Seaflax: The Next Frontier in Eco-Friendly Composite Manufacturing

Polysachaaride Based Green Composites

Master Thesis Report
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TU Delft

Seaflax: The Next Frontier in Eco-Friendly Composite Manufacturing?

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by

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Preface

I would like to express my deepest gratitude to several individuals whose guidance and support have been invaluable during my work.

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I would also like to extend my heartfelt appreciation to my family, who have stood by me throughout this study. Their unwavering support and love have been the bedrock of my perseverance and success.

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My sincere thanks to all for their invaluable contributions to my academic and personal growth.

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Abstract

Composite materials offer superior mechanical performance with lower weight than traditional materials. As a result, they are widely used in various industries, such as aerospace, automotive, construction, and sports. The composite industry is increasingly utilizing natural fibers and developing biodegradable composites in response to environmental sustainability concerns. Natural fibers have comparable physical and mechanical properties to glass fiber, making them suitable for use in the production of bio-composites. Despite this, natural fiber cannot fully replace glass fiber due to a variety of factors that influence the material's variable properties such as the type of fiber used, the conditions in which the fiber grows, the processing methods, and any modification of the fiber. Hence most of the research done on bio-composites has concentrated on using them in non-structural parts.

This project aims to develop and characterize a green and sustainable bio-composite system, to overcome existing application challenges. The constituent materials include a bio-resin extracted from seaweeds and Unidirectional Flax fibers as reinforcements to stiffen and strengthen for semi-structural applications. Although alginates have been studied in-depth for their biomedical applications, their potential as a bio-based matrix for biocomposites has not yet been explored.

In addition to the materials used in the composite preparation, the processing technique significantly impacts the final properties of the composite. Therefore, in the first half of the work, thorough research was conducted to study the constituent properties for their processing. The second half of the work defined a new approach to manufacturing bio-composites from natural constituents. The corresponding analysis useful for product design are thoroughly demonstrated in this thesis.

However, using natural fibers in composites and water alginate soluble matrices has three main concerns: the fiber/matrix interaction and their sensibility to moisture absorption and residual water within the composite structure. Their surfaces can be modified using physical and/or chemical methods to improve the bonding between fibers and matrix. In most studies cited in the literature, the chemical modifications employed are synthetic and toxic. It would be ideal if the chemicals used to modify natural fibers were bio-based and preserved the biodegradable nature of natural fibers.

The development of an optimized seven-step manufacturing approach is a key innovation for water removal, to enhancing fiber reinforcement and boosting overall composite performance, particularly in the use of flax fibers. This approach is notable for its novelty and challenge, as evidenced by the limited literature on the subject. It focuses on achieving sufficient impregnation by utilizing low water percentages in resin, specifically around 7%, and applying appropriate consolidation pressure and temperatures. The most effective results were observed at 5 MPa and 95°C, which facilitated homogeneous plasticization and mouldability. Additionally, the method of wet/dry cycling, incorporating pre-soaking and heating, has proven beneficial in providing dimensional stability to flax fibers and limiting water absorption, further contributing to the technique's effectiveness.

Analytical techniques like microscopy and SEM reveal promising compatibility between components. No degradation of the bio-resin or the fibers relatable to the heat press was identified.

Finally, the research aimed to establish a meaningful relationship between the critical process variables and the properties of the bio-composite, with the ultimate goal of optimizing the production process and enhancing the quality of the final product by varying the fiber volume fraction within the range of 41-47%.

The maximum tensile and flexural strengths achieved were 219MPa and 56Mpa, respectively. The elastic tensile and bending moduli in the composites were approximately 6.64GPa and 1.83GPa, respectively.

However, the observed properties fell below the predicted values for the biocomposite system, which were calculated using the rule-of-mixtures and Halpin-Tsai methods. Nonetheless, the experimental data confirm that these biocomposites can be used as secondary structural elements. The observed discrepancy was due to the presence of huge voids further leading to poor adhesion.

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Nomenclature

Abbreviations

Abbreviation	Definition
ASTM	American society for testing and materials
CO2	Carbon dioxide
COOH	
carboxyl group DSC	differential scanning calorimetry
FRP	Fiber reinforced polymer
HT	Halpin-Tsai
MROM	Modified rule of mixtures
NFRP	Natural fiber reinforced polymer
NFRPCs	Natural fiber reinforced polymer composites
OH	hydroxyl
PCL	Polycaprolactone
PGA	Polyglycolic acid
PHA	Polyhydroxyalkanoates
PLA	Polylactic acid
ROM	Rule of mixtures
RTM	Resin transfer molding
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UTS	Ultimate tensile strength
VARTM	Vacuum Assisted Resin Transfer Molding
VIP	Vacuum Infusion Process

Table 1: List of Abbreviations

Symbols

Symbol	Definition	Unit
A_c	cross-sectional area of composite	[m^2]
V	Velocity	[m/s]
A_f	cross-sectional area of fiber	[m^2]
A_m	cross-sectional area of matrix	[m^2]
E	Elastic Modulus	[GPa]
E_b	Elastic Bending Modulus	[GPa]
E_c	Elastic Modulus of Composite	[GPa]
E_f	Elastic Modulus of Fiber	[GPa]
E_m	Elastic Modulus of Matrix	[GPa]
E_T	Transverse Composite Modulus	[GPa]
M_w	Average Molecular Weight Number	[g/mol]
P_c	Load Carried by Composite	[N]
P_f	Load Carried by Fiber	[N]
P_m	Load Carried by Matrix	[N]
ρ_c	Density of composite	[kg/m^3]
ρ_{ce}	Theoretical Density of Composite	[kg/m^3]
ρ_{ct}	Experimental Density of Composite	[kg/m^3]
ρ_f	Density of Fiber	[kg/m^3]
ρ_m	Density of Matrix	[kg/m^3]
ε_c	Strain in Composite	[mm/mm]
ε_f	Strain in Fiber	[mm/mm]
ε_m	Strain in Matrix	[mm/mm]
SCF	stress concentration factor for Halpin-Tsai model	
σ	Tensile Strength	[MPa]
σ_c	Tensile Strength of Composite	[MPa]
σ_f	Tensile Strength of Fiber	[MPa]
σ_m	Tensile Strength of Matrix	[MPa]
σ_{mu}	Ultimate Tensile Strength of Matrix	[MPa]
σ_{Tu}	Ultimate Transverse Tensile Strength of Composite	[MPa]
T_g	Glass Transition Temperature	[^oC]
v_c	Volume of Composite	[m$\hat{3}$]
v_{ce}	Experimental Volume of Composite	[m$\hat{3}$]
v_f	Volume of Fiber	[m$\hat{3}$]
v_m	Volume of Matrix	[m$\hat{3}$]
v_v	Volume of Void	[m$\hat{3}$]
V_f	Volume Fraction of Fiber	[m$\hat{3}$]
V_{fe}	Experimental Volume Fraction of Fiber	[m$\hat{3}$]
V_m	Volume Fraction of Matrix	[m$\hat{3}$]
V_{me}	Experimental Volume Fraction of Matrix	[m$\hat{3}$]

Symbol	Definition	Unit
V_v	Volume Fraction of Void	
w_c	Weight of Composite	[gm]
w_{ef}	Weight of End Fibers	[gm]
w_f	Total Weight of Fiber	[gm]
w_{f1}	Weight of Fibers in Layer One	[gm]
w_{f2}	Weight of Fibers in Layer Two	[gm]
w_m	Total Weight of Polymer Matrix	[gm]
w_{m1}	Weight of matrix in Layer one	[gm]
w_{m2}	Weight of matrix in Layer two	[gm]
W_f	Weight Fraction of Fiber	
W_m	Weight Fraction of Matrix	

Table 2: List of Symbols

Chapter 1

General Introduction

The extensive usage of petroleum-based polymer items has become essential in modern society, owing to their diverse applications in packaging, agriculture, food, medical appliances, and construction materials. Petroleum-based, Fiber reinforced polymer (FRP) composites heavily dominate these industries due to their lucrative properties such as elevated mechanical performance characterized by improved strength-to-mass ratios surpassing those of classical metal and plastic materials. Nevertheless, the environment is adversely affected by the CO2 emissions and extended degradation period of plastics that are produced from petroleum-based matrices. The effect of synthetic composite materials with reinforcements like glass, carbon, and kevlar on biodegradability and recycling ability made the researchers look for substitute materials derived from nature. The need for zero environmental impact and sustainability catalyzes the increased use of new and improved materials that promote environmental advancement. One such alternative development is that of ”biocomposites”. Materials classified as biocomposites are composed, either in part or entirely, of composed of constituent materials that are bio-based or biodegradable. These innovative materials, derived from natural or biodegradable sources, present a viable solution to the detrimental ecological impacts associated with traditional polymers, like high CO2 emissions and prolonged degradation times. Natural fibers like flax, hemp, kenaf, and jute are used as reinforcements and already have a vital role in the ”green” and circular economy. They have been a noteworthy alternative to the mineral fibers. These fibers are efficient in terms of energy, use renewable feedstocks, have low CO2 manufacturing processes, and are recyclable. Additionally, they help to reduce weight and minimize waste. The use of natural fibers has been historically employed for a variety of applications based on their composition and properties. The use of natural fibers as reinforcement in composite materials has become increasingly popular, driven by the growing need for sustainable materials in industries such as automotive, construction, and aerospace. The primary reasons for their incorporation in composites include their cost-effectiveness (when measured volumetrically), low density, high specific stiffness, ease of processing, minimal tool wear, ready availability, and biodegradability. Flax, a prominent natural fiber, is widely used in biocomposites with thermoplastic, thermoset, and biodegradable matrices due to its excellent mechanical properties. In the last two decades, the biocomposites industry has seen continuous growth, driven by technological innovations and expanding applications. However, much of the technology in biocomposites has primarily focused on using short, randomly aligned fiber reinforcements.

Green fibers can be added to polymer composites without affecting their mechanical strength. However, they only partially enhance degradability. Biopolymers like PLA, PGA, PCL, and PHA are gaining popularity due to their usage in high-performance and traditional commodity applications, as well as in the medical field, automotive, and construction sectors. However, challenges such as higher prices, lack of standards, optimized production, and sustainable sources of extraction have prevented them from entering the market. The advancement of biocomposite materials for enhanced economic and environmental advantages lies in the creation of biopolymers reinforced with aligned natural fibers, exhibiting strong performance traits. Recent explorations have included using sources like crops, textile waste, and industrial by-products to develop biodegradable composites. This approach aims to decrease global reliance on fossil fuels and offer easier disposal solutions at the end of the product's life. As the search for new sustainable and renewable resources to develop green biodegradable composites continues, this report discusses the development of a new all-green composite. It bridges the gap between the need for eco-friendly practices and the innovative use of natural materials in composite manufacturing. Specifically, it explores the use of flax and seaweed, both offering promising avenues for sustainable development due to their unique properties. Seaweeds have been extensively studied as a potential solution for promoting a circular biomass-based economy. Seaweeds offer several advantages and have considerable economic value compared to terrestrial crops. They have unique compositions, including functional ingredients like lipids, proteins, polysaccharides and polyphenols. Polysaccharides; in particular, are abundant in hydroxyl (-OH) functional groups, which makes them ideal for film-forming applications due to the formation of hydrogen bonding networks that stabilize the intra and inter-polymeric chain interactions. Alginates primarily have been known for their features of emulsifiable films, possessing good mechanical and barrier properties and providing better protection to the encapsulated active substances.[169], [75] Considering its increasing demands within the consumable goods in the past few years, raw seaweed as a polymer matrix is less studied, even though no chemical and energy consumption is needed for isolation, which makes material preparation easier and cheaper. Additionally, knowledge on Flax and seaweed composites will increase the usage of seaweed-based industrial by-products as raw materials and promote research on their use in the growing green and circular economy. In this study, a preliminary investigation on the fabrication of Flax/Seaweed based resin composites are presented. To achieve this aim, the following tasks were planned to be conducted during the literature study phase to:

- Understand the properties of various textile structures to optimize processing, fiber orientation, ease of use, and final properties of the compound.
- Explore various biopolymers extracted from seaweed and their feasibility to be used as resin films in composite materials.
- Study on modifying natural cellulosic fibers to enhance adhesion and stability in biopolymer matrices.
- Conduct a critical review of the existing literature covering the development of biocomposites and establish the current state of the art.

Chapter 2

Thesis Structure and Layout

This chapter has been included to aid readers in navigating through the structure of the academic report that presents the development process of bio-based composite panels, along with the experimental results. The report in total consists of ten chapters, each containing the following:
Chapter 1 provided a general introduction to the various elements of this research.

Chapter 2 helps readers understand the report layout with an inclusive storyboard to help them navigate the report.
Chapter 3, titled ″State of the Art,″ presents a literature review of various aspects of the project, such as textile composites, unidirectional plant fiber composites, relevant technologies, and properties of flax and bio-based resins. Additionally, this chapter covers a broad range of bio-composite materials, including the description of reinforcing natural fibers, their composition, and their properties. The chapter also includes the theoretical models used for predicting composite properties, mainly mechanical properties.

Chapter 4 outlines the objectives of the next phase, which begins with the progression of developing and characterizing the bio-composites. Chapter 5, titled ″Material Selection and Characterization,″ follows the knowledge assessment and focuses on the selection of two forms of resin formulations required to impregnate the fiber reinforcement for developing the bio-composite. his chapter presents an in-depth analysis of selecting the optimal two components for designing superior bio-composite panels, considering factors such as environmental benefits, expected mechanical properties, cost-effectiveness, availability, and their suitability as composite materials. Through experimental testing, the mechanical properties and processing capabilities of flax fibers and alginate polymers were assessed. These findings laid the groundwork for establishing the most effective and durable fabrication process for the bio-composite panels, utilizing the best processing conditions identified

Chapter 6 Composite Process Development: It focuses on the development of the composite process, with the primary goal of enhancing the adhesion between the fiber and matrix in the composites. This chapter provides an overview of the most effective processes that can be employed for impregnation, which contribute to the development of sustainable composites. The chapter also outlines the various techniques used for composite production, including the fabrication and treatment of non-crimp fibers. Through a process of parameter identification and process characterization, the chapter describes the determination of an optimized manufacturing procedure for the bio-composite system
Chapter 7 SEAFLAX Composites: This chapter focuses on the finalized newly developed composite panels under the defined novel processing scheme (chapter 4). Multiple samples were manufactured and

Chapter 8 Test Methods and Composite Characterisation: This chapter summarises all the materials characterization methods used during the thesis. Experimental testing was conducted to evaluate the performance of the five composite systems under tension, flexure, and thermal conditions. Following the analysis of these test results, an optimized composite system was identified. Additionally, the chapter includes a concise overview of the conditions employed in these characterization techniques
Chapter 9 Results and Discussion This chapter includes the results and discussion regarding the effect of process variables on the physical, mechanical, and thermal properties of flat bio-composite panels based on the standard testing methods. This chapter also focuses on the stability of bio-composite panels by evaluating the thermal properties analysis and the effect of process variables on the physical and mechanical properties of bio-composite.
Chapter 10 ends the thesis with conclusions and recommendations for future work.

Chapter 3

Literature Review

3.1 Introduction to Biocomposites: Sustainable Solutions for Environmental Preservation and Innovation

Composites are naturally occurring or engineered materials. Composites consist of two or more inherently different material constituents with their properties, including reinforcements providing strength and stiffness and a matrix or resin bonding the reinforcements together and adding toughness.

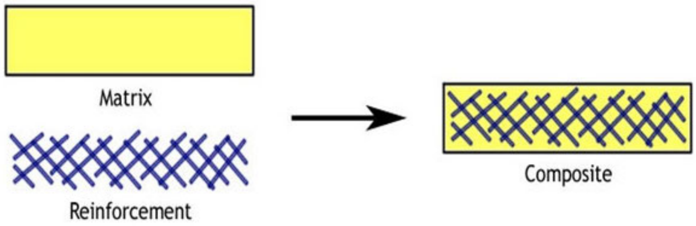


Figure 3.1: Components of a composite

The market for fibre-reinforced composites is worth billions and is used in various industries such as automotive, construction, marine, electronics, sporting goods, appliances, aerospace, and consumer products. The 20th century, marked by the rise of polymers, witnessed the ascent of polymer matrix composites. During World War II, the scarcity of metallic materials propelled fibre-reinforced polymers (FRP) to gain prominence in various applications. In the 1970s, the infusion of short glass fibres into thermoplastic polymers, like polypropylene or polyamides, through injection processes significantly bolstered stiffness and strength. Traditionally, synthetic fibres such as carbon, glass, and aramid have been the most popular choice for reinforcing FRP composites due to their superior physical and mechanical properties compared to other fibre types. Synthetic polymers, including thermoset and thermoplastic, have been widely used as polymer matrices due to their excellent adhesive properties, chemical resistance, moisture resistance, and outstanding mechanical properties. These materials possess desirable properties, such as good fatigue resistance, low shrinkage, and strong durability at low and high temperatures. However, they also have significant environmental impacts as they are non-biodegradable and can remain in the environment for hundreds of years. Furthermore, their production from fossil fuels releases a substantial amount of excess greenhouse gases, contributing to global warming. As a result, researchers and innovators have been forced to shift towards manufacturing sustainable composites due to the increasing awareness of the environmental crisis and sustainability in general.

Plastic waste is a significant contributor to water and soil pollution, with approximately 75-80 million tons of packaging plastics ending up in oceans annually. Moreover, plastic waste degrades into microplastics, posing challenges in detection and facilitating the transportation of pollutants into marine and other organisms, exacerbating pollution. These factors drive industries and academia to seek and develop materials from sustainable resources, leading to bio-based materials and the development of innovative ”biocomposites”, composites containing either the matrix or reinforcement component obtained from nature.

Biocomposites are broadly classified into bio-based and green composites, encompassing diverse compositions. According to Mohanty et al.[115]; it comprises of three main categories:

- Composites of synthetic matrix and natural fibres.
- Composites of bio-based matrix and synthetic fibres.
- Composites of bio-based matrix and natural fibres or ”green composites”.

As shown in 3.2, the last group, also known as ”green composites”. Biocomposites offer improved properties, such as increased mechanical strength and stiffness, making them a promising alternative to conventional fossil-based materials. They have various applications in the automotive, construction, and packaging industries.[116]

Biocomposites have been adopted and developed by many industrial companies since the 1990s. These materials are used in medical applications and commercial car interiors, including door panels, roof linings, dashboards, seats, and engine covers. They are also used in exterior parts, such as commercial exterior underfloor panelling or the bodywork of some electric concept vehicles.

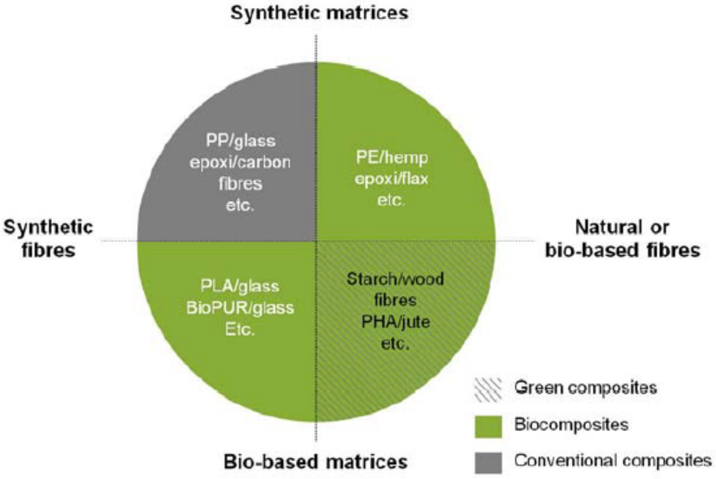


Figure 3.2: Biocomposites definition.

The aircraft industry is using natural fibre-reinforced composites for interior panelling. Biocomposites are used in construction for non-structural applications such as door and window frames, roof structures, floors, and wall insulation. The possibility of using natural fibres for cement reinforcement is also under consideration ([135], [88]).

Biocomposites are used in surfboards, snowboards and fishing rods in the sport and leisure industries. Hybrid biocomposites, which contain other fibres like carbon fibres, are also used in tennis rackets and bicycle frames ([135],[9],[51]). However, it is crucial to note that these biocomposites may contain partially non-biodegradable components. Different biocomposites vary in environmental friendliness, depending on their constituent materials and biodegrading ability. This creates difficulties in disposing of them at the end of their life, requiring new recycling methods that may have a lasting impact on the environment. Researchers have introduced a new biocomposite classification focusing on biodegradability to address these challenges. The categories of composites under this classification are shown in 3.3 Bio-based composite materials are made from natural or synthetic fibres and fossil oil-derived non-biodegradable or biodegradable polymers. Green composite materials, on the other hand, are made from all biodegradable polymers from natural renewable resources through fractionation, fermentation, genetic modification, and chemical synthesis[18]. They contain bio fibres, obtained chiefly from biological sources such as plants (cotton, flax, or hemp), recycled wood, waste paper, crop processing byproducts, regenerated cellulose fibre (viscose/rayon), and animal-based fibres like wool, silk, and feathers. The use of bio-based polymers as a matrix can be classified as fossil-based but biodegradable, bio-based but non-biodegradable, and bio-based and biodegradable, as shown in 3.4 The biodegradability of these materials ultimately depends on their biopolymer matrix components.

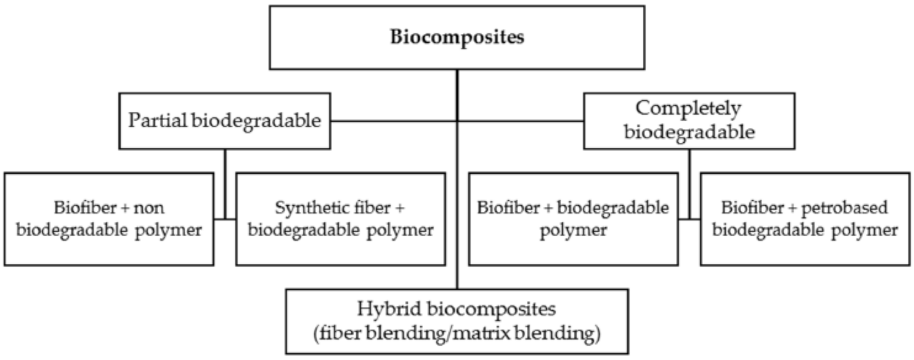


Figure 3.3: Classification of biocomposites.Adapted from [58]

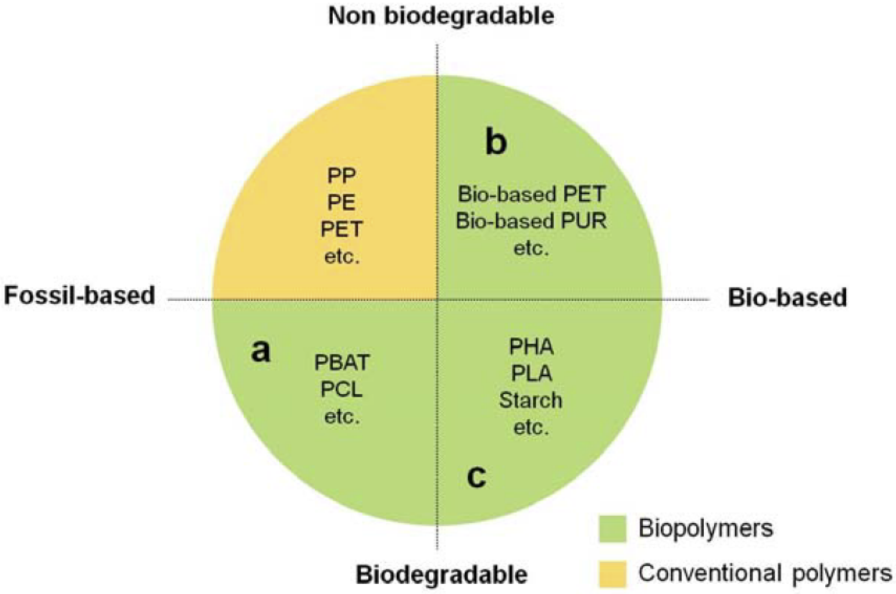


Figure 3.4: Difference between a conventional polymer and a biopolymer, showing that biopolymers can be: a) fossil-based but biodegradable; b) bio-based and non-biodegradable; and c) bio-based and biodegradable. Adapted from [135]

Incorporating these polymers with bio-fibres reduces reliance on non-renewable resources and enhances the environmental image of companies, appealing to eco-conscious consumers.

Green composites, which can be wholly decomposed without environmental impact, have gained significant attention from industry and research due to their renewable origin and lower environmental impact[214]. They are a viable alternative to conventional petroleum-based materials, and with further developments and improvements in performance, they could soon become the most promising alternative material.

The following section will describe each of the bio-based categories in detail to discuss the ongoing work and trend in each field:

3.2 Classification of Biocomposite

3.2.1 Composites of synthetic matrix and natural fibres

Natural fibres Reinforced Polymer Composites (NFRPCs) are an exciting material class that offers several advantages over traditional composites. They are lightweight, biodegradable, less expensive, and exhibit excellent mechanical properties. These NFRPCs are also called bio-composites and are further categorized into complete or partial green composites. Plant fibres, especially bast and leaf fibres, have applications in various industries, including automotive.

There are three major types of natural fibres used in NFRPCs production The three major types which produced NFs are:

- Animal-based fibres
- Mineral fibres
- Natural lignocellulosic fibres (NLF)

Plant fibres containing cellulose as their primary component are the most commonly used reinforcement media due to their availability and cost-effectiveness. Animal-based fibres, such as wool, silk, feathers, and hair, and mineral-based fibres, such as asbestos and basalt, are less commonly used due to their high price and unavailability. To make NFRPCs, these fibres are mixed with other constituents such as epoxies, PEEK, PP, low-density polyethylene (LDPE), high-density polyethylene (HDPE) as the polymer plastic matrices to make the two-phase fibre-reinforced composites. The production of NFRPCs consumes lower energy (9.55 MJ/kg) than traditional fibre-reinforced composites, such as glass (54.7 MJ/kg). Moreover, NFRPCs have lower environmental impacts than synthetic fibre-reinforced composites. These products equipped with economic qualities like biodegradability and renewability are raising the market volume, mainly due to their lower climate effects. Even though the usage of natural fibres is very lucrative at this stage, however, these fibres inherently pose many problems. Combined with hydrophobic matrices, they weaken interphases and compromise the composites' potential mechanical qualities. Moreover, animal fibres exhibit inferior hydrophilic properties than plant fibres, are highly sensitive to some alkalis, and are poor conductors of heat. These fibres must be treated further to optimize interfaces so they can be manufactured into a composite.

The mechanical properties of natural fibre polymer composites (NFPCs) depend on several factors, such as the interface provided by the fibre-matrix, stress transfer function, fibre orientation[149], moisture absorption[130], impurities[85], physical properties[35], and volume fraction[147]. The mechanical properties of PLA, epoxy, PP, and polyester matrices can be affected by various types of natural fibres [175] [[109], [184]

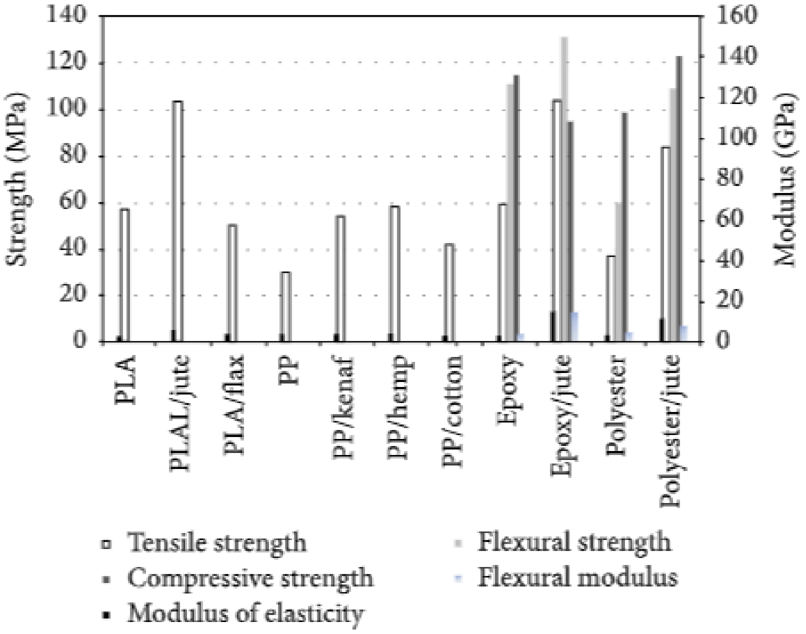


Figure 3.5: Some of the mechanical properties of natural fibre reinforced polymer composite

NFPCs show even better mechanical properties than a pure matrix in cases where jute fibres are added in PLA (polylactic-acid); in this case, 75% of PLA's tensile strength was improved; however, introduction or incorporation of flax fibres showed a negative impact on this addition. The addition of flax fibres resulted in 16% reduced tensile strength of the composites. Conversely, composites of PP were improved with the incorporation of hemp, kenaf, and cotton [167]. By far, maximum improvement is only seen in composites where jute or polyester has been incorporated where a total of 121% improvement is evident compared to pure polyester [167]. However, due to the rubber phase in gum compounds, a greater range of flexibility is present in such materials, resulting in reduced stiffness and storage modulus.

Owing to their excellent thermal and insulation properties, these composites have been used in various packaging, automotive, and construction sectors.

3.2.2 Composites of bio-based matrix and synthetic fibres

In biocomposites, matrix materials are derived from agricultural waste and reinforcement materials are natural fibres derived from biomass and agricultural waste. There are numerous natural and synthetic biodegradable polymers available such as poly-lactic acid (PLA), poly-lactic-co-glycolic acid (PLGA), polyethylene glycol (PEG), poly-hydroxy butyrate (PHB), polycaprolactone (PCL), etc, that can be used as matrix materials for the development of biocomposite. In recent times, considerable research works have been performed in developing completely biodegradable materials (green composites) by combining biodegradable polymer matrix with biofibres [124]. Biodegradable polymers can be broadly classified into two types based on the source, bio and synthetic polymers [13]. 3.6 summarizes the classification of these polymers. Based on their synthesis methodology, biopolymers can be grouped as biomass and microorganism products, while synthetic polymers can be grouped as biotechnology and petroproducts.

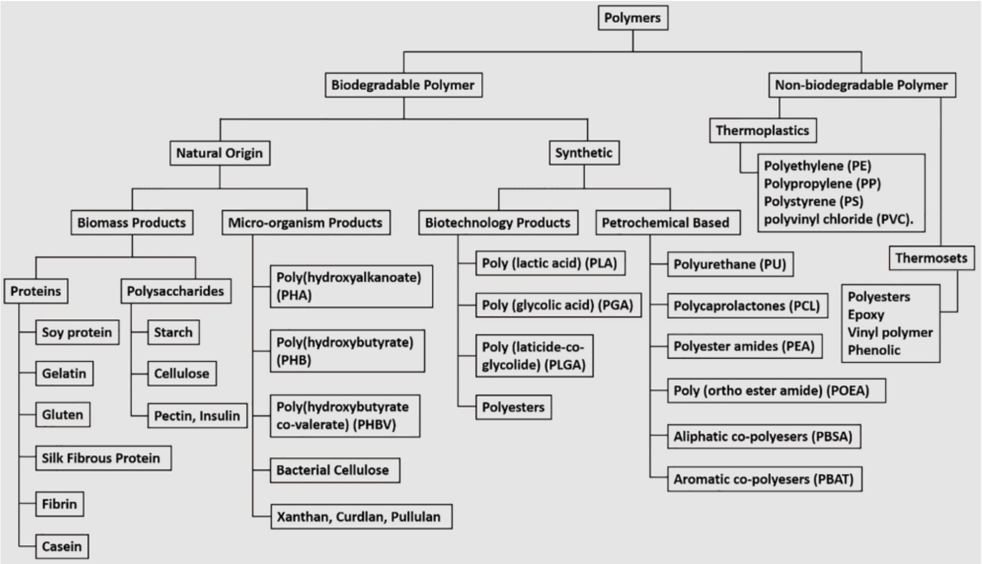


Figure 3.6: Classification of biodegradable and non-biodegradable polymers, adapted from[214]

Except for the polymer that originated from fossils, most of the polymers are originated from sustainable biomass. Biopolymers are produced commercially on a large scale for varied applications. Even though biopolymers make up only a small percentage of the polymer market, it has been predicted that they might replace petroleum-based polymers by about 30–90% in the future. Most biopolymers are biodegradable except a few; that is, they can microbiologically decompose into carbon dioxide (CO2), water (H2O), methane (CH4), and inorganic compounds. The degradation capacity of biopolymers depends on many factors like type of polymer, chemical composition and environmental conditions [38]. Recently produced biodegradable polymers possess a more comprehensive range of properties that are very much comparable with traditional polymers used in the market. The biopolymers are employed in specific fields depending upon their cost, availability, moisture absorption, thermal stability, mechanical behaviour, degradation stability, and biocompatibility [23]. The chemical constituents, molecular weight, morphological characteristics, mechanical attributes, and processing technique of a biocomposite are governed by the biopolymer part of the composite [191]. Despite wider applicability, biopolymers have a few shortcomings, such as their hydrophilic nature, low mechanical properties, and low durable degradation ratio in moist environments. One major limitation commonly referred to is its high price and commercial shortage compared to conventional plastics. Thermoplastic starch (TPS) has also been used for replacing petroleum-based plastics [1],[54]]. However, TPS has lower mechanical properties, making it unsuitable for packaging applications [112]. Thus, one of the ways to overcome this problem is by reinforcing TPS with fibre, which can improve its mechanical properties. The fibres used as fillers are generally more effective in improving the mechanical properties of the PLA matrix because the latter is much stronger than the former. Compared with the natural fibres, the synthesized fibres are generally much stronger, and hence they are more effective in enhancing the mechanical properties of PLA. Due to its good mechanical properties and low cost, GF is a popular reinforcing filler in the industry, along with carbon nanotubes and nanofibres. Recycled carbon fibres are also used to develop eco-friendly composites using a bio-based epoxy such as vitrimer/CANs derived from epoxidized; the study is still in progress.

Biobased composites made up of carbon fibre along with biobased thermoplastic polymer, polyamide 11 (PA11), as the matrix material showed significant mechanical and thermal properties as reported by Butenegro JA et.al, leading to recycled carbon fibre prepregs to be a suitable reinforcement, enhancing the reinforcement-matrix adhesion and leading to higher mechanical properties.[38] Adding biochar to biobased content epoxy resin and carbon fibres improved the mechanical and thermal properties of carbon fibre-reinforced composite[108]. These composites are widely studied owing to the maintained circularity of composites.

3.2.3 Composites of bio-based matrix and natural fibres or green composites

Green composites are those whose constituents- The resins and fibres used in the green composites are biodegradable when dumped and decomposed by the action of microorganisms. They are converted into the form of H2O and CO2. These H2O and CO2 are absorbed into the plant systems. The two main components of green composites are Biodegradable resin and natural fibres. The well-known biopolymer matrices are polybutylene succinate (PBS), poly hydroxyalkanotes (PHA), polylactic acid (PLA), poly (poly ε-caprolactone) (PCL) and thermoplastic starch. Due to their biocompatibility, biodegradability and environmental friendliness, these biopolymers have been used for various applications. The natural fibres include ramie, sisal, coir, hemp, etc. The whole idea of preparing natural fibre green composites is to ensure that the resultant material is eco-friendly and cost-comparable compared to conventional materials.

Biofibres include a huge amount of cellulose, hemicelluloses, pectin, lignin, etc., which make them highly hydrophilic materials and, in turn, result in poor interfacial bonding when embedded into hydrophobic polymers[136]. These features can lead to the loss of final composite properties; such a synergic combination of features resulting from the constituents and their interfaces determines their performance. A lot of chemical treatment must be done to manufacture compatible interfaces, which leads to further high-strength composites. This leads to significant energy loss. The bonding strength between the fibre and polymer matrix in the composite is considered a significant factor in getting superior fibre reinforcement composite properties. Unlike synthetic matrices-based composites, the identical polarities amid the biofibres and biopolymers (cellulose, collagen, polylactic acid (PLA), etc.,) generate the resulting biocomposites with superior compatibility and interfacial adhesion.

Many biocomposites are useful in non-load bearing capacities, even though they lack the inherent strength provided by synthetic fibre composites. These biocomposites are commonly used in sports equipment, housing for electronics, internal and external vehicle panelling, and furniture. Flax is known to be the strongest mechanically, and it shows properties comparable to glass fibre when woven in optimum arrangements. Flax bio-composites are hard but lightweight, making them suitable for various products. Among the bio-resins mentioned, those containing cashew nutshell liquid are perhaps the most applicable to varied conditions. Composites made of sisal fibre reinforced with CNSL (cashew nut shell liquid) resin were tested and exhibited an average strength of 24.5 MPa and a Young's modulus of 8.8 GPa. Their suitability for roofing applications was affirmed through bending tests, demonstrating adequate strength. In the realm of natural-based construction materials, Plant Fibre Technology, a venture originating from the BioComposites Centre, has developed various products. Among these is Isonat® insulation fibre, crafted from hemp cultivated on UK farms and utilizing waste cotton fibres. Isonat® contains 15% polyester fibres to provide loft and stability. Isonat® can be harmlessly disposed of by composting or incineration. The ability of Isonat® to absorb and release humidity actively assists in controlling moisture in buildings without any loss in thermal performance and without affecting the durability of the insulation. Ongoing research is addressing obstacles like the nascent stage of biopolymers and the inconsistency in fibre properties, striving to enhance the performance and market viability of biocomposites compared to conventional synthetic materials. With expected continuous progress, the prospect of a high-performing, eco-friendly, and financially viable biocomposites industry is emerging. Consequently, these bio-based composites are currently under investigation and are viewed as promising subjects for future development.

However, the philosophy of tailoring new products within a sustainable development perspective has gained traction, promoting environmentally safe alternatives like natural fibres and biodegradable polymers. The biodegradable composites, which are "Green Composites" designed to decompose entirely, offer a sustainable solution to end-of-life disposal concerns. The demand for environmentally friendly materials is increasing rapidly, positioning biodegradable fibres and polymers as crucial contributors to high-performance industrial composites. when recycling is not an appropriate option, the fact that the whole material—matrix and reinforcement—can biodegrade, which helps to face the problem of end-of-life disposal of the final good/product. These biodegradable composites are the the sort of biocomposites under the scope of the thesis, and hence, the possible candidates for such a material are further reviewed.

This recognition underscores the significance of investigating and understanding the properties and applications of these materials in the broader context of sustainable development.

In the further sections going ahead, a detailed overview of each of the green constituents is addressed.

3.3 Natural fibres as reinforcement in biocomposites and Criteria for Selection

After examining various categories of biocomposites, this section will throw deeper insights into the first constituent, which plays a significant role in composite development: natural fibres. The selection of such materials during the design and manufacturing of sustainable composites plays a crucial role in determining their performance[84],[102][114][156]. Various natural fibres have been used or have the potential to be used for sustainable FRP composites, which have been discussed here.

Natural fibres are lucrative alternatives to synthetic fibres in the composite industry due to their versatility, local availability, and eco-friendliness. They offer lightweight, low density, easy production and processability, and cost-effectiveness. They are also preferred as they cause less wear and tear during processing and are environmentally friendly [191]. These fibres are widely used for reinforcement in polymer matrices, providing dimensional stability and excellent strength-to-mass ratio [12], [17]. Around 30,000,000 tonnes of natural fibres are produced annually and have been used as suitable raw materials in sectors like clothing, paper making, packaging, sports equipment, automobiles, and building materials.[84] The European natural fibre composites market was valued at US$ 1,998.59 million in 2022 and is expected to reach US$ 3,155.01 million by 2028, registering an annual growth rate of 7.9% from 2022 to 2028. The critical factors attributed to the European natural fibre composites market expansion are the focus on eco-friendly and sustainable products and the increasing demand for natural fibre composites from the automotive industry. Based on raw material, the European natural fibre composites market is segmented into wood, cotton, flax, kenaf, hemp, and others. The wood segment held 42% market share in 2022, amassing US$ 839.93 million. It is projected to garner US$ 1,360.52 million by 2028 to expand at 8.4% CAGR during 2022–2028. The spiralling demand for lightweight products from the automotive and construction sectors due to their thermal insulation and the growing awareness regarding green products fuelled the increased interest in these natural resources. However, the moisture sensitivity of natural fibre composites and other structural scarcities is still hindering further market growth [132].

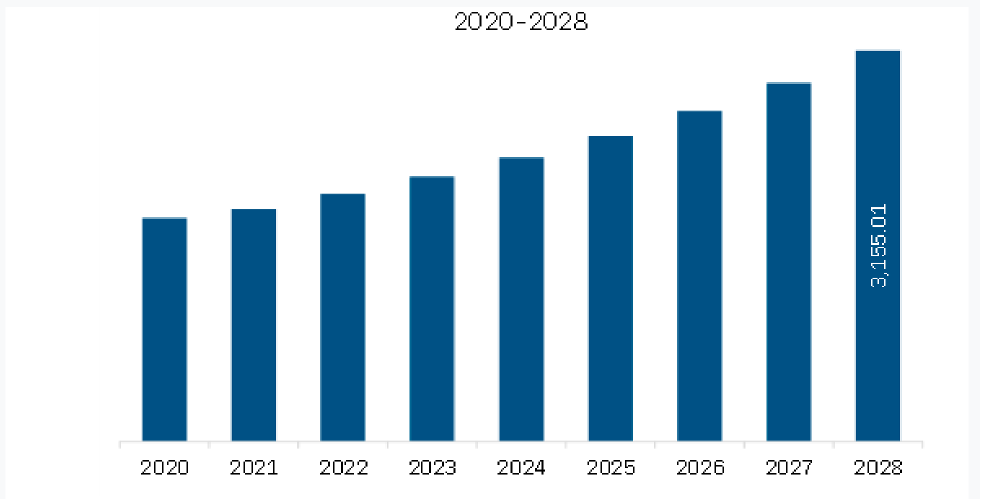


Figure 3.7: Europe Natural fibre Composites market Revenue and Forecast to 2028 (US$ Million)[132]

3.3.1 Classification of Natural fibres

Depending on their origin, natural fibres can be sorted into minerals, such as basalt or asbestos; animals, such as silk or wool; and vegetal, also known as plant fibres. The use of vegetable fibres as reinforcements in composite materials [24] has emerged as an alternative reinforcement to the conventional carbon and glass fibres or other inorganic fillers [160],[10]. Animal fibres mostly comprise proteins, while plant fibres are composed of cellulose. Plant fibres are abundantly available and cost effective; on the other hand, animal fibres have recently gained attention as reinforcing material for biopolymer composites. Animal fibres have received appreciable interest because of their flexibility, high surface roughness, high aspect ratio, and low hydrophilic nature compared to plant fibres [110]. Plant fibres like hemp, kenaf, flax, cotton, ramie and animal fibres like wool and silk are usually used in the textile sector[135]. Figure3.8 illustrates the classification of reinforcing fibres.

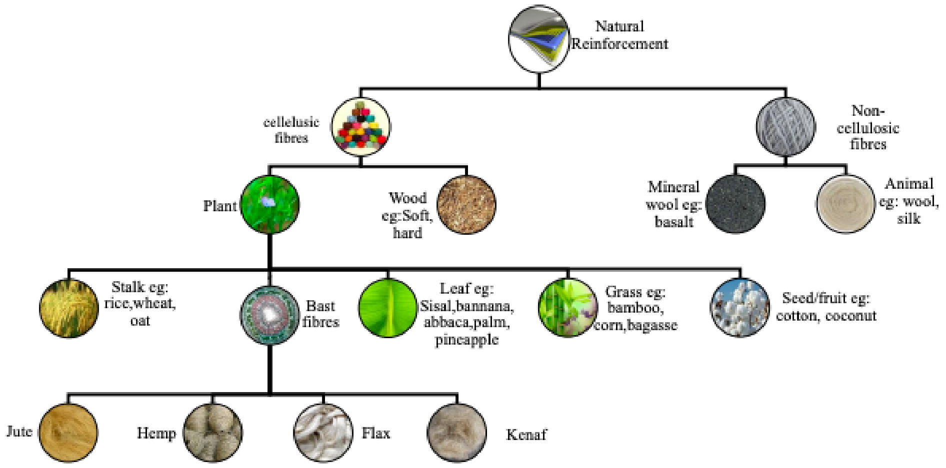


Figure 3.8: Classification of various reinforcement with natural fibres: cellulosic and non-cellulosic fibres

In the following subsections, a detailed summary of usage and its types are described.

Animal fibres

Animal fibres are highly valued for their exceptional chemical, physical, and mechanical properties, which make them ideal for reinforcing polymer composites. Silk, hair of different animals, and bird feathers are all such fibres. Wool, for instance, is obtained from mammals like sheep, alpaca, bison, angora rabbit, and cashmere/pashmina goats and is a widely used textile fibre produced primarily in China, New Zealand, and Australia. The properties of wool vary depending on its origin, with different diameter ranges for angora, alpaca, qiviut, and cashmere wool fibres. Wool fibres possess hydrophilic characteristics, absorbing water up to one-third of its weight. They also have low flame spread rates, heat release, and combustion. Other commonly used animal fibres include goat, horse, and camel hairs. On the other hand, Avian fibres consist of feathers and feather fibres from chickens and other birds. Chicken feathers, composed mainly of keratin, are a by-product of slaughterhouses and have applications in microbial corrosion resistance, absorbent sponges, and composite sponges for cleaning lenses and polished surfaces. Studies have demonstrated that chicken feather fibre-reinforced composites exhibit favourable mechanical, acoustic, and thermal properties due to their chemical composition, low density, and morphological structure. [145][155]

Silk, obtained from approximately 14,000 species of butterfly larvae and

4,000 species of spiders, is secreted by glands during cocoon development. Silk contains chitin, a highly structured protein that provides the fibre's chemical resistance and mechanical strength. The most commonly used silk is mulberry (Bombyx mori), consisting of fibroin and sericin components. Mulberry silk has a tensile strength of about 600 MPa, which surpasses most plant fibres. Silk finds applications in biomedical fields like tissue engineering and the production of medical scaffolds through fibre reinforcement in polymers.[145][191] Dragline silk, produced by giant wood spiders or banana spiders (Nephilia), is another type of silk. It comprises two repetitive proteins, spidroin I and spidroin II, and exhibits a semi-crystalline structure with lower crystallinity than mulberry silk. Among various silk fibres, dragline silk is one of the strongest, with a tensile strength of 1.1 GPa, comparable to high-tensile steel (1.5 GPa).[155]

Plant fibres

Typically sourced from rapidly renewable plants, plant fibres are considerably more affordable and less prone to economic variability. However, they also alleviate environmental concerns related to the exhaustion of natural resources. The density of these cellulose-based fibres can be almost half that of conventional reinforcing fibres, like those made from glass. Historically, cellulosic fibres have reinforced thermoplastic and thermosetting resins derived from petroleum or natural sources. In bio-composites, these natural fibres act as the reinforcing phase, enhancing the performance of the composite material. Cellulose-based fibres can come from bast, leaf, seeds, or other plant parts. Their incorporation typically increases strength and stiffness while often reducing the weight, leading to more efficient systems. Applications such as roping, textiles, tools, and housing materials have historically and currently utilized plant fibres, leveraging their unique mechanical characteristics. Consequently, natural fibre-reinforced polymer (NFRP) composites, which are lighter than conventional composites, facilitate more efficient systems and reduce transportation costs. Vegetable fibres are widely available, economical, and non-hazardous, promoting safer working environments. Their biodegradable nature supports sustainable disposal methods, yet they also offer CO2-neutral energy recovery through incineration. With low density, these fibres provide balanced stiffness, toughness, strength, and excellent thermal and acoustic insulation properties. The processing of vegetable fibres is tool-friendly, minimizing wear, and their surface characteristics are adjustable for greater hydrophilicity or hydrophobicity [46],[199],[37]. These fibres are available in diverse morphologies, such as long fibres, staple, pulp, strands, tufts, and technical fibres [46]. The energy consumption for producing a natural fibre mat, including the entire process from cultivation to fibre digestion (9.55 MJ/kg), is substantially lower than that for producing a glass fibre mat (54.7 MJ/kg) [9].

3.3.2 Chemical composition and properties of cellulosic fibres

As natural fibres are derived from various plant types and plant parts, their chemical compositions exhibit slight variations. These differences manifest in the quantities of cellulose, hemicellulose, lignin, and other compounds present. Nonetheless, a shared characteristic among all these natural cellulosic or lignocellulosic fibres is their fundamental composition, which primarily comprises cellulose, lignin, and hemicellulose as major constituents. In addition to these main components, there are also minor constituents, including pectin, waxes, and inorganic compounds, among others in table 3.1.

Fibre	Cellulose ($wt.\%$)	Hemicellulose ($wt.\%$)	Lignin ($wt.\%$)	Pectin ($wt.\%$)
Flax	60-81	14-18.6	2-3	1.8-2.3
Jute	51-72	12-20.4	5-13	0.2
Sisal	43-88	10-13	4-12	0.8-2
Kenaf	36	21	18	2
Hemp	70-78	17.9-22	3.7-5	0.9
Ramie	68.6-76	13.1-15	0.6-1	1.9-2
Cotton	82.7-92	2-5.7	0.5-1	5.7
Coir	43	0.3	45	4.0
Banana	60-65	6-19	5-10	3-5
Wood fibres	45-50	23	27	-

Table 3.1: Chemical composition of selected natural fibres. Data from [72]

In the following section, a detailed discussion of the chemical composition of such fibres is discussed to understand the properties like swelling and hydrophilicity. Plant fibres can be considered composite materials, consisting of (cellulose) microfibrils embedded into an amorphous matrix of lignin and hemicellulose [34]. The combination of these components, which present variable contents depending on multiple factors, is responsible for cellulosic fibres' properties and their aforementioned variability. Cellulose is the main component of plant fibres, a strictly linear—unbranched [122] polymer formed by β linked D-glucose repeating units(see figure3.9). Cellulose chains form random amorphous pockets and well-packed crystalline regions [117][177].

It presents high tensile strength and large stability in normal environments [72], and as the main structural component, cellulose content influences the strength and stiffness of the fibre Hemicellulose is an amorphous polymer consisting of random short, highly branched chains, which forms some cross-

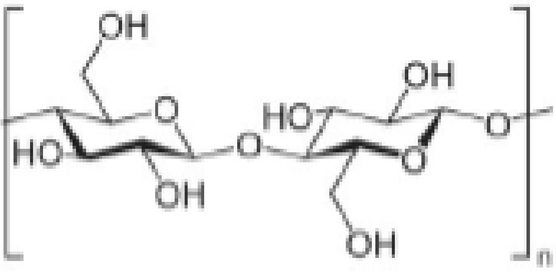


Figure 3.9: Cellulose

linking with the cellulose molecules, resulting in a higher structural integrity [30]. It presents poor strength and thermal stability, and high sensitivity to water is the most hydrophilic component [135]. Due to that, hemicellulose plays a key role in moisture absorption and biological and thermal degradation of vegetable fibres. Lignin is a long-chain and high molecular weight substance that presents aromatic structures and is resistant to the attack of microorganisms and anaerobic processes [72]. It is hydrophobic [153], has a high contribution to the char formation [135] and confers to the fibre its resistance against UV degradation.

Lignin and hemicellulose do not contribute too much to the fibre tensile strength, but due to their branched and cross-linked nature acting as a "natural cement", providing some degree of structural integrity and rigidity to the walls to harness the cellulose strength, while conferring flexibility [72],[120].Lignin and hemi-cellulose do not contribute too much to the fibre tensile strength, but due to their branched and cross-linked nature acting as a "natural cement", providing some degree of structural integrity and rigidity to the walls to harness the cellulose strength, while conferring flexibility In figure 3.10, the influence of the chemical components in some of the properties of cellulosic fibres are schematised: Typically, varieties with a higher cellulose content and those with cellulose microfibrils aligned along the fibre direction tend to exhibit superior performance. This alignment is commonly found in bast fibres like flax, hemp, kenaf, jute, and ramie, which are crucial in supporting the plant's stalk. These fibres' structural characteristics and their relation to performance are discussed in more detail in the following section (refer to figure3.11).

3.3.3 Bast fibres

Vegetable fibres can be classified into six botanical types [151],[189] with the most common division being non-wood fibres and wood fibres[106]. Non-wood fibres can further be classified based on their plant origins, including bast fibres (flax, hemp, jute, kenaf, ramie), leaf fibres (abaca, sisal, henequen, pineapple), seed/fruit fibres (cotton, coir), straw (corn, wheat, rice), and

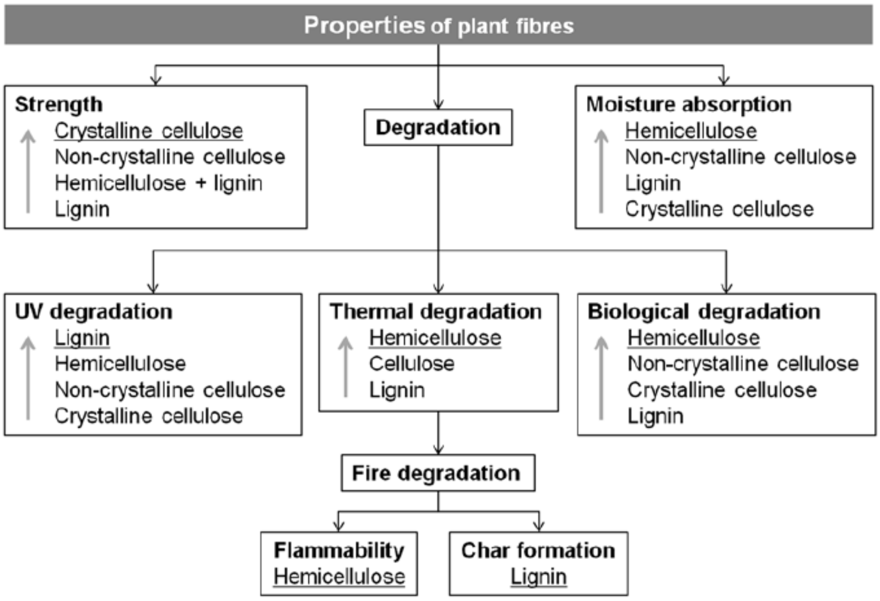


Figure 3.10: Influence of the constituents on some of the properties of the plant fibres [26,28]

grass fibres (bagasse, esparto, bamboo, switch grass). Bast fibres, such as jute, flax, ramie, and sisal, are widely used in polymer composites [34] for high-performance applications [177] due to their desirable and comparable

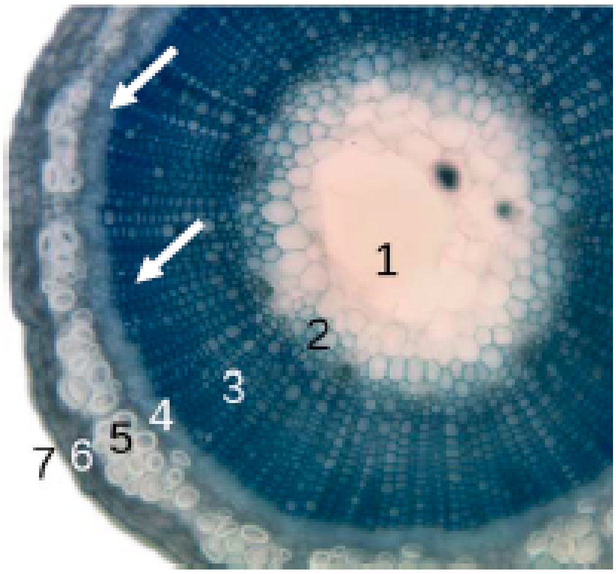


Figure 3.11: Stem cross-section—of a flax plant—showing: (1) pith; (2) protoxylem; (3) xylem; (4) phloem; (5) bast tissue; (6) cortex; and (7) epidermis. Arrows mark the bast fibre bundles.

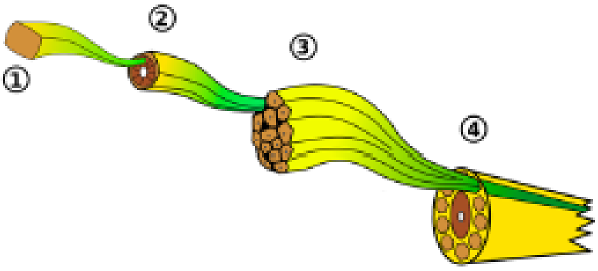


Figure 3.12: Diagram of a stem configuration: (1) microfibril; (2) elementary fibre; (3) bast fibre bundle; (4) stem.

physical properties, which can be seen in the table 3.2 below. These fibres, containing 60-75% cellulose, are found in fibre bundles within the inner stem, providing structural strength and stability. Figure 3.11 shows a section of a flax stem, highlighting the bast fibre bundles beneath the stem bark. Each bundle comprises 10-40 elementary fibres linked together mainly by pectin [106]. These elementary fibres, seen in figure 3.12, have concentric layers composed of parallel microfibrils. The microfibrils form helices with either an S or Z orientation [177], impacting the fibre's microfibrillar angle and axial tensile properties. Fibres with a spiral orientation of microfibrils often exhibit good ductility.

At the nano-scale, microfibrils comprise crystalline cellulose chains embedded in an amorphous matrix, primarily consisting of pectins and hemicelluloses.[106].

In figure 3.12, the stem configuration is presented, showing the hierarchical structure of the bast fibres. Each bundle contains around 10-40 elementary fibres mainly linked by pectin (3.12-3). At the microscopic scale, elementary fibres (3.12-2) are composed of concentric layers, which are, in turn, composed of parallel microfibrils (3.12-1), organised in helices with S or Z orientation, forming a determined angle of the microfibrils concerning the fibres axis: the microfibrillar angle. This angle strongly influences the axial tensile properties of the fibre [177], and good ductility is often observed in fibres that present a spiral orientation of these microfibrils [106]. At the nano-scale, microfibrils comprise cellulose chains in a crystalline configuration embedded in an amorphous matrix, mainly made of pectins and hemicelluloses [106].

Fibre	Density (g/cm3)	Diameter (μm)	Elongation at break (%)	Tensile Strength (Mpa)	Young Modulus
Flax	1.4-1.5	40-620	2.7-3.2	343-1035	27-80
Jute	1.3-1.5	30-140	1.4-3.1	187-773	3-55
Sisal	1.3-1.5	100-300	2.0-2.9	507-855	9-28
Kenaf	1.22-1.4	40-90	3.7-6.9	2.95-930	22-53
Hemp	1.4-1.5	16-50	1.3-4.7	580-1110	3-90
Ramie	1.5	40-60	3.6-3.8	400-938	44-128
Cotton	1.5-1.6	16-21	2-10	287-597	5.5-12.6
Coir	1.25-1.5	11-450	15-47	106-270	3-6
Banana	1.3-1.35	50-280	3-10	529-914	7.7-32

Table 3.2: Physical Properties of bast fibres

Referring to table 3.2, we see the flax fibre has the strength and Young's Modulus which would be desirable to develop a stronger biocomposite, so going forward, further sections will give a detailed overview of Flax and its structure, which will enlighten us about flax properties.

Flax; fibre Structure and properties as reinforcements

Flax is one of the most widely used fibres since ancient times. Flax textiles have been dated back to 5000 BC in Egyptian burials. Despite being traditionally used for high-quality textiles, flax fibres, especially lower fibre grades, are increasingly used in the composites industry due to their excellent mechanical properties, low price, and availability. Flax's high cellulose content and high crystallinity contribute to its strength, stiffness, and ease of wrinkling. Flax (Linum usitatissimum L.) is an ancient plant cultivated by the Egyptians and brought to Europe 2000 years ago. It has specific growing requirements and is sown between March and May when temperatures are below 30°C. The life cycle consists of 12 stages, which include vegetative growth, flowering, and maturation. During the first 30 days, the plant develops fibre cells and roots. The flowering period lasts 50-60 days, during which the stem extends and leaves are produced. After flowering, the maturation period lasts 30-40 days, and cellulose is deposited in the fibre cells. At maturity, the fibre flax stems can reach a height of 80-120 cm and a diameter of 3 mm. There are around 20 stem varieties, but only four major categories are sown in Western Europe, covering 90% of the areas. Bundles of primary fibres rapidly form inward, with the outermost bundles coming first. These bundles elongate during flowering, representing 25% of the stalk's dry weight. A flax stalk can have 20-40 fibre bundles, each containing 20-40 primary fibres. Refer to figure3.13 for a visual representation. The composites industry increasingly uses flax fibres, particularly lower fibre grades, due to their excellent mechanical properties, low cost, and easy availability. Flax fibres are rich in cellulose and have a high degree of crystallinity, which makes them strong, stiff, and easy to fold. Flax fibres are mainly composed of cellulose —fibres,

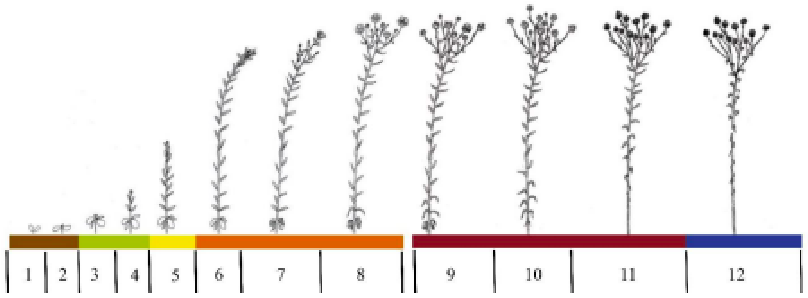


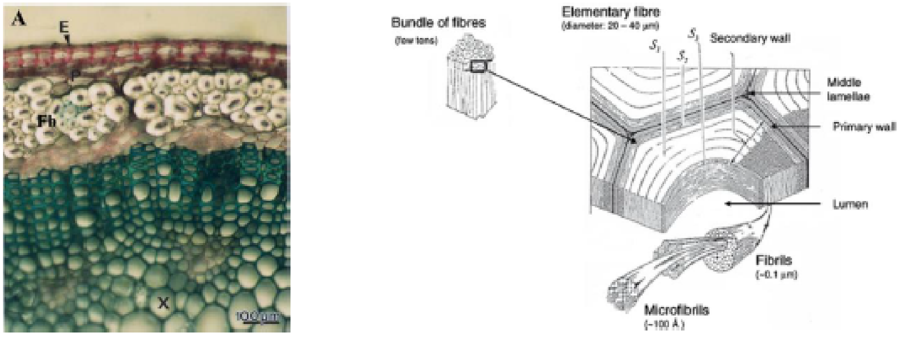
Figure 3.13: Flax plant 12 growth stages

consisting of helically wound cellulose microfibrils bound together by an amorphous matrix. Plant fibres, in particular flax fibres, consists of a complex structure comprising four main components: cellulose, hemicellulose, lignin, and pectin, but also waxes and water. Flax fibres are typically long, polygonal, and hollow, with a smooth surface and nodes. These nodes, also called dislocations, have thick walls and a well-defined central lumen. These fibres are grouped into bundles, which are either entire or partial, and referred to as "technical fibres". The elementary fibres comprise concentric cell walls or layers surrounding a central open channel or lumen. Each layer is made up of microfibrils with diverse chemical compositions and structures.

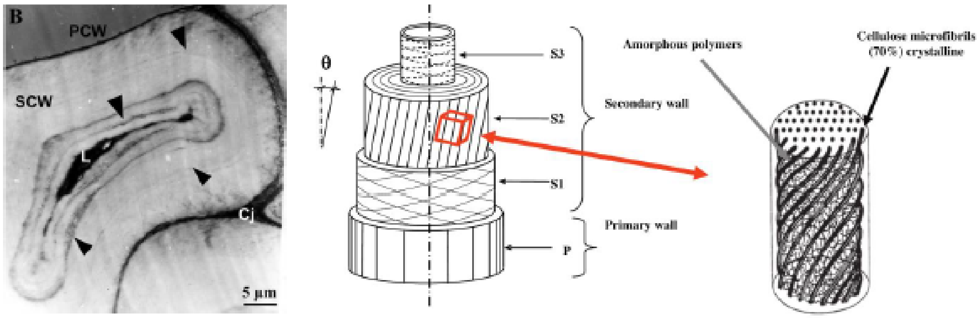
For Flax, the outer thin layer, the primary cell wall that acts as a coat, is around $0.2\mu m$ thick and the microfibrillar angle—respects the fibre axis—is of 35°.

The outer thin layer, the primary cell wall in Flax that acts as a coat is around $0.2\mu m$ thick and the microfibrillar angle—respect the fibre axis—is of 35°.

The secondary cell wall, the inner layer of fibre, is typically between $5\mu m$ and $15\mu m$ thick and makes up most of the fibre. According to a review by [67], the secondary cell wall comprises three layers. The first layer, S1, limits lateral cell expansion and ensures fibre stability in compression. The second layer, S2, is the most critical layer due to its relative size compared to the other layers (S1 and S3). It contains mainly amorphous hemicelluloses and cellulose that is oriented at 10°. The S2 layer plays a significant role in defining the properties of the fibre. Because the microfibrillar angle in the secondary cell wall is minimal, Flax has a high tensile strength. The final layer, S3, is closer to the fibre lumen and contributes to fibre stability by supporting the hydrostatic pressure. Figure 3.14 presents the general structure of a flax fibre. Plant fibres, in particular flax fibres, comprise four main components: cellulose, hemicellulose, lignin, and pectin, but also waxes and water. Main component proportions are summarized and determined in



(a) flax stem (b) bundle of fibers



(c) elementary fiber (d) elementary fiber (S1–S3 reversed)

Figure 3.14: Sructure of flax fibre from stem to microfibrils[15][119].

several studies as in table 3.3. A significant variation of the values has been found in the literature. That is mainly because of a set of parameters such as the variety, quality of the soil, the climatic conditions, the quality of the retting process, the degree of maturity or measurement conditions.

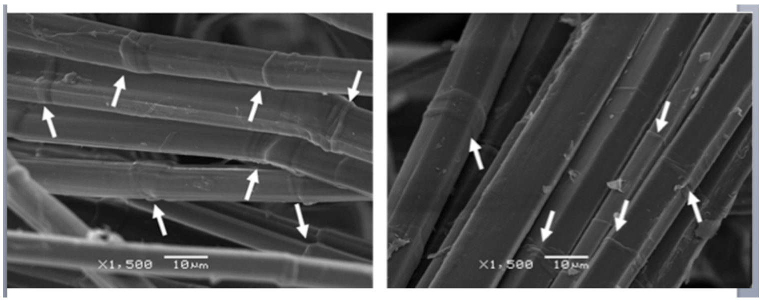


Figure 3.15: SEM images of flax bundles showing several fibres. Arrows mark the nodes.

Cellulose	Hemi-cellulose	Pectin	Lignin	Wax	Water soluble	Water	References
65.2-72.2	10.1-17.1	2.8-5.6	2.3-7.7	2.2-3.0	-	-	[40]
61.5-86.5	-	2.4-3.8	2.1-3.6	-	-	-	[59]
77	8.7	-	2.8	-	-	4.5	[118]
71	19.6	2.3	2.2	1.7	-	10	[50]
60-80	10-15	-	0.4-4	-	-	-	[56]
65	16	3.0	2.5	1.5	4	8	[25]
64.1	16.7	1.8	2.0	1.5	3.9	10	[27]
62-72	18.6-20.6	2.3	2-5	1.5-1.7	-	8-12	[52]

Table 3.3: Component Proportion in fibre

Physical Properties

As previously mentioned, flax fibres are highly desirable for composite reinforcement because of their impressive mechanical properties. Flax is also biodegradable has a low cost of around 0.4 €/kg-1.1 €/kg in 2014, according to, low density— 1.4 g/cm^{-}3 - 1.54 g/cm^{-}3, moisture absorption—of approx. 7 % [193]. Additionally, flax offers good thermal and acoustical insulation properties. However, flax fibres are highly interesting for composite reinforcement owing to their mechanical properties3.2. When examining the specific properties of flax fibres, they exhibit high stiffness 27 GPa- 80 GPa—and good strength— 345 MPa- 1830 MPa—[135].

When considering the specific properties, flax fibres have an outstanding performance, equal to or higher than those of glass fibres, for instance, [193]. Also, the elongation of the flax fibres is very low; 1.2 % - 3.2 % [135], which is beneficial for producing rigid composites and ensuring good stress transfer. It is crucial to note that various factors heavily influence flax properties and are subject to unavoidable variability. This variability is evident in the wide range of values in previous data.

The mechanical performance of flax fibres is affected by various factors, as reviewed in [53],[200]. These factors include the plant species, crop cultivation, fibre location in the plant, weather conditions, and the extraction method used. Additionally, the fibre's cell wall thickness, coarseness, microfibril angle, porosity, and size and shape of the lumen, which are determined by the harvesting stage, can also affect the mechanical performance of the fibres.

However, some variability in the results obtained can also be attributed to measurement conditions, such as the type of fibre, moisture or temperature conditions, fibre diameter, and determination of the cross-section, testing speed, or clamping distance (gauge length), among others [200], [185]. The intrinsic variability of natural fibres also contributes to the scatter of the results, leading to significant variations in the measured properties.

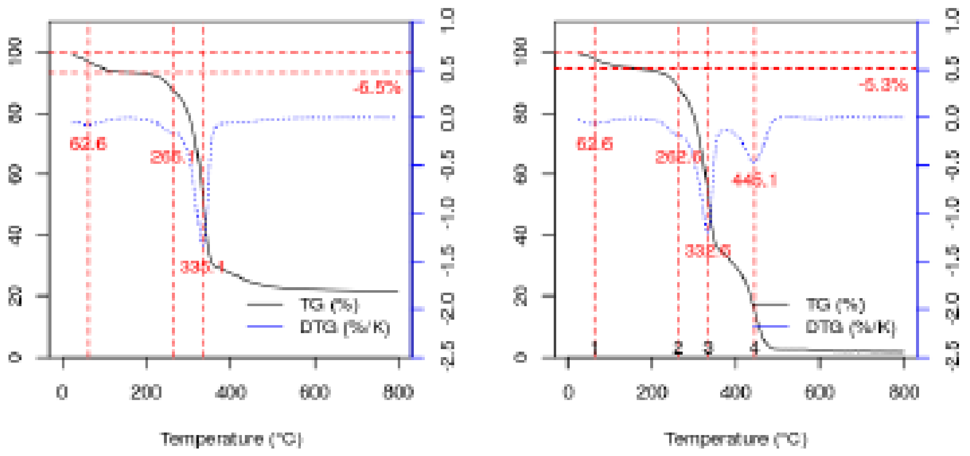
In general, natural fibres' flexural and tensile performance depends on environmental conditions [5]. Moisture absorption, and hence, environmental humidity, can affect the mechanical properties of cellulosic fibres. An increasing clamping distance can lead to a decrease in the strength values [185]. The stiffness of flax fibres is known to decrease with the increase in fibre diameter [181].

Furthermore, the properties of flax fibres can be tailored by applying surface treatments. Chemical or physical treatments can modify the hydrophobic/hydrophilic nature of the fibres, surface chemistry, surface roughness, dimensional stability, stiffness, strength, or elongation.

Density And Defect The mass density values of a flax fibre reported in the literature are widely scattered, ranging from 1380 kg m^{-}3 to 1550 kg m^{-}3 ([101], [27], [135], [193], [52]). The plants' growth conditions may partly explain this difference, as well as the fibre's position in the rod, the species in question, and the measurement method. Particularly, considering the volume of the lumen on one hand and the humidity inside the fibre on the other hand, it has an important effect on the measured density. One retains the value 1540 kg m^{-3} for fibre percentage computation of FFRP ([139], [106]). Elementary flax fibres contain cell wall defects known as various organizational forms called dislocations, kink bands, nodes, or slip planes, etc. [16] Defective secondary walls also exist in the growth of plant cell walls. Ultrastructural studies reveal a common set of cell wall defects in dividing embryonic and root cells. These defects are linked to a specific reduction in cellulose coupled with ectopic callose and lignin deposits, resulting in cell wall gaps. The most obvious defect observed was the appearance of incomplete cell walls[162].

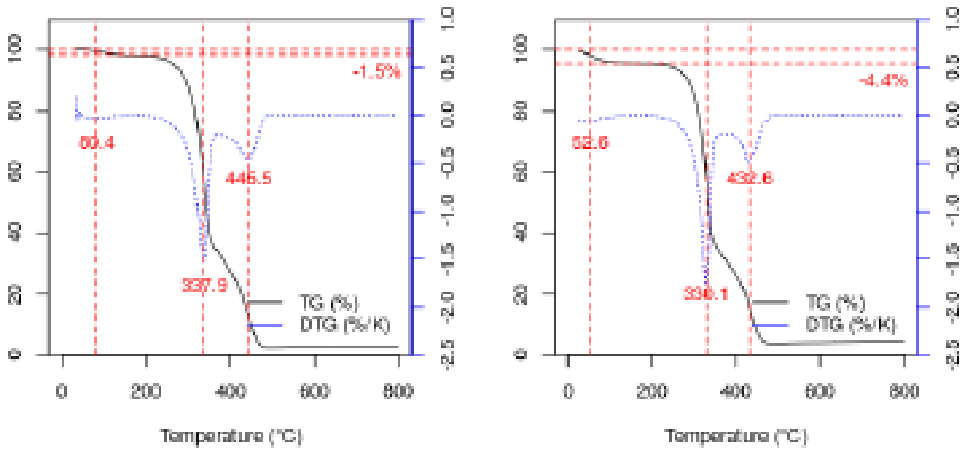
The rupture properties of the flax fibre are affected by the defects of those weakest links of a chain (kink bands zone), causing initiated failure under load. A non-homogeneous distribution of defects in the fibres may be one reason for the significant variations in the mechanical properties of the flax fibres. Many defects are also induced through the standard mechanical preparation of the flax, typically scutching, hackling, spinning and weaving in addition to the discontinuity and possible misalignment of the fibres. These defects lead to the weakening of the fibres and result in a decrease of composite mechanical properties[98].

Thermal Stability Their structure and chemical composition greatly influence the thermal degradation of cellulose-based fibres. Thermal stability seems to be one drawback limiting the application of flax fibre. Several condition thermogravimetric analyses carried on between room temperature and $800°C$ with $10°C$ are shown in Fig.3.16 where the mass of the fibres remains stable until $160°C$and weight loss of the previous portion below $100°C$ is mainly due to the evaporation of water. After that, the fibres gradually begin to decompose. Derivative thermogravimetry in the blue dotted curve shows



(a) Standard flaxtape, under argon

(b) Standard flaxtape, under air



(c) Dry spinning yarn, under air

(d) Wet spinning yarn, under air

Figure 3.16: Thermogravimetric analyses of flax fibre

that the maximum weight loss rate is around 334°C. It should be the same with other flax products because oxidation reaction occurs at around 440°C in the air atmospheres.

The first decomposition of the fibre components is the wax (above 120°Cand pectin (above 180°C then cellulose and hemicelluloses[49] followed by the lignin[39]. According to the literature, the first loss of mass at around 60°Con Fig3.16 is due to the release of water, the third loss of mass at around 334°C is due to cellulosic substance degradation, and the fourth loss of mass at around 440°Cis due to oxidation of some woody matter (lignin). The second loss of mass at around 264°C is mainly due to pectin degradation[173]. (Fig.3.16a& Fig.3.16b). That is due to the use of pectin as a binding agent in the case of Flax, which was tested for literature study purposes. These pectins are mainly eliminated in the case of traditional textile processes (Fig.3.16c, d). Beyond this simple analysis, it is well known that when cellulose-based materials are heated in the range of 100°C to 250°Csome of the changes in physical properties of the fibres can be explained in terms of alteration in either physical or chemical structure such as depolymerization, hydrolysis, oxidation, dehydration, decarboxylation and recrystallization.

Thermal stability is a key factor for the flax fibre used as reinforcement during composite production, and temperature has a greater effect on the resistance mechanical properties. Normally, for exposure temperatures up to 170°C both the recrystallization and the differences in thermal expansion coefficient seem not to be significant enough to have a remarkable influence on the tenacity of untreated flax fibres[49] reported that after exposure to 120°C up to two hours, no significant decrease of the tensile strength is observed in hackled long Flax. However, after two hours exposure to 180°C stress retentions of (64 %-68 %) and retained strains of (44 %-60 %) are observed, respectively. Strain properties are more influenced than stress properties.

Mechnical Properties The tensile mechanical properties of flax fibres are an essential performance considering that they are used as reinforcement in the composite. The tensile deformation is influenced by various factors such as external conditions of strain rate, humidity, temperature, etc. and internal conditions of fibre variety such as chemical composition (e.g. cellulose rate) and the structure (e.g., size of the lumen, microfibril angle), fibre diameter, fibre length considering the defect, etc. Generally, flax fibres' mechanical properties (Young's modulus and failure stress and strain) exhibit significant dispersions. In addition, the extraction process of the fibre operations can vary, resulting in a variation in mechanical properties. Charlet et al.[43] performed a tensile test with a displacement rate of 1 mm min^-1 and gauge length 10 mm in room condition. Results show a mean strength 1200 MPa Young's modulus 56 GPa respectively.

The stress-strain curve of a tensile test of a flax fibre is shown as in Fig 3.17 with three regions considering: first linear region (strain from (0 % to 0.3 %); second non-linear region (0.3 %-1.5 %) and the final linear region (1.5 % to rupture). Bos et al.[36] evaluated the hand-decorticated elementary fibre can give strength as high as 1800 MPa lamping length 3 mm strain rate 0.005 s^-1. The clamping length influences the tensile mechanical properties, especially when small.

Pillin et al.[138] investigated different flax fibre varieties from the same cultivation environment. The test parameters, such as gauge length and speed, are the same as Charlet et al.[43]. The ultimate stress of different kinds of flax fibres varies from 733 to 1111 MPa for modulus; it is from 45.6

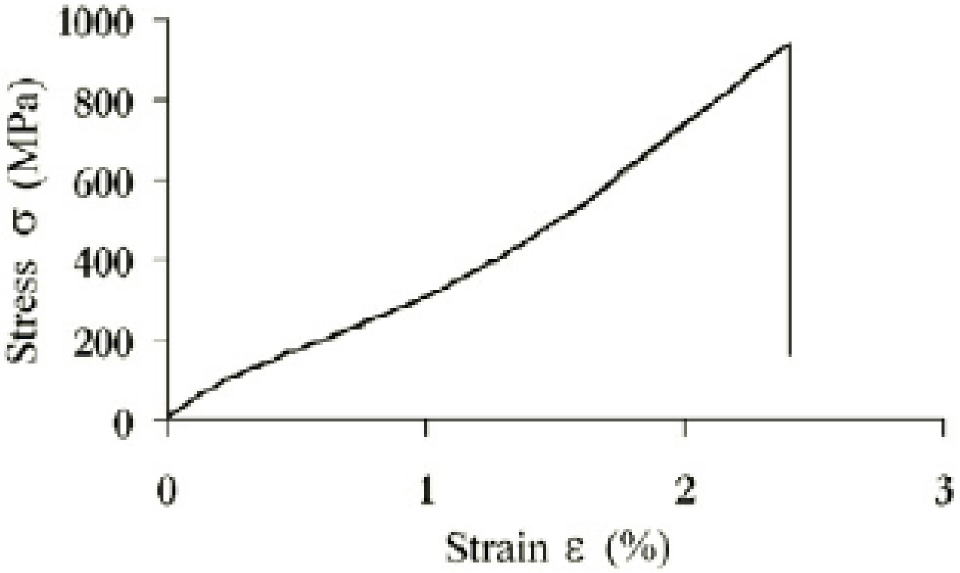


Figure 3.17: Stress-Strain curve of elementary flax fibre

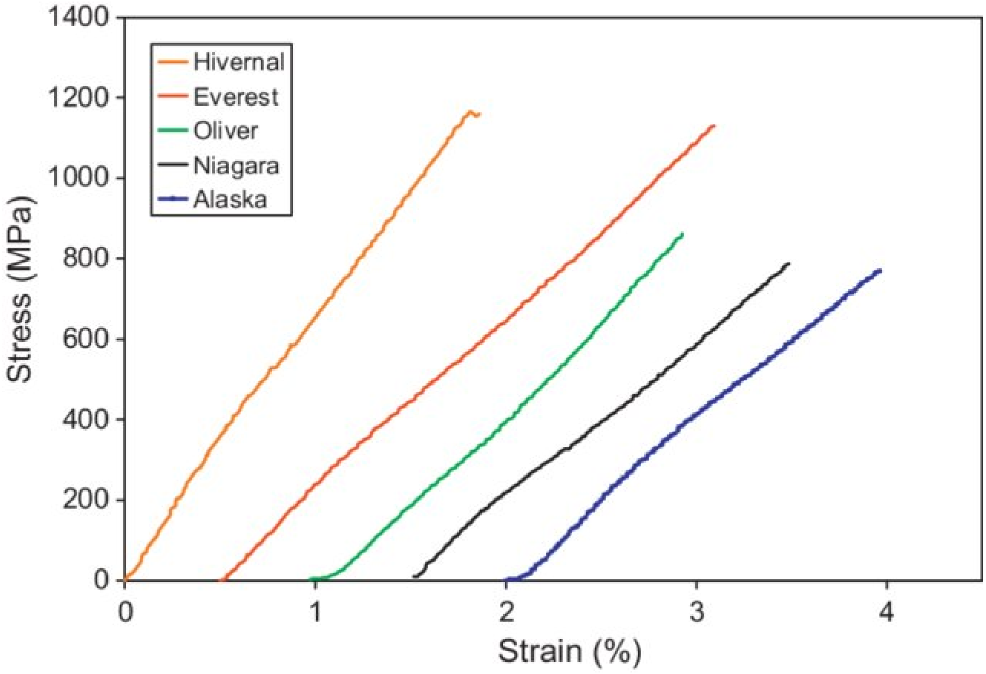


Figure 3.18: Tensile stress-strain curves of different varieties of flax fibre[137]

to 71.7 GPag the second region to calculate. Both Pillin et al. and Charlet et al. show a typical stress-strain curve with linear and nonlinear regions in small deformation (0.3 %-0.5 %) or higher deformation about the flax fibres (actually, they hold different views on the linear region), referring to Fig.3.17 and Fig.3.18. The structure parameters described here in the study could explain the nonlinear tensile mechanical behaviour. A widely accepted view is due to the deformation of each cell wall caused by the reorganization and alignment of the cellulose microfibrils along the tensile axis direction of the flax fibre. It was noted that there is a decrease in the mechanical properties (tensile rigidity and strength) of flax fibre and an increase in fibre diameter. One reason could be the size change of the lumen; another reason could be that defective secondary walls do not have as many defects as when they are okay.

Manufacturing Process Of Flax

Since extraction and manufacturing play a significant role in generating varied mechanical properties for Flax, this section will focus on flax processing, which can provide a comprehensive study of how the desired reinforcement is obtained.

Plant fibres are classified based on their extraction regions from the plant, such as leaf fibres, seed fibres, stem fibres, and various other types (including grasses, reeds, roots, wood fibres, etc.). Flax fibre, for instance, is derived from the plant's stem and undergoes additional reinforcement processes. These processes include retting, scutching, hacking, and folding, varying according to the desired end reinforcement product. A schematic representation of flax fibre processing is provided in fig.3.19.

In the normal way, flax fibre bundles have been obtained by a retting process, which consists of the biological action of bacteria in an aqueous medium where some waxes and pectins are removed[8]. Then, the mechanical processes are implemented, including scutching and hacking. Scutching is the process consisting of extracting fibre bundles contained in the stems. The hacking process makes phloem fibre bundles into the technical fibres, which contain several dozen elementary flax fibres in an increasing fine status. Folding/drawing of the flax reinforcement allows coalescing fibres into greater lengths to obtain ribbons or tapes several meters long. At the same time, the variability of reinforcement decreases and the flax colour homogenizes itself. In the spinning process by flax spinning mills, the ribbons undergo successive torsions and stretches by which the flax ribbons are transformed, and the desired yarn titration or woven reinforcement can be obtained. Experienced more or less process steps, flax fibre reinforcements with different forms (mat, sew, UD) can be acquired fig.3.20

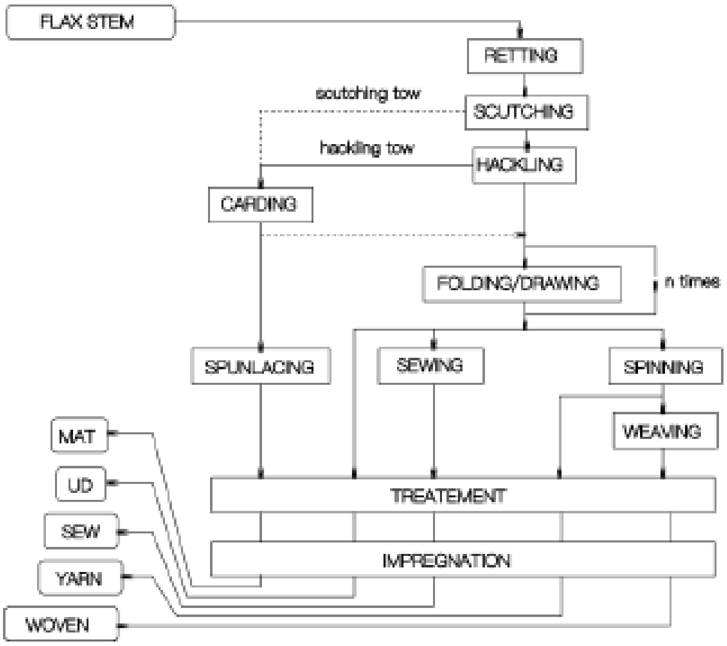


Figure 3.19: Production processes of technical flax fibres as reinforcement [16]

Non-Crimp Unidirectional plant fibre composite Fibres can be added to the composites in the form of randomly dispersed fibres or forming textile structures. Two types of composites are defined based on the form of fibre reinforcement- Fibre Reinforced Composites (FRC) with non-entangled fibres and Textile Reinforced Composites (TRC) with fibres forming structures. FRC contains micro or nano fibres, while TRC contains textile structures. The textile structures can be woven or nonwoven fabrics, knitted, multiaxial, or braided structures. The reinforcing capability depends on the amount, type of fibre, its geometry, adhesion to the matrix, and structure [91]

The traditional method of producing composite parts with high specific stiffness and strength uses prepreg tapes. However, the use of prepreg has been limited to high-tech applications due to the high cost of the material and processing. In today's world, where cost is a significant concern, even in the aircraft and aerospace industry, there is an increasing interest in developing cheaper materials and manufacturing techniques for high-tech applications. An alternative method for manufacturing composites with continuous fibres has been developed in composite materials. This method involves setting the reinforcement orientation during the textile manufacturing stage by stitching several layers of unidirectional plies of fibres. These fabrics are commonly known as Non-Crimp Fabrics (NCF), and they offer better mechanical prop-

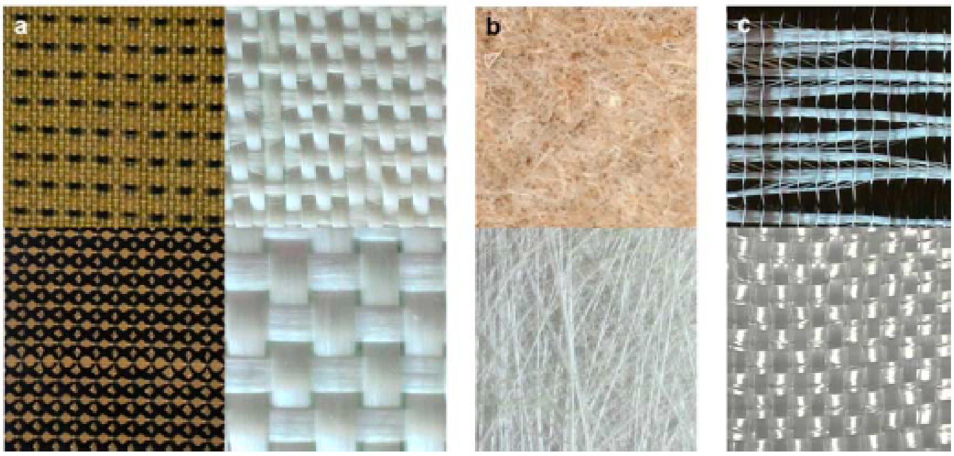


Figure 3.20: Typical structures of fibre reinforcements: a) woven fabrics with several structures; b) nonwoven fabrics (mats); c) non-crimp fabrics

erties than woven fabrics due to the primarily straight orientation of their fibres. The lay-up of NCF reinforcements is much quicker than the lay-up of prepreg tapes, as several layers of unidirectional fibres can be assembled at the fabric manufacturing stage. NCF fabrics can be manufactured using almost any reinforcing fibre, and their mechanical properties depend on the type, amount, and orientation of the fibre used. Tailoring the fibre architecture allows for optimized performance, resulting in weight and cost savings. However, to be suitable for high-tech applications, NCF composites must exhibit high quality with low variation in properties. Hence, more knowledge is required about their mechanical properties. Different types of fibres exhibit varying bundle sizes, stitch parameters, and mechanical properties. Therefore, arranging fibres to facilitate their handling is essential for most applications. In polymeric composite terms, a fabric is a manufactured assembly of long fibres that form a flat sheet with one or more layers of fibres. The layers are held together either by mechanical interlocking of the fibres themselves or by a secondary material that binds them together and holds them in place. In the case of secondary materials, some manufacturers use adhesives, while others use stitching, which maintains the drapeability of the fabric. Stitched fabrics can be made using glass, carbon, or aramid fibres, among others, and they can be oriented in different ways to create various fabrics, each with unique characteristics. There has been a growing interest in using multiaxial fabrics to design composite components in recent years. Stitch fabrics produced by ”advanced warp knitting technology” are often called Directionally Orientated Structure Fabrics (DOS Fabrics) or Non-Crimp Fabrics (NCF) because there is no crimp on the inserting yarns, resulting in better-aligned fibres and improved mechanical properties. Unidirectional fabrics offer oriented strengths, which is often preferred in high-performance applications. However, multiple orientations are sometimes beneficial to obtain a quasi-isotropic reinforcement. raditional textile architectures—woven, knitted, or braided preform structures are used in composites [91] and it was found that the optimum mechanical strength could not be achieved in these preform-based composites due to the crimp, which is usually generated at the interlacement of warp/weft yarns during the fabrication processes of textile preforms. Therefore, designing the fibre placement technique to remove any crimp is becoming a significant concern for achieving optimal mechanical performance in composites. Plenty of works reported in the literature are related to the development of natural-based continuous or unidirectional dry-fibre preforms for avoiding yarn interlacement or crimps for composite application.

Fabric Construction Stitched fabrics, also known as non-woven, non-crimped, or knitted fabrics, have excellent and repeatable mechanical properties that are predictable because of the fibre architecture. Stitched fabrics are produced by putting together layers of aligned fibres, Typically, the fibre orientations are 0° (warp), 90° (weft or fill), and ±45° (bias). Other orientations can be manufactured on order, but they are not especially common as they necessitate significant machine changes.

Advantages Advantages of NCF The two critical improvements with stitched multiaxial fabrics compared to woven fabrics are: (i) Better mechanical properties, primarily because the fibres are always straight and non-crimped. In the case of woven fabrics, the fibres embedded in resin will straighten during loading/impact, which causes resin cracks. When the load is transmitted along the many kinks in woven roving, a stress concentration occurs due to the shearing between fibre and resin. If repeated loading and unloading takes place, this will cause a more rapid breakdown of the laminate (fatigue). Furthermore, in the case of NCF, more orientations of fibres are available from the increased number of layers of fabric. (ii) Improved component build-up speed because fabrics can be made thicker and with multiple fibre orientations, so fewer layers are needed. The properties of non-crimp fabric-based composites are determined by: i) Fibre properties. The mechanical properties of most fibre-reinforced resins are considerably higher than those of unreinforced resins. The mechanical properties of fibre/resin composites are, therefore, dominated by the contribution of the fibre to the composite.

This chapter provides an overview of plant fibre composites, explicitly focusing on flax fibre and its composites. Compared to artificial fibres like carbon and glass fibre, plant fibres offer several advantages for composites, such as high specific ultimate stress and stiffness, renewability, and environmental friendliness. However, plant fibres are also sensitive to moisture. Flax fibre, a member of the plant fibre family, exhibits superior mechanical properties compared to other plant fibres and even some alloys like magnesium and aluminium. It can be used as reinforcement in various resin systems and has been utilized in many consumer products.

This study employs unidirectional flax non-crimp fibre to create a biocomposite. The focus is on the mechanical properties and sorption behaviour of unidirectional flax fibre composite, which performs better in tensile properties along the fibre orientation than textile flax fibre composite. The chapter reviewed the characteristics of plant fibre composite, specifically flax fibre and its composites, highlighting their advantages and disadvantages. While plant fibres offer many benefits, they are also sensitive to moisture. Flax fibre, with an ultimate stress of over 1000 MPa, exhibits superior mechanical properties compared to other plant fibres and some alloys. It has been utilized in many consumer products and can be used as reinforcement in various resin systems.

This chapter comprehensively reviews the properties and potential applications of flax fibre composite, particularly unidirectional flax fibre composite. The study highlights the superior mechanical properties of flax fibre and its potential as a sustainable and environmentally friendly alternative to artificial fibres.

3.4 Biopolymers as matrix in biocomposites

Biopolymers play a crucial role in forming matrices for biocomposites and are highly beneficial due to their biodegradability, biocompatibility, air permeability, and low-temperature sealability. These properties make them ideal for semi-structural applications. The increasing demand for natural polymers among consumers, industry, and governments has led researchers to focus on alternative materials derived from annually renewable agricultural and biomass feedstocks. These materials, such as chitin, cellulose, and lignin, are sourced from renewable origins, which makes them environmentally friendly and sustainable. In light of the current emphasis on reducing environmental impact, there is a growing interest in renewable resources and new technologies for developing sustainable materials.

Although biopolymers are considered a promising alternative to conventional polymers due to their potential for end-of-life disposal, their cost and availability are crucial factors for widespread adoption. The production capacity of biopolymers has been steadily increasing over the past decade, as seen in figure 3.21, which shows a positive trend in the biopolymer production capacity forecast for 2016.

Despite the increase in production capacity, the current capacity of biopolymers still needs to be higher than that of conventional plastics. Nevertheless, the demand for bio-based polymers is high in Europe[2]. To promote the widespread use of biopolymers as a replacement for conventional polymers, it is necessary to increase their production capacity while maintaining similar properties and competitive prices.

In conclusion, the growth in biopolymer production capacity and the rising demand for environmentally friendly materials indicate that biopolymers in green composites will continue to expand in various industries.

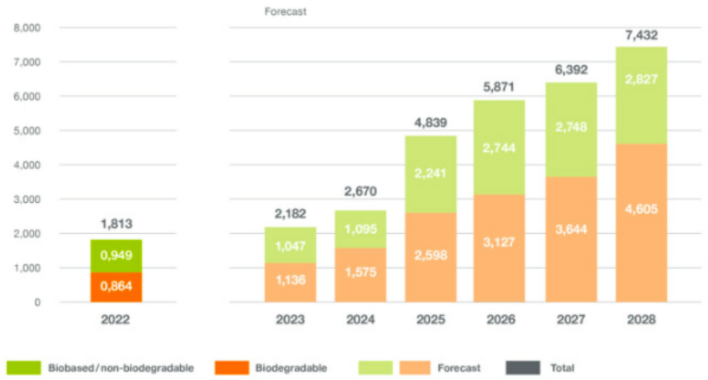


Figure 3.21: Global production capacities of bioplastic,[107]

The increase in the price of fossil fuels, particularly oil, climate change concerns, and growing eco-consciousness among consumers are driving factors for expanding biopolymer usage. These factors significantly influence the price of biopolymers, which has been decreasing, and continuous advancements in research and innovation may further accelerate this trend.

The production rates for starch blends, polylactic acid (PLA), and polyhydroxyalkanoates (PHAs) are expected to increase in the next five years. In recent decades, various starches, such as soy protein, corn starch, wheat starch, tapioca starch, and potato starch, have been used to produce green resins for composites[183][74]. These starches are abundant in nature and biodegradable, making them suitable substitutes for petroleum-based polymeric resins. However, these biopolymers have lower mechanical properties, hydrophilicity, and lower thermal stability than conventional polymers.

Commonly used methods to overcome the disadvantages of biodegradable polymers include blending them with other polymers and reinforcing them with fillers or fibres, which can improve their mechanical and thermal properties, processability, and humidity resistance.[214](Vroman and Langan, 2009; Luckachan and Pillai, 2011)

The term ”biopolymer” comprises a range of materials of a bio-based origin and/or biodegradable nature. All the polymers that fulfil at least one of these two principles are considered biopolymers, thus leading to three main groups:

- Petrochemical-based biodegradable polymers: such as polybutylene adipate-co-terephthalate (PBAT) or polycaprolactone (PCL).
- Bio-based non-biodegradable polymers: such as bio-based polyethylene (bioPE), bio-based polyethylene terephthalate (bioPET) or bio-based polyamides (bioPA).
- Bio-based biodegradable polymers: such as polyhydroxyalkanoates (PHAs), polylactic acid (PLA) or polybutylene succinate (PBS). Considering that the cellulosic fibres are biodegradable, using these fibres combined with a biodegradable matrix leads to an exciting solution since it is possible to obtain completely biodegradable materials.

In general, composite materials are difficult to recycle because of the heterogeneity of their components and the difficulties in matrix/reinforcement separation. Therefore, producing biodegradable composites simplifies the product's final disposal at the end of its life since compostability is a more economical and viable option.

3.4.1 Biopolymers classification

As can be seen in figure 3.22, bio-based polymers can be divided into three main categories based on their origin and production.

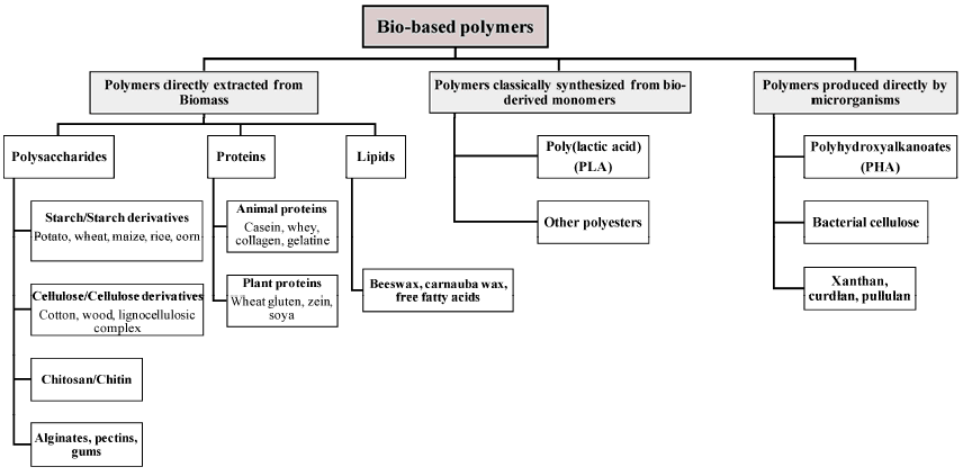


Figure 3.22: Schematic overview of bio-based polymers[148]

- Natural: directly extracted/removed from biomass, such as polysaccharides (starch, alginate, and cellulose) and proteins (casein and gluten).

- Synthetic: produced by classical chemical synthesis using renewable bio-based monomers, such as PLA.
- Microbial-fermented: produced by microorganisms or genetically modified bacteria, such as PHAs.

3.4.2 Alginate: From Seaweed to bioplastics/Resins

In response to the escalating environmental concerns associated with synthetic plastics, the exploration of biodegradable polymers has gained significant momentum. Seaweeds, categorised as marine macroalgae, present a promising alternative source for the production of bioplastics. Their unique attributes, including higher biomass, rapid reproduction, adaptability to various environments, and cost-effectiveness, place them as an ideal polysaccharide source for creating environmentally friendly, high-quality bioplastics.

As multicellular photosynthetic organisms found in diverse aquatic environments, seaweeds offer a renewable biomass resource. The sugars within seaweeds, constituting polymers containing carbon, serve as a foundation for developing biodegradable and non-toxic bioplastics. They are divided into three main groups according to their colour, which is produced by the presence of pigments. Beyond their potential in bioplastics, seaweeds find applications in various industries, such as fertiliser production, aquaculture feed, biofuels, and wastewater treatment[190],[26],[79]]. Additionally, they contribute to the development of innovative and ecologically sound materials, offering sustainable alternatives to traditional plastics[95],[194],[144].

The interest in seaweed-derived materials intensifies due to their inherent biodegradability and additional antimicrobial properties. Seaweeds produce antimicrobial compounds, including phenols, fatty acids, carbohydrates, proteins, and minor compounds, as part of their antibiotic defence mechanisms. Among the three main seaweed-derived hydrocolloids, alginate, agar, and carrageenan alginate stand out for their unique physical, optical, mechanical, thermal, antioxidant, and antibacterial characteristics.

Advancements in seaweed-based research have opened up opportunities for commercialising bioplastics made from alginate. This approach offers several advantages, including avoiding competition for land and resources dedicated to traditional crops and the potential to mitigate deforestation concerns, given that seaweed cultivation can happen in outdoor or laboratory settings. Large-scale seaweed production also helps to reduce costs, making these bioplastics an even more sustainable solution.

The journey from seaweed to alginate-based bioplastics is a groundbreaking step in developing eco-friendly, cost-effective, and non-toxic alternatives to traditional plastics. The many properties of seaweed-derived materials make them a vital contributor to a sustainable future, addressing both environmental and economic challenges associated with plastic waste.

Source, Structure and Extraction Process

Alginates, which are polysaccharides, are naturally present in the cell walls of seaweeds. Given the abundant availability of seaweeds, alginates present a promising alternative to the dwindling petroleum resources traditionally used in polymer production. Alginate, an alginic acid derivative, is an anionic polymer found in brown algae (Phaeophyceae), especially in their cell walls. The commercial extraction of alginates is carried out from various brown seaweed species, including Laminaria hyperborea, Laminaria Digitata, Macrocystis pyrifera, Ascophyllum nodosum, Ecklonia maxima, Saccharina japonica, Lessonia nigrescens, Durvillea Antarctica, and Sargassum spp[62]. Approximately 23,000 tons of alginate are produced annually from around 85,000 tons of algae, with significant contributions from commercially valuable species [22]. Commercial brown seaweeds, including Laminaria, Ecklonia, Macrocystis, and Sargassum, are particularly rich sources of valuable sodium alginate. This polysaccharide, characterized by its water-solubility, is isolated from brown algal species.

Alginate, a water-soluble polysaccharide, is derived from brown algae with alginic acid as its primary constituent. Its sodium form, Sodium alginate (SA), is a polymer rich in hydroxyl and carboxyl groups on its backbone. This anionic polysaccharide comprises two types of 1,4-linked hexuronic acid units: b-d-mannuronopyranosyl (M) and a-l-guluronopyranosyl (G) residues. These units are organized into specific blocks: blocks of M residues (MM blocks), blocks of G residues (GG blocks), and mixed blocks containing both M and G residues (MG blocks)[76][111][192].

It has the chemical formula (C6H7NaO6)n and an average molecular weight of 216.121 g/mol[207]. By a partial hydrolysis reaction in an acidic medium, the alginate molecule can be cleaved into three successive fractions: manuronic (MMMMM), glucuronic (GGGGG) and a mixture of manuronic fractions with glucuronics (MGMGMG), as shown in figure 3.23 and 3.24[100][146].

Alginates' physical and chemical properties depend on how each monomer is placed in the chain and their molecular weight. In addition to the aforementioned features, the length of the uronic acid chain and the percentage of each monomer (meaning guluronic and mannuronic acids) are also important. These factors cause significant structural differences as well as specific physico-chemical properties. The abundance, composition and M/G ratio of alginate can vary not only by plant species and algae age but also by natural alginate source, plant location, geographical location, and season. These factors affect the functional properties of alginate, such as solubility,

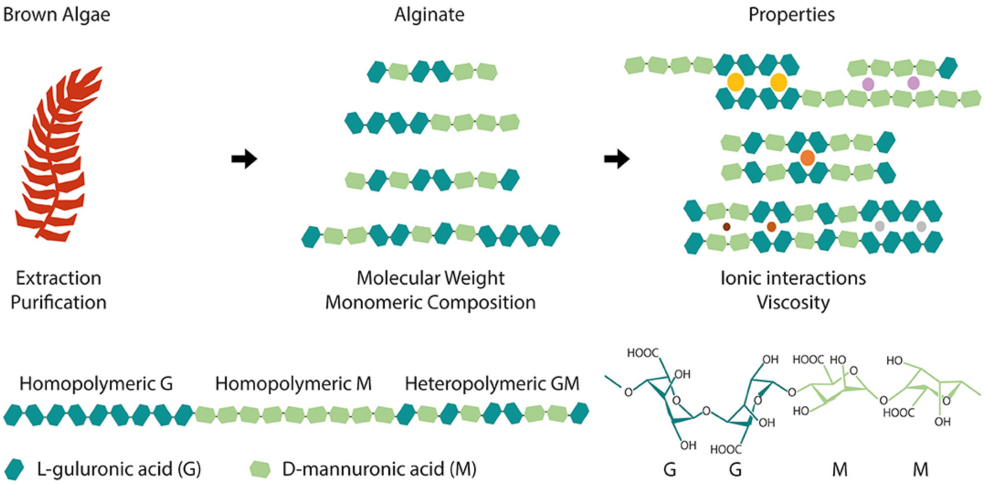


Figure 3.23: Alginate is extracted and purified from a wide variety of brown algae, and it is composed of α-L-guluronic acid (G) and β -D-mannuronic acid (M) blocks. These differences impact its material properties, such as affinity towards ions and viscosity, which ultimately influence its development and potential applications

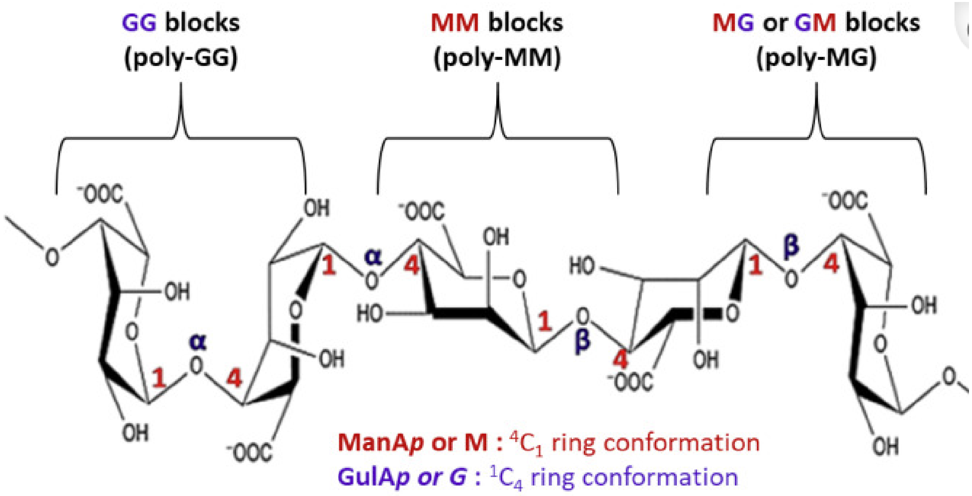


Figure 3.24: Schematic overview of bio-based polymers[209]

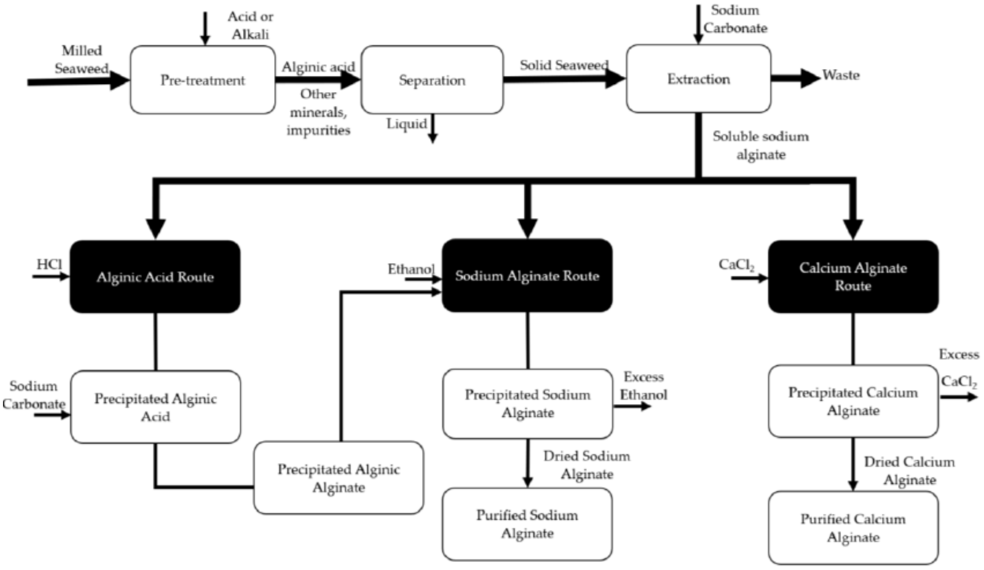


Figure 3.25: Schematic overview of alginate production routes

reaction with metal ions, viscosity, and gel-forming properties.[68],[63][4]. As we know by now, alginates are biodegradable, biocompatible, and nontoxic. Their most important property is related to their viscosifying, stabilizing and gelling properties and their ability to retain water. Owing to these properties, they have a broad range of applications. Thus, it is of technological interest to understand the mechanism of how alginate affects the overall dynamics of soft matter samples. Such insights are also interesting from a fundamental point of view. Already in relatively small amounts, alginate dramatically affects the rheology of aqueous solutions. Their properties and biodegradability, as well as their origin in a renewable source and their no-dependence on oil, make these polymers interesting for a wide range of applications. The current and potential uses of alginates have been reviewed for packaging, film formation, bags, paper-coating, and biomedical uses such as drug delivery, among others.

The extraction of alginate from brown algae involves a multi-stage process. Firstly, seaweed biomass is washed, dried, and milled into powder. Subsequently, the biomass undergoes rehydration in water with the addition of chemicals to remove unwanted compounds. Acid or alkali pre-treatment is applied to break the plant cell wall, followed by sodium carbonate extraction to obtain water-soluble alginate from the seaweed biomass matrix. The extracted alginate is then filtered and purified to produce water-soluble sodium alginate powder [157]. Figure 3.25 shows a simplified schematic diagram of conventional alginate production routes.

Alginate is present in the cell walls of brown algae as the calcium, magnesium and sodium salts of alginic acid. The extraction process aims to obtain dry, powdered sodium alginate. The calcium and magnesium salts do not dissolve in water; the sodium salt does. The rationale behind alginate extraction from the seaweed is to convert all the alginate salts to sodium salt, dissolve this in water, and remove the seaweed residue by filtration. The alginate must then be recovered from the aqueous solution. The solution is very dilute, and evaporating the water could be more economical. There are three precipitation routes to recover alginate from the solution, namely the sodium alginate route, calcium alginate route and alginic acid route, with the final product usually isolated in the form of sodium alginate. The sodium alginate route is a very widely used process, in which an organic solvent, mainly ethanol is added to the sodium alginate solution to reduce the alginate solubility and therefore precipitate sodium alginate. The fibre-like solid form of sodium alginate is then separated from the solution via. filtration or centrifugation. Research showed that the sodium alginate route not only had the simplest steps but also resulted in the highest yield with good overall rheological properties. The other route is to add acid, which causes alginic acid to form; this does not dissolve in water and the solid alginic acid is separated from the water. The alginic acid separates as a soft gel and some of the water must be removed from this. After this has been done, alcohol is added to the alginic acid, followed by sodium carbonate which converts the alginic acid into sodium alginate. The sodium alginate does not dissolve in the mixture of alcohol and water, so it can be separated from the mixture, dried and milled to an appropriate particle size that depends on its particular application. In both, calcium alginate and alginic acid routes, the separated solid form of alginate is commonly converted to sodium alginate solution again by reacting with sodium carbonate and subsequently is precipitated by organic solvent, e.g., ethanol. The main objective of applying the calcium alginate or alginic acid route is to reduce the usage of organic solvents by introducing alternative purification pathways. In alternative purification pathways, organic solvent can be used only once in the final purification step, while the sodium alginate route normally uses organic solvent twice; in the initial precipitation and final purification step, The calcium route led to a product with the lowest molecular weight and poor mechanical properties. It is explained that the degradation of the ether bond by HCl (which is used in both the calcium alginate and alginic acid routes) was responsible for the low molecular weight and weak mechanical properties.

The second way to recover sodium alginate from the initial extraction solution is to add a calcium salt. This causes calcium alginate to form with a fibrous texture; it does not dissolve in water and can be separated from it. The separated calcium alginate is suspended in water, and acid is added to convert it into alginic acid. This fibrous alginic acid is easily separated and placed in a planetary-type mixer with alcohol, and sodium carbonate is gradually added to the paste until all the alginic acid is converted to sodium alginate. The sodium alginate paste is sometimes extruded into pellets that are dried and milled.

The processes mentioned above are very straightforward; certainly, the chemistry is simple: convert the insoluble alginate salts in the seaweed into soluble sodium alginate; precipitate either alginic acid or calcium alginate from the extract solution of sodium alginate; convert either of these back to sodium alginate, this time in a mixture of alcohol and water, in which the sodium salt does not dissolve.[157]

The physical properties of Sodium Alginate are as follows: The solubility of sodium alginate in cold water is slow, and it results in a viscous solution. It cannot dissolve in alcohol, hydroalcoholic solutions with alcohol content above 30%, chloroform, and ether. Its solubility depends on various factors, such as pH, molecular weight, ionic strength, the nature of the ions present in the structure, and concentration. The pKa value of guluronic acid is 3.6, while that of manuronic acid is 3.3. On the other hand, calcium alginate is insoluble in water and organic solvents but is soluble in sodium citrate.

Sodium alginate is compatible with most anionic substances and a few cationic substances. It has better stability against external factors in the form of a dry powder than a solution. Sodium alginate gradually forms an alginic acid gel with acids at low pH values. At elevated pH values, alginic acid dissolves and restores its original viscosity[19]. In an alkaline environment, sodium alginate can tolerate short periods. However, pH values higher than 11 reduce its viscosity. Sodium alginate can withstand high temperatures in the short term, making it sterilizable. However, in the long term, the high temperature in sterilization can reduce the degree of viscosity.[73][165]

The viscosifying capacity of alginate depends on the molecular weight and concentration of the polymer. Gelling (affinity for cations) depends on the amount of glucuronic acid in the structure. Therefore, the higher the amount of glucuronic acid present in the structure, the more the solubility of alginate in water and the gelling capacity increases. This results in a more resistant, viscous, strong, and stable gel. According to studies, sodium alginate solutions are not Newtonian fluids but pseudoplastic fluids whose viscosity changes drastically when dissolved in water and diluted with water. The viscosity of alginate is dependent on temperature. Alginate films' thermal and viscoelastic properties can be studied using differential scanning calorimetry (DSC). Studies on various thermosensitive alginate gels obtained in the temperature range between 0 and 100°C showed low rigidity at high temperatures. The noncovalent bond between the adjacent polymeric groups kept the alginate intact under oscillatory deformation conditions at temperatures below 100°C. However, this equilibrium was interrupted by constant magnetic stirring.

Commercially used sodium alginate has varying degrees of viscosity. The resulting 1% aqueous solutions have viscosities that can range from 20 to 400 cP (centipoise) and 0.02–0.4 Pa.s (pascals second) at 20°C [68],[154],[44].

Functionality and Physico-Chemical Modification of Alginates

Alginates are copolymers made up of β -d-mannuronic acid (monomer M) and α -l-guluronic acid (monomer G) residues. They are linear and unbranched. These two acid residues (saccharide unit) present stereochemically differences at C-5. Alginate presents several free hydroxyl and carboxyl groups distributed along the backbone, which allow reactions and chemical functionalization. The alginate polymer accepts different conformations of M and G saccharides in its chain. The chain can be composed of homopolymeric regions of β -d-mannuronic acid residues (M-blocks:MMMMMM), homopolymeric regions of β -d-mannuronic acid residues (G-blocks: GGGGGG), and heteropolymeric regions where G and M exist in alternating sequence (MG-block:MGMGMG). Figure3.26 represents both M and G monomers and the chain conformation of alginate.

Alginate contains all four possible glycosidic linkages within the alginate molecule: diequaorial linkages connect mannuronic acid residues in M-blocks, diaxial linkages connectguluronic acid residues in G-blocks, and equatorial-axial (MG) and axial-equatorial (GM)glycosidic bonds connect both uronic residues in MG blocks. Due to these linkages, the M-bock is a relatively straight polymer, such as a flat ribbon, while the G-block presents a buckled arrangement. Figure 3.26 reports the conformation of linkages and chain alginate. The diaxial linkage in G-blocks results in a significantly hindered rotation around the glycosidic linkage, which, combined with the polyelectrolyte nature of the alginate molecule, may account for its stiff and extended nature. G-blocks are stiffer than alternating blocks, which, in turn, are more soluble at low pH. In the uronic blocks, the rigidity decreases along the series $GG >$MM$> MG$. Electrostatic repulsion caused by charged groups on the polymer chain increases chain extension and intrinsic viscosity. The most crucial feature of alginate properties is its ability to form hydrogels with divalent cations. The alginate chelation with multivalent cation is the basis for gel formation. Selective binding of earth metal ions increases significantly with the increase of G content in the alginate backbone chain.[57].

The G blocks can form gels by complexing with divalent cations forming tightly held junctions, and their structure varies depending on the monomer position in the chain, forming either homopolymeric (MM or GG) or heteropolymeric (MG or GM) blocks. The divalent cations, such as Ca2+, Cu2+, Zn2+ or trivalent metal cations, such as Fe3+, Al3+, Cr3+, Cu2+, Ba2+, Sr2+, Ca2+, et al. act as crosslinks between the functional groups of alginate chain, “zipping” the G-blocks in alginate chain, that is, the G-block of one poly-

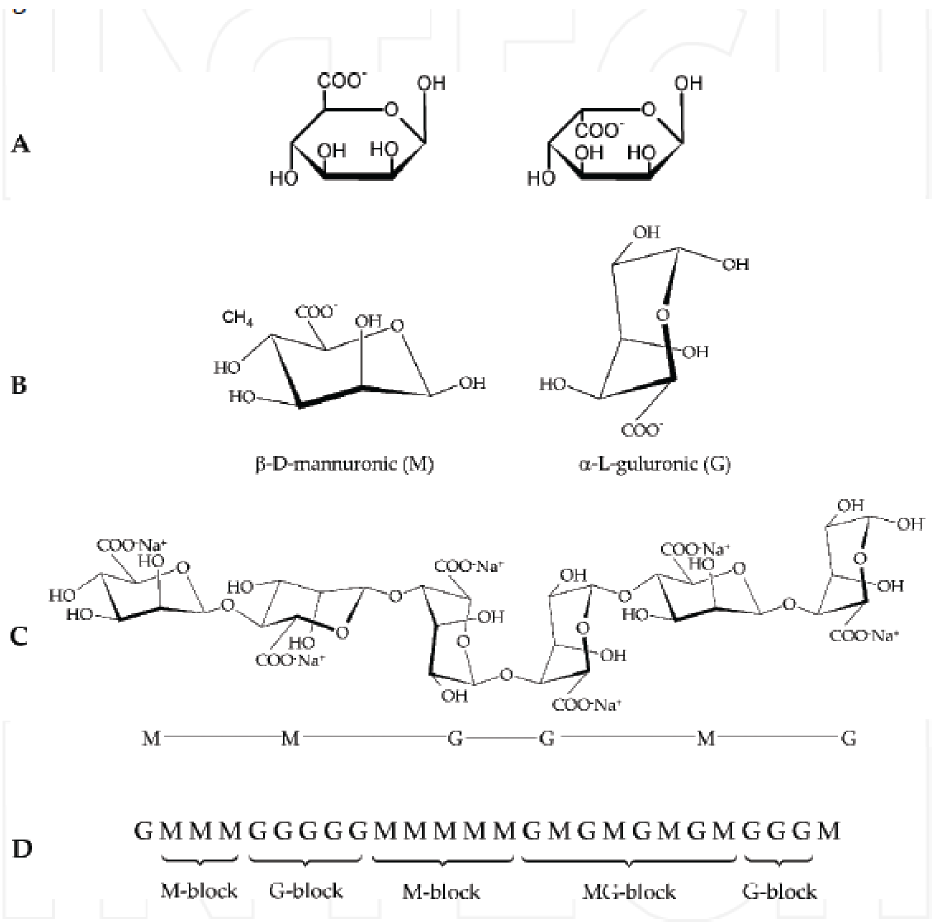


Figure 3.26: Chemical Structure of Sodium Alginate

mer forms junctions with the G-block of adjacent polymer chain through interactions with the carboxylic groups in the sugars, which leads to the formation of a thermo irreversible gel network[41]. Because of the structural form of the G-block, the metal chelation-binding chain is called the eggbox crosslinking model. Figure 3.27 shows the eggbox model for alginate gel formation. The gelation mechanism is the coordination between the carboxyl groups of alginate and the metal ions. Currently, because of the cost and no toxicity, Ca2+ is the most used ion to produce alginate gel.

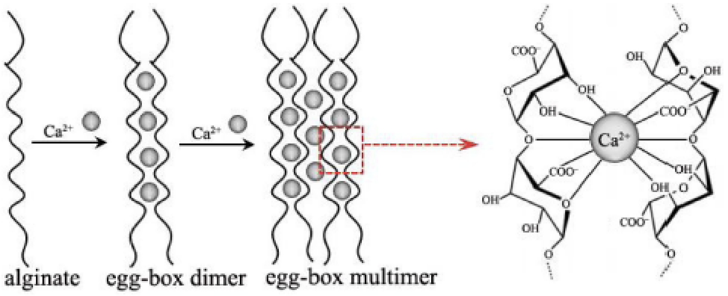


Figure 3.28: Egg box of Alginate gels

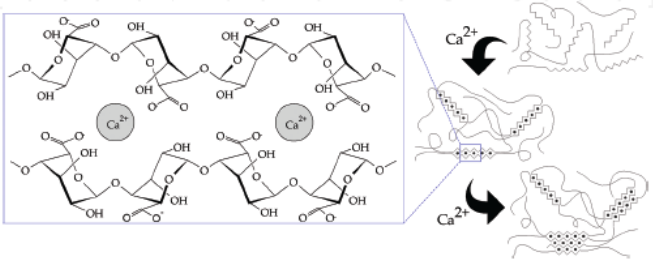


Figure 3.27: Chemical Structure of Calcium Alginate

Different types of physical or chemical modifications are used to synthesize alginate-based materials, which have various applications in the plastic industry, paper-making, food industry, drug delivery, hydrogels or making materials for the adsorption of heavy metals.[202],[152]

The sodium alginate gel is soft and soluble in alkaline solutions and cold water, forming viscous and colloidal solutions, but is insoluble in alcohol, hydroalcoholic solutions, organic solvents, viz. ether, and in acids. However, the crosslinked gel-calcium alginate is practically insoluble in water and organic solvents. If Ca2+ ions can be removed, a Ca2+ crosslinked alginate gel can be degraded. The diverse modifications and unique properties of alginates position them as versatile biomaterials with applications spanning from biomedical uses to environmental remediation, offering innovative solutions across various industries.[133],[55].

Commercial alginate-based bioplastics consist of thermoplastic blends or crosslinks with various divalent ions to overcome hydrophilicity and low thermal and mechanical properties. Various attempts have been made to overcome these problems, such as their weak mechanical properties, high hydrophilicity, etc. However, several limitations restrict the application of alginate. Hence, a trend exists to develop "value-added" alginates by per-

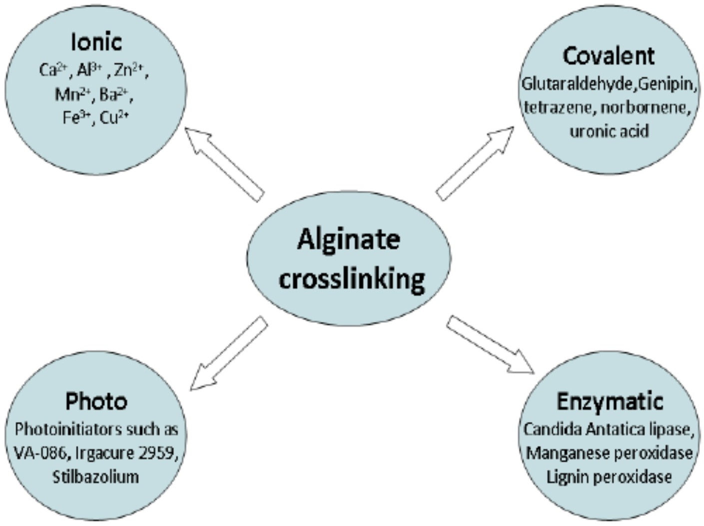


Figure 3.29: Method of Crosslinking Alginate

forming derivatization reactions on the polysaccharide's backbone. Since plenty of free hydroxyl and carbonyl groups spread all along the polymer backbone, alginate provides a good opportunity for various chemical modifications. Modification of alginate can be performed using various approaches such as chemical bonding with synthetic biopolymers, coating the surfaces of alginate with micro-or nanospheres made from biocompatible artificial polymers, crosslinking with physical or chemical reagents, hydrophobization, a variation of guluronic/mannuronic ratio, etc. Further, chemical methods can be combined with biochemical techniques if required. This, in turn, allows for altering alginate properties such as solubility, affinity for specific proteins, hydrophobicity, etc. Solubility and reactivity are the key parameters to consider before choosing any modification. Alginates can dissolve in aqueous, organic or mixed organic solvents.

Further, modification of alginates depends not only on the solvent but also on the location of the carbon and substituent groups. The two secondary OH positions (C2 and C3) or the COOH C6 position can be modified. In addition, the reactivity of the alginates is reliant on the type of functional groups and very selective to the type of chemical modification. Variation in reactivity between the functional groups can be an advantage in altering alginate selectively for specific applications. Among alginate's various chemical/physical modifications, crosslinking has been widely used due to its flexibility, ability to achieve desired properties, convenience, and relatively low cost. Fig 3.29 shows the various methods of crosslinking alginate and examples of reagents used.

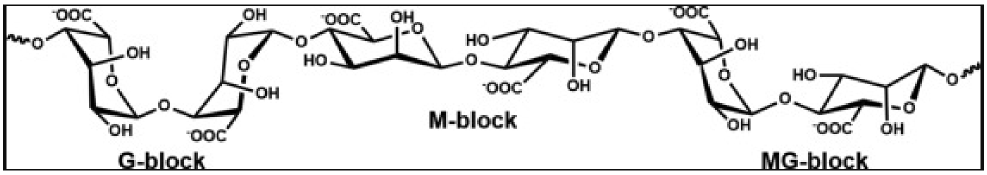


Figure 3.30: Chemical Structure of Sodium Alginate

Processability and degradation of Alginates Sodium alginate, as previously discussed, possesses the unique ability to form water-resistant gels when exposed to multivalent ions through a cross-linking mechanism. This capacity for gel formation, coupled with the nearly temperature-independent sol/gel transition in the presence of multivalent cations, renders alginate an ideal candidate for creating biomaterials with significant industrial applications. Structurally, alginate is made up of mannuronic acid residue blocks (M-blocks), guluronic acid residue blocks (G-blocks), and alternating M and G residue blocks (MG-blocks)[117].3.30

The ratio M/G is important because the properties of alginate solution, gels, and its produced biomaterials depend on the G and M contents. Depending on the alginate material that must be developed, this is critical in choosing the raw alginate source.

Physical and mechanical properties of alginates and the formation of gels depend on the relative proportion of these blocks, in which higher concentration of alginate promotes better strength.Gels prepared from alginate with a high content of G residues (high M/G ratio) exhibit higher stiffness than those with a low amount of G residues. The quantity of Ca2+ ions present in the system interferes in the stability of these polymeric nets, forming permanent or temporary inter-chain associations. Studies are showing that the chemical structure and the size of the alginate molecule, as well as the gel formation kinetic connected to the type of ion used are determining factors on its properties, such as swellability, porosity, biodegradability, biocompatibility, gel resistance and its immunological characteristics.

Concerning alginate particles, the preparation method of calcium alginate particles also interferes with their physical properties, such as porosity, volume of water, sphericity, and elasticity. Methods such as atomization, emulsification, and dripping are also employed. Calcium cross-linking of alginates can be performed by mainly two methods: diffusion method and internal setting method. In the "diffusion" method, the ions diffuse into the alginate solution from an outside reservoir. In the "internal setting" method, the ion source is located within the alginate solution and a controlled trigger (typically pH or solubility of the ion source) sets off the release of cross-linking ions into the solution. The diffusion method yields gels having a Ca2+ ion concentration gradient across the thickness, while the internal setting gives gels with uniform ion concentrations throughout. The gelation rate is an important factor that affects the uniformity and strength of hydrogels. Lower rates can be achieved by temperature control (lower temperature implies slower ionic cross-linking), alginate composition (high G content implies higher stiffness), pH control, and Ca2+ concentration of calcium solution source. Calcium chloride ($CaCl_2$) is one of the most frequently used agents for ionically cross-linking alginate. However, it typically leads to rapid and poorly controlled gelation due to its high solubility in aqueous solutions [117]. The fast gelation rate with $CaCl_2$ results in varying crosslinking densities and a polymer concentration gradient within the gel bead. By contrast, the use of $CaCO_3$ and $CaSO_4$, at the internal setting method, which has very low solubility in pure water, allows its uniform distribution in alginate solution before gelation occurs. The journey to alginate-based bioplastics addresses environmental challenges and offers versatile applications, from packaging to biomedical uses. The following sections study the optimization of extraction exploration of greener technologies, which is crucial for sustainable production. As we harness the diverse properties of seaweed-derived materials, we pave the way for a more sustainable future, reducing the environmental impact of traditional plastics.

3.5 Critical factors for biocomposite production

The previous chapter provided an overview of various natural fibres and biopolymer materials suitable for biocomposite manufacturing. While comprehensive reviews of biocomposite technologies that use these materials are available [114],[28],[124]], a complete examination of all research in the biocomposites field is outside the scope of this work. However, a summary of more significant studies in this area is presented in Table3.4.

Polymers	Bast Plant fibres				
	Hemp	Flax	Jute	Ramie	Kenaf
Soy protein/oil	[140]	[106]	xx	[48]	[14]
Poly-lactic acid	xx	xx	xx	[113]	[61]
Starch	[24]	[24]	[189]	[24]	[212]
Cellulose	[13]	[74]	xx	[24]	xx
Plant oil	[200]	xx	xx	xx	[86]
PHA	[37]	[46]	[24]	[46]	[24]
Polypropylene	[9]	[121]	[82]	xx	[27]
Polyethylene	[172]	xx	xx	xx	xx
Nylon	[174]	xx	xx	xx	xx
Polyester	[83]	[72]	[205]	xx	[90]
Epoxy	[178]	[83]	xx	xx	xx

Table 3.4: Table of published natural fibre-reinforced composites

This work will primarily concentrate on studies involving bast fibre reinforcements and biopolymers derived from renewable resources as composite components. These selections are due to their strong mechanical properties and minimal environmental impact. Essential factors contributing to enhanced composite performance, including specialized processing methods and fibre surface treatments to improve fibre/matrix adhesion, will also be examined. A summary of current and prospective future uses of biocomposites will also be provided.

Exploring the production of biocomposites using natural fibres and biopolymer resin presents some critical factors. As reviewed by Pickering et al. [135], fibre and matrix selection, interfacial strength, fibre dispersion and orientation, porosity and manufacturing processes have a great influence on the mechanical properties obtained. These critical factors, among others, are here briefly reviewed:

Fibre and matrix selection

Multiple variables can be considered for the fibre selection, despite the probably most relevant are: availability, cost, mechanical properties, length and quality. Given their influence on the fibre's properties, chemical composition, harvesting time, extraction methods, treatment, or growing and storage conditions are relevant parameters to be taken into account in the fibre selection. In this sense, differences around 15-20% in fibre strength due to optimal harvesting time or manual extraction methods have been reported in the literature, as reviewed in [135]. For optimal mechanical performance, fibres with high cellulose contents and microfibrils aligned in multiple directions are preferred, as is the case of bast fibres. Also low moisture absorption and high lignin content—for better long-term resistance and better thermal stability—are preferred [67]. However, geographical location often plays a major role in fibre selection for composite applications, since the fibre availability depends on the climate conditions for growth. A favourable climate makes flax a common crop in Europe and due to that, flax is the most widely used natural fibre for composite reinforcement in this region. Regarding the matrix selection, also multiple considerations are required. From a technical point of view, the polymer selected has to fulfil the mechanical and other functional requirements for the application, as well as being suitable for the production process defined. In this sense, the matrix selection is limited by the processing temperature, which has to be low to avoid degradation of the natural fibres—that are thermally unstable above 180 °C

On the other hand, surface treatments are based in the generation of bonds between chemical groups of the fibre's and the matrix's surfaces. The increase in the interfacial strength depends, in this case, in the sort and density of the bonds generated. This chemical bonding can be produced by coupling agents bridging the fibre/matrix interface, by grafted groups on the fibre surface, or by activation of surface groups, for example the most popular chemical treatments are the use of alkaline treatments—such as mercerization, which consists of a treatment with NaOH—, acetylation, silane treatment, or use of maleated coupling agents, among others [5],[28],[134],[61]]. Enzymatic treatments can be cost-effective and environmentally-friendly solutions to achieve good quality fibres, which have been shown to improve composite properties due to the removal of adverse fibre components and the increase of fibre surface area—mainly due to fibrillation. Regarding the matrix modification, a possibility—used in conventional thermoplastic matrices such as PP—is the addition of coupling agents such as maleic anhydride that react with the hydroxyl groups increasing the fibre/matrix adhesion. However, the modification of the natural fibres according to the aforementioned techniques is more common.

Fibre content and porosity The increase in fibre content is generally translated into a rise in the mechanical properties of the composite. A higher amount of fibres will be translated in higher stiffness, and in higher composite strength, whether the fibre/matrix adhesion is optimised, as mentioned

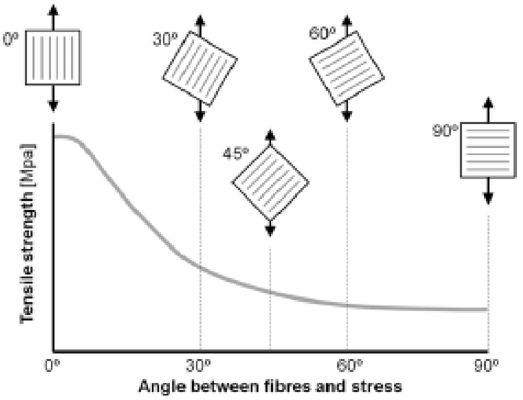


Figure 3.31: Orientation of fibres w.r.t direction

before. However, some limitations can be reached, especially in plant fibre composites. On the one hand, the fibre content can be increased up to a threshold in which the water uptake and the odour of the composite become relevant side effects.

On the other hand, these limitations are related to achieving a balance between fibre content and proper wettability, and hence good stress transfer. In this sense, there is a critical volume fraction—expectedly 10 % — from which lower contents of natural fibres produce a negative effect in the composite strength, acting as simple pores/holes in the matrix, but also there is a maximum volume of fibres fraction—around 50%- 60%that leads to a poor wetting due to a deficient fibre/matrix ratio [135]. The former is not often observed given that higher fibre contents are normally used; the latter is produced because of the amount of matrix cannot cover all the fibre surface and a large porosity is obtained, thus affecting the stress transfer and hence, the mechanical properties. Regarding porosity and in addition to the aforementioned, cellulosic fibres present intrinsic porosity due to their lumen—for flax, lumen is the 6.80% of the fibre section[103]. The porosity has an important effect in lowering the final properties of the composite. Madsen, Lilholt and co-workers have worked on the relationship between fibre contents and porosity—which is of special interest for modelling the mechanical behaviour of the composites—, and have developed correcting factors for the modified rule of mixtures that have shown a better accuracy in the stiffness prediction in natural fibre composites [106].

Fibre orientation and dispersion The orientation of the fibres concerning the direction in which the load is applied plays a key role, as can be observed in figure 3.31.

Regarding mechanical properties, fibres aligned with the direction of the applied load demonstrate optimal performance [14]. While aligning natural fibres is more challenging due to their finite length, unlike continuous synthetic fibres, there are methods utilizing carding systems to align natural fibres for reinforcement. Alternatively, yarns made from spun natural fibres can be used, though they involve some degree of twisting and thus do not achieve perfect alignment.

However, fibre orientation can be a positive or negative factor depending on the composite's processing technique and final application. For instance, sandwich structures of uniaxial fibres oriented in multiple directions can be of interest in high-performance applications, such as the bike structure or the surfboard fin. However, having oriented short fibres following the flux direction in a composite part that has been produced by injection moulding can result in inhomogeneity on the stress transfer throughout the material, which can lead to a premature fracture. Regarding fibre dispersion, the reinforcement of thermoplastic biopolymers with long fibres, the use of textile structures is an interesting option to solve or minimize the problems of fibre orientation and dispersion, despite it leads to limitations in what to the manufacturing processes available is concerned.

Processing Conditions Moreover, cellulosic fibres can present symptoms of degradation at relatively low temperatures 180°C. As aforementioned, this limits their use in matrices that require high-temperature conditions for processing. This is a minor drawback, given that most thermoplastic biopolymers can be processed at lower temperatures than those at which the cellulosic fibres start to degrade. However, some biopolymers like Alginate present a very narrow processing window and undergo thermal degradation when exposed to temperatures just above their melting point. Other factors such as viscosity, pressures or shear rates that depend on the processing require an optimisation. Therefore, a critical factor in the final properties of the composite material is the determination and setting of the proper processing conditions for its production.

Durability and Degradation The structure of cellulosic fibres and their hydrophilic nature—favoured by the chemical composition—is responsible for their sensibility to moisture and water absorption. Therefore, biocomposites, typically, tend to absorb water when exposed to humid environments or when immersed in water. In this sense, water transport is associated with diffusion throughout the matrix, to cracks, pores or other imperfection in the matrix, and capillarity along the fibre and or the fibre/matrix interface [213]. Anyhow, once the water absorption reaches the fibres causes their swelling, thus inducing cracks in the surrounding matrix— matrix damaging—and debonding of the fibres—weakening the fibre/matrix adhesion—, among other effects [213][113]. The fibre debonding is translated into an ineffective stress transfer, and hence, to the impoverishment of the mechanical properties of the biocomposites—sometimes referred to as ageing. Therefore, the moisture absorption of the cellulosic fibres is an important drawback for biocomposites since affects their durability. In this sense, given that the water uptake is related to the fibre content, the use of large amounts of cellulosic fibres can have a potentially negative effect in the long-term properties due to higher degradation by water/moisture absorption [135]. Due to that, several fibre treatments that can be used to reduce the hydroxyl groups—and hence the hydrophilicity of the cellulosic fibres—can be found in the literature, causing an increase in the mechanical behaviour and higher dimensional stability, too. On the other hand, moisture absorption increases the potential microbial attack that is related to the biodegradation of the biocomposites, thus being a benefit for those applications in which such an effect is desired.

3.5.1 Treatment of Woven Flax fibres

As aforementioned, Flax fibres present two main drawbacks for their use in polymer matrix composites: fibre/matrix compatibility and moisture absorption [60]. In this sense, numerous studies focussing on treatments to overcome these difficulties have been published. As previously mentioned, the fibre/matrix adhesion governs the stress transfer and hence, the mechanical performance of the composite. Therefore, it is a key parameter in composites production. Literature reports there are two main mechanisms which increase interfacial bonding. The first type works by changing the structure of the fibre to form stronger bonds with the matrix which is the alkaline treatment section. The second category of treatment is the use of a coupling agent. A coupling agent is a chemical bonded to the surface of the fibre to create a chemical bridge between the fibre and matrix. This compatibility depends on the nature of both the matrix and reinforcement. Cellulosic fibres—which present a hydrophilic nature—present poor adhesion with most of the matrices commonly used—mainly hydrophobic[61]. The improvement of wettability can be addressed by chemical or physical methods or by modifying the matrix or the fibre surface, such as: alkaline treatment, silane treatment, acetylation of natural fibres, benzoylation treatment, acrylation and acrylonitrile grafting, maleated coupling agents, isocyanate treatment, or plasma treatments, among others. Anyhow, this modification must be consistent with the matrix, because different matrices require different fibre surface properties. In general, alginates shall present better adhesion to natural fibres than polyolefins due to the presence of polar groups that can interact with the hydroxyl groups of cellulose [27],[18]. However, fibre treatment can enhance this favourable adhesion and increase the mechanical properties between the Alginate matrix and the flax fibres.

Given the marked environmentally friendly character of the composites focussed in this thesis the green composites, an interesting option is the use of eco-friendly methods to perform the aforementioned enhancements. In this sense, a treatment which is non-toxic and derived directly from a renewable natural source would be favourable for further exploration. Various surface treatments of natural fibres using eco-friendly compounds such as polyphenolic compounds or proteins have been explored to enhance interfacial adhesion in natural fibre-reinforced composite. In a study referring to Ovlaque et al, alkali treatment was proven to induce an increase in the surface roughness of milkweed floss fibres (from 10.03 to 20.9 nm) and thus, better mechanical interlocking with PLA [128]. Yu et al. investigated three different chemical treatments, namely, alkali, maleic anhydride-PP (MAPP) coating and silanization, to improve inter-facial adhesion between PP and flax fibres. Studies also found that MAPP coating and silanization (on alkalized fibres) were more effective in improving the interfacial shear strength of composites (IFSS) than alkali treatment alone because these two treatments allow bridges to be generated between the fibres and the matrix through the formation of chemical covalent bonds (highest IFSS increases of (60 %,(109 % and (125 % with the alkali,MAPP coating and silanization treatments, respectively)[203]. The effectiveness of MAPP was confirmed in previous work, as well as its ability to limit fibre degradation, which is often seen with other treatments (e.g. alkali treatment) [20]. Previous studies also focused on the coating of flax with silica nanoparticles dispersed in epoxy or a thin film of titanium dioxide [142]. The researchers have successfully demonstrated a strong adhesion between flax and PLA through an intermediate interfacial layer in such cases. However, the proposed surface treatments often degrade NF or are either expensive or require the use of non-environmentally friendly chemicals. They can be used for technical applications where high performances are required but, in the case of larger-scale production, the development of cheaper and more ecological treatments is awaited with great interest. Various chemical modifications of flax fibres have been proven beneficial in terms of increasing the strength of the fibres as well as the moisture absorption and the interfacial bonding with the resins in the composites. The effects of corn zein protein- a bio-based coupling agent on the properties of the flax UD fibres and used as a reinforcement in unsaturated polyester resin was studied by researchers and they found an improvement in the properties of the composites with the modified flax fibres. [88]. Results demonstrate the environmentally friendly zein treatment successfully increased tensile strength 8 % , flexural strength 17 %, and shear strength 30 % compared to untreated samples. [210] developed 100 % green composites, by investigating interfacial adhesion between modified flax fibres and polylactic acid (PLA) using lignin and tannin, two types of eco-friendly polyphenolic compounds derived from waste or paper industry byproducts. They reported an increase in interfacial adhesion of the composites. Tannin, on the other hand, showed better compatibility with PLA and flax fibres with a 17 % and 29 % increase in the ultimate flexural strength and interlaminar shear strength of the composites, respectively.

Various other researchers have also explored the use of alginates as a compatibiliser in flax-reinforced PLA and PHBV composites. Composites containing alginate-modified flax fibres were found to exhibit improved viscoelastic and thermal properties[87]. Many other studies have incorporated fillers to toughen brittle resin matrices such as the incorporation of rubber, silkworm silk, wool, and various other plant modifiers to improve mechanical properties.

Researchers have extensively explored the integration of flax into polymer matrices, yielding composites with notable advantages in stiffness-critical structures. Shah et al. compare flax composites with E-glass composites as a replacement material for a small wind turbine structure. The flax turbine is 10% lighter than the E-glass structure. Many other researchers have found that NFC can have very good specific stiffness and reasonably specific tensile strength[166].

Fibre modification and treatment have been essential in addressing challenges such as lower impact strength and improving adhesion. These composites have diverse applications, ranging from consumer goods to automotive components. For instance, flax fibres have been used as polymer reinforcement in car interior parts such as car roofs, doors, and panels, and even in-car disk brakes as a substitute for asbestos fibres. This showcases the adaptability and economic viability of these composites. The shift towards green composites further highlights their potential for tailoring properties to specific needs. Flax fibres serve as the foundation for advanced materials, paving the way for innovation and optimization in various industrial applications. Furthermore, fibre treatment plays a crucial role in incorporating these fibres into resin matrices. The subsequent section explores traditional composite manufacturing techniques and the important considerations for achieving optimal results.

3.5.2 Composite Manufacturing Processes

In the realm of natural fibre polymer composites, the adaptation of conventional manufacturing techniques designed for traditional fibre-reinforced polymer composites and thermoplastics is a common practice. These techniques encompass a wide array of methods, including hand lay-up, spray lay-up, filament winding, pultrusion, extrusion, injection molding, carding, hot pressing, film-stacking, compression molding, resin transfer molding (RTM), resin infusion, sheet molding compounding (SMC), and hot pressing.

The choice of an appropriate consolidation method relies on several factors, such as the type and orientation of fibres, fibre content, moisture content of fibres, matrix material (i.e., polymer type and rheology), thermal stability, and the desired properties of the final composite. Additionally, it is crucial to consider the processing temperature limits of natural fibres, as they cannot withstand temperatures exceeding 180 – 200 °C or 175 °C for extended durations without experiencing a significant reduction in mechanical properties [65]. Consequently, the selection of suitable matrix systems becomes a critical consideration.

The advancement of biopolymers, characterized by lower processing temperature requirements, such as plasticized starch, cellulose, and soy-based polymers, has broadened the scope of available composite matrix materials. This development has effectively mitigated the challenges associated with high-temperature composite processing.

A wealth of literature exists on the processing techniques for natural fibre composites (NFCs), categorizing them based on the type of matrix system utilized, namely thermoplastic and thermoset-based systems [61]. The natural fibre reinforcements within these composites can vary from short to long lengths, with structural orientations ranging from random to highly aligned.

For composites reinforced with short fibres and favouring a random orientation, techniques such as injection molding (IM), resin transfer molding (RTM), and various hot press methods have demonstrated their efficacy in producing composites endowed with favourable physical and mechanical properties.

Conversely, composites demanding long fibre reinforcements with a high degree of alignment often rely on processing techniques like pultrusion, filament winding, and the creation of prepregs followed by compression molding.

The diverse range of materials and the specific performance criteria associated with biocomposites frequently necessitate the utilization of highly specialized processing techniques to manufacture tailored biocomposite systems.

Compression Moulding Compression molding (CM) serves as a widely employed technique for both thermoplastic and thermoset matrices, accommodating loose chopped fibres or short and long fibre mats. This versatile method involves the stacking of fibres in alternating layers with thermoplastic matrix sheets, followed by the application of heat and pressure ([135]).

In the compression molding process, plastic material is introduced directly into an open, heated metal mold cavity. Under the influence of heat, the material softens and conforms to the shape of the mold as it closes. Electric heaters maintain the mold's temperature, while hydraulic cylinders or toggle clamps keep the mold securely shut ([31]). The material, subjected to high pressure and temperature, interacts with the heated mold surface, achieving softening and complete cavity filling. This interaction initiates a chemical reaction, leading to the curing of the part. The duration of the curing process is determined by factors such as the thickest cross-section, mold temperature, material type, and grade. Following curing, the mold is opened, and the part is ejected. Hydraulic presses are commonly used as compression molding machines.

Various types of reinforcements can be employed in advanced composite thermoplastics, including unidirectional tapes, woven fabrics, randomly oriented fibre mats, or chopped strands. Thermoplastic resins can be loaded into the mold in various forms, such as pellets, film, sheets, solutions, or fibres. Alternatively, the mold may receive material from a plasticizing extruder. In the case of thermoplastic materials, they are heated above their melting points, shaped, and subsequently cooled.

Ensuring the even distribution of material over the mold surface during the compression step is critical, and this is achieved through the proper material feed. Historically, incorporating fibres into thermoplastic resins faced challenges due to low fibre wet-out caused by the high viscosity of thermoplastics compared to low-viscosity thermoset resins. However, innovative techniques have emerged for the commercial production of thermoplastic prepregs. These prepregs offer extended storage life and can be consolidated into laminated composites by applying heat and pressure ([186][187]). The thermoset compression moulding process entails spraying rather than immersing the natural fibre mats with resin. The mats are then compressed into the final part in a hot tool. Typical applications of this process in the automotive industry include interior parts such as door trims, seatbacks, and vehicle under-trays.

Sheet moulding compounding (SMC) Sheet moulding compound (SMC) is a thermoset-based compression moulded composite which is mainly used for producing thin, strong, stiff and lightweight structural parts. Common thermoset resins for SMC sheets are polyester and vinyl esters, whereas epoxies' longer cure time has limited their use in SMC. SMC composites are manufactured in a two-step production process, the first step is the preparation of the so-called prepreg and compression moulding is the second step ([161] Prepregs of fibres, in the form of continuous roving or nonwoven mat or woven fabrics, impregnated with predetermined amounts of uniformly distributed resin. The pre-pregging process uses a bath containing a resin liquid of a controlled viscosity by applying the appropriate solvent to the catalysed resin. Unlike other processes which can sometimes damage fibres due to the rotating screw for example in the extrusion or injection moulding, CM eliminates such damage as the fibres can be gently placed inside the mould without shear stress or vigorous motion, thus preserving the isotropic properties of the composite. Chopped glass fibre in thermosetting resins used to be the conventional SMC process output, however nowadays, the process has been developed for natural fibres such as flax [187], hemp [150] and jute([99]. Furthermore, the moulding temperature and pressure affect the mechanical properties of natural fibre composites. On one hand, the higher temperature reduces the thermoplastic viscosity hence better fibre wetting but on the other hand, there is a risk of fibre degradation[182]. Simultaneously, sufficient moulding pressure is important to remove air trapped inside the mould and reduce void contents [93].

Hand lay-up Hand lay-up, the simplest method of composite manufacturing, is suitable for natural fibre composites although it does not necessarily involve the application of heat but labour intensive process and is widely used for prototype part manufacturing and in the marine industry. This process yields low fibre fraction contents compared to hot pressing and compression moulding and consequently produces only moderate mechanical properties. The process entails fibre wet-out with the application of resin on the reinforcement layers continuously until the required thickness is achieved, then allowed to cure. In a study on the impact and fatigue behaviour of non-woven hemp polyester composites, a hand lay-up process using dead weight (40 kPa) during curing produced a low fibre weight fraction of 16 %fibre. However, to provide a significant reinforcing effect it was necessary to apply higher pressure using moulder (2 MPa) which resulted in a much higher fibre fraction of 44 %[204]. Similar results reported in a study by [45], the measurements of fibre volume fractions were found as low as 8 % - 11 %due to the low compaction pressure of such process and porous structure of natural fibres that increase the amount of resin absorbed when lamina are impregnated. Alternatively, a higher volume fraction of 30 % could be achieved if liquid molding techniques RTM were employed.

Resin Transfer Moulding Liquid composite moulding processes encompass Resin Transfer Moulding (RTM) whose basic approach is to separately inject the liquid resin into the bed of stationary preforms. In the RTM technique, firstly the two-part mould needs to be cleaned and coated with a release agent. Once these coats are cured, dry fibre preform or porous preform having the mould size is placed into the cavity. Then, the two matching mould halves are clamped tightly to avoid leakage of resin during the injection process. A pressurised molten resin is then injected into the heated mould through single or multiple ports depending on the final part complexity. Once the mould is filled with resin and after the cooling cycle has been completed, the part can be removed. Post-cure is often required to allow the chemical reaction between the resin and its catalyst. This technique is capable of serving industries with high-volume production demands at effective costs, as it bridges the gap between labour-intensive hand lay-up and capital-intensive compression moulding. The main variables of RTM process are mould temperature, injection pressure, resin viscosity, preform architecture and permeability, preform placement, gate location and configuration and vent control [77] Generally, low viscosity resin is achieved at higher temperatures allowing fast resin flow at higher injection pressure, as a result shorten the manufacturing cycle time. However, an excessive injection pressure may cause deformation of the mould and wash-out of the fibre preform. An excessively high mould temperature may induce pre-mature resin gelation and cause short shot [77]. Lower temperature requirements of natural fibre to avoid thermomechanical degradation making RTM the preferred process over other processes [64]. In a comparative study between RTM and CM; Sisal reinforced polyester composites elucidated the benefits of the former process in reducing the void contents and water absorption. Tensile and flexural properties of the RTM composites were higher than the CM fabricated composites due to the good fibre/matrix interaction [176]

The Resin Transfer Molding (RTM) process offers several benefits, including reduced investment and operational costs, precise dimensional accuracy, the ability to manufacture complex parts, a high-quality surface finish, and low volatile emissions due to its closed moulding approach. Specifically, using natural fibres in the RTM process lessens tool abrasion risk, unlike glass fibres. Additionally, the absence of airborne particles in this process diminishes respiratory issues for workers. However, there are challenges: the tooling design can be complex, and considerable trial-and-error experimentation or flow simulation modelling may be needed to manufacture complex parts. The compaction in this process is influenced by the natural fibres' structure, including the lumen's closing. Due to lower degrees of fibre alignment, natural fibre composites are less compact than glass fibre composites.

Resin infusion- Vacuum Infusion Process Resin infusion also known as vacuum infusion process (VIP) or vacuum bagging is also considered one of the liquid composite moldings whereby only a vacuum is used to drive the resin flow and the laminates are enclosed in a one-sided mould covered with a bag [182]. This technique is basically an extension of the hand lay-up process, it is referred to as the open mould process. Vacuum bagging involves layering the preform with peel ply, resin infusion film and resin infusion mesh then sealing the wet laid-up laminate with a sealing plastic film to form a vacuum bag. Air under the bag is then extracted by a vacuum pump thus the laminate is consolidated through the pressure effect of one atmosphere. The pipework consists of two parts, on one side of the preform applying vacuum so that extra air is removed. On the other side, resin is infused through a tube from a container (cup or glass) into the sealed bag. Vacuum causes the resin to flow through the preform and proper wetting of the fibres is achieved. Unlike hand lay-up, vacuum bagging achieves higher fibre contents lower void contents and better fibre wet-out resulting in: i) stronger interface strength thus increased strengths and moduli, ii) minimise fibers abrasion thus eliminating damage and fracture, iii) avoiding crack initiation and growth due to void [32]Ȧlthough the process reduces volatile emission during cure, it is costly for consumables and labour intense which require specialist skills to carry out the steps of mixing and controlling the resin flow and content [198] Biocomposite panels, for large structures like trucks and automotive parts, of soybean oil resin reinforced with various natural fibres mats were prepared using vacuum-assisted resin transfer moulding (VARTM) and cured at room temperature due to the associated cost inefficiency with post-cure at elevated temperature [126]. The static and dynamic test results of these panels proved that VARTM is suitable for the manufacture of large-scale components without the need to generate a large mechanical force via a press for molding.

Film stacking and hot pressing This technique employs alternate layers of dry fibres and polymer, most commonly thermoplastic, films followed by heating and compressing the stack using a hot press to force the thermoplastic into the reinforcement layers and thus form prepregged sheet. Initially, this technique involves converting the polymer resin into a film form by heating and compressing the polymer pellets. The reinforcement fibre can take many forms such as nonwoven or continuous comingled, wrapped and coweaved fibre arrangements. The reinforcing fibres are then cut to the desired dimensions and shape then placed between the heating plates equipped with a hydraulic press. The stack of the layered polymer films and fibres achieving the desired thickness is then placed for processing. The assembly is heated and pressed and once the polymer has melted the composite is cooled to room temperature under constant pressure. Process parameters, time and temperature as well as pressure, are dependent on the nature of composite constituents i.e. polymer and fibres and are controlled as these parameters affect the melting temperature and viscosity but also on the degradation of the reinforcing fibres. Jute fibres have been consolidated with polypropylene films using a combination of film stacking and compression moulding to produce samples for mechanical and optical characterisation. A pressure of 2 MPa, a holding time of 15 minutes and cooling at ambient temperature were used for three moulding temperatures 140°C, 150°Cand 160°Cproduced samples of fibre volume fraction 49.2%. Optical micrographs revealed visible voids caused due to the incomplete fusion of polypropylene films and partly melted matrix of samples pressed at 140°Cand 150°Chindered the adequate impregnation of the reinforcing jute yarns. In contrast, composites moulded at 160°CPP films were adequately fused and its complete melt penetrated the fibre bundles [94]. In another study, biocomposite samples were manufactured by stacking alternate layers of treated kenaf fibres and PLA films. The whole assembly was then placed between heated platens with a controlled temperature of 190°Cand a two-stage pressure process of 700 psi for 12 minutes and 1700 psi for 5 minutes followed by cooling under pressure. At 90°C, the mould platens were opened and the composite of various fibre volume fractions namely 27%, 37%, 47% were removed for conditioning and then testing [78]

Injection moulding Injection moulding (IM) of composites is a process that forces a measured amount of mixture which contains molten polymer and fibre into mould cavities. This process can be employed in the production of NFCs. This technique is capable of producing in great numbers parts of complex geometries with accurate dimensions while the process is fully automated [61]. Other advantages include economics of scale, minimum warping and shrinkage high high-function integration and the possibility of using recycled materials. Difficulties associated with achieving high fibre fraction and longer fibre limit the use of injection moulding in the production of natural fibre biocomposites. Although this process was originally designed for plastic pellets to produce thermoplastic components however this process was later adopted for fibre-reinforced composites. In such a process, the pellets with chopped fibres are fed individually through a funnel-shaped feed hopper into a heated compression barrel with a rotating screw. The solid pellets are transformed into a viscous liquid, the mixture is then channelled through the sprue nozzle effect and finally forced into the tightly clamped mould cavities against the injection pressure. The closed mould is then cooled allowing the polymer to solidify and locking the fibres in place. Finally, once the assembly is sufficiently cooled, the composite is ejected from the closed mould to form the desired part. Fibres used in the injection moulding are usually chopped first into short fibre according to the critical fibre length criterion to ensure efficient load transfer assuming a good fibre/matrix interfacial bonding is resulted. However, the fibre length in practice is normally shorter than the predicted fibre length due to the high shear rate in the barrel. In extreme cases where the fibre length is less than the critical fibre length, therefore inability to carry load effectively or even worse by acting as a defect in the material. A possible solution is to increase the fibre content which would theoretically improve the strength and stiffness, but a risk of fibre cluttering in the narrow gate and sprue would limit the amount of fibres to be injected. Many studies have been conducted to assess the potential of using IM in natural fibre composite production.

Extrusion is an essential pre-IM step and often considered for producing a pre-cursor for IM process. This is because injection moulding machines and screws are much shorter than extruders and therefore, the ratio of length to diameter for injection moulding screws is lower than for extruders. The lower length-to-diameter ratio of the screw in the injection machine makes it less efficient in mixing and non-homogenous melt comparison with extruders. For this reason, if the composite is processed by injection moulding, prior extrusion compounding is necessary for the materials.

Other composite processes The pultrusion process is a less commonly used method in the production of NFCs. In this process, fibres are pulled from creel through a resin bath and then on through a heated die to form composite shapes with constant cross-section. Typical components produced via pultrusion are rods, beams, channels, tubes, walkways and bridges, handrails, light poles, etc. However, a variant known as pulforming allows for some variation in the cross-section of the part. This process is continuous, low cost and high-volume manufacturing. Filament winding is primarily used for making tubular parts, generally circular or oval sectioned, for application-specific structures like pressure vessels, pipes and tanks. The process involves passing fibre tows through a resin bath before the impregnated fibres are wound in a variety of orientations angles over a rotating mandrel. The fibres move through the resin bath and after impregnation, they move back and forth utilizing the guide while the mandrel rotates at a specified speed. The desired angle is achieved by controlling the motion of the guide and the mandrel. In summary, NFCs are manufactured through various processes depending on the application specifications, geometry, final product performance and most importantly costs at high volume production. Careful consideration of several factors such as the properties degradation during processing, fibre loading and porosity i.e. void contents when choosing a manufacturing technique for NFCs. Table 3.5 provides a summary of NFC manufacturing techniques with composite parameters.

Manufacturing Technique	Consolidation Pressure(bar)	Fibre volume fraction(%)	Porosity volume fraction(%)	Matrix Used
Injection Moulding	> 1000	Upto to 45% (Typically 15-30%)	None	Thermoplastic
Compression Moulding	Up to 40 (typically 20-30)	Up to 85% (typically 25-50%)	Up to 25% (typically 2-8%)	Thermoplastic or Thermoset
Prepregging (With autoclave)	0-10 typically 4-6	Up to 60% (typically 35-50%)	Up to 10% (typically 0-4%)	Thermoset
VIP(RTM)	0-4 (typically 0-2)	Up to 60% (typically 25-50%)	Up to 10% (typically 1-4%)	Thermoset

Table 3.5: Manufacturing techniques to produce NFCs with composite parameters

3.6 Applications for Biocomposites

Despite increased research in bio-based materials over recent decades, the biocomposite industry continues to confront various challenges. Many of these stem from difficulties in composite processing and the natural vulnerability of certain natural fibres and biopolymers to moisture, heat, and environmental factors. The long-term durability of these materials has yet to be fully assessed. However, significant progress has been made in addressing these issues, including developing new techniques to improve fibre-matrix adhesion, the creation of innovative bio-based polymers, and an enhanced understanding of the impacts of reinforcement and processing parameters on composite characteristics. As biocomposite science progresses, it is anticipated that new uses for these materials will emerge. Biocomposites are already finding applications in geotextiles, transportation, building/housing, packaging, and consumer products.

3.6.1 Research Applications

The word 'green' affiliated with composites refers to materials that are biodegradable and renewable and thus attributed to twin sustainability issues. and 'environmental impact'. Green composites are becoming more popular recently due to persistent problems such as fossil fuel depletion, increase in oil prices and need for a clean environment[168]. Using yearly renewable resources is a simple solution to all the abovementioned problems. Green composites are a particular class that uses biodegradable polymeric material as the resin reinforced with natural fibres. Polymer composites with plant fibres are manufactured using compounding and mixing and applying polymer processing techniques such as extrusion, injection or compression molding. The most commonly used plant and microbe-derived resin materials include polylactic acid (PLA), poly(butylene succinate) (PBSu) and Poly(hydroxyl alkanoate) (PHA).94 Aliphatic polyesters such as PHAs are fully degradable in normal environments as opposed to aromatic polyesters. However, aliphatic polyesters have poor thermal and mechanical properties.94 But copolymerization of aromatic and aliphatic diacids with an aliphatic diol leads to combining copolyesters with balanced mechanical and biodegradable properties. Such polymers are called alipharomatic polyesters. Poly(butylene terephthalate-co-butylene adipate) copolyesters or similar copolymers are already commercially available under. the trade names as Ecoflex® or others. while numerous other types of such materials have been investigated. These alipharomatic polyesters have higher degradability than aromatic polyesters like poly(ethylene terephthalate), which is the most used polyester, but lower mechanical properties. To increase their properties several kinds of fibres can be used. Several other biodegradable, natural polymers exist, such as polysaccharides (starch, chitin, collagen, gelatins, etc.), proteins (casein, albumin, silk, elastin, etc.), polyesters (e.g., PHA, PHB, PLA), lignin, lipids, natural rubber. These are used as matrices for green composites, 96. Oksman et al. fabricated flax-PLA composites and compared it with flax-PP composites which are used in many automotive panels. They found that the composite strength is about 50% better for flax-PLA (44 MPa) compared to similar flax-PP composites (29 MPa). While a similar modulus value was observed in both. Thus, PLA can be used to replace conventional resins such as PP. Plackett et al. reported the tensile strength value of 100 MPa and modulus of 9.5 GPa jute-PLA composites (using 40% jute on a wt. basis). Various nanocomposites have been fabricated using organo-modified montmorillonite clays to improve the thermal stability of the PLA-based composites. Various plant oils can also be used to obtain bio-based resins or adhesives. Many active sites from the triglycerides like double bond, allylic carbons and ester groups can be used to introduce polymerizable groups. Wool and Sun99 prepared soybean oil-based resins by functionalizing the triglycerides by attaching polymerizable chemical groups such as maleinates and acrylic acid. This made the triglyceride capable of polymerizing via ring opening, free-radical or polycondensation reactions. Composite materials made out of plant oil-based resin and plant fibres using the VARTM process showed properties desired for many applications. Research on biodegradable polymer composites containing lignocellulosic fibres is also generating increasing attention due to dwindling petroleum resources, low cost of lignocellulosic reinforcements with a variety of properties and increasing ecological considerations. Luo and Netravali21 used Biopol® (poly(hydroxybutyrate-co-hydroxyvalerate) or PHBV resin from Monsanto Company) with pineapple and henequen fibres to make green composites. The tensile and flexural strengths of green composites were reported to be significantly higher than many wood varieties in the grain direction, even at a low fibre content of 28%. With higher fibre content and better processing, the mechanical performance could be improved further for use in applications such as secondary structures in housing and transportation. Lodha and Netravali102 fabricated green composites using soy protein isolate as resin and reinforced it with ramie fibres. They further modified the soy protein resin with stearic acid to reduce moisture absorption and obtain better tensile properties. Huang and Netravali104 incorporated nanoparticles such as nano clay into the soy protein-based resins and further reinforced it with flax fibres and characterized the composites. Nanoclay incorporation increased the Young's modulus of the resin as well as that of the composite. Nanoclays also reduce the moisture absorption of the resin. Rout et al. studied the effects of different fibre treatments including alkali treatment, bleaching and vinyl grafting on coir fibres and the effect of treatment on the composite performance. They showed that all modifications of the fibre surfaces increased the mechanical properties of the composite.[211] [201]

3.6.2 Commercial Applications

The role of the automotive industry in the field of green composites is of prime importance. The first carmaker to use polymer (epoxy) filled with natural fibres was Mercedes-Benz in 1960 by manufacturing door panels containing jute fibres. Another paradigm of greener composites' application appeared commercially in 2000 when Audi launched the A2 midrange car: the door trim panels were made of polyurethane reinforced with a mixed flax/sisal material. Mitsubishi Motors also used green/greener composites in the interior components which combine bamboo fibres and a plant-based resin polybutylene succinate (PBS), and floor mats made from PLA and nylon fibres. Toyota has claimed to be the leading brand in the adoption of environmentally friendly,100% bioplastic materials.38 The natural fibre-reinforced green composite was used in the RAUM 2003 model in the spare tire cover. The part was made using PLA resin from sugar cane and sweet potato and was reinforced with kenaf fibres. Toyota added the Matrix and RAV4 models to the list of vehicles using soy-based seat foams in the summer of 2008. Recently, Ford selected wheat straw as reinforcement for a storage bin and inner lid in its 2010 Flex crossover vehicle while BMW, for the 7 Series sedan used prepreg natural fibre mats and a unique thermosetting acrylic copolymer for the lower door panel.107 The shift to more sustainable construction in the automotive industry, particularly in Europe, is not only the company initiative towards a more viable environment and cost efficiency but also a requirement through European regulations. According to the European Guideline 2000/53/EG issued by the European Commission, 85% of the weight of a vehicle had to be recyclable by 2005. This recyclable percentage was expected to be increased to 95% by 2015. Composites made of renewable materials are now commonly used in interior and exterior body parts. Similar components are used as trim parts in dashboards, door panels, parcel shelves, seat cushions, backrests and cabin linings. In recent years there has been increasing interest in the replacement of fibreglass in reinforced plastic composites by natural plant fibres such as jute, flax, hemp, sisal and ramie. Materials experts from various automakers estimate that an all-advanced-composite auto-body could be 50 %–67 %lighter than the current similarly sized steel auto-body as compared with a 40 %– 55 %mass reduction for an aluminum auto-body and a 25 %– 30 % mass reduction for an optimized steel auto-body. Specifically for the future electrical vehicle's chassis, the light-weighting materials approach is vital to offset the added weight of batteries while at the same time lowering the curb weight and increasing their maximum range. Such an automobile body could be even lighter with the addition of natural fibres in the composite because these are less dense than the synthetic types. The concept of natural fibre incorporation in exterior car parts is not new. Dealing with an exterior part though is more complex in comparison to the interior parts which are protected from the weather, particularly water. In addition, the exterior components must be able to withstand extreme conditions such as exposure to heat and cold and mechanical impacts resulting in chipping and splintering. The first release of exterior greener composites appeared in 2000, when the Mercedes-Benz Travego travel coach model, was equipped with a polyester/flax-reinforced engine and transmission enclosures for sound insulation. These are the first examples of natural fibres' use for standard exterior components in a production vehicle and represent a milestone in the application of natural fibres.[211] [201]

INTERIOR PARTS	**Model year**	**No. of parts**	**Weight (kg)**
Mercedes-Benz			
C Class	2000	33	22
S Class	1998	32	24.6
E Class	1995	21	20.5
A Class	1997	27	11.9
C Class	1992	30	18.3
Other manufacturers			
BMW Series 3	1998	-	12
Audi A4 (B6)	1999	-	10
VW Passat	1997	-	1.5
Audi A4 (B5)	1993	-	1.5
EXTERIOR PARTS			
Mercedes-Benz			
Travego	2000	3	12.3
Top Class	2000	3	14.1

Table 3.6: Commercial Application of Natural fibre composites

Through various molding techniques, biopolymers and natural fibre-reinforced biocomposites are tailored to suit consumer product requirements, often achieving lower production costs and lighter product weights. The expectation is that almost any component presently crafted using neat synthetic polymers or those incorporating inorganic fillers might be substituted with biocomposites created using similar methods. Among the consumer products already transitioning to biopolymer and biocomposite materials are items like tool handles, clothing hangers, food trays, compostable planting cups, hygiene products, laptop computer casings, and various furniture pieces, including tables and chairs.

Chapter 4

Research Goals

In light of the pressing concerns surrounding plastic waste and the ethical dilemmas associated with utilizing food sources for materials, our research endeavors to explore sustainable alternatives, particularly focusing on seaweed-based composites. As we read in the previous section, seaweed presents a promising avenue due to its eco-friendly properties, offering sustainable fibers and binders while minimizing ecological footprints and land competition. Despite challenges related to cost, natural fibers, complicated extraction process of biopolymers from seaweed, these materials nonetheless hold potential as reinforcements and resins, driving the development of eco-friendly composites in the future.

Transitioning into research objectives, this section highlights the gaps determined from the previous literature study to define the further action course for this project. This is achieved by investigating the potential of seaweed-based composites and clean technologies to unlock new realms of sustainable materials, contributing to a greener future and fostering novel solutions for environmental challenges.

4.1 Research Objectives

This study explores and strives to formulate an eco-friendly material. The primary objective is to harness the potential of seaweed-derived matrices and enhanced natural fibers, particularly unidirectional flax fibers (UD), to craft a fully natural, biodegradable composite. The research also aims to delve into the feasibility, properties, and optimal processing parameters of these eco-friendly composites while navigating the ethical challenge of choosing between edible sources for food and sustainable material production.

By achieving these milestones, the study aspires to make substantial contributions to the advancement of sustainable materials, uncover new markets, and offer solutions that align with eco-conscious practices. This endeavor aims to carve a path toward a more sustainable and eco-friendly future. Additionally, the research aims to unlock the untapped potential of alginates, celebrated for their biocompatibility, biodegradability, and cost-effectiveness, as a matrix for biocomposites. This exploration intends to fill a critical research gap, paving the way for innovative applications and broader adoption of these versatile materials in various industries. In order to achieve these aims, the following tasks were planned to be conducted during the experimental phase in order to :

- Raw Material Selection: Identify suitable biopolymer and natural cellulosic fibers for processing in the laboratory machine, and determine appropriate blend ratios of reinforcing fiber to matrix for composite fabrication.
- Composite Manufacturing: Utilize various manufacturing techniques to produce flat composites and assess the quality of the plates.
- Processing Variable Investigation: Study the impact of different processing variables on the physical, thermal, and mechanical properties of the bio-composites to establish the optimum processing parameters.
- Application Identification: Identify potential applications for the developed composites based on their properties and performance characteristics.

Chapter 5

Material Selection and Characterisation

5.1 Material Selection

This section focuses on the meticulous selection and characterization of materials essential to developing high-strength biocomposites sourced entirely from renewable resources. Traditional biocomposites have encountered limitations compared to conventional materials, prompting recent studies to explore enhanced properties through careful material selection and precise processing techniques. Within this study, emphasis is placed on alginates, naturally occurring polysaccharides found in abundance in seaweed. Renowned for their biocompatibility, biodegradability, and cost-effectiveness, alginates have found applications across various industries. This section explores the rationale behind selecting the correct concentration and type of alginates as resin and flax as constituents. It employs a rigorous characterization process to optimize its performance in developing robust and sustainable biocomposites.

An extensive evaluation of natural fiber reinforcements was performed to create composites from renewable resources, focusing on hemp, flax, jute, and ramie. The study began with an in-depth literature review to understand the application of these plant fibers in composite reinforcement. The review's findings led to the selection of bast fibers, especially flax, for reinforcement in this research. The preference for flax fibers was based on their high mechanical strength, moisture and environmental resistance, cost efficiencies, and agricultural benefits, such as rapid growth, high yield, and suitability for cultivation in diverse geographic regions, including Europe.

This led to investigating flax yarns, commonly used in textile applications, as potential reinforcement materials for high-strength biocomposites.To maximize the mechanical strength of these biocomposites, traditional textile architectures like woven, knitted, or braided preform structures were considered [[105][208],[11]]. However, using these textiles introduced challenges, such as crimp formation, typically occurring at the warp/weft yarn interlacings in textile perform fabrication, which constrained the achievable mechanical strength. Recent studies have focused on the development of unidirectional (UD) fiber-based preforms using flax and jute fibers to remove yarn interlacement and crimps, thereby improving composite performance ([92],[6],[159],[188]). Although these UD preforms offer superior mechanical properties, they face challenges such as limited draping ability, making them susceptible to tearing under shear forces while manufacturing 3D composite structures. Despite the difficulty in handling, with two major concerns—twist and crimp, these fabrics are still in demand. Our research has given special attention to Non-crimp UD fabrics due to their high mechanical properties and excellent manufacturability despite handling difficulties.

These fabrics are ideal for further exploration in this project, especially for manufacturing composite structures, offering a balance between exceptional strength and ease of production. Non-crimp fabrics find applications in critical load-bearing aerospace structures, making them an area of focus for research in this project for manufacturing composite structures due to a combination of high mechanical properties and excellent manufacturability. Typical applications of non-crimp fabrics include load-bearing aerospace structures. Their physical properties are discussed in the following sections.

Alginates are widely used in various industries and possess exceptional biocompatibility, biodegradability, and cost-effectiveness. However, their potential as a matrix for biocomposites remains underexplored. Leveraging the abundance of seaweed, alginates emerge as an appealing substitute for petroleum resources in polymer production. The general chemical structure of Alginates is depicted in the figure 5.1.

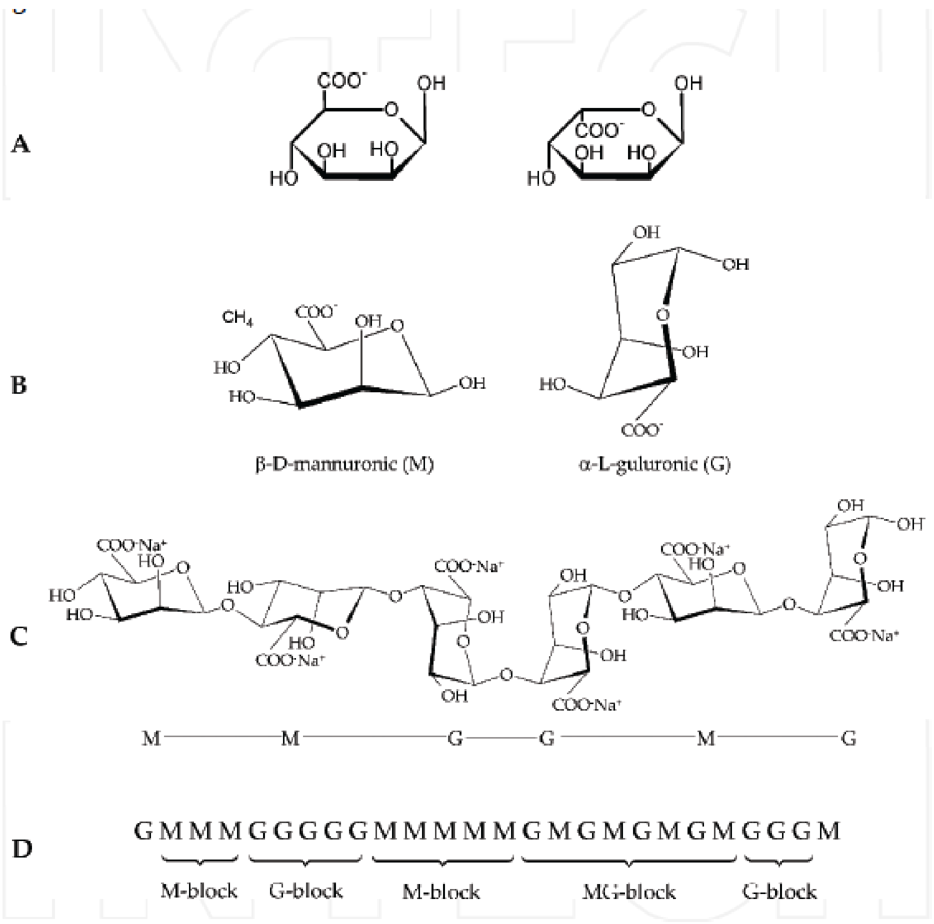


Figure 5.1: Chemical Structure of Sodium Alginate

Alginates constitute a family of linear binary unbranched copolymers composed of 1,4-linked β -d-mannuronic acid (monomer M) and α -l-guluronic acid (monomer G) residues [71] [70]. These two acid residues (saccharide unit) present stereochemically differences at C-5 [57], [143]. Alginate presents several free hydroxyl and carboxyl groups distributed along the backbone which allow reactions and chemical functionalization [202]. The general chemical structure of Alginate is shown in figure 5.1 represents both M and G monomers and the chain conformation of alginate.

The ratio M/G is an important factor because the properties of alginate solution, gels, and its produced biomaterials depend on the G and M contents. Depending on the alginate material that must be developed, this is a critical feature in choosing the raw alginate source.

Alginates can form water-resistant gels in the presence of multivalent ions, making them suitable for developing biomaterials. The gel formation and the almost temperature-independent sol/gel transition in the presence of multivalent cations make alginate suitable for the development of biomaterial that has great industrial significance.

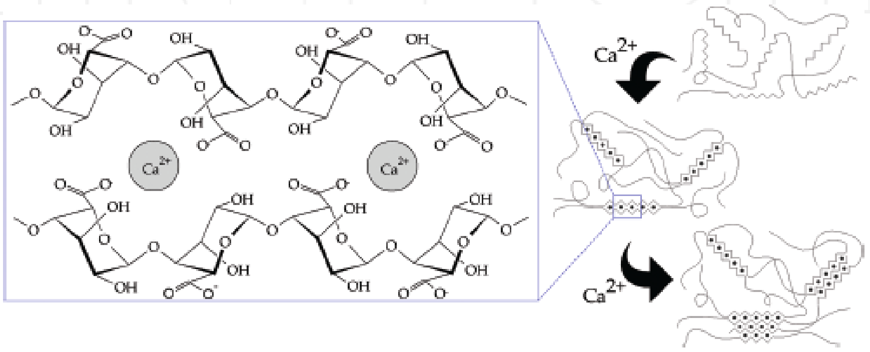


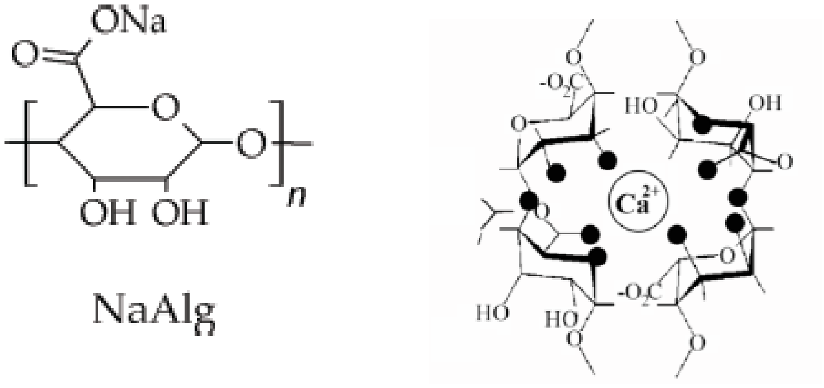
Figure 5.2: Chemical Structure of Calcium Alginate

The alginate chelation with multivalent cations is the basis for gel formation. Selective binding of earth metal ions increases significantly with the increase of G content in the alginate backbone chain.

The G blocks can form gels by complexing with divalent cations forming tightly held junctions and their structure varies depending to the monomer position in the chain, forming either homopolymeric (MM or GG) or heteropolymeric (MG or GM) blocks [71] as shown in figure 5.2. The divalent cations, such as Ca2+,Cu2+, Zn2+ act as cross-links between the functional groups of alginate chain [10], "zipping" the G-blocks in alginate chain, that is, the G-block of one polymer forms junctions with the G-block of adjacent polymer chain through interactions with the carboxylic groups in the sugars, which leads to the formation of a gel network as shown in figure5.2

In addition, ample hydroxyl groups (-OH), and carboxyl acid (-COOH), are covalently anchored on the periphery of the glucose unit, thereby providing a versatile platform for functionalization, crosslinking and hydrogen bonds with the hydroxyl groups of cellulosic fibers.

The chemical structure of sodium alginate allows for various chemical reactions and functionalizations, enabling the formation of versatile, eco-friendly water-resistant films for biocomposite applications. This research seeks to leverage these properties to create sustainable materials with competitive strengths, paving the way for the development of eco-friendly biocomposites.



(a) Without Cross-linking **(b)** NaAlg with Crosslinking

Figure 5.3: Chemical structure

5.1.1 Constituent Properties

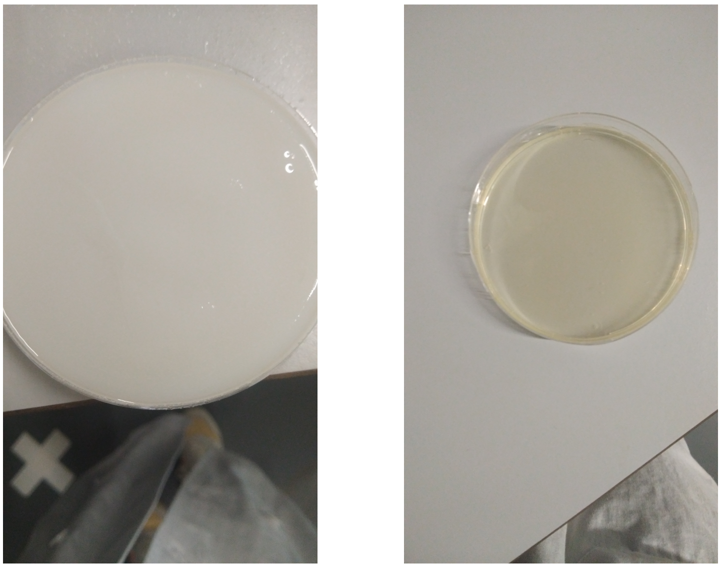
Resin- Sodium Alginate

The sodium Alginate was obtained in the powdered form from Carl Roth[80], Germany. Two variants of alginate gels namely Sodium Alginate- resin A and crosslinked Sodium alginate with divalent ions, here with Ca+2, referred to as Resin B were chosen for further exploration.

It can be seen that the carboxyl and hydroxyl from the chemical structures, that the contents of the two resins are nearly identical; however, the viscosity and melt characteristics of the two resins differ greatly Two formulations of Sodium alginate- one with crosslinking and one without cross-linking were further selected for use on natural fiber composite based on mechanical and processing tests conducted(mentioned in the table below)

	Viscosity	**Melting Range**	**Molecular weight**
Resin A	350-550 mPas	$> 200^oC$	398.316 g/mol
Resin B	Not measurable	$> 300^oC$	240,000 g/mol

Table 5.1: Properties of Alginate resin



(a) With Cross-linking **(b)** Without Crosslinking

Figure 5.4: Sodium Alginate Formulations

Flax fiber Reinforcement

The project aimed to produce high-strength composites reinforced with flax. A non-crimp fabric featuring a predominantly unidirectional (UD) weave architecture with minimal weft yarn insertion was chosen to achieve this. This selection was made to minimize the percentage of crimp. A critical requirement was having a very low number of warp/weft yarn interlacements, which helps maintain the original shape of the weave. This characteristic is essential for resisting shear forces that occur during the manufacturing processes of complex-shaped composites. Considering these specifications, Industrial grade long flax fiber non-crimp UD fabric was obtained from Bcomp, Amplitex, Switzerland. These fibers were oriented at 0°C. The fabric has an area density of 280 g/m2. The manufacturer provided specific values needed for composite manufacturing, such as linear density mechanical properties, as shown below. A detailed investigation was further skipped.

	Areal Density	**Linear Density**	**Construction**
Flax (EU)	280gsm	106	0^o

Table 5.2: Properties of Flax as provided by manufacturer.

(a) Flax Tape obtained from Bcomp **(b)** Cut and trimmed

Figure 5.5: Flax Noncrimp UD fabric

5.1.2 Test Methods

Resin Characterisation

Processing Parameters for Matrix The manufacturer did not supply detailed information on the ideal processing parameters for manufacturing Alginate resin composites. Initial experimental observations indicated that the resin systems' viscosity, concentration, and melting range temperatures were not directly applicable as processing parameters for fiber impregnation. Consequently, a set of experiments involving powder resin under different conditions, including varying temperatures, solvent concentrations, and gelation times, were conducted. These experiments aimed to identify specific processing parameters and establish a suitable processing window for each resin system. The temperature range was selected for each batch of Alginate formulations tested based on the melt temperature and findings from earlier published studies. Two techniques were used to produce Alginate gel films: solution casting with subsequent solvent evaporation and pressing between heated platens. Two varieties of films were created: SA films, which are Sodium Alginate without crosslinkers, and SA films that include crosslinkers (Ca-Alg with Calcium ion crosslinking).

For the preparation of reference films (SA and Ca-Alg):

- SA solution of 1-40 wt% was prepared by dissolving 1-40gms of SA dried powder in 100mL distilled water at room temperature.
- The solution was stirred with a magnetic stirrer at 1200rpm at 50°C.

- **For Ca-Alg gel films**, 1-40gms of SA was dissolved in 100mL distilled water.
- A mixture of Calcium Carbonate and citric acid (10mL) at the concentration of 4.6 g/L was added to varying concentrations of Sodium Alginate solution.
- The mixture was stirred with a magnetic stirrer at 1200rpm at 50°C and left to sit for 1 hour.
- The added Ca2+ ions were sufficient to bind 40 mol% of ACOONa groups in both solutions.

  To make thin dried films, the following procedures and parameters were followed:

- **For films prepared by solution casting:**
- The SA and Ca-Alg solution/mixtures of varying concentrations were poured into a glass Petri dish.
- The films were left to dry in an oven from 40°C to 95°C for film formation over 12 hours.
- Subsequently, the films were further dried in a vacuum oven for 1 day at 35°C to eliminate the effect of absorbed water on the determined property.
- **For films casted by Heat Press:**
- A defined amount (30gms) of solution/mixture of varying concentrations of SA and Ca-Alg was placed under the heat press.
- The films were heated at a constant temperature ranging from 40°C to 95°C for a total period of 10 minutes.
- The films inside the mold were then cooled in the hot press at room temperature for another 10 minutes until the ambient temperature was reached.

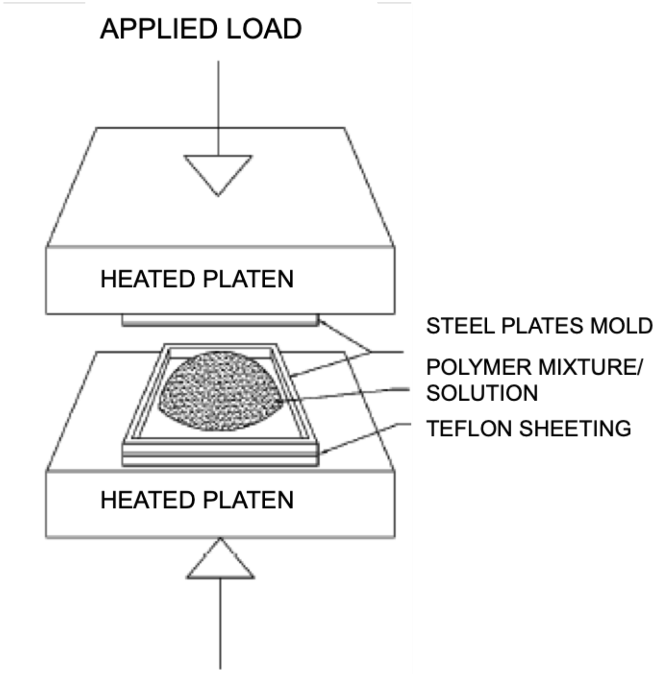


Figure 5.6: Schematic of resin film formation using steel plates

Mechanical Properties The mechanical properties of the Alginate resins were not provided by the manufacturer, and a literature review also revealed significant variation in the reported mechanical values of alginate resins among different research groups. The research is very unclear, especially for higher-concentration alginate mixtures above [6%]. To ascertain the mechanical properties of the resin, tension tests conforming to ASTM D638 were conducted at a cross-head speed of 3 mm/min on resin samples processed at various concentrations.

For these tests, rectangular specimens measuring approximately 50 mm x 10 mm x 0.04 mm were prepared using a mechanical knife, as depicted in picture 5.7. To eliminate any moisture absorbed during the machining process, these specimens were subsequently dried for 1 hour at 40°C in an oven.

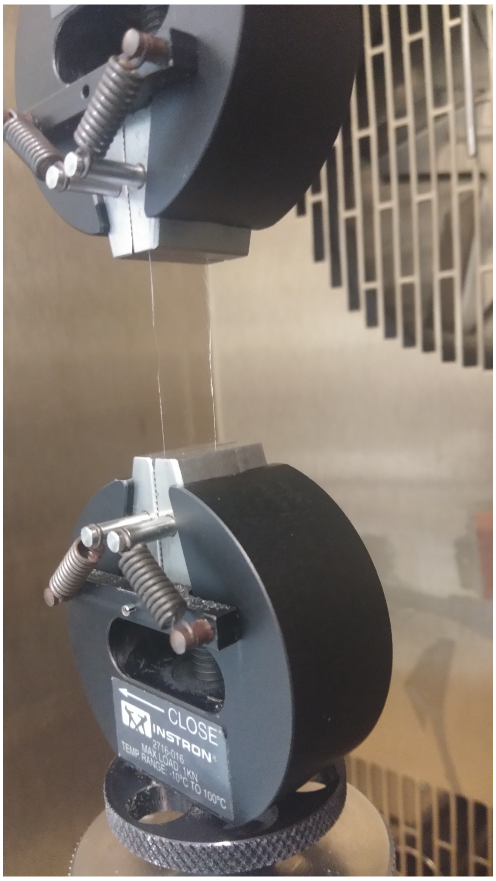


Figure 5.7: Tensile testing of Alginate sample

The overall gauge length of the test specimens was 30 mm. A minimum of 5 samples at each concentration profile for resin A and B were tested and averaged results are shown in the following section below and compared in the Figure 5.8.

fiber Characterisation

Mechanical Properties The mechanical data, linear density, average density was provided by the Supplier Bcomp, Amplitex.[21] Attached table 5.3shows all the mechanical properties.

	Ultimate Elongation%	Ultimate Elongation%	Tensile Modulus(Gpa)	Ultimate Elongation%
Tension	Parallel	580	61	1
	Perpendicular	x	6.4	x
Flexural	Flexural Parallel	663	57	x
	Perpendicular	x	6.3	0

Table 5.3: Mechanical Properties of fibers

5.1.3 Results of Constituent Characterization

Resin

In assessing the alginate resin systems for their application in natural fiber-reinforced composites, both mechanical properties and processing parameters were evaluated. A key factor in determining these properties is the molecular weight of the polymer, which is directly proportional to its polymer chain length. Generally, longer polymer chains lead to a higher degree of chain entanglement, enhancing the mechanical characteristics of the polymer, including tensile strength. It is commonly proposed that for a polymer to exhibit satisfactory physical and mechanical properties, its molecular weight should be at least around $25,000$ g/mol. It was expected that both alginate resins in this study will have sufficient mechanical properties for use as a matrix in natural fiber composites as both have average molecular weights well above this value, With manufacturer-provided values of 300000 g/mol and 350000 g/mol for resins A and B, respectively.

When manufacturing composites, considering the melt flow characteristics or the viscosity of the resin under varying temperatures and pressures is crucial. In the context of fiber-reinforced composite applications using thermosets, resins with lower viscosity are generally preferred. This preference is due to their enhanced ability to thoroughly impregnate the reinforcing fibers, leading to a composite with lower void content and improved bonding between the fiber and the matrix. Additionally, the mechanical properties of a polymer resin, such as strength, stiffness, and elongation, are vital parameters to assess. These properties have a direct impact on the mechanical characteristics of the final composite product.

Physical Effects of Processing Conditions

For resin A-(Sodium Alginate) - Thin films designed by varying concentration of the resin from 1-40%. These were the following observations made during processing:

- **Lower viscosity(1-5%)**: It was observed, that it was easier to dissolve Sodium Alginate and obtain a uniform solution by varying concentration upto 5% using a magnetic stirrer at 50°C. Making films using these concentrations by solution casting at temperatures from 40°C-90°C was easier as uniform thin films could be obtained.
- At temperature of 40°C-60°C, all the films with concentration from 1-5%; after 12 hours show needed further drying. At a temperature of 65-75°C, the film's shrinkage was considerable and had dried effectively. At temperatures 85°C and above, the films shrunk highly had become very brittle, and were susceptible to crumbling due to prolonged drying. There was however a change in the color of films which was observed. These observations suggested that an extended period of drying at a higher temperature than 75°C led to the degradation of the polymer. These concentration resins also faced similar problems of drying under the heat press.
- These concentrations of films were not able to set under a heat press and films could not be obtained as the solvent was not able to evaporate from the molds and under the application of pressure from the press these solutions. disintegrated since the viscosity was less.
- **Medium viscosity**: Post to that, higher concentration 6% - 14% resin solution was difficult to obtain as uniform mixing was not possible even with increased temperatures greater than 50°C. Bubbles were seen being formed during mixing. It further led to discoloration and the resin system gave off a unique odor at a prolonged mixing time. The films produced using solution casting were uneven, and crumbly after exposure to various temperatures leading to increased brittleness and discoloration due to the creation of pores while drying.
- These polymer solution/mixture concentrations were also put under a heated press to form thin films. This solution/mixture did flow however due to a considerable amount of water as the temperature changed from 40-95°C. These concentrations had a considerable amount of trapped water and therefore drying was a big concern. Due to the presence of the high amount of water, the films were not strong and ended up becoming a paste-like structure
- **Higher Viscosity**: On Further increasing the concentration, $>$ 15% mixing led formation of a dough-like structure which was difficult to be solution cast and dried to prepare uniform thin films. For concentration above 15%, it was easier to make films using the heat press. The mixture was able to sustain the pressure from the heated plates and did not break. These mixture concentrations showed good flow properties as temperature was raised from 40-95°C However drying under 30 mins

at various temperatures was still a concern as the water was not able to escape the heat press.

For resin system B- (Ca-Alg), The cross-linked gels were formed by mixing Calcium Carbonate with citric acid into a mixture of Sodium Alginate. This formulation was used to obtain a uniform gel. Thin dried films were prepared by varying the concentration from 1-40%. The following observations were made for the resin system:

- **Lower Viscosity**: For concentration from 1-5%; the gels were more homogeneous but they appeared milky and colloidal with the usage of calcium carbonate.
- It was observed, that it was easier to make cross-linked films by using the solution casting technique for concentrations from 1-5% as uniform mixing was possible followed by uniform gelation.
- At temperature of 40^oC- 60^oC, all the films with concentration from 1-5%; after 12 hours show very little shrinkage as compared to resin system A but need further drying. At a Temperature of 65-75°C, the film shrinkage was considerable and had dried effectively as compared to Resin system A. At temperatures 75^oC and above, the films shrunk highly but they were stiff and not discoloured as compared to Resin A.
- For concentration 5%, due to the crosslinking, a strong gelation was obtained; the mixing of the resin was highly difficult, which led to the non-uniform clumpy mixture, which was difficult to be cast into a film. uniform gel could not be obtained thereby creating macro pores within the gels. Further forming nonuniform films leads to disintegration during drying. These highly viscous uneven gels were also kept under the heat press for about 30 minutes. These mixtures did not flow under the application of heat and on further application of pressure from the heated plates to form films, they were observed to be disintegrated and formed smaller broken gels
- From the outcomes observed with resin A, there was an anticipation that resin B might exhibit similar degradation signs when subjected to the selected processing temperatures, especially at elevated levels. Surprisingly, resin B showed no signs of discoloration or odor, even when exposed to higher temperatures for an extended drying period.

Although the two Alginate resins have almost similar average molecular weights, the difference in chemical structure, due to the addition of cross-linkers, led to changes in the viscosity of the solution. Resin B was more viscous as compared to Resin A. While it was anticipated that cross-linking would benefit the processing of composites, the specific influence of this characteristic on the ultimate performance of the final composite remained uncertain.

Moreover, Resin system A at higher concentrations around $> 15\%$ was also found to be easily processable and pliable as compared to resin B.

Mechanical Effects of Processing Conditions Tension tests were conducted on samples of neat resin processed at room temperature. For each type of resin A and B, a minimum of five samples per resin content were tested. The average results of these tests are presented in Figure 5.8 and comparisons are drawn in Figure 5.9. Analysis of the test data revealed how different concentrations impact the mechanical properties of the resins. These findings, along with other observations, were instrumental in determining the optimal composition for the resin system. It should be noted, however, that variations in viscosity and water content between the two resin systems are likely to influence their processing parameters and mechanical properties.

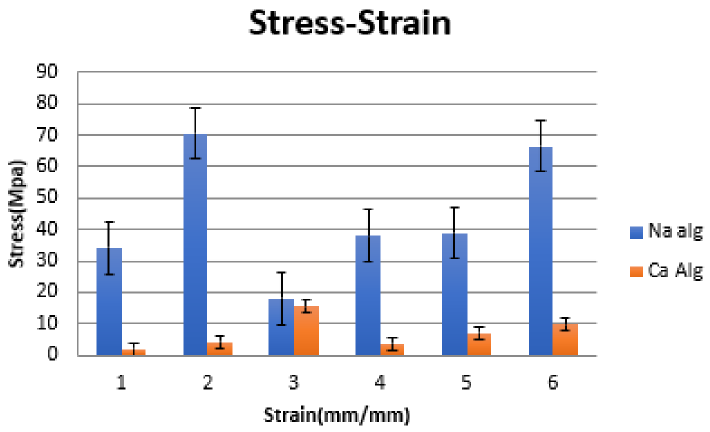


Figure 5.8: Tensile Strength Comparison

Crosslinking and Mechanical Properties: Crosslinking has been reported to increase the tensile strength and cohesion of the structure, resulting in stronger films with low water solubility. These films exhibit excellent water stability and resistance to water-induced thickness changes. Moreover, crosslinking can reduce water vapor permeability, making the films water-insoluble. Calcium alginate films were found to be stiffer when fully crosslinked, with a higher Young's modulus and lower elongation, affecting their tensile strength. The higher the concentration of Ca2+, the better water resistance and swelling behavior is observed.

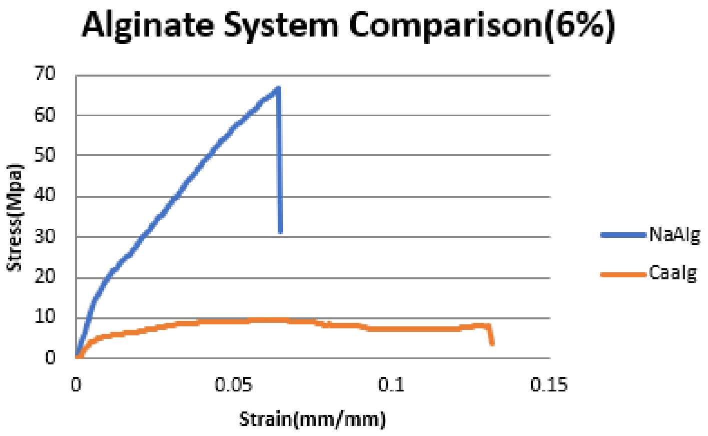


Figure 5.9: Tensile Strength 0f Alginate films 6% Conc

Mechanical Properties Comparison of Resin A and Resin B: The investigation of the two alginate polymers revealed significant differences in their mechanical properties. Resin A, without crosslinking, exhibited better mechanical properties compared to Resin B with crosslinkers. The latter showed lower average values of strength and stiffness, as well as lower elongations during mechanical testing. Although literature studies suggest that resin B at low concentrations (1-5%) should have better mechanical properties compared to resin A of the same concentration, the actual results did not align with these expectations. Porosity was observed during the drying phase of resin B with crosslinkers, which further diminished its mechanical properties.

Resin System	**Concentration (%)**	**Tensile Strength (Mpa)**	**Elongation at Break (%)**
Resin A	1	34.12	5.1
	2	70.56	3.5
	3	18.01	7.0
	4	37.93	1.5
	5	38.89	2.6
	6	66.60	6.5
Resin B	1	1.91	7.1
	2	4.25	2.1
	3	18.01	0.91
	4	3.66	1.8
	5	7.20	9.1
	6	9.64	13.2

Table 5.4: Mechanical Properties Comparison of Alginate System

Selection of Resin A for Composite Fabrication: Consequently, for higher concentrations beyond 5% for both resins, conclusions, and comparisons could not be drawn due to significant porosity and increased brittleness in resin B films. Despite the initial expectation that the lower mechanical properties of Resin A (without crosslinkers) might affect the composite performance, the actual testing showed comparable tensile strengths to those of commercial bio-resin PLA. However, the relative impact of polymer parameters derived from Resin A on the final composite performance remained unknown. Considering the ease of processing and observed mechanical properties, it was decided to use Resin A without crosslinking to fabricate the bio-composite. Furthermore, the production of composites using Resin A is anticipated to yield critical insights into how these resin properties impact composite performance. This knowledge can be expected to be beneficial in guiding future materials selection

5.1.4 Conclusion

- Sodium Alginate Viscosity and Film Formation: Water, as the primary solvent, leads to high viscosity in sodium alginate with increasing concentration. Intra-molecular electrostatic repulsion between negatively charged carboxyl groups causes extended random coil conformation. Uniform films were achieved only for low alginate concentrations (1% to 5%) in both Resin System A and B.
- Drying Time and Temperature Effects:

  Drying time for both Resin Systems A and B is around 12 hours at temperatures 80°C. Prolonged exposure to high temperatures results in brittleness, shrinkage, and compromised polymer quality. Reducing exposure time is advised for temperatures 80°C to avoid damage.

- Mechanical Properties and Porosity:

  Resin System B, expected to have better mechanical integrity, showed lower properties due to porosities and shrinkage. No conclusive comparisons for concentrations above 5% in both resin systems due to difficult film processing.

- Resin System A and B Solutions:

  Uniform solutions beyond 15% concentration are not achievable for both Resin Systems A and B. Resin System A allows thin films with higher concentrations (up to 40%) due to superior handling and pliability. Resin System B disintegrates under pressure, unsuitable for thin films at higher concentrations.

- Optimal Water Concentration and Film Processing:

  Concentrations exceeding 40% water content lead to tough, hard-to-process gel mixtures. Resin A can still be used for film-making at concentrations up to 40% with water acting as a plasticizer.

- Drying Challenges for Resin A Films:

  Drying films from Resin A in the heated press is difficult due to evaporation challenges. Need for a suitable drying technique for Resin A thin film fabrication.

- Choice of Resin for Composite Fabrication:

  Resin A without crosslinking was chosen for bio-composite fabrication due to ease of processing and observed mechanical properties. Further research and thermal tests are recommended to explore the processing window for Resin A and optimize film quality.

- Valuable Insights for Future Materials Selection:

  Findings contribute to future materials selection and development of bio-based materials:
  Preliminary observations indicated that two resins with a similar processing window exhibited different viscosities due to their distinct chemical structures and cross-linking. The viscosity played a crucial role in processing the biocomposite. While a stronger and stiffer gel formed by crosslinking with Calcium seemed advantageous, Resin A was chosen for composite processing due to its better flow properties, ease of handling, and decent mechanical properties.

Importance of understanding resin properties and behaviors for film-making and composite applications:
The impact of these characteristics on the final composite performance remained uncertain. Manufacturing composites with Resin A without crosslinking was expected to provide valuable insights into the resin properties' importance for future material selection.

Chapter 6

Composite Process Development

The project aimed to develop natural fiber-reinforced biopolymer composites as replacements for traditional synthetic materials in semi-structural applications. The limited use of biocomposites is attributed to their insufficient mechanical performance compared to materials like wood, plastics, and glass fiber-reinforced polymer (GFRP) composites.

This chapter explores the success of manufacturing composite materials by selecting constituent materials with appropriate mechanical properties and using an appropriate manufacturing procedure. fiber characteristics, such as mechanical properties, length, and orientation, greatly influence composite performance, and the matrix's ability to encapsulate and transfer load to reinforcing fibers is essential.

To enhance the properties of the Flax fiber and Alginate composite, parameters like high fiber content, good matrix impregnation, drying time, and viscosity were carefully controlled during fabrication.

For the higher concentration Alginate resin, resembling starch-based thermoplastics, procedures used for thermoplastic manufacturing were explored to design the bio-composite effectively.

6.1 fiber Treatment and Lay ups

Most of the existing research on natural fiber-reinforced biocomposites has focused on injection or compression molding techniques. These methods involve molding a thermoplastic polymer with randomly oriented fibers at high temperatures and pressures. While these processes offer quick production, the random fiber alignment limits the composite's properties. Although their specific strengths are comparable to commonly used chopped fiberglass fiber reinforced polymer (GFRP) composites, it is expected that controlled fiber alignment could surpass the properties of randomly aligned GFRPs.

Lately, manufacturers of fiber-reinforced composites have been exploring the use of natural dry-fiber preforms in structural composite applications. For this study, composite laminates were made using six plies at 0° orientation. It is essential to note that Flax fibers are susceptible to moisture absorption. Thus, the selected plies were dried in a vacuum oven for 15 minutes at 110 °C before further processing. Before drying, steps such as cutting the plies with the same orientation and optimizing their size were carried out.

The development of the composite plates involved a custom-designed composite processing method, which will be discussed in detail in subsequent chapters.

6.2 Composite Matrix Applications

The achievement of high composite performance in this study relied heavily on attaining good resin dispersion and fiber wet-out. However, it has been observed that at high fiber volume fractions (0.5), obtaining good fiber wet-out and matrix adhesion is challenging in natural fiber-reinforced composites. To address this, various resin application methods, such as thin film stacking, hand layup, powder impregnation, vacuum infusion, and solution impregnation, were investigated to determine the most effective approach for achieving optimal resin dispersion and fiber wet-out.

Throughout the process development, special attention was given to determining the maximum concentration of alginates with the lowest water content possible to impregnate the fibers. The goal was to achieve high fiber volume fractions suitable for semi-structural applications

Powder Resin It was hypothesized that the fine particulates of powdered resin would facilitate effective application and uniform distribution among the reinforcing yarns. The method of applying this powdered resin, as depicted in figure6.1, entailed evenly spreading a specific amount of powdered cellulose polymer over aligned Flax fibers. This was followed by a light application of water as a solvent, sprayed onto the mixture, ensuring the maintenance of desired fiber volume fractions. Subsequently, all components were hot-pressed to form a single composite material. The quantity of polymer used was determined by the target final weight or volume fractions of the constituents. Aiming for high mechanical properties in the composite, a high fiber volume fraction of 0.4 or more was targeted. However, achieving even distribution of the polymer matrix proved challenging at these high fiber volume fractions, where the resin fraction is relatively low.

Figure 6.1 shows a schematic illustration of this process.

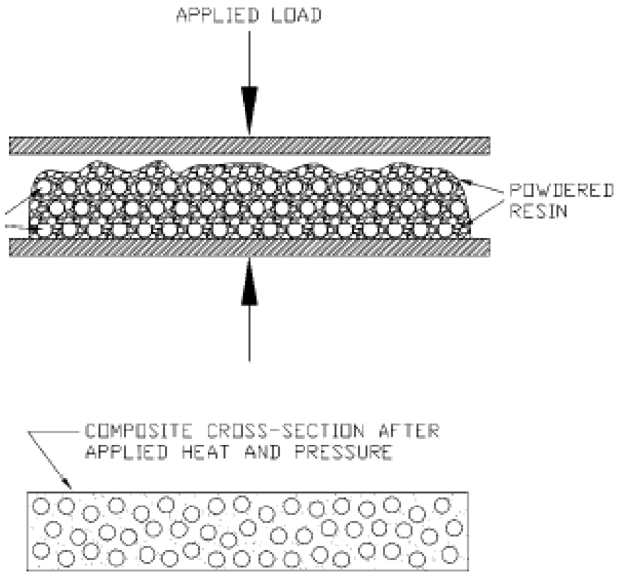


Figure 6.1: Powder resin application system Set up

To address the surface wetting issue caused by hand spraying the solvent on the dried powder, vacuum infusion of the solvent was introduced in a controlled manner. The final composites, after further heating and consolidation, exhibited variable thickness and noticeable dry patches on the surface, indicating poor fiber wet-out. Examination under an optical microscope revealed poor resin distribution and areas of inadequate fiber wet-out throughout the composite cross-section. The addition of extra powdered resin to improve resin distribution resulted in lower-than-desired fiber volume fractions. Additionally, resin clumping in certain areas caused non-uniform drying within the fabric.

The challenge of achieving uniform resin distribution resulted in uneven dispersion of fibers across the composite's cross-section. Similar difficulties were encountered in previous research, like the studies by Seavey and colleagues[27], which also used powdered resin. These studies highlighted issues in producing composites with high fiber volume fractions, evenly distributed matrix, and smooth surface finishes. The primary cause of these issues was identified as the large size of the resin particulates, which impeded their ability to uniformly fill the spaces between fiber reinforcements.

Solution Imprgegnation Due to the shortcomings of the earlier method, where clumping of alginate powder led to inadequate resin flow and resin-deficient areas, compromising adhesion, a different strategy was considered.

The focus shifted to using an appropriate amount of water as a solvent to improve the final biocomposite's quality. This led to the development of a resin solution system, designed to counteract the issues of poor resin flow and uneven dispersion. The goal was to enhance fiber alignment and ensure thorough wet-out in the produced biocomposites.

Figure 6.2 shows a schematic illustration of this process.

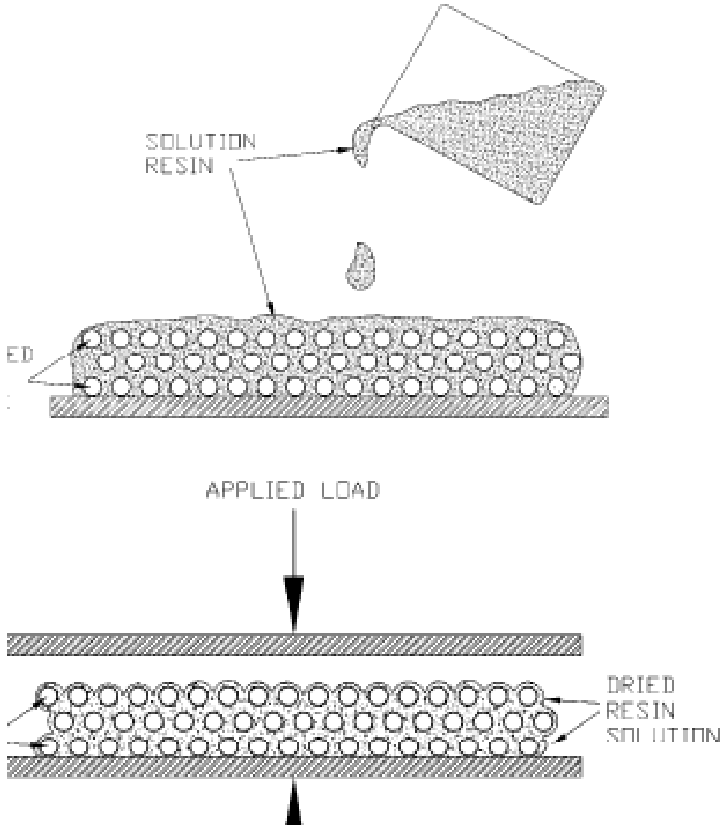


Figure 6.2: A two-step solution resin application system and composite cross-section

Polymer solutions were prepared with weight percentages ranging from 1% to 40% to determine the optimal resin concentration to water ratio. Beyond 10% weight percent, the polymer started to gel and form clumps due to very high viscosity. At lower weight percentages $< 5\%$ the polymer dissolved quickly in water, resulting in a uniform resin without air-trapped voids, but with a high water percentage, necessitating multiple applications to achieve sufficient resin coating on the fibers.

After experimentation, it was found that a 4% weight percent concentration provided the best results for impregnating the fibers, displaying good mechanical properties and clear flow properties. The process involved heating water to 50°C, adding 4% weight of dry alginate polymer, and allowing it to dissolve using a magnetic stirrer at 1200 rpm for an hour at 50°C. The prepared resin solution was poured onto aligned fiber plates and dried in a vacuum oven at 70°C until the solvent evaporated. The prepregs were then heated and pressed under a heated press for final consolidation, resulting in reinforcing fibers coated with a dried polymer matrix, similar to prepregs in traditional fiber-reinforced polymer (FRP) composites.

Through the solution resin application method, the composites demonstrated outstanding consolidation, fiber dispersion, and wet-out properties. Yet, the final composites had visible voids, primarily due to air entrapment during the processes of solvent evaporation and consolidation. To resolve this, the adoption of vacuum consolidation was contemplated, as suggested by existing literature studies. This technique could effectively diminish the void content in the final composites [163].

A notable limitation of this method was that the solvent evaporation left behind thin films of matrix on the surface, resulting in very low matrix content composites, which were insufficient for proper adhesion. Additionally, the use of a solution resin necessitated extra processing time to accommodate solvent evaporation before the heating and consolidation stages.

Thin Film Stacking To improve the amount of resin within the composite, a higher weight percentage of resin was desired, as a lower weight percent would require multiple applications of resin to achieve a sufficient coating on the fiber preforms. However, exceeding 40% weight percent led to the formation of a dark-colored dough with an unpleasant odor, making it difficult to use even with excessive shear forces.

For film preparation, a water/alginate mixture was placed in a sealed plastic beaker inside a vacuum mixer. The mixture was combined at 2000 rpm with the temperature maintained at 50 °C, containing 40% dry weight alginate polymer. Thin sheets, 0.5 to 1.0 mm thick, were pressed from this mixture for impregnation, alternating with aligned flax fibers, and heated at 95 degrees for 5 minutes. While the melt flow of the resin sheets adequately impregnated the fibers, uniform dispersion of the resin throughout the composite cross-section was poor, resulting in a defined fiber-rich and resin-rich layer.

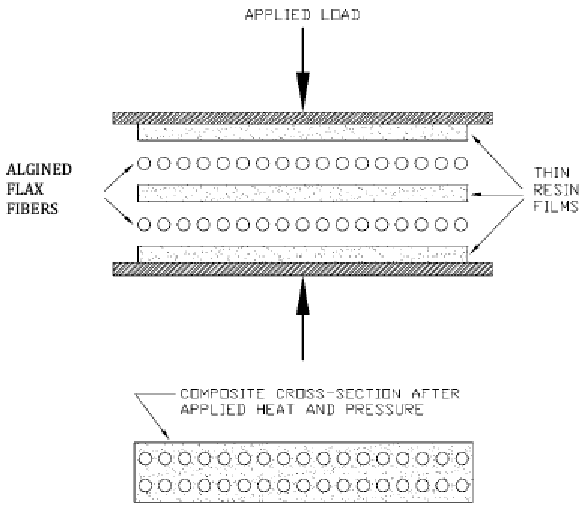


Figure 6.3: Thin film resin impregnation setup

In the figure 6.3the composite created, as depicted in the process diagram, displayed a structure with distinctly irregular layers of fiber-rich and resin-rich areas. This issue of uneven fiber distribution was also observed by Seavey and co-workers [163] in their use of a thin film stacking approach. Efforts to use slimmer resin films, aimed at reducing the resin-rich layer thickness, faced practical challenges as films thinner than 0.3 mm were tough to produce with consistency and manage. The use of resin in form of thin film or dry powder led to bio-composites with reduced fiber volume fractions. Moreover, both methods presented difficulties in evenly dispersing fibers, resulting in uneven forces exerted on the fibers during the heating and consolidation phases. Given the low melt flow of the polymer, these forces were significant and could misalign the fibers if the resin was not evenly distributed before the heating and consolidation processes.

6.2.1 Determination of processability window

To determine the ideal processing window for each resin, a careful balance of temperature, pressure, and processing time during hot-pressing was optimized. This ensured sufficient resin flow for consolidation without compromising fiber wet-out or material integrity. It is crucial to consider the potential detrimental effects of elevated thermal conditions on natural fibers' mechanical properties, as they have lower thermal stability compared to traditional reinforcements like glass fibers.[196],[65],[197] Studies on flax fibers have shown comparable outcomes, with temperatures exceeding 160°C resulting in a gradual decrease in the mechanical properties of natural fibers [67]. Brief exposure to processing temperatures at or above 200°C can also lead to substantial degradation of the fibers. Thermogravimetric analysis (TGA) of the flax fibers used in this study indicates that fiber degradation initiates around 220°C, as shown in figures: 6.4(literature) and 6.5(experimental). It is essential to take these temperature thresholds into account when determining the appropriate processing parameters to ensure optimal mechanical performance and prevent unnecessary fiber degradation during the hot-pressing process[66]

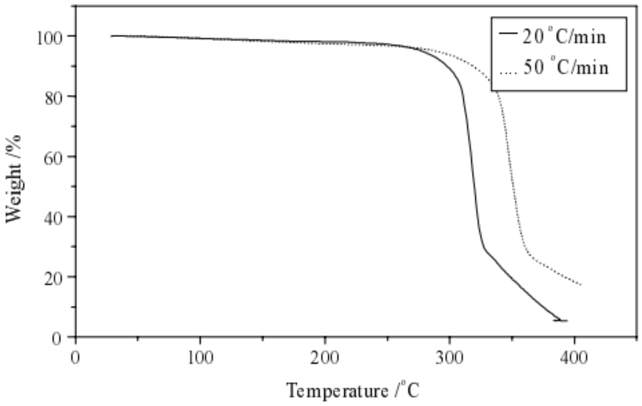


Figure 6.4: TGA of flax fibers

The processing parameters for manufacturing the composites were carefully optimized to ensure the preservation of flax fiber's mechanical properties while allowing for good resin flow. Thermal analysis indicated that the mechanical properties of flax fibers started to degrade at temperatures below those resulting in weight loss in thermal analysis. To avoid this, processing temperatures were kept below the critical threshold while still allowing for sufficient resin flow.

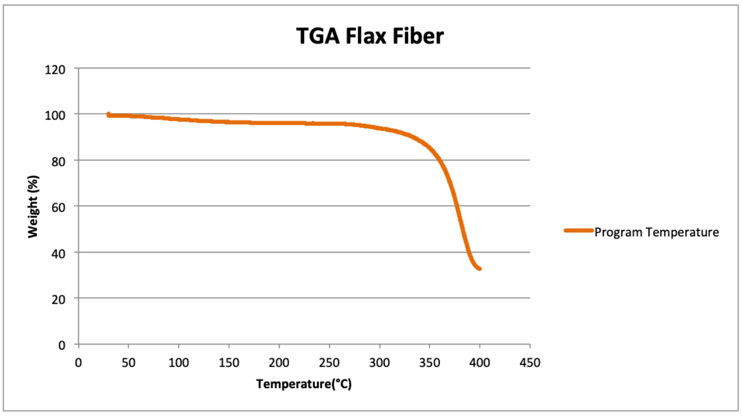


Figure 6.5: TGA Flax fiber experimental of flax fibers

The study by Wielage et al. [195] points out that the start of fiber weight loss isn't necessarily an indicator of the beginning of fiber mechanical property degradation. In their analysis of flax fibers, a significant decline in mechanical properties was observed at temperatures lower than those causing weight loss in thermal tests. The breakdown of cellulosic fibers is often attributed to the scission of cellulose chains, which can be seen as an increase in 'broken bonds'. In light of this, the processing temperatures for the hemp yarns in this study were maintained below the levels where mechanical properties might be detrimentally affected, yet high enough to ensure effective resin melt flow Literature analysis on thermal studies of Alginates suggested that degradation occurred beyond 230°C, with dehydration initiating at 100°C. Physical observation as discussed in sub-section section 5.1.1also indicated discoloration at exposure to temperatures above 75°C for extended periods. It was found that resin flow was optimal between 80-95°C, and temperatures above 80°C allowed for good melt flow without degradation while being within the recommended upper limit for short-term processing of natural fibers.

To achieve maximum resin impregnation of the reinforcing fibers without fiber crushing, it was essential to ensure a complete melt of the alginate polymer matrix before applying pressure. A method involving the use of an oven equipped with heavy plates was developed to effectively heat and facilitate impregnation, which was then succeeded by applying pressure for a predetermined period. Applying a pressure of 1.5 MPa ensured thorough melting of the resin, uniform thickness, and effective consolidation of the composite.

The composite plates were then cooled under pressure until they reached ambient temperatures. The entire alignment, resin impregnation, and consolidation process was repeated in thin layers until the desired composite thickness was achieved. After only a few repetitions, the composite thickness was sufficient for mechanical testing. The resulting cross-section images in the figure below 6.6showed good resin impregnation of the flax fiber fabric for the preliminary composites made using the optimized processing procedure.

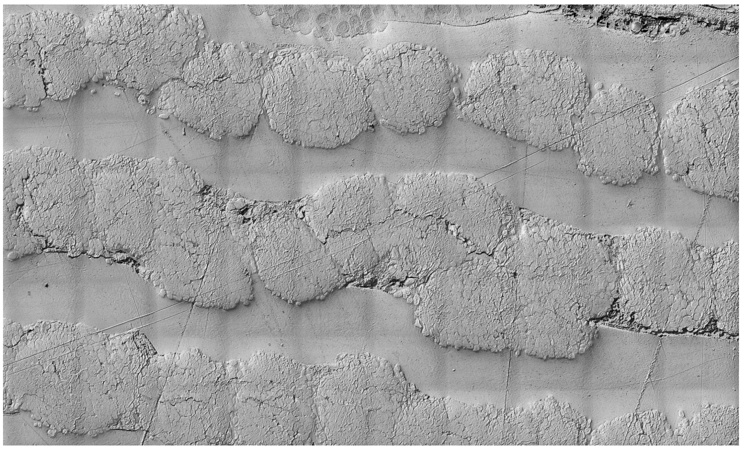


Figure 6.6: Optical Images of flax/alginate resin interface

In conclusion, the careful selection of processing parameters allowed for effective resin flow and impregnation of the fibers without compromising their mechanical properties. The resulting composites showed promising characteristics for further testing and evaluation.

6.3 Summary

Given the aforementioned limitations in the existing processes, a customized approach was essential to achieve uniform wet-out and resin dispersion while maintaining a substantial resin concentration for a favorable fiber volume ratio. The custom-designed processing procedure employed in this study integrated four composite processing techniques:

(a) Hand layup was used to prepare prepregs akin to those used in traditional fiber-reinforced composite applications, ensuring even wet-out on the fiber surface.

(b) The introduction of films via stacking allowed for a desirable fiber volume ratio.

(c) Vacuum infusion provided the platform for effective diffusion and maximum impregnation of the fibers.

(d) Vacuum drying was employed to reduce void content and facilitate solvent (water) evaporation.

(e) Hot-press consolidation was utilized to achieve overall consolidation of the composite.

Throughout the process, careful consideration was given to optimizing temperature, concentration profiles, and drying temperature to achieve the desired results

Chapter 7

SEAFLAX Composites Processing

7.1 Introduction

The search for greener materials has led to the rise of biopolymers as a promising alternative. Alginates, a bio-based biodegradable polymer, hold potential, but they face challenges due to their high viscosity, narrow processing window, and brittleness. To enhance their properties, flax non-crimp fabrics are explored as reinforcement in the composite, offering good mechanical properties and cost-effectiveness. To improve fiber-matrix adhesion, the fibers are treated and coated with alginate resin

This chapter aims to develop all-natural fiber-reinforced composites using an alginate matrix reinforced with flax non-crimp fabrics. We explore the ideal processing window by optimizing temperature, viscosity, pressure, and processing time for efficient and strong composite plates. The selection of materials and processes from previous chapters guides our approach. Preliminary manufacturing experiments inform the processing conditions.

7.2 Experimental Section

The process of sample preparation for the composite is outlined in Figure 3.10. This section will describe the step-by-step combination of all the constituents involved in developing the composite.

- Prepreg Production: The first step involves treating the non-crimp fiber to create prepregs. This treatment is done to ensure easy handling of the dry preforms and to facilitate even resin wet-out on the surface of the dry fiber preforms.
- Matrix Formulation: Resin A, which is Sodium alginate, is used as the matrix. The formulation of the matrix involves preparing Sodium alginate with varying water content. This variation in water content is

intended for different processing methods, such as infusion and film formation, which will be used to prepare the composite.

- Impregnation Stages: Stages of impregnation are introduced to ensure even wet-out of the fiber with the resin. This step is crucial to achieve a high fiber volume content in the composite.
- Evaporation of Water: After impregnation, the water content is extracted from the composite to prepare it for consolidation.
- Composite Consolidation: The final step involves consolidating the composite using a heat press once the solvent (water) has evaporated. This process ensures the complete formation and solidification of the composite.

7.2.1 Fiber Treatments/Pre-soaking

The experimental setup for preparing the flax non-crimp fabric cutouts involved the following steps:

Flax fiber Preparation: Flax fibers, with an average length of 30*30 cm and an average diameter of 98 µm, were obtained from Bcomp. The fibers were provided in roll form.

Fabric Drying: The UD flax fabrics, with a weight of 300 g/m2 and a thickness of 1.9 ± 0.1 mm, were further dried in a vacuum oven for 15 minutes at 110°C. This step was essential to remove any moisture present in the fabric.

Fabric Modification: The flax non-crimp fabric cutouts were used in their original untreated form. Additionally, some fabric cutouts were modified with resin treatments as summarized in figure 7.1.

Wet/Dry Cycling Treatment: The modified fabric cutouts underwent a wet/dry cycling treatment. This treatment involved coating the fabric with a 4% (w/w) liquid resin solution using the hand layup method. The coated fabric was then dried in an air-circulating oven at 75°C for about 15 minutes to allow the solvent to completely dry off. The fabric was further placed inside a vacuum oven with perforated steel plates to facilitate solvent (water) evaporation, enhance the handling of the dry preform, and prevent warpage of the fabric. To vary the fiber volume content and prepare modified composites, this coating and drying step was repeated a variable number of times (1-4 times) per side.

By following these steps, flax non-crimp fabric cutouts were prepared in their original untreated form and with modified resin treatments for subsequent composite fabrication. The wet/dry cycling treatment allowed us to control the fiber volume content and tailor the characteristics of the final modified composites

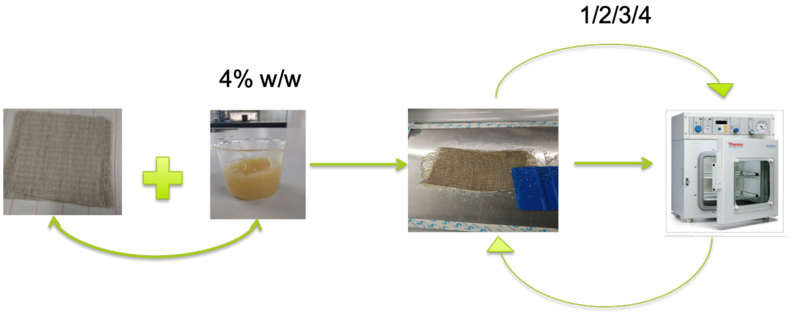


Figure 7.1: Schematic of thin film resin impregnation system and the resulting composite cross-section

7.2.2 Preparation of Matrix

The dried powdered sodium alginate was obtained from Carl Roth. This was used as a matrix. This dried powder was mixed with 1% ethanol to increase the dissolution of sodium alginate with water at 50°C. The mixture was then mixed using a magnetic stirrer on top of a hot plate at a speed of 1200 rpm, under a vacuum. The mixture was allowed to diffuse at 4°C overnight. Three different weight percentages of resins were prepared, one with 1%, another; with 4%, and a third one of weight percent 40%. This was done to cater to different impregnation steps to maintain even wet out and high fiber volume fractions.

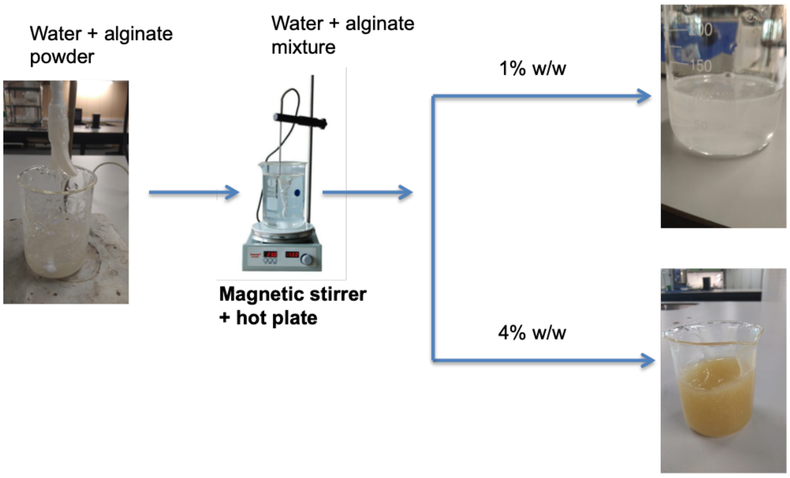


Figure 7.2: Schematic of resin preparation of varying concentration

Film Preparation A sodium alginate mixture with a 40% weight was used to produce 0.8mm thickness films in a hot plate press. The process consisted of mixing the powder and water on a hot plate to facilitate mixing. This dough was further put inside a vacuum speed mixer and mixed at 2500 rpm to eliminate any trapped bubbles. 40 grams of the wet mixture was then transferred in between two steel plates coated with a layer of marbo coat (release agent) and peel-ply. The mixture with the steel plates was heated the resin from 40-95°C for 5 minutes without pressure to allow the polymer to flow and further applying pressure for about 1 minute at 1 MPa, followed by cooling to room temperature under no pressure for another 4 mins. These films were stacked and kept inside a cool chamber at 4^oC to be used for further manufacturing the biocomposites. 8 films of 0.8mm thickness were prepared for each biocomposite sample.

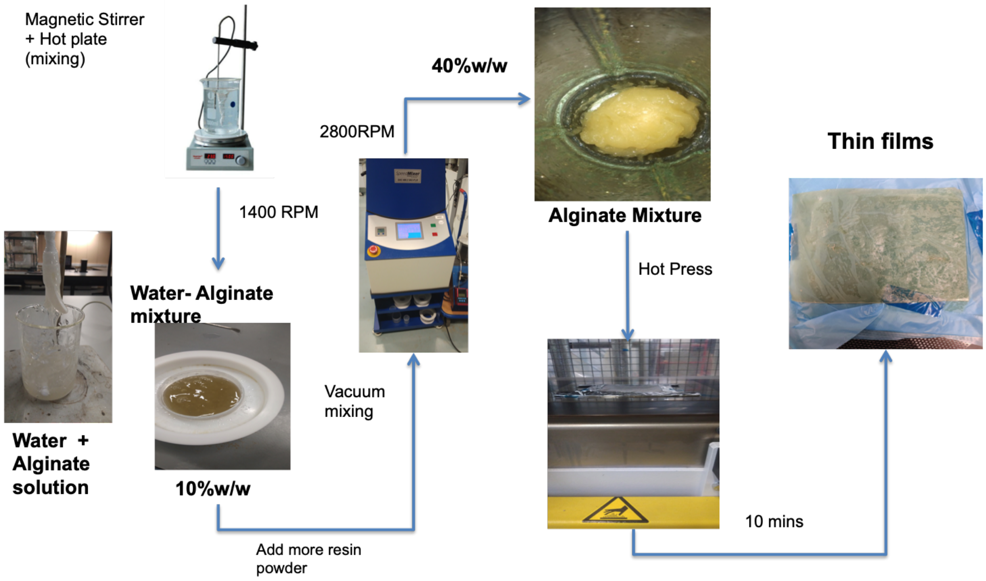


Figure 7.3: Schematic of resin preparation of varying concentration

Regardless of the use of the matrices and reinforcements, samples were named after the number of cycles used in fiber treatment and were referred as Untreated/alginate(0P-FlaAlg), 1cycle-Flax/alginate(1P-FlaAlg), 2Cycle-Flax/alginate(2P-FlaAlg), 3Cycle-Flax/alginate(3P-FlaAlg), 4cycle-flax/alginate(4P-FlaAlg).

Preparation of the composite Gravimetric measurements were conducted on the composite system at each stage throughout the composite processing procedure.

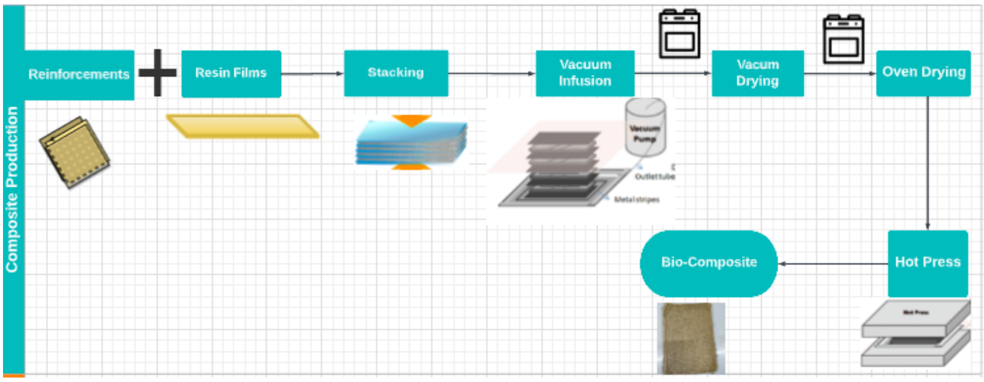


Figure 7.4: Resin preparation of varying concentration

The fabrication process for the biocomposite can be broken down into the following steps:

A) Flax fiber Preparation:

- Six layers of flax fibers, each measuring 30 × 30 cm^2, were cut.
- The flax fibers were pre-dried in a vacuum oven at 110°C for 10 minutes.

B) Coating with Alginate Resin:

- The pre-dried flax fibers were coated with a 4% weight percent viscous alginate solution.
- The coated fibers were then dried again for 15 minutes at 95°C.

C) Repeated Coating for fiber Volume Control:

- All six layers of flax fibers were coated with the resin solution on one side and immediately dried.
- To vary the fiber volume content and improve fiber handling, the coating process was repeated 0-4 times on each side until a thick resin layer coated each side of the fiber.

D) Preparation of Higher Weight Percent Films:

- Films containing 40% weight of dried alginate and water were prepared in a hot press.
- The temperature was increased from 40°C to 90°C over 10 minutes, followed by pressing at 1 Mpa for 1 minute and cooling for 4 minutes at 0 pressure to room temperature.
- Eight layers of films were prepared for each sample variation.

E) Stack Assembly for Vacuum Infusion:

- Both untreated (uncoated) and coated fibers (1-4P) were stacked with the films.
- Six layers of treated or untreated fibers were stacked together with 8 resin films on a steel plate coated with a release agent and peel ply.
- The wet composite stack was covered with another release film and an infusion mesh, and then sealed with a vacuum bag for vacuum infusion.

F) Vacuum Infusion:

- Complete vacuum was obtained using a pressure pump.
- A highly fluid alginate resin solution of 1% weight was allowed to flow through the composite stack for 5 minutes under vacuum.
- resin impregnation, excess resin was collected in a pot.

G) Vacuum Oven Curing:

- The setup was placed inside a vacuum oven and heated gradually to 95°C over 8 hours.
- Volatiles, water, and excess resin were expected to evaporate during this time.

H) Drying and Moisture Removal:

- After allowing evaporation and resin diffusion, the biocomposites were further dried in the oven at 95°C for 1 hour under perforated steel plates to remove any remaining moisture.

I) Heat Press Consolidation:

- The semi-dried biocomposites were further consolidated under a heat press at 95°C for 10 minutes under 5 MPa pressure.
- The step-by-step process ensured the proper preparation, coating, and consolidation of the biocomposite materials, resulting in the desired properties for the final product 7.5.

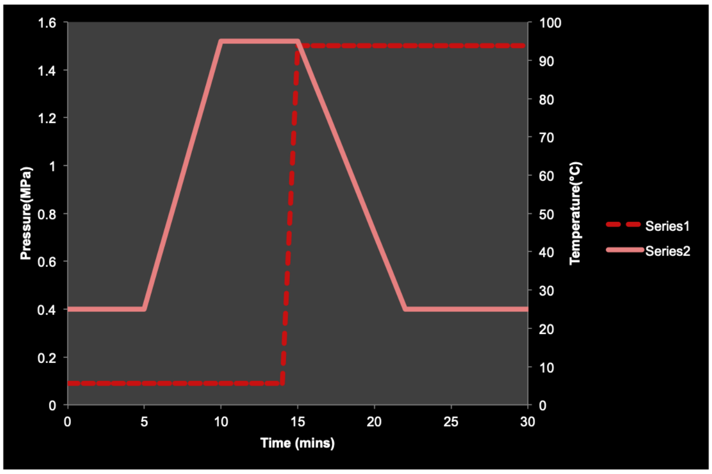


Figure 7.5: Processing Cycle Bio-Composite

7.2.3 Degree of Repeatability in Composite Manufacturing

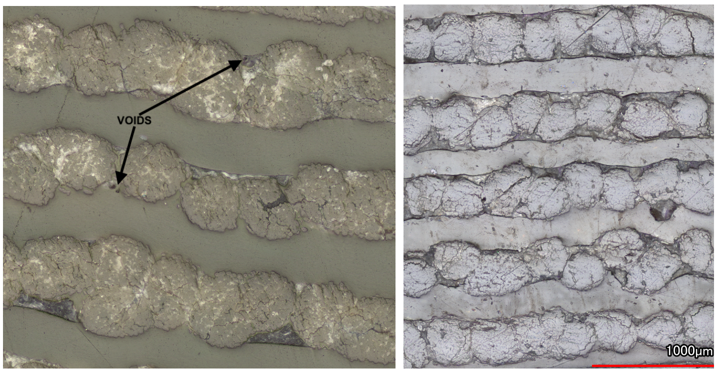
To ensure repeatability and control of the fiber and resin content ratios in the composite, a systematic bio-composite manufacturing approach was adopted. The goal was to maintain the fiber volume fractions of the composite specimens around 0.5 for comparison in subsequent mechanical, impact, and thermal characterizations.

The process involved a series of controlled experiments. At every stage of the composite processing, gravimetric measurements were systematically taken. This began with recording the weight of the dry fiber and continued with additional measurements after applying each layer of fiber and resin. The process concluded with weighing the final dried and pressed composite.

Using these weight data, the total weights of the fiber and resin in each composite sample (w_f and w_m) were established. The fiber and matrix weight fractions (W_f and W_m) were then calculated using specific equations 7.1 and 7.2. The known fiber density of 1.3 g/cm3 (referenced in section 5.1.1) and the manufacturer's specified alginate polymer density of 1.40 g/cm3 were utilized to determine the total fiber and matrix volumes within the composite samples.

Furthermore, theoretical volume fractions of the fiber and matrix (V_f and V_m) were calculated as per equations 7.3 and 7.4. It is important to recognize that these theoretical volume fractions are indicative and for comparison only, as they presuppose an ideal scenario of zero void content in the composites. However, visual inspection of both the surface and cross-section of the composites revealed voids within the matrix, indicating that the theoretical assumption of zero void content does not hold true in practice.

By systematically analyzing the weight fractions and volume fractions, the manufacturing process's repeatability and consistency in controlling the fiber and resin content ratios were assessed. This data would prove vital in the subsequent characterization of the mechanical, impact, and thermal properties of the four composite systems manufactured in the study. The assumption of no void content in the composites is contradicted by visual examination of both the surface and the cross-section of the composite. This inspection clearly reveals the presence of voids in the matrix, as shown in Figure 7.6, indicating that the assumption is not accurate.



(a) 1 pass **(b)** 4 pass

Figure 7.6: Optical pictures of the manufactured Flax/alginate composite showing voids formed during manufacturing

$$W_f = \frac{w_f}{w_c} = \frac{w_f}{w_f + w_m} \tag{7.1}$$

$$W_m = \frac{w_m}{w_c} = \frac{w_f}{w_f + w_m} \tag{7.2}$$

$$V_f = \frac{v_f}{v_c} = \frac{v_f}{v_f + v_m} \tag{7.3}$$

$$V_f = \frac{v_f}{v_c} = \frac{V_m}{v_f + v_m} \tag{7.4}$$

Weight measurements obtained during the experimental controlled manufacturing studies of the five prepared biocomposite systems are shown in table 7.1. Composite fiber and matrix weights and weight fractions were calculated for the four composite systems and the results are summarized in table 7.2, where

Layers	F.W	R+F (Wet)	R.W	R.w+F (Dry)	R+F (Wet)	R.W	R+F (Dry)	R+F (Wet)	R.W	R+F (Dry)	R+F (Wet)	R.W
	1c			2c			3c			4c		
1	14.3	45.6	31.3	14.7	45	30.3	16.9	40	23.1	16.1	41	24.9
2	14.4	45	30.6	14.7	43	28.3	15	43	28	15.8	42	26.2
3	14.3	43	28.7	16.6	42	25.4	15.7	43	27.3	16.3	42	25.7
4	13.9	43.2	29.3	15.5	43	27.5	17.2	43	25.8	19.4	41	21.6
5	14.1	43.2	29.1	14.7	43	28.3	15.6	43	27.4	16.7	42	25.3
6	14	45.2	31.2	14.7	43	28.3	15.8	43	27.2	16.9	41	24.1

Table 7.1: Summary of sample weight measurements recorded during experimental controlled manufacturing studies

Composite weight-based calculations	0p	1p	2p	3p	4p
Total fiber weight	72.8	89.5	80.45	88.7	85.55
Total matrix weight	102.2	109.45	111.95	125.05	111.95
Total composite weight	175	198.95	192.4	213.75	197.5
fiber weight fraction (Wf)	0.416	0.449	0.418	0.414	0.433
Matrix weight fraction (Wm)	0.584	0.550	0.581	0.585	0.566

Table 7.2: Weight-based calculations to determine fiber and matrix fractions in alginate biocomposite

Composite volume-based calculations	0p	1p	2p	3p	4p
Total fiber volume (cm3)*:	53.92	66.29	59.59	65.70	63.37
Total matrix volume (cm3)*:	63.85	68.36	69.92	78.10	82.41
fiber volume fraction (Vf)**	0.45	0.49	0.46	0.45	0.43
Matrix volume fraction (Vm)**	0.54	0.50	0.53	0.54	0.56

Table 7.3: Volume-based calculations to determine fiber and matrix fractions in Alginate biocomposite

$$\begin{aligned} w_f &= w_{f1} + w_{f2} - w_{ef} \\ w_m &= w_{m1} + w_{m2} \\ w_c &= w_f + w_m \\ v_f &= \frac{w_f}{\rho_f} \\ v_m &= \frac{w_m}{\rho_m} \end{aligned} \tag{7.5}$$

Composite fiber and matrix volumes, as well as their volume fractions, were also computed, with the outcomes presented in table 7.3. The aim during the manufacturing of the composite specimens was to achieve a fiber volume fraction of around 0.4. The findings from this study showed that the fiber volume fractions for all four composite systems ranged between approximately 0.4 and 0.46. This result implies that a minor adjustment in the fiber resin fraction might be necessary to more precisely meet the target fiber volume fraction of 0.4. In terms of manufacturing consistency, a comparison across the four biocomposite systems - 0P, 1P, 2P, 3P, and 4P - demonstrated a notable degree of uniformity in the production process. For an in-depth evaluation of surface quality, the dispersion of fibers, the quality of resin impregnation, and the extent of void content, sections from these composite samples were scrutinized under an optical microscope.

Visual examination of the five composite systems revealed slight variations, which were more attributable to the different melt parameters of the polymer resins than to the composite processing technique. For instance, composites produced using fiber pretreatment generally had a lower void content and exhibited better fiber wet-out compared to those made with and without fiber pretreatment.

Figure 7.6 presents optical microscope images of the composite cross-sections, which generally demonstrate effective resin impregnation of the flax fiber in composites manufactured using the described procedure. Typically, poor resin impregnation leads to a weaker fiber/matrix interface, adversely affecting the load transfer between the fiber and matrix materials and consequently diminishing the composite's properties. Interestingly, composites with a densely packed 6-ply structure displayed encouraging impregnation throughout the fiber direction.

Chapter 8

Test Methods And Composite Characterisation

8.1 Characterisation Methods

A comprehensive testing procedure was conducted on the composite systems developed using the aforementioned manufacturing process. This testing aimed to evaluate their mechanical and thermal performance, assessing their suitability as semi-structural materials. The flax fiber-reinforced alginate polymer biocomposites were subjected to an extensive characterization program, including tensile, flexural, and thermal tests. These tests were crucial to gauge the composites' potential for semi-structural applications and to understand how the physical and mechanical properties of the composite constituents influenced the overall performance.

Further, the results of these tests were not only analyzed for their practical application potential but also compared against theoretical model predictions and findings from similar biocomposite studies in existing literature. Tension and flexure tests were specifically conducted on the various flax/alginate systems to quantify their mechanical performance. As detailed in Section subsection 7.2.3 of this report, it was noted that the actual fiber volume fractions in individual composite panels slightly varied from the target 0.4, due to manufacturing variances and high void content. Consequently, the experimentally determined mechanical properties were normalized to a fiber volume fraction of 0.4 to facilitate comparison. The report includes both the actual and normalized data.

8.1.1 Mechanical characterisation techniques

Tensile testing

Tensile tests based on standards were used to characterize the resins and the solid composites. All the tests in samples containing fibers were performed in the longitudinal direction.
The samples from the solid composites were characterized in a Universal testing machine (Instron, UK), following ASTM D3039[180]. These solid composites were in the form of rectangular samples test specimens, tested with a 20kN load cell at a displacement rate of 2 mm/min. The gage length of test specimens was kept to be at 150 mm, with fibers aligned along the length, and an extensometer was used during testing with a gauge length of 75 mm. After adjusting the speed, the samples to be tested were fixed in the grip of the machine and the loading started. Before fixing the specimen to be tested into the grip, the thickness, width, and gauge length were measured. The loading of the machine was started simultaneously with a computer which was used to record the data with the help of the mechanical tensile test software. A minimum of five specimens were tested for each material and the results were then averaged to produce mean values. After the the specimen had deformed, the final length, width and thickness of the specimen was also measured. The data recorded shows the load as the specimen was deformed and the various times of deformation. This data was used to calculate the strain rate and stress, and the strain of the specimen tested was also determined from the measured initial and final length. Strength, elastic modulus, and elongation values for the composites were obtained following the procedures of ASTM D 3039 [180].

Flexural Test

Flexure tests were performed on the unidirectional Flax reinforced composites according to ASTM D 790 [47]. The tests were performed using an Instron mechanical testing machine model 5583 with a 20 kN load cell. A cross-head speed of 0.5 mm/min was chosen based on the requirements of testing procedure A of ASTM D 790. Rectangular-shaped composite specimens of approximately 120.8 mm x 12.7 mm were cut from composite panels having thicknesses varying from 2.0 -3 mm. The samples underwent 3-point bending tests with a span length of 50 mm, ensuring the necessary span-to-depth ratio of 16:1 for inducing appropriate flexural failure. A minimum of five specimens from each material type were subjected to these tests. From each test, values for flexural strength and bending modulus were acquired and subsequently averaged. The purpose of this process was to compare the flexural mechanical performance across different composite types and to assess how the material properties of the composite constituents affected the composite's performance under out-of-plane loading conditions.

8.1.2 Thermal characterisation techniques

DSC

Differential scanning calorimetry (DSC) is a useful technique to determine melting temperatures and crystallinity, as well as to reveal differences in the samples produced during processing. DSC analysis is used in Chapter 6 to study differences in the resin and to study the developed biocomposite. The DSC data were recorded on a DSC-862 (Mettler Toledo). A three-cycle DSC was performed in all the essays, under a nitrogen flow of 60 mL/min: first heating cycle from 25 °C to 180 °C at 10 °C/min with 2 min of annealing at 180 ºC; cooling cycle from 180 ºC to 25 ºC at 10 ºC/min; second heating cycle from 25 ºC to 180 ºC at 10 ºC/min. Melting temperatures (Tm) and crystallisation temperatures (Tc) were obtained as the maximum of the peaks from the endothermic and exothermic curves, respectively.

TGA

The thermal gravimetrical analysis (TGA) was used to evaluate thermal stability. The assays were performed in a TGA/SDTA 861 equipment (Mettler-Toledo). Samples of about 5.5 mg were heated from room temperature up to 400 °C with heating rates of 10°C/min under a nitrogen atmosphere at a flow rate of 60 mL/min while recording the weight loss.

8.1.3 Composition and microstructural characterization

Porosity and fiber volume fraction Gravimetric measurements with Ethanol were performed following the ASTM D792 standard [81]. The gravimetric technique involves the measure of the Archimedes density (ρethanol), the FVF density V_f (density), and the FVF porosity v_f shown below. The specimens used here were 10 mm long, approx 6 mm wide, and 3-4 mm thick. The Archimedes mass of the samples was measured immediately after immersion. contains the term that represents the mass of the composite at room humidity (about 48 % RH). The density is referred to as the ethanol (0.7877 g/cm3), while is the mass of the whole composite measured in the ethanol. The density of the composite was used in 9.10 to determine the FVF(V_f-density).

Visual measurements of the porosity The specimens used for the visual measurements were prepared by polishing and cutting the samples before the test. Polishing was performed by embedding specimens in resin pots and sanding their cross-section. Further polishing was made with a micro diamond aqueous solution. The measurement via optical microscope was performed using a Keyence confocal microscope. The magnification was large enough to detect as many porous features as possible and was also lowered (zoomed out) sufficiently to obtain an image representative of the internal structure of the specimen.

CT-scanner measurement The samples for the CT scanning were 50 mm long, 5 mm wide, and 1 mm thick. The scanner was a Nikon XTH320 with a 65 kV scanning voltage, a 135 A scanning current, a 708 ms exposure time, and an 8.26 A scanning resolution. Scanning was performed with 455 projections and 2 frames

8.2 Other Techniques

8.2.1 FTIR

The presence of interfacial bonds in the SF and composites was studied using FTIR. Using the kBr pellet, The FTIR transmittance spectra were recorded after an average of 16 scans from 4,000 to 500cm^{-1} and the resolution is 4cm^{-1}. The characteristic functional groups of fibers and Alginate were analyzed at room temperature by using a Nicolet iS-10 spectrometer (Thermo Fischer Scientific, Waltham, USA).

8.3 Summary of the Characterisation Techniques

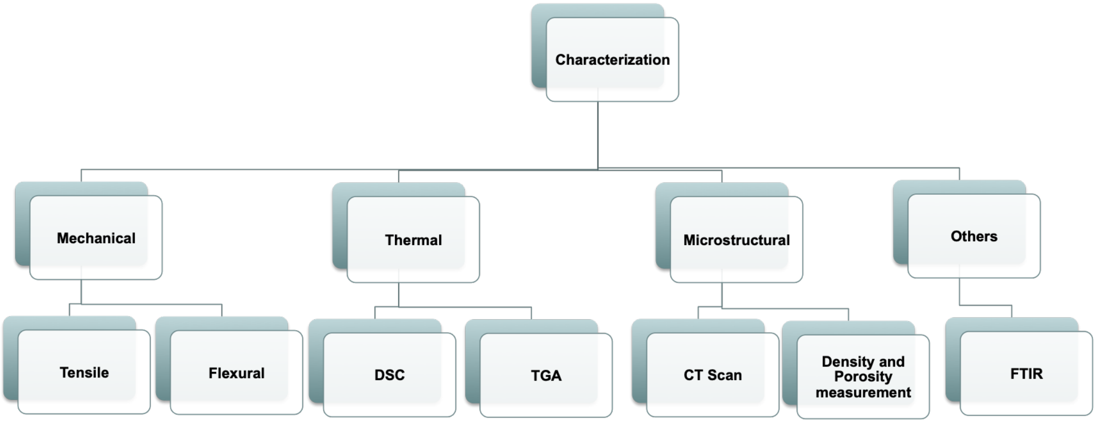


Figure 8.1: Summary of tests conducted

Chapter 9

Composite Theoretical Analysis, Results and Discussion

In this study, a series of composite systems, namely 0P, 1P, 2P, 3P, and 4P, were developed using specific manufacturing procedures and aiming for predefined constituent fractions. Each of these systems was designed as unidirectional composite laminates, featuring only six layers aligned at zero degrees. Analysis of the test data highlighted how the physical and mechanical properties of the constituents influenced the overall performance of the composites produced under these specific manufacturing conditions. Through this analysis, several critical factors essential for enhancing composite performance emerged.

9.1 Determination of Composite Properties

A crucial aspect in determining the properties of unidirectional composites is the relative proportions, either in weight or volume fractions, of the matrix and reinforcing fibers. The definitions of these constituent volume and weight fractions are detailed in 7.2.3 of this report. As previously mentioned, the weights of both fiber and matrix materials were meticulously controlled during the manufacturing process, which facilitated the calculation of their respective weight and volume fractions in the composite. Utilizing the known densities of the fiber and polymer, equation 9.1 allows for the establishment of a relationship to compute the theoretical composite density ρ_{ct} based on volume fractions, as illustrated in equation 9.3

$$w_c = w_f + w_m \tag{9.1}$$

$$\rho_c v_c = \rho_f v_f + \rho_m v_m \tag{9.2}$$

$$\rho_{ct} = \rho_f \frac{v_f}{v_c} + \rho_m * \frac{v_m}{v_c} = \rho_f V_f + \rho_m V_m \tag{9.3}$$

In these equations, the subscripts c, f, and m correspond to the composite, fiber, and matrix, respectively. The symbols w, v, and ρ stand for weight, volume, and density, respectively. Additionally, ρ_{ct} represents the theoretical density of the composite. The terms W_f, W_m, V_f, and V_m denote the weight and volume fractions of the fiber and matrix components, respectively. Furthermore, the composite's density can also be expressed in terms of the constituent weight fractions, as illustrated by the equations 9.4-9.6.

$$\frac{w_c}{\rho_{ct}} = \frac{w_f}{\rho_f} + \frac{w_m}{\rho_m} \tag{9.4}$$

$$\frac{1}{\rho_{ct}} = \frac{(\frac{w_f}{\rho_f} + \frac{w_m}{\rho_m})}{w_c} \tag{9.5}$$

$$\rho_{ct} = \frac{1}{(\frac{W_f}{\rho_f} + \frac{W_m}{\rho_m})} \tag{9.6}$$

While obtaining constituent weight fractions is more straightforward in an experimental context, theoretical analyses of composites exclusively utilize volume fractions. By employing the theoretical composite density, specific expressions (Equations 9.7 - 9.12) can be formulated. These expressions enable the conversion between weight and volume fractions, thereby facilitating the correlation of experimental composite findings with theoretical predictions.

$$W_f = \frac{\rho_f}{\rho_c} V_f \tag{9.7}$$

$$W_m = \frac{\rho_m}{\rho_c} V_m \tag{9.8}$$

and inversely,

$$V_f = \frac{\rho_c}{\rho_f} W_f \tag{9.9}$$

$$V_m = \frac{\rho_c}{\rho_m} W_m \tag{9.10}$$

In this study, the constituent fractions of the composite panels made from six flax fibers and alginate polymers were calculated to evaluate the consistency in composite manufacturing. These results are detailed in tables 7.2 and 7.3 in subsection 7.2.3. The formulas utilized for determining these fractions operate under the premise that the composite's volume is solely the sum of the fiber and matrix volumes. However, most composites contain small voids, leading to an actual volume that exceeds this theoretical calculation, which is based on the weights of the constituents. Interestingly, this increase in volume doesn't correspond to an increase in the composite's weight, resulting in a real composite density that is lower than what would be theoretically predicted using Equations 9.3- 9.6.

In these equations, the subscripts c, f, and m correspond to the composite, fiber, and matrix, respectively. The symbols w, v, and ρ stand for weight, volume, and density, respectively. Additionally, ρ_{ct} represents the theoretical density of the composite. The terms W_f, W_m, V_f,V_m denote the weight and volume fractions of the fiber and matrix components, respectively. Furthermore, the composite's density can also be expressed in terms of the constituent weight fractions, as illustrated by the equations 9.4-9.6.

$$\frac{w_c}{\rho_{ce}} = \frac{w_c - w_{ethanol}}{\rho_{ethanol}} \tag{9.11}$$

$$v_{ce} = v_f + v_m + v_v \tag{9.12}$$

$$\frac{w_c}{\rho_{ce}} = \frac{w_f + w_m}{\rho_{ct}} + V_v = \frac{w_c}{\rho_{ct}} + V_v \tag{9.13}$$

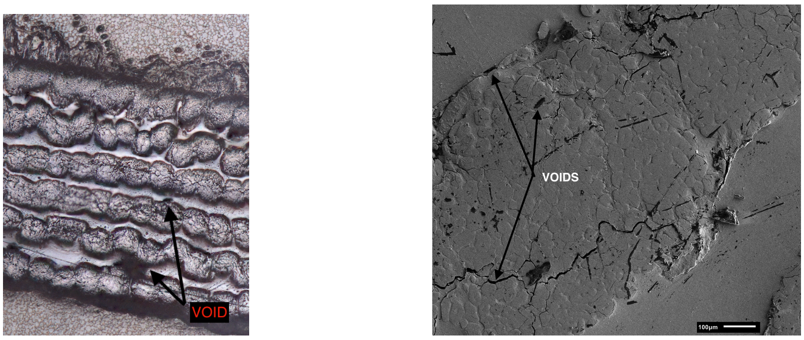
$$V_v = \frac{\rho_c t - \rho_c e}{\rho_c t} \tag{9.14}$$

$$V_v = \frac{v_v}{v_c e}, \qquad V_f e = \frac{v_f}{v_c e}, \qquad V_m e = \frac{v_m}{v_c e} \tag{9.15}$$

$$V_f e + V_m e + V_v = \frac{(v_f + v_m + v_v)}{v_c e} = 1 \tag{9.16}$$

In the composite analysis, the experimental density of the composite (ρ_{ce}) and the density of ethanol ($\rho_{ethanol}$) play key roles. The experimental volume of the composite, v_{ce}, incorporates the volume of voids, v_v. Additionally, V_v, V_{fe}, and V_{me} denote the volume fraction of voids and the experimental volume fractions of fiber and matrix, respectively.

Research, including studies by Agarwal et al. [3] and Madsen [106], has demonstrated the significant impact of void content on the mechanical properties and overall performance of composites. Even a void content as low as 1% can affect the shear and compression properties of composites, while a void content above 5% is likely to substantially degrade general composite properties. High void contents typically lead to decreased fatigue resistance, reduced shear strength, and stiffness, more variability in strength properties,



(a) Optical **(b)** SEM

Figure 9.1: Optical images of composite cross-sections showing voids in

and heightened vulnerability to water penetration and weathering [3]. Table 9.1 presents the calculated theoretical and experimental densities, along with the void volumes and corresponding void fractions for the composites in this study.

The void contents in this study's composites ranged from 4 to 8 percent across different samples. These high void contents are believed to be the result of solvent evaporation during composite processing and residual moisture in the flax fibers, which is predominantly water. Optical images of the composites' cross-sections, as shown in 9.1 a-b, reveal the presence of substantial voids in the resin layers around and between the reinforcing fibers. Furthermore, part of the void content in these composites is thought to originate from the hollow cellular structure of the flax fibers used for reinforcement (9.1).

Experimental Density and Composite Constituent Calculations					
	0p	1p	2p	3p	4p
Theoritical composite density (ρ ct) g/cm3	1.486	1.476	1.485	1.486	1.491
Exp composite density (ρ ce)(g/cm3):	1.362	1.404	1.425	1.424	1.426
Volume fraction of voids,Vv:	0.082	0.049	0.040	0.041	0.043
Exp. Volume fraction of fibers, Vfe:(vf/vce)	0.419	0.468	0.441	0.437	0.415
Exp. Volume fraction of matrix,Vme:(vm/vce)	0.497	0.482	0.518	0.520	0.540

Table 9.1: Overview physical properties of manufactured composite panels

Once the void content was determined for each composite system, adjusted experimental fiber and matrix volume fractions of the composites could be calculated from 9.15 such that the relation in equation 9.16 was satisfied. The calculated values for fiber, matrix, and void contents will be used later in this report to study the effect of voids on the composite properties as well as to back-calculate the effective fiber properties.

The properties of a composite material mainly depend on the properties and contents of the constituents as well as the orientation and distribution of them within the composite volume. The determination of composite properties can be simply and directly achieved through experimental testing. ′

For a composite with a defined material, produced through a consistent manufacturing procedure, fabrication and testing is a viable means for determining the composite properties. However, this process can be very time-consuming when trying to develop and analyze a variety of composite systems resulting from changes in constituent volumes and processing parameters. For this study, flax fibers with bio-resin derived from seaweed were investigated for developing unidirectional biocomposites. During the material characterization phase of the project, the mechanical properties of these constituent materials were determined. The constituent properties were then used in conjunction with known models to theoretically predict the properties of the flax/alginate biocomposites in this study.

The following equations 9.17-9.22 are used to predict the longitudinal composite properties for the unidirectional flax fiber-reinforced composites, where, the subscripts c, f, and m denote composite, fiber and matrix, respectively: and variables ε, σ and E represent the material strain, stress and stiffness in the direction of applied load, respectively; P, represents the load carried by the material; and A, represents the area of the material in the composite cross-section perpendicular to the loading direction. Equation 6.22, known as the rule of mixtures (ROM), indicates that the contributions of the fiber and matrix constituents to the overall composite material properties are proportional to their volume fractions.

$$\varepsilon_f = \varepsilon_m = \varepsilon_c \tag{9.17}$$

$$P_c = P_f + P_m \tag{9.18}$$

$$\sigma_c A_c = \sigma_f A_f + \sigma_m A_m \ \ or\ \sigma_c = \sigma_f \frac{A_f}{A_c} + \sigma_m \frac{A_m}{A_c} \tag{9.19}$$

$$\sigma_c = \sigma_f V_f + \sigma_m V_m \tag{9.20}$$

$$\frac{d\sigma_c}{d\varepsilon} = \frac{d\sigma_f}{d\varepsilon} V_f + \frac{d\sigma_m}{d\varepsilon} V_m \tag{9.21}$$

$$E_c = E_f V_f + E_m V_m \tag{9.22}$$

The transverse composite modulus, E_T, can be predicted using the Halpin-Tsai equation 9.23. Where η is defined as shown in Equation 9.24 and ξ is a measure of reinforcement characteristics including fiber geometry, packing geometry, and loading conditions. For circular or square fiber cross-sections ξ is generally assumed to equal 2. Predictions for the ultimate transverse tensile strength of the composite, σ_{TU} are based on the strength of materials approach (Equation9.22), where,$\sigma_m u$ represents the matrix's ultimate strength and SCF is a stress-concentration-factor defined by Equation 9.25

$$\frac{E_T}{E_m} = \frac{1 + \xi \eta V_f}{1 - \eta V_f} \tag{9.23}$$

$$\eta = \frac{(E_f/E_m) - 1}{(E_f/E_m) + \xi} \tag{9.24}$$

$$SCF = \frac{1 - V_f[1 - (E_m/E_f)]}{1 - (4V_f/\pi)^{(}1/2)[1 - (E_m/E_f]} \tag{9.25}$$

$$\sigma_{TU} = \frac{\sigma_{mu}}{SCF} \tag{9.26}$$

9.1.1 Predicted Values for Unidirectional Flax/Alginate Biocomposites

It was expected that below 20 percent fiber volume content the high fiber properties would not be efficiently used, and at fiber volume content greater than 60 percent poor fiber impregnation in the natural fiber-reinforced composites were expected to result in high voids and significant reductions in composite performance, hence all predictions were made for composites with fiber volume fractions between 0.25 and 0.55 [3], [105]. A few studies [42]-[164] on composites with unidirectional natural fiber reinforcement has, however, manufactured composites with fiber volume contents between 60 and 77 percent having very good properties. For the composite predictions, literature data sets of mechanical properties were used for the flax fiber reinforcements. This was done because of lack of equipment setup available. The translation of these unique fiber characteristics when embedded in resin to overall composite performance is not easily determined; therefore, commonly reported properties were used to predict composite performance. The values for strength and modulus of flax fibers reported in the literature, however, are 300–1500 MPa and 50–60 GPa, respectively[21][33][26]

Preliminary tensile tests showed the flax fiber reinforced composites to fail at an average strain of approximately 0.06mm/mm. However, due to the brittle nature of the polymer, it was only possible to test the matrix film until 0.1mm/mm strain. So from the polymer stress-strain diagrams, the stress in the matrix, σm, at a strain of 0.06 was determined to be 64.20Mpa and for resin a which was sodium alginate. Therefore, this matrix property was used in the prediction of composite longitudinal properties. For transverse properties, however, the maximum tensile strength of the matrix which is 70.61 Mpa used. For longitudinal and transverse predictions, an average elastic modulus of 2.45 GPa was used for the alginate polymers. It is also important to note that although the matrix is known to be an isotropic material, such that the properties are independent of the material axis, the structure of the fiber reinforcements most likely implies the fibers are a non-isotropic material. Therefore, the variation in fiber properties must be accounted for when predicting the transverse composite properties.

Predicted Longitudinal Properties

Theoretical longitudinal strength and stiffness values for the unidirectional flax-reinforced alginate polymer biocomposites manufactured in this study were based on the strength-of-materials approach shown in equations 9.22 and 9.20. Composite predictions were made using the experimentally calculated matrix strength and stiffness values and pre-assigned fiber measurements from the average of the values reported for flax fibers and experimentally calculated matrix values in table 9.2. Using Figure 9.2 and 9.3, a comparison of the composite predictions using the different fiber properties can be made in table 9.3

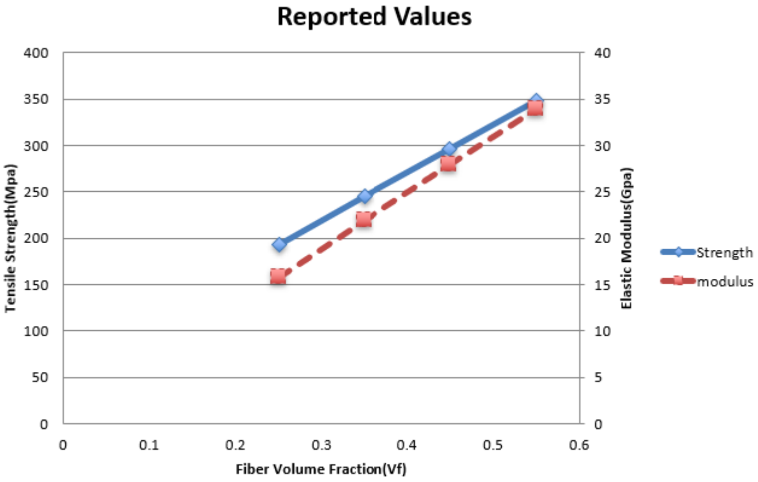


Figure 9.2: Prediction of composite strength and modulus values at varying fiber contents using ROM with flax and alginate properties reported in the literature

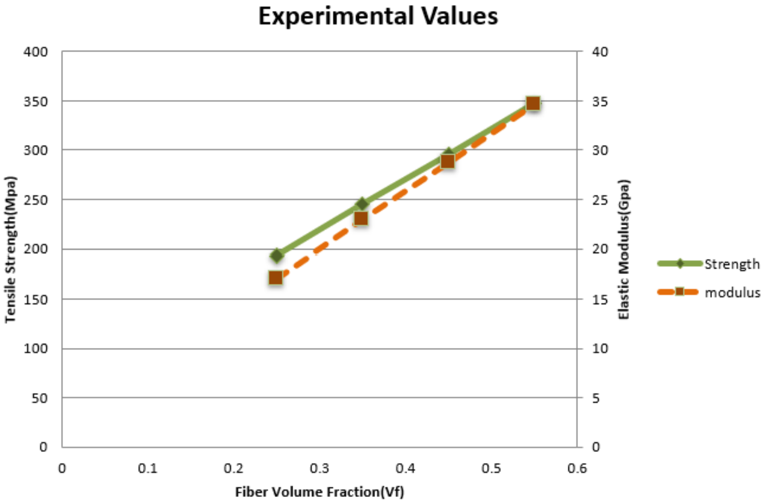


Figure 9.3: Prediction of composite strength and modulus values at varying fiber contents using ROM with experimentally determined flax fiber and alginate properties

Longitudinal	Material	Reported	Experimental	Reported	Experimental
		Modulus	*Modulus*	*Strength*	*Strength*
	Resin	0.8	2.42	65	64.20
	fiber	61	61	580	580

Table 9.2: Overview of fiber and polymer properties for computing longitudinal composite strength and modulus predictions

Longitudinal	fiber Vol. Frac(Vf)	Reported	Experimental	Reported	Experimental
		Modulus(Er)	*Modulus(Ec)*	*Strength*	*Strength()*
	0.25	15.8	17	193.7	193.1
	0.35	21.8	22.9	245.2	244.7
	0.45	27.8	28.7	296.7	296.3
	0.55	33.9	34.6	348.2	347.8

Table 9.3: Comparitive Predicted longitudinal properties with respect to varied fiber contents and dused for predictions

It can be seen that the ROM approach predicts a direct increase in composite properties with increasing fiber volume fraction. The slope of the model is also proportional to the ratio of fiber properties to matrix properties. Therefore the higher the fiber material values used in the model, the greater the slope of the relationship between composite properties and fiber volume fraction. These predictions are, however, based on material strength properties only and are not able to predict the effect of physical properties and processing characteristics on the final composite properties. For that, we must examine the results from experimental testing.

Predicted Transverse Properties

Predictions for transverse composite strength were done using the strength-of-materials approach as presented in Equation 9.25. Similarly, the predictions for the composite transverse modulus were calculated using the Halpin-Tsai (HT) equation presented in equation 9.22.The HT equation was used in replacement of the strength-of-materials approach because it is a better approximation of the exact solutions found through more rigorous mathematical predictions [3]. The polymer matrix is an isotropic material; therefore, the modulus and strength values calculated experimentally for the Alginate polymer matrix were used in the model predictions for the composite transverse properties. In contrast, the transverse strength and modulus properties of the flax fibers are not expected to equal the fiber properties in the longitudinal direction. No published mechanical properties for flax fibers in the transverse direction could be found, therefore, these details were taken from the supplier's data sheet[21].

Transverse	**Material**	**Reported**	**Experimental**	**Reported**	**Experimental**
		Modulus	*Modulus*	*Strength*	*Strength*
	Resin	0.8	2.4	65	70.6
	fiber	6.3	6.3	348	348

Table 9.4: Comparison of predicted transverse properties for biocomposites with respect to varied fiber contents and material values used for predictions

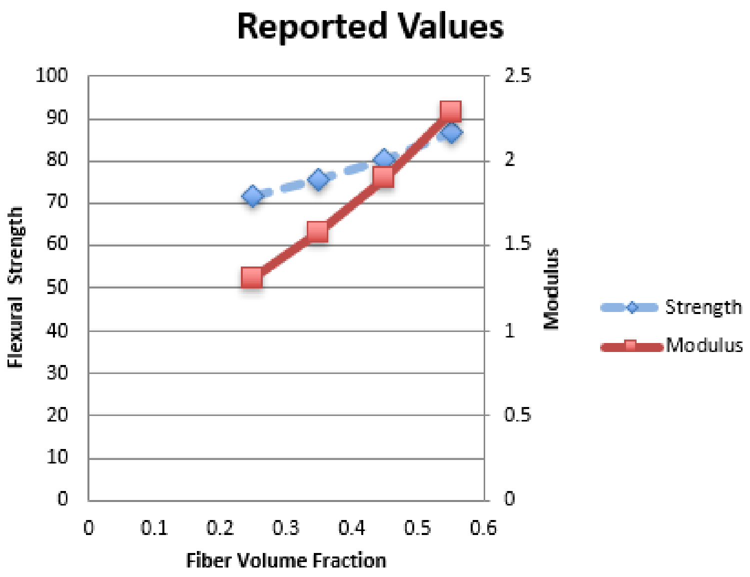


Figure 9.4: Transverse composite strength and modulus predictions using literature reported fiber properties versus composite fiber volume fraction

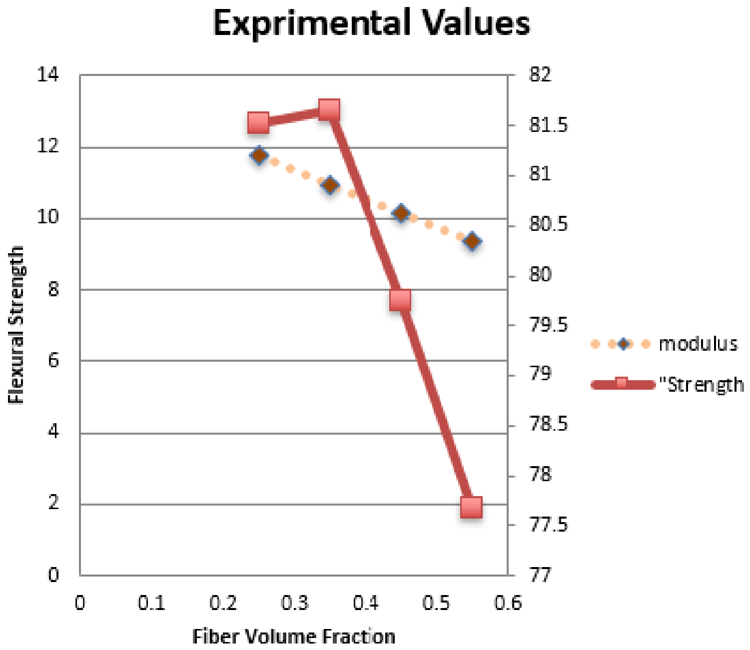


Figure 9.5: Transverse composite strength and modulus predictions using experimentally determined fiber properties versus composite fiber volume fraction

An overview of the material properties used for these predictions is outlined in 9.4 The transverse mechanical composite predictions using the experimentally determined and the literature reported properties for hemp fibers are depicted in 9.4 and 9.5, respectively.

Firstly, it should be noted that the fiber properties have a less significant effect on transverse properties than was seen in the longitudinal composite predictions. Due to the nonavailability of experimental fiber modulus values, therefore the modulus predictions based on literature-reported fiber values are expected to predict the composite transverse modulus. The HT approach predicts an increase in composite transverse modulus with increased fiber volume fraction when the fiber modulus is greater than the matrix modulus, as is the case for the literature-reported values. The strength of materials approach used to predict the composite transverse strength shows a decrease in composite properties with increasing fiber content. This negative trend is a result of an increase in the stress-concentration factor for composites with higher fiber volume fractions. It is therefore important to choose fiber volume fractions that offer a balance of transverse strength and modulus properties if loading in this direction is anticipated

9.2 Experimental Results

The four composite systems, 0P, 1P, 2P,3P, and 4P were produced in this study under a defined manufacturing procedure with a target fiber volume fraction of 0.4. The results of tensile, flexural, and thermal testing following the procedures outlined in 8.1.1 of this report are presented below

9.2.1 Mechanical Characterisation

The composites were tested in tension and flexure to quantify the mechanical performance of the various flax/Alginate systems. It was realized that the actual fiber volume fraction of the individual composite panels deviated slightly from the target value of 0.5 as a result of manufacturing and high void content. Therefore, the experimentally determined mechanical properties were normalized to a fiber volume fraction of 0.4 for comparison purposes. Both the actual and normalized data is reported.

Tension

Polymeric materials are mostly tested for mechanical properties using the tensile test. This was achieved by continuously measuring the force that deforms the test specimen. The test specimen was continuously elongated at a constant rate of extension. Stress-strain curves were developed from the data obtained from the tensile test conducted. Likewise, was obtained by using the expression in equation 9.27. The results of the tensile test are depicted in equation9.28, which illustrates the test's progression over time (in seconds).

The tensile test provides various properties of interest, including tensile strength, modulus of elasticity, and elongation at break. Tensile strength (as per equation 9.27) is determined by dividing the force causing deformation by the cross-sectional area of the specimen.

Stress-strain curves serve as crucial tools in understanding how materials behave under loading. These curves display stress on the y-axis and the corresponding strain on the x-axis.

The plasticity and elasticity of materials are key insights gained from stress-strain curves. As shown in figure 9.6, materials demonstrate varied tensile responses, ranging from brittle to strong yet non-ductile, ductile, and plastic. Brittle materials, for instance, undergo elastic deformation and possess a high Young's modulus, yet they are susceptible to shocks and tend to break easily. On the other hand, plastic materials feature regions of both elasticity and plasticity, offering ease of deformation and reduced sensitivity to flaws and shocks.

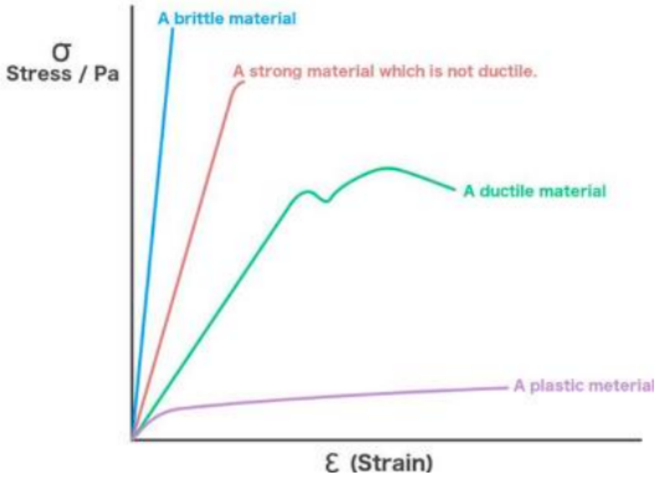


Figure 9.6: Stress-Strain for different materials

A brittle material typically shows elastic deformation and possesses a high Young's modulus. Such materials can withstand a certain level of deformation but are highly susceptible to breaking under shock. In contrast, a strong, non-ductile material exhibits high elasticity but limited plasticity. Materials known for their plasticity have a small elastic region but a larger plastic region, making them easily deformable and less sensitive to flaws and shocks. Materials that are both strong and tough and exhibit ductility, combine a high Young's modulus with plastic deformation capabilities. These materials effectively resist deformation and shocks and are less prone to flaws and deflections. Our composite material, based on the observed curves, tends to exhibit characteristics similar to brittle materials, being strong yet lacking in ductility.

The mechanical behavior of most fiber-reinforced composites is affected by various factors, including the volume fraction and the quality of the interface adhesion between the fiber and the matrix. The selection of fiber and matrix materials is crucial. We explored how the content of particulates/-fibers and their surface modifications impact the tensile properties of these biocomposites.

$$TensileStrength(stress) = F/A_0 \tag{9.27}$$

$$TensileStrain = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0} \tag{9.28}$$

Where F is the load applied, A_0. is the initial area of the test specimen, L is the instantaneous length of the test specimen at a particular load and time and L_0 is the gage length of the test specimen. The area of the test specimen was calculated from the width and thickness of the test specimen. This was calculated from the various widths, thicknesses, gage lengths, and final lengths of the individual test samples.

The mechanical properties of most fiber-reinforced composites are affected by the volume fraction and kind of interfacial adhesion between fiber and matrix. Most times also, the kind of fiber and matrix (polymer) used affects the quality of the interfacial bonding. The effects of particulate/fiber content and surface modification on the tensile properties of the biocomposites fabricated.

In our study, tension tests were carried out on five composite material systems following the outlined procedure in section subsection 8.1.1. The setup is shown below in figure 9.7

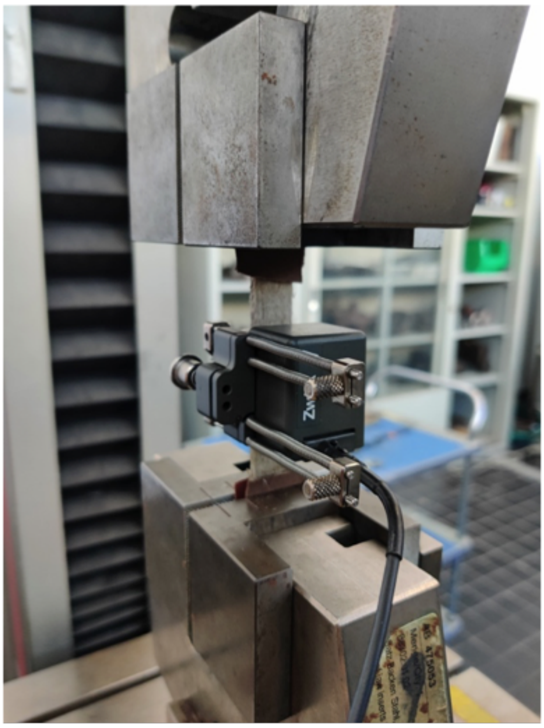


Figure 9.7: Tensile setup for testing samples

Table 9.5 shows a summary of the original and normalized axial tensile properties of the composites calculated according to the specifications of ASTM D3039[180]. Additionally, a comparison between the mean tensile strengths, stiffness, and elongation at failure of the normalized composite systems are shown in figures 9.8-9.9 below, respectively.

			Actual Properties			Normalised Properties		
Tensile	**Composite Sample**	**Vf**	**Tensile Strength(Mpa)**	**Tensile Modulus (Gpa)**	**Elongation at Break (%)**	**Tensile Strength (Mpa)**	**Tensile Modulus (Gpa)**	**Elongation at Break (%)**
	0p	0.42	149.76	2.52	6.40	142.65	2.40	6.09
	1p	0.47	219.77	5.70	8.77	187.80	4.87	7.49
	2p	0.44	180.03	4.44	8.02	163.10	4.02	7.27
	3p	0.43	202.00	6.12	5.30	184.56	5.59	4.84
	4p	0.41	198.37	6.64	6.2	190.90	6.39	5.96

Table 9.5: Actual and normalized (Vf = 0.4) tensile properties for unidirectional Flax/SA

For the flax/alginate composite systems with an average fiber volume fraction of 0.44, the average longitudinal tensile strength ranged from 149 MPa to 219 MPa, the composite stiffness from 2.5 GPa to 6.6 GPa, and the ultimate elongation ranged from 6% to 23%. These properties were compared with results from other studies on unidirectional-aligned natural fiber composites in the literature.[105],[29]-[158].

Composite Materials (fiber/matrix)	Vf	Tensile Strength (MPa)	Tensile Modulus (GPa)	Norm. Tensile Strength (MPa)	Norm. Tensile Modulus (GPa)	Ref
Flax/Alginate	0.43	202	6.12	184.56	5.59	*Current Study
Hemp/polyester	0.4	148	14	185	18	[[158]]
Flax/VE	0.37	248	24	335	32	[69]
Flax/Epoxy	0.47	280	39	298	41	[127]
Jute/PLA	0.38	78	8.5	103	11	[93]

Table 9.6: Actual and normalized (Vf = 0.5) tensile properties of published values for unidirectional natural fiber-reinforced composites

By normalizing the data from these studies to represent composites with equivalent fiber volume fractions, it is seen that the tensile properties of the composites in this study are comparable to a majority of the properties reported for these composite systems in table9.6. In addition, the composite in this study has the advantage of being made with polymers derived from biodegradable matrix as well as natural fiber reinforcements, making them more environmentally friendly.

Figure 9.8 shows the relationships between fiber content and tensile strength. From this figure, it can be seen that tensile strength has a linear relationship with increasing fiber content. The tensile strengths were 219 MPa, in the samples with a fiber fraction of 47%. The untreated fibers for sure have the least tensile strength with a fiber volume content of 42%, so conclusively, it can be inferred that soaking the fibers and making prepregs using the resin does lead to an increase in the strength of the used flax fibers. However, further increasing the number of treatment cycles leads to an increase in the matrix content. As a result, the fiber content decreases further, leading to decreased tensile strength. However, with 43.8%(3pass cycle) volume fraction, the strength has shown an un-predicted increase in the value. This is assumed to be due to processing influence. Nonetheless, with an increase in matrix content, we induce more voids and fiber contacts caused by an insufficient amount of resin observed in the specimen. Therefore, the fiber content used for fabricating flax fiber reinforced composites should be kept below 70% and matrix content should be kept well below 30-35% for better adhesion.

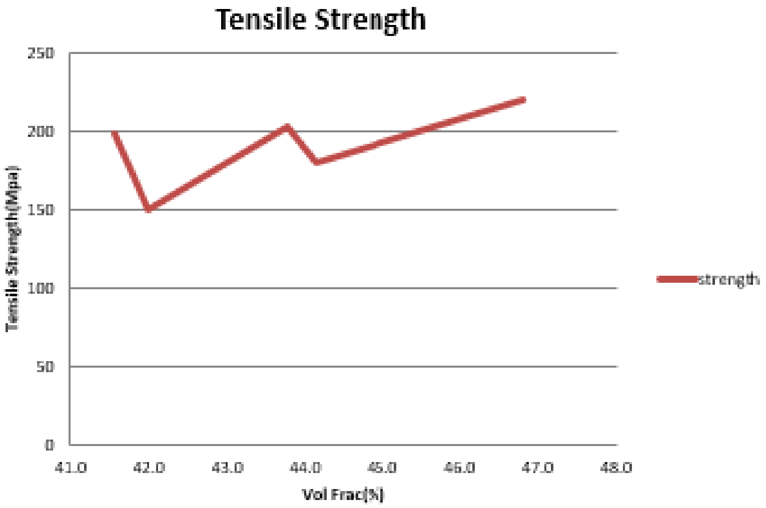


Figure 9.8: Graph of the relationship between tensile strength and Vol. Frac

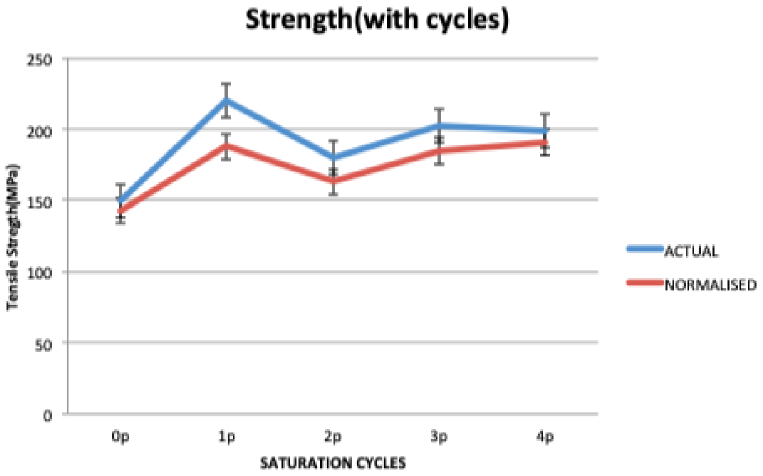


Figure 9.9: Graph of the relationship between tensile strength and passes

As expected, the higher the flax fiber content, the stiffness values would increase leading to a decrease in elongation at break. Increased tensile strength was observed significantly with treating the fibers after one cycle leading to fiber content up to 47 wt %, after which it likely plateaued, due to reduced stress transfer across the fiber-matrix interface at higher fiber loading

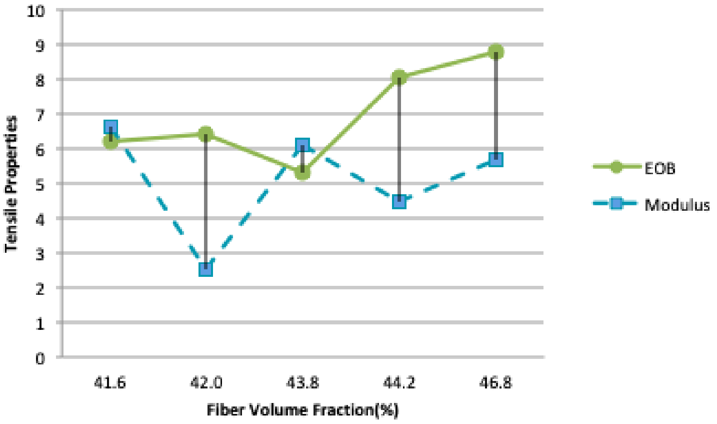


Figure 9.10: Trend of tensile properties

This behavior is very common to other similar bio-composite systems encountered in literature. By increasing the number of saturation cycles, the fiber content decreased moreover poor wetting of the fibers with the matrix could be present leading to reduced stress transfer across the fiber-matrix interface with consequent reduction of the tensile strength The alginate treatment of flax fibers has led to an increase in the tensile properties as compared to the untreated fibers.

The tensile failure behavior observed for the composite specimens varied depending on the number of passes which further was dependent on the degree of adhesion between the fiber and matrix. Preliminary visual inspection of samples showed with increasing passes, tensile failure by fiber pull out and the fracture was commonly exhibited across samples of higher saturation passes 9.11. In the sample without any pre-saturation treatment, failure mostly occurred by delamination.

Figure 9.11: Failure Modes in Samples

Further fracture surface inspection of tensile specimens could have provided valuable information about composite failure modes, such as delamination and fiber breakage, which can further lead to the study of the effect of fiber-matrix adhesion in detail.

By normalizing the data from these studies to represent composites with equivalent fiber volume fractions, it is seen that the tensile properties of the composites in this study are comparable to a majority of the properties reported for these composite systems are mentioned in table9.6.In addition, the composite in this study has the advantage of being made with polymers derived from seaweed biomass as well as natural fiber reinforcements, making them more environmentally friendly.

Flexural

Composite samples were tested in 3-point bending following the procedure outlined in subsection 8.1.1 of this report. Test results were analyzed according to ASTM D790 [179] to determine the bending strength and stiffness values for each composite system at a varied fiber volume fraction of 0.41-.47. The actual and normalized (Vf = 0.4) flexural properties for the composite in this study are shown in tables 9.7 and 9.8.

Figure 9.12: Processing Cycle Bio-Composite

It can be seen that the experimentally determined composites flexural properties for most of the samples are lower than the tensile properties reported in the previous section of this report. Maximum flexural strength 150.90 MPa in longitudinal direction and 50.11 MPa in transverse direction for a 4pass composite sample. The flexural properties of the other three composite systems were significantly lower values. However, modulus values are higher than tensile modulus for samples that were pre-soaked with alginate resin two or more times. With modulus values of 9.44Gpa(longitudinal)and approximately 1.83GPa(transverse) direction, respectively. The composite stiffness depends on the fiber and matrix properties, fiber content, and its dispersion inside the matrix. In the case of the flexural modulus, the quality of the interface between polymer and matrix has little impact as it has been observed before for different thermoplastic-reinforced composites. Moreover, it can be observed that the flexural strength, when calculated in the transverse direction, the sample with the lowest void content(2p,vf-0.44,Vv-) yields the highest value-56Mpa. Numerous studies in the literature have focused on assessing the flexural properties of unidirectional natural fiber-reinforced composites. While a majority of these studies have examined composite systems featuring conventional petroleum-based thermosetting or thermoplastic polymers, and some have incorporated coupling agents or additives to enhance their properties, it is valuable to compare the reported data with the findings obtained for the flax/alginate composites investigated in this study.

Flexural (Longitudinal)	**Composite sample**	**fiber vol frac (Vf)**	**Actual Properties**				**Normalised Properties**			
			Flexural Strength (Mpa)		**Flexural Modulus (Gpa)**		**Flexural Strength (Mpa)**		**Flexural Modulus (Gpa)**	
			Average	**Std.Dev (FS)**	**Average**	**Std.Dev (FM)**	**Average**	**Std. Dev**	**Average**	**Std. Dev**
	0p	0.42	20.08	4.66	0.40	0.17	19.13	4.44	0.38	0.16
	1p	0.47	69.52	22.20	3.70	3.00	59.41	18.97	3.16	2.57
	2p	0.44	88.17	13.02	6.63	1.87	79.88	11.80	6.012	1.69
	3p	0.43	96.76	10.26	6.11	1.42	88.41	9.38	5.58	1.30
	4p	0.41	150.90	19.73	9.44	0.88	145.21	18.99	9.088	0.85

Table 9.7: Actual and normalized (Vf = 0.4) flexural properties for unidirectional Flax/SA

Flexural (transverse)	**Composite sample**	**fiber vol frac (Vf)**	**Actual Properties**				**Normalised Properties**			
			Flexural Strength (Mpa)		**Flexural Modulus (Gpa)**		**Flexural Strength (Mpa)**		**Flexural Modulus (Gpa)**	
			Average	**Std.dev(FS)**	**Average**	**std dev (FM)**	**average**	**Std. Dev**	**Average**	**Std. Dev**
	0p	0.42	9.30	9.30	0.02	0.027	8.86	8.86	0.02	0.02
	1p	0.46	21.08	10.06	0.68	0.50	18.01	8.59	0.58	0.43
	2p	0.44	56.20	25.10	1.57	0.29	50.92	22.74	1.42	0.26
	3p	0.43	40.09	4.32	1.58	0.11	36.62	3.95	1.44	0.10
	4p	0.41	50.11	2.78	1.83	0.13	48.23	2.67	1.76	0.13

Table 9.8: Actual and normalized (Vf = 0.4) flexural properties (through-thickness) for unidirectional Flax/SA

The flexural strength and stiffness properties for unidirectional natural fiber-reinforced composites with thermoplastic polymers vary greatly depending on the fiber and matrix constituent properties, method of composite manufacture, and resulting in fiber volume fraction. Pal et al. [129] reported flexural properties of several unidirectional-aligned polyester composites, including those with jute, sisal, and ramie fiber reinforcements.

The composites, which featured reinforcement with ramie, sisal, and jute fibers, exhibited significant variations in their respective fiber volume fractions: 0.62, 0.64, and 0.68. Consequently, these composite materials demonstrated high levels of flexural strength, measuring at 197 MPa, 250 MPa, and 280 MPa, along with corresponding bending stiffness values of 43 GPa, 49 GPa, and 41 GPa, respectively. In a separate study conducted by Bledzki et al., hemp and flax yarn-reinforced polypropylene (PP) composites were explored.[29], hemp and flax yarn-reinforced polypropylene (PP) composites were created by alternating filament-wound fiber layers and resin films, followed by hot pressing. The resulting hemp/PP and flax/PP composites had fiber volume fractions ranging from 0.3 to 0.35 and exhibited flexural strengths of 125 MPa and 149 MPa, respectively. Khondker et al.[93] reported flexural strength and stiffness values for jute yarn-reinforced composites in polypropylene (PP) and polylactic acid (PLA) matrices. For composites with a PP matrix and a fiber volume fraction of 0.21, the reported bending strength and stiffness properties were 122 MPa and 9.1 GPa, respectively. Jute/PLA composites, with a fiber volume fraction of 0.22, exhibited lower flexural strength and stiffness properties of 85 MPa and 7 GPa, respectively. Most recently, Angelov et al.[7] reported results for unidirectional flax yarn-reinforced PP composites produced through pultrusion followed by compression molding. These composites had fiber volume fractions of 0.4 and demonstrated flexural strength and stiffness properties of 135 MPa and 11 GPa, respectively.

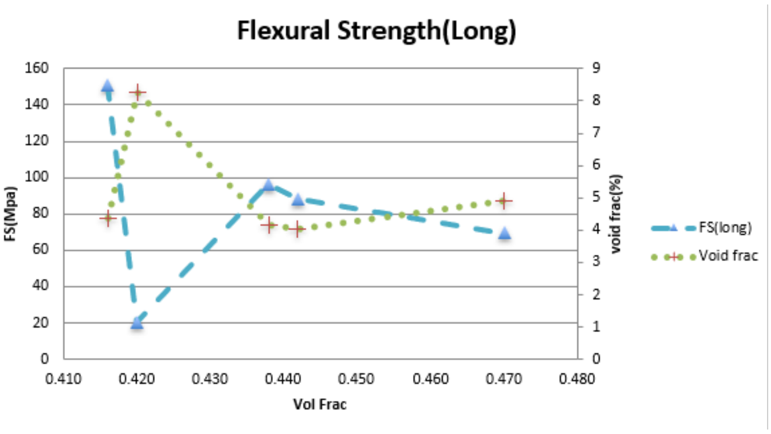


Figure 9.13: Flexural Properties comparison in-plane direction: Flexural Strength

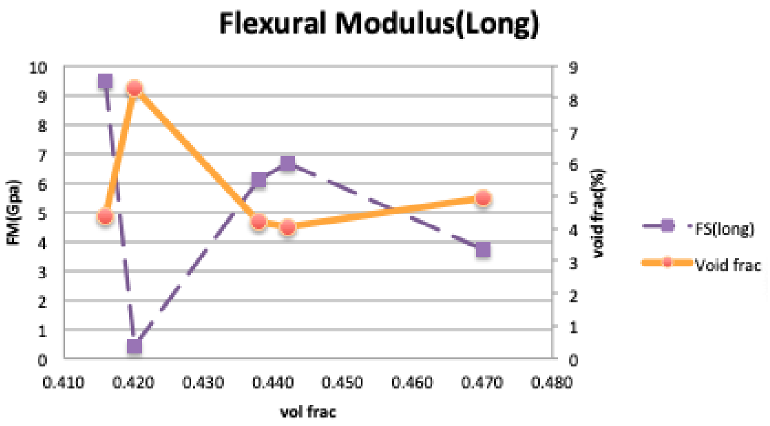


Figure 9.14: Flexural Properties comparison in-plane direction: Flexural Modulus

Studies focusing on natural fiber-reinforced composites utilizing thermosetting polymers as the matrix have reported significantly higher flexural properties. These findings suggest that if bending strength and stiffness are the primary concerns, more brittle and highly cross-linked thermosetting polymers should be employed in biocomposites. Goutianos et al. conducted several studies on unidirectional flax and jute fiber-reinforced composites. The reported flexural strength and stiffness properties for flax yarn-reinforced composites with an unsaturated polyester (UPE) matrix, produced by hand lay-up with a fiber volume fraction of 0.28, were 170 MPa and 15 GPa, respectively. Using the same materials but with a fiber volume fraction of 0.31 and employing the resin transfer molding (RTM) process, slightly higher flexural strength and stiffness properties of 198 MPa and 17 GPa, respectively, were achieved.[69]

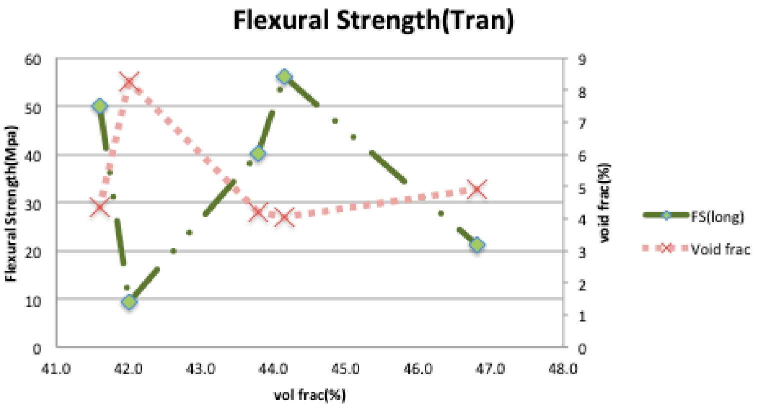


Figure 9.15: Flexural Properties comparison through-thickness direction: Flexural Strength

Composite Materials (fiber/matrix)	Vf	Flexural strength (MPa)	Bending modulus (GPa)	Norm. Flexural strength (MPa)	Norm Bending modulus (GPa)	Ref
Flax/Alginate	0.43	40.0	1.5	45.7	1.80	*Current Study
Hemp/CAB	0.51	133	22	129	21	[141]
Flax/PP	0.	135	11	169	14	[7]
Flax/Polyester	0.31	198	17	319	27	[69]
Jute/PLA	0.21	85	7	202	17	[93]

Table 9.9: Actual and normalized (Vf = 0.5) tensile properties of published values for unidirectional natural fiber-reinforced composites

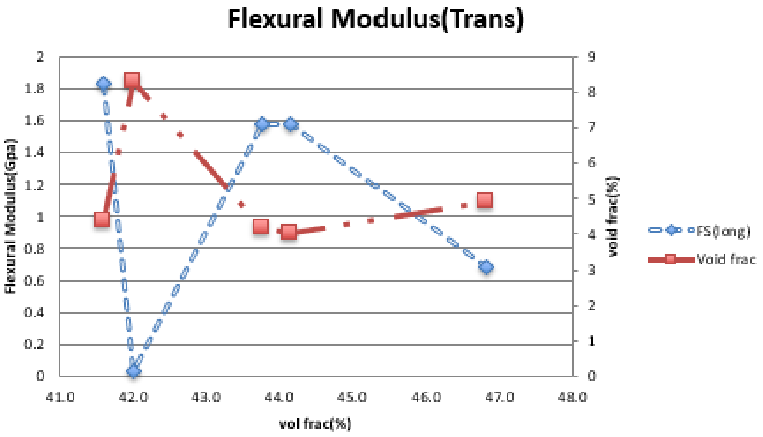


Figure 9.16: Flexural Properties comparison through thickness direction:Flexural Modulus

Bledzki et al.[29] reported flexural strength and stiffness values of 228 MPa and 12 GPa, respectively, for filament-wound hemp-reinforced epoxy composites with a fiber volume fraction of 0.35. Additionally, Netravalli [123] reported flexural strength and stiffness values of 225 MPa and 12 GPa, respectively, for consolidated unidirectional composites with fiber volume fractions up to 0.65, made from long ramie fiber and a soy-based thermosetting polymer. This study indicates that with further advancements in biobased thermosetting resins, natural fiber composites could achieve significantly higher performance levels.

9.2.2 Thermal Characterisation

TGA

Thermogravimetric analysis was performed on the flax fibers, alginate polymers, and composites, according to the procedure outlined in subsection 8.1.1 of this report, to determine their respective degradation temperatures as well as water contents. The percent weight loss of the samples plotted concerning temperature is shown in figures 9.17 and 9.18 .

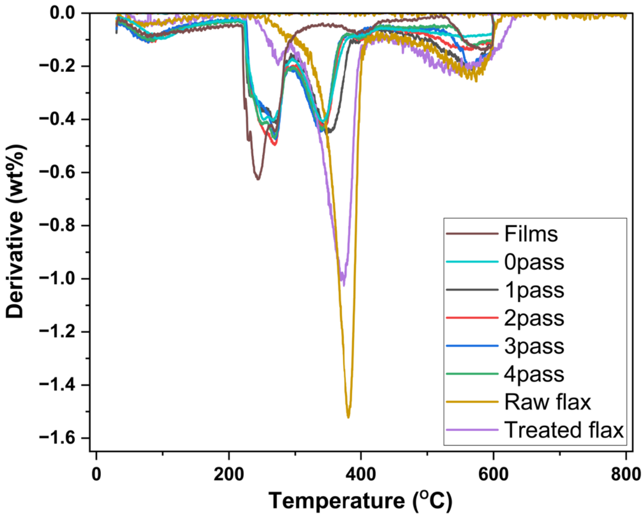


Figure 9.17: DTG of Flax Alginate composite.

The thermogram for pure sodium alginate shows thermogravimetric effects, with the first being a 5% mass loss at starting at 65 °C due to the dehydration of water linked by hydrogen bridges (adsorbed). The energy of bonding between water molecules and the sorption sites is higher than the energy that holds the molecules of pure water[131]. The second weight loss of about 43% was observed at 230°C; this weight loss is typically associated with the destruction of glycosidic bonds [104], [171] and corresponds to alginate fragmentation due to chain breakage. Further thermogravimetric effect above 500°C was observed. It could be due to the fragments and monomeric units of the alginate getting converted into Na2CO3. It was expected that the degradation temperature of the constituent samples would be very close as both the fiber and polymers are polysaccharides. The degradation temperature of the pure alginate resin was, however, much lower than for the flax fiber and composites suggesting a more irregular molecular structure in the Alginate polymers as compared to the fibers. Since the solvent used was water, its effect combined with the hydrophilic nature of these fibers is well known and therefore, the presence of moisture in the composites and its effect on composite properties should be further investigated. Flax fiber has three stages of degradation and weight loss against temperature. The initial weight loss of flax fiber is around 120–220°C and it is due to the evaporation of water molecules and wax content. Efficient drying is required for the weight loss of fiber at this stage. Meanwhile, the thermal stability of the flax fiber has started to reduce at 160°C. The second stage of degradation is around 345–380°C. It is mainly due to the degradation of lignin and hemicelluloses of the flax fiber. After 380°C, the quick decomposition of the flax fiber is found due to the complete depolymerization of the cellulose, hemicellulose, and lignin components. The final decomposition and complete weight loss of the flax fiber occurred at 578 °C.

Initially, all the components including fiber, matrix, and the designed composites, undergo a weight loss, indicating the presence of water in all the samples.

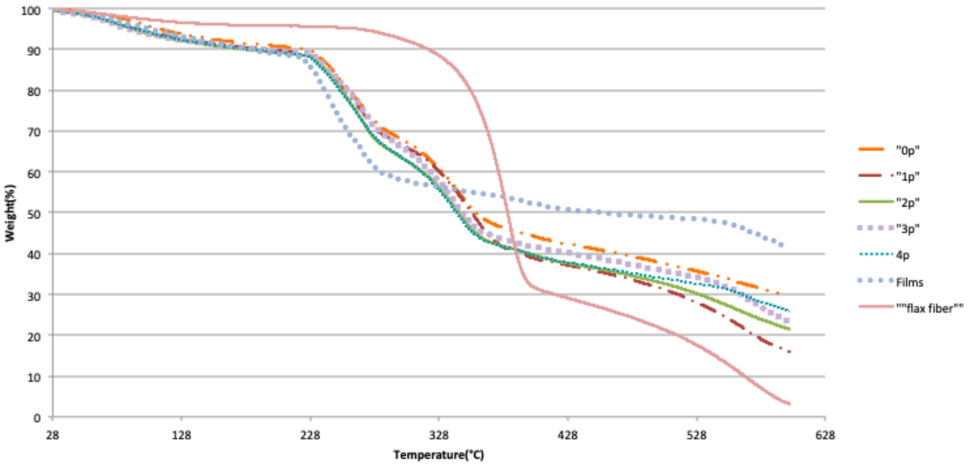


Figure 9.18: TGA weight loss curve showing the temperature-dependent degradation profiles

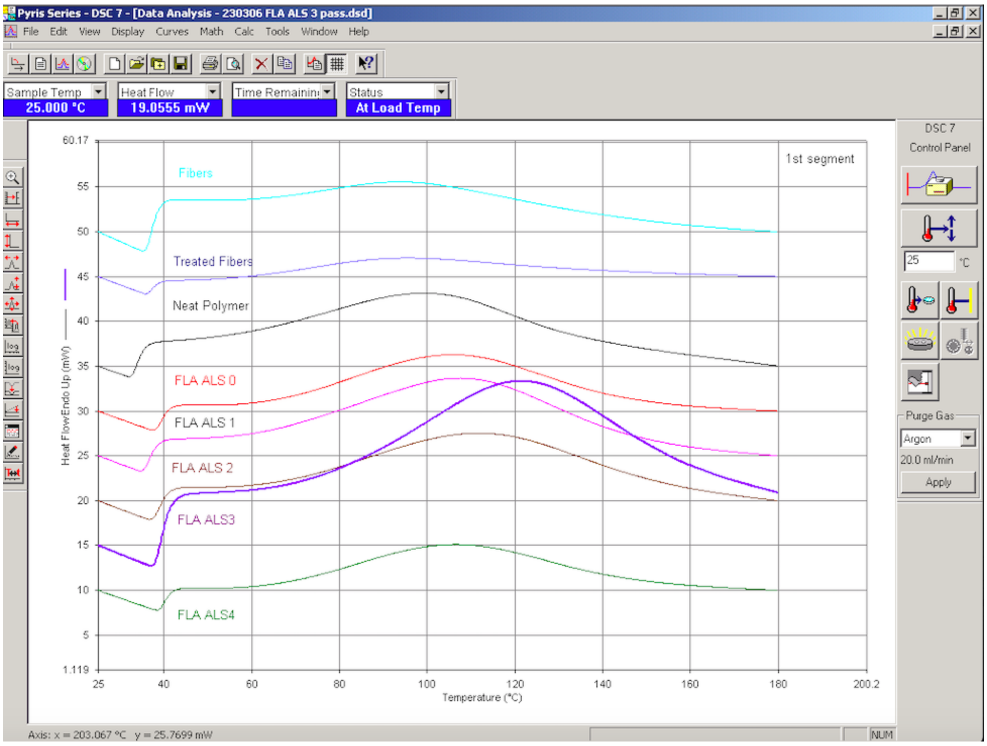
Compared to pure Alginate films, the thermal stability of the composites has increased, however, it can also be seen that in the case of alginate-treated composites, the temperature of the major peak increases —. It indicates that the thermal stability of the composites is increased by the addition of alginate-treated fibers. Flax/Alginate composite also displays two mass loss steps, the first step occurs between 200 and 250 °C, with 25% mass loss and the second between 280 and 340 °C with 40% mass loss. Except for the delayed start of the decomposition in flax/Alginate, the mass loss profiles and mass losses in both steps for both composites are similar throughout.

While these properties effectively characterize temperatures leading to substantial material loss, studies have demonstrated that the performance characteristics of materials can deteriorate at temperatures considerably lower than those identified by TGA for degradation [105, 125, 195].

The loss of mechanical properties in natural fibers as a result of exposure to elevated temperatures have already been described in this report (Section subsection 3.3.3). Additionally, visual degradation and the loss of mechanical properties for the alginate polymers processed at elevated temperatures was shown during the material characterization portion of this report (Sections subsection 5.1.3). It is important that both mechanical testing, as well as thermal testing, should be considered when determining the processing parameters for natural fiber composites.Comparing the degradation curves for these materials to their mechanical performance is essential.

DSC

To study the effect of the flax fibers on the thermal properties of the neat polymers, DSC analysis of fibers, neat polymers, and the corresponding biocomposites was performed. Differential scanning calorimetry (DSC) serves as a common thermal technique employed for the assessment of temperature-related transitions within polymers. In this study, DSC was employed to both validate the glass transition temperature (Tg) of the pristine polymers and investigate the impact of incorporating fiber reinforcements on these material transitions. This method involves providing energy to the sample and subsequently monitoring changes in heat capacity. An elevation in heat capacity is indicative of heightened molecular motion within the polymer. Consequently, the glass transition temperature is determined as the temperature at which half of the increase in heat capacity has occurred. The glass transition temperatures were determined from these curves and a summary of the values of the glass transition temperatures for each polymer and composite sample can be seen in table9.10. The curves for neat polymer and polymer reinforced with different percentages of treated fibers are shown in the picture below. Determination of the Tg for the neat polymer resins was straightforward, however, for the highly reinforced composite materials determination becomes more challenging because the specific heat capacity of the sample is only slightly changed by the polymer glass transition. Determination is further complicated by the poor thermal conductivity introduced by the reinforcing fibers [195]. However, the glass transition temperature of the treated composites has shifted marginally indicating that pre-treating the fibers with sodium alginate can affect the thermal stability of the composites and is increased by the addition of alginate-treated fibers. This can be further observed in the figure 9.19below



Pyris Series - DSC 7 - [Data Analysis - 230306 FLA ALS 3 pass.dsd]

Sample Temp: 25.000 °C

Heat Flow: 19.0555 mW

Time Remaining:

Status: At Load Temp

Purge Gas: Argon

20.0 ml/min

Axis: x = 203.067 °C y = 25.7699 mW

Figure 9.19: DSC curves for neat alginate polymer and flax alginate samples

The dehydration was evidenced by an endothermic peak close to 100°C across all the test samples. There is a wide endothermic peak, which starts around 80°C and ends at 150°C, and Δ H = 317 $Jg\hat{} - 1$, where the area under the endotherm associated with Tg is defined as enthalpy recovery or relaxation and evaporation of water linked. Several authors generally attribute this process to gelatinization 39. However, we consider that claim to be inaccurate, and would not attribute it to gelatinization but relaxation enthalpy 38. On the other hand, the TGA analysis of AlgNa shows a loss of mass in this interval, which could also be due to the evaporation enthalpy of water molecules linked to the polysaccharide corresponding to non-freezing bound water [32]. Glass transition is often referred to as a second-order phase transition that occurs without the release or absorption of latent heat. However, due to the non-equilibrium nature of the glassy states, the glass transition is preferably called a state transition, rather than a phase transition [41].

		Temperature		
2nd heating		**Tg**	**Onset**	**Endset**
	fibers	39.7	38.41	41.61
	Treated fibers	39.36	38.28	40.94
	Neat Polymers	38.03	36.96	40.11
	0p	40.86	39.42	43.19
	1p	39.86	38.34	42.13
	2p	41.03	39.505	43.58
	3p	41.7	40.17	44.13
	4p	41.7	40.52	43.83

Table 9.10: Summary of glass transition temperature (Tg) for neat polymer and reinforced composite samples obtained by DSC

9.3 Other techniques

The CT Scans were conducted to study void volume which further helped to gauge the presence of voids with the help of Scanning Electron Microscopy.(See appendix 11.2- 11.8)

FTIR scans were done to analyze if there were any bonding observed. Since they did not base the major part of the work a detailed was not carried out after a few initial observations. The data regarding the void volume fraction can be can be found in the appendix.11.7.

Based on these data, a new set of calculations of all the predicted and experimental values can be re-assessed.

9.4 Discussion: Evaluation of Flax/Alginate Composite Performance

9.4.1 Comparison of Experimental and Predicted Longitudinal Properties

The evaluation of tensile properties for Flax/Alginate unidirectional biocomposites, as discussed in 9 reveals intriguing findings. Specifically, when comparing experimentally determined properties with predictions, notable disparities emerge. The tensile strength properties observed through testing fall significantly below the anticipated range (0.45-0.5), whether considering the strength values of flax fibers from literature or experimental matrix data. Moreover, the elastic modulus of the flax/alginate composites is notably lower than the predicted values, even when utilizing the modulus values reported in the literature for flax fibers .

In the estimation of theoretical longitudinal properties for the composite constituents employed in this study, a series of simplifying assumptions were applied concerning the physical variables governing the system. In practice, however, achieving the fulfillment of all these assumptions throughout the composite manufacturing process is a rare occurrence. The disparities observed between the experimental values and the anticipated values of composite system properties are likely attributed to the non-realization of these assumptions.

Several factors have been identified as significant influencers on the longitudinal properties, such as strength and stiffness, of composites possessing a defined fiber volume fraction. These factors encompass:

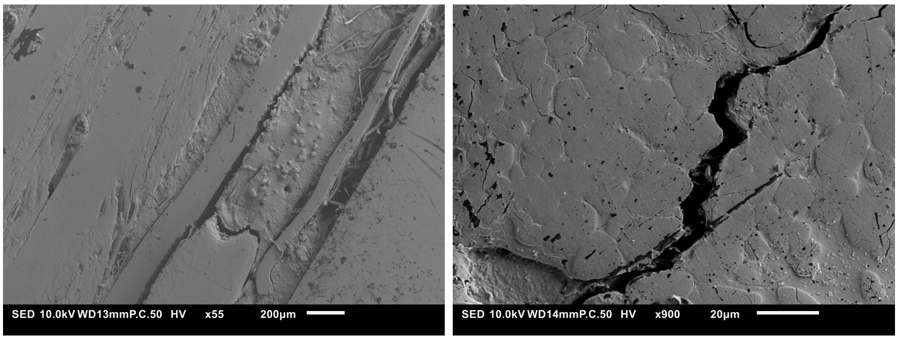
- Variability in fiber properties
- Discontinuous fiber structure
- Fiber misalignment during pre-treatment cycles
- Interfacial conditions
- Fiber undulations
- Presence of voids

These elements collectively contribute to the deviations between predicted and experimental composite properties.

Natural fibers are known to have a high variation in mechanical properties as a result of defects, changes in diameter, and growing conditions. The flax fabrics used in this study are no exception and it is expected that the variability in the fiber properties would directly affect the composite properties.

The orientation of fibers concerning the loading axis stands as a critical parameter, as it directly influences both the capacity of the fibers to bear loads and the transmission of stresses between the fibers and the matrix within a composite material. Although alignment in the non-crimp fabric was highly controlled, due to handling during the pretreatment soaking cycle, there might be some degree of misorientation within individual fibers during the process. Moreover, since the fibers were not individually tested for their mechanical properties, these obtained composite values are mostly based on theoretical data provided by the manufacturer's datasheet.

Poor fiber/matrix adhesion is another likely reason for reduced composite properties. With the help of a CT scan and microscopy, the presence of poor adhesion between the fiber and the matrix was verified. The poor fiber/matrix adhesion is due to inadequate transfer of stress between the composite constituents resulting in premature failure by fiber debonding and matrix failure.



(a) Debonding between **(b)** CT-Scan

Figure 9.20: SEM images for fiber/matrix adhesion of Flaxalginate composite

Investigating the discrepancies between predicted and experimental longitudinal properties of the composite, as detailed in 9.1.1, involved examining the impact of void contents on the composite. Several models were employed to back-calculate the effective fiber properties, considering both composite performance and void contents. A consistent approach was maintained across these methods by equating the matrix strength, σm, with the strength observed on neat resin stress-strain curves at the point of ultimate composite elongation, as mentioned in previous composite predictions.

To provide further clarification on the disparities between the anticipated and observed longitudinal properties of composites, an examination of the influence of void content, as computed in chapter 9, was carried out. In this process, multiple models were employed to retroactively determine the effective fiber properties based on the composite's performance and void content. In each method employed, it was ensured that the matrix strength denoted as σ_m, matched the matrix strength observed on the stress-strain curves of the pure resin at the point where the composite reached its ultimate elongation. This was done to maintain consistency with previous composite predictions.

Across all composite systems analyzed, the elongation to break fell within the range of 5.7% to 8% 9.3, thus a standardized value of strain, equivalent to 0.06 mm/mm, was utilized to estimate the approximate strength of the matrix at the point of composite failure. These estimates were derived from typical stress-strain curves for the polymer resin (sodium alginate) used, yielding an approximate value of 64.2 MPa.

Initially, the conventional ROM equations were applied to retroactively determine the effective fiber strength and stiffness, as represented by 9.28 and 9.29 respectively. This was accomplished using the original fiber and matrix volume fractions, which were derived from the constituent weight percentages and theoretical composite densities for each composite sample. It's important to note that in this context, the sum of the fiber and matrix volume fractions, denoted as Vf and Vm, equaled 1.

$$E_f = \frac{E_c - (1 - V_f)E_m}{V_f} \tag{9.29}$$

$$\sigma_f = \frac{\sigma_c - (1 - V_f)\sigma_c}{V_f} \tag{9.30}$$

The modified rule of mixtures (MROM) approach, which includes equations for predicting composite properties in the presence of voids, is often employed as an adaptation to the traditional ROM approach that doesn't consider void contents. The theoretical basis of the MROM equations remains the same as the ROM approach, but there's a key difference in how the volume fractions of the fiber and matrix are determined. In MROM, these fractions, denoted as Vfe and Vme, are experimentally calculated instead of theoretically derived, leading to a sum that is not equal to one as outlined in equation 9.31. Consequently, in the MROM equations, the (1-Vf) term from the ROM approach is substituted with the experimentally determined matrix volume fraction Vme, as demonstrated in equations 9.32-9.33

$$V_{fe} + V_{me} = (\frac{v_f}{v_(ce)}) + (\frac{v_m}{v_{ce}}) = (1 - V_v) \tag{9.31}$$

$$E_f = \frac{E_c - (E_m V_{me})}{V_{fe}} \tag{9.32}$$

$$\sigma_f = \frac{\sigma_c - \sigma_m V_{me}}{V_{fe}} \tag{9.33}$$

The MROM equations signify a notable improvement in the prediction of composite properties when contrasted with the conventional ROM approach. Nevertheless, these equations predominantly regard voids as regions devoid of strength and stiffness, resulting in a reduction in the composite's load-bearing volume or cross-sectional area. Recent studies have highlighted that voids also induce stress concentrations within the composite material. In response to this concern, Madsen and Lilholt [106] introduced a model that builds upon the ROM approach.

This model includes an extra term to compensate for the diminished material properties due to reduced load-bearing volume and the stress concentrations caused by voids, as outlined in Equations 9.34-9.37. Similar to the ROM and MROM methods, these equations are used to calculate Ef and σf, thereby determining the effective fiber properties.

$$E_c = (E_f V_f + E_m(1 - V_f))((1 - V_v))^2 \tag{9.34}$$

$$\sigma_c = (\sigma_f V_f + \sigma_m(1 - V_f))((1 - V_v))^2 \tag{9.35}$$

$$E_f = \frac{((E_c(1 - V_v)^{-2}) - E_m(1 - V_f))}{V_f} \tag{9.36}$$

$$\sigma_f = \frac{(\sigma_c(1 - V_v)^{-2}) - \sigma_m(1 - V_f))}{V_f} \tag{9.37}$$

Table 9.11 provides a summary of the back-calculated effective fiber properties, Ef and σf, derived from the three models discussed earlier. In the case of flax reinforcing fibers used in this study, the fiber modulus values in the longitudinal direction obtained through ROM, MROM, and the model by Madsen were found to be considerably lower than those values previously reported in section 5.1.1 of this report. Similarly, the back-calculated fiber strength values were also lower than the range typically seen in the literature for flax fibers. These reduced effective strengths of the fibers might indicate a couple of factors: (i) the composite's longitudinal strength and modulus are more influenced by void content than predicted by the Madsen and Lilholt model, and (ii) the adhesion quality between the fiber and matrix layers significantly impacts the composite's strength and modulus. These lower-than-average values are probably due to a mix of these issues. Furthermore, the strength of highly concentrated matrix films (40%) can be precisely determined, which would help in more accurately back-calculating the fiber values. The back-calculated fiber properties using the Madsen and Lilholt model were then used to make predictions about the 0p(no treatment),1p, and 4p composite systems, assessing their competitiveness with other unidirectional natural fiber composites 9.21.

	Effective fiber Modulus			Effective fiber Strength		
	Ef(Gpa)			f(Mpa)		
composite sample	**ROM**	**MROM**	**M&L**	**ROM**	**MROM**	**M&L**
0p	2.649788889	3.146016605	3.697550287	251.4017899	70.57966466	313.5124998
1p	9.117644898	9.687343614	10.34825771	379.2016366	151.0709393	426.6123511
2p	6.819693478	7.231260789	7.642051476	313.1939815	101.7140139	346.4884052
3p	10.64134444	11.11756018	11.82958037	367.5026844	122.5671889	406.707197
4p	12.24528372	12.85599535	13.66582774	373.040607	111.509263	415.4287797

Table 9.11: Effective fiber strength and stiffness, derived through back-calculation from various prediction models, for longitudinal properties of the composite

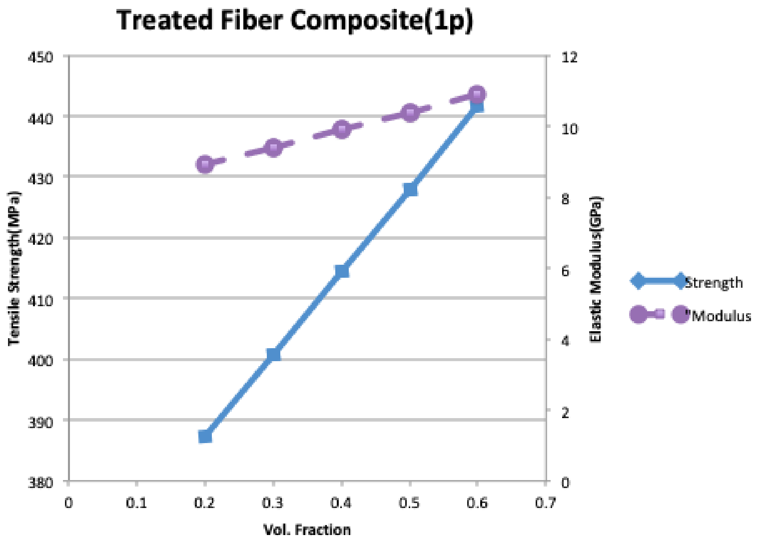


Figure 9.21: Predicted composite strength and stiffness values for biocomposite for 1p at various fiber volume fractions using the back-calculated effective fiber

The results indicate that enhanced processing conditions, lower void content, and improved adhesion between fiber and matrix could lead to Flax/Alginate composite tensile properties surpassing those obtained in this study.

9.4.2 Comparison of Flax/Alginate biocomposites with existing materials

In this study, the biocomposite system developed was compared not only with other unidirectional natural fiber composites but also with conventional building materials like GFRPs and wood products. The primary goal was to create a biocomposite system that rivals these materials, offering a greener alternative for semi-structural applications. Previous research [89],[206] has highlighted the environmental advantages of using natural fibers and biopolymers over synthetic or petroleum-derived composites. Moreover, the

Composite Materials (fiber/ matrix)	Vf	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (Mpa)	Bending Modulus (Gpa)	[Ref]
Glass/Epoxy	0.48	817	31	x	x	[127]
Hemp/PP	0.48	280	28	x	x	[106]
Flax yarn/Soy	0.45	x	x	126	2.24	[42]
Flax yarn/Soy	0.6	x	x	259	3.7	[170]
Flax/Epoxy	0.25	x	x	182	19.5	[69]
Flax/Vinylester	0.37	248	24	x	x	[69]
Flax/Epoxy	0.47	280	39	x	x	[127]
Flax/PP	0.4	x	x	135	11	[7]
Jute/PLA	0.38	78	8.5	x	x	[93]
Jute/PLA	0.23	x	x	85 7	11	[93]
Ramie/SPC	0.65	271	4.9	225	12.5	[123]
Sisal/Epoxy	0.58	310	9.8	240	17.8	[214]
Flax/Alginate	0.47	219.7	5.7	69.5	3.7	*
Flax/Alginate	0.41	198.3	6.6	150.9	9.4	*

Table 9.12: Summary of some unidirectional composite properties *Current Study

rapid growth and high yield of plant crops enhance the sustainability of natural fiber composites compared to wood products.

While aligned natural fiber-reinforced polymer composites have shown promise in the automotive industry, suggesting they could be alternatives to traditional GFRP composites in some cases, their application in directionally aligned formats is largely unexplored. 9.12table presents an overview of the reported mechanical properties of unidirectional aligned biocomposites, alongside values for unidirectional GFRP composites. Though natural fiber composites have lower strength than GFRP composites, their stiffness is on par. Considering that natural fibers are often much lighter than glass fibers, the specific strength and stiffness of natural and glass-fiber-reinforced composites are more closely matched. This study demonstrates that the mechanical performance of natural fiber-reinforced composites can be significantly enhanced by strategically aligning the reinforcements. Furthermore, replacing traditional petroleum polymers with biopolymer resins in these composites has been proven effective both in manufacturing and performance.

table9.13 shows typical properties of wood and plant-based materials used in construction. The study's unidirectional non-crimp fiber composites outperform traditional wood. Their unique advantage lies in customizing orientation by stacking angle plies. The composites developed could be effectively used as face sheets or veneers in the construction of particle and fiberboards, with the potential to enhance their tensile and flexural strengths.

Material	**Density (g/cm3)**	**Tensile Strength**	**Elastic modulus (GPa)**	**Flexural strength (MPa)**
Flax/Alginate	1.43	219	5.7	69.52
HARDWOOD				
Red Maple Wood	0.6-0.75	N.A	11.3	92
White Oak Wood	0.6-0.9	N.A	12.3	105
SOFTWOOD				
Douglas Fir	0.53	N.A	13.4	85
Pine (ponderosa)	0.35-0.6	N.A	8.9	65
Spruce	0.4-0.7	N.A	8.9	64
PARTICLEBOARDS				
Flax	0.6	N.A	N.A	16-18
Hemp	0.6	N.A	N.A	15-16
Bagasse	0.6	N.A	N.A	20-21
Jute	0.58	N.A	N.A	15-16
Bamboo	0.625	N.A	N.A	18-19
MEDIUM DENSITY fiberBOARDS				
Flax	0.785	N.A	N.A	29-35
Hemp	0.88	N.A	N.A	7.8-20.8
Kenaf	0.817	N.A	N.A	19.3
NATURAL fiber/POLYESTER COMPOSITE LAMINATES				
Sisal (Wf = 0.5)	1.05	40	N.A	N.A
Jute (Wf = 0.3)	1.22	66	N.A	N.A
Coir (Wf = 0.3)	1.4	20.4	N.A	N.A

Table 9.13: Comparison of properties for several common wood and plant based[97],[96],[170] building materials

However, there are still limitations to these materials due to insufficient knowledge regarding their long-term load-bearing behavior, as well as their moisture resistance and durability. Before these materials can be confidently used in applications that demand substantial long-term load-bearing capacity, further investigation into these properties is necessary.

Chapter 10

Conclusion

10.1 Summary

This study on unidirectional biocomposites has highlighted their substantial potential usage in secondary and non-primary load-bearing applications. Their properties, derived from experiments and predictions, align closely with those reported in other studies on unidirectional non-crimp natural fiber composites. These biocomposites show promise in competing with commercial timber products, especially when weight is a consideration and they are further developed.

The performance of the composite materials was evaluated by considering the impact of void content on their properties. This approach revealed that the back-calculated effective fiber properties aligned closely with those reported in the literature for flax fibers. Furthermore, when applying the ROM approach with these effective fiber properties, the predicted properties of the composites suggest an enhanced capability for bearing high loads.

The biocomposites in this study are entirely made from renewable resources, offering an environmentally superior alternative. Flax fibers, known for their rapid growth and eco-friendliness, were utilized as the reinforcing phase, exhibiting impressive performance. The use of non-crimp textile fibers brought several advantages. It simplified the process of cutting and drying the flax to remove impurities and weaker components. Additionally, the non-crimp structure allowed for easier composite processing, controlled alignment of reinforcements, and facilitated consolidation, resulting in lower void content.

However, the study indicates that improvements in reinforcement characteristics, void content, and fiber-matrix adhesion are needed to optimize the biocomposite system. Future research should address issues such as water removal, durability, biodegradation, and long-term behavior, especially for load-bearing applications.

The study also explored the use of brittle alginate resin systems as matrix materials. These systems displayed satisfactory mechanical and processing properties, with an optimal processing window between 65-100°C. Sodium alginate polymer composites showed acceptable properties, and the polar nature of the polymer matrix enhanced the bonding between the composite constituents. Nonetheless, challenges in achieving strong bonds between natural fibers and matrix were observed, necessitating further research.

A manufacturing procedure for biocomposites using dilute matrix systems was developed, demonstrating good repeatability and control over fiber and matrix contents. The study successfully produced unidirectional composites with high fiber volume fractions using this technique. Water, essential for reducing resin viscosity and ensuring effective impregnation, posed challenges in terms of potential higher void content. However, this can be mitigated using a vacuum or more environmentally friendly solvents. The study also highlighted the potential for developing other processing methods compatible with natural fibers and biopolymers, crucial for their industrial application in high-performance composites.

10.2 Aspects for Further Research

The current study has effectively shown that Flax/Alginate biocomposites with satisfactory performance levels can be produced. However, significant enhancements are possible, aiming to elevate these materials beyond just their environmental appeal in secondary structural applications, to being chosen for their performance alone. True sustainability in construction materials will come from making environmental benefits an integral, but not the sole, aspect of the system. Further research is required in several areas, as detailed below:

Further Investigation of Fiber Treatment Methods:

Explore additional physical and chemical techniques to lessen the hydrophilic nature of fibers, thereby improving adhesion with the matrix. This includes:

- Chemical treatments like Mercerization or acetylation to remove impurities and non-structural elements from fibers, increasing surface roughness for better mechanical interlocking with the biopolymer matrix.
- Use of chemical coupling agents or plasticizers to strengthen chemical bonding between different types of composite materials.

Development of Automated Composite Manufacturing Systems:

- Implement systems that combine vacuum and drying processes with pressing mechanisms to:
- Facilitate easier adjustment of fiber and matrix compositions.
- Decrease void content in composites.
- Reduce the time required for composite processing.

Research on Durability and Long-Term Performance:

- Study the water absorption, long-term behavior of biocomposite systems and its durability, particularly under conditions of high humidity, temperature fluctuations, and continuous stress.

Exploration of Degradation Techniques:

- Investigate degradation processes for the flax/alginate composite system to determine the final degradation timeline, ensuring the product's design follows a "cradle-to-cradle" approach.

Processing of Dilute Matrix Systems:

- Identify methods to process dilute matrix systems for biocomposite development.

Prototype Manufacturing and Testing:

- Create and evaluate structural biocomposite prototypes as alternatives to traditional GFRP composites, wood, or metal in structural elements like beams, ceiling or wall panels, or fenestration products such as windows and doors.

Chapter 11

Appendix

	Literature Prediction	**Strength**					**Modulus**					
	sig f	**sigf*Vf**	**Vm**	**Sigm**	**Sigm*Vm**	**Sigc**	**Ef**	**Ef*Vf**	**Em**	**Vm**	**Em*Vm**	**Ec**
0.25	580	145	0.75	65	48.5	193.75	61	15.25	0.8	0.75	0.6	15.85
0.35	580	203	0.65	65	42.25	245.25	61	21.35	0.8	0.65	0.52	21.87
0.45	580	261	0.55	65	35.75	296.75	61	27.45	0.8	0.55	0.44	27.89
0.55	580	319	0.45	65	29.25	348.25	61	33.55	0.8	0.45	0.36	33.91

Table 11.1: Predicted Values

Longitudinal	**Material**	**Reported**	**Experimental**	**Reported**	**Experimental**
		Modulus	*Modulus*	*Strength*	*Strength*
	Resin	0.8	14	65	400
	Fiber	61	61	580	580

Table 11.2: Literature Data

Density Final	**0pass**	**1pass**	**2pass**	**3pass**	**4pass**
	1.37855534	1.40241982	1.44190448	1.40407795	1.42014539
	1.23692073	1.41374728	1.41996895	1.43577676	1.43337819
	1.24155964	1.4013897	1.44621253	1.41830861	1.4383712
	1.47416171	1.37761	1.41494915	1.43256416	1.47318089
	1.46006429	1.4162487	1.42311116	1.41913862	1.37202952
	1.386678	1.41374728	1.40471616	1.43590734	1.42249293
Mean	**1.36298995**	**1.4041938**	**1.42514374**	**1.42429557**	**1.42659969**
SD	**0.11462048**	**0.01446075**	**0.01598088**	**0.01269811**	**0.0328352**

Table 11.3: Density Calculations

no of passes	**fw%**	**Densitykg/m3**
0p	41.6	63.1111111
1p	45.0	69.0476191
2p	41.8	61.0793651
3p	41.6	63.1111111
4p	41.5	55.5555556

Table 11.4: Volume Fraction and Density Data

No of passes	**Void%**	**Wt%**
0p	0.08285782	0.42
1p	0.04922471	0.45
2p	0.04040967	0.42
3p	0.04176589	0.41
4p	0.04376477	0.43

Table 11.5: Void, Cycles and Weight Percentage

Experimental Density and Composite Constituent Calculations					
	0p	**1p**	**2p**	**3p**	**4p**
Theoretical composite density (ρct) g/cm3	1.48612721	1.47689345	1.4851585	1.48637537	1.49189199
Experimental composite density (ρce)(g/cm3):	1.467113	1.41374728	1.43093671	1.41992735	1.42676179
Volume fraction of voids Vv:	0.08285782	0.04922471	0.04040967	0.04176589	0.04376477
Exp. Volume fraction of fibers, Vfe:(vf/vce)	108.453849	137.348833	115.027736	126.246219	117.22603
Exp. Volume fraction of matrix, Vme:(vm/vce)	128.382824	141.631593	134.971805	150.079334	152.459986

Table 11.6: Experimental Density Calculation

void fraction(%)		
Passes	**Archimedes**	**CT**
0p	8.28578204	19.5015
1p	4.922471	14.6988
2p	4.04096677	17.1268
3p	4.17658929	15.9932
4p	4.37647683	9
SD	1.77905684	3.92158481

Table 11.7: Void Fraction Comparison From CT and Gravimetric Analysis

sample number	**Fiber weight fraction**	**Density**	**Fiber volume fraction**	**Matrix Volume fraction**	**Porosity Volume fraction**
0p	0.416	1.36298995	0.420	0.497	0.08
1p	0.450	1.4041938	0.468	0.482	0.049
2p	0.418	1.42514374	0.442	0.518	0.04
3p	0.415	1.42429557	0.438	0.52	0.041
4p	0.433	1.42659969	0.416	0.54	0.043

Table 11.8: Volumetric Calculations

Fibre		Density (g cm-3)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)	Equilibrium moisture content (%)
Eco-friendly sustainable natural fibers	Cotton	1.5–1.6	287–597	5.5–12.6	7–8	–
	Jute	1.44	393–773	10–30	1.5–1.8	12
	Flax	1.54	345–2000	27–85	1–4	7
	Hemp	1.47	368–800	17–70	1.6	9
	Kenaf	1.2	240–930	14–53	1.6	–
	Ramie	1.5–1.56	400–1000	27–128	1–4	9
	Coir	1.25	220	6	15–25	10
	Abaca	1.5	980	–	–	15
	Oil palm (empty fruit bunch)	0.7–1.55	248	3.2	2.5	–
	Sugar palm	1.5	421.4	10.4	9.8	–
	Baggase	1.2	20–290	19.7–27.1	1.1	8.8
	Sisal	1.33	600–700	38	2–3	11
	Pineapple	1.5	170–1627	82	1–3	13
	Banana	1.35	355	33.8	5.3	–
	Bamboo	0.6–1.1	140–230	11–17	–	8.9
	Henequen	1.4	500	13.2	4.8	–
	Nettle	1.51	650	38	1.7	–
Conventional fibers	E-glass	2.5	2000–3500	70–77	4.5–4.9	–
	S-glass	2.5	4570	86–90	4.5–4.9	–
	Carbon	1.8–1.9	3400–5400	230–440	1.4–1.8	–
	Aramid	1.45	3400–4000	130–185	2.5	–

Table 11.9: Mechanical properties of different natural fibers compared to conventional reinforcing fibers

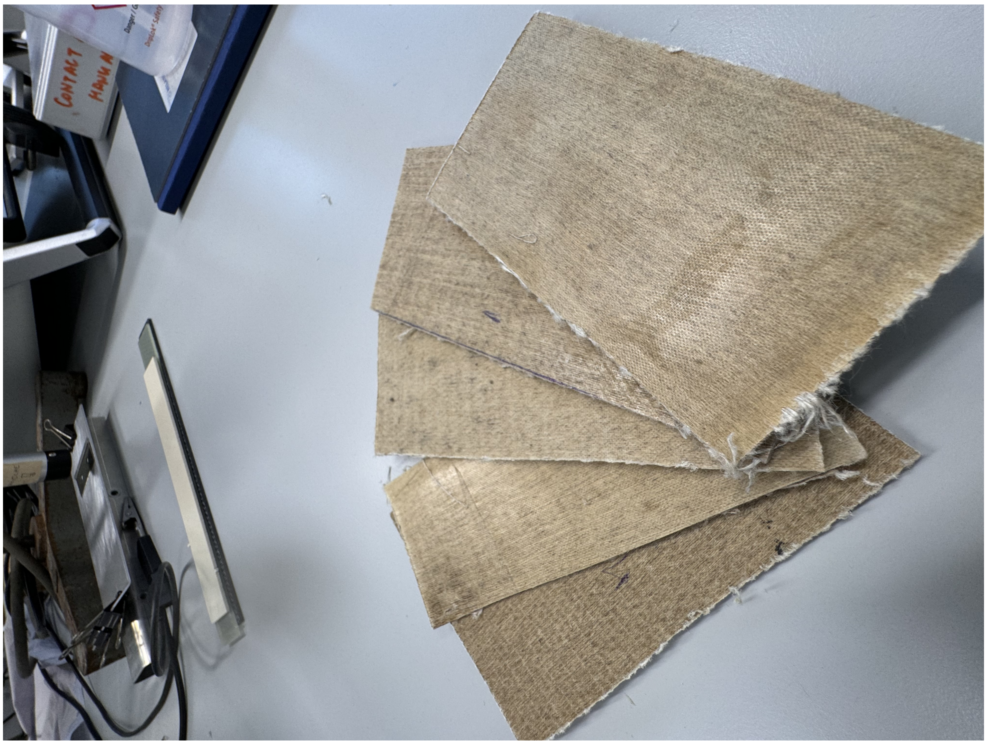


Figure 11.1: Prepared Samples

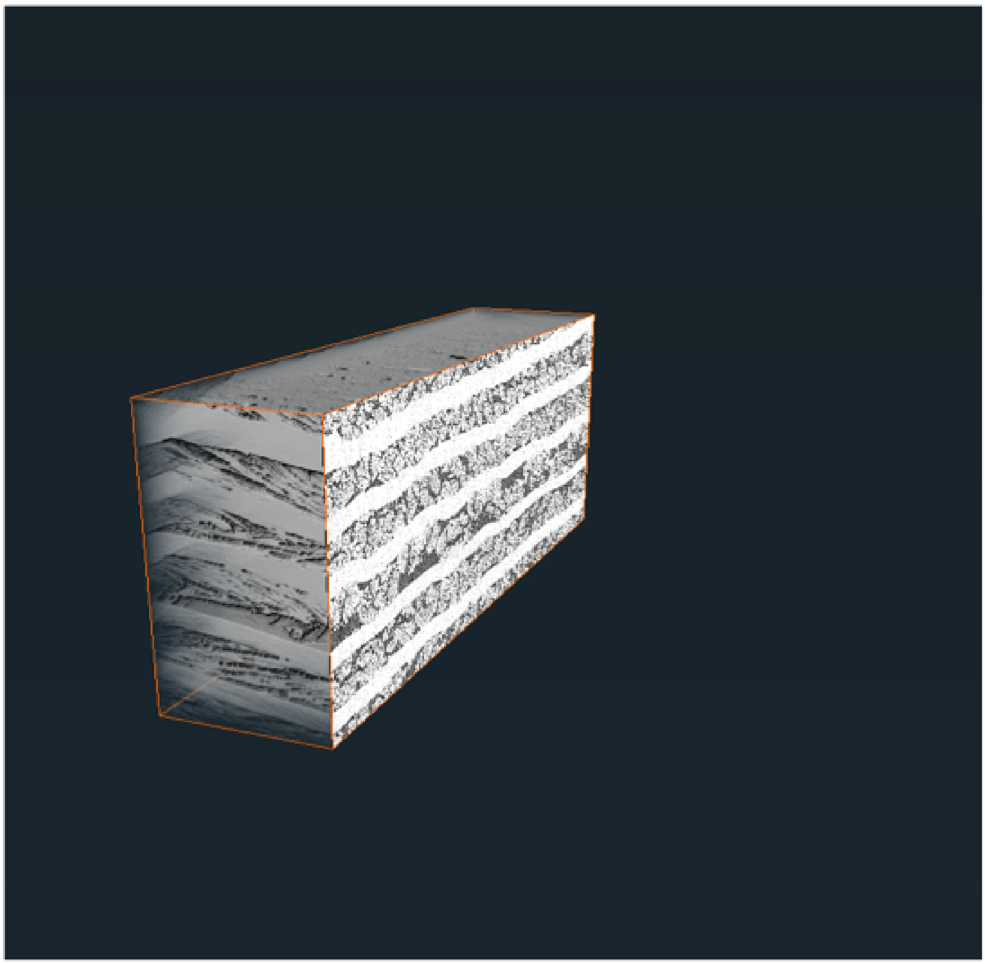


Figure 11.2: CT-scan 1

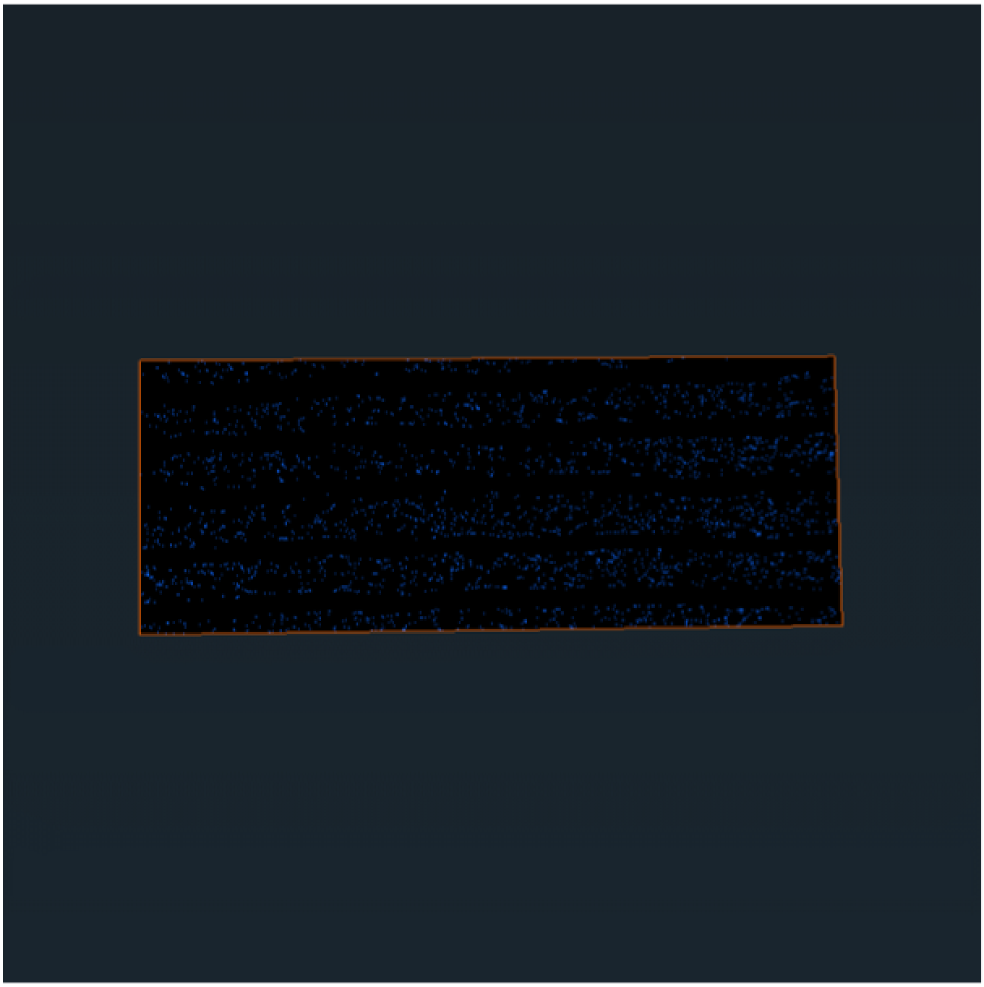


Figure 11.3: CT-scan 2

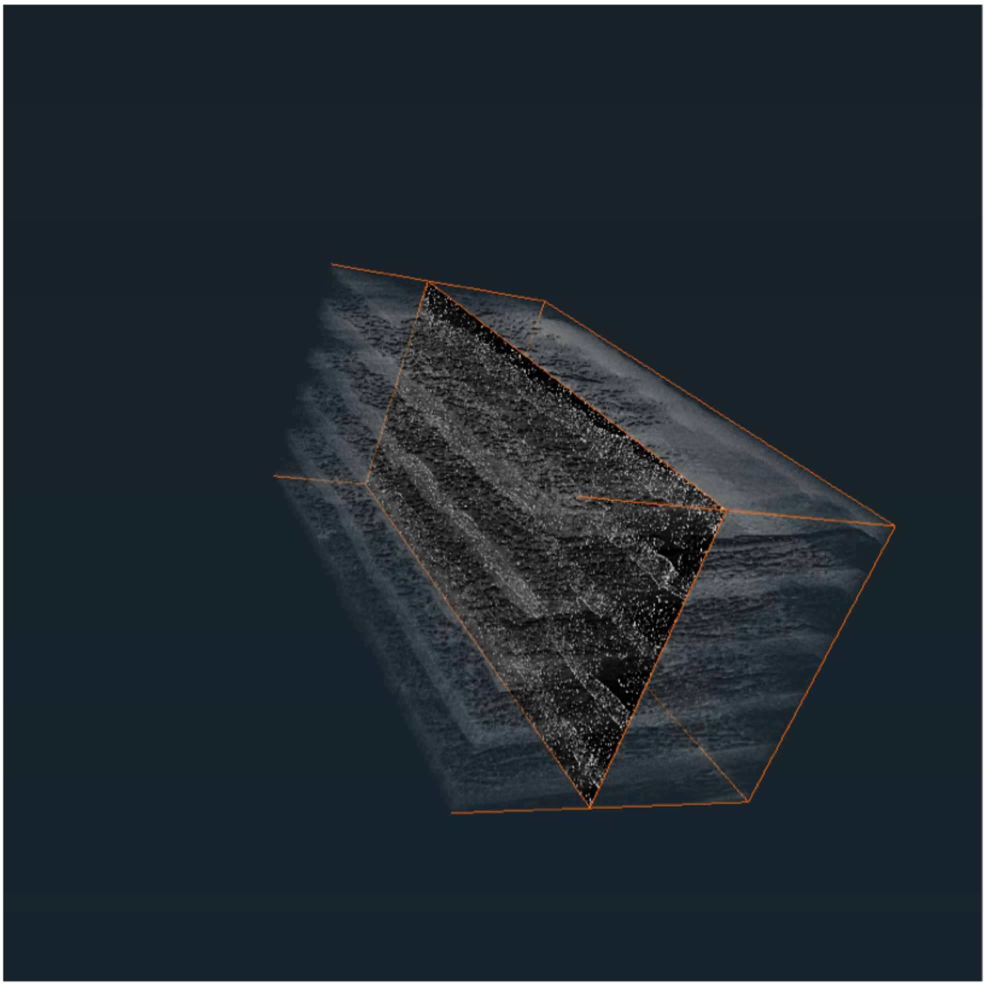


Figure 11.4: CT-scan 3

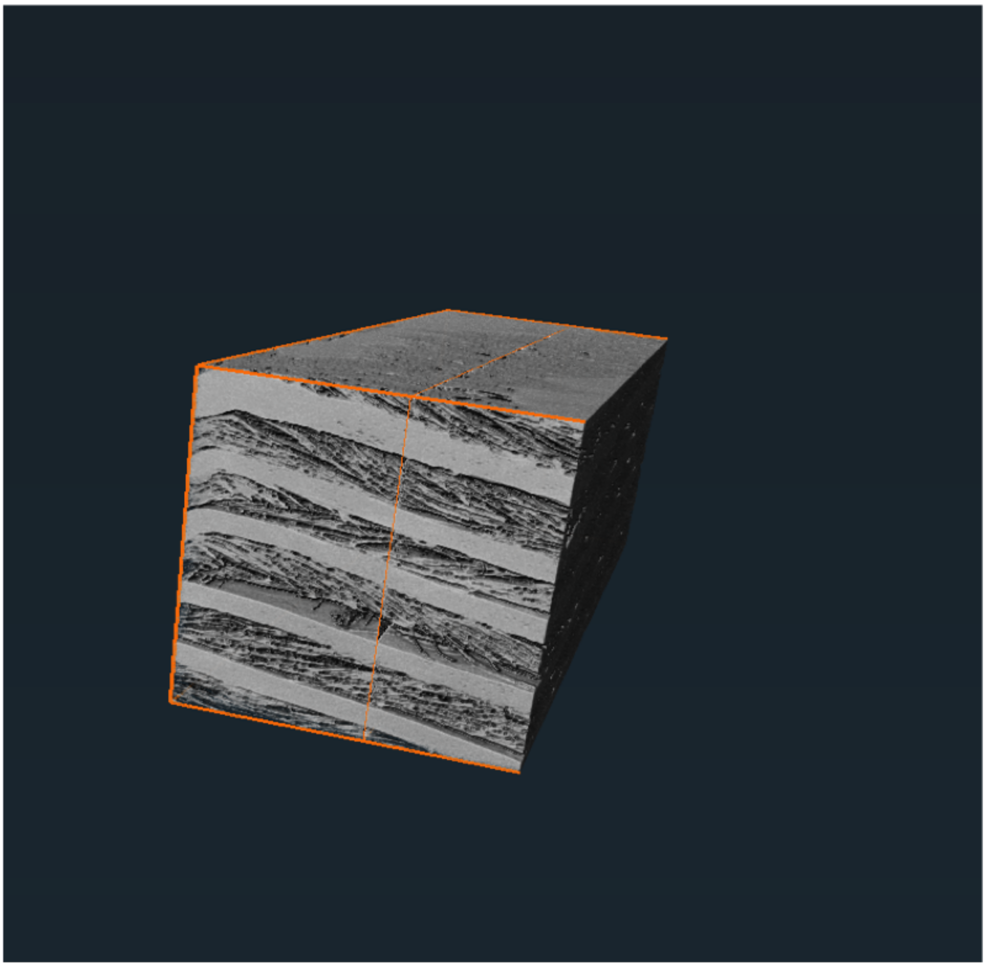


Figure 11.5: CT-scan 4

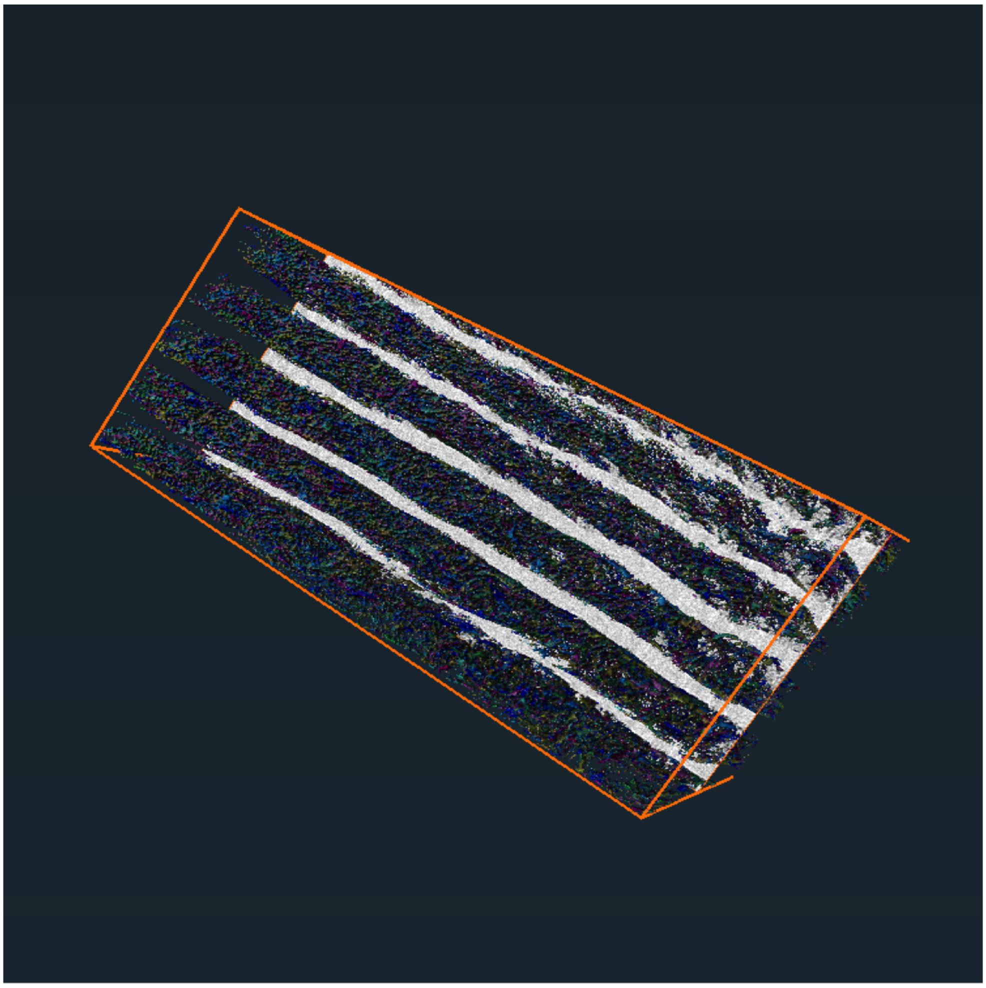


Figure 11.6: CT-scan 5

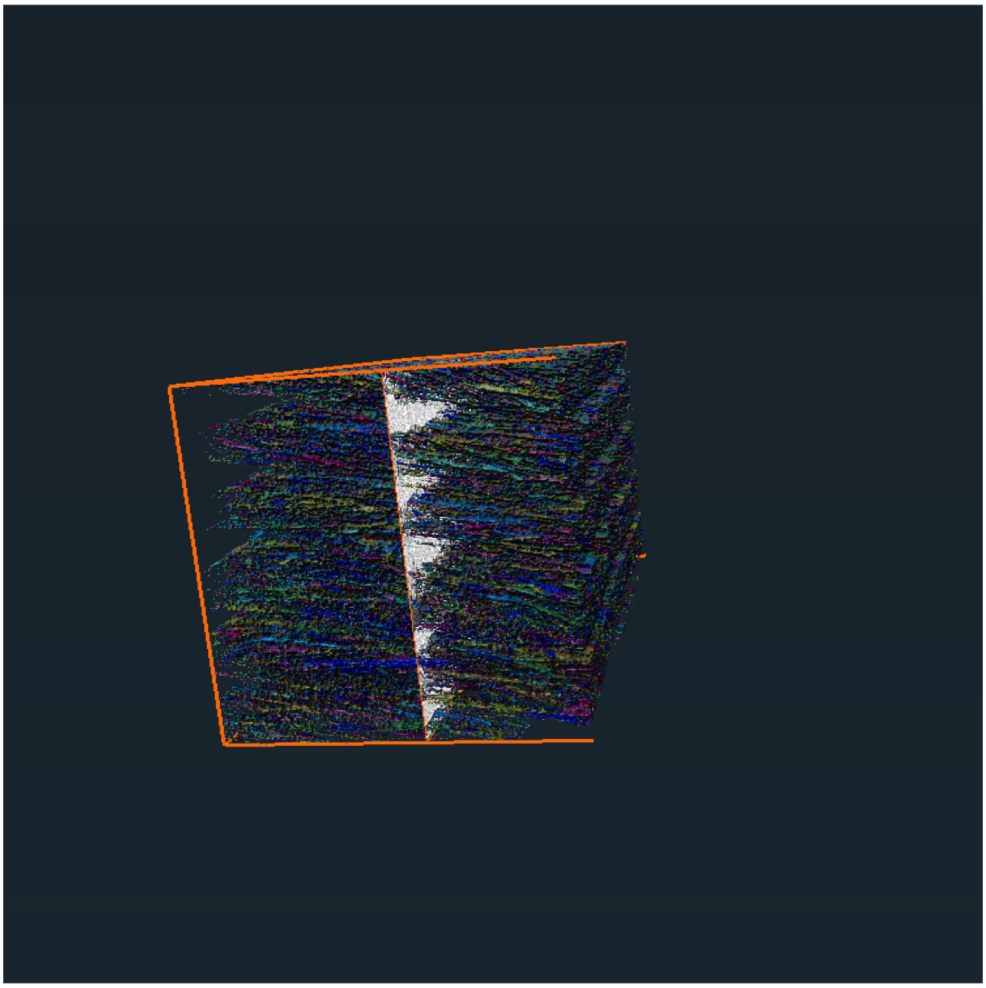


Figure 11.7: CT-scan 6

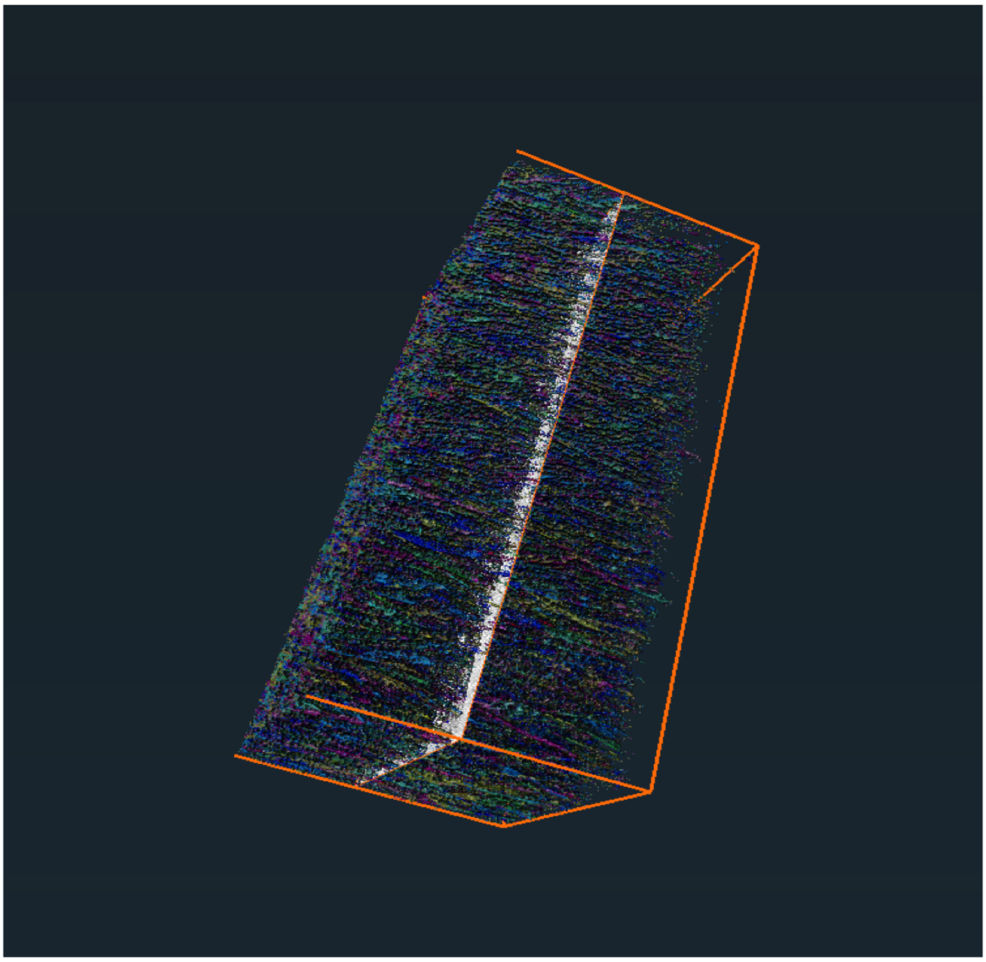


Figure 11.8: CT-scan 7

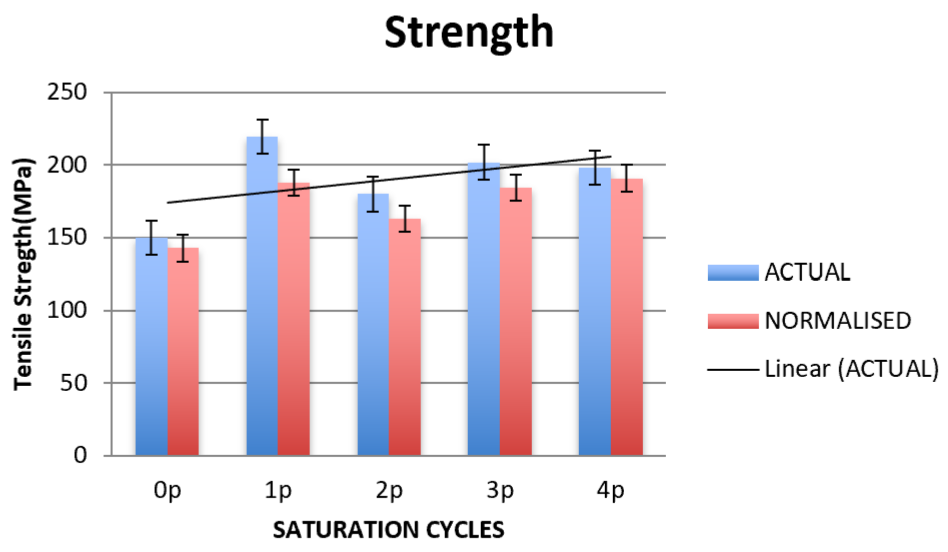


Figure 11.9: Tensile strength

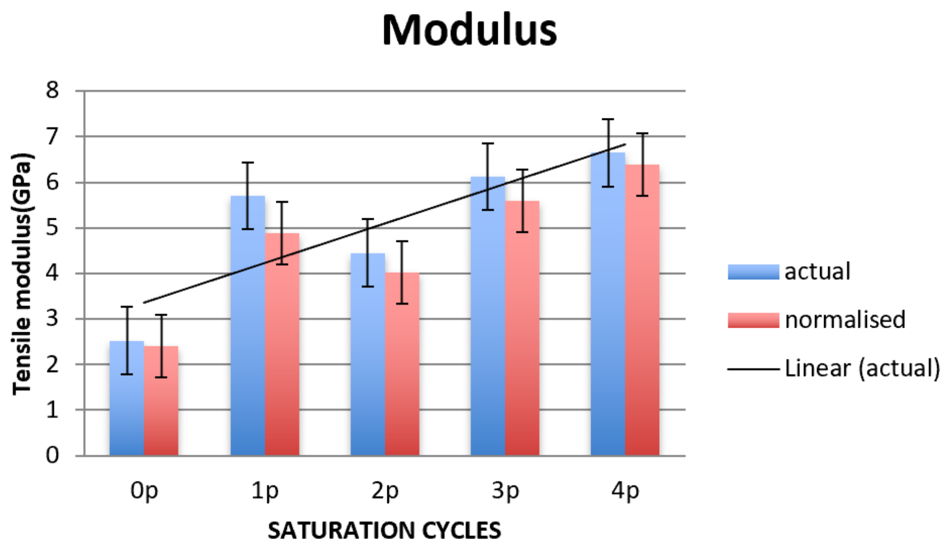


Figure 11.10: Tensile modulus

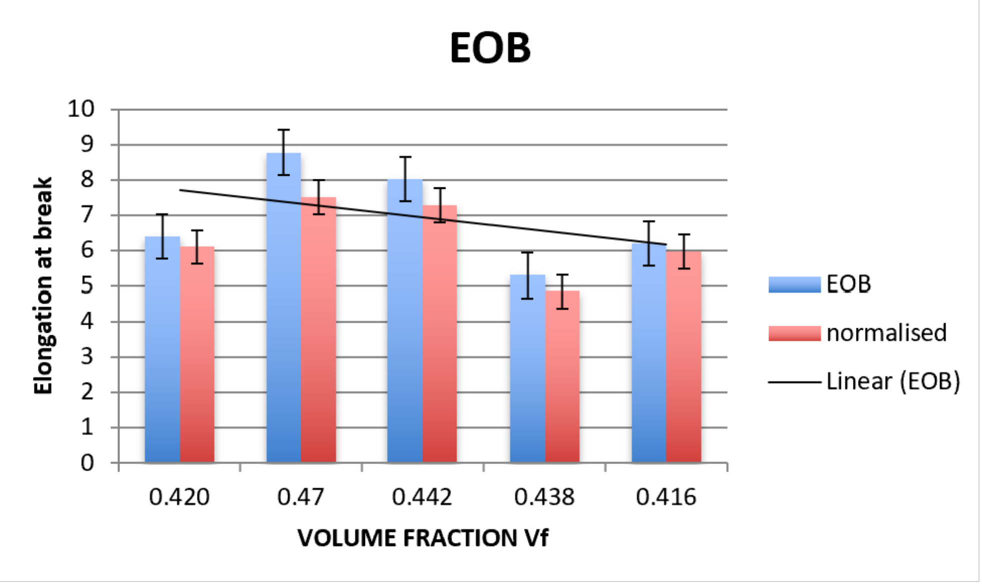


Figure 11.11: EOB

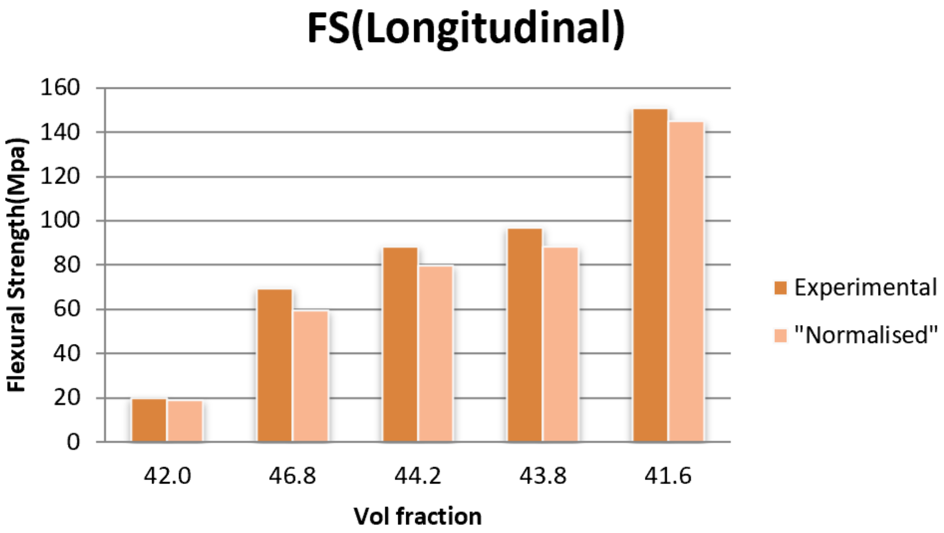


Figure 11.12: Flexural Strength

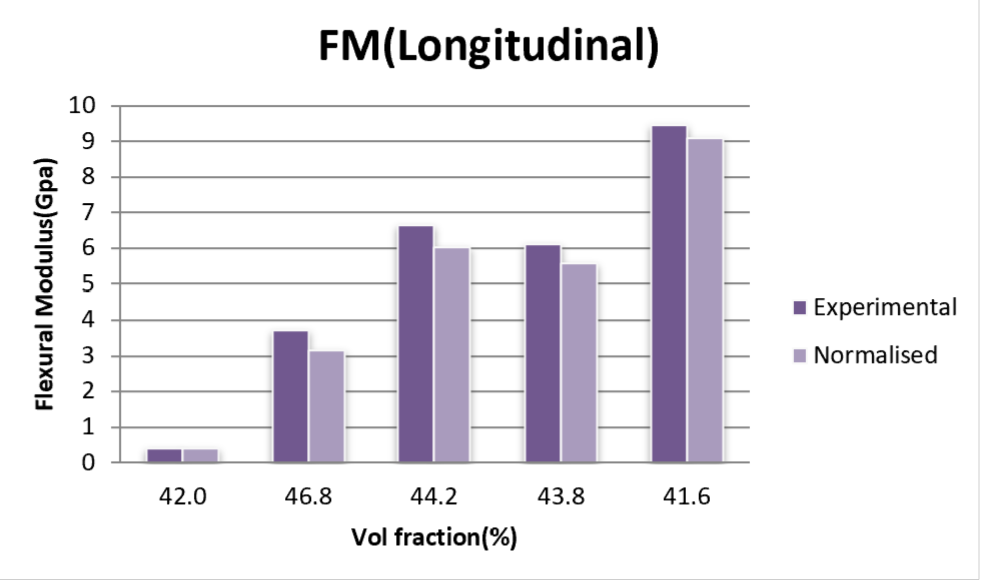


Figure 11.13: Flexural Modulus (long)

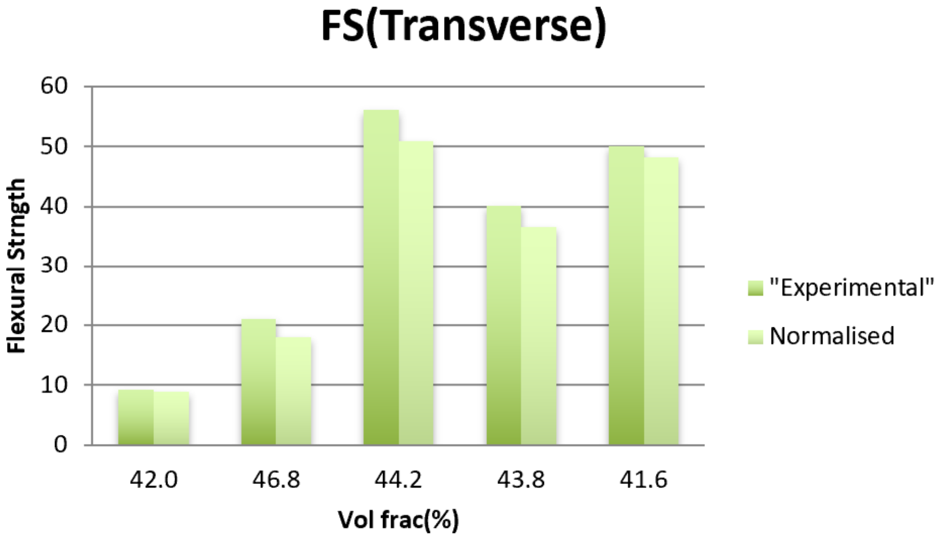


Figure 11.14: Flexural Strength (Trans)

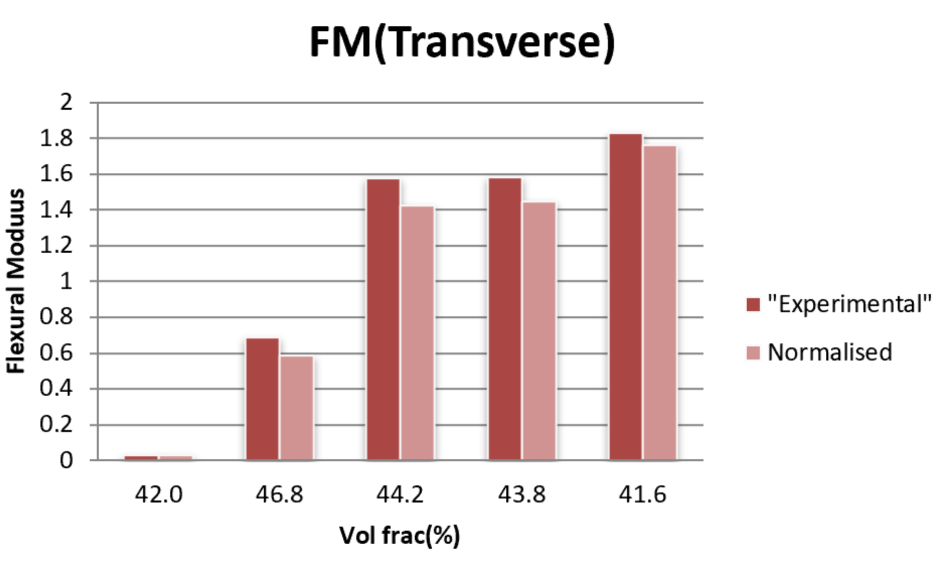


Figure 11.15: FM Trans

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