FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO

Biocomposite pellets for direct extrusion-based 3D printing

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Abstract

Nowadays, the increasing search for more sustainable, biodegradable and recyclable products has brought a challenging development on new materials in order to achieve a solution for the sustainability problem. For that, there is an increasing development on the research of biocomposites that could reduce a product's through-life environmental impact relative to wholly synthetic composites. On the other hand, 3D printing has also been widely explored due to reduced waste, reduced production time, and great versatility when compared to conventional manufacturing methods.

This project aimed to create a new biocomposite with only green constituents for 3D printing. The goal was to develop filaments of various blends: colophony and wood powder, Polylactic acid (PLA) and wood powder, PLA and colophony, and PLA and colophony reinforced with wood powder. At first, numerical simulations were run based on the Asymptotic Homogenization technique with the support of the commercial software ABAQUS®. Afterwards, the filaments were produced on a extruder and then experimentally characterized through tensile tests to compare the experimental results with simulation results.

During this project it was possible to conclude that wood fibers help to increase the tensile properties, however it is a challenge to combine the fiber with the matrix without the use of additives. On other hand, comparing PLA with colophony, PLA has better results for the elastic properties. The results obtained from the numerical predictions were compared to those obtained experimentally and the final analysis showed that they were not in good agreement. The potential causes and issues for this deviation are addressed in details throughout the present work and suggestions to improve the overall results are discussed accordingly.

Keywords: biocomposites, natural fibers, 3D printing, ecocomposites

Resumo

Actualmente, a procura crescente de produtos mais sustentáveis, biodegradáveis e recicláveis trouxe um desenvolvimento desafiante sobre novos materiais, a fim de alcançar uma solução para o problema da sustentabilidade. Para isso, há um desenvolvimento crescente na investigação de biocompósitos que poderiam reduzir o impacto ambiental de um produto durante toda a sua vida útil em relação aos compósitos totalmente sintéticos. Por outro lado, a impressão 3D também tem sido muito explorada devido à diminuição do desperdício, reduzido tempo de produção e grande versatilidade quando comparada com os métodos convencionais.

Este projecto visava criar um novo biocomposto com apenas constituintes verdes para impressão 3D. O objectivo era desenvolver filamentos de várias misturas: colofónia e pó de madeira, ácido poliláctico (PLA) e pó de madeira, PLA e colofónia, e PLA e colofónia misturados com pó de madeira. No início, foram realizadas simulações no software comercial ABAQUS® utilizando uma técnica de modelação de Homogeneização Assimptótica. Posteriormente, os filamentos foram produzidos numa extrusora e depois expostos a ensaios de tracção para comparar os resultados experimentais com os resultados da simulação.

Durante este projecto foi possível concluir que as fibras de madeira ajudam a aumentar as propriedades mecânicas, mas ainda se revela ser um desafio combinar as fibras com a matriz sem a utilização de aditivos. Por outro lado, comparando o PLA com a colofónia, o PLA tem melhores resultados para as propriedades elásticas. Os resultados obtidos a partir das previsões numéricas foram comparados com os obtidos experimentalmente e a análise final mostrou que não estavam em bom acordo. As causas e questões potenciais para este desvio são abordadas em pormenor ao longo do presente trabalho e as sugestões para melhorar os resultados globais são discutidas em conformidade.

Palavras-chave: biocompósitos, fibras naturais, impressão 3D, ecocompósitos

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Catarina Nunes

"Failure is not the opposite of success.
It is a part of it."

Allistair McCaw

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Abbreviations

3D	Tridimensional
ABS	Acrylonitrile-butadiene-styrene
AM	Additive Manufacturing
HEC	Homogenized Elastic Constants
LCA	Life Cicle Assessment
MaPO's	Maleated polyolefin
NFCs	Natural Fiber Composites
NFPCs	Natural Fiber Polymer Composites
PCD	Process Control Documents
PLA	Polylactic Acid
RVE	Representative Volume Element
SPC	Statistical Process Control
VOCs	Volatile Organic Compounds
WPCs	Wood Polymer Composites

List of Symbols

A_s	Sectional area [m^2]
D	Diameter [m]
E	Young's Modulus [Pa]
E^H_{ijkl}	Homogenized properties
E_{ijkl}	Material constitutive tensor
F	Load [N]
$f^{0(kl)}$	Nodal forces obtained after prescribing $\chi^{0(ij)}$
$f^{*(kl)}$	Nodal forces after prescribing $\chi^{*(ij)}$
G	Shear Modulus [Pa]
r	Radius of the fiber
wt	Mass fraction [%]
Y	Unit cell volume
y_n	Set of coordinates
Vf	Volume fraction [%]
x	Number of fibers
δl	Displacement [m]
ε	Derformation [m/m]
ν	Poisson's ratio
σ	Tensile strength [N/m^2]
$\chi^{kl}_m(y)$	Auxiliary displacement fields
$\chi^{0(ij)}$	Prescribed nodal displacements
$\chi^{*(ij)}$	Nodal displacements after prescribing $f^{0(kl)}$

Chapter 1

Introduction

1.1 Context and Motivations

The growing ecological and environmental consciousness has driven efforts to develop new innovative materials for several end-use applications. This awareness triggered the interest for more sustainable materials that are able to be processed with lower energy consumption, as are natural fiber composites. As a consequence, research and development of these materials has increased in recent years, which is reflected in their applications in various industries, particularly the automotive and construction industries.

The primary goal is to replace current synthetic petroleum-based composites with natural resources. Materials derived from nonrenewable petroleum-based sources are hazardous and expensive to produce. On the other hand, biocomposites derived from natural sources are biodegradable, recyclable, non-abrasive, and compostable in addition to have properties comparable to synthetic fiber composites.

Natural fibers are low-cost, lightweight, biodegradable, renewable, and environmentally friendly alternatives to synthetic fibers like glass fiber and carbon fiber. The long-term viability of natural fiber-based composite materials has led to increased use in various production industries. However, the manufacturing process of natural fiber-based biocomposites is still characterized by some difficulties, such as poor adhesive propensity, moisture absorption, poor fire resistance, low impact strength, and low durability.

The forest represents in Portugal an important asset that lacks a higher level of development and solutions to increase the value of forest resources. In this context, it is of high importance the development of high added value solutions for forest waste and subproducts, identifying alternative solutions with greater economic potential in the face of energy recovery, including the production of biocomposite materials. Besides, these solutions could be an alternative and a motivation for the development of a circular economy.

The circular economy is an economic model that makes effective use of resources by minimizing waste, retaining value over the long term, using fewer raw resources, and utilizing closed

production cycles within the bounds of socio-environmental policy. Figure 1.1 illustrates the main cycles of a circular economy.

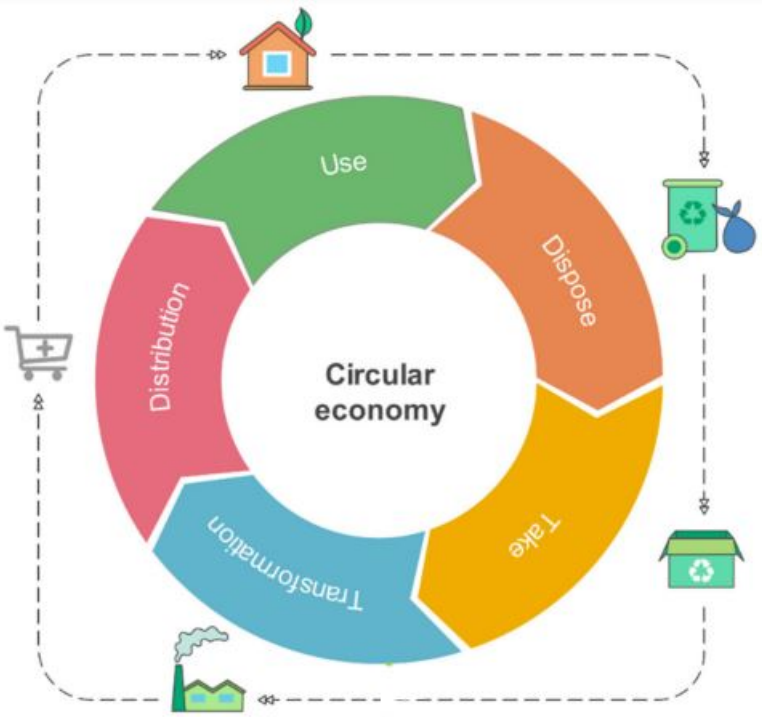

Figure 1.1: Scheme for a circular economy cycle. Adapted from [1].

The internal cycles of manufacture, reuse, and reconditioning consume less energy and materials in addition to be more cost-effective than traditional recycling. The most pressing environmental issue the world is now experiencing is climate change. The impacts of rising global temperatures on ecosystems, animals, food chains, and human existence are critical. For that, United Nations have some goals for 2030 to achieve sustainable management and efficient use of natural resources, encouraging companies, especially large and transnational companies, to adopt sustainable practices and to integrate sustainability information into their reporting cycles [2].

In this sense, and taking into account the economic and environmental interest associated with the use of forest waste, this dissertation aims at the development of a composite material with totally green constituents. In addition to mixing and extruding the material, filaments were experimentally characterized in tension and numerical modelling was employed to predict the resulting stiffness properties.

1.2 Goals

The main objective of this dissertation is to create pellets of a new biocomposite material with all-green constituents for direct extrusion based-3D printing. To ensure that this goal is achieved,

the following milestones have been set from the outset:

- State-of-the-art on the existing literature, focusing on biocomposite materials, more specifically their constituents, processes, properties, and applications associated with 3D printing;
- Development of numerical models that would support and predict the experimental results through Asymptotic Homogenization;
- Mixing and extruding the material into filament form, followed by tensile testing to obtain the filament properties;

1.3 Summary

This dissertation is divided into 6 separate chapters:

- Introdution: It contains not only the context and motivation for the adopted research line, but also the main objectives of the performed work and the structure of the data presentation;
- State-of-the-art: A compendium of current literature related to the main topics covered in this dissertation, i.e. composite materials, biocomposites, and additive manufacturing;
- Experimental Procedure: A detailed description of the tests performed, the conditions under which they were performed, and the equipment, materials and methods that were adopted;
- Numerical Modelling: A detailed description of the employed models, the respective adopted methods, and their execution;
- Methodologies for Future Works: Exposure of possible methodologies that could have been used during the process and should be considered in future work;
- Conclusions and Future Work: The relevant conclusions are drawn from the obtained results, and future work is indicated. It is believed that may continue, enrich, and validate the work done during the dissertation in an even more substantiated way.

Chapter 2

State of the Art

In order to make the best decisions on the selection of the materials to use, as well as the processes to achieve what is proposed in this thesis, it is required to acquire knowledge of the concepts, technologies, previous work, and research related to the topic. In this chapter, the goal is to describe the highest level of general development, and the evolution of such level of development.

2.1 Introduction

Nowadays, there are social and environmental challenges that can grow as new opportunities for new business concepts, using a sustainable development. Saying that, the sustainable development allied with the technology evolution could reduce the waste and create better materials for the future. This would depend on more skilled jobs and new ways of organization that could handle the consumers necessities without putting at risk the future generations.

Through the years, the use of composite materials has increased with special attention to the bio composites. Studies have been developed to use natural fibers and resins in order to obtain materials that are more sustainable.

2.2 Composite Materials

The study and development of new materials have been the focus of some technology areas so it is possible to achieve properties that could not be found on traditional materials. Some of these properties combine low density and good performance in high efficiency applications with lower costs. The search for such materials led to the development of composite materials [3].

The composite materials are characterised for being the combination of two or more materials that together have better properties than alone. This properties could be related to weight, density, strength or stiffness. The fiber reinforced composites are the most known example, which are the result of the combination of fibers with a binding material, also designated as matrix [4, 5, 6].

The main constituents of a composite material are the matrix and the reinforcement. The reinforcement is responsible for the internal structure of the composite. On the other side, the matrix guarantees a stable form and a efficient distribution of the loads on the reinforcement.The matrix can also be responsible for the maximum service temperature of the composite and for controlling its resistance to the surrounding environment [4, 7].

The classification of composite materials depends of many factors like the type of matrix used and the reinforcing phase. These combinations are responsible for the balance of their properties. Composite materials behavior and properties are mostly influenced by the nature of the constituents, their phase and distribution, and how good is the interface between the reinforcement and the matrix [4, 6, 7]. The classification based on the matrix can be divided into three groups that are related to the material used, as presented in Figure 2.1. On the other side, the classification based on the reinforcement is divided into three types related to the reinforcement phase, which can be seen in Figure 2.2 [8].

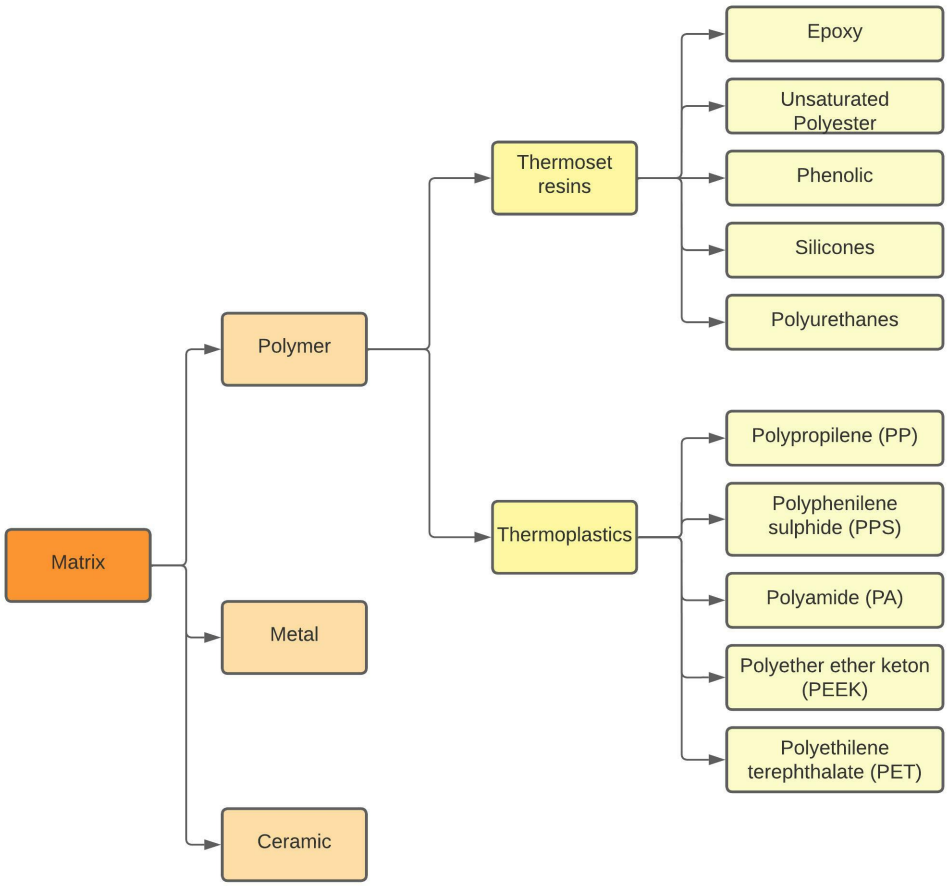

Figure 2.1: Representative diagram of the classification of the composite based on the matrix.

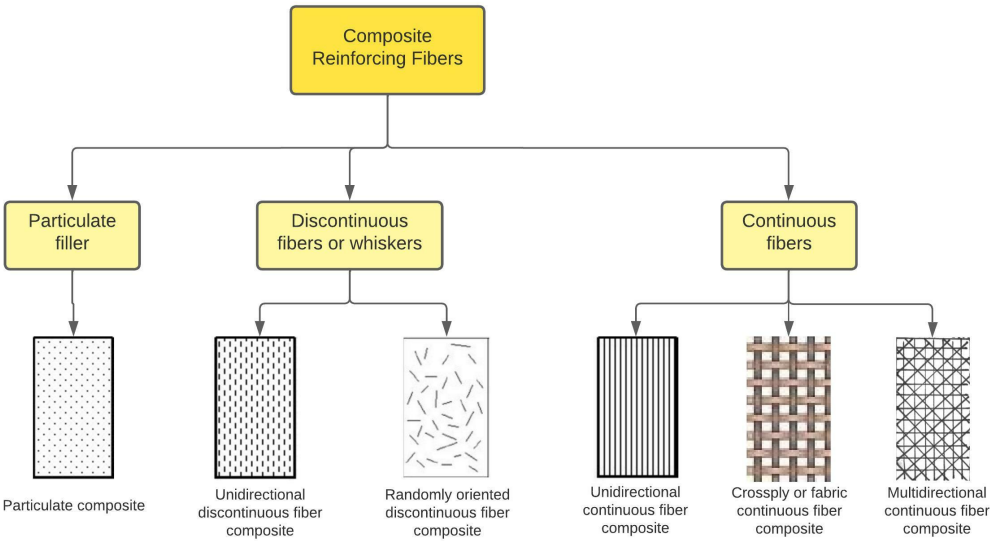

Figure 2.2: Classification of composite material systems based on the reinforcement. Adapted from [9].

In general, a lot of new possibilities arise by having properties like light weight, high strength, high stiffness and fatigue resistance, and low thermal expansion. However, they can also bring some disadvantages as the real cost of the materials, their long development time, and manufacturing constraints [4, 10]. Furthermore, due to the importance of bringing more sustainable materials to the industry there was a big development of composite materials with natural fibers and polymer matrices called biocomposites or green composites. These materials generated composites with lower density and a lower cost in a more sustainable way [3, 4]. As this project focus is on the biocomposite materials for more sustainable applications, there will be given more attention to natural fibers and polymer matrices.

2.3 Biocomposites

In response to the increase of environmental issues related to the use of petroleum-based plastics in an excessive way, researchers started developing bio-based sustainable materials that can be an alternative to petroleum-based plastics. At first, the focus was on the production and characterization of polymer composites based on recyclable polymers filled with natural-organic fillers, i.e. fibers and particles extracted from plants [11, 12]. These fillers showed to be better than inorganic-mineral counterparts in many different areas, such as being less abrasive to processing machinery and less dangerous for the production employees in case of inhalation. In addition, they are easy to incinerate and lead to final composites with lower specific weight, allowing to obtain interesting properties in terms of thermal and acoustic insulation [12].

For the sake of clarification, green composites usually come from the combination of biodegradable and/or bioderived polymer matrices with natural fibers/particles, which can be as mere fillers

or reinforcements. Wood flour and fiber are the most known natural-organic fillers, being the flour easily obtained from sawmill wastes and the fibers produced by thermo-mechanical processes on wood waste [12, 13]. Wood flour and fiber have low costs, but poor adhesion between the filler particles and the polymer matrix, low impact strength, and thermal decomposition at temperatures over 200°C [12, 14, 15].

The investigation of the suitability of natural fiber composites has shown more interest in structural and infrastructure applications where moderate strength, lower cost, and environmentally friendly properties are required. For example, in Germany, the major car manufactures such as Mercedes, Volkswagen, Audi and Ford uses natural fiber composites for various interior and exterior applications. The usage of the biocomposite makes the car lighter, renders greater resistance to heat, external impact, and improves fuel capacity [16]. On Figure 2.3 it is possible to see a car door inner trim panels that are precast using mats of 60% natural fiber in a Baypreg® polyurethane resin (Courtesy of Bayer Polymers).

Figure 2.3: Modern door inner trim panels molded using mats of 60% natural fiber in a Baypreg polyurethane resin (Courtesy of Bayer Polymers). Reproduced from [17].

2.3.1 Polymer matrices

As shown on Section 2.2, polymer matrices can be classified as thermoplastics or thermoset resins. The matrix system must be selected based on the intended application since it directly affects the final properties of the resulting composite material. Even if the tensile property on the longitudinal direction of the composite depends on the reinforcement, the other properties like the tensile property in the transverse direction, the shear strength, the compressive strength, and the resistance to heat and environment are influenced by the selection of the matrix [18, 19].

At first, thermoset resin matrices were used and developed for military aircraft applications because of their superior mechanical properties. However, some flaws were discovered related to epoxy based composites, which brought the discover of the thermoplastic matrices. Polymer

matrix composites are usually used in structural applications like automotive area, aircraft building materials, sport, acoustic furniture, and naval packaging [18, 20, 21].

Researchers have studied the physical and mechanical properties of the most used thermosets and thermoplastics, and concluded that thermosets show better properties than thermoplastics [18] in different applications. On the other hand, there is a huge contrast between thermosets and thermoplastics when referring to the their capability of being reused and recycled. Thermosets, generally speaking, cannot be reused once cured, while thermoplastics have repeatable use and recyclability [22, 23, 24], which opens the door for new applications and opportunities.

2.3.2 Natural fibers

Due to the recent worries related to environmental issues, as well as many other advantages, natural fibers started to replace synthetic fibers. In fact, natural fibers have become popular on the automotive industry because of some of these advantages [18, 25, 26]. Table 2.1 summarizes a qualitative comparison between synthetic and natural fibers [27].

Table 2.1: Comparison between natural and synthetic fibers [27].

Criteria	**Synthetic fiber**	**Natural fiber**
Density	High	Low
Structure of fiber	Can be modified	Cannot be modified
Nature	Hydrophobic	Hydrophilic
Durability, usage, cost	High	Low
Renewable and recyclable	No	Yes
Biodegradability	No	Yes
Specific strength and modulus	Low	High
Strength and modulus	High	Low

Natural fibers can be classified based on their origin as plant fibers, animal fibers or mineral fibers (see Figure 2.4) [27]. From Table 2.1, it can be seen that natural fibers are better in terms of density, costs, recyclability, biodegradability, and specific strength and modulus than synthetic fibers. According to the literature [18, 28], their hydrophilic nature could be solved with chemical treatments that would help to improve the mechanical properties. In addition, there are some important factors that influence the selection of natural fibers, which are represented in Figure 2.5 [18, 29].

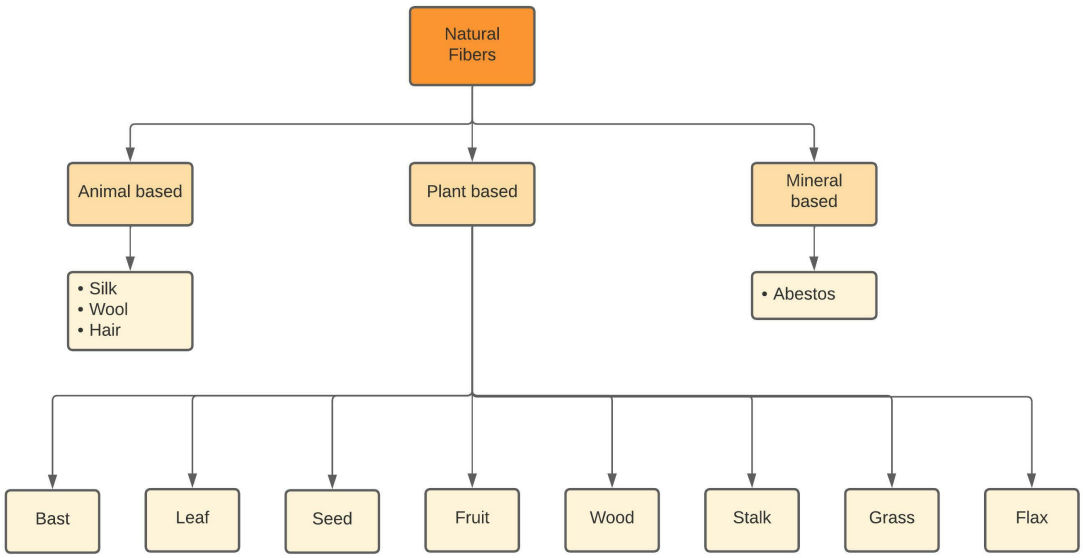

Figure 2.4: Representative diagram of the classification of natural fibers. Adapted from [18].

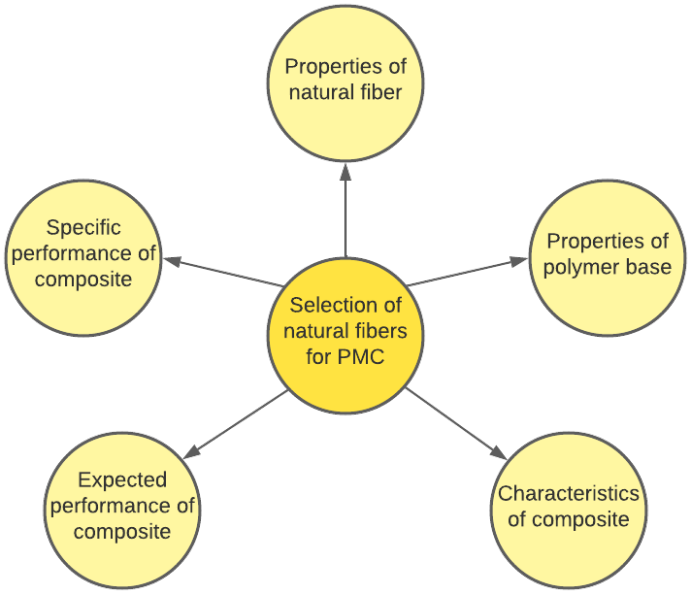

Figure 2.5: Factors that have influence on natural fiber selection in composite materials. Adapted from [18].

2.3.3 Processes

Over the years, new techniques were developed to process polymer composites. Among the processes, some are only suitable for thermoplastic-based composites, others only for thermoset-based composites, and there are a few that work for both. They can also be distinguished by the

type of fiber reinforcement. Most of these techniques can also be used to process biocomposites [30, 31]. The most used manufacturing techniques are:

- Hand layup
- Autoclave molding
- Filament winding
- Pultrusion
- Extrusion
- Injection molding
- Resin transfer molding
- Compression molding
- Automated fiber placement (AFP)
- Automated tape lying (ATL)

The composite processing techniques mentioned before may be divided into three main systems: melt blending, in-situ polymerization, and solution blending.

In solution blending or casting, the polymer and fibers are dissolved in a suitable solvent to make the composites, and the solvent is then dried once the composites have been processed [32, 33]. Even if there are polymers that may be dissolved in water, finding the right solvent to dissolve the particle, and make it easy to remove, is a crucial step in the foundation of solution casting process [32, 34, 35]. The solution casting aids in preventing the thermomechanical degradation often seen with other methods of processing polymers that include heating and vigorous mixing. It is mostly used in the production of films. The amount of solvent used in this method makes the foundation with solvent unsustainable for the environment. In addition, the majority of organic solvents are hazardous to health and temperature-sensitive [32]. Figure 2.6 shows a schematic example of the process.

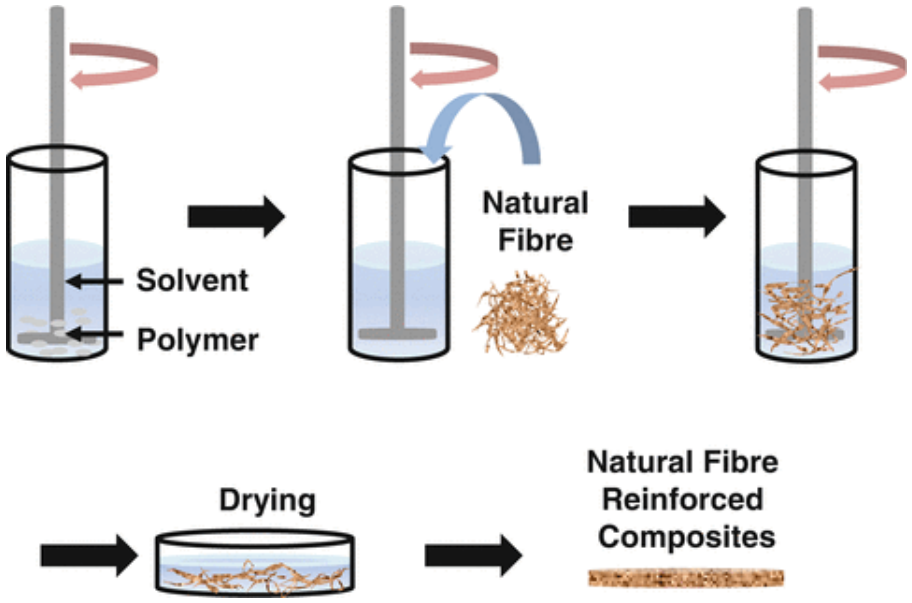

Figure 2.6: Schematic example of solution casting. Adapted from [36].

On other hand, melt blending has become the favourite technique for the creation of natural fiber composites. It consists in heating the polymer matrix to between 10°C and 30°C over the point of fusion before adding the fiber and properly blending it under compression, as represented in Figure 2.7.

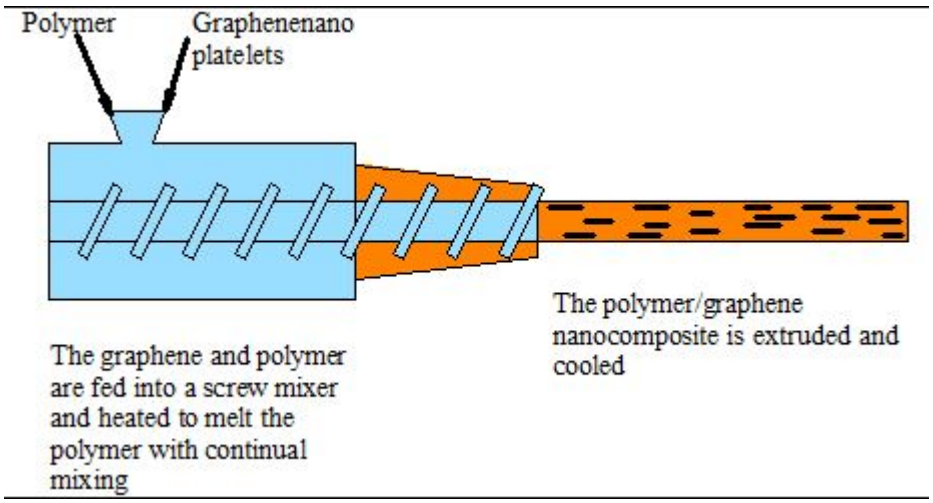

Figure 2.7: Schematic example of melt blending. Adapted from [37].

Melt blending has been considerably more widely accepted as a result of its compatibility with current processing technologies, such as injection molding and extrusion [32, 38]. As an additional advantage, these methods are environmentally friendly and do not involve the use of hazardous solvents. However, there is still some concern related to the processing conditions and the level of interactions between the fibers and the matrix that are used. In Ref. [39], the author concluded that good distribution of fibers inside the matrix, which is one of the requirements for

improving the mechanical and thermal properties, requires a favorable interface between the fibers and the polymeric matrix. Without this, the fibers will be poorly dispersed on the matrix.

For last, in-situ polymerization consists on the polymerization of a monomer in the presence of another polymer, typically in small amounts, being this technique referred to as one of the key methods for the compatibility in polymer blends [32, 40]. It enables the formation of a covalent bond between the constituents, which may lead into graft or block copolymers that, in the final analysis, lead to the development of a stable interface [38]. Additionally, it is possible to obtain composite materials with higher fiber weight fractions [41], since the resulting materials have a far higher degree of homogeneity than those produced by solution casting and melt blending. Figure 2.8 presents a representative diagram of the in-situ polymerization method.

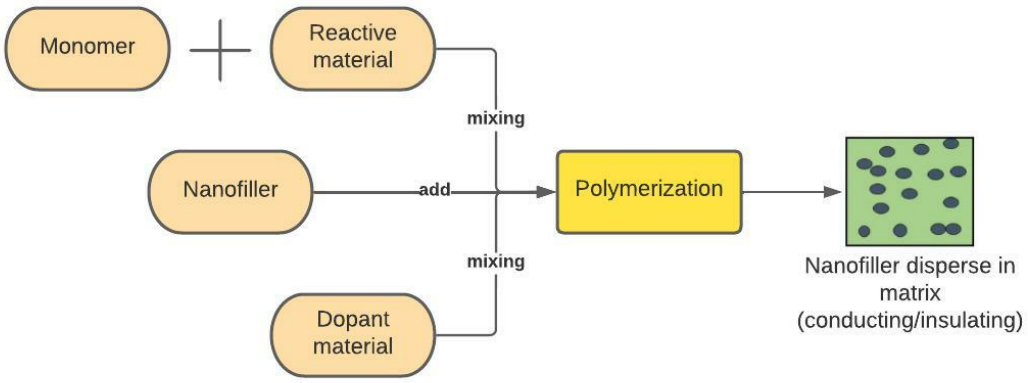

Figure 2.8: Schematic representation of the in-situ polymerization method. Adapted from [42].

In general, the processing of composites requires good control of pressure and temperature once they have direct influence on the degradation of the fiber and guarantee the quality of the composites during the manufacturing process. In injection and compression moldings, there is a desirable effect on applying high pressure that ensures the fiber volume fraction. The degradation temperature of constituents in a typical natural fiber usually is between 200-400°C. However, the higher the temperature the bigger is the potential to the loss of mechanical strength. The range of the processing temperature of most polymeric resins is about 200-500°C, which means it could damage the natural fibers during the production process of composites [30, 43]. A representative diagram of degradation temperature ranges, and consequent effects on their material constituents, are illustrated in Figure 2.9.

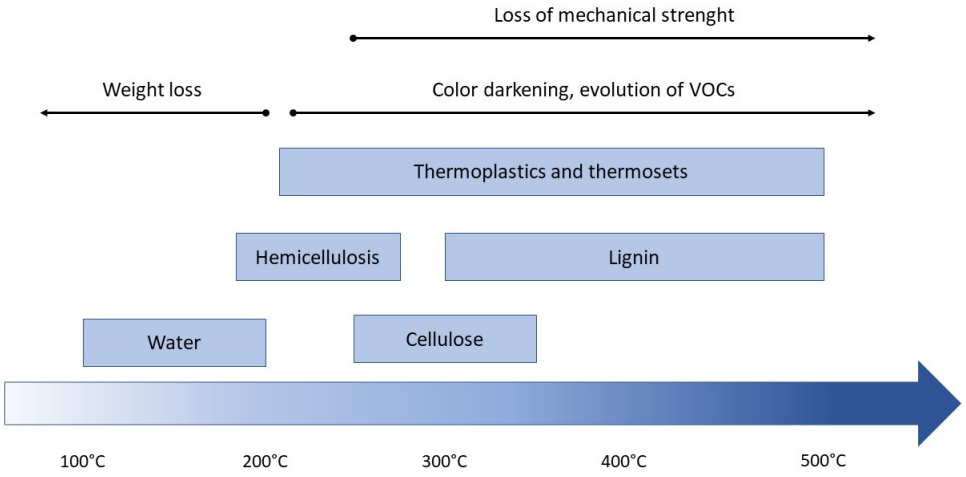

Figure 2.9: Thermal degradation ranges for natural fiber reinforcing and resulting consequences on the characteristics of the composite constituents. Adapted diagram from [43].

Extra caution is required in controlling the processing temperature because if it is too high it could over-heat some local regions, but if it is too low, the viscosity of the resin could not reach the required level. In such cases, the wettability of the fiber and the distribution uniformity of the resin within the composite material would be affected [30, 43].

On the specific case of wood-polymer composites, ensuring that the melted polymer disperses through the wood particles in a uniform manner is one of the challenges of the compounding process. The extent of blending is a critical parameter for short fiber-reinforced composites, since it can affect the mechanical properties of the final product in a negative way [44, 45, 46]. There is also a problem related to the mixing, in which the result of ineffective or excessive mixing could damage the wood fibers. Usually, these composites are produced by single screw extrusion, twin screw extrusion or injection molding. The extrusion process generates less heat because of its lower shear, being this an advantage over injection [44].

There are some factors that must be considered before and during the processing of natural fiber polymer composites (NFPCs). These factors are mainly related to the fiber properties, the polymer matrix, and the fiber-matrix interface properties. As mentioned on Section 2.2, the reinforcing fiber properties directly influence the strength and the stiffness of the composite, while the matrix helps in keeping the fiber distribution and helps in transfer the load from fiber to fiber. In summary, the main factors that can contribute to the fiber-matrix relationship are:

- Fiber types and surface treatment;
- Fibers distribution;
- Processing condition;
- Addition of other materials.

Chemical and physical treatments

In order to improve the mechanical and surface properties of composites due to the problem associated to the hydrophilic characteristic of natural fibers, it is necessary to adopt some chemical treatments. This is of high importance, since the pure mix of natural fibers to a matrix could lead to poor mechanical properties, being this even more problematic on low length-to-diameter ratio particles [12, 28]. Natural fibers, when compared to synthetic fibers, are more moisture absorbent and show lower strength. To solve this problem many studies were developed to discover pre-treatment processes to enhance the mechanical properties and the compatibility of natural fibers with the polymer matrices [28, 47]. Table 2.2 summarizes the different chemical treatments and their effects on natural fibers.

Table 2.2: Different chemical treatments and their effects [28, 48, 49, 50].

Chemical Treatments	**Coupling Agent**	**Specific Effects on Natural Fibers**
Benzoylation treatment	Benzoyl chloride	Makes fibers hydrophobic
Peroxide treatment	Polyethylene	Improve the adhesion of fibers with a matrix
Sodium Chlorite treatment	Sodium Chlorite ($NaClO_2$)	Remove moisture from fiber
Acrylation and acrylonitrile grafting	($CH_2 = CHCOOH$)	Bonding capacity and stress transfer of the interface increases
Oleoyl Chloride treatment	Oleoyl Chloride	Improves wettability and adhesion properties
Triazine treatment	Triazine ($C_3H_3N_3$)	Improves the adhesion of the fibers
Permanganate treatment	Potassium Permanganate ($KMnO_4$)	Improves the thermal stability of the fibers
Fungal treatment	Specific Enzymes	Enhance the linking/meshing of fibers in the matrix

Chemical and physical approaches are employed to modify the filler particles, with the major focus on grafting chemical groups capable of enhancing the interfacial interactions between the filler particles and the polymer matrix. Although there are some drawbacks related to the costs, in the case of complicated techniques, this is a particularly interesting approach to improve the properties of green composites [12]. Still, some industrial applications demand faster and cheaper methodologies, therefore chemical modifications are still unlikely to meet these requirements [12, 51].

Currently, the preferred solution for industrial applications relies less on manipulating the chemistry of the fibers and more on adding small amounts of a "third compound". This new addition may operate as a catalyst for the formation of chemical bonds between a matrix of polymers

and cellular components due to its intrinsic chemical characteristics [12]. Detailed information about this solution is given on Chapter 5.

2.3.4 Quality Control

The quality control for composites begins at a supplier level, being the Process Control Documents (PCD) used to regulate the manufacture of a given composite material. Usually, it defines and controls everything related to the composite: the raw materials, the processes and equipment, and the test methods. On other hand, to monitor the data generated during the manufacturing and to keep the material as uniform as possible (batch to batch method), there is the Statistical Process Control (SPC). This control checks the variability through the standard deviation and establishes a tolerance limit. The lesser products produced outside specification limits the better, meaning the process is more capable [52].

There are also ways to control the production at a user level such as inspecting incoming material and supervising supplier traceability, which can ensure that the materials used in composite construction will meet the engineering requirements [52]. Besides, there are shelf life and out time control. The quality of the starting material form and the processing route selected to manufacture the composite can impact its final properties and performance, though the properties of the reinforcing phase have a huge influence on the final properties of the composite [52]. Furthermore, there are other aspects that can minimise any risk of quality deviations, such as [52]:

- Characterizations of the thermal profile of the empty mold;
- Trial runs combining grid strain analysis with finite element methods to validate performance;
- Combination of new sensor techniques for process monitoring with new non-destructive component testing;
- Tools with real-time monitoring for clamping pressure, vacuum level between diaphragms, forming rate, consolidation etc;
- Control residual stresses;
- Fiber volume and void content measurements.

2.4 Additive Manufacturing

Additive manufacturing, commonly referred to as 3D-printing, has been given more attention for the relatively low starting cost of open-source printers, the promise of repeatable, customized, and high-resolution prints, and compatibility with a wide variety of materials [53]. Very recent research has been conducted on the investigation of continuous fiber reinforced 3D-printed materials either adapting conventional printers [54, 55, 56, 57, 58] or using commercial solutions

[59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69]. The use of continuous fiber reinforced composites in the 3D-printing field is also supporting developments that include complex and multifunctional load-bearing materials [70].

Additive manufacturing (AM) is a "process of joining materials to make parts from 3D model, usually layer upon layer" [71] with less waste material and without requiring additional tooling. It has been used for a long time to make architecture models since it opens the door to complex geometries and automates the process starting by the digital modelling [72, 73, 74, 75]. Additive manufacturing has unique characteristics [76, 77, 78, 79], namely:

- No need for tooling, which significantly reduces production time and costs;
- Product optimization for a certain function;
- More economical custom product manufacturing (mass customization and mass personalization);
- Potential for simpler supply chain, shorter lead times, and lower inventories.

The main goals of Additive Manufacturing processes have been printing high-load bearing, light-weight, and recyclable structural parts, making possible complex designs that it would be impossible to produce using conventional manufacturing processes [52]. The AM processes can be classified in 7 different types, as it is shown in Figure 2.10 [80].

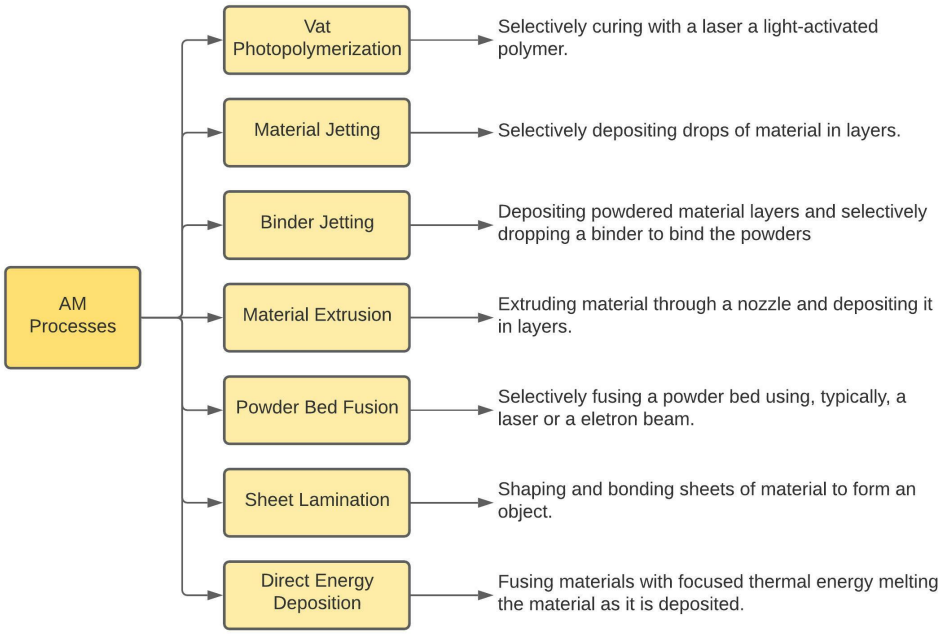

Figure 2.10: Types of Additive Manufacturing processes.

Additive manufacturing has a lot of applications in many areas, as represented in Figure 2.11. Aerospace and automotive industries are the ones who have explored more this area. Initial focus was on the rapid prototyping to reduce time to get these parts.

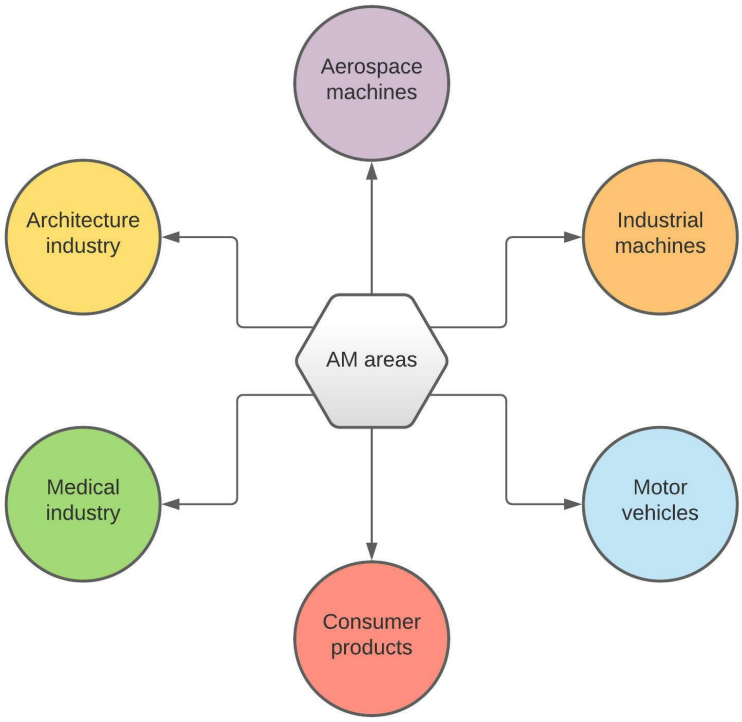

Figure 2.11: Additive manufacturing areas of application.

Additionally, AM technology brought a lot of advantages for the medical field when it was incorporated into their methodologies. For instance, it can be mentioned the high quality of bone prototypes, its ability to be used to craft artificial teeth in dentistry, and its high efficiency in manipulating tissue growth in orthopedic surgery [73].

According to a report published by the World Economic Forum, the construction industry currently accounts for about 6% of the world GDP [81], providing 18 million jobs worldwide, and is expected to reach around 14.7% in 2030 [82, 83]. Indeed, 58% of all construction supplier and contractor respondents identified skilled workforce shortages as an obstacle for a future modernized construction sector [83]. Furthermore, a 1% rise in productivity could save $100 billion a year in construction costs at global level [84].

Also, when considering the climate implications of construction we must understand that construction uses around 50% of the global steel production, and it is responsible for 30% of the world greenhouse gas emissions [83].

However, the total replacement of traditional methods will probably not occur. Nevertheless, the use of hybrid techniques can improve resolution and surface finish while not increasing the

printing time. If we use AM for low resolution and then finish the part with a subtractive technology, then we take the best of both to get a faster and better result [72]. This can be advantageous to build components using AM and finishing processes to provide the external aimed geometrical tolerance as well as the overall appearance.

Additive Manufacturing adds value by the fabrication of parts with complex geometries or end-use materials with enhanced functions, customized geometries, and either biodegradable materials or reusable. There are solutions, like printing moulds for reinforced concrete using wax material, being developed. The Laing O'Rourke Engineering Excellence Group idea was that the wax would act as the mould during construction, and later it could be heated to recover or reused for other moulds, reducing the waste [85].

In extrusion-based 3D-printing, the most common feedstock materials are synthetic thermoplastics, that can be reinforced with natural fibers such as hemp. Natural fibers are themselves composites of multiple biopolymers and extracted single-component polymer fibers, such as cellulose [53].

A lot of experimental research employing acrylonitrile-butadiene-styrene copolymer (ABS) or polylactic acid (PLA) focused on the impact on the qualities of the produced systems. For example, Kariz et al.[86] studied the effect of wood content up to 50% in 3D-printed samples printed in PLA and ABS. They discovered that the presence of wood particles on the filaments reduced the density of the filaments because the lower density of wood compared to PLA. Beyond that, the tensile strength increased with the an addition of wood until 10% to the filament, however, it started to decrease with 20% of wood.

Ferreira et al. [87] investigated the mechanical properties of unreinforced and short carbon fiber reinforced PLA. In their work, specimens were tested in tension and in-plane shear, and the results were very promising in terms of stiffness and strength. They also performed microscopical analyses in order to support their finds. Duigou et al. [88] researched the properties of 3D-printed PLA filled with continuous flax fibers. Although the Young's modulus showed significant increase compared to the unfilled PLA, the properties in the transverse direction were lower than those obtained on the same systems.

In an attempt of exploring the use of lignin, Gorbodil et al. [89] investigated PLA composites filled with lignin, discovering that the lignin prevents the hidrolytic degradation of PLA. However, it decreases the crystallinity, leading also to the reduction of the elastic modulus and tensile strength, while the elongation at break increased. On other hand, Gao et al. [90] explored the effect of different types of lignin reinforcing PLA, which showed an increase on the elastic modulus on the overall results. However, the higher percentages of lignin caused the decrease of the other properties.

Chapter 3

Experimental Procedure

This chapter aims to present in detail the processes and methods adopted to create biocomposite pellets for 3D printing. The experimental procedure includes the materials selection, mixing the materials, extrusion of filaments and tensile testing of the filaments.

3.1 Materials and Methods

First, it was decided to use colophony as matrix since there have been a huge exploration of pine resin in Portugal being this a way to get advantage of it. For that, the company Eurochemicals was fundamental in supplying the colophony used during the project. After selecting the matrix, one had to decide a material for the fiber. For this choice, one contacted Wood Pellet Services and went to the FuTerra Fuels factory who are experts in making pellets to "replace fossil fuels and reduce greenhouse gas emissions in a cost effective-way" [91]. They provided us wood powder/fillers (one third of pine, one third of eucalyptus, and one third of various trees) that we decided to use as material for the fibers. This choice was made in order to evaluate the possibility to reutilize forest residues.

3.1.1 Colophony

Colophony is a variation of pine resin obtained through distillation, being a mixture of small molecules consisting of different isomers. These isomers are generally known as "resin acids". A resin acid's chemical structure typically consists of cyclic rings, doubly conjugated bonds, and a carboxylic group. These characteristics brings to colophony several potential pathways for structural changes [92, 93]. In addition, colophony, also known as rosin, is used as a raw material in the production of adhesives, glues, culinary items, depilatory waxes, tires, rubber, and printing inks [94].

Genusa et al. [95] examined the structural behavior of a biocomposite material made of natural resin (colophony) and plant fibers (hay). Three-point flexure and compression experiments

were conducted. Samples with less fiber content turned to be more resistant. The experimental characterization demonstrated that the mechanical properties of the biocomposite, i.e. colophony replacing lime as an aglutinant, significantly increased when compared to the properties obtained for a mixture of lime and hay. Table 3.1 summarizes the Colophony properties used on this project based on the technical datasheet provided by Eurochemicals.

Table 3.1: Colophony properties.

Properties	**Typical**
Color	white/pile yellow
Color Gardner (50% toluene)	4/5
Softening point (R. B.) (ºC)	70/71
Acid number (mgKOH/g)	160/163
Abietic acid (%)	0.2/1.0
Dehydroabietic acid (%)	45/55
Unsaponifiables (%)	3/4
Solubility	Hidrophobic
Density	1.11-1.12
Tensile Strength (MPa)	0.077+/- 0.06
Tensile Modulus (GPa)	0.009 +/- 0.001
Max Strain (%)	1.71 +/- 0.03
Poisson's ratio	0.39

It is clear that colophony is a versatile chemical resource that has found use in many different fields, whether as colophony itself or as a close derivative. Opportunities to investigate colophony as a primary constituent for polymer-based materials are supported by the richness of its chemical reactivity.

3.1.2 Wood powder

Wood flour or powder is produced from postindustrial sources such as planer shavings and sawdust, which it usually used on wood polymer composites (WPCs). In general, natural fiber composites (NFCs) and WPCs have drawn a lot of attention on the last decades. The reason for this is that natural fibers are low-cost and renewable resources that increase mechanical properties like stiffness, strength, and heat deflection temperature under load. The natural fiber composites are widely used for applications in decks and automobiles as well as a building material, where the relatively low density of natural fibers is a significant advantage [96, 97].

In their work, Hristov et al. [98] concluded that wood fillers enhance the matrix polymer, but they also cause a reduction in ductility and a decrease in impact resistance. On other studies, the addition of wood fillers to thermoplastic polymers showed increases on the melt viscosity, which creates additional processing difficulties [99, 100, 101].

Typically, an extruder is used in a single compounding process or in a two-step process, along with an in-line injection molder, to create wood polymer composites. However, flat pressed wood polymer composites have the benefit of hot presses being accessible in traditional wood composite manufacturing facilities, as well as the ability to easily regulate the panel's density.

As FuTerra Fuels does not characterize the mechanical properties of the wood powder used on the fabrication of their pellets, they could not provide information about these properties. Nevertheless, it is known that they use a mixture of pine and eucalyptus, so it was decided to search for the properties on the database GRANTA EduPack 2021 and used the average between these two materials, as shown on Table 3.2.

Table 3.2: Pine and Eucalyptus mechanical properties from GRANTA EduPack 2021.

Properties	**Pine**	**Eucalyptus**	**Average**
Young Modulus [MPa]	1.700E+04	1.970E+04	1.835E+04
Shear Modulus [MPa]	6.182E+03	7.164E+03	6.673E+03
Poisson's ratio	0.375	0.375	0.375

3.1.3 Polylactic acid (PLA)

Polylactic acid is a thermoplastic monomer derived from renewable and organic sources such as corn starch or sugar cane. In contrast to the majority of plastics, which are made from fossil fuels by distilling and polymerizing petroleum, PLA is created from biomass resources. PLA is considered a promising biodegradable thermoplastic biopolymer, which is mainly used in medical applications, food packaging industry, and 3D printing. However, when compared to other biopolymers it exhibits a high degree of stiffness and fragility. As a result, the pursuit of conferring PLA with higher ductility remains a research issue of interest. Additionally, restricted features like as hydrophobicity, melt flow rate, and high temperature resistance have prompted researchers to study and create new sustainable polymer formulations based on PLA and other materials [102, 103, 104]. Figure 3.1 shows the PLA mechanical properties of the database GRANTA EduPack 2021 used during this project.

PLA (general purpose)

Datasheet view: All attributes | Show/Hide | Find Similar

Mechanical properties					
Young's modulus		3,3	-	3,6	GPa
Specific stiffness		2,63	-	2,87	MN.m/kg
Yield strength (elastic limit)		50	-	55	MPa
Tensile strength		55	-	72	MPa
Specific strength		43,8	-	57,4	kN.m/kg
Elongation		2,5	-	6	% strain
Elongation at yield		2	-	3,5	% strain
Compressive modulus		* 3,3	-	3,6	GPa
Compressive strength		66	-	86,4	MPa
Flexural modulus		3,1	-	3,6	GPa
Flexural strength (modulus of rupture)		83	-	108	MPa
Shear modulus		* 1,2	-	1,29	GPa
Bulk modulus		* 5,7	-	6,3	GPa
Poisson's ratio		* 0,38	-	0,4	
Shape factor		5,6			
Hardness - Vickers		17	-	22	HV
Hardness - Rockwell M		* 50	-	54	
Hardness - Rockwell R		* 32	-	35	
Hardness - Shore D		79	-	83	
Elastic stored energy (springs)		445	-	742	kJ/m^3
Fatigue strength at 10^7 cycles		* 22,2	-	27,7	MPa

Figure 3.1: PLA mechanical properties from the database GRANTA EduPack 2021.

3.2 Procedure

For the experimental procedure one adopted different steps as represented on the diagram in Figure 3.2.

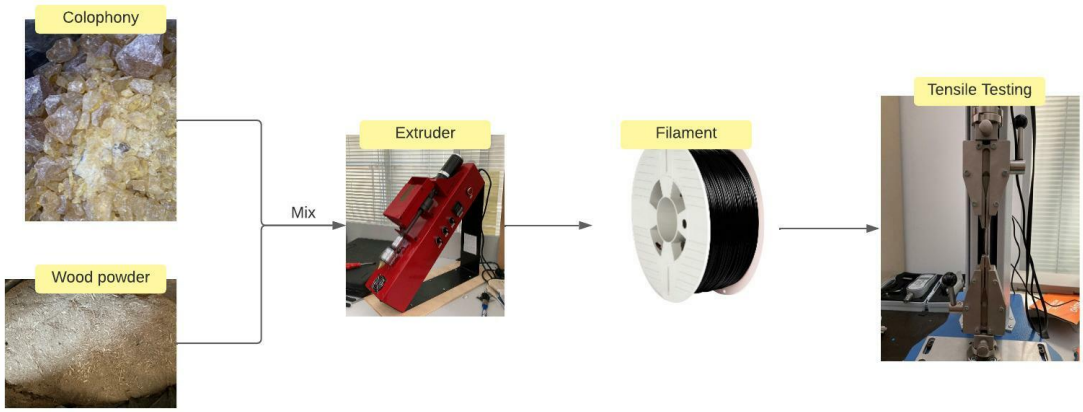

Figure 3.2: Schematic diagram of the experimental procedure.

3.2.1 First attempt

Initially, one had to make sure that the materials were ready to be mixed. As the colophony was solid and had pieces that were too big to use in the extruder, one started by putting some pieces on a plastic bag into the freezer and then they were crushed with a hammer into smaller pieces and powder. As there still remained some pieces that were too large, it was decided to sift. For some uniformity, it was decided to also sift the wood powder/fillers.

After having both materials sifted, the first tryout consisted in making 5kg by mixing 3wt% of wood fillers and 97wt% of colophony (150g/4850g). The next step was to extrude the mixture on the extruder Noztek Pro at 140°C, since it was a reference temperature above the softening point of the colophony to start. However, the equipment was not extruding well the material, so it was decided to increase the temperature gradually until 160°C, which led the material to accumulate in the hopper without being extruded, as shown in Figure 3.3.

Figure 3.3: Accumulated material at first attempt.

As this process failed, it was decided to not go any further, clean the extruder, and try another attempt with a different percentage of colophony and wood in a lower quantity.

3.2.2 Second Attempt

After the failure of the first attempt, it was decided to increase the percentage of wood powder to 30wt% in a 1kg mixture. Once again it was needed to sift both the colophony and the wood fillers, weight them, and mix, as shown in Figures 3.4 and 3.5.

Figure 3.4: Sifting wood fillers.

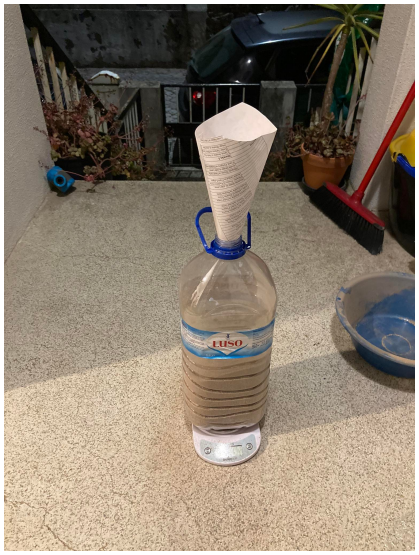

Figure 3.5: Weighting and mixing of the materials.

After the first step, the extruder hopper was filled with the mixture and the material seemed to be extruded well, as it is seen in Figure 3.6. However, after few minutes the material was stuck again and the nozzle seemed to be clogged (Figure 3.7).

Figure 3.6: First filament extruded.

Figure 3.7: Accumulated material on the second attempt.

After getting the material stuck once again it was clear that there was no material coming out from the nozzle, so it was decided to remove the nozzle and clean the extruder, as it is shown on Figures 3.8 and 3.9.

Figure 3.8: Extruder without the nozzle and material removal.

Figure 3.9: Cleaning the nozzle by adding PLA to the extruder.

After cleaning the nozzle, it was verified that it was not a viable process. Hence, it was decided that pure colophony and wood powder could not the best approach. So, another strategy was adopted to continue this project:

1. Mix PLA with colophony;

2. Mix PLA with wood powder;

3. Mix PLA with colophony and wood powder.

3.2.3 Third Attempt

PLA

To make sure the extruder was clean and working accordingly, it was decided to do some trials with pure PLA to find the best extrusion conditions since it was a little different from the literature. We started with 170°C since it was the reference temperature to melt PLA but the filament was too liquid and thin so one decreased the temperature to 160°C. After cooling the extruder the filament thickness increased a little but it was still too liquid, so one decreased the temperature to 155°C and with this new condition the filament started to be properly extruded, as shown in Figure 3.10.

Figure 3.10: Continuous filament of PLA being extruded.

PLA and Colophony

At first, one extruded the new mixture at 155°C, but the the mixture was too liquid and thin so it was decided to decrease the temperature to 150°C and then to 140°C to ensure the filament would extrude in the best conditions. After it stabilized and started to get difficult to extrude, one increased the temperature again to 155°C. In Figure 3.11 one can see the filament being extruded.

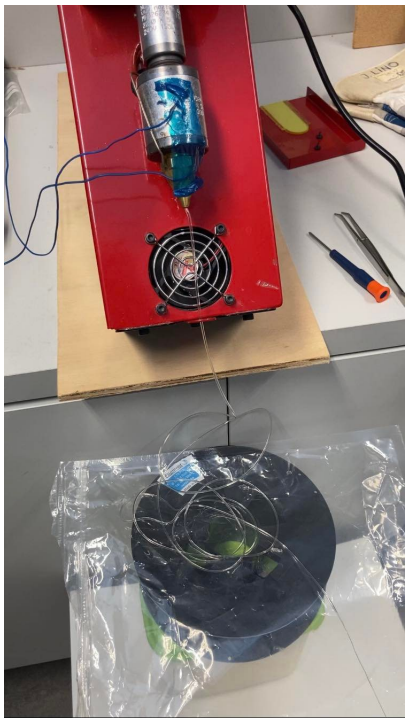

Figure 3.11: Test of PLA (97wt%) with colophony (3wt%).

As one could not see a significant difference between the pure PLA filament and the one consisted of PLA and colophony, it was decided to increase the percentage of colophony to 10wt%.

3.2.4 Tensile Tests

In order to determine the longitudinal properties of the extruded filaments, tensile tests were performed each type of filament, i.e. pure PLA, PLA with colophony at 3wt%, and PLA with colophony at 10wt%. For each filament three samples were tested. The tensile test's fundamental concept is to clamp a sample of a material between two fixtures known as "grips", as shown in Figure 3.12. The material's length and cross-sectional area must be measured before starting the test. The material is then put under weight while the other end is fastened and held in place. As the weight (also known as the load or force) is continuously increased, the sample's length is also measured. For the current tests, the load was measured using a load cell with 2500N capacity.

Figure 3.12: Tensile test equipment.

The raw data obtained from the machine acquisition system can be plotted creating a graph of load (amount of weight) versus machine crosshead displacement (amount it stretched). When the sample fractures or breaks it can be obtained the maximum force before failure and the displacement associated. After having the overall testing information, it is possible to compute the Young's Modulus for each sample, through the Equation 3.1:

$$E = \frac{\Delta\sigma_i}{\Delta\varepsilon_i}, \tag{3.1}$$

where $\Delta\sigma_i$ is the difference in applied stress between two strain points i, and $\Delta\varepsilon_i$ is the difference of the respective strain points i. The stress σ_i is defined as

$$\sigma_i = \frac{F_i}{A_s}, \tag{3.2}$$

with F_i the force measured at a given point i and A_s the cross-sectional area of the filament. The strain ε_i can be obtained as

$$\varepsilon_i = \frac{\Delta l_i}{l_0}, \tag{3.3}$$

where Δl_i is the displacement at a given point i and l_0 is the initial distance between the grips, i.e. the initial length-span of the filament.

In Figures 3.13, 3.14 and 3.15 it is possible to see the samples after the test. It is worth noting that all the samples were loaded until failure. Some of them were broken at the grip, which in theory, invalids their testing results. However, for the sake of comparison the computed values are still presented.

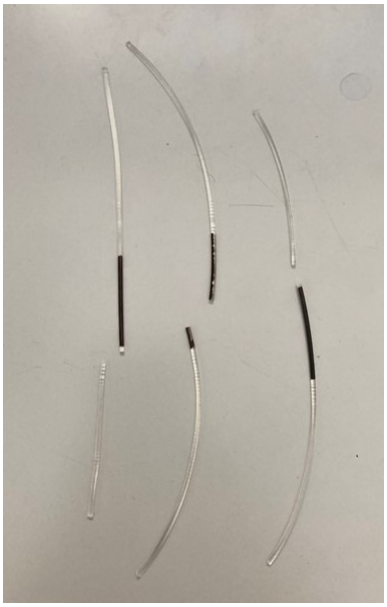

Figure 3.13: Samples of pure PLA filament tested in tension.

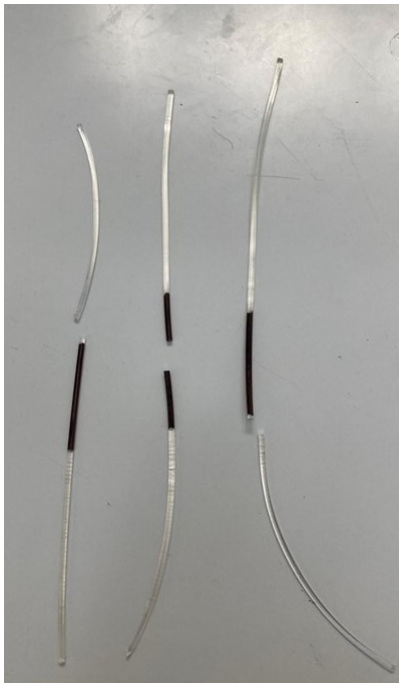

Figure 3.14: Samples of PLA with colophony (3wt%) filament tested in tension.

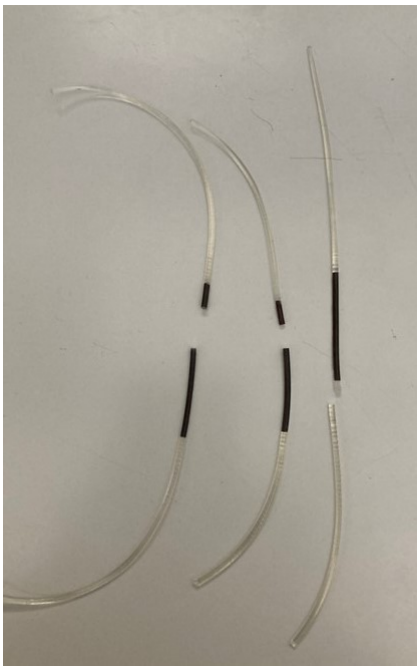

Figure 3.15: Samples of PLA with colophony (10wt%) filament tested in tension.

3.3 Results and Discussion

Figures 3.16, 3.17, and 3.18 present the force-displacement curves recorded throughout the tensile tests of samples from pure PLA, PLA with colophony (3wt%), and PLA with colophony (10wt%) respectively. From Figures 3.17 and 3.18 it can be noticed a good consistency in the elastic zone of the tested samples, which is not seen in Figure 3.16. In regards to the the maximum force before failure, some deviations can be observed in Figures 3.16 and 3.18.

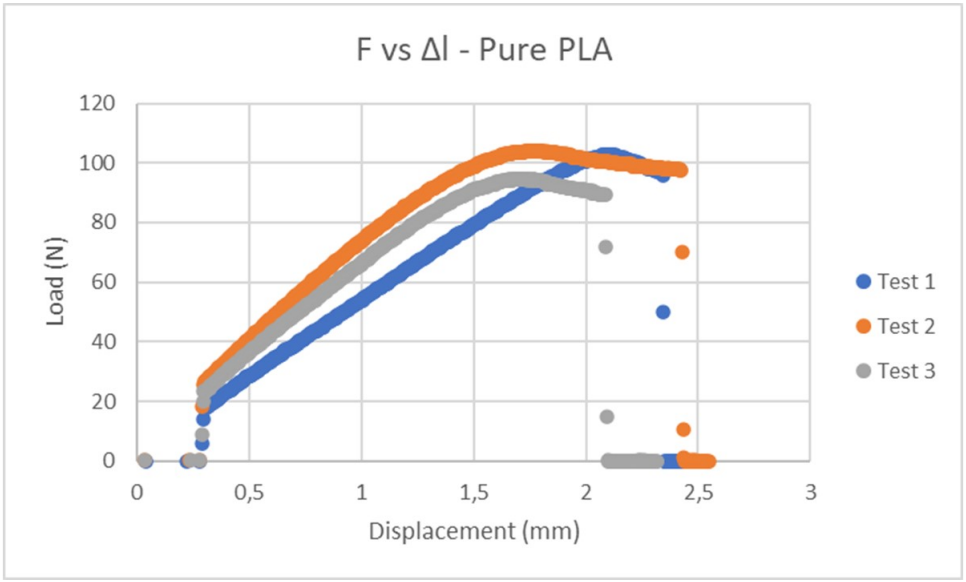

Figure 3.16: Force versus displacement results obtained for the pure PLA filaments.

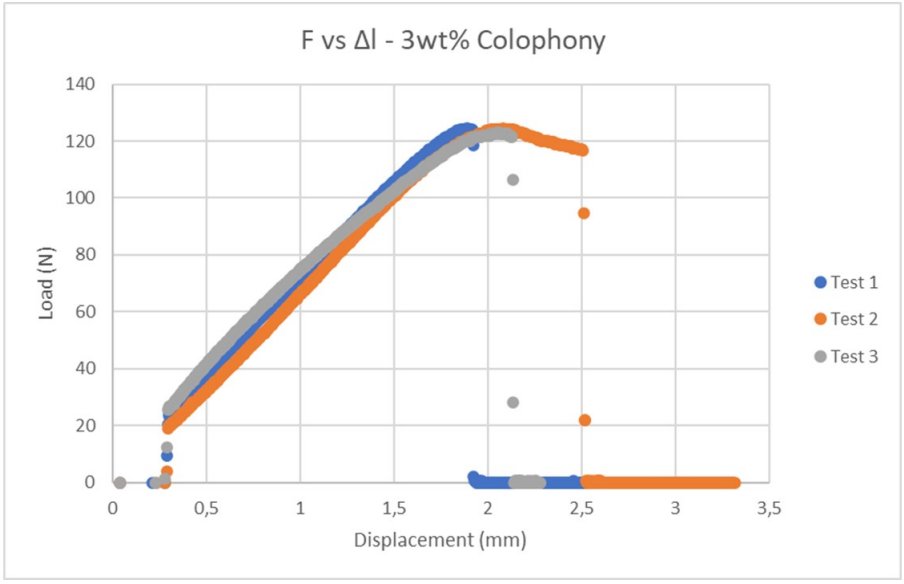

Figure 3.17: Force versus displacement results obtained for the PLA with colophony (3wt%) filaments.

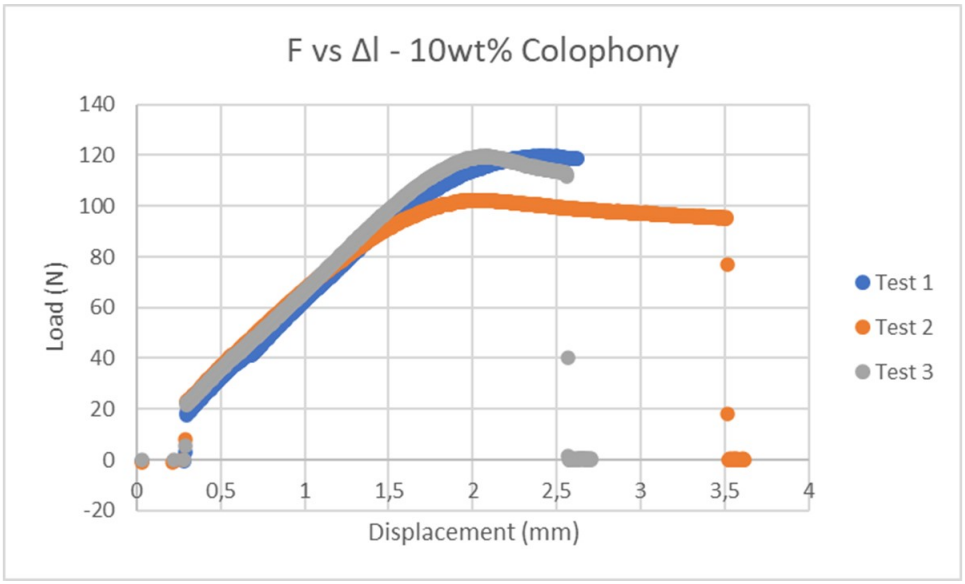

Figure 3.18: Force versus displacement tensile tests results for the PLA with colophony (10wt%) filaments.

Figures 3.19, 3.20 and 3.21 present the stress-strain curves computed after post-processing the load-displacement data recorded throughout the tensile tests of samples from pure PLA, PLA with colophony (3wt%), and PLA with colophony (10wt%) respectively. From Figures 3.20 and 3.21 it can be noticed a good consistency between the elastic moduli of the tested samples. In contrast, the results for sample Test 1 in Figure 3.19 presented some deviations when compared to the results obtained for the other samples of pure PLA. Regarding to the ultimate tensile strength, some premature failure can be noticed in Figure 3.20.

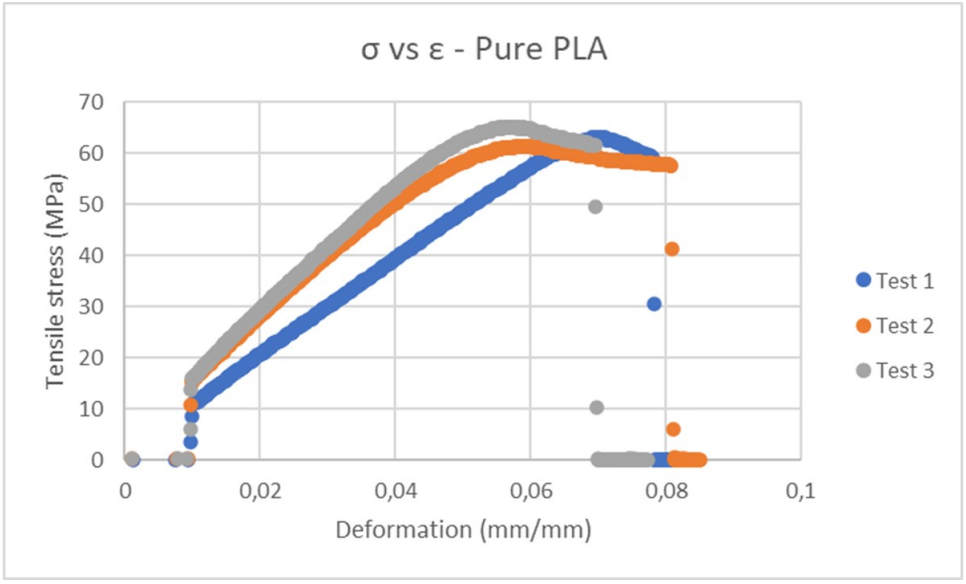

Figure 3.19: Tensile stress versus deformation results for the pure PLA filaments.

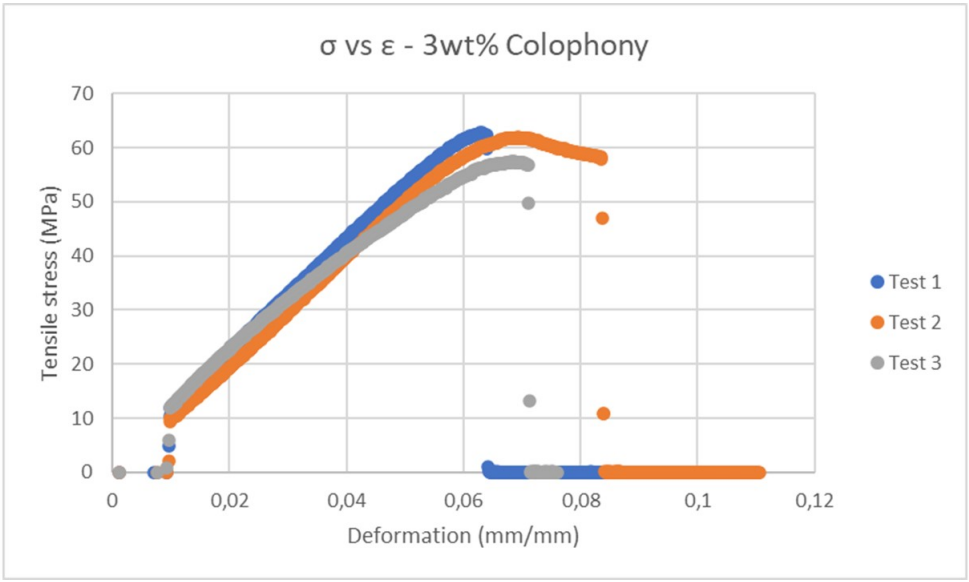

Figure 3.20: Tensile stress versus deformation results for the 3 wt% colophony filaments.

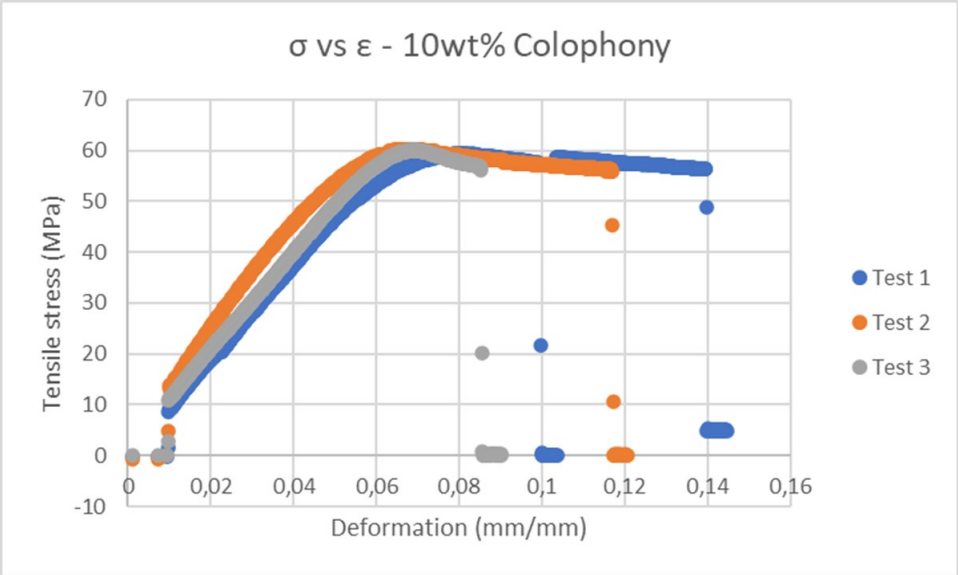

Figure 3.21: Tensile stress versus deformation results for the 10 wt% colophony filaments.

Table 3.3 lists the elastic data computed from the graphics according to Equation 3.1 for each sample of the filaments. As mentioned before, the results obtained for the samples that were broken at the grip are still reproduced in Table 3.3 for the sake of comparison. In Table 3.3, D is the averaged diameter of the sample, ΔF is the difference in applied force between two displacement points, and $\Delta(\Delta l)$ is the difference of two displacement points.

Table 3.3: Young's Modulus of samples from the three extruded filaments for a given $\Delta(\Delta l)$ and the respective ΔF.

	Trials	**D (mm)**	**ΔF (N)**	**$\Delta(\Delta l)$ (mm)**	**$\Delta\varepsilon$ (mm/mm)**	**E (MPa)**	**Average E (MPa)**
Pure PLA	**1**	1.44	51.00	1	0.033	939.46	1060.55
	2	1.47	58.50	1	0.033	1034.08	
	3	1.36	58.50	1	0.033	1208.12	
PLA + 3wt% Colophony	**1**	1.59	67.50	1	0.033	1019.86	963.44
	2	1.60	68.00	1	0.033	1014.61	
	3	1.65	61.00	1	0.033	855.84	
PLA + 10wt% Colophony	**1**	1.60	61.25	1	0.033	913.90	948.94
	2	1.47	55.50	1	0.033	981.05	
	3	1.59	63.00	1	0.033	951.87	

After analysing the overall test results, it is possible to conclude that some errors occurred throughout the experiments. For instance, the displacement measured by the machine ended in deformations that are particularly high, leading to low Young's modulus that do not correspond to the reality. The explanation for this could be related to the absence of an extensometer, since the strains were computed from the displacement recorded by the machine, and the tests were not standard, lacking a dimensional control of the filament. Other explanation could be related to the fact that it was not considered the sliding at the grips during the tests, which would cause the increase on the displacement without existing deformation. Furthermore, the filaments could have

porosities that were not considered and would decrease the cross-sectional area of the filament, which means that the expected Young's Modulus should be lower in this case.

In order to provide more elements for the discussion, a cause and effect analysis was performed with the support of Ishikawa diagrams. In Figures 3.22 and 3.23 it is possible to see the diagrams summarizing potential causes for the non-expected results obtained throughout the experimental procedure.

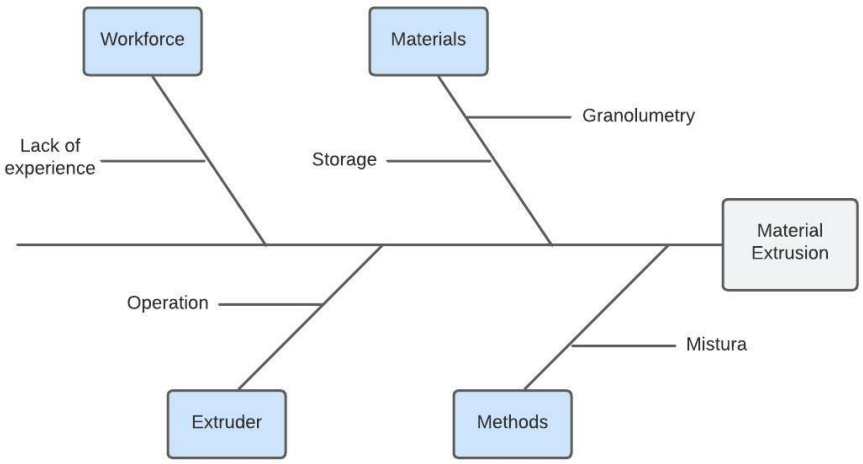

Figure 3.22: Ishikawa's diagram for material extrusion.

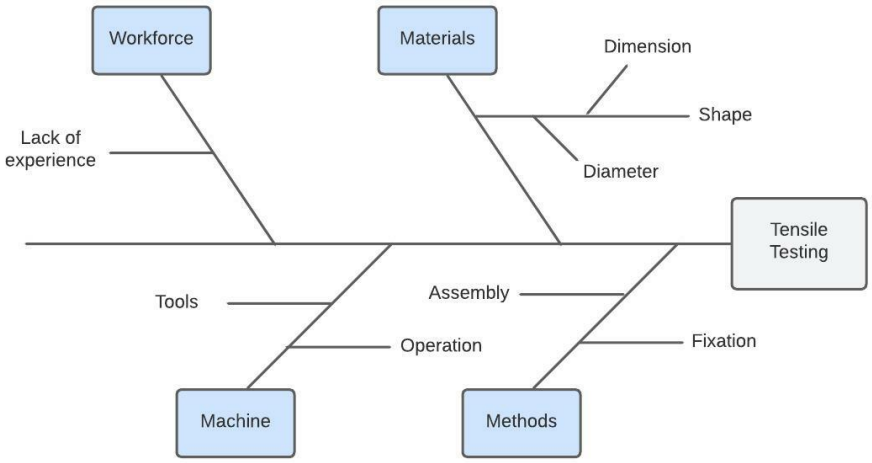

Figure 3.23: Ishikawa's diagram for tensile testing.

Chapter 4

Numerical Modeling

This chapter explains in details the numerical modeling adopted to predict the elastic properties of the aimed biocomposite, using the Asymptotic Homogenization technique implemented in the commercial software ABAQUS®. In summary, this work consists in 2 different models of a wood-fiber reinforced PLA-colophony biocomposite material with 10% and 20% of fiber volume fractions respectively. In order to compute the resulting elastic properties of the matrix system consisting of PLA and colophony, the models were defined with a colophony volume fraction of 10% for different sizes of representative volume elements until convergence. Details are given as follows.

4.1 Asymptotic Homogenization

In order to predict the biocomposite mechanical behavior, one decided to use the Asymptotic Homogenization technique. The Asymptotic Homogenization technique lies on a concept of a unit cell that is assumed to be periodic in the whole material. In structural problems, this technique provides an elastic model capable of predicting the homogenized equivalent properties of a heterogeneous material and also determining the stress in the domain of the periodic unit cell [68]. The Asymptotic Homogenization technique "presents a rigorous mathematical foundation providing accurate results when compared to experiments" [105]. Its implementation can be facilitated using commercial software of finite element analysis [106] such as the ABAQUS® software.

Depending on the microstructure that is modeled, a volume that is larger than a unit cell is required. To this end, Representative Volume Elements (RVEs) are often adopted. Typically, a RVE can be defined as volume of heterogeneous material that is representative of the whole composite structure containing matrix, fibers, grains, etc. [105, 107, 108]. In terms of modeling fiber reinforced materials, recent studies [109, 110, 111] have presented methodologies to create random fiber distributions that simulates the real fiber arrangement in a composite system.

4.1.1 Asymptotic Homogenization Model Implementation

According to Guedes and Kikuchi [112], the homogenized properties E^H_{ijkl} of a periodic composite material are given by

$$E^H_{ijkl} = \frac{1}{|Y|}\int_Y \left(E_{ijkl} - E_{ijmn}\frac{\partial \chi^{kl}_m(y)}{\partial y_n} \right) dY, \tag{4.1}$$

where Y corresponds to the unit cell volume, y_n denotes the set of coordinates used to define the problem at the microscopic level, E_{ijkl} is the material constitutive tensor and $\chi^{kl}_m(y)$ are the auxiliary displacement fields defined at the domain of the unit cell.

The auxiliary displacement fields $\chi^{kl}_m(y)$ can be obtained solving the problem at microscopic level defined as

$$\int_Y E_{ijmn}\frac{\partial \chi^{kl}_m}{\partial y_n}\frac{\partial \delta u_i}{\partial y_i} dY = \int_Y E_{ijkl}\frac{\partial \delta u_i}{\partial y_i} dY. \tag{4.2}$$

The solution of the problem at the microscopic level for the $\chi^{kl}_m(y)$ can be obtained by the finite element method, discretizing the domain of the unit cell. A implementation using the finite element commercial software ABAQUS ® is applied according to [105]. At first, the Eq.4.1 is rewritten in the bi-linear form and assuming unitary pre-strains

$$E^H_{ijkl} = \frac{1}{|Y|}\int_Y E_{ijkl}\frac{\partial}{\partial y_l}\left(P^{kl} - \chi^{kl} \right)\frac{\partial}{\partial y_j}\left(P^{ij} - \chi^{ij} \right) dY. \tag{4.3}$$

From the bi-linear form [113], it is possible to define the homogenized properties in function of strains as

$$E^H_{ijkl} = \frac{1}{|Y|}\int_Y E_{pqrs}\left(\varepsilon^{0(kl)}_{pq} - \varepsilon^{*(kl)}_{pq} \right)\left(\varepsilon^{0(ij)}_{rs} - \varepsilon^{*(ij)}_{rs} \right) dY, \tag{4.4}$$

which rewritten in the matrix form gives

$$\left[E^H\right] = \frac{1}{|Y|}\int_Y \left(\{\varepsilon^0\} - \{\varepsilon^*\} \right)^T [E] \left(\{\varepsilon^0\} - \{\varepsilon^*\} \right) dY. \tag{4.5}$$

Equation (4.5) can still be described in terms of characteristic displacements, where $\{\varepsilon\} = [B]\{\chi\}$, as

$$\left[E^H\right] = \frac{1}{|Y|}\int_Y \left(\{\chi^0\} - \{\chi^*\} \right)^T [B]^T [E] [B] \left(\{\chi^0\} - \{\chi^*\} \right) dY. \tag{4.6}$$

It is known from the finite element formulation that the stiffness matrix is defined by

$$[K] = \frac{1}{|Y|}\int_Y [B]^T [E] [B] dY, \tag{4.7}$$

and the reaction force vector is

$$\{f\} = [K]\{\chi\}. \tag{4.8}$$

Finally, as presented in [105], the homogenized properties in terms of nodal displacements and nodal forces are given by

$$E^H_{ijkl} = \frac{1}{|Y|}\left(\chi^{0(ij)} - \chi^{*(ij)}\right)^T \left(f^{0(kl)} - f^{*(kl)}\right) dY \tag{4.9}$$

where $\chi^{0(ij)}$ is the prescribed nodal displacements which results in unit strains, $f^{0(kl)}$ nodal forces obtained after prescribing $\chi^{0(ij)}$, $\chi^{*(ij)}$ nodal displacements obtained after prescribing $f^{0(kl)}$ and $f^{*(kl)}$ nodal forces after prescribing $\chi^{*(ij)}$.

It is worth mentioning that the authors of Ref. [105] kindly made their developed Python code available in order to perform the numerical analysis in the present work. In regards to the finite element model, it was discretized using the eight nodes, reduced integration, C3D8R solid elements available in AbaqusTM. More details about the element formulation can be found in [114].

4.2 Numerical Models

Table 4.1 summarizes the steps that were adopted for the creation of the numerical models.

Table 4.1: Steps for the numerical modeling on ABAQUS®.

Step	Description
Part	Create a cube $10 \times 10 \times 10$ [mm^3]. Create Partition of circles with 1.26 [mm] radius.
Properties	Create the materials with the respective properties. Create sections and assign them to the materials.
Instance	Create the instance dependent on the mesh.
Mesh	Create the mesh by the edges number (the same size of the edge for the y and z directions and for 1 on the x direction).
Job	Create a Job and Write Input to use the created file in the script.
Script	Run the script of the Asymptotic Homogenization
Results	See the results on the Output file.

4.2.1 Colophony and Fiber

At first, the modeling started with making the RVE by defining the part that was a 10 mm $\times$ 10 mm $\times$ 10 mm cube. After, it was time for making a partition for the fibers that one decided to make with a radius of 1.26 mm. As the radius was 1.26 mm and the first model had 10% of fiber volume fraction, Equation 4.10 was employed to determine how many fibers the RVE would contemplate.

$$\frac{\pi * r^2 * x * 10}{10 * 10 * 10} * 100 = 10\% \Leftrightarrow x = 2 \tag{4.10}$$

Once the number of fibers was defined, it was needed to randomly distribute them across the RVE cross-section. For that, it was used the function "*rand(1,2)*" on the software Matlab to generate random coordinates between 0 and 10 and then select the ones that were valid. For this part, it was decided that the fibers would have to be fully inside the square face, excluding the coordinates that could not fill this criterion, as shown in Figure 4.1.

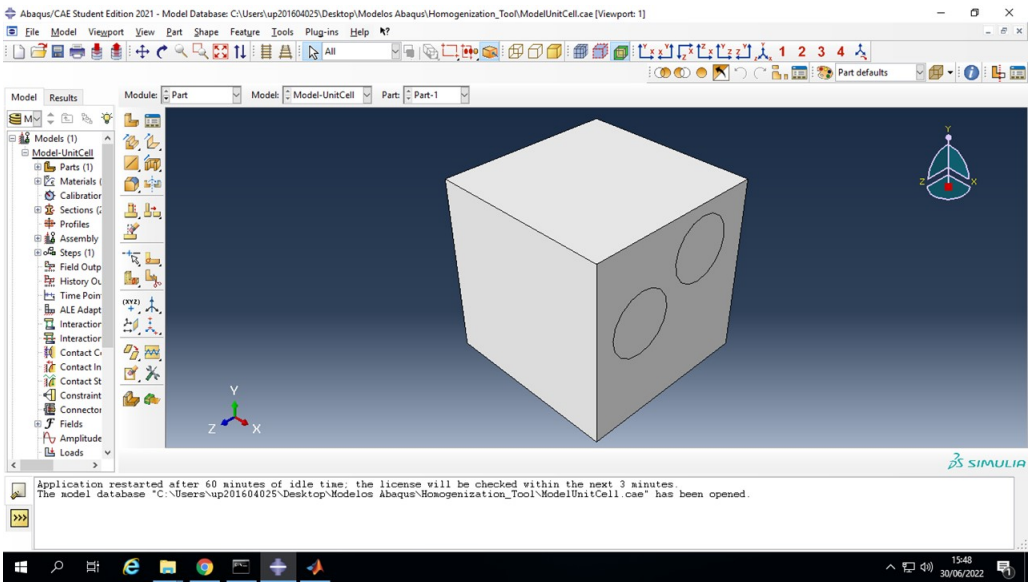

Figure 4.1: Example of Representative Volume Element on ABAQUS® for 10% of volume fraction.

The next step was to define the properties, as shown in Figure 4.2, by creating the materials with the elastic properties, previously described in Tables 3.1 and 3.2 in Chapter 3. In the present work, it was assumed that both the materials were isotropic. After the materials were created, the sections associated to each material were also created and then assigned to the respective elements. Thus, the material orientation was assigned for all the elements within the RVE.

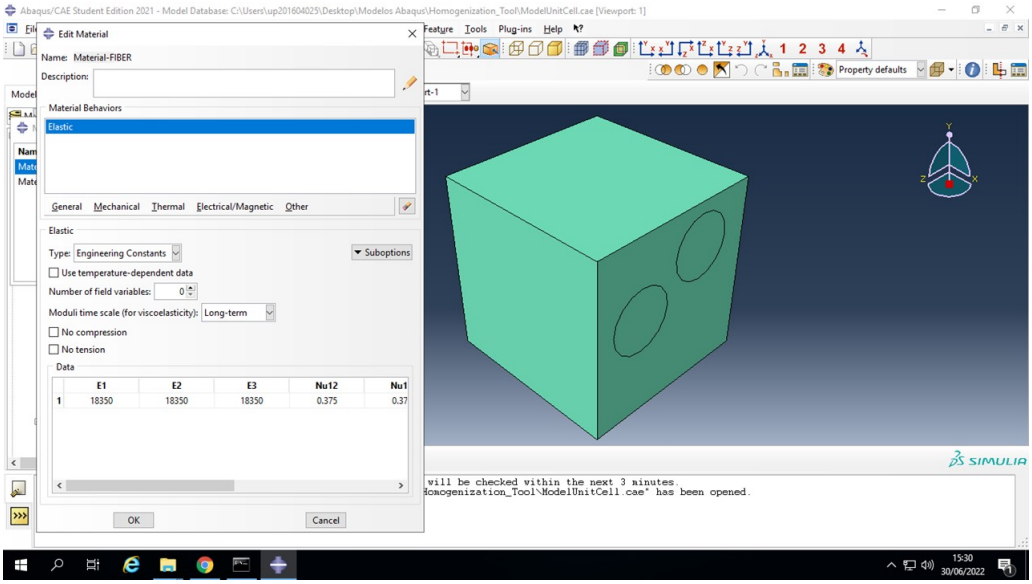

Figure 4.2: Example of the definition of the mechanical properties on ABAQUS®.

The next step was to create the instance and the mesh with 10 elements on y and z directions and with only one element on the x orientation as it would remain constant, as shown in Figure 4.3.

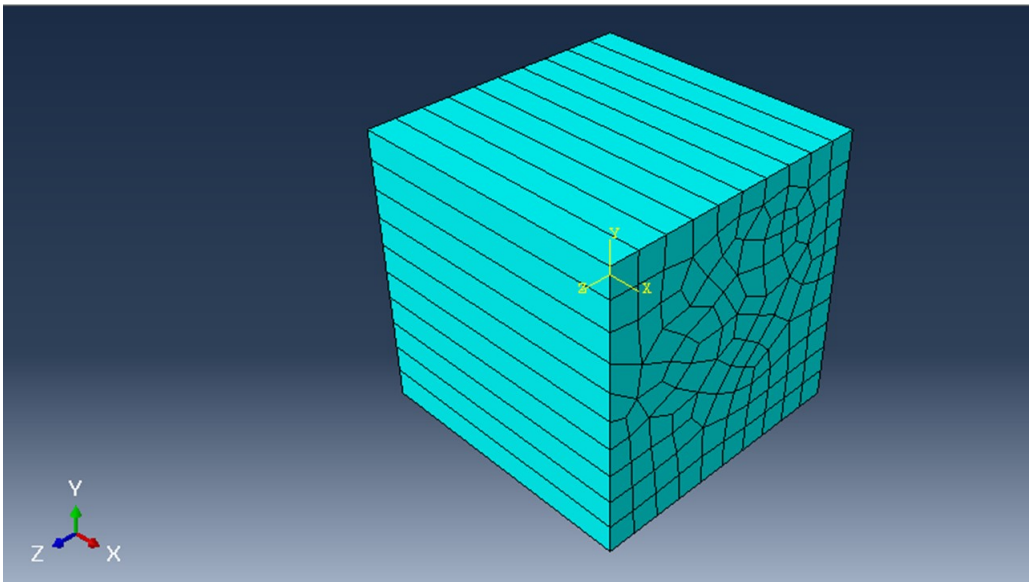

Figure 4.3: Example of the Mesh definition on ABAQUS®.

Afterwards, an Abaqus Job was created in order to write an input file that is used on the Python code to compute the Homogenized Elastic Constants (HEC) [105]. The same process was repeated for 20% of volume fraction, i.e., with 4 (four) fibers on the Representative Volume Element, as shown in Figure 4.4. Table 4.2 presents the results obtained for the models of wood-fiber reinforced colophony with fiber volume fractions of 10% and 20% respectively.

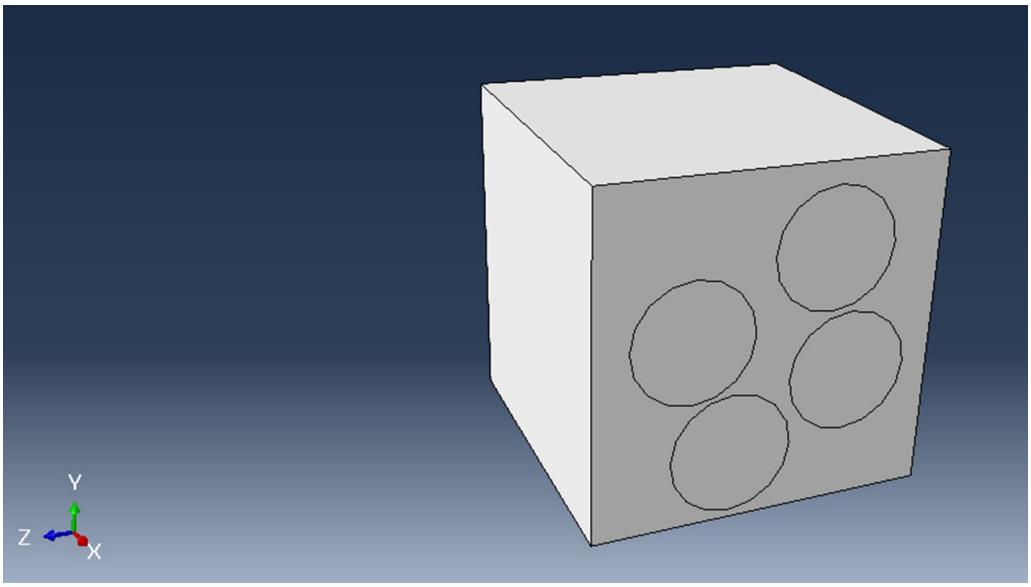

Figure 4.4: Example of Representative Volume Element on ABAQUS® for 20% of volume fraction.

Table 4.2: Results for the simulations with a volume fraction of 10% and 20% for Colophony with fibers.

HEC	**Colophony + Fibers - 10%Vf**	**Colophony + Fibers - 20%Vf**
E1 [MPa]	3.43E+03	6.86E+03
E2 [MPa]	1.46E+01	2.66E+01
E3 [MPa]	1.51E+01	2.42E+01
ν_{12}	0.38721	0.38271
ν_{13}	0.38617	0.38436
ν_{23}	0.59553	0.53371
G12 [MPa]	4.58E+00	8.08E+00
G13 [MPa]	4.98E+00	6.98E+00
G23 [MPa]	4.49E+00	6.65E+00

4.2.2 PLA and Fiber

For the models with PLA and fibers, it was used the same process adopted for the colophony and fibers, since it was also applied the Asymptotic Homogenization technique. The only difference was in changing the properties of the matrix for the PLA properties. Table 4.3 lists the results obtained for the Representative Volume Element with 10% and 20% of fiber volume fraction respectively.

Table 4.3: Results for the simulations with a volume fraction of 10% and 20% for PLA with fibers.

HEC	PLA + Fibers - 10%Vf	PLA + Fibers - 20%Vf
E1 [MPa]	6.23E+03	9.01E+03
E2 [MPa]	4.54E+03	6.31E+03
E3 [MPa]	4.62E+03	6.13E+03
ν_{12}	0.38719	0.3833
ν_{13}	0.38644	0.38429
ν_{23}	0.43861	0.4316
G12 [MPa]	1.58E+03	2.19E+03
G13 [MPa]	1.64E+03	2.06E+03
G23 [MPa]	1.56E+03	1.99E+03

4.2.3 PLA and Colophony

As two matrix materials were being mixed, the same model could not be applied to this simulation. So it had to be simulated as the colophony was randomly mixed with the PLA. For that, it was decided that was better to do a simulation with a volume fraction of 10% of colophony. Thus, the best way was to assign random elements of the mesh to colophony. Three models with different RVE sizes were defined, i.e. $5 \times 5 \times 5$, $10 \times 10 \times 10$, and $20 \times 20 \times 20$, under the condition that in every model each element of the mesh would have a volume $V_e = 1mm^3$. On this models it was not made a mesh convergence, but it was increased the RVE, since the elastic constants also depend of the total volume.

First, it was created the Part as a cube with $5 \times 5 \times 5$, then created the materials PLA and colophony with their respective properties and sections, and then the PLA section was assigned to the entire part. The next step was to create the Instance and then the mesh of the part with 5 elements in each direction, which resulted in 125 elements, as shown in Figure 4.5.

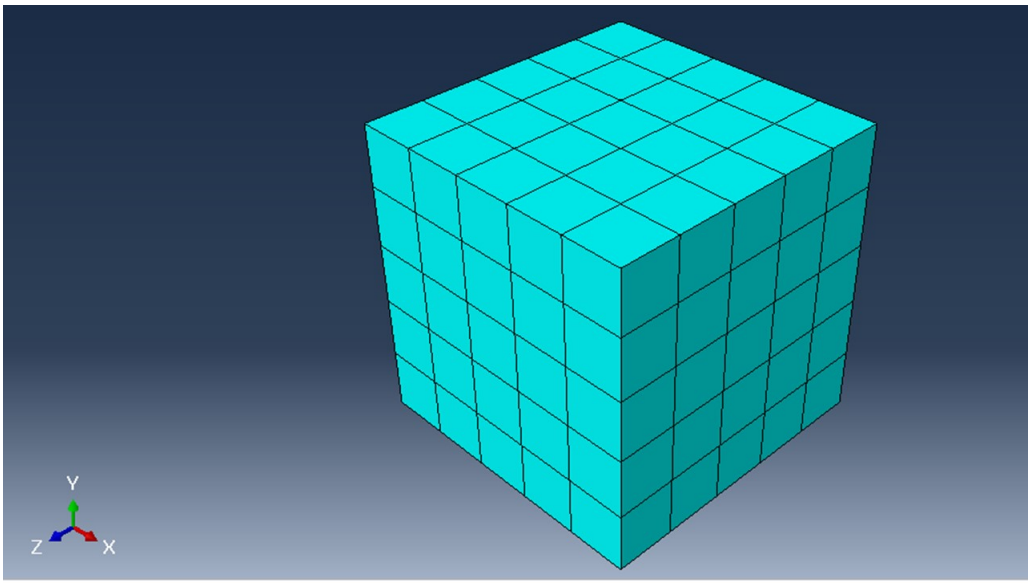

Figure 4.5: Representation of the mesh on the model 5x5x5 of PLA with colophony.

As the volume fraction was 10%, there were 13 elements that would be randomly distributed with colophony properties. To randomly select the colophony elements, it was developed a Matlab script that returns random coordinates and then some functions were developed on Excel to assign the coordinates to the respective element. Afterwards, it was created a Python script to assign the colophony section to the elements obtained by the Matlab function an then ran, as shown in Figure 4.6.

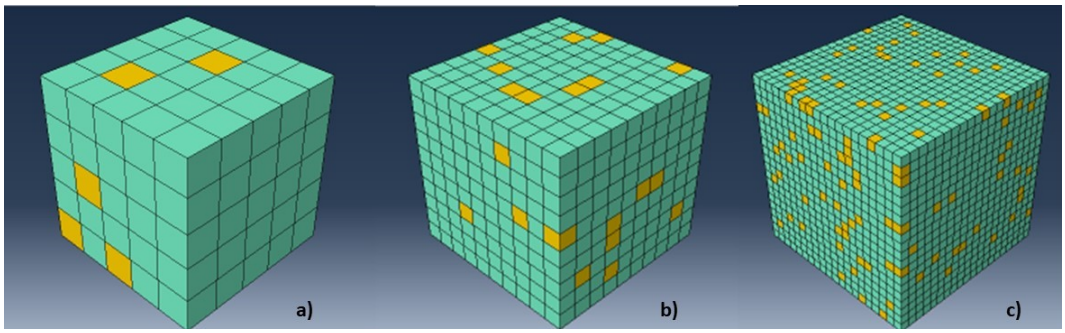

Figure 4.6: Elements section assignment after running the script.

Having all the elements assigned to the respective material, it was created the Abaqus Job to write the input file. The final script of the Asymptotic Homogenization modeling was run to obtain the results of the homogenized elastic constants. The same process was applied to the models with size $10 \times 10 \times 10$ and $20 \times 20 \times 20$ but changing the size of the cube to be in accordance with the model. However, as the size of the RVE increased, the complexity of the formulas to attribute the coordinates to the elements got higher. Table 4.4 describes the results obtained for the homogenized elastic constants from the three models with PLA and Colophony.

Table 4.4: Results of the simulations for the RVEs of PLA with Colophony with sizes $5 \times 5 \times 5$, $10 \times 10 \times 10$, and $20 \times 20 \times 20$.

HEC	$5 \times 5 \times 5$	$10 \times 10 \times 10$	$20 \times 20 \times 20$
E1 [MPa]	2.83E+03	2.77E+03	2.87E+03
E2 [MPa]	2.90E+03	2.84E+03	2.87E+03
E3 [MPa]	2.76E+03	2.79E+03	2.88E+03
ν_{12}	0.36224	0.3569	0.36333
ν_{13}	0.36069	0.35657	0.36246
ν_{23}	0.37378	0.36432	0.36232
G12 [MPa]	1.01E+03	9.82E+02	9.97E+02
G13 [MPa]	9.72E+02	9.62E+02	9.96E+02
G23 [MPa]	1.00E+03	9.83E+02	9.97E+02

4.2.4 PLA, Colophony and Fiber

Lastly, to compare the results and evaluate the influence of the fibers and the colophony together it was made the model "PLA + Colophony" to use the results of the converged simulation as the properties of the matrix on a model with fibers. For this, it was needed to analyse the results of the three models to see which one would suit better to use on the simulation with the fiber. It was decided that the criterion would be how the properties converge since the constants should be isotropic. From Figures 4.7, 4.8, and 4.9, it is possible to conclude that the simulation $20 \times 20 \times 20$ is the one which the results are better converged to a point that is expected for assumed isotropic materials.

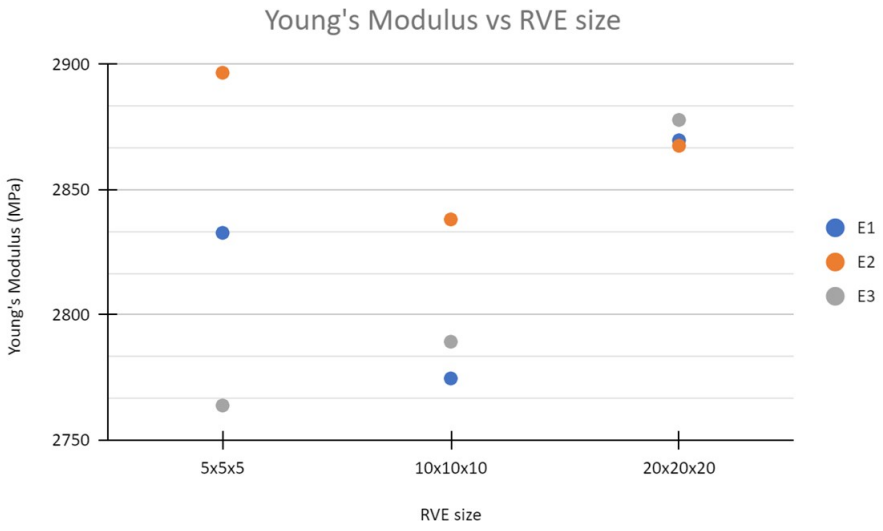

Figure 4.7: Graphic of the Homogenized Young's Modulus of each RVE size.

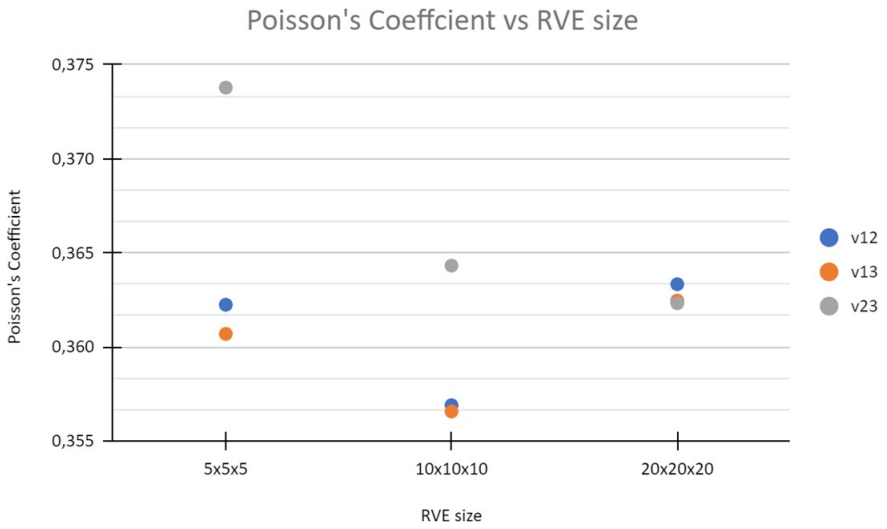

Figure 4.8: Graphic of the Homogenized Poisson's coefficient of each RVE size.

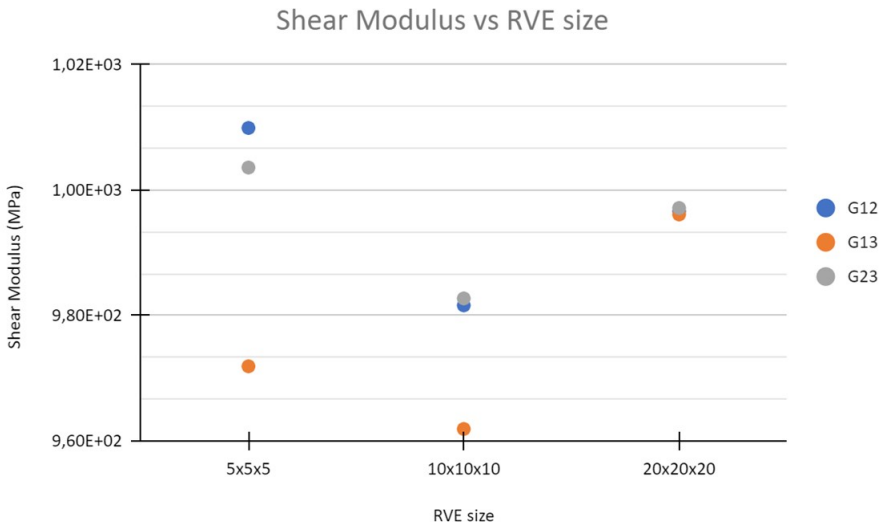

Figure 4.9: Graphic of the Homogenized Shear Modulus of each RVE size.

The rest of the modeling followed the same steps described in Section 4.2.2 by only changing the properties of the matrix for the results of the model $20 \times 20 \times 20$, as this now became the new matrix for the final simulations. Table 4.5 shows the results of the simulations for the wood-fiber reinforced PLA-colophony with fiber volume fractions of 10% and 20% respectively.

Table 4.5: Results for the simulations with a volume fraction of 10% and 20% for PLA and colophony with fibers.

HEC	PLA+Colophony+Fiber - 10%Vf	PLA+Colophony+Fibers - 20%Vf
E1 [MPa]	5.76E+03	8.65E+03
E2 [MPa]	3.80E+03	5.40E+03
E3 [MPa]	3.89E+03	5.21E+03
ν_{12}	0.3656	0.36867
ν_{13}	0.36553	0.36744
ν_{23}	0.41143	0.40364
G12 [MPa]	1.29E+03	1.85E+03
G13 [MPa]	1.35E+03	1.73E+03
G23 [MPa]	1.28E+03	1.65E+03

4.3 Discussion

After using the Asymptotic Homogenization as numerical modeling technique, it was possible to compare the results and draw some preliminary conclusions. Comparing the results for both fiber volume fractions, it is possible to verify that the Young's Modulus and the Shear Modulus increases with the presence of PLA on the matrix and decreases in the presence of Colophony, as shown in Tables 4.6 and 4.7.

Table 4.6: Results of all simulations with a volume fraction of 10%.

HEC	Colophony + Fibers	PLA + Fibers	PLA+Colophony+Fiber
E1 [MPa]	3.43E+03	6.23E+03	5.76E+03
E2 [MPa]	1.46E+01	4.54E+03	3.80E+03
E3 [MPa]	1.51E+01	4.62E+03	3.89E+03
ν_{12}	0.38721	0.38719	0.3656
ν_{13}	0.38617	0.38644	0.36553
ν_{23}	0.59553	0.43861	0.41143
G12 [MPa]	4.58E+00	1.58E+03	1.29E+03
G13 [MPa]	4.98E+00	1.64E+03	1.35E+03
G23 [MPa]	4.49E+00	1.56E+03	1.28E+03

Table 4.7: Results of all simulations with a volume fraction of 20%.

HEC	**Colophony + Fibers**	**PLA + Fibers**	**PLA+Colophony+Fibers**
E1 [MPa]	6.86E+03	9.01E+03	8.65E+03
E2 [MPa]	2.66E+01	6.31E+03	5.40E+03
E3 [MPa]	2.42E+01	6.13E+03	5.21E+03
ν_{12}	0.38271	0.3833	0.36867
ν_{13}	0.38436	0.38429	0.36744
ν_{23}	0.53371	0.4316	0.40364
G12 [MPa]	8.08E+00	2.19E+03	1.85E+03
G13 [MPa]	6.98E+00	2.06E+03	1.73E+03
G23 [MPa]	6.65E+00	1.99E+03	1.65E+03

On other side, when comparing the simulation of PLA with fibers and PLA with colophony it gets clear the influence of the colophony on the elastic constants, as shown in Table 4.8. This could be explained by the high elastic properties of the wood-fibers over the low properties of the colophony.

Table 4.8: Results of the homogenized elastic constants for the mixture PLA with fibers (10% Vf) and PLA with colophony with a volume fraction of 10% colophony.

Properties	**PLA + Fibers**	**PLA + Colophony**
E1 [MPa]	6.23E+03	2.87E+03
E2 [MPa]	4.54E+03	2.87E+03
E3 [MPa]	4.62E+03	2.88E+03
ν_{12}	0.38719	0.36333
ν_{13}	0.38644	0.36246
ν_{23}	0.43861	0.36232
G12 [MPa]	1.58E+03	9.97E+02
G13 [MPa]	1.64E+03	9.96E+02
G23 [MPa]	1.56E+03	9.97E+02

Chapter 5

Methodologies for Future Work

On this project, the initial goal was to create a biocomposite with only natural constituents to be the most greener as possible. However, there are ways that could have been explored in order to find a better solution for this project to work. This chapter explores some possible solutions.

However, these solutions need to be evaluated since their addition could mean losing the biodegradable and sustainable properties. To effectively convey the benefits of biocomposites, engineers, designers, manufacturers, and researchers are increasingly using Life Cycle Assessment (LCA) as a tool for environmental impact study. This is a comprehensive strategy that records data on material input and waste production over the course of a product system's entire life cycle. A variety of scientific methods are used to characterize the inventory data that determines the system's causal effects on the environment and human health.

The inclusion of natural fibers to replace all, or parts of, the synthetic fibers in a biocomposite consequently results in a lower environmental effect, according to published LCAs, available for biocomposites [115].

5.1 Use of additives

When speaking of polymer composites, it is a great concern the interaction between matrix and fibers in the interphase. The type of interfacial contact present in composites can be linked to a large number of flaws. Highlighting the variables that determine the nature and extent of interactions in the interphase is therefore crucial. Composites made of natural fibers and polymers have applications in many different areas. The elements that regulate the establishment of excellent contact of the interphase need to be understood, so they can be modified for a better outcome.

The functions of natural fiber polymer composites (such as mechanical and thermal properties) are determined by the kind of interfacial adhesion. Other types of interactions include electrostatic forces, inter diffusion, and mechanical interlocking [32].

To improve certain properties, additives are included in the composites-making process. For instance, the use of nanoparticles improves the mechanical and thermal characteristics by improving crystallinity development and stabilizing phase and morphology [116, 117]. Additives seek to improve the final material properties. Since stresses are transferred between the matrix and fibers at the interface level, coupling agents are crucial and lead the mechanical properties of composites to be dependent on interfacial bonding. As mentioned in Section 2.3.3, one way to improve the bonding is using chemical treatments.

According to the literature [118, 119], it can be seen that there was a significant reduction of the water absorption and an increase of the Young's Modulus, hardness, and impact strength, after adding maleic anhydride on sisal and banana fibers surface adhesion. In similar lines of research, other studies addressing the creation of hybrid composites consisted of polymeric matrices reinforced with fibers and nano or microparticles of ceramic minerals have been published in open literature [120, 121, 122, 123].

In conclusion, some of the issues related to the fiber matrix interface of NFPCs have been reduced as a result of the incorporation of other components. Compatibility has reduced fiber aggregation, enhanced matrix dispersion, and reduced water absorption.

5.1.1 Compatibilizers

To improve the interfacial interactions between polymer-polymer in blends and polymer-fiber in composites, compatibilizers can be added [32]. Maleated coupling agents are frequently applied to reinforce composite materials that contain reinforcement fibers and fillers. Maleic anhydride's effective interaction with the functional surface of fiber reinforcements and cost-effective manufacture are the two primary causes of Maleated Polyolefin's (MaPO) established role. By selecting a maleated coupler with the ideal balance of molecular weight and maleic anhydride concentration, peak performance in agrofibre polypropylene composites was achieved [124].

Li et al. [125], searched for the possibility of using two different species of silane as coupling agents in the treatment of sisal fibers surfaces. The experimental procedure consisted in diluting the coupling agents in acetone to 6% concentration and then immerse the sisal fibers on the coupling solution for 24h. After the immersion, it was washed with acetone and dried up in the oven for 4h at 60°C. The results showed that the sisal surfaces were etched and they were very rough, leading to the unbundling of the fiber bundle into smaller fibers, which increased the surface area presented for contact with the polymer matrix.

Other studies have reported the existence of additional coupling agents that functioned rather well [124, 126, 127]. However, it is recommended that the fibers be altered to the nanoscale in order to chemically change the surface characteristics of the cellulose fibers to the level that they can considerably affect the properties of polymer composites [32, 128].

5.1.2 Nanoparticles

Recently, adding nanoparticles to NFPC in order to enhance their properties has gain more interest by researchers [32]. It has been noted that adding nanoparticles to polymer composites increases their strength and Young's Modulus. The mechanical properties of the NFPCs were influenced with the addition of a small concentration of 0.1-1.0% of these nanoparticles [129]. When some researchers studied the modifications of the particles, it led to the increased of chemical interactions when added to composites. Thereby, improving interfacial bonding and by extension, mechanical and thermal properties were also improved [130, 131]. Additionally, Ibrahim et al. [132], discovered that the addition of inorganic nanoparticles helps to improve the thermal and mechanical properties, which has influenced the crystallization process when processing the composite. The increased crystallinity can lead to superior mechanical interlocking of the polymer-fiber interface.

5.1.3 Hybrid fibers

Hybrid fibers are a combination of two or more different fibers to make a composite. The addition of glass and/or carbon fibers to form hybrid fibers has proved to help improve the composite properties. In Ref. [133], Allamraju discovered that the percentage increase in mass fraction of jute fibers resulted in the increase of the compression and tensile strength of jute/glass hybrid fibers epoxy composite.

Hybrid composites properties can be dependent of many elements such as extent of intermingling of fibers, fibers orientation, fiber surface roughness etc. Thereby, they are prepared as a combination of two or more different type, shape or size of reinforcement [134, 135]

The goal in using hybrid natural fiber polymer composites is to maximize the pluses of the fibers while minimizing some downsides [32]. On other side, it is possible decrease the costs of the finished composite material. Substituting partially wood fibers by cotton fibers could bring large improvements in the composite performance and reduce the manufacture costs at the same time. Ayrilmis et al. [136] reported that addition of larger amounts of waste cone flour content (20-40 wt%) on a wood flour-polypropylene composite affected negatively the water resistance and the flexural properties of the composite. Nevertheless, it was noticed that for 10 wt% of pine cone flour the composite did not show significant consequences on water absorption or flexural strength properties. Reducing the pine cone flour added to the composite could reveal positive results [136].

5.1.4 Lubricants

Wood polymer composites are mainly produced using lubricants as additives. The lubricant is added to the WPC mixture during melting in order to provide a consistent flow of melt through to the equipment and a mold during the manufacture of WPCs. Due to the high viscosity of plastic, excessive lubrication might prevent connection at the wood/plastic contact in the interface. To prevent this issue and choose the best kind of handling for wood fiber composites, the quantity of lubricant should be maintained to a minimum [44].

According to the literature survey, studies have evaluated the influence of some lubricants types used in sawdust composites, through rheological and mechanical properties [137, 138]. On these studies, not only the maleic anhydride showed to be a good compatibilizer but also to work as an internal lubricant. However, the compatibilization may be reduced depending on the nature of the lubricant. Santi et al. [138], found out that when ester-based lubricants and PE-g-MA compatibilizer are employed together, the mechanical properties of the HDPE/sawdust composites might suffer a decrease.

Bettini et al. [51], investigated the influence of the presence of compatibilizers and lubricants in a PP/sawdust composite and noted that when both additives were present the tensile strength decreased. This could suggest that a possible interaction between compatibilizer and lubricant reduces the efficiency of the latter. All polymer composites have substantial fiber-matrix interfacial interactions. In summary, the type of fiber-matrix interfacial bonds that are produced has a significant impact on the performance properties.

Chapter 6

Conclusions and Future Work

6.1 Conclusions

The main objective of this dissertation was to develop biocomposite pellets for 3D printing by direct extrusion. Unfortunately, this goal was not successfully completed in its entirety, since, due to reasons unrelated to this project, it was not possible to print. However, the tensile tests had positive results for the elastic properties of the filaments and predictions were left through numerical models that may help in the continuation of the work done throughout this dissertation. Mixing colophony with wood powder did not work as expected, however, the experimental results of PLA with colophony were successful. The numerical results for the mixture of PLA and colophony with wood powder will be of great help for further experimental work. The following conclusions can be drawn from this research:

- Wood fibers increased the tensile properties of the composite in theory, however, in practical experiments it is difficult to combine with the matrix without additives;

- Based on the numerical models, the Asymptotic Homogenization predicts a superior loss of properties, which aproximates the values to reality;

- The experimental results do not correspond to reality probably due to the absence of an extensometer, since the strains were computed from the displacement recorded by the machine, and the tests were not standard,lacking a dimensional control of the filament. Other explanation could be related to the fact that it was not considered the sliding at the grips during the tests, which would cause the increase on the displacement without existing deformation. Furthermore, the filaments could have porosities that were not considered and would decrease the cross-sectional area of the filament, which means that the expected Young's Modulus should be lower in this case.

6.2 Further Work

In order to continue and enrich the research carried out in this dissertation, some of the possible suggestions for future work are:

- Perform the extrusion trials of colophony with the wood fillers instead of powder;
- Experiment the extrusion of PLA with wood powder or wood fillers;
- Use of additive of the mixtures to help the compatibilization between the matrix and the fibers;
- Comparing future experimental procedures with the numerical models used on this project;
- Cutting the filament to obtain the pellets and perform the printing tryouts.

References

[1] S. A. Acevedo, A. J. D. Carrillo, E. Flórez-López, and C. D. Grande-Tovar. Recovery of banana waste-loss from production and processing: A contribution to a circular economy. *Molecules*, 26(17), 2021.

[2] Sustainable development goals.

[3] D.Dias. *Comportamento ao Impacto a Baixa Velocidade de Laminados de Epóxido/Fibra de Vidro, com Camadas de Cortiça*. PhD thesis, FEUP, Universidade do Porto, 2009.

[4] R. L. Fernandes. *Caracterização à Fratura de um Material Compósito com Carbono-Epóxido e Cortiça*. PhD thesis, Faculdade de Engenharia da Universidade do Porto, Porto, 2013.

[5] T. Reinhart, W. Smith, J. Quinlivan, and G. Bourland. *Composites*. USA: ASM International, vol. 1 edition, 1987.

[6] A. Arteiro. Lecture presentation. Advanced Materials. Composite Systems, Constituent Materials and Semi-products, 2021.

[7] M. M. Schwartz. *Composite Materials Handbook*. USA: McGraw-Hill Companies, 1984.

[8] Y. Yang, R. Boom, B. Irion, D. van Heerden, P. Kuiper, and H. Wit. Recycling of composite materials. *Chemical Engineering and Processing: Process Intensification*, 51:53–68, jan 2012.

[9] A. Ramsaroop. Fracture properties of fibre and nano reinforced composite structures. 2007.

[10] A. B. Strong. *The Fundamentals of Composite Manufacturing - Materials, Methods and Applications*. Society of Manufacturing Engineers, second edition, 2008.

[11] S. Wasti, E. Triggs, R. Farag, M. Auad, S. Adhikari, D. Bajwa, M. Li, and A. J. Ragauskas. Influence of plasticizers on thermal and mechanical properties of biocomposite filaments made from lignin and polylactic acid for 3d printing. *Composites Part B: Engineering*, 205, jan 2021.

[12] F. P. la Mantia and M. Morreale. Green composites: A brief review. *Composites Part A: Applied Science and Manufacturing*, 42:579–588, jun 2011.

[13] R. Scaffaro, A. Maio, E. F. Gulino, G. Alaimo, and M. Morreale. Green composites based on pla and agricultural or marine waste prepared by fdm. *Polymers*, 13, may 2021.

[14] A. N. Netravali and S. Chabba. Composites get greener. *Materials Today - MATER TODAY*, 6:22–29, april 2003.

[15] D. R. Carroll, R. B. Stone, A. M. Sirignano, R. M. Saindon, S. C. Gose, and M. A. Friedman. Structural properties of recycled plastic/sawdust lumber decking planks. *Resources, Conservation and Recycling*, 31:241–251, mar 2001.

[16] T. R. K. Reddy, H. Kim, and J. Park. Renewable biocomposite properties and their applications. In Matheus Poletto, editor, *Composites from Renewable and Sustainable Materials*, chapter 10. IntechOpen, Rijeka, 2016.

[17] K. N. Bharath and S. Basavarajappa. Applications of biocomposite materials based on natural fibers from renewable resources: a review. *Science and Engineering of Composite Materials*, 23(2):123–133, 2016.

[18] V. Mahesh, S. Joladarashi, and S. M. Kulkarni. A comprehensive review on material selection for polymer matrix composites subjected to impact load. *Defence Technology*, 17:257–277, feb 2021.

[19] R. Wang, S. Zheng, and Y. Zheng. 3 - matrix materials. In *Polymer Matrix Composites and Technology*, Woodhead Publishing Series in Composites Science and Engineering, pages 101–548. Woodhead Publishing, 2011.

[20] I.Y. Chang and J.K. Lees. Recent development in thermoplastic composites: A review of matrix systems and processing methods. *Journal of Thermoplastic Composite Materials*, 1(3):277–296, 1988.

[21] R.R. Naslain and MR Pomeroy. Ceramic matrix composites: Matrices and processing. In *Reference Module in Materials Science and Materials Engineering*. Elsevier, 2016.

[22] X. Tian, A. Todoroki, T. Liu, L. Wu, Z. Hou, M. Ueda, Y. Hirano, R. Matsuzaki, K. Mizukami, K. Iizuka, A. V. Malakhov, A. N. Polilov, D. Li, and B. Lu. 3d printing of continuous fiber reinforced polymer composites: Development, application, and prospective. *Chinese Journal of Mechanical Engineering: Additive Manufacturing Frontiers*, 1(1):100016, 2022.

[23] W. Hao, Y. Liu, H. Zhou, H. Chen, and D. Fang. Preparation and characterization of 3d printed continuous carbon fiber reinforced thermosetting composites. *Polymer Testing*, 65:29–34, 2018.

[24] Y. Ming, Y. Duan, B. Wang, H. Xiao, and X. Zhang. A novel route to fabricate high-performance 3d printed continuous fiber-reinforced thermosetting polymer composites. *Materials*, 12(9), 2019.

[25] J. Holbery and D. Houston. Natural-fiber-reinforced polymer composites in automotive applications. *The Journal of Minerals*, 58:80–86, nov 2006.

[26] S. Thomas, S. A. Paul, L. A. Pothan, and B. Deepa. *Natural Fibres: Structure, Properties and Applications*, pages 3–42. Springer Berlin Heidelberg, Berlin, Heidelberg, 2011.

[27] M. R. Sanjay, G. R. Arpitha, L. Laxmana Naik, K. Gopalakrishna, and B. Yogesha. Applications of natural fibers and its composites: An overview. *Natural Resources*, 7:108–114, feb 2016.

[28] M. Y. Khalid, A. A. Rashid, Z. U. Arif, W. Ahmed, and H. Arshad. Natural fiber reinforced composites: Sustainable materials for emerging applications. *Results in Engineering*, 11:100263, 2021.

[29] F. M. AL-Oqla and S.M. Sapuan. Natural fiber reinforced polymer composites in industrial applications: feasibility of date palm fibers for sustainable automotive industry. *Journal of Cleaner Production*, 66:347–354, 2014.

[30] K. Lau, P. Hung, M. Zhu, and D. Hui. Properties of natural fibre composites for structural engineering applications. *Composites Part B: Engineering*, 136:222–233, 2018.

[31] S. Ramakrishna and Z.-M. Huang. 9.06 - biocomposites. In *Comprehensive Structural Integrity*, pages 215–296. Pergamon, Oxford, 2003.

[32] O. J. Shesan, A. C. Stephen, A. G. Chioma, R. Neerish, and S. E. Rotimi. Fiber-matrix relationship for composites preparation. In António B. Pereira and Fábio A. O. Fernandes, editors, *Renewable and Sustainable Composites*, chapter 2. IntechOpen, Rijeka, 2019.

[33] N.A. Churochkina, S.G. Starodoubtsev, and A.R. Khokhlov. Swelling and collapse of the gel composites based on neutral and slightly charged poly(acrylamide) gels containing na-montmorillonite. In *Polymer Gels and Networks*, volume 6. 1998.

[34] S. Wang, L. Chen, and Y. Tong. Structure–property relationship in chitosan-based biopolymer/montmorillonite nanocomposites. *Journal of Polymer Science Part A: Polymer Chemistry*, 44(1):686–696, 2006.

[35] X. Wang, B. Liu, J. Ren, C. Liu, X. Wang, J. Wu, and R. Sun. Preparation and characterization of new quaternized carboxymethyl chitosan/rectorite nanocomposite. *Composites Science and Technology*, 70(7):1161–1167, 2010. Special issue on Chiral Smart Honeycombs.

[36] I. Kong, K. Y. Tshai, and M. E. Hoque. *Manufacturing of Natural Fibre-Reinforced Polymer Composites by Solvent Casting Method*, pages 331–349. Springer International Publishing, Cham, 2015.

[37] J. Deepak, A. Pattanaik, and M. Scholar. Polymer matrix composites with improved thermal conductivity: A review. 08 2019.

[38] L. M. Robeson. Polymer blends: A comprehensive review. 641, 2007.

[39] S. S. Ray. *Clay-containing polymer nanocomposites: from fundamentals to real applications*. 2014.

[40] V. K. Thakur and M. K. Thakur. Processing and characterization of natural cellulose fibers/thermoset polymer composites. *Carbohydrate Polymers*, 109:102–117, 2014.

[41] Z. Spitalsky, D. Tasis, K. Papagelis, and C. Galiotis. Carbon nanotube–polymer composites: Chemistry, processing, mechanical and electrical properties. *Progress in Polymer Science*, 35(3):357–401, 2010.

[42] V. Shukla. Review on the electromagnetic interference shielding materials fabricated by iron ingredients. *Nanoscale Advances*, 1, 04 2019.

[43] T. Väisänen, A. Haapala, R. Lappalainen, and L. Tomppo. Utilization of agricultural and forest industry waste and residues in natural fiber-polymer composites: A review. *Waste Management*, 54:62–73, 2016.

[44] M. Ramesh, L. Rajeshkumar, G. Sasikala, D. Balaji, A. Saravanakumar, V. Bhuvaneswari, and R. Bhoopathi. A critical review on wood-based polymer composites: Processing, properties, and prospects. *Polymers*, 14(3), 2022.

[45] K.L. Pickering, M.G. Aruan Efendy, and T.M. Le. A review of recent developments in natural fibre composites and their mechanical performance. *Composites Part A: Applied Science and Manufacturing*, 83:98–112, 2016. Special Issue on Biocomposites.

[46] D. Mohankumar, V. Amarnath, V. Bhuvaneswari, S. P. Saran, K. Saravanaraj, M. Srinivasa Gogul, S. Sridhar, G. Kathiresan, and L. Rajeshkumar. Extraction of plant based natural fibers – a mini review. *IOP Conference Series: Materials Science and Engineering*, 1145(1):012023, apr 2021.

[47] F. S. da Luz, F. C. G. Filho, M. T. G. del Río, L. F. C. Nascimento, W. A. Pinheiro, and S. N. Monteiro. Graphene-incorporated natural fiber polymer composites: A first overview. *Polymers*, 12(7), 2020.

[48] D. Puglia, Jerico Biagiotti, and J.M. Kenny. A review on natural fibre-based composites - part ii: Application of natural reinforcements in composite materials for automotive industry. *Journal of Natural Fibers*, 1(3):23 – 65, 2004.

[49] R. Gallego, C. C. Piras, L. A. J. Rutgeerts, S. Fernandez-Prieto, W. M. De Borggraeve, J. M. Franco, and J. Smets. Green approach for the activation and functionalization of jute fibers through ball milling. *Cellulose*, 27(2):643 – 656, 2020.

[50] P. K. Jena, J. R. Mohanty, and S. Nayak. Effect of surface modification of vetiver fibers on their physical and thermal properties. *Journal of Natural Fibers*, 19(1):25 – 36, 2022.

[51] D. Harper and M. Wolcott. Interaction between coupling agent and lubricants in wood-polypropylene composites. *Composites Part A: Applied Science and Manufacturing*, 35(3):385 – 394, 2004.

[52] A. Arteiro. Lecture presentation. Technological processes for PMCs, 2021.

[53] J. L. Fredericks, H. Iyer, R. McDonald, J. Hsu, A. M. Jimenez, and E. Roumeli. Spirulina-based composites for 3d-printing. *Journal of Polymer Science*, 59(22):2878–2894, 2021.

[54] Nanya Li, Yingguang Li, and Shuting Liu. Rapid prototyping of continuous carbon fiber reinforced polylactic acid composites by 3D printing. *Journal of Materials Processing Technology*, 238:218 – 225, 2016.

[55] Florian Baumann, Julian Scholz, and J´urgen Fleischer. Investigation of a New Approach for Additively Manufactured Continuous Fiber-reinforced Polymers. *Procedia CIRP*, 66:323 – 328, 2017. 1st CIRP Conference on Composite Materials Parts Manufacturing (CIRP CCMPM 2017).

[56] Chuncheng Yang, Xiaoyong Tian, Tengfei Liu, Yi Cao, and Dichen Li. 3D printing for continuous fiber reinforced thermoplastic composites: mechanism and performance. *Rapid Prototyping Journal*, 23(1):209–215, 2017.

[57] Huiyan Luo, Yuegang Tan, Fan Zhang, Jun Zhang, Yiwen Tu, and Kunteng Cui. Selectively enhanced 3d printing process and performance analysis of continuous carbon fiber composite material. *Materials*, 12(21):3529, Oct 2019.

[58] Jun Zhang, Zude Zhou, Fan Zhang, Yuegang Tan, Yiwen Tu, and Baojun Yang. Performance of 3d-printed continuous-carbon-fiber-reinforced plastics with pressure. *Materials*, 13(2):471, Jan 2020.

[59] L. G. Blok, M. L. Longana, H. Yu, and B. K. S. Woods. An investigation into 3D printing of fibre reinforced thermoplastic composites. *Additive Manufacturing*, 22:176 – 186, 2018.

[60] Frank Van Der Klift, Yoichiro Koga, Akira Todoroki, Masahito Ueda, Yoshiyasu Hirano, Ryosuke Matsuzaki, et al. 3D printing of continuous carbon fibre reinforced thermo-plastic (CFRTP) tensile test specimens. *Open Journal of Composite Materials*, 6(01):18, 2016.

[61] Garrett W. Melenka, Benjamin K.O. Cheung, Jonathon S. Schofield, Michael R. Dawson, and Jason P. Carey. Evaluation and prediction of the tensile properties of continuous fiber-reinforced 3D printed structures . *Composite Structures*, 153:866 – 875, 2016.

[62] Andrew N. Dickson, James N. Barry, Kevin A. McDonnell, and Denis P. Dowling. Fabrication of continuous carbon, glass and Kevlar fibre reinforced polymer composites using additive manufacturing. *Additive Manufacturing*, 16:146 – 152, 2017.

[63] J. Justo, L. Távara, L. García-Guzmán, and F. París. Characterization of 3D printed long fibre reinforced composites. *Composite Structures*, 185:537 – 548, 2018.

[64] Haider Al Abadi, Huu-Tai Thai, Vidal Paton-Cole, and V.I. Patel. Elastic properties of 3D printed fibre-reinforced structures. *Composite Structures*, 193:8 – 18, 2018.

[65] G.D. Goh, V. Dikshit, A.P. Nagalingam, G.L. Goh, S. Agarwala, S.L. Sing, J. Wei, and W.Y. Yeong. Characterization of mechanical properties and fracture mode of additively manufactured carbon fiber and glass fiber reinforced thermoplastics. *Materials & Design*, 137:79 – 89, 2018.

[66] Miguel Araya-Calvo, Ignacio López-Gómez, Nicolette Chamberlain-Simon, José Luis León-Salazar, Teodolito Guillén-Girón, Juan Sebastián Corrales-Cordero, and Olga Sánchez-Brenes. Evaluation of compressive and flexural properties of continuous fiber fabrication additive manufacturing technology. *Additive Manufacturing*, 22:157 – 164, 2018.

[67] M. A. Caminero, J. M. Chacón, I. García-Moreno, and J. M. Reverte. Interlaminar bonding performance of 3D printed continuous fibre reinforced thermoplastic composites using fused deposition modelling. *Polymer Testing*, 68:415 – 423, 2018.

[68] Thiago Assis Dutra, Rafael Thiago Luiz Ferreira, Hugo Borelli Resende, and Alessandro Guimarães. Mechanical characterization and asymptotic homogenization of 3D-printed continuous carbon fiber-reinforced thermoplastic. *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, 41(3):133, Feb 2019.

[69] Thiago Assis Dutra, Rafael Thiago Luiz Ferreira, Hugo Borelli Resende, Brina Jane Blinzler, and Leif E. Asp. Mechanism based failure of 3d-printed continuous carbon fiber reinforced thermoplastic composites. *Composites Science and Technology*, 213:108962, 2021.

[70] T. Fruleux, M. Castro, P. Sauleau, R. Matsuzaki, and A. Le Duigou. Matrix stiffness: A key parameter to control hydro-elasticity and morphing of 3d printed biocomposite. *Composites Part A: Applied Science and Manufacturing*, 156:106882, 2022.

[71] ISO/ASTM 52900:2015(en), Additive manufacturing – General principles – Terminology. International Organization for Standardization, Case postale 56, CH-1211 Geneva 20, 2015.

[72] D. D. Camacho, P. Clayton, W. J. O'Brien, C. Seepersad, M. Juenger, R. Ferron, and S. Salamone. Applications of additive manufacturing in the construction industry – a forward-looking review. *Automation in Construction*, 89:110 – 119, 2018.

[73] K. Jamali, V. Kaushal, and M. Najafi. Evolution of additive manufacturing in civil infrastructure systems: A ten-year review. *Infrastructures*, 6(8), 2021.

[74] C. Beyer. Strategic implications of current trends in additive manufacturing. *Journal of Manufacturing Science and Engineering, Transactions of the ASME*, 136(6), 2014.

[75] W. E. Frazier. Metal additive manufacturing: A review. *Journal of Materials Engineering and Performance*, 23(6):1917 – 1928, 2014.

[76] B. P. Conner, G. P. Manogharan, A. N. Martof, L. M. Rodomsky, C. M. Rodomsky, D. C. Jordan, and J. W. Limperos. Making sense of 3-d printing: Creating a map of additive manufacturing products and services. *Additive Manufacturing*, 1:64 – 76, 2014.

[77] J. Holmström, J. Partanen, J. Tuomi, and M. Walter. Rapid manufacturing in the spare parts supply chain: Alternative approaches to capacity deployment. *Journal of Manufacturing Technology Management*, 21(6):687 – 697, 2010.

[78] S. H. Khajavi, J. Holmström, and J. Partanen. Additive manufacturing in the spare parts supply chain: hub configuration and technology maturity. *Rapid Prototyping Journal*, 24(7):1178 – 1192, 2018.

[79] S. Mellor, L. Hao, and D. Zhang. Additive manufacturing: A framework for implementation. *International Journal of Production Economics*, 149:194 – 201, 2014.

[80] ISO/ASTM f2792 12a, Standard Terminology for Additive Manufacturing Technologies. International Organization for Standardization, Case postale 56, CH-1211 Geneva 20, 2012.

[81] Shaping the future of construction - future scenarios and implications for the industry, 2018.

[82] Future of construction - a global forecast for the construction industry to 2030, 2021.

[83] F. Craveiro, J. Duarte, H. Bártolo, and P. Bartolo. Additive manufacturing as an enabling technology for digital construction: A perspective on construction 4.0. *Automation in Construction*, 103:251–267, 04 2019.

[84] Shaping the future of construction- a breakthrough in mindset and technology, 2016.

[85] D. Turney. History of 3d printing: It's older than you think, 2021.

[86] M. Kariz, M. Sernek, M. Obućina, and M. K. Kuzman. Effect of wood content in fdm filament on properties of 3d printed parts. *Materials Today Communications*, 14:135 – 140, 2018.

[87] Rafael Thiago Luiz Ferreira, Igor Cardoso Amatte, Thiago Assis Dutra, and Daniel Burger. Experimental characterization and micrography of 3D printed PLA and PLA reinforced with short carbon fibers. *Composites Part B: Engineering*, 124(Supplement C):88 – 100, 2017.

[88] A. Le Duigou, A. Barbé, E. Guillou, and M. Castro. 3d printing of continuous flax fibre reinforced biocomposites for structural applications. *Materials and Design*, 180, 2019.

[89] O. Gordobil, I. Egüés, R. Llano-Ponte, and J. Labidi. Physicochemical properties of pla lignin blends. *Polymer Degradation and Stability*, 108:330–338, 2014.

[90] Y. Gao, W. Qu, Y. Liu, H. Hu, E. Cochran, and X. Bai. Agricultural residue-derived lignin as the filler of polylactic acid composites and the effect of lignin purity on the composite performance. *Journal of Applied Polymer Science*, 136(35), 2019.

[91] Futerra Fuels. Company. Last accessed 13 June 2022.

[92] G. R. Mitchell, V. Mahendra, and D. Sousa. Biopolymers based on rosin. *Current Research in Biopolymers*, CRBP-102, 2018.

[93] G. R. Mitchell, V. Mahendra, and D. Sousa. Biopolymers based on rosin. *Curr Res Biopolymers: CRBP-102*, 2018.

[94] P. Simões and F. A. Rocha. A transição de matéria prima de origem fóssil para fontes vegetais renováveis e biocompostáveis/biodegradáveis. *Ciências Tecnologia dos Materiais*, 32(Nº1), 2020.

[95] M. L. Gennusa, P. Llorach-Massana, J. I. Montero, F. J. Peña, J. Rieradevall, P. Ferrante, G. Scaccianoce, and G. Sorrentino. Composite building materials: Thermal and mechanical performances of samples realized with hay and natural resins. *Sustainability*, 9(3), 2017.

[96] V. Hristov and J. Vlachopoulos. A study of viscoelasticity and extrudate distortions of wood polymer composites. *Rheologica Acta*, 46:773–783, 05 2007.

[97] A.K. Bledzki and J. Gassan. Composites reinforced with cellulose based fibres. *Progress in Polymer Science*, 24(2):221–274, 1999.

[98] V. N. Hristov, ST. Vasileva, M. Krumova, R. Lach, and G. H. Michler. Deformation mechanisms and mechanical properties of modified polypropylene/wood fiber composites. *Polymer Composites*, 25(5):521–526, 2004.

[99] S. N. Maiti and M. R. Hassan. Melt rheological properties of polypropylene–wood flour composites. *Journal of Applied Polymer Science*, 37(7):2019–2032, 1989.

[100] S. N. Maiti, R. Subbarao, and M. N. Ibrahim. Effect of wood fibers on the rheological properties of i-pp/wood fiber composites. *Journal of Applied Polymer Science*, 91(1):644–650, 2004.

[101] Z. Charlton, J. Vlachopoulos, and D. Suwanda. Profile extrusion of highly filled recycled hdpe. In *ANTEC 2000: SOCIETY OF PLASTICS ENGINEERS TECHNICAL PAPERS, CONFERENCE PROCEEDINGS, VOLS I-III*, pages 2914–2918, 2000.

[102] H. D. L. Rosa-Ramírez, M. Aldas, J. M. Ferri, J. López-Martínez, and M. D. Samper. Modification of poly (lactic acid) through the incorporation of gum rosin and gum rosin derivative: Mechanical performance and hydrophobicity. *Journal of Applied Polymer Science*, 137(44):49346, 2020.

[103] J. Urquijo, S. Dagréou, G. Guerrica-Echevarría, and J. I. Eguiazábal. Morphology and properties of electrically and rheologically percolated pla/pcl/cnt nanocomposites. *Journal of Applied Polymer Science*, 134(36):45265, 2017.

[104] M. Liu, G. Zeng, K. Wang, Q. Wan, L. Tao, X. Zhang, and Y. Wei. Recent developments in polydopamine: an emerging soft matter for surface modification and biomedical applications. *Nanoscale*, 8:16819–16840, 2016.

[105] T. A. Dutra, R. T. L. Ferreira, and H. B. Resende. A complete implementation methodology for asymptotic homogenization using a finite element commercial software: preprocessing and postprocessing. *Composite Structures*, 245(112305), 2020.

[106] E. J. Barbero. *Finite element analysis of composite materials using AbaqusTM*. 2013.

[107] W.J. Drugan and J.R. Willis. A micromechanics-based nonlocal constitutive equation and estimates of representative volume element size for elastic composites. *Journal of the Mechanics and Physics of Solids*, 44(4):497 – 524, 1996.

[108] T. Kanit, S. Forest, I. Galliet, V. Mounoury, and D. Jeulin. Determination of the size of the representative volume element for random composites: Statistical and numerical approach. *International Journal of Solids and Structures*, 40(13-14):3647 – 3679, 2003.

[109] J. Zeman and M. Šejnoha. From random microstructures to representative volume elements. *Modelling and Simulation in Materials Science and Engineering*, 15(4):S325–S335, 2007.

[110] A. R. Melro, P. P. Camanho, and S. T. Pinho. Generation of random distribution of fibres in long-fibre reinforced composites. *Composites Science and Technology*, 68(9):2092 – 2102, 2008.

[111] L. Yang, Y. Yan, Z. Ran, and Y. Liu. A new method for generating random fibre distributions for fibre reinforced composites. *Composites Science and Technology*, 76:14 – 20, 2013.

[112] José Miranda Guedes and Noboru Kikuchi. Preprocessing and postprocessing for materials based on the homogenization method with adaptive finite element methods. *Computer methods in applied mechanics and engineering*, 83(2):143–198, 1990.

[113] Ole Sigmund. Materials with prescribed constitutive parameters: an inverse homogenization problem. *International Journal of Solids and Structures*, 31(17):2313–2329, 1994.

[114] Dassault Systemes Simulia Corp. Abaqus 6.14-1 documentaton, 2014. v6.14-1.

[115] A. Fitzgerald, W. Proud, A. Kandemir, R. J. Murphy, D. A. Jesson, R. S. Trask, I. Hamerton, and M. L. Longana. A life cycle engineering perspective on biocomposites as a solution for a sustainable recovery. *Sustainability*, 13(3), 2021.

[116] I. D. Ibrahim, T. Jamiru, E. R. Sadiku, W. K. Kupolati, S. C. Agwuncha, and G. Ekundayo. Mechanical properties of sisal fibre-reinforced polymer composites: a review. *Composite Interfaces*, 23(1):15–36, 2016.

[117] I. D. Ibrahim, T. Jamiru, R. E. Sadiku, W. K. Kupolati, and S. C. Agwuncha. Dependency of the mechanical properties of sisal fiber reinforced recycled polypropylene composites on fiber surface treatment, fiber content and nanoclay. *Journal of Polymers and the Environment*, 25(2):427 – 434, 2017.

[118] S. Mishra, J. B. Naik, and Y. P. Patil. The compatibilising effect of maleic anhydride on swelling and mechanical properties of plant-fiber-reinforced novolac composites. *Composites Science and Technology*, 60(9):1729–1735, 2000.

[119] J. B. Naik and S. Mishra. Esterification effect of maleic anhydride on swelling properties of natural fiber/high density polyethylene composites. *Journal of Applied Polymer Science*, 106(4):2571–2574, 2007.

[120] L. Silva, T. Panzera, A. Christoforo, J. C. Rubio, and F. Scarpa. Micromechanical analysis of hybrid composites reinforced with unidirectional natural fibres, silica microparticles and maleic anhydride. *Materials Research*, 15:1003–1012, 12 2012.

[121] P. Rosso, L. Ye, K. Friedrich, and S. Sprenger. A toughened epoxy resin by silica nanoparticle reinforcement. *Journal of Applied Polymer Science*, 100(3):1849–1855, 2006.

[122] A. Haque, M. Shamsuzzoha, F. Hussain, and D. Dean. S2-glass/epoxy polymer nanocomposites: Manufacturing, structures, thermal and mechanical properties. *Journal of Composite Materials*, 37(20):1821–1837, 2003.

[123] J. Tsai and Y. Cheng. Investigating silica nanoparticle effect on dynamic and quasi-static compressive strengths of glass fiber/epoxy nanocomposites. *Journal of Composite Materials*, 43(25):3143–3155, 2009.

[124] T.J Keener, R.K Stuart, and T.K Brown. Maleated coupling agents for natural fibre composites. *Composites Part A: Applied Science and Manufacturing*, 35(3):357–362, 2004. AIChE 2002.

[125] Y. Li, C. Hu, and Y. Yu. Interfacial studies of sisal fiber reinforced high density polyethylene (hdpe) composites. *Composites Part A: Applied Science and Manufacturing*, 39(4):570–578, 2008. Fifth Asian–Australian Conference on Composite Materials (ACCM-5).

[126] W. Heinen, C. H. Rosenmöller, C. B. Wenzel, H. J. M. de Groot, J. Lugtenburg, and M. van Duin. 13c nmr study of the grafting of maleic anhydride onto polyethene, polypropene, and ethenepropene copolymers. *Macromolecules*, 29(4):1151–1157, 1996.

[127] S. Ranganathan, W. E. Baker, K. E. Russell, and R. A. Whitney. Peroxide-initiated grafting of maleic anhydride onto linear and branched hydrocarbons. *Journal of Polymer Science Part A: Polymer Chemistry*, 37(20):3817–3825, 1999.

[128] P. Sobolčiak, A. Tanvir, A. Popelka, J. Moffat, K. A. Mahmoud, and I. Krupa. The preparation, properties and applications of electrospun co-polyamide 6,12 membranes modified by cellulose nanocrystals. *Materials Design*, 132:314–323, 2017.

[129] M. Ptak, P. Kaczyński, J. Wilhelm, J. Margarido, P. Marques, S. Pinto, R. A. de Sousa, and F. Fernandes. Graphene-enriched agglomerated cork material and its behaviour under quasi-static and dynamic loading. *Materials*, 12:151, 01 2019.

[130] R. Sadeghian, S. Gangireddy, B. Minaie, and K. Hsiao. Manufacturing carbon nanofibers toughened polyester/glass fiber composites using vacuum assisted resin transfer molding for enhancing the mode-i delamination resistance. *Composites Part A: Applied Science and Manufacturing*, 37(10):1787–1795, 2006.

[131] D. Pedrazzoli, A. Pegoretti, and K. Kalaitzidou. Synergistic effect of exfoliated graphite nanoplatelets and short glass fiber on the mechanical and interfacial properties of epoxy composites. *Composites Science and Technology*, 98:15–21, 2014.

[132] I. Ibrahim, T. Jamiru, R. Sadiku, W. Kupolati, and S. Agwuncha. Impact of surface modification and nanoparticle on sisal fiber reinforced polypropylene nanocomposites. *Journal of Nanotechnology*, 2016, 01 2016.

[133] K. V. Allamraju. Study of mechanical behaviour of hybrid jute nano fiber composite. *Materials Today: Proceedings*, 5(9, Part 3):20750–20753, 2018. Materials Processing and characterization, 16th – 18th March 2018.

[134] A. Ashori and S. Sheshmani. Hybrid composites made from recycled materials: Moisture absorption and thickness swelling behavior. *Bioresource Technology*, 101(12):4717–4720, 2010.

[135] N. Saba, M. Jawaid, Othman Y. Alothman, and M.T. Paridah. A review on dynamic mechanical properties of natural fibre reinforced polymer composites. *Construction and Building Materials*, 106:149–159, 2016.

[136] N. Ayrilmis, U. Buyuksari, and T. Dundar. Waste pine cones as a source of reinforcing fillers for thermoplastic composites. *Journal of Applied Polymer Science*, 117(4):2324–2330, 2010.

[137] K. B. Adhikary, C. B. Park, M.R. Islam, and G. M. Rizvi. Effects of lubricant content on extrusion processing and mechanical properties of wood flour-high-density polyethylene composites. *Journal of Thermoplastic Composite Materials*, 24(2):155–171, 2011.

[138] C. Santi, E. Hage Jr, J. Vlachopoulos, and C. Correa. Rheology and processing of hdpe/-wood flour composites. *International Polymer Processing - INT POLYM PROC*, 24:346–353, 09 2009.