sawdust composite, the same approach as for the preparation of the polyglycerol citrate pre-polymer was used. Only after the pre-polymer was ready, the sawdust was mixed.

Polyglycerol citrate/sawdust samples were prepared with pre-polymer of 1:1 and 2:1 stoichiometries (figure 40). For each stoichiometry, samples with different amounts of wood were made. The sawdust mass percentage was tried to be as high as possible. Finally, oven and microwave curing were done.

The preparation of the pre-polymer polyglycerol citrate was carried out as already described in chapter 3.6. Then, the wood was mixed in the pre-polymer and homogenisation was carried out. Samples were prepared with a mass of wood above 10% of the total mass of the composite. The maximum value of wood that could be added was for the pre-polymer with 2:1 stoichiometry, where the sawdust mass was 42% of the total mass of the composite, cured in the oven. Other samples were made with smaller amounts of wood, namely 15, 20 and 30% of the total mass of the composite. The results obtained when using oven curing were interesting, regardless of the polymer stoichiometry. It was noted that the greater the amount of wood inserted in the composite, the more fragile the material became. However, some qualitative characteristics were kept, such as its behaviour as a rigid foam, without compromising the goal of having a large amount of wood. Given the impossibility of studying other characteristics of this composite, such as its mechanical properties and its stiffness/density ratio, these studies are projected for future works.



Figure 40 - Polymer in the ratio 2:1 on top and 1:1 on the bottom, with sawdust, after curing in the oven.

In addition to the curing process in an oven, the composite was also cured in a microwave. It was found that the result of the samples cured in the microwave was different from those samples cured in the oven. Although the composite was completely polymerised, the sawdust, previously homogeneously mixed by the polymer matrix, partially migrated to the surface (figure 41).



Figure 41 - Microwave-cured polyglycerol citrate/ sawdust.

4.4. Preparation of Sawdust/ Corn Starch/ Glycerine composite

The preparation of this composite was performed in two different ways. In the first one, sawdust was added at the same time as glycerine and corn starch. Distilled water was also added during the pre-curing process. In the second version, the pre-polymer was prepared and only then sawdust was added, without the addition of distilled water. The curing of these materials was always performed in an oven.

In the first iteration, the composite constituents were all added at once. Then, they were stirred in the beaker in an attempt to have some homogeneity before being heated. This was not possible, regardless of the amount of wood that was added, so distilled water was added. This was done not only to favour

the homogenisation of the solution but also to improve the miscibility during the composite cooking. Different masses of wood were used, representing 26%, 33.3% and 43% of the total mass of the samples. There were no major differences in the preparation of the composite before curing, and their colour and viscosity were similar. The composite baking process took place on the hot plate until the excess water was evaporated. Since it was not possible at this point to determine the amount of free¹ water remaining in the solution, it was removed from the heating plate when it began to resist being stirred.

Then, the composite was placed in the oven, initially in an aluminium bowl and later in the moulds for the specimens for the mechanical tests. As both the samples in the moulds and in the bowl were exposed to the same curing time and temperature conditions, similar results could be expected. This was not verified. The composite in the bowl dried, verifying only the mass variation corresponding to the evaporated water. On the other hand, the composite that was inserted in the mould through the syringe was expelled from its curing place, as can be seen in figure 42. This distinct behaviour was due to the fact that the mould composite was in a practically closed environment and, with the evaporation of the water present there, air bubbles were created. For the air bubbles to be released, they forced the polymer to leave the moulds. It was thus concluded that the polymer should already be inserted in the moulds without water. It was also possible to verify that varying the amount of wood in the composite did not cause relevant changes in its qualitative behaviour, since only a slightly more brittle behaviour was observed with the increase in wood content.



Figure 42 - Condition of the dies after an attempt to cure the non-dried polymer.

In the second iteration, an attempt was made to solve the problem of the presence of water in the composite before its curing. Now, the glycerine was preheated before the addition of the corn-starch, water was not added, and the sawdust was added after the pre-polymer was prepared. The mixing of the pre-polymer with the wood was done using a mortar and pestle. The specimens were made using the composite with only 16.67% of the wood mass. The mould was filled with the composite, it was pressed and placed in the oven for 12 hours at a temperature of 145°C. An attempt was made to cure the polymer in 8 hours, however, it was found that this wasn't time enough to polymerise the matrix.

¹ The amount of water remaining in the mixture not bonded to the polymer nor the sawdust

Figure 43 shows a specimen still in the mould. The specimens looked flexible and weak. Specimens with 28.6% of wood mass were made, however, they easily crumbled.



Figure 43 - Specimen for tensile test after curing in the oven for 12 hours at 140/150°C. Composite with 16.67% of sawdust by mass was used.

4.5. Physical-Chemical Characterization

4.5.1. Thermogravimetry

Thermogravimetries were performed, according to the conditions mentioned in chapter 3.1.9, to the glycerine/corn starch/ sawdust composite. For these analyses were used samples obtained in the 3d filament extruder using the 4mm and 2mm nozzles. The results of this characterisation are visible in the graphic in figure 44, in which in the left y-axis we can see the sample mass (TG) and in the right y-axis the thermal degradation speed (DTG).

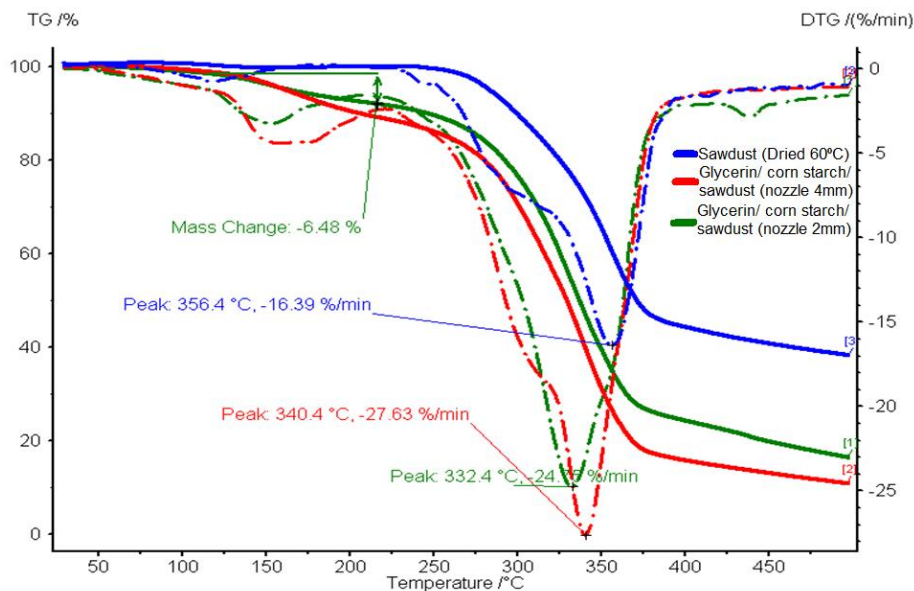


Figure 44 - Thermogravimetry graphic for glycerine/corn starch/ sawdust composite.

By analysing the results obtained, it is possible to note that the initial section of the TG curves show that the composites do not adsorb a great quantity of water, which means that it is not a hygroscopic polymer. It can also be observed that the maximum degradation speed temperature of the wood that is

used in the preparation of these composites (356.4°C) is higher than that of the composite (<345°C). This behaviour from the composites may show that there is an interaction between the wood and the polymeric matrix.

4.5.2. Tomography

The images obtained in the tomography performed to the composite glycerine, corn starch and sawdust are presented in figure 45. Analysing the monochrome image it is possible to see, in white, the wood particles dispersed throughout the composite. It was possible to identify 2 types of heterogeneity. It is visible that the particles are not equally dispersed throughout the sample since there are areas with a higher wood flour concentration than others (heterogeneity in the wood particle dispersion); heterogeneity can also be seen in the wood particle orientation in the polymer matrix.

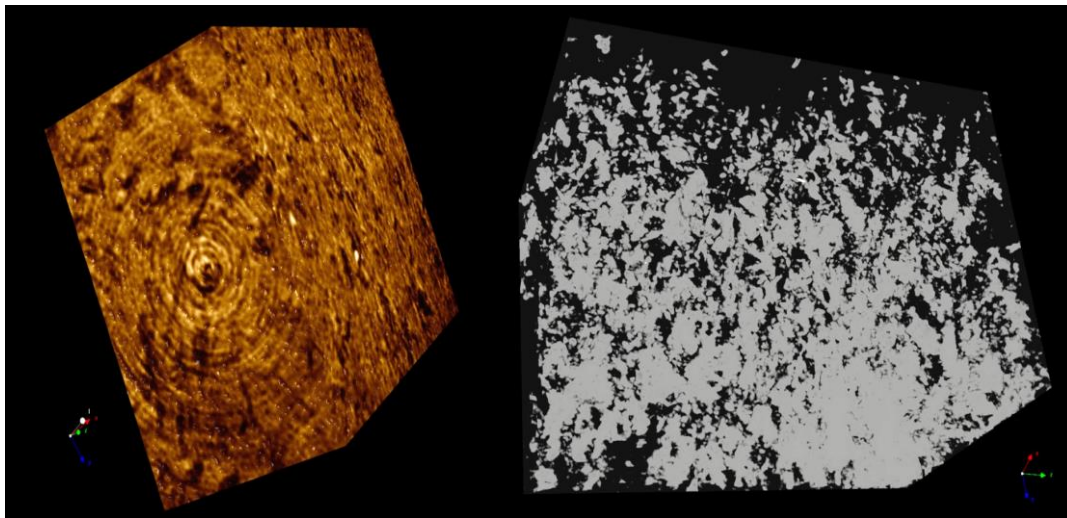


Figure 45 - Images obtained in the tomography.

4.5.3. Assessment Thermoplastic/ Thermoset behaviour

Polyglycerol Citrate/ Sawdust composite was characterized regarding its type. For this, the device designed to identify if it is either thermoplastic or thermosetting was used (chapter 3.9.3). Thus, it was placed the composite, in powder form, inside the container and compressed at a temperature of 380°C, for 24h. When the polymer was removed from the device, it was found that there was no difference in the appearance of the composite, except that the wood had carbonised. Given that the composite did not change its state at a temperature very near its degradation temperature, it may be assumed as a thermoset. The initial and final phases of the process can be observed in figures 46a and 46b, respectively.

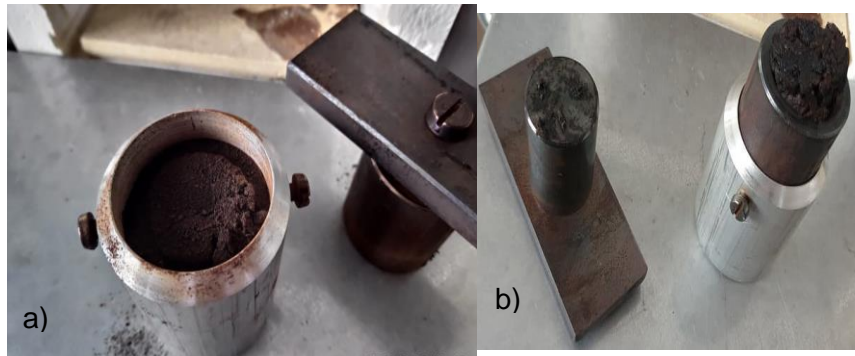


Figure 46 - a) Polyglycerol citrate shredded before putting in the oven; b) Polyglycerol citrate shredded after having been in the oven at 380°C.

The glycerine/ corn-starch/ sawdust composite was also submitted to the polymer type characterization test. After shredded, the composite was placed in the device, compressed and taken to the oven at 380°C for one day. It was verified a complete change of the composite aspect because it changed its state from solid to liquid, at the same time that it overflowed of the container where it was placed (figure 47). Analysing its behaviour and comparing it with that of polyglycerol citrate/ sawdust it is possible to verify that it is a thermoplastic.



Figure 47 - Sawdust/ Corn Starch/ Glycerine composite after the test in which it was found to be a thermoplastic.

4.6. Mechanical Tests

4.6.1. Tensile Tests

The tensile tests were performed using a sample of 5 specimens, all of them with the same dimensions. Given the apparent weakness of the material, it was decided to use a 500N load cell, the smallest available in the laboratory. The maximum load achieved for these tests was 23.20496N, so this load cell proved adequate for these tests. A total of 6 tensile tests were performed; however, only 4 of these tests are reliable. The second specimen had a problem related to the inappropriate measurement of the specimen extension. Another fact that led to the loss of results from this specimen was the fact that the specimen fracture occurred outside the test length, close to the ties that hold it.

The remaining tests were performed normally. In none of them the fracture occurred in the centre of the specimen, but in the test area immediately before the variation in the width of the specimen, either in the upper area or in the lower area. As it will be observed in chapter 5, there was some heterogeneity in the results obtained. Since the test conditions were the same in all tests, this suggests a lack of reproducibility of the specimen production. The fracture of two of the specimens used in these tests can be observed in figure 48.



Figure 48 - Fracture of 2 specimens used in the tensile tests.

4.6.2. Compressive Tests

The compressive tests were performed using a sample of 8 specimens, with an effort to ensure that the surfaces of the specimens were flat and straight. Since the cutting was done using manual methods of low precision, it was not possible to ensure that height was the same for all specimens nor the precision of the cutting surfaces was flat and normal to the axis of the specimen. The diameter of the section was the same for all specimens. As the height of all specimens was measured after cutting and inserted in the Bluehill program, the difference in heights was taken into account by the program when comparing the final results. Before initiating each test, to ensure that the specimens were perpendicular to the compression plates, they were carefully aligned, thereby mitigating some of the less desirable effects caused by deficiencies in their cuts. Since the maximum force reached was 467.4404 N, the load cell used proved to be sufficient to perform these tests (max. 500N). A total of 8 compression tests were performed, however, only 6 of these tests are reliable. The first test did not represent any kind of reliable value, as it served only for machine setup and explanation of its operation.

Except for the case explained below, all the tests occurred as expected, as can be observed in figure 49. The material showed an appreciably elastic behaviour. Contrary to what was expected, there was no fracture in any of the tests, and only at the end of them, small cracks opened at the tops of the specimens when the specimen was already substantially compacted. As will be observed later, there

was some variability in the results obtained, which, since the test conditions were the same in all tests, was ascribed due to the effects of the low reproducibility of the composite production.

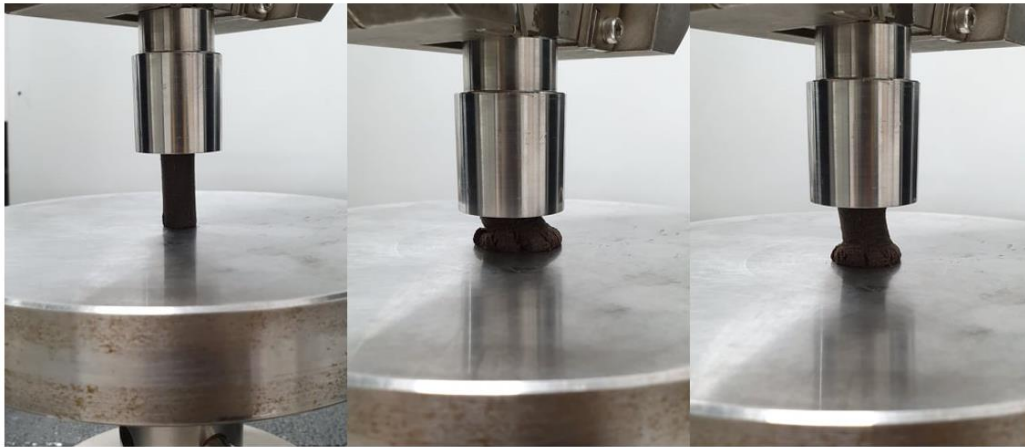


Figure 49 - General behaviour of the composite under compressive stress.

Another invalidated test was the last one because as soon as the force started to be applied to the specimen, it collapsed (figure 50). It was performed using one specimen that had a higher mass of wood than the others. Part of the wood from this specimen migrated to the extremities, and crumble as soon as they were compressed. So, this was considered an outlier and it was removed from this study.



Figure 50 - Compression test of the specimen with the highest wood content.

4.7. Filament Extrusion

The filament extrusion process had several stages of research, and several parameters were modified throughout it. It should be noted that although different preparations of the composite were made to be used in the production of the filament, they all had the same amount of glycerine, corn-starch and sawdust, 33.3% of each.

The process started by using the largest extrusion nozzle, 4mm. It began by using a constant temperature along with the 4 temperature control points, 160°C, with a worm gear speed of 3.5rpm. A uniform filament was obtained, with good elasticity, which favoured its winding, however, the diameter obtained was higher than 4mm. It was decided to increase the temperature to 180°C, keeping the linear temperature profile. There was a change in the composite behaviour since it became less compliant. The filament diameter decreased to a size between 3.5 and 3.7 mm. The filament came out with the

wood carbonised (figure 51). Keeping the same temperature, the worm gear speed was increased to 7.5rpm. it was verified that the wood started to come out lighter than in the previous configuration, however, the filament diameter increased again to 4mm. Then, the worm gear speed was maintained, and a step temperature profile was chosen, with temperature steps of 10°C. The highest temperature was near the nozzle, to ensure the fluidity of the composite and, consequently, a smaller diameter. The filament obtained kept the flexibility, but this time with a colour that was neither as clear as with the linear temperature profile of 160°C, nor as dark as when the temperatures were all 180°C. However, the lowest diameter obtained was 3.2mm, which is far from the 2.85mm that was aimed at. Therefore, it was concluded that a smaller extrusion nozzle should be used.



Figure 51 - Filament obtained using the 4-mm nozzle.

The tests proceeded with a 3mm extrusion nozzle. From the experience previously acquired, it was decided to maintain the rest of the machine configuration. The filament obtained under these conditions had a diameter of 3.4mm. The filament diameter was larger than the nozzle diameter presumably because the worm gear speed was not enough, allowing the material to accumulate at the nozzle exit. The worm gear speed was increased to 10 rpm and a reduction of the filament thickness to values around 3mm was verified. Besides still not being the diameter targeted in this study, the filament was brittle, which made its winding impossible. It was decided to go back to linear temperature profiles, having set the temperature at 160°C, to avoid dark colour and the worm speed at 3.5rpm, to increase the dwell time inside the extruder. Due to the temperature being too low, the extruder started to present difficulties in expelling the filament from the heating zone, so it started to auto shut down, for the safety of its components. The temperature was increased to 170°C, maintaining the extrusion speed, as shown in figure 53. It was found out that wood carbonised again. In the last iteration performed, in figure 52, a temperature of 180°C and a worm gear speed of 10rpm were used. The problem of the material being too brittle before the winding and the sawdust carbonisation was significantly reduced, although its diameter was irregular, varying between 2.70 mm and 2.95 mm in the same strand.



Figure 52 - Filament obtained using the 3-mm nozzle.



Figure 53 - One of the setups used in the filament extrusion tests, under cooldown conditions.

The iteration process occurred in the same way with the nozzle of 2mm, however, it was not obtained filament with a diameter inferior to 2mm nor superior to 2.5mm, therefore, far from the desired values. The filament was very brittle. A sample of filament extruded with this nozzle can be seen in figure 54.



Figure 54 - Filament achieved using the 2-mm nozzle.

Due to the fact that the filament was brittle, which made its winding impossible, further efforts to obtain filament for 3d printing were left for future work.

Note that, after 1 month in the air, the filament gained some flexibility, already allowing its coiling, however, it did not have the ideal diameter for 3d printing.

5. Results & Discussion

From the tensile tests performed to characterise the glycerine/corn starch/ sawdust composite, the following results in figure 55 were obtained.

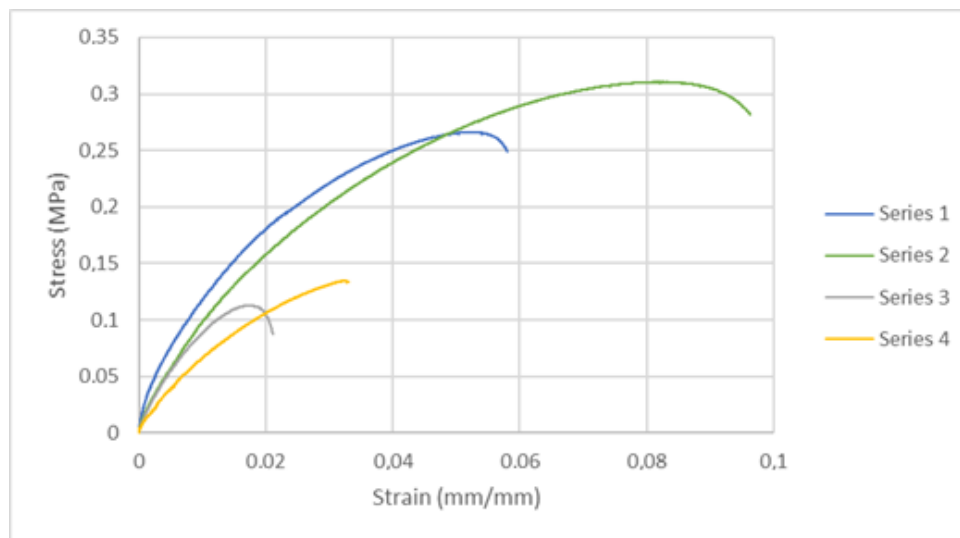


Figure 55 - Stress-strain curves of the various tensile tests performed on glycerine/corn-starch/ sawdust.

As can be seen in the same figure, the results obtained in each of the tensile tests were very disparate. Although the behaviour of the curves was similar in all tests, the stress-strain values obtained were quite different from each other. For the determination of a Young Modulus (E) only tests 2 and 3 showed some similarity. This difference of results between tests, taking into account that the test conditions were the same, was ascribed to the difficulty of obtaining repeatability between preparations of the composite under study. The preparation of the pre-polymer and the addition of wood was done manually and could not be ensured a completely uniform distribution of sawdust through the polymeric matrix. This problem may be responsible for the high variability in the results of the mechanical tests. With the research development of this composite and its progressive approximation to a commercial version, it may be possible to obtain more homogeneous tensile test results.

It is also noticeable nowhere tests shows a linear behaviour. This behaviour of the material makes it more complex to obtain the Young Modulus of the material. To obtain these values an iterative process was used. Knowing that the Young Modulus is determined according to equation 1, the derivative definition was used to obtain the Young Modulus for each test.

Equation 1 - Hooke's Law, where σ represents stress, E represents Young Modulus and ϵ represents strain.

$$\sigma = E * \epsilon$$

Considering that the test curves correspond, through an interpolation, to functions of the type $y=f(x)$, the derivative of the functions $f(x)$ in relation to the variable x is the function f' whose value at x is:

Equation 2 - Derivative definition (adapted from Bastos & Bravo, 2010)

$$f'(x) = \lim_{h \rightarrow 0} \frac{f(x+h) - f(x)}{h}$$

Thus, Young's Modulus (E) can be calculated as the derivative of $\sigma(\epsilon)$ at the origin, i.e., by applying the definition of derivative at the origin:

Equation 3 - Definition of derivative applied to obtain the Young modulus, where E represents the Young Modulus, σ the stress and ϵ the strain.

$$E = \lim_{\epsilon \rightarrow 0} \frac{\sigma(\epsilon) - \sigma(0)}{\epsilon}$$

By applying this equation to the various stress values obtained in the tests and extrapolating these values to the origin, the graphic in figure 56 is obtained. Making the average of the obtained results, it was determined a Young Modulus of 20.317 MPa. Note that this value is only indicative, given the disparity of the results obtained.

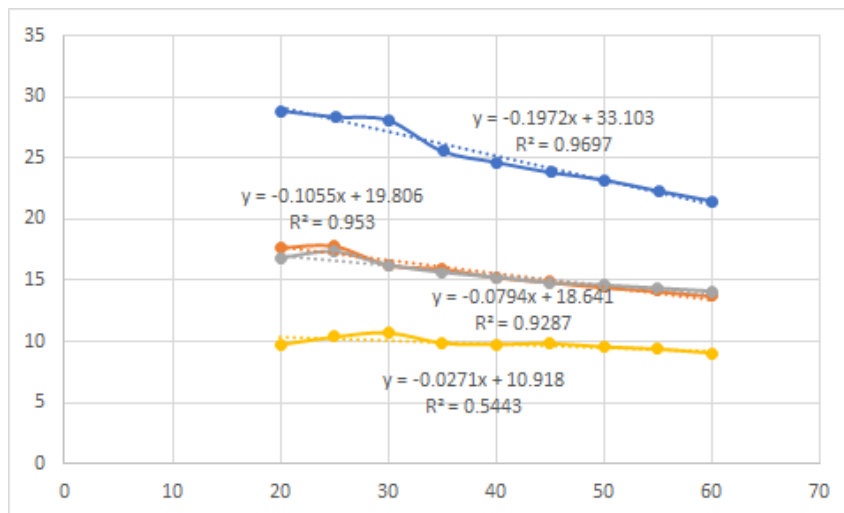


Figure 56 - Graphic used to obtain Young Modulus for each of the tensile tests.

Compressive tests were also performed to characterise this composite. The following results shown in figure 57 were obtained.

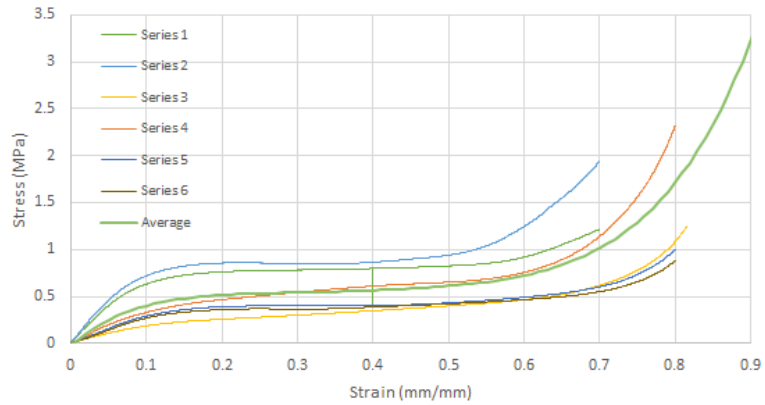


Figure 57 - Stress-strain curves of the various compression tests performed with glycerine/corn starch/ sawdust, including the average of the results obtained.

Similarly to what happened in the tensile tests, there were visible variations in the experimental results. Although the stress-strain curves presented a similar shape in all tests, the stress-strain results varied significantly from test to test. Then, to facilitate the obtention of a representative Young Modulus, interpolations were made to the stress-strain curves of figure 58. After obtaining the approximate equations of the curves, their analytical average was calculated.

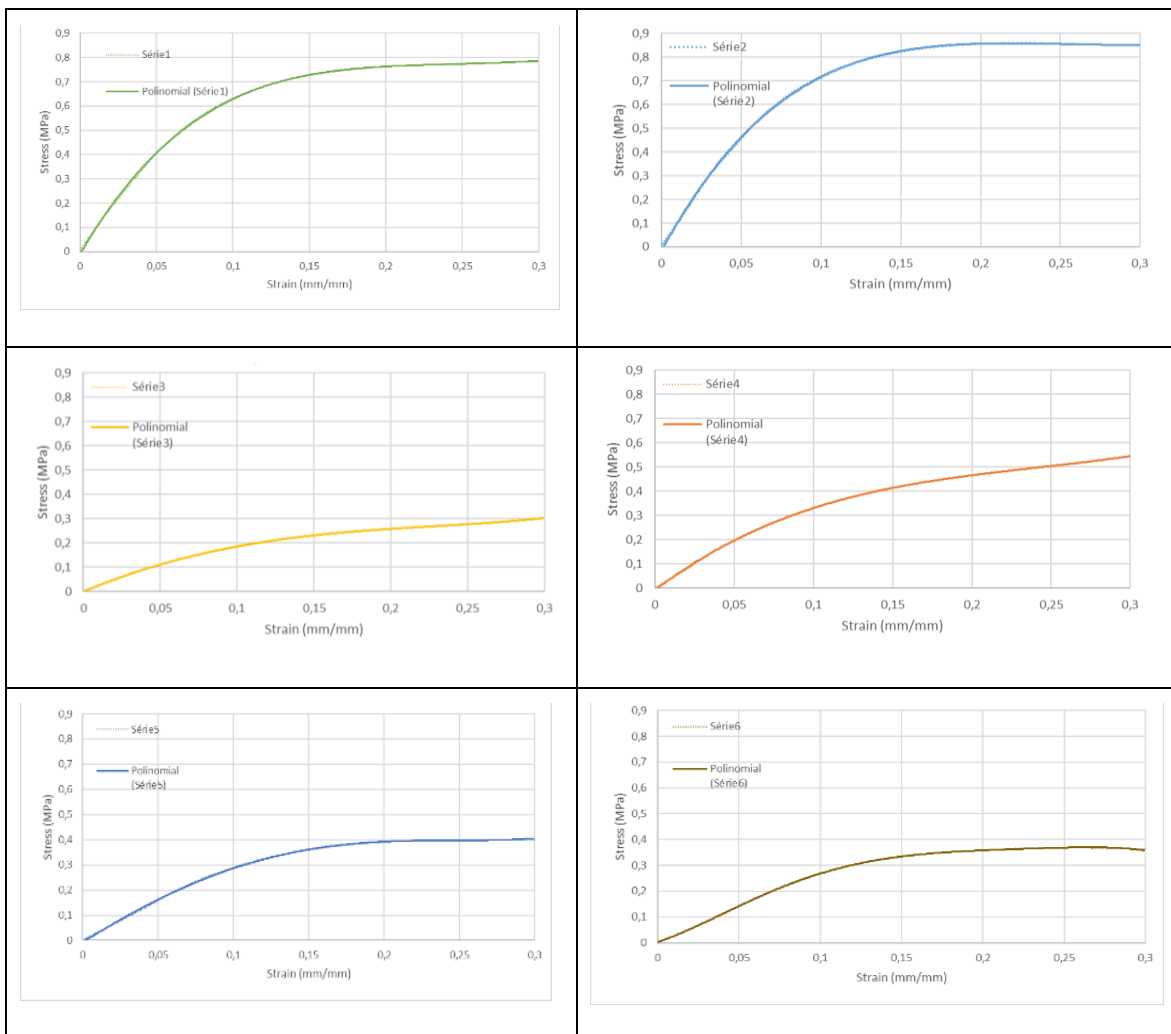


Figure 58 - Comparison of the stress-strain curves with their interpolations.

Then, the stress-strain curve corresponding to the average equation was graphically represented. In figure 59, the derivative at the origin was obtained, as a way to determine the young modulus representative of the compressive strength of this material. The Young Modulus obtained was 6.9MPa. These values should be considered a rough estimate, given the dispersion of the results obtained between tests.

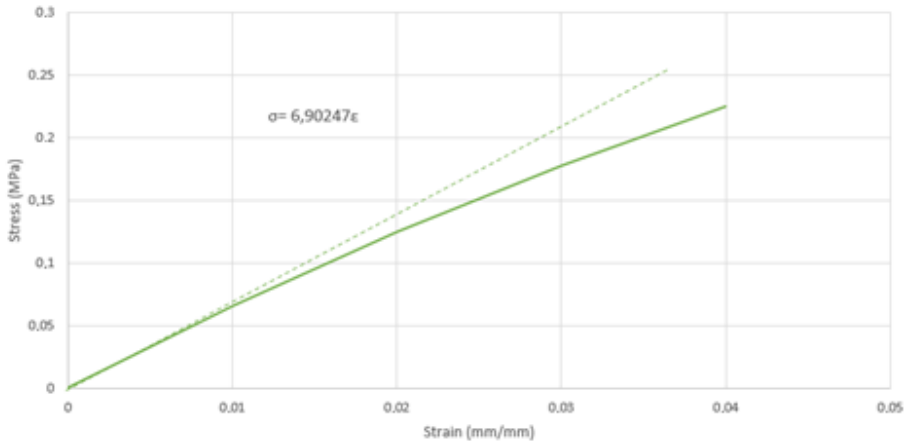


Figure 59 - Graphic representing the calculation of Young Modulus to compressive strength.

Figure 60 shows the specimens used for the tensile (a) and compressive (b) tests. It is possible to visualize in them the final aspect of the thermoplastic composite that was created.



Figure 60 - a) Tensile Tests Specimens; b) Compressive Tests Specimens

6. Conclusions

6.1. Original Contributions

The following points are considered as original contributions in this work:

- Development and preliminary study of 2 new composites: polyglycerol citrate/sawdust and glycerine/corn starch/sawdust.
- Creation of a device to characterize the type of polymers regarding their behaviour under temperature variation.
- It was verified that polyglycerol citrate behaves as a thermoset and glycerine/corn starch as a thermoplastic.
- Creation of moulds for specimens for tensile, compression and bending tests of polymers.
- Mechanical and physical-Chemical characterization of glycerine/corn starch/ sawdust.
- Exploratory study of filament production for FDM 3D Printing using glycerine/corn starch/ sawdust.

6.2. Lessons Learned

During this work, 2 composites were developed. Each of these materials provided a different experience. Both materials showed the importance of the reproducibility of their manufacturing process and how complex it is to achieve the repeatability of a process in the laboratory. It can also be seen that small variations and iterations in the research process of one material can generate large differences in its behaviour.

Firstly, when developing polyglycerol citrate with sawdust, it was observed that this composition behaves like a foam. It is a thermoset with low density that, combined with sawdust, may have an interesting application in low weight applications and with an interesting apparent hardness, besides the aesthetic factor of being able to resemble wood.

The composite composed of glycerine, corn starch and sawdust also presented interesting characteristics. It is presented as a material that uses components of biological origin, the reuse of by-products and wood waste, establishing connections between them that aesthetically resemble wood. As it is a thermoplastic, as it was proved, it makes possible its application in 3d printing.

Although in this work only an initial study of these materials has been carried out, much more progress has to be made in their improvement.

6.3. Future Work

There is still a lot of work ahead in the development and application of these materials. Each of which can be improved in different ways.

Thus, for polyglycerol citrate and its composite with wood the following explorations can be made:

- Application of glycerine without any kind of treatment, as it is obtained as a by-product from biodiesel transesterification.
- Exploration of different stoichiometries of citric acid and glycerine, and their conjugation with wood.
- To investigate the importance of wood particle sizes in the preparation of the composite.
- Increase the amount of wood inserted in the composite.
- Explore the use of sawdust produced from sanding in the preparation of the composite.
- To search for processes of curing the polymer and the composite in a way that it is possible to obtain a given form.
- Discover methods of controlling the number and size of gas bubbles formed in the polymer elaboration.
- To explore in more detail the curing of the polymer and of the composite using microwaves, trying to solve the dispersion of the wood particles and the polymerisation deficit inside the samples.
- To discover ways of demoulding for the polymer and the composite given its high adherence to the walls of other materials
- Perform the mechanical and physical-chemical characterisation of the polymer and the composite.
- To develop methods of surface protection for the polymer and the composite to avoid their too early degradation.

In the development of the polymer glycerine/corn starch and its composite with wood, the following improvements can be made:

- Use of glycerine without any kind of treatment, as it is obtained as a by-product of biodiesel.
- To investigate the importance of wood particle sizes in the preparation of the composite.
- Increase the wood volume inserted in the composite.
- Explore the use of sawdust produced from sanding in the preparation of the composite.
- Carry out a more refined study of the preparation of the pre-polymer, studying more intensely the need of adding distilled water in the pre-polymer, the moment in which the addition of sawdust is made and, finally, the whole curing process of the same.
- To research a bio-filler that can be applied on the polymer and the composite to reduce the water absorption due to its hygroscopicity, as well as to increase its longevity without degradation.
- To study the longevity of these materials.
- Characterize the polymer regarding its mechanical and physical-chemical properties.
- To proceed with the development of filament for 3d printing using the polymer and the composite, studying the mechanical and physical-chemical properties after printing.

6.4. Final Remarks

It may be concluded that all these materials show remarkable potential and applicability, either at the insulation level or merely for aesthetic application or non-structural functionalities. All these materials are biocompatible and, therefore, can be used, for example, in the creation of spoons to stir coffee, cups, among other applications.

It is considered that the process of development of these materials is still in an embryonic state, as tests and characterisations have only been carried out on them in their purest state, but they may still be improved on several fronts, such as using additives.

It is considered that the goal of creating new composites that would allow the reuse of sawdust, while still being bio, was successfully concluded, although it is necessary to improve the work carried out so far.

The glycerine/corn starch and the glycerine/corn starch/ sawdust have a high potential of applicability in FDM, and in this work, several tests were already developed aiming to achieve this goal. Given the increasing use of rapid prototyping (RP), it would be interesting to introduce these materials, which are environmentally friendly and promote the reduction of raw material waste.

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