Development of Flax- and Hemp-based Polylactic Acid Films for Bioplastic Applications

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In Partial Fulfillment of the Requirements
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Saskatoon

by

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ABSTRACT

Plastic, widely used for packaging fresh food, poses environmental risks. It threatens marine and terrestrial ecosystems, while also contributing to global greenhouse gas emissions. To tackle this problem, bioplastics has emerged as a promising alternative to traditional plastics. Bioplastics, such as polylactic acid (PLA), offer advantages like wide availability, cost-effectiveness, and non-reliance on petroleum. PLA is non-toxic, biodegradable, strong, and has excellent film-forming properties, making it suitable for single-use applications like food packaging. Bioplastics holds promise, but sustainable raw material sources are necessary. Saskatchewan's crop production yields agricultural biomass, like flax straw, which can enhance the province's agriculture industry. While hemp is increasingly grown in Saskatchewan, its biomass quality may not meet high-quality fiber production standards. The utilization of excess agricultural by-products in composites remains unexplored, with limited studies on agricultural waste utilization for composite creation.

In this work, the effects of particle size, loading and treatment (alkali and acetylation) of biomass fillers on the mechanical, moisture absorption, vapor barrier, and surface wettability characteristics of the flax and hemp-based PLA films have been studied. The study emphasizes the importance of optimizing the particle size, treatment, and loading of fillers to achieve desirable properties for specific applications. This study has explored the addition of alkali and acetylation treated fillers of particle sizes <75 µm and 149-210 µm to the PLA films and compared the properties of the treated films with untreated ones. The addition of untreated flax fillers did not improve the tensile strength and elongation at break of flax bioplastic, and Young's modulus decreased as the filler loading increased. However, alkali-treated flax fillers showed an improvement in tensile strength at 2.5% and 5% loading. Acetylation treatment improved elongation at break at lower loading percentages but became less effective as the percentage of filler loading increased. The addition of flax fillers, whether untreated or alkali-treated, resulted in a decrease in tensile strength and Young's modulus. However, at 2.5% and 5% filler loadings, both untreated and alkali-treated fillers increased the elongation at break of the films. For hemp fillers, the tensile strength and Young's modulus decreased at all filler loadings, while the elongation at break increased until 5% loading and then started reducing. These trends can be
attributed to factors such as changes in crystallinity, interfacial adhesion, and the presence of defects. The addition of fillers to bioplastics increased moisture absorption and water vapor permeability (WVP), with a more pronounced effect observed in untreated fillers compared to treated ones. The water contact angle of the films decreased as the filler content increased for both particle sizes. However, the decrease in water contact angle was more prominent for untreated fillers compared to treated ones.

The balance between the ability of the filler particles to fill gaps between polymer chains and the formation of a more porous structure as loading percentage increases should be carefully considered when selecting bioplastics for specific applications. Therefore, it is essential to consider several factors such as particle size, treatment, and loading of the filler and their interaction while designing bioplastics with tailored properties for various applications.
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The years spent pursuing my master's degree have been both immensely challenging and undeniably fulfilling. I must acknowledge that the support and assistance I received from those around me, both in my academic and personal life, were instrumental in achieving this milestone. Without their guidance and encouragement, obtaining my master's degree would not have been possible.

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CHAPTER ONE
INTRODUCTION

1.1 Research Background

Owing to exceptional properties such as lightweight, flexibility, accessibility, and good mechanical properties, synthetic-based plastics have become an integral part of modern society with both industrial and commercial attractiveness (Nanda et al. 2022). Their importance has led to a spike in the global industrial production, reaching about 370 megatonnes in 2020 and being forecast to hit an estimated 1.3 gigatonnes by 2060 (Development 2022). Being comprised of complex materials, plastics represent diverse components, with the bulk of their components developed from repeating monomer units. Despite their fascinating advantages, the use of synthetic-based plastics has triggered ecological and environmental concerns ascribed to their long-term effect on pollution (Ahsan et al. 2023; Chae and An 2018). This perspective has given birth to seeking a greener alternative and benign solutions to the rising demand for plastic products. Thankfully, the use of natural materials is gradually drawing the attention of many industries and researchers owing to their ability to mitigate the environmental setbacks of traditional plastics.

Bioplastics, also known as bio-based plastics or biopolymers, are a promising alternative to petroleum-based plastics and can be derived from biomass sources such as corn and sugar cane, in line with the biorefinery concept (Shogren et al. 2019). These materials have gained popularity in recent years due to their ability to biodegrade into carbon dioxide in just a few months under suitable conditions, making them a contributor to carbon capture and storage (Lambert and Wagner 2017). Polylactic acid (PLA) and bio-polyethylene are examples of bioplastics that can be obtained directly from natural materials, such as cellulose, starch, or sucrose, through fermentation and chemical synthesis from renewable biological monomers (Dedenaro et al. 2016). Alternatively, bacterial cultures can produce bioplastics such as polyhydroxyalkanoates (PHAs) and polyhydroxybutyrate (PHBs) (Ciriminna and Pagliaro 2020; Tamburini et al. 2021).

Plastic materials produced from such as cellulose, starch, vegetable oils, and vegetable fats (Babu et al. 2013; Tokiwa et al. 2009). PCL (polycaprolactone), PBS (polybutylene succinate),
PHA, PLA, PHB are typical examples of biodegradable bioplastics. Their popularity has gained attention in recent years. Based on a recent study, bioplastic production worldwide is predicted to rise from 2.11 million tonnes in 2019 to 2.42 million tonnes by 2024 (Mat Yasin et al. 2022). The characteristics of bioplastics, such as degradability, are a function of the degree of crystallinity, environmental factors, production process, and filler properties in blends and composites (Endres 2019; Thakur et al. 2018). This imparts distinct characteristics and peculiar advantages to each bioplastic and their overall use. Starch- and cellulose-based bioplastics are highly sought after owing to their affordability and biodegradability, but the former has a limited application and is most tailored for edible films, while cellulose-based bioplastics are highly characterized with weak hydrogen bonds, resulting in lower mechanical properties (e.g., strength, flexibility, etc.) and rapid degradation when subjected to heat. Notwithstanding, polylactic acid, when compared to other biodegradable polymers, has promising properties and stands out as a versatile and multipurpose choice for packaging applications due to its biodegradability and other favorable aspects.

Polylactic acid has been investigated as a viable option for creating bioplastic films due to their wide availability, cost-effectiveness, and non-reliance on petroleum. Additionally, the development of PLA has resulted in a biopolymer that is non-toxic, biodegradable, possesses superior strength and modulus, and has excellent film-forming properties, making it suitable for short-term applications. These properties have expanded the utilization of PLA in various fields, including food packaging and drug delivery (Gbadeyan et al. 2022).

Utilizing natural fibers obtained from agricultural by-products in composite applications is attractive due to its various advantages, including lightweight properties, low processing costs, and contribution to CO₂ sequestration (Al-Oqla and Sapuan 2017; Jubinville et al. 2023). Examples of natural fibers include industrial hemp, banana fiber, jute, kenaf, flax, wood, and others, although the specific choice depends on their availability in each geographical area. However, when it comes to creating durable composite products, the use of natural fibers as reinforcing fillers presents certain drawbacks in terms of long-term durability. This is due to their tendency to absorb moisture and their limited ability to resist crack propagation (Stevulova et al. 2013). The affinity of natural fibers to water leads to the separation between the fiber and the polymeric matrix, resulting in poor mechanical properties of the resulting composites. The existence of waxy substances on the fiber surfaces poses a challenge in achieving strong adhesion between the fibers and the matrix. Additionally, compared to
synthetic fibers like fiberglass and carbon fibers, lignocellulosic-based fibers lack uniformity and require added refinement such as mechanical grinding and chemical treatments to enhance their properties. Researchers have shown that the transfer of stress from the matrix to the fiber is heavily influenced by the interface, and several approaches have been explored to enhance the adhesion between the matrix and natural fibers (Hu and Lim 2007; Lee et al. 2009; Mohanavel et al. 2021; Pokharel et al. 2022). Physical and chemical treatments have been among the most popular methods used. The treatment of fillers with alkali (Mohamad et al. 2020; Pannu et al. 2021; Pokharel et al. 2022; Silva et al. 2019; Tran et al. 2014) and acetylation (Chung et al. 2018a; Pokharel et al. 2022) is regarded as the most efficient way to enhance the compatibility of natural fillers in the matrix.

Although natural fibers have immense potential in composites, we have only just begun to explore the possibilities of incorporating unused agricultural by-products (at present, only a few research studies have concentrated on using agricultural waste to make composites (Ashok et al. 2014; Mohan and Panneerselvam 2022; Ortega et al. 2022; Radusin et al. 2019; Ranjeth Kumar Reddy and Kim 2019)). Using agricultural by-products as a filler is a relevant strategy for creating financially sustainable and environmentally friendly products, while also reducing the negative effects of traditional plastics (Pokharel et al. 2022; Stevulova et al. 2013).

1.2 Knowledge Gaps, Hypothesis, and Research objectives

1.2.1 Knowledge Gaps

- The use of crops such as hemp and flax, which are grown for seed purposes in Canada, in composite materials has not been extensively studied.
- The effects of particle size, treatment and loading of fillers and the interaction among these factors on the composite material has not been largely studied.

1.2.2 Hypothesis

- Agricultural waste obtained from harvesting of crops such as flax and hemp can be effectively repurposed as fillers in composite materials, resulting in sustainable and environmentally friendly products.
• The treatment of flax and hemp fillers with alkali and acetylation improve the characteristics of the bioplastic films.

1.2.3 Research Objectives

The overall aim of this research is to explore the potential of using agricultural waste fillers, specifically flax and hemp, in polylactic acid (PLA) matrix composites. The specific research aims are as follows:

• To investigate the effect of alkali treatment on the mechanical, moisture, barrier and surface wettability properties of composite films made from PLA and flax/hemp agricultural waste fillers.
• To investigate the effect of acetylation treatment on the mechanical, moisture, barrier and surface wettability properties of composite films made from PLA and flax/hemp agricultural waste fillers.

1.3 Organization of the thesis

This thesis consists of six chapters, each serving a specific purpose. In Chapter One, an overview is provided, including the identification of knowledge gaps, hypotheses, and research objectives.

Chapter Two offers a comprehensive introduction and literature review on bioplastics, covering their components, natural fibers, treatment methods for natural fibers, biopolymers, and various manufacturing techniques employed in bioplastic production.

In Chapter Three, the materials and methods used for sample preparation and characterization in this research are presented.

Chapter Four is dedicated to the thorough characterization of polylactic acid (PLA) films incorporating flax and hemp fillers treated with alkali. This investigation focuses on assessing the impact of these fillers on film performance by examining essential properties such as surface transparency, wettability, mechanical characteristics, and using advanced spectroscopic and thermal techniques like FTIR, XPS, and TGA.
Chapter Five conducts an in-depth study on PLA films incorporating flax and hemp fillers treated with acetylation. The aim is to analyze the effects of these fillers on film performance by exploring various properties, including surface transparency, wettability, mechanical properties, and employing sophisticated spectroscopic and thermal techniques such as FTIR, XPS, and TGA. Additionally, this chapter investigates the water vapor permeability and moisture absorption of the composite films.

Finally, Chapter Six provides the key conclusions drawn from the research, along with recommendations and suggestions for future work.
CHAPTER TWO
LITERATURE REVIEW

The contents of this chapter have been published with following citation.

Contribution of the M.Sc. Candidate
Anamol Pokharel: conceptualization, literature review, writing—original draft, writing—review and editing, and visualization; Kehinde James Falua: literature survey, writing, and source knowledge gaps; Amin Babaei-Ghazvini: writing—review and editing; Bishnu Acharya: conceptualization, funding, source introduction, supervision, and writing—review and editing.

Contribution of this chapter to overall research
In this chapter, a literature review of the research has been conducted. An introduction and literature review are provided in this chapter. This chapter aims to provide information on bioplastics, with a focus on the various treatment methods, modes of compatibilization, and environmental impacts of the functional components in bioplastics. In addition, the use of bioplastics in many applications are documented in this chapter. The research gaps, the perspectives and uncertainties, and the outlook are summarized in this chapter.

Abstract
Global environmental concerns, as well as the rapid depletion of non-renewable fossil fuel-based resources, have prompted research into the development of sustainable, environmentally friendly, and biodegradable materials for use in a variety of high-end applications. To mitigate the environmental setbacks caused by nonbiodegradable materials, the development of biocomposites with improved mechanical performance is gradually gaining momentum. Natural fibers such as hemp, flax, and sisal have been well incorporated into biocomposite development. Nonetheless, the impact of functional moieties in their life cycle cannot be underestimated. In this review paper, a detailed discussion of the characteristics and components of biocomposites is presented. The treatment of composite materials (alkali and acetylation), as well as several manufacturing processes (hand layup, 3D printing, extrusion, etc.) and the applications of biocomposites, which are not limited to the aerospace industry,
packaging, biomedicine, etc., are presented. Biocomposites with excellent durability, performance, serviceability, and reliability must be produced to expand their applications.

2.1 Biocomposites

The durability of petrochemical-based plastics has been verified to last for many decades, highlighting the pressing need to switch to bioplastics. PET packaging, like drink bottles, can survive for over 90 years (Karan et al. 2019). Biopolymer production relies on living organisms and exploits different qualities, including toughness, resilience, and adaptability. Plants, crops, animals, and microorganisms serve as the fundamental raw materials that can be utilized to create biopolymers (Aggarwal et al. 2020).

Creating innovative bioplastics using organic materials is expected to bring about substantial benefits in certain domains, such as the environment and the economy (Brodin et al. 2017). There are many ways to categorize biopolymers into diverse groups since there is a vast array of resources that can be used to produce them (Kumar and Thakur 2017). One classification system entail dividing them based on their biodegradability and biomass content, which results in three categories: (i) bio-based and non-biodegradable, (ii) biodegradable and bio-based, and (iii) biodegradable and fossil-based options (Acquavia et al. 2021). Another way to classify them is based on the source of their materials, which means they can either be derived entirely from renewable resources or be a blend of biopolymers and commercial polyesters (Kumar and Thakur 2017). Biodegradable and bio-based biopolymers can also be categorized into three subgroups: synthetic biopolymers (produced from bio-derived monomers), microbial biopolymers (generated by microorganisms), and natural biopolymers (extracted from biomass) (Nilsen-Nygaard et al. 2021). The standout feature of bioplastics is their ability to biodegrade and be naturally recycled, thus offering various end-of-life options (Agarwal 2020; Podkościełna et al. 2022). The potential of bioplastics to support a circular economy and enhance recycling efficiency marks them as a crucial player in reducing carbon emissions (Abraham et al. 2021; Briassoulis et al. 2021; García-Depraect et al. 2021). Biodegradable plastics made from renewable resources that are suitable for the purpose include PHAs, such as PHB and PHV, and their copolymers, such as PHBV (Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)), as well as chemically produced polymers such as PGA (polyglycolic acid), PCL, PVOH (polyvinyl alcohol), and PLA (Mohan and Panneerselvam 2022; Rhim 2007; Roy and Rhim 2020). PLA (Cisneros-López et al. 2018; Hu and Lim 2007; Lee et al. 2009;

Natural fibers and the matrix part make up bioplastics. Biodegradable or non-biodegradable polymers can be used to create the matrix. Polymer matrix bioplastics are formed of natural (PLA, PHA, PCL) or synthetic matrix materials (thermoplastic and thermosetting plastics) coupled with addition to one or more reinforcements such as carbon fibers, glass fibers, or natural fibers (Sharma et al. 2020). The fibers give strength to the material and the resin holds it together which ensures that the product stays rigid and protects the fibers from moisture. The effect of reinforcement on polymer matrix composite was reviewed in the literature of (Das Lala et al. 2018). The authors noted that animal-fiber, protein, and biochemical-reinforced polymer matrix composites have a mechanical strength that makes them a potential material for scaffold and implants in biomedical applications but recommended that relevant research should concentrate efforts into finding other potential of applications for polymer matrix composites. The aspect ratio and fiber size play essential roles in the strength of the composite (Migneault et al. 2009). Although the integration of the small particles into the processing equipment is effective, low aspect ratios gives rise to stress concentration resulting in the lower strength when compared to neat polymer (Gamstedt et al. 2007; Wolcott and Englund 1999). Higher aspect ratio results in the superior mechanical characteristics as the load is transferred more effectively with increasing L/D ratio (Migneault et al. 2009). Bioplastics made from biopolymers and natural fibers are very appealing because of their ability to provide required functions at a cheaper price (Satyanarayana et al. 2009). They are biodegradable and recyclable; they can be disposed effortlessly after they have fulfilled their purpose without negatively affecting the environment. This is not possible in case of synthetic composites derived from fossil fuel resources. According to the bioplastics market prediction research, the industry will expand from $23.90 billion in 2021 to $80.55 billion by 2029 (Greyviews 2022). Plastic composites are being effectively substituted by bioplastics (Drzal et al. 2001).

2.2 Characteristics of biocomposites

Natural fibers and the matrix component make up biocomposites. Biodegradable or non-biodegradable polymers can be used to create the matrix. Polymer matrix biocomposites are
formed of natural (PLA, PHA, PCL) or synthetic matrix materials (thermoplastic and thermosetting plastics) coupled with addition to one or more reinforcements such as carbon fibers, glass fibers, or natural fibers (Sharma et al. 2020). The fibers give strength to the material and the resin holds it together which ensures that the product stays rigid and protects the fibers from moisture. The effect of reinforcement on polymer matrix composite was reviewed in the literature (Das Lala et al. 2018). The authors noted that animal-fiber, protein, and biochemical-reinforced polymer matrix composites have a mechanical strength that makes them a potential material for scaffold and implants in biomedical applications but recommended that relevant research should concentrate efforts into finding other potential of applications for polymer matrix composites. The aspect ratio and fiber size play essential roles in the strength of the composite (Migneault et al. 2009). Although the integration of the small particles into the processing equipment is effective, low aspect ratios give rise to stress concentration resulting in the lower strength when compared to neat polymer (Gamstedt et al. 2007; Wolcott and Englund 1999). Higher aspect ratio results in the superior mechanical characteristics as the load is transferred more effectively with increasing L/D ratio (Migneault et al. 2009). Biocomposites made from biopolymers and natural fibers are very appealing because of their ability to provide required functions at a cheaper price (Satyanarayana et al. 2009). They are biodegradable and recyclable; they can be disposed effortlessly after they have fulfilled their purpose without negatively affecting the environment. This is not possible in case of synthetic composites derived from fossil fuel resources. According to the biocomposites market prediction research, the industry will expand from $23.90 billion in 2021 to $80.55 billion by 2029 (Greyviews 2022). Plastic composites are being effectively substituted by biocomposites (Drzal et al. 2001).

2.3 Natural fibers

Plant fibers, for example, bast, leaf, and wood fibers, have piqued the interest of many scholars when being considered as a reinforcing agent (Sorieul et al. 2016; Summerscales et al. 2010). They contain cellulose, lignin, hemicellulose, and pectin in different quantities (Nirmal et al. 2015). The chemical composition of plant fibers is also affected by the growth period, stalk height and botanical classification of the fibers (Dittenber and GangaRao 2012). Hemp, flax, kenaf, and jute, which are all component of bast fiber are derived from the plant's stem and are widely employed for reinforcing composites because of their longer length as well as their highest strength and stiffness (Carruthers 2012). Interestingly, various non-wood fibers (e.g.,
Flax, kenaf, sisal and hemp) are also currently used commercially in biocomposites in proportion with polypropylene for applications in automotive sectors. Native grass fibers are also attracting scientists' attention as reinforcement fibers. Some of the widely available fibers are rice, wheat or corn straw fibers which can be used as a very economical reinforcement for biocomposite materials (Aladejana et al. 2020). Low embodied energy, good influence on agriculture, CO₂ sequestration is some of the benefits of using natural fibers in composite materials (Carruthers 2012). Natural fibers are recyclable and biodegradable which has resulted in increased use of these fibers in composite reinforcement applications. Natural fibers absorb CO₂ while growing which ultimately reduces their carbon footprint compared to the petroleum-based fibers. Table 2.1 summarizes the characteristics of natural fibres.

### Table 2.1: Characteristics of Fibers (Bledzki and Jaszkiewicz 2010; Faruk et al. 2012)

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Density (g/cm³)</th>
<th>Modulus (GPa)</th>
<th>Specific Strength</th>
<th>Production (10³ ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flax</td>
<td>1.4-1.5</td>
<td>27.6-70</td>
<td>19.7-50</td>
<td>830</td>
</tr>
<tr>
<td>Cotton</td>
<td>1.5-1.6</td>
<td>5.5-12.6</td>
<td>3.4-8.4</td>
<td>-</td>
</tr>
<tr>
<td>Jute</td>
<td>1.35-1.46</td>
<td>13-26.5</td>
<td>8.9-19.6</td>
<td>2300</td>
</tr>
<tr>
<td>Hemp</td>
<td>1.48</td>
<td>70</td>
<td>47.3</td>
<td>214</td>
</tr>
<tr>
<td>Ramie</td>
<td>1.45</td>
<td>61.4-128</td>
<td>42.3-88.3</td>
<td>-</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.33-1.45</td>
<td>9.4-38</td>
<td>6.5-28.6</td>
<td>378</td>
</tr>
<tr>
<td>Coir</td>
<td>1.15</td>
<td>4-6</td>
<td>3.48-5.2</td>
<td>-</td>
</tr>
<tr>
<td>E-glass</td>
<td>2.5-2.55</td>
<td>70-73</td>
<td>27.5-29.2</td>
<td>-</td>
</tr>
<tr>
<td>Aramid</td>
<td>1.44</td>
<td>60-140</td>
<td>41.2-97.2</td>
<td>-</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.4</td>
<td>230-240</td>
<td>168</td>
<td>-</td>
</tr>
</tbody>
</table>

#### 2.3.1 Flax

Flax (*Linum usitatissimum* L.) has piqued the interest of users owing to the possibilities of creating highly valued products from it. Importantly, flax fibers are cost-expensive, biodegradable, and characterized by excellent mechanical characteristics (Ramesh 2019). Due to its economic worth, flax has been a contributor to the gross domestic product (GDP) of several economies. At present, Canada, Russia, and Kazakhstan remain the leading producers
of flax, followed by China, France, and India (Griga and Bjelková 2013; Saleem et al. 2020). The flax fiber is of particular interest in composite development. Flax fiber have been deployed for composites development because of their mechanical strength, which is hugely ascribed to the significant presence of cellulose (64.1-75%), hemi-cellulose (11-20.6%), and lignin (2-30%) (Akin 2013; Cristaldi et al. 2010; Lilholt et al. 1999; Ramesh 2019; Tröger et al. 1998). Although studies have reported the development of composite materials using flax, scanty reports are available on flax and poly (lactic) acid as a sustainable route to non-biodegradable plastics. Dog-bone-shaped PLA/flax was developed using compression moulding (Pantaloni et al. 2022). The authors observed decreased mechanical properties because of environmental conditioning (75 and 95% RH) of the PLA/flax composite samples. Slicing parameters such as layer height, interfilament distance, number of layers, and microstructure, tensile properties of 3D-printed PLA/flax have also been investigated (Le Duigou et al. 2020). By application, Kandola et al. (2020) deduced the importance of PLA/flax as an excellent material for flame retardant. Generally, improved mechanical properties have been reported in PLA/flax composites (Kanakannavar and Pitchaimani 2022). In a similar study, Laziz et al. (2020) investigated the surface treatment of PLA/flax fiber. The authors reported better flexural strength, higher energy, and good surface properties.

During the production of flax fibers, shives, which are agricultural waste, are separated from the flax stem. Currently, these shives are used as animal bedding, particleboard, thermal insulation material for buildings (Le Duigou et al. 2012), and as an alternative to wood flour plastic composites (Goudenhooft et al. 2017). Shives contribute to about 30% of the bending stiffness of the dry flax stem (Evon et al. 2019). Research conducted by Nuez and his team explored the potential of flax shives as reinforcement in a polymer matrix, showing an enhancement in the mechanical properties of a flax shive/polypropylene composite (Nuez et al. 2021). Another study by Soete and colleagues investigated the flax fiber breakage during the injection moulding process. They found that the high shear forces during compounding and injection moulding lead to fiber breakage, resulting in the rupture of flax fibers and adjacent wooden parts or flax shives in the composite (Soete et al. 2017). Tensile tests revealed improved mechanical properties when flax shives were used in a polypropylene matrix (Tanguy et al. 2018). Considering the promising results of using flax shives and the whole flax stem as reinforcements in a polypropylene matrix, there is potential for valuable applications of this agricultural waste product.
2.3.2 Hemp

Hemp (*Cannabis sativa* subspecies L.), one of the most utilized plant-based fibers, has been produced for millennia and used in several food and non-food applications (Liao 2022). In North America, the cultivation of industrial hemp (*Cannabis Sativa* L.) is an advantageous practice due to its minimal requirement for chemical fertilizers and herbicides (Stevulova et al. 2014). On a global scale, the market size of industrial hemp was estimated to be 4.7 billion USD in 2019, and it is projected to reach 15.2 billion USD by 2027 (Jubinville et al. 2023). This growth is primarily driven by the increasing demand for hemp oils and fibers in industries such as automotive, construction, food and beverage, pharmaceutical, personal care, and textiles (Jubinville et al. 2023). In its natural state, the hemp plant is made up of seed, leaf, flower, stalk, and root. Essential oils and other vital biproducts could be recovered from hemp plants according to literature (El Bakali et al. 2022; Sainz Martinez et al. 2023; Visković et al. 2023). However, industrial hemp has a sizeable proportion of bast fibers (approximately 20 to 40 wt.%) and woody core fibers (hurds or shives) (around 60 to 80 wt.%), compared to the weight of the entire plant, which varies depending on growth conditions (Jubinville et al. 2023; Stevulova et al. 2013, 2014). Despite being the largest weight fraction, the hurd part of the hemp plant is currently considered the least valuable. Hemp stalks and roots are created as waste in the hemp sector and typically end up in landfills. As a result, researchers have taken a keen interest in initiating ways of converting these green wastes into value-added products (Ahmed et al. 2022; Berzin et al. 2018; Sarangi et al. 2023). The high tensile strength (sometimes >1000 MPa) and stiffness of extracted hemp fibers positioned them as a promising reinforcing material for biocomposites. Another key advantage of hemp fiber is its high aspect ratio (549) and low density. Notwithstanding, non-uniform and non-smooth surfaces, restricted processing temperature (<230 ºC), variability of properties, and low resistance to water absorption and decay have been reported as drawbacks of hemp fibers (Shahzad 2011a). As such, studies have evaluated their performance when developed with bioplastics. Considering the peculiarity of hemp fibers, especially their processing temperature, thermoplastics such as polyamides, polyesters, and polycarbonates, which need higher processing temperatures above (>250 ºC), cannot be used with natural fibers. This scenario is, however, different for PLA. Several authors have studied PLA/hemp composites or hemp with other bioplastics (Baghaei et al. 2013; Mazzanti et al. 2020; Momeni et al. 2021; Pickering and Aruan Efendy 2016), but insight from these studies still demands intensive research to investigate how developed biocomposites are affected by factors such as source of the natural fiber, extraction procedure,
type of treatment, and type of technology used. In the spectroscopy study of PLA/hemp fibers, Smoca (2020) opined that the biocomposite is an excellent candidate for furniture and construction purposes. Sitticharoen et al. (2022) observed that PLA/micro-fillers hemp fiber could be a novel material in non-construction industrial sector owing to thermal stability and excellent water absorption property reported in their results. In a more recent study, the physico-chemical degradation through weathering acceleration of PLA/hemp fiber biocomposite have been studied (Hedthong et al. 2023). The incorporation of hemp hurd into polymer matrices has proven its ability to enhance the mechanical, thermal, and acoustic properties of the resulting hemp-polymer composites (HPCs) (Stevulova et al. 2013). HPCs are considered a practical substitute for both wood plastic composites (WPCs) and pure wood products (Jubinville et al. 2023; Schirp and Stender 2010). Insights from all these scientific reports on PLA/hemp suggest more investigation of several important parameters and processes on development of eco-friendly bioplastics.

2.4 Treatment of natural fillers

Natural fillers are hydrophilic in nature i.e., they attract water molecules. The hydrophilicity of natural fillers results in the delamination between the fiber and the polymeric matrix which reduces the mechanical characteristics of the resulting composites (Faruk et al. 2012). As depicted in Figure 2.1, the poor interfacial bonding gives rise to the fiber pull-out phenomena that further deteriorates the mechanical properties (Khan et al. 2021). The thermal degradation temperature of the natural fillers is low (around 200 °C). The presence of waxes on the fillers’ surfaces makes it difficult to achieve good bonding between the fiber and the matrix. These disadvantages such as hydrophilicity, poor bonding, and thermal instability, can be overcome by subjecting fillers to physical and chemical treatments.
Physical treatments, for instance, plasma discharge and corona discharge improve the bonding between the fiber and the matrix without changing the fibers’ chemical characteristics (Faruk et al. 2012). However, these physical treatment methods only affect the surface characteristics of the fiber. While plasma discharge roughens up the surface of the fiber to enhance better interfacial bonding, corona discharge, on the other hand results in surface oxidation and leads to the better compatibility between the fiber and the matrix (Ragoubi et al. 2012). Other examples of physical treatment methods include ultraviolet bombardment, laser, and gamma-ray (Jawaid and Khalil 2011). Chemical treatment of biocomposites is somewhat like plasma discharge but are usually carried out via chemical reaction pathway. Most reported chemical treatment methods in literature are alkali treatment (mercerization) (Abdullah et al. 2022) and acetylation (Zaman and Khan 2021). Nonetheless, chemical treatments such as silane treatment (Dehouche et al. 2020), benzyolation treatment (Mohd Izwan et al. 2021), maleated coupling agents (Daghigh et al. 2018), permanganate treatment (George et al. 2012; Rabhi et al. 2022), and peroxide treatment (Li et al. 2007; Sabri et al. 2020) have been widely reported in the literatures. Alkali treatment disrupts the H-H bond in the structure and hence increases the roughness in the fiber’s surface, promoting better interlocking between matrix and fibers. Furthermore, the waxes, oils and lignin present in the fibers’ external surface are washed away depolymerizing the cellulose and the short crystallites are exposed due to this treatment (Li et al. 2007). In acetylation treatment, acetyl group is introduced in the cell wall of the fibers replacing the hydroxyl group. The acetyl group repels water molecules thus making the fibers
hydrophobic. The hygroscopicity of natural fibers can be reduced by the acetylation treatment. As a result, the resulting composites have increased dimensional stability (Hill et al. 1998). Given the increased popularity of these two chemical approaches, it is critical to provide more detailed information about their distinctiveness and applications.

2.4.1 Alkaline treatment

Treatment of natural fibers with alkali solution removes waxes, hemicellulose, and oils thereby increasing the roughness of the external surface of the fibers and rendering the fibers thermally stable. The increased roughness leads to better interlocking between the fibers and the matrix enhancing the overall mechanical characteristics of the resulting composites (Ray et al. 2001). Concentration of the alkaline solution, temperature and time of the alkaline treatment highly influences the effectiveness (Ariawan et al. 2018). Fiber fragmentation and separation rate increases with alkaline treatment (Iannace et al. 2001). Sodium hydroxide (NaOH) is generally used for the treatment of natural fibers. Hemicellulose, waxes, oils, lignin are removed when the fibers are treated with NaOH solution. As a result, the fibrils are revealed, and the roughness of the fiber surface increases. Amorphous regions are created in the tightly packed cellulose lattice thereby altering the orientation of the cellulose lattice. The new cellulose lattice has larger distance between the cellulose molecules and water molecules fill the space between the cellulose molecules (Campilho 2015). OH groups sensitive to NaOH are thus broken down and eventually removed from the fiber structure. Hence, water loving OH groups are removed resulting in increased moisture resistance. Moreover, oils, waxes, and hemicelluloses are also removed (Campilho 2015). Na⁺ ion reacts with fiber as shown in the following chemical reaction (Muthu et al. 2019). Figure 2.2 shows the schematic representation of the chemical reaction of alkali treatment process.

\[
\text{Fiber-}\text{OH} + \text{NaOH} \rightarrow \text{Fiber-}\text{O-Na}^+ + \text{H}_2\text{O} + \text{Surface Impurities}
\]
Figure 2.2: Schematic showing the alkaline treatment of raw natural fibers (Redrawn from Ref. (Silva et al. 2021))

Pannu et al (Pannu et al. 2021) investigated the influence of alkaline treatment on the mechanical properties of composites and found that the tensile strength and impact energy of the treated composites both increased by around 34% compared to the untreated one. The findings of the scholars were corroborated by (Abdullah et al. 2022) who observed that alkaline treatment of seaweed fibers increased the tensile strength of composites by around 48% compared to the untreated one. This increment in tensile strength can be accounted to the greater adhesion between seaweed fibers and polypropylene. The study also showed the increment of impact strength of the composites by 106%. The authors also noticed the lower water absorption in treated composites compared to the untreated ones (Abdullah et al. 2022). In most of the surveyed literatures (Table 2.2), many of the scholars saw that alkaline treatment of the natural fibers leads to greater adhesion between fiber and the matrix, which improves the composites' mechanical performance. Considering the mechanical features, different matrix materials such as PLA, Polypropylene, amongst several other matrix precursors offers significantly higher tensile strength.
<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>Matrix</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana Fibers</td>
<td>PLA</td>
<td>Increment in tensile strength and impact strength both by around 34%.</td>
<td>Pannu et al. 2021</td>
</tr>
<tr>
<td>Seaweed Fibers</td>
<td>Polypropylene</td>
<td>Tensile strength improved by around 48% and the impact strength by around 106%. Water absorption rate was seen to be lower in treated composites.</td>
<td>Abdullah et al. 2022</td>
</tr>
<tr>
<td>Rice and Einkorn Wheat Husk</td>
<td>PLA</td>
<td>The bending stress and modulus were increased showing the better interfacial adhesion</td>
<td>Tran et al. 2014</td>
</tr>
<tr>
<td>Hemp fiber</td>
<td>Polypropylene</td>
<td>The tensile properties of the resulting composite increased for fibers treated at higher temperature.</td>
<td>Sunny et al. 2020</td>
</tr>
<tr>
<td>Alfa fiber</td>
<td>Modified sunflower oil</td>
<td>Interfacial adhesion was improved resulting in better mechanical properties and thermal stability of the composites.</td>
<td>Kadem et al. 2022</td>
</tr>
<tr>
<td>Eucalyptus microfibers</td>
<td>PLA</td>
<td>Mechanical properties were increased.</td>
<td>Silva et al. 2019</td>
</tr>
<tr>
<td>Ground coffee</td>
<td>HDPE</td>
<td>There was an improvement in interfacial adhesion, water resistance, impact and tensile characteristics.</td>
<td>Tan et al. 2017</td>
</tr>
<tr>
<td>Kenaf fiber mat</td>
<td>PLA</td>
<td>The mechanical performance of the treated bio-composite was higher than that of untreated one.</td>
<td>Mohamad et al. 2020</td>
</tr>
<tr>
<td>Pineapple leaves</td>
<td>Polypropylene</td>
<td>Tensile and water resistance characteristics increased and the biocomposites were more thermally stable.</td>
<td>Gnanasekaran et al. 2021</td>
</tr>
</tbody>
</table>
Aloe Vera Fiber
poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)
The rheological properties and thermal stability increased. Dehouche et al. 2020

| Combretum dolichopetalum fiber | HDPE | Ultimate tensile strength and flexural strength increased by 7.64% and 76.19%, while impact strength decreased by 5.33%. | Oladimeji et al. 2018 |

### 2.4.3 Acetylation treatment

Acetylation treatment changes the mechanical and thermal properties plasticizing the natural fibers. Acetic anhydride is the commonly used chemical in this treatment. Acetyl groups are introduced in the fibers' cell wall, replacing the OH groups, making the fibers hydrophobic (Hill et al. 1998). Acetic acid is also produced as the by-product which must be removed before using the fiber. The chemical reaction (Hill et al. 1998) is shown below:

\[
\text{Fiber-OH} + \text{C}_4\text{H}_6\text{O}_3 \rightarrow \text{Fiber-OCOCH}_3 + \text{CH}_3\text{COOH}
\]

Chung et al (Chung et al. 2018b) investigated the effect of acetylation treatment on the mechanical performance of kenaf fiber reinforced PLA biocomposites and reported the increment in tensile strength and flexural strength of the treated composites compared to untreated one. The findings agree with the study carried out by (Kivade et al. 2021) who reported that the tensile strength, impact strength and flexural strength of the acetylation treated banana fiber reinforced composites was increased by around 98%, 58% and 24 % compared to the untreated one. The study also showed that the water absorption rate was lower in treated composites (Kivade et al. 2021). With acetylation treatment, the water absorbing tendency of the natural fibers is reduced and the resulting composites are more dimensionally stable (Table 2.3).
Table 2.3: Effect of Acetylation treatment

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>Matrix</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combretum dolichopetalum fiber</td>
<td>HDPE</td>
<td>Ultimate tensile strength and impact strength increased by 18.78% and 58.73% respectively compared to untreated one.</td>
<td>Oladimeji et al. 2018</td>
</tr>
<tr>
<td>Kenaf fiber</td>
<td>PLA</td>
<td>Increased mechanical characteristics and water resistance as well as the thermal stability.</td>
<td>Chung et al. 2018b</td>
</tr>
<tr>
<td>Banana fiber</td>
<td>Polyvinyl alcohol (PVA)</td>
<td>Showed an increase of 98%, 58% and 24% in tensile, flexural and impact strength of the treated composites. The water absorption rate also reduced.</td>
<td>Kivade et al. 2021</td>
</tr>
<tr>
<td>Hemp Fiber</td>
<td>Unsaturated Polyester</td>
<td>Increased chemical and mechanical fiber-matrix bonding resulting in improvement in mechanical performance.</td>
<td>Wang et al. 2014</td>
</tr>
<tr>
<td>Wood Fiber</td>
<td>Poly(ε-caprolactone) (PCL)</td>
<td>Increased ultimate strength and Young’s modulus by 46% and 248% respectively compared to untreated fiber.</td>
<td>Lo Re et al. 2018</td>
</tr>
<tr>
<td>Wood fiber</td>
<td>HDPE</td>
<td>Resulted in improved interfacial adhesion, higher Young’s modulus and lower strain at failure.</td>
<td>Mbarek et al. 2013</td>
</tr>
<tr>
<td>Softwood Pulp Fiber</td>
<td>LDPE</td>
<td>There was no increment in mechanical characteristics but significant increment in moisture resistance properties.</td>
<td>Lepetit et al. 2017</td>
</tr>
<tr>
<td>Material</td>
<td>Polymer</td>
<td>Properties and Improvements</td>
<td>Authors and Year</td>
</tr>
<tr>
<td>--------------------------</td>
<td>--------------------</td>
<td>---------------------------------------------------------------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Kenaf</td>
<td>Starch</td>
<td>Increased interfacial bonding.</td>
<td>Jung et al. 2021</td>
</tr>
<tr>
<td>Kenaf</td>
<td>HDPE</td>
<td>Increment in water resistance, tensile and thermal stability characteristics.</td>
<td>Ismail et al. 2011</td>
</tr>
<tr>
<td>Kraft based dissolving pulp</td>
<td>Polypropylene</td>
<td>Increased thermal stability and mechanical performance.</td>
<td>Duan et al. 2022</td>
</tr>
<tr>
<td>Japanese cedar sapwood</td>
<td>Polypropylene</td>
<td>Increased tensile and flexural strength as well as improvement in creep resistance.</td>
<td>Hung et al. 2016</td>
</tr>
<tr>
<td>Banana fiber</td>
<td>Polypropylene</td>
<td>Improved homogeneous dispersion, interfacial adhesion, water resistance and thermal stability compared to the untreated and alkaline treated one.</td>
<td>Zaman and Khan 2021</td>
</tr>
</tbody>
</table>

2.5. Biopolymers as matrix

Biopolymers are biodegradable and eco-friendly. Biopolymers are derived from agricultural resources, by-products, chemical processing and microbiological actions (Satyanarayana et al. 2009). They may also be created by blending two biopolymers. The structure and origin of the polymer and the degradation conditions decide the polymers' biodegradability (Mohanty et al. 2002). Microbes attack the polymer during degradation and decompose it into small molecules along with the emission of CO₂ (Mohanty et al. 2000). Biopolymers alone have weak mechanical characteristics; however, the addition of natural fibers improves their mechanical performance (Van de Velde and Kiekens 2002). Traditional polymers such as polypropylene, polyester, polyethylene and epoxy have been around for a long time and have gone through the various stages of research and commercialization process (Alavudeen et al. 2015; Carrillo-Escalante et al. 2016; Eagan et al. 2017). Significant amount of time and resources have been poured in the development of these polymers which have resulted in their superior mechanical performance. Nevertheless, the problem of recycling and underlying environmental concerns about their usage have moved the interest towards biopolymers (Isikgor and Becer 2015). Out of 7 billion metric tonnes of plastics generated, more than three-fourth end up in landfills. 
are some of the widely used biopolymer matrices. The intriguing features of these materials are succinctly elucidated in the following subsections.

**PHA**

PHA is a renewable, eco-friendly polymer produced from fatty acids, sugar, sucrose, molasses, starch, wheat, methane, and corn (Zwawi 2021). Sucrose and glucose are used for the commercial production of PHA (Keshavarz and Roy 2010; Zwawi 2021). Biodegradability of PHA depends upon its surrounding, water content, crystallinity, chemical composition, pH level and surface area (Zwawi 2021). Hong et al. developed novel heart valves for replacing diseased natural valve using PHA (Hong et al. 2009). Use of PHA can also be seen in drug delivery and packaging (Bugnicourt et al. 2014). Nevertheless, poor physical and mechanical characteristics and relatively higher cost of production (7-10 Euro/kg) limits the introduction of PHA into broader market (Bugnicourt et al. 2014; Singh et al. 2015).

**PBS**

PBS is biodegradable and produced from 1,4 butanediol and succinic acid with outstanding thermal (melting temperature of 115 °C) and mechanical performance (Young’s modulus of 500 MPa, and tensile yield strength of 35 MPa) (Zwawi 2021). Blending PBS with other biopolymers such as PLA, starch, carbohydrates can improve its mechanical performance. PBS is used to manufacture bottles, packages, shopping bags, etc (Frollini et al. 2015).

**PLA**

Poly(lactic) acid (PLA) is a biodegradable thermoplastic polymer material commonly used in small to large scale processes such as packaging, textiles, medical implants, etc. They are preferred as a “green” alternative to traditional petroleum-based plastics owing to their renewability characteristics and origin. Usually formed by polymerization of lactic monomers in agricultural biomass such as corn starch, sugarcane, and tapioca roots (Lunt 1998; Morão and De Bie 2019; Rai et al. 2023; Vink et al. 2004), PLA is the most widely desired biodegradable plastic because of its better formability, biocompatibility with other polymers, non-toxicity, and excellent insulating properties. The significant properties of PLA from
commercial perspective include its good mechanical properties (Young’s modulus 5–10 GPa, and flexural strength of up to 140 MPa) (Oksiuta et al. 2020) and its manufacturing from renewable raw materials (Yu 2009). PLA production has several advantages compared to other biopolymers. PLA production consumes CO₂ (Dorgan et al. 2001). It is compostable, recyclable, and biodegradable (Drumright et al. 2000; Sawyer 2003). Its thermal processability is better compared to PHA, PEG, and PCL. PLA can be produced using 25-55% less energy than that of conventional polymers (Rasal et al. 2010). The tensile strength and elastic modulus of PLA and PET (Polyethylene Terephthalate) are comparable (Farah et al. 2016). From a biodegradability standpoint, many authors have affirmed the positive impact of PLA, especially when it comes to providing a greener world with a smaller environmental imprint. Fewer greenhouse gas emissions, the potential to reduce fossil energy consumption, faster decomposition, and the absence of toxic biproducts during processing of PLA have positioned them as a potent biopolymer material (Karamanlioglu et al. 2017). Despite the appealing advantages of PLA, their sole use is highly induced with many drawbacks. When exposed to elevated temperatures, softening or quick deformation occur which limits their use in high-temperature applications such as those in the electronic and automotive industries. Similarly, their high brittleness makes them unfit for important processes where high durability and flexibility are needed. Also, PLA’s physical and mechanical properties could be adversely altered and affected due to their sensitivity to high moisture and, potentially, may not be an excellent candidate in outdoor applications that require long-term durability. Notwithstanding, scientists have been experimenting with many ways to sidestep these limitations. A popular panacea is the incorporation of plant-based fibers such as sisal, flax, hemp, coir, jute, etc. into bioplastics (Prakash et al. 2022). With respect to biocomposites, application of natural fibers to biodegradable plastics requires a significant understanding of the inherent characteristics (e.g., fiber length, fiber orientation, type of treatment, etc.) of the fibers. Fiber orientation, for example, is assigned isotropic and mechanical properties of fibers, while typical fiber treatments (e.g., ultrasonic, chemical) can increase fiber-matrix adhesion and reduce moisture absorption. Several sources of plant-based fibers exist in nature, as previously stated; nonetheless, specific application needs and considerations such as cost, and availability is critical to their utilization. The comparison of mechanical properties of PLA and PBS with synthetic polymers is summarized in Table 2.4.
Table 2.4: Comparison of mechanical properties of PLA and PBS with synthetic polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Young’s Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>5-10</td>
<td>53</td>
<td>5</td>
<td>Oksiuta et al. 2020; Sanivada et al. 2020</td>
</tr>
<tr>
<td>PBS</td>
<td>1.43</td>
<td>18.62</td>
<td>-</td>
<td>Saffian et al. 2021</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>1.5-2</td>
<td>31</td>
<td>80-350</td>
<td>Sanivada et al. 2020</td>
</tr>
<tr>
<td>HDPE</td>
<td>0.4-1.5</td>
<td>14.5-38</td>
<td>2-130</td>
<td>Sanivada et al. 2020</td>
</tr>
<tr>
<td>Polyamide</td>
<td>2</td>
<td>56-90</td>
<td>70</td>
<td>Sanivada et al. 2020</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>4-5</td>
<td>25-69</td>
<td>1-2.5</td>
<td>Sanivada et al. 2020</td>
</tr>
</tbody>
</table>

**Bio-epoxy Resins**

Several bio-epoxy resins can be obtained from natural sources like epoxidized vegetable oils (including soya oil and pine oil residues) or residues from other industrial processes such as cellulose and biofuel production (Tan and Chow 2010). Sorbitol derived from corn starch and glycerine derived from triglyceride vegetable oil are two common and crucial bio-epoxies. Glycerol derived epoxy resins, like polyglycidyl ethers of polyglycerol and glycerol, are inexpensive, commercially available, and used in paper and textile industries. Takada and colleagues explored the use of glycerine-epoxy bio-resins to make composite materials and said that glycerine-epoxy resins, because of their high thermal properties and mechanical performance, could be a potential replacement for fossil-based epoxy resins (Takada et al. 2009). Shibata’s co-workers shared a similar standpoint when experimenting with glycerol and polyglycidyl ether of sorbitol polymerized with a tannin-based agent that had relatively good and balanced thermomechanical characteristics (Shibata and Nakai 2010). Epoxy resins derived from vegetable oils are another broad category, and the most common ones used today are epoxidized linseed oils and soy vegetable oils. Miyawaga et al. (Miyagawa et al. 2006) prepared bio-based soybean oil nanocomposites and carbon fiber reinforced organic clay and
tested their thermal and mechanical performance. Their efforts have resulted in new and advanced materials with high modulus and strength properties. Ahmetli et al. (Ahmetli et al. 2012) used sunflower residue fatty acids to alter a commercial synthetic epoxy resin. All modifications improved mechanical performance with greater strength and elongation, while a resin hardness was also considerably improved (Ahmetli et al. 2012). Some other bio-based resins are polyfurfuryl bioresin (Deka et al. 2013), hemp oil based bioresin (Cardona et al. 2015), furfuryl alcohol (Fam et al. 2013), epoxidized soybean oil (Díez-Pascual and Díez-Vicente 2014), castor oil derivatives (Díez-Pascual and Díez-Vicente 2015), and epoxidized hemp oil (Manthey et al. 2013). Despite the advantages, biopolymers have some disadvantages such as thermal instability, flammability, and low production volume which in turn increases the processing costs. Microbial attacks can cause damage to biopolymers (Beck et al. 2019). So, depending on the uses, various antibacterial and antifungal components are required. Moisture uptake is high in starch-based biopolymers (Andrew and Dhakal 2022). Future significant areas of research for matrix materials include the design and creation of novel biopolymers that are thermally stable, have lower processing temperature, recyclable, stable while storage, transportation and service life and demonstrate good mechanical performance. New uses will emerge as these materials become resistant to moisture, more dimensionally stable, robust, and fire-resistant. The field of nanotechnology provides a good platform to develop the novel biocomposites possessing the aforementioned properties. Figure 2.3 shows the chemical structure of commonly used biopolymers.
2.6. Compatibilization of biocomposites

Despite the fact that the combination of various polymers create a product having superior properties than either of the parent polymer, the most polymer pairs are thermodynamically immiscible (Stamm n.d.). Therefore, the interactions between phases are weak resulting in poor mechanical performance (Wang et al. 2015; Xu et al. 2015). Hence, there is an increasing interest in compatibilization of polymers in the academic research and industry.

2.6.1 Non-reactive compatibilization

One of the compatibilization techniques is adding the third component in polymer blends. This technique falls under the non-reactive compatibilization. Mostly the additives are graft or block copolymer. The compatibility is improved via non-covalent reactions (Chen et al. 2017; Lin et al. 2005). Theoretically, it is suggested that the compatibilizer’s effectiveness rises with its molecular weight (Utracki 2002). Compatibilization by addition affects the interfacial characteristics as well as the flow behaviour which in turn affects the processing and performance (Utracki 2002). Various non-reactive compatibilizers reported in the literature are
PE-PLA di-block copolymers (PE-b-PLLA) (Anderson and Hillmyer 2004; Wang and Hillmyer 2001), maleic anhydride grafted PE (MAPE) (Boubekeur et al. 2020; Quiles-Carrillo et al. 2019; Singh et al. 2011), ethylene-glycidyl methacrylate copolymer (EGMA) (Brito et al. 2016; Djellali et al. 2013), and ethylene-methyl acrylate-glycidyl methacrylate (EMA-GMA) terpolymer (Brito et al. 2016; Zolali and Favis 2018). MAPE and MAPP are commonly used compatibilizers for producing natural fibers reinforced biocomposites (Daghigh et al. 2018). At temperatures higher than 170°C, maleated polymer reacts with natural fibers via esterification. As a result, the long polymer chains are in a covalent bond with natural fibers (Kabir et al. 2012). This increases the interfacial adhesion between matrix and the fibers. Therefore, various studies have reported that the addition of maleated polymer significantly enhances the characteristics of the biocomposites (Baykus et al. 2015; Chun et al. 2013; Daghigh et al. 2018; Saeed et al. 2021).

2.6.2 Reactive compatibilization

Another technique is reactive compatibilization. It is presently the dominant technique of compatibilization. In this strategy, the graft or block copolymers are formed in situ at the interface because of the specific chemical reaction between the polymers (Dong et al. 2015; Wang et al. 2016). In this method, the copolymers are formed at the region where they should remain. As a result, the interfacial tension between polymers is reduced, coalescence of the particles is suppressed and eventually, the interfacial adhesion is improved (Eklind et al. 1996; Wang et al. 2015). This method is employed in the extruder during compounding. Functionalized Compatibilizers which possess isocyanate, maleic anhydride, oxazoline, epoxide as reactive groups are utilized in this method. The compatibilizers are fed into the extruder along with polymers at the same time. Also, an appropriate initiator, generally the peroxide having low decomposition temperature (dicumyl peroxide) is introduced. The rapid decomposition of DCP takes place. The free radicals are formed along the polymers. The reaction between these active points and compatibilizers takes place. Hence the compatibilization occurs in the extruder via reaction. The product formed has a complicated structure with grafted polymers and compatibilizers at the interface. As a result, there is a reduction in interfacial tension and increment of interfacial adhesion. There is a substantial reduction in gap between the two incompatible polymers. There is an interplay between the polymers and the transmission of load is permitted from the dispersion to the matrix phase, which improves the overall characteristics (Detyothin et al. 2015). Using DCP as the initiator,
the improvement in the interaction between PLA/PBS (Srimalanon et al. 2018), PHB/PCL (Semba et al. 2007), thermoplastic dry starch (DTPS)/PLA with maleic anhydride as the compatibilizer has been reported in the literature. Ferri et al. conducted a study on the impact of various compatibilizers like polyethylene vinyl acetate, polyvinyl alcohol and DCP on PLA/bio-polyethylene blend (Ferri et al. 2020). The writers report the increment in ductile properties in compatibilized blend. Highest impact energy and highest elongation at break was observed when Polyethylene vinyl acetate was used as the compatibilizer (Ferri et al. 2020).

Naturally occurring lignin acts as a promising compatibilizer between hydrophobic matrices and hydrophilic fibers. Lignin, which is the second most prevalent renewable bio-resource after cellulose, is regarded as a waste product in a variety of industrial processes. Many studies and reviews have documented attempts to valorise lignin in recent years (Figueiredo et al. 2018; Rinaldi et al. 2016; Schutyser et al. 2018). Lignin has many advantages, including many functional groups, strong biocompatibility, high carbon content, and low toxicity that can be converted into carbon materials and composites. Lignin-based materials are often low in cost and eco-friendly. The compatibility of hemp (Thielemans and Wool 2005) and flax fibers (Thielemans et al. 2002) with thermoset matrices have improved by treating fibers with lignin, hence increasing the mechanical characteristics of the resulting biocomposites. According to Graupner, the tensile characteristics of compression-moulded PLA-cotton composites were improved when treating the fibers with lignin (Graupner 2008). Kraft lignin as compatibilizer was used in the preparation of jute fiber reinforced polypropylene composites by Acha et al. (Acha et al. 2009). The writers report that the thermal degradation temperature increased by around 8 °C in the Polypropylene-lignin blend (5% lignin) compared to the neat polypropylene. However, the study shows that there was improvement in impact characteristics only (Acha et al. 2009). Investigation of introducing kraft lignin to hemp reinforced epoxy composites was conducted by Wood and his colleagues (Wood et al. 2011). The authors noticed increment in impact strength with increment in lignin content. The study further reports that the tensile and flexural modulus also increased till 2.5 wt. % addition of lignin. This study showed an increase in structural properties of the composites to a certain extent compared to the composites without lignin (Wood et al. 2011). The effect of kraft lignin obtained from pulping waste on poplar wood flour reinforced polypropylene composite was studied (Luo et al. 2017). The study shows that the water absorption property was reduced, and the composites were more thermally stable compared to the composites without lignin. Moreover, the authors found that the impact strength, flexural strength, and tensile modulus increased when small amount of lignin (0.5 wt.
% and 1 wt. %) was added albeit at higher lignin content there was no change or even decrease in properties was observed. This study suggested that the industrial lignin acts as a potential additive in wood flour reinforced polypropylene composite (Luo et al. 2017).

2.7. Moieties in polymer compatibilization-environmental impact and applications

To a certain extent, when compared with plastic-based materials, it is widely agreed that biocomposites are safer for people and other living things owing to their unique and appealing attributes. Flax, hemp, jute, etc. which are common sources of lignocellulosic fibers have been reported in a plethora of report owing to their compatibility with biodegradable hydrophobic polymers such as PLA and PBAT to form bio-composite (Mazzanti et al. 2019). Findings of several scholars have documented enormous benefits of in the use of biodegradable hydrophobic polymers with natural fibers (Karimah et al. 2021; Thyavihalli Girijappa et al. 2019) whereas the manufacturing of biocomposite from recycled polypropylene (PP) matrix have shown possibility of several phenolic compounds, as well as oxidized chemicals such as alcohols, aldehydes, ketones, and carboxylic acids (Chamas et al. 2020; Vera et al. 2019). The significance of this is that uncontrolled consumption of manufactured composites materials incorporated with non-biodegradable moieties may cause adverse environmental impacts. It is worth mentioning that the chemicals produced by the breakdown of lignocellulosic fibers, such as carboxylic acids, alcohols, and esters, appear to be more prevalent than other components in materials as they age. Depending on the type of polymer components and their environmental conditions, polymer blends experience diverse types of deterioration (e.g., photodegradation, oxidation, erosion, and hydrolysis) throughout processing, storage, use, and disposal. Even though the exact implications of polymeric compatibilization of functional moieties on the environment are relatively known, these products have gained popularity and have been discovered to be important in practically every element of human life. In this regard and as previously captured in this review, the need for fossil fuels and the problems with plastic waste's sustainability has prompted continued research developments in the field of more environmentally benign materials of natural origin. Utilizing some natural materials such as vegetable oils, waste-derived liquids, and essential oils profoundly creates new possibilities as reactive compatibilizers, active additives, or even natural plasticizers for the development of new polymer formulations with improved sustainability characteristics (Balart et al. 2020). Numerous studies have dwelled more on the mechanical performance and end-use of functional moieties than the environmental impacts. The interactive effect of block copolymer (BC) and
ionic liquid (IL) as a functional moiety on PLA/PCL blends was studied (Long et al. 2018). The authors observed that BCIL copolymer strengthened the contacts between the two polymeric phases, and the particle size of PCL reduces owing to interfacial reinforced compatibility of IL moiety. In addition, it was discovered that the dialkoxybenzene/dihydroxybenzene moieties either improved the polymers' already-existing features or merely introduced new ones. The dihydroxybenzene moiety guaranteed the polymer's metallic adsorption, redox activity, adhesion-promoting, and lacquer coating abilities, whereas the dialkoxybenzene moiety increased the electrical conductivity and electroluminescence of the poly(para-phenylene)s (PPPs) and poly(phenylenevinylenes) (PPVs) and their associated properties. Cazin and co-workers (2021) indicated novel applications such as 4D printing, soft robotics, medication delivery systems, bioimaging, and tissue engineering are potential areas where functional moiety such as coumarin could play a significant role in the future owing to their electro-optical properties (e.g., absorbance and fluorescence). Despite these appealing outcomes of researchers, it is still imperative to provide up-to-date information on the associated environmental impacts of functional moieties in biocomposites.

One of the most widely reported functional moieties with an excellent flexibility and tensile strength in polymer compatibilization is epoxy (Berzins et al. 2022; Zhao 2022). Their strong mechanical properties, good heat resistance and abrasion, adhere well to a variety of substrates. Being distinguished by a combination of these beneficial and outstanding properties, epoxy resins are often used in a vast array of different applications as structural adhesives. This suggests that an increase in the demand for epoxy in the upcoming years. Currently, photosensitive (e.g., cinnamate, chalcone, stilbene, maleimide, and anthracene), ionic liquids, and coumarin moieties have been documented in the literatures. Suresh and colleague opined that most photo-sensitive moieties easily go through photo-crosslinking upon irradiation (Suresh and Arun 2022). Ishiguro and colleagues’ (2007) report also provided insight into the photosensitivity and birefringence properties of amorphous polymers having azobenzene and tolane moieties. In their findings, the scholars saw the degradation effects of the moieties. Degradation is an externally induced irreversible change in the physical characteristics of the compatibilized biocomposites brought on by chemical reactions in the main or side chains macromolecules (Bryll et al. 2017; Vohlidal 2020). Chemical, thermal, mechanical, biological, and radiation-related degradation processes have been reported by many scholars. While chemical degradation is essentially promoted by chemical agents like oxygen, water, acids, or
bases, specifically oxidation and hydrolysis (Chamas et al. 2020), thermal and mechanical degradation processes are caused by heat application and influence of external stress (including UV light and electromagnetic exposure), respectively (Fajardo Cabrera de Lima et al. 2020; Yousif and Haddad 2013). On the other hand, biological agents such as fungi or bacteria act on decomposed biocomposites leading to a disintegration of the polymer matrix, resulting in the creation of fragmented particles of varied sizes and leached additives. Nonetheless, some chemical industries have taken the advantage of the leached additives and have used them in the manufacture of chemicals (Campanale et al. 2020). Leached additives, however, may be wrongly considered as food for mammals such as birds and could potentially threaten their existence in the ecosystem (Smith et al. 2018). As seen by Lambert and Wagner (2018), lower molecular weight additives travel more readily through a polymer matrix that shows higher pore size; the rate at which additives are leached depends on the pore diameter of a certain polymer structure and the additives used. Hammer and co-workers (2012) also stressed that the occurrence of plastic-based materials and their associated chemical additives in the aquatic environment is an emerging worldwide problem, and their impacts are now gaining a wider scientific and social audience. Plastic-based composite materials contaminate the environment through the ocean and/or land routes with human activities being the major carrier. In parallel to this, some degradable biocomposites incorporated with functional moieties takes some years to completely degrade and it is often found by users of these materials to discard them into the ocean. Although, this menace is increasingly being curbed through legislation and enforcement of laws. However, the huge volume of uncontrollable environmental factors such as wind or subsequent runoff of rainfall still compromises the waste reduction efforts (Lambert and Wagner 2018). Likewise, a wide range of volatile and other low molecular weight compounds from polymerization residues may have been kept from synthesis, incorporation of additives which further contaminates bio-based composites during degradation. This leads to the emission of toxic substances with foul odors under high processing temperatures. As such, this drawback may not be beneficial to the textiles and construction industries. In our opinion, the assessment of the life cycle analysis (LCA) of biocomposites may be necessary to expand their application and overall sustainability. A unique advantage of LCA is that it could be used for evaluating products using the circular economy models by figuring out their shortcomings and their impact on variables like climate change, water use, acidification, and global warming to build methods for continual improvement (Ghoroghi et al. 2022; Mongo et al. 2022). According to Ita-Nagy and colleagues (2020), the LCA of sugarcane-reinforced biocomposites outperformed 100% sugarcane bioPU and fossil-based PE when parameters such as global
warming, ozone generation, terrestrial acidification, and the scarcity of fossil fuels were considered. The researchers came to the opposite conclusion to findings of some scholars, noting that while the environmental impact of the original materials was lessened using bagasse fiber reinforcements, more property enhancement is needed to make it more useful as a replacement for fossil-based PE. Similarly, De Vegt and Haije (1997) in their study showed that flax fiber-based biocomposites had better LCA points (1.85) compared to carbon and glass fiber composites. Schmehl and co-workers (2008) adopted three crucial factors – human health, ecosystem quality, and resource availability, in the LCA of polycarbonate acid anhydride and hemp and glass fibers composites. Their findings revealed that the LCA value of hemp fiber composite, 0.36, was 50% lower than that of glass fiber composite (0.74).

Biocomposites' short- and long-term reactions to environmental conditions including temperature, moisture, and biological attack can restrict their usability (John 2017). To the best of our knowledge, the degradation of polymers is gradually receiving an attention over the past few decades. A panacea to the recycling of useful materials with a promising value into the environment requires an adequate understanding of the structural and functional stability during processing and use, along with an appropriate waste management technique when discarded. In addition to existing body of knowledge, studies should focus on degradability characteristics of bio-based composites when composting and designing a suitable waste management method. This is because the analysis of degradation processes in biocomposites is even more important than in conventional composites due to the environmental susceptibility of their components to many physical and chemical reactions.

2.8. Manufacturing Process of Biocomposites

2.8.1 Hand layup

This process involves spreading over a mould after the fibers have been trimmed. A vacuum bag is then wrapped around the part to prevent air from escaping and make the assembly more secure. Thermosetting polymer-based biocomposites lend themselves well to the hand-layup approach. Compared to other composite processing processes, the capital investment is smaller, but the rate of production is lower. High reinforcement volume fraction is challenging to attain in final composites. Hand layup technique is widely used with thermoplastic polymers such as polyester/epoxy/MDI(diphenylmethane diisocyanate) (Faria et al. 2020; Kikuchi et al. 2014;
Hand layup technique is often used in integration with other techniques such as compression moulding (Shahzad 2011b) and 3D printing (Milenkovic et al. 2021). Milenkovic et al (Milenkovic et al. 2021) integrated the hand layup method with 3D printing. The PLA was 3D printed while adding long continuous polyvinylidenfluorid (PVDF) fibers by hand to produce reinforced PLA composites. The authors reported the improvement in ductility (Milenkovic et al. 2021). Laying fibers by hand might lead to imperfections between layers. A simple hand layup process is shown in Figure 2.4.

Figure 2.4: Hand Layup (Redrawn from Ref (Aljibori et al. 2016))

2.8.2 Resin transfer moulding

Resin transfer moulding is used to produce components with a smooth surface finish at low pressure. The fibers are initially spread out by hand in the mould and then the resin is poured into it. Then the mould is heated and cured under pressure. Thermoset resins are preferred, however thermoplastic resins having low viscosity are also being used (Sozer et al. 2012). Vacuum assisted RTM is a variation of RTM technique which uses vacuum to fill the mould with resin. VARTM is preferred for manufacturing synthetic fiber reinforced composites at large scale. The technique delivers safer, cleaner, and more cost-effective way of manufacturing composites. Voids and bubbles formation and impurities are reduced producing homogeneous
product with superior mechanical characteristics (Paglicawan et al. 2021). Sun et al. (Sun et al. 2018b) used CRTM techniques (integration of compression moulding and RTM) to produce composites that demonstrated superior mechanical characteristics than that of RTM prepared composites. The CRTM process has considerable mass production potential and might be utilised to mould structural components of vehicles (Sun et al. 2018b). A schematic representation of RTM is shown in Figure 2.5.

![Figure 2.5: Schematics of resin transfer moulding process (Redrawn from Ref. (Erden and Ho 2017))]()
of this technique. Accidental fires may occur while handling highly flammable epoxy resins during resin transfer moulding. Many researches have been conducted to reduce the flammability of the epoxies with significant advancements (Dong et al. 2016; Rwei et al. 2017; Zhang et al. 2017; Zhou et al. 2017). Zhang et al. (Zhang et al. 2017) produced flame retardant epoxy composites having Limiting Oxygen Index (LOI) greater than 30%.

2.8.4 Extrusion process

Extrusion is a method of producing long items having uniform cross-section. The polymer is forced through a die containing an opening in this technique. Through a hopper, pellets of polymer are inserted into an extruder. A feeding screw then propels the material ahead and forces it through a die, transforming it to continuous product. The polymer is softened and then melted by placing heating sources above the barrel. Thermocouples are used to regulate the material's temperature. Air or water bath is used to cool the final product exiting the die. Unlike metal extrusion, polymer extrusion is a continuous process that lasts till the raw pellets are provided (Dmitri Kopeliovich 2014). A schematic representation of this process is presented in Figure 2.6.

![Figure 2.6: Schematic diagram of a polymer extrusion machine. Barrel and screw are the two major industrial components (Redrawn from Ref. (Senthilkumaran et al. 2022))](image)

Depending on the product, single or double screw extruders are used. Single screw provides the limited mixing whereas twin screw provides the intense mixing of the melt (Zwawi 2021). The thermal and mechanical characteristics are highly influenced by the processing parameters of the extrusion (Haag et al. 2017). Despite better aspect ratio is achieved at high temperature and pressure, natural fibers are deteriorated resulting in the high porosity in the end product (Du et al. 2014). Under the combined action of high temperature and shear loading during extrusion, delignification of
wood flour resulted in greater plastic deformation (Migneault et al. 2009). Wood flour obtained after delignification process has low melt viscosity because of the highly porous and flexible structure of holocellulose (Migneault et al. 2009). The plasticity of rigid cell wall can be enhanced by altering its composition which might improve the processability of Wood plastic composites (WPCs) (Migneault et al. 2009). Previous research has used extrusion to manufacture biocomposites (Ettxabide et al. 2016; Gupta et al. 2021; Hietala and Oksman 2018; Panariello et al. 2021; Silva et al. 2022; Vandi et al. 2019). Gupta et al. (Gupta et al. 2021) used hemp powder as a filler to reinforce reinforced Polybutylene adipate-co-terephthalate (PBAT) for producing PBAT-HP bio-composite via extrusion. The authors reported the homogeneous dispersion of the hemp powder in PBAT matrix and a significant improvement in mechanical performance of the biocomposites (Gupta et al. 2021). Vandi et al. (Vandi et al. 2019) conducted statistical analysis to study the impact of processing conditions on the mechanical characteristics of the composites. The authors reported that although the thermal stability of polyhydroxyalkanoate (PHA) is relatively low, its processing can be done even at a temperature as high as 190 °C by adjusting the extrusion parameters such as feeding rate and speed of the screw (Vandi et al. 2019). Ettxabide et al. (Ettxabide et al. 2016) manufactured a fish gelatin biocomposites via novel approach combining the extrusion and injection moulding techniques. Panariello et al. (Panariello et al. 2021) studied the effect of biobased chain extenders (epoxidized soybean oil (ESO) and biobased dicarboxylic acid (DCA)) on the PLA/PBSA blend. The authors reported the fair increment in melt viscosity of the blend (Panariello et al. 2021). Silva et al. (Silva et al. 2022) successfully produced polyvinylidene fluoride – hydroxyapatite composite filaments at various angular velocities by twin screw extruder and found that the produced filaments were suitable for 3D printing. Hietala et al. (Hietala and Oksman 2018) found that pelletizing cellulose fibers with the help of lubricant is a potential method for compacting them. The authors reported the reduction in fiber breakage and increased dispersion of the fibers with the addition of lubricant. Introducing lubricant directly to the cellulose fiber pellets increased the mechanical properties of the composite as compared to adding lubricant while melt compounding (Hietala and Oksman 2018).

2.8.4 Injection moulding

Injection moulding is a popular technique for manufacturing complex shaped plastic parts due to its high accuracy, low cost, and high productivity (Semlali Aouragh Hassani et al. 2019). This technique accounts for more than 30% plastic parts manufactured worldwide (Mathivanan
et al. 2010). Injection moulding is used with polymers like polycarbonate, polystyrene, polypropylene, polyamide, ABS, polybutylene terephthalate (PBT) (Singh and Verma 2017). The process may be divided into three different stages for a certain injection moulding process: filling, post-filling, and cooling (Nguyen et al. 2011). Initially, polymer melt at high pressure is injected into the mould so that the melt takes the shape of the desired mould. The part is then released from the mould after solidification and cooling. Complications arise in the filling stage as various phenomena such as heat and mass transfer are happening. Quick hardening of polymer melt upon contact with the mould may cause issues like incomplete filling of the mould at narrow areas (Semlali Aouragh Hassani et al. 2019). This issue can be resolved by heating the mould at higher temperature, however doing so would lengthen the cooling cycle. Therefore, optimization of the process is necessary. Fibers are oriented in the melt flow direction in injection moulded samples whereas random orientation was observed in extruded samples (Migneault et al. 2009). Gigante et al. produced horticulture pots using paper sludge as a filler via injection moulding (Gigante et al. 2021). Considering these major sources are from fiber components, it may be interesting for scholars to address injection moulding technology on other biomass components, especially sources having less fiber content such as starch and protein. A schematic representation of this process is presented in Figure 2.7.

![Schematic diagram of injection moulding of polymers](Redrawn from Ref. (Senthilkumaran et al. 2022))

### 2.8.5 Three-dimensional (3D) printing

In recent years, three-dimensional (3D) printing has advanced quickly. Through digitised and computer-assisted procedures, this technology enables the creation of one-of-a-kind, complicated, and customizable structures, thereby lowering manufacturing costs and time
(Nguyen et al. 2018). Furthermore, when compared to typical processing manufacturing, this technology produces less waste and requires less chemical usage. Among 3D printing technologies, Fused deposition modeling (FDM) is popular, that involves melting thermoplastic materials at high temperatures and then solidifying them after they cool. Many people have shown interest in using biomass and biomass-based components in FDM 3D printing in recent years. 3D printing allows the feasible and economical manufacturing of composites (Brenken et al. 2018). Complex structures along with good fiber percentage and orientation can be obtained easily (Tran et al. 2017). Recently, researchers are attracted towards using natural fibers as composite fillers for 3D printing. But the mechanical performance of the composites is low. This may be due to the improper fiber orientation, presence of pores, low aspect ratio of the fibers, poor characteristics of the chosen fibers, and the less fiber content in the printed structure (Kariz et al. 2018; Milosevic et al. 2017; Stoof et al. 2017). Various works have been reported in literature to produce 3D printing filaments reinforced with flax fibers (Depuydt et al. 2019), hemp fibers (Coppola et al. 2018; Milosevic et al. 2017; Stoof et al. 2017; Stoof and Pickering 2018), hemp hurds (Xiao et al. 2019), bagasse fibers (Liu et al. 2019), coconut fibers (Gama et al. 2022), bamboo fibers (Depuydt et al. 2019; Long et al. 2019), wood particles (Kariz et al. 2018; Tao et al. 2017), cocoa shell (Morales et al. 2021; Tran et al. 2017), waste macadamia nutshell (Girdis et al. 2017), and Harakeke fibers (Milosevic et al. 2017; Pickering and Stoof 2017; Stoof et al. 2017). PLA and ABS are widely used filaments for FDM 3D printing (Song et al. 2017; Weng et al. 2016). The 3d printing of these filaments require that the nozzle and the printing bed be maintained at a high temperature of 200°C for PLA and 220°C for ABS (Kreiger and Pearce 2013; Sarazin et al. 2008). But, melting lignocellulosic components for extrusion and injection moulding techniques is quite difficult, unlike petroleum-based thermoplastic compounds. As a result, developing novel biomass-based materials suited for 3D printing is a challenging task (Le Duigou et al. 2016; Henke and Treml 2012; Zhao et al. 2016). The high resistance to flow and high thermal transition temperature of pure lignin composites limit their production (Nguyen et al. 2018). As a result, lignin is combined with other polymers, enhancing its melting and flow. Kraft softwood lignin (Domínguez-Robles et al. 2019) and organosolv hardwood lignin (Nguyen et al. 2018) have recently been used to make FDM filaments based on PLA and acrylonitrile-butadiene-styrene polymers, respectively. There are some disadvantages associated with using natural fibers in 3D printing. The fibers need to be fully dried before processing otherwise voids and pores will be present in printed part (Rajendran Royan et al. 2021). Moreover, the natural fibers need to be sieved to very fine particles less than 75 µm. Otherwise, agglomeration
may occur and there will be clogging in the nozzle of the 3D printer (Petchwattana et al. 2019). A schematic representation of this process is presented in Figure 2.8.

![Diagram of FDM 3D Printing](image)

Figure 2.8: FDM 3D Printing (Redrawn from Ref (Olivera et al. 2016))

### 2.8.6 Compression moulding

Compression moulding refers to the moulding of the material through compression. The feed material is placed in a heated mould cavity in this method. Then the mould is enclosed within the upper and lower part of the die and the pressure is applied to spread the material inside the mould. The material is allowed to cure while maintaining heat and pressure. A schematic representation of this process is presented in Figure 2.9. Low processing time and high production rate makes compression moulding the reliable method. Fibers are generally placed within layers of matrix (Zwawi 2021). There are several routes to compression moulding techniques. However, the most popular one vastly used in several manufacturing processes is hot compression moulding (HCM). HCM is typically used to manufacture thermoplastic polymer composites reinforced with long fibers. Hot presses are effective techniques for providing the required high pressure and temperature necessary for complete thermoplastic
composite consolidation (Hoa 2009; Kim et al. 1989). But the heating rate is limited (less than 5 °C/min) in traditional hot presses that are equipped with heat cartridges. There might already be the degradation of natural fibers at the isothermal stage (Ramakrishnan et al. 2019). High pressure, temperature and processing time favours the matrix flow and the impregnation of fibers but may thermally degrade the natural fibers resulting in the formation of macro pores (Ramakrishnan et al. 2019). Several techniques have been investigated by scholars to preserve the integrity of natural fibers such as vacuum assisted oven consolidation (VAOC) (Kazmi et al. 2014) and fast heating systems (Ramakrishnan et al. 2019). Ramakrishnan et al. (Ramakrishnan et al. 2019) used the fast inductive heating system and noted that fibers had limited thermal degradation.

Zhao et al. (Zhao et al. 2020) used a new approach combining paper manufacturing and compression moulding techniques to produce biocomposites from waste paper and poly(butylene succinate). The product demonstrated the excellent biodegradability and robust mechanical characteristics.

![Mould open](image)

Figure 2.9: Schematic diagram of compression moulding for polymers (Redrawn from Ref. (Wang et al. 2019b))

The various processing techniques, components, and the characteristics of the biocomposites that have been reported in literature have been reviewed in Table 2.5.
Table 2.5: Manufacturing techniques of various composites.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Manufacturing Technique</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsaturated polyester</td>
<td>Vacuum assisted Resin Transfer Moulding</td>
<td>Alkali treated composites showed better durability than heat treated one.</td>
<td>Ariawan et al. 2018</td>
</tr>
<tr>
<td>PLA</td>
<td>3D printing + Hand Layup</td>
<td>Increased failure resistance and yield stress whereas decreased flexural strength compared to neat PLA.</td>
<td>Milenkovic et al. 2021</td>
</tr>
<tr>
<td>PP, polyethylene, PLA, polyhydroxybutyrate</td>
<td>Hand Layup</td>
<td>Hybrid glass-curaua fiber composite effectively reduced water absorption than that of curaua fiber composite.</td>
<td>Silva et al. 2009</td>
</tr>
<tr>
<td>PLA</td>
<td>Hot compression</td>
<td>Alkali treated hemp fiber PLA composites showed higher tensile strength, bending strength and elastic modulus compared to neat PLA.</td>
<td>Hu and Lim 2007</td>
</tr>
<tr>
<td>PLA</td>
<td>Carding, punching followed by hot-pressing</td>
<td>Silane coupling has highly beneficial impact on the mechanical performance, moisture resistance and heat distortion temperature.</td>
<td>Lee et al. 2009</td>
</tr>
<tr>
<td>PLA</td>
<td>Hot pressing</td>
<td>Reduction in fiber contacts and voids because of the emulsion type biodegradable resin.</td>
<td>Ochi 2008</td>
</tr>
<tr>
<td>PLA with lignin as compatibilizer</td>
<td>3D Printing</td>
<td>Mechanical performance reduced with increasing lignin concentration.</td>
<td>Tanase-Opedal et al. 2019</td>
</tr>
<tr>
<td>Material</td>
<td>Fiber Type</td>
<td>Process</td>
<td>Description</td>
</tr>
<tr>
<td>---------------</td>
<td>--------------------------------</td>
<td>--------------------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>PLA</td>
<td>Rice Husk</td>
<td>3D Printing</td>
<td>-</td>
</tr>
<tr>
<td>PLA</td>
<td>Carbon Fibers; Jute Fibers</td>
<td>3D Printing</td>
<td>Continuous fiber impregnation resulted in higher tensile strength compared to traditional 3D printed composites.</td>
</tr>
<tr>
<td>PLA</td>
<td>Agave Fiber</td>
<td>Compression moulding</td>
<td>Improvement in crystallinity, tensile modulus and impact strength by 30%, 14%, and 71% respectively compared to neat PLA.</td>
</tr>
<tr>
<td>PLA</td>
<td>Kenaf Fiber</td>
<td>Compression moulding</td>
<td>Improvement in tensile modulus, storage modulus, flame retardancy, thermal stability and thermo-dimensional stability with increasing ammonium polyphosphate content.</td>
</tr>
<tr>
<td>Polyester</td>
<td>Kenaf</td>
<td>Vacuum Infusion and Hand Layup</td>
<td>Composites produced by vacuum infusion process showed higher tensile strength and young’s modulus value than Hand layup method.</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>Coconut husk</td>
<td>Hand Layup</td>
<td>Tensile strength improved by around 28%.</td>
</tr>
<tr>
<td>Unsaturated polyester resin</td>
<td>Hemp Fiber + Glass Fiber</td>
<td>Hand layup + Compression moulding</td>
<td>Glass-hemp reinforced composites showed an improvement in tensile strength and tensile modulus by 75% and 15%</td>
</tr>
<tr>
<td>Resin Type</td>
<td>Fiber Type</td>
<td>Manufacturing Method</td>
<td>Improvement in Properties</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>---------------------------------------------</td>
<td>-----------------------------------------------------------------</td>
</tr>
<tr>
<td>Bisphenol A-type epoxy resin</td>
<td>Carbon Fiber</td>
<td>Compression resin transfer moulding (CRTM)</td>
<td>Improvement in tensile strength by 43%, bending strength by 41%, interlaminar shear strength by 77% was observed in CRTM composites compared to RTM composites.</td>
</tr>
<tr>
<td>Unsaturated polyester</td>
<td>Kenaf fibers</td>
<td>Resin Transfer moulding</td>
<td>Interfacial shear strength improved significantly in alkali treated kenaf fiber reinforced composites.</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>Glass fiber</td>
<td>Resin Transfer Moulding</td>
<td>The composites demonstrated excellent flame retardancy while not affecting the mechanical performance.</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>Bamboo fibers</td>
<td>Vacuum Assisted Resin Transfer Moulding</td>
<td>Alkali treated and silane treated composites demonstrated better interfacial adhesion, mechanical and thermal performance opening the door towards structural applications.</td>
</tr>
<tr>
<td>Material System</td>
<td>Fiber Type</td>
<td>Processing Method</td>
<td>Remark</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------------------</td>
<td>--------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>Flax</td>
<td>Resin Transfer Moulding</td>
<td>Water uptake was lower and at lower rate. Good interfacial bonding was observed.</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>Carbon Fiber</td>
<td>Vacuum Assisted Resin Transfer Moulding</td>
<td>Microwave radiation reduced the resin curing time by 15 times.</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Jute fibers</td>
<td>Single screw extrusion + injection moulding</td>
<td>Urea treatment of fibers led to improvement in mechanical performance compared to raw and oxidized jute fibers.</td>
</tr>
<tr>
<td>Polyolefins (PP, PE)</td>
<td>Flax and hemp fibers</td>
<td>Twin screw extrusion</td>
<td>Improvement in mechanical characteristics with fiber loading till 25%.</td>
</tr>
<tr>
<td>Poly-L-lactic acid</td>
<td>Kenaf</td>
<td>Wet impregnation method</td>
<td>Higher thermal and mechanical performance due to good interfacial adhesion between PLLA and kenaf fiber.</td>
</tr>
<tr>
<td>PP</td>
<td>Poplar (Populus deltoides) in particle form</td>
<td>Twin screw extrusion + injection moulding</td>
<td>Smaller size of filler resulted in higher tensile modulus than that of large size. Wood flour could be a promising cheap natural fiber source.</td>
</tr>
<tr>
<td>High density polyethylene</td>
<td>Kenaf fiber with maleated polyethylene (MAPE) as compatibilizer</td>
<td>Melt compounding (internal mixing) + compression moulding</td>
<td>Increased mechanical and water resistance characteristics with adding MAPE.</td>
</tr>
<tr>
<td>Polymer Type</td>
<td>Fiber Type</td>
<td>Manufacturing Process</td>
<td>Result Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
<td>-----------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Unsaturated polyester resins</td>
<td>Raw and plasma-treated jute fiber</td>
<td>Hand layup</td>
<td>Improvement in interfacial bonding and hydrophobicity was developed after plasma treatment.</td>
</tr>
<tr>
<td>Bio-polyethylene</td>
<td>Pulp Fibers</td>
<td>3D Printing</td>
<td>Increased tensile strength by 127%.</td>
</tr>
<tr>
<td>Green Epoxy</td>
<td>Sisal Fiber</td>
<td>Compression moulding</td>
<td>-</td>
</tr>
<tr>
<td>Polyester</td>
<td>Drumstick fibers + Glass Fiber</td>
<td>Hand Layup</td>
<td>Orientation of fibers in longitudinal direction increased bending strength by 200% compared to transverse orientation.</td>
</tr>
<tr>
<td>PLA</td>
<td>Waste silk fiber</td>
<td>Hand Layup</td>
<td>Increased tensile strength and modulus by 75.92% and 75.64% respectively at 30% wt. fiber.</td>
</tr>
<tr>
<td>Hytrel™ 4056</td>
<td>Hydrolysed soyhull fiber</td>
<td>Single screw extrusion</td>
<td>-</td>
</tr>
<tr>
<td>Polyamide 6 PA6</td>
<td>Kenaf; Flax</td>
<td>Twin Screw Extrusion</td>
<td>Improvement in mechanical performance compared to neat PA6.</td>
</tr>
<tr>
<td>epoxy</td>
<td>Banana fibers+ glass fibers; Jute fibers+ glass fibers</td>
<td>Hand Layup</td>
<td>Hybrid composites made up with banana fibers showed increment in ultimate tensile stress and yield strength with increasing fiber content. The jute fiber-based hybrid composites showed up a similar pattern in ultimate</td>
</tr>
</tbody>
</table>
2.9. Notable applicable areas of biocomposites

Only a few biocomposites have been marketed while the majority are still in research and development phase. For the cheaper production cost of biocomposites, new production techniques and technologies are being developed. Although the natural fibers are abundant in developing nations, lack of technology and resources hinders them from being used to produce composites. On the other hand, developed nations in Asia and Europe are manufacturing biocomposites (Evans et al. 2002). There are various issues associated with biocomposites such as low reliability, poor mechanical performance, and production costs that need to be addressed for producing these biocomposites at a large scale (Satyanarayana et al. 2009). Despite these obstacles, biocomposites offer enormous promise for utilisation in a variety of applications. Although research has yielded encouraging results, further research and development are necessary for the successful commercialization of biocomposites (Khalil et al. 2012). The goal is to acquire characteristics equivalent to synthetic composites. Public awareness and new environmental policies will result in significant advancements in production of biocomposites. Furthermore, progress in the field of agricultural science will aid in the harvesting of fibers with better qualities. Biocomposites have the potential to fully eliminate the need for synthetic products in the coming future (Mohanty et al. 2011). Synthetic composites require a lot of energy to make, but biocomposites use less (Banik et al. 2017). Various governments have encouraged the use of biodegradable materials to combat waste and pollution (Al-Oqla and Omari 2017). Mechanical properties of plant fibers vary from place to place making it difficult for its proper utilization in biocomposites (Al-Oqla and Sapuan 2015). Various chemical treatments and processing mitigate these flaws. The key fields where biocomposites are utilized the most are automotive, construction, and food packaging.

2.9.1 Automotive industry

Composites reinforced with synthetic fibers such as carbon and glass fibers dominate the automotive industry. Growing environmental concerns and carbon footprint has attracted the usage of biocomposites in this industry. Biobased composites can become promising
alternative sustainable and eco-friendly materials in the automotive industry. They are light weight which improves the fuel efficiency of the vehicles. It has been reported that using biocomposites instead of synthetic fiber composites, the energy and weight can be saved up to 80% and 10% respectively (Zwawi 2021). The damping characteristics of biocomposites reduce vibrations and noise (Akampumuza et al. 2017). Due to the comparatively poor mechanical characteristics and moisture resistance, the biocomposites are mostly used in interior of the automotive components like dashboards, door panels, cabins, etc. (Li et al. 2020). Automobile manufacturer Ford uses seats made out of soy foams, bio-based cushions and the front grills made out of hemp based composites in its several models (Andresen et al. 2012). There are currently around 8 million Ford vehicles with seats made from soy foam, reducing fossil fuel utilization by around 5 million pounds per year. Nylon 11 derived pure castor bean oil used in the fuel tank tubes of Ford vehicles resulted in reduction of approximately 1 million pounds CO$_2$ per year (Akampumuza et al. 2017). Interior panels, shelves and trunk covers, and rear panel shelves in Mercedes Benz vehicles are made out of jute fiber composites, flax fiber composites, and sisal based composites, respectively (La Mantia and Morreale 2011). Similarly, various automobile manufacturers use biocomposites in seats, tire covers, toolbox areas, package trays, door panels, door inserts, dashboards, etc (Zwawi 2021). Table 2.6 summarizes the applications of biocomposites in automotive sector.

Table 2.6: Biocomposites in automotive industry

<table>
<thead>
<tr>
<th>Brand</th>
<th>Bio-composite Units</th>
<th>Applications</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ford</td>
<td>Soy foams</td>
<td>Seats</td>
<td>Reduction of oil consumption by 5 million pounds per year.</td>
<td>John and Thomas 2008</td>
</tr>
<tr>
<td></td>
<td>Hemp/propylene composites</td>
<td>Front grills</td>
<td>-</td>
<td>Holbery and Houston 2006</td>
</tr>
<tr>
<td></td>
<td>Nylon 11 derived from castor oil</td>
<td>Fuel Tank tubes</td>
<td>Reduction of 1 million CO2 emission annually.</td>
<td>Akampumuza et al. 2017</td>
</tr>
<tr>
<td>Material</td>
<td>Reinforcement</td>
<td>Applications</td>
<td>Weight Reduction</td>
<td>Authors</td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------------</td>
<td>---------------------------------------------------</td>
<td>------------------</td>
<td>----------------------------------------------</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>Inner lids and</td>
<td>Weight reduction by 20%.</td>
<td>-</td>
<td>Akampumuza et al. 2017</td>
</tr>
<tr>
<td></td>
<td>Storage bins</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jute-reinforced Plastics</td>
<td>Interior door panels</td>
<td>Weight reduction by 20%.</td>
<td>La Mantia and</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Morreale 2011;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Marsh 2003</td>
<td></td>
</tr>
<tr>
<td>Flax/polyester composite</td>
<td>Engine</td>
<td>Weight reduction by 5%</td>
<td>Koronis et al. 2013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>enclosures</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood fibers</td>
<td>Seat, interior of</td>
<td>Reduction of car weight by around 43 kg.</td>
<td>Finkbeiner and</td>
<td></td>
</tr>
<tr>
<td></td>
<td>front door linings</td>
<td></td>
<td>Hoffmann 2006;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Wallenberger 2001</td>
<td></td>
</tr>
<tr>
<td>Flax fibers</td>
<td>Rear trunk covers</td>
<td>Reduction of car weight by around 43 kg.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>and parcel shelves</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood veneer</td>
<td>Trim strips and</td>
<td>Weight reduction by 10%, energy savings by 80%</td>
<td>Mohanty et al. 2002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>panels</td>
<td>and cost reduction by 5%.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sisal reinforced</td>
<td>Rear panel shelves</td>
<td>Weight reduction by 10%, energy savings by 80%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>composites</td>
<td></td>
<td>and cost reduction by 5%.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abaca/PP composite</td>
<td>Tire wheel covers</td>
<td>Earned 2005 Society Plastics Engineers Award</td>
<td>Koronis et al. 2013; Sinon et al. 2011</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kenaf/PLA composite</td>
<td>Spare tire cover</td>
<td>-</td>
<td>Cunha et al. 2006</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kenaf/PP composite</td>
<td>Door trims, and other interiors</td>
<td>-</td>
<td>Akampumuza et al. 2017</td>
<td></td>
</tr>
<tr>
<td>Soy foams</td>
<td>Seats</td>
<td></td>
<td>Akampumuza et al. 2017</td>
<td></td>
</tr>
<tr>
<td>Biobased PP/PLA</td>
<td>Package trays, side trims</td>
<td>-</td>
<td>Akampumuza et al. 2017</td>
<td></td>
</tr>
<tr>
<td>Material/Composite</td>
<td>Application</td>
<td>Properties</td>
<td>Source</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------</td>
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<td>--------</td>
<td></td>
</tr>
<tr>
<td>Zytel (biobased nylon)</td>
<td>Radiator end tank</td>
<td>-</td>
<td>Akampumuzza et al. 2017</td>
<td></td>
</tr>
<tr>
<td>Biobased PET</td>
<td>Luggage compartment</td>
<td>Durable, heat resistant, and less susceptible to shrinkage.</td>
<td>Koronis et al. 2013</td>
<td></td>
</tr>
<tr>
<td>Volkswagen flax/sisal hybrid mats reinforced polyurethane</td>
<td>Door trim panels</td>
<td>-</td>
<td>Ashori 2008; John and Thomas 2008</td>
<td></td>
</tr>
<tr>
<td>General Motors Flax/PP composites</td>
<td>Inner door panels</td>
<td>-</td>
<td>Shinoj et al. 2011</td>
<td></td>
</tr>
<tr>
<td>BMW Cotton fibers</td>
<td>Sound proofing</td>
<td>-</td>
<td>Pickering 2008</td>
<td></td>
</tr>
<tr>
<td>BMW Acrodur/sisal composite</td>
<td>Lower door panel</td>
<td>Weight savings of 2.7 kg, lower consumption of fuels, and reduced emissions.</td>
<td>Akampumuzza et al. 2017</td>
<td></td>
</tr>
</tbody>
</table>

### 2.9.4 Packaging

The growing global economy and population necessitates a more efficient management of the Earth's natural resources. In 2015, with 15 million jobs, the combined plastic and food sector is a significant portion of the EU economy (Commission 2021). Unleashing the potential for innovation in the packaging and cosmetics industries will help to boost job creation and competitiveness. Starch based plastics are renewable, biodegradable, and combustible due to which they have piqued a lot of interest in industrial applications (Lescher et al. 2012). Lescher
et al. (Lescher et al. 2012) have demonstrated unique manufacturing applications. Starch derived foam has insulation properties like that of polystyrene foam which are being produced commercially (Kalambur and Rizvi 2006). Starch based foams can be used as loose-fill packaging materials to fill empty spaces in packages effectively substituting polystyrene foams (Guan and Hanna 2004). Loose-fill packing materials protect, stabilise, and cushion packed goods and must have low density, sufficient resilience, and compressibility (Tatarka and Cunningham 1998). When stored in atmosphere having high relative humidity, TPS foams are prone to moisture. The hydrogen bonds in starch are attacked by water molecules. As a result, they are weakened and their functional characteristics are reduced (Lescher et al. 2012). The blends of TPS with hydrophobic polymers are being utilized as oxygen barriers in a commercial level (Alavi and Rizvi 2005). In multi-layered materials, incorporating water free TPS with hydrophobic polymers is beneficial in protecting gas barrier layers and foamed cores from moisture (Lescher et al. 2012). Blends containing higher amylose content starch appeared to be more dimensionally stable (Lescher et al. 2012). The synthesis of polyhydroxyalkanaotes from agro-food by-products, as well as the synthesis of lactic acid co-polymers, are both viable options for creating sustainable polymeric matrices (Cinelli et al. 2020). Natural fibers, polysaccharides (starch, cellulose, chitin, chitosan), cutin, and protein-rich by-products can all be found in abundance in the agro-food business. A research have evidenced the impact of bio-composite film based on high methoxyl pectin reinforced with zeolite Y in prolonging the shelf life of fruits (Nesic et al. 2022). Table 2.7 summarizes the application of biocomposites in food packaging.

Table 2.7: Bio-based plastics for food packaging.

<table>
<thead>
<tr>
<th>Material</th>
<th>Uses</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>Jars, bottles, bags, bowls, cups, and films.</td>
<td>Halonen et al. 2020; Shogren et al. 2019</td>
</tr>
<tr>
<td>PBS</td>
<td>Direct melt paperboard coating in food packaging</td>
<td>Thurber and Curtzwiler 2020</td>
</tr>
<tr>
<td>PA</td>
<td>Structures for providing toughness and strength</td>
<td>Halonen et al. 2020</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Material Type</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTT</td>
<td>Beverage bottles</td>
<td>Ohishi and Otsuka 2021</td>
</tr>
<tr>
<td>PHA</td>
<td>Snacks bags</td>
<td>Halonen et al. 2020; Shogren et al. 2019</td>
</tr>
<tr>
<td>Cellulose based polymers</td>
<td>Packaging of dried foods</td>
<td>Babaie-Ghazvini et al. 2022; Babaie-Ghazvini and Acharya 2022; Halonen et al. 2020; Shogren et al. 2019</td>
</tr>
<tr>
<td>Starch Based Polymers</td>
<td>Disposable tableware, bottles, cutlery, films, and coffee machine capsules</td>
<td>Babaie-Ghazvini et al. 2020a, 2018; Halonen et al. 2020; Shahabi-Ghahfarrokh and Babaie-Ghazvini 2019</td>
</tr>
<tr>
<td>PEF</td>
<td>Films and bottles</td>
<td>Halonen et al. 2020</td>
</tr>
</tbody>
</table>

### 2.9.2 Construction industry/interior decorations

Biocomposites are used to make windows, doors, window frames, ceilings, floor mats, and roof tiles in the building sector. Floor slabs, beams, pipes, and tanks are all examples of load-bearing applications (Zwawi 2021). Wood Plastic Composites (WPCs) are used in making tables, decks, benches, floorings, and landscape timbers. Similarly, biocomposites are also used in the repair and rehabilitation of a variety of structural components (Mosallam et al. 2014). Natural fiber composites are employed as insulating and soundproofing materials because of their superior thermal and acoustic qualities. Hemp/lime/concrete composites have outperformed all other binders in terms of sound absorption (Kinnane et al. 2016). The thermal characteristics of the concrete can be improved by adding hemp. However, hemp needs to be mineralized first.
for its use with cement (Novakova and Sal 2019). Novakova et al. (Novakova and Sal 2019) successfully used hemp hurds as filler in lightweight concrete. Dweib et al. (Dweib et al. 2004) successfully fabricated unit beams and structural beams out of natural fibers and soybean oil based resin and noted some promising results. Blok et al. (Blok et al. 2019) designed and manufactured a 14 m long footbridge out of biocomposites. The study reported that all the required tests such as creep tests, tensile tests, and moisture content tests was passed by the bridge. However, before utilizing any biocomposites as a construction material, life cycle assessment, durability qualities, and environmental concerns are considered. Low weight and equivalent mechanical qualities with synthetic composites are critical for building purposes. In addition, many countries are using bio-composite materials to combat environmental challenges. Due to future demand, many companies are investing in biocomposites (Kinnane et al. 2016).

2.9.3 Biomedicine

Extending life expectancy requires the use of novel technologies. Various innovative procedures and new technology have been developed in this direction, resulting in lower morbidity and mortality rates (Baranwal et al. 2022). Tissue engineering, an aspect of biomedicine is one of the key areas where biocomposites are profoundly used because of the exceptional qualities of biocomposites to modify mechanical characteristics, degradation kinetics, and bioactivity (Alatawi et al. 2019). Nonetheless, the characteristics of biomaterial polymers could be improved by adding mineral polymer fillers (HA) to the primary polymer PET, which has poor bioactivity when compared to other biobased composites such as PLA, PLGA, PCL (Hu et al. 2017). Combining these two polymers creates a new nano-bio-composite scaffold with better capabilities, which is deemed unusual because it concentrates on skin application rather than the more common application on hard tissues (Sughanthy et al. 2020). Recently, there have been advances in other biomedical areas such as wound healing, drug delivery in which the use of biocomposites is highly craved in these areas. Drozdov and colleagues (Drozdov et al. 2015) in their efforts to create a healing biocomposites prepared four medicaments with different characteristics. The authors observed that the wound healing rate with a biocomposite was 1.5 times faster than the control group (21 and 14 days for complete healing, respectively). They further observed that the use of a magnetite-based biocomposite resulted in a significant reduction in scar size. Other scholars such as Bagheri et al. documented the synergistic antibacterial effects of chitosan nanofiber for biocomposites with an
outstanding scratches repair potential of chitosan fiber and polyethylene oxide (Bagheri et al. 2022). Efforts of scholars should be tailored towards addressing the overall long-term effect of these materials on other functional body parts of human.

2.9.5 Aerospace industry

Increasing fuel prices have led the aircraft sectors in search of lightweight materials. Around half of operational costs in aircraft is accounted by fuel costs. Fiber reinforced polymer composites increases the fuel efficiency of Boeing 787 by more than 20% (Njuguna et al. 2012). Lightweight aircraft use less fuel, allowing them to carry heavier cargo and cover longer distances. The primary goals of the aviation industry are to reduce carbon dioxide emissions, costs, and fuel consumption; hence, the use of biocomposites is gaining popularity in the aerospace industry. Biocomposites can be used to make aircraft interior sections (such as seats, decks, and floor) and external body panels. To be used in aircraft structures, biocomposites must possess high moisture resistance, flame retardancy, and high specific strength (Kuram 2022). Biocomposites have low flame retardancy making it questionable to be used in aircraft. External structure of aircraft needs to be flame resistant but interior structure such as cabin, decks, seats, and floors which are less prone to fire hazards can be manufactured with biocomposites. Cabin interior panels were made from phenolic resin and woven flax (John et al. 2008). 12-14% weight reduction in the wing box was observed when compared to 7000 series aluminium alloy using ramie fiber-reinforced composite (Boegler et al. 2015). Composite laminates made using goat hair and banana fibers might be employed in aeronautical applications (Rao et al. 2020).

2.10 Summary

Natural materials, particularly those derived from plant materials, have been used for hundreds of years. Researchers have discovered improved ways for these materials to fulfill both social and industrial needs. Biocomposites provide advantages owing to their exceptional attributes such as biodegradability, availability of raw materials, and applications. Even though many industrial sectors have tapped into the benefits, commercialization of manufactured biocomposite materials is still in its initial stages. The influence of moieties has various downsides, including the likelihood of harmful chemical release. Nonetheless, since this research area is attracting the interests of many academic and industrial contributions, it
indicates that commercialization of biocomposites is projected to rise in the future as people become more environmentally conscious, manufacturing processes become more efficient, and new applications are discovered. Scholars must also contend with the obstacles of establishing norms and standards for these materials. It is important to emphasize that, because of the poor mechanical and thermal characteristics, replacing standard synthetic composites entirely with biocomposites would require a series of scientific evidence necessary to create the change. At present, research work involving multiple reinforcing fibers and polymer blends appears to be scarce, even though such materials may offer greater production and tailoring flexibility. Because of the possibilities for novel applications, this subject must be researched further. Biocomposites having excellent durability, performance, serviceability, and reliability must be produced to broaden their applications. As scientific breakthroughs and technology advance, fresh areas of applications of natural fiber reinforced composites will emerge, influencing the always expanding market for bio-based composites.
CHAPTER THREE

METHODOLOGY

This chapter covers a detailed discussion of various aspects, including materials and methods, sample preparation, film production procedure, and casting method. It also provides an overview of the analytical techniques used for characterizing the bioplastics and the software utilized for assessment.

3.1 Material

The materials used in this study include PLA 3D850 pellets obtained from Natureworks (Minneapolis, Minnesota, USA), flax fiber sourced from local farmers in the Saskatchewan province and hemp fiber of “Katani” cultivar provided by KF Hemp (Lajord, Saskatchewan) respectively. PLA pellets were dried at 50°C for 24 hours before use. The flax and hemp biomass were processed into powder form prior to being incorporated into the composite material. Sodium hydroxide, acetic anhydride, sulphuric acid and chloroform were purchased from Sigma Aldrich Company (Oakville, Ontario, Canada) and were used as it is without any modification. The flax and hemp fiber are shown in Figure 3.1.

Figure 3.1: (a) Flax (b) Hemp
3.2 Treatment of fillers

3.2.1 Alkali treatment

About 100 grams pre-dried biomass was submerged in a 5% solution of sodium hydroxide at room temperature for a period of three hours. After the treatment, the biomass was thoroughly washed with water until a pH of 7 was attained to remove any residual alkali on its surface. Finally, the treated biomass was dried in an oven.

3.2.2 Acetylation treatment

About 100 grams flax biomass was immersed in a glass beaker containing enough acetic anhydride to submerge it completely. This would cause the moisture in the biomass to be converted into acetic acid through hydrolysis by the acetic anhydride. The acetic acid would enhance the swelling of the fibers, making the hydroxyl groups of the biomass more accessible, eliminating the need for a solvent (Zafeiropoulos et al. 2002). To facilitate the reaction, about 5 ml sulfuric acid was added. After 15 minutes, the biomass was transferred to a reagent bottle and subjected to autoclaving at 121 °C to promote esterification. Finally, the treated biomass was thoroughly washed to eliminate residual chemicals until the pH reached 7, and then dried in an oven. In similar way, hemp biomass was treated.

The alkali and acetylation treated biomass are shown in Figure 3.2.
3.3 Grinding of biomass

Following the alkali treatment and acetylation treatment process, the next step in the preparation of biomass involves grinding. In this study, a hammer mill (Serial no. 6M13688; Glen Mills Inc., Maywood, NJ, USA)) was used for grinding the biomass. The biomass is fed into the mill through a hopper, and the blades rotate at high speeds, cutting the biomass into small particles. The resulting pulverized biomass was then sieved to obtain two different particle sizes; $<75 \mu m$ and $149-210 \mu m$. The biomass was placed on top of the sieve and shaken to allow smaller particles to pass through the openings, while larger particles were retained on the sieve. This process was repeated until the desired particle size was obtained.

3.4 Preparation of PLA/filler composite films

The composite films were prepared using the solvent casting method. First, a mother liquor solution was prepared by dissolving PLA in chloroform at a 1:12 ratio using a magnetic stirrer. Then, biomass was added at varying concentrations (2.5%, 5%, 10%, 20%, and 30% weight based on PLA) to the mother liquor solution. The resulting mixture was thoroughly mixed for 48 hours using a magnetic stirrer. The film-forming solution was then poured onto a glass plate and allowed to dry at room temperature. For comparison, neat PLA films without any fillers were also casted in a similar manner. The films were designated as “PLA/Filler name Loading**".
3.5 Characterization of the film

In order to gain a comprehensive understanding of the properties and performance of the composite film, a detailed characterization is imperative. The following characterization techniques are employed to understand the behaviour of the films.

3.5.1 Fourier transform infrared spectroscopy (FTIR)

The attenuated total reflectance-FTIR spectrophotometer (Spectrum 3 Tri-Range MIR/NIR/FIR Spectrometer, PerkinElmer, USA) was utilized to examine the FTIR spectra of the film samples. The analysis was conducted within the wavenumber ranges of 4000-650 cm\(^{-1}\), with a resolution of 4 cm\(^{-1}\).

3.5.2 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) data was acquired using an AXIS Supra System manufactured by Kratos (Manchester, UK) at the Saskatchewan Structural Sciences Centre (SSSC). The system is equipped with a 500 mm Rowland circle monochromated Al K-\(\alpha\) (1486.6 eV) X-ray source and a combined hemispherical and spherical mirror analyzer (HSA/SMA). For the analysis, a hybrid slot with a spot size of 300-700 \(\mu\)m was employed. During the survey scan, binding energies ranging from 0 to 1200 eV were collected in 1 eV increments, with a pass energy of 160 eV. High-resolution scans were performed in 0.1 eV steps. The data analysis was carried out using CASA XPS software (Babaei-Ghazvini and Acharya 2023; Fairley et al. 2021).

3.5.3 Thermogravimetric analysis (TGA)

To assess the thermal stability of the film samples, thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (Perkin-Elmer TGA 8000, Llantrisant, UK). Approximately 6 mg of film sample was subjected to heating from 50 to 900 °C at a heating rate of 20 °C/min, under a constant nitrogen gas flow of 30 cm\(^3\)/min. The differential form of TGA (DTG) was obtained by differentiating the TGA values, which helped in identifying the maximum disintegration temperature at each stage of thermal degradation.
3.5.4 Colour analysis

The colour of the samples was measured with a portable colorimeter (WR10QC-8), which used the CIE standard illuminant D65 and a pointer from the CIE chromaticity diagram. The measurement process was repeated five times. Additionally, digital photographs were taken of the samples. The device then recorded the tristimulus colour values of L (lightness), a (redness/greenness), and b (yellowness/blueness) at five random points on each film sample. These readings were then averaged to provide a more precise and accurate depiction of the film's colour. To further analyse the colour data, the total colour difference (ΔE), whiteness index (WI), and yellowness index (YI) were calculated using the following equations:

$$
\Delta E = \left\{ (\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2 \right\}^{0.5}
$$  
$$
WI = 100 - \left\{ (100 - L)^2 + (a)^2 + (b)^2 \right\}^{0.5}
$$  
$$
YI = \frac{(142.86 \times b)}{L}
$$

3.5.5 Water contact angle

To measure contact angles, the researchers employed the Sessile droplet method. This involved placing a tiny 5-μL droplet of distilled water on the surface of the film, and then using a drop shape analyser (AM2111, Dino-Light, Taiwan) to take a picture of the droplet. The contact angle, which is the angle formed between the baseline of the droplet and the tangent line at the point where it touches the surface, was then determined. To obtain an average value, eight droplets of water were used for each film (Goudarzi et al. 2017).

3.5.6 Moisture absorption

The moisture absorption was ascertained by comparing the weight of the specimens before and after conditioning at a humidity level between 50-55%. Test specimens with dimensions of 20 mm x 20 mm were used in this experiment. Initially, the specimens were dried in a laboratory oven set to a temperature of 105 ± 1 °C until a constant weight was achieved and measured (M₃ in g). Once the specimens were weighed (M₃ (g)), they were placed in a desiccator containing a saturated magnesium nitrate solution conditioned to ensure a humidity level of 53-55% at 20 °C. Their weight was recorded at specific intervals, until the specimens reached equilibrium (M₄ (g)). To obtain reliable results, this process was repeated three times. Following Equation (3.4) was used to calculate the moisture absorption of each specimen.
3.5.7 Water vapor permeability

To determine the water vapor permeability (WVP) of film specimens, the ASTM E96 standard was used (Babaei-Ghazvini et al. 2020b). The WVP of the films was measured using glass vials containing desiccant particles made of calcium chloride (CaCl₂) that had been dehydrated at 150°C for 2 hours. Before the experiment, the film specimens were conditioned for 48 hours in a desiccator at 20°C and 53-55% relative humidity using a magnesium nitrate (Mg(NO₃)₂) saturated solution. The film samples were then affixed to the tops of the vials containing and the vial mouths were tightly sealed with a screw cap that had a hole in the center. To counterbalance moisture absorption, three vials without desiccant were used. The vials were placed in a desiccator maintained at 75% relative humidity using a saturated solution of sodium chloride (NaCl) to create a water vapor partial pressure (∆P) of 1753.55 Pa. The weight of each vial and affixed polymer sample was measured and recorded with an accuracy of 0.0001 g for 24 hours. The weight of each vial and attached polymer sample was recorded with precision, and the weight vs. time plot was analyzed to calculate the WVP. The slope (S) was determined from the plot, which was then divided by effective film area (A) to calculate water vapor transmission rate (WVTR). The experiment was performed in triplicate to improve the accuracy of the results.

\[
WVTR = \frac{S}{A} \quad (3.5)
\]

\[
WVP = \frac{WVTR \times X}{\Delta P} \quad (3.6)
\]

Where 
- \( S \) = Slope of the weight vs time plot  
- \( A \) = Film Area  
- \( X \) = Film thickness, m  
- \( \Delta P \) = Water vapor partial pressure, Pa  
- WVTR = Water vapor transmission rate  
- WVP = Water vapor permeability
3.5.8 Mechanical properties

The tensile strength (TS), elongation at break (EB), and elastic modulus (EM) of the films were determined using an Instron Universal Testing Machine according to the ASTM D 882-88 standard. A series of rectangular film strips, measuring 100mm X 10mm, were meticulously cut. The machine was set in motion with an initial grip separation of 50mm, moving with a steady crosshead speed of 75 mm/min while utilizing a 1 kN load cell. The Young’s Modulus (YM) was obtained from the slope of the initial portion of the stress-strain curve that was generated during the tensile test. To ensure accuracy, five replicates were performed for each film specimen, and TS and EB were calculated using Equations (3.7) and (3.8), respectively.

\[ UTS = \frac{F_{\text{max}}}{A_{\text{min}}} \quad \text{(MPa)} \quad \text{(3.7)} \]

\[ EB = \frac{L_{\text{Max}}}{L_{0}} \]

\[ YM = \frac{\text{Stress}}{\text{Strain}} \quad \text{(MPa)} \quad \text{(3.9)} \]

3.6 Statistical analysis

After performing each test using an independently prepared film as the experimental unit, the results were then expressed as mean ± SD (standard deviation). To determine the significance of each mean value, a statistical analysis system was employed to perform one-way analysis of variance (ANOVA). Duncan's multiple range test was then used to ascertain the statistical significance of each mean value, with a significance level of \( p < 0.05 \). Furthermore, to understand the effect of particle size, treatment and loading of fillers and their interaction on the properties of the film, three-way ANOVA was conducted.
CHAPTER FOUR
RESULTS AND DISCUSSION

This chapter focuses on the comprehensive characterization of polylactic acid (PLA) films incorporating alkali-treated flax and hemp fillers. The investigation encompasses various essential properties to understand the impact of these fillers on the performance of the films. The characterization involves an analysis of surface transparency and wettability, mechanical characteristics, and the use of advanced spectroscopic and thermal techniques such as FTIR, XPS, and TGA. Additionally, the chapter explores the water vapor permeability and moisture absorption of the composite films. The findings presented in this chapter provide valuable insights into the influence of alkali-treated flax and hemp fillers on the properties of PLA films.

4.1 Fourier transform infrared spectroscopy (FTIR) analysis of composite films

FTIR analysis was used to evaluate changes in the chemical composition of flax and hemp filler resulting from alkali and acetylation treatment. As shown in Figure 4.1, the peak at 1740 cm\(^{-1}\), which is related to the C = O stretching of acetyl or carboxylic acid groups of hemicellulose in untreated fillers, disappeared after treatment due to the removal of hemicellulose (Oliveira et al. 2021; Le Troedec et al. 2008). The peak at 1232 cm\(^{-1}\), corresponding to the C-O stretching vibration in lignin disappeared after the treatment. These findings suggest that alkali treatment reduced the lignin content of hemp filler (Oliveira et al. 2021; Le Troedec et al. 2008).
As shown in Figure 4.2, the increase in the peak at approximately 1735-1737 cm\(^{-1}\) occurs due to esterification of the hydroxyl groups, resulting in a stronger stretching vibration of the carbonyl (C=O) group present in the ester bonds. In untreated fillers, the band around 1740 cm\(^{-1}\) in the spectrum is mainly related to the C=O stretching vibration of the carboxyl and acetyl groups in the hemicellulose 'xylan' component and lignin chemical groups. The appearance of the peak around 1740 cm\(^{-1}\) in treated fillers suggests that the acetyl groups are forming an ester bond with the hydroxyl groups of the fillers. Ester bond formation is also confirmed by the emergence of a new peak around 1229 cm\(^{-1}\), which is attributed to the C-O stretching of the ester carboxyl group. The strong absorption between 3320 cm\(^{-1}\) in the spectra is caused by the OH groups of the fillers, but this band is noticeably reduced due to esterification (Tserki et al. 2005).
As shown in Figure 4.3, several absorption bands were observed in the neat PLA, including those at 3659 cm\(^{-1}\), corresponding to the terminal OH group, and those at 2994 and 2946 cm\(^{-1}\), corresponding to the asymmetric and symmetric stretching vibrations of the CH3 groups in the side chains, respectively. The band at 1454 cm\(^{-1}\) was assigned to the bending vibration of CH, while the strong absorption band at 1743 cm\(^{-1}\) corresponded to the stretching vibration of carbonyl (-C=O) groups from the repeated ester units. Another strong absorption band at 1182 cm\(^{-1}\) was assigned to the stretching vibration of C-O in CH-O of polymer chains. The rocking triplet peaks at 1130, 1082, and 1038 cm\(^{-1}\) corresponded to C-O stretching vibrations in CO-O groups. The absorption bands at 956 and 870 cm\(^{-1}\) were assigned to C-C stretching of the single bond. The strong absorption band at 749 cm\(^{-1}\) was assigned to the deformation vibration of CH3 groups. These FTIR results of PLA were consistent with those reported in the literature (Ashok et al. 2014; Roy and Rhim 2020). The PLA/fillers spectra were found to be similar to the PLA spectrum for all untreated, alkali treated and acetylation treated samples, indicating that physical interactions were predominantly present without the formation of new functional groups as can be seen in the Figure 4.3. Similar FTIR results were reported on addition of fillers
to PLA films in the literature (Mohan and Panneerselvam 2022; Roy and Rhim 2020; Zhang et al. 2020).

Figure 4.3: FTIR Spectra of films

### 4.2 Thermogravimetric analysis of composite films

Thermogravimetric analysis was utilized to assess the thermal stability of the neat PLA film and the PLA/filler composite film. The TGA and DTG thermograms presented in Figure 4.4 and Figure 4.5 illustrated that both films displayed a two-step thermal degradation pattern, with the initial mass loss occurring near 100°C because of the remaining solvent evaporation. The second weight change, which was more significant, was observed in both the neat PLA and the PLA/filler composite films within the temperature range of 270-410°C. The composite film's maximum degradation temperature was at 360°C.

The addition of fillers, such as hemp and flax, did not show a significant effect on the PLA film's thermal stability. Both the neat PLA film and the PLA/filler composite film had the same maximum thermal decomposition temperature of 362.5°C, indicating that the presence of fillers did not influence the overall thermal stability of the composite film. These results suggest
that PLA-based composites with fillers may be a practical option for various applications that necessitate both strength and thermal resistance, as the fillers do not seem to negatively impact thermal stability. Similar trend of thermal stability was observed in PLA/curcumin film (Roy and Rhim 2020).

Figure 4.4: TGA and DTG of PLA/Flax films (a) Alkali treatment (b) Acetylation treatment

Figure 4.5: TGA and DTG of PLA/Hemp films (a) Alkali treatment (b) Acetylation treatment
4.3 Surface chemistry analysis with X-ray photoelectron spectroscopy (XPS)

The samples of untreated and treated flax and hemp fillers was investigated through X-ray photoelectron spectroscopy (XPS) to ascertain their elemental composition, atomic concentrations, and mass concentrations. This analytical technique allowed for a deeper comprehension of the surface chemistry of the samples.

Flax and hemp consist of cellulose, hemicellulose, lignin, and small amounts of extractives, with carbon (C), hydrogen (H), and oxygen (O) as the primary components. Hence, XPS can be employed to determine the chemical properties of these fillers before and after the treatment to assess the efficacy of the treatment method. In this study, the assessment focused solely on the C and O elements in the biomass samples, as XPS cannot detect H elements. The primary focus of XPS detection and analysis is on the 1s electrons found in the inner shells of C and O atoms. Valuable information regarding the chemical properties of flax and hemp surfaces were obtained by analysing the intensities and chemical shifts of the C1s peaks. The C1 peaks were composed of components associated with C and O functional groups in the samples, respectively. These components were categorized as C1 (C–C, C–H), C2 (C–O), C3 (O–C–O, C=O), and C4 (O–C=O) based on their binding energy levels. The different atomic binding states of C and O originate from various sources (Watling et al. 2011; Yu et al. 2022). As depicted in the Figure 4.6, in the C1s spectra, the peak of C1 primarily stemmed from lignin and extracts (C–C, C–H), while C2, C3, and C4 were predominantly derived from cellulose and hemicellulose. After undergoing alkaline treatment, the C1 intensity decreased, indicating the effective removal of lignin by sodium hydroxide. In both cases of biomass, it is evident that C2 peak intensity increased due to the introduction of hydroxyl groups to the surfaces. In addition, the π-π interaction which probably sourced from lignin phenolic rings has been disappeared after the treatment for both biomass samples. Higher O/C ratios indicate a higher carbohydrate content, while lower ratios suggest the presence of more lignin and extracts on the flax and hemp surfaces (Kocaefe et al. 2013). Consequently, the increased O/C atomic ratio observed in this study following the delignification treatment further confirms the degrading effect of sodium chloride on lignin (Reale Batista and Drzal 2021).
Figure 4.6: High Resolution XPS Spectra. Signal assessments in different binding energies (a) Untreated Flax (b) Alkali Treated Flax (c) Untreated Hemp (d) Alkali Treated Hemp

As observed in the Figure 4.7, the C1 and C2 components were the primary constituents of the C1s spectrum for both untreated and acetylated samples. However, the contribution of the C1 component decreased, suggesting the degradation of lignin and the dissolution of extractives. Conversely, the C2 signal increased, indicating the acetylation of carbohydrates. Furthermore, there was an increase in the C4 signal, suggesting that acetylation occurred (Karoyo et al. 2020; Sun et al. 2019; Tserki et al. 2005).
Figure 4.7: High Resolution XPS Spectra. Signal assessments in different binding energies (a) Untreated Flax (b) Acetylated Flax (c) Untreated Hemp (d) Acetylated Hemp

4.4 Surface transparency of the composite films

The results of the color test clearly demonstrate that the addition of both flax and hemp filler has a significant effect on the total color difference (ΔE), yellowness index (YI), and whiteness index (WI) values of the PLA film. As presented in Tables 4.1, 4.2, 4.3, and 4.4 interestingly, as the filler content increases, the ΔE value also increases, suggesting a more pronounced deviation from the original color of the PLA film. Similarly, the YI value increases, indicating an increased degree of yellowing in the material. This is likely by the natural color of flax and hemp fillers, which can give a yellowish color to the final product. On the other hand, the WI value decreases with the addition of flax and hemp filler, possibly due to the brown color of the fillers, which can darken the PLA film as shown in Figure 4.8 and Figure 4.9 and reduce its overall whiteness.

Figure 4.8: Colour of PLA/Flax films (a) Neat PLA (b) PLA/Flax\textsuperscript{2.5} (c) PLA/Flax\textsuperscript{5} (d) PLA/Flax\textsuperscript{10} (e) PLA/Flax\textsuperscript{20} (f) PLA/Flax\textsuperscript{30}
Table 4.1: Colour Results Of PLA/Flax films (particle size <75 µm

<table>
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<tr>
<th>Blends</th>
<th>Untreated</th>
<th>Alkali Treated</th>
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<tbody>
<tr>
<td></td>
<td>ΔE</td>
<td>WI</td>
</tr>
<tr>
<td>Neat PLA</td>
<td>9.85±1.42&lt;sup&gt;e&lt;/sup&gt;</td>
<td>90.75±1.47&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>PLA/Flax&lt;sup&gt;2.5&lt;/sup&gt;</td>
<td>15.7±0.98&lt;sup&gt;d&lt;/sup&gt;</td>
<td>83.81±1.06&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>PLA/Flax&lt;sup&gt;5&lt;/sup&gt;</td>
<td>19.71±4.28&lt;sup&gt;d&lt;/sup&gt;</td>
<td>79.61±4.29&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>PLA/Flax&lt;sup&gt;10&lt;/sup&gt;</td>
<td>31.49±1.55&lt;sup&gt;c&lt;/sup&gt;</td>
<td>67.65±1.52&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>PLA/Flax&lt;sup&gt;20&lt;/sup&gt;</td>
<td>44.16±3.04&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>55.18±2.3&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>PLA/Flax&lt;sup&gt;30&lt;/sup&gt;</td>
<td>51.15±2.96&lt;sup&gt;a&lt;/sup&gt;</td>
<td>48.38±2.93&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
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</table>

‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

Table 4.2: Colour Results of PLA/Flax films (particle size 149-210 µm)

<table>
<thead>
<tr>
<th>Blends</th>
<th>Untreated</th>
<th>Alkali Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔE</td>
<td>WI</td>
</tr>
<tr>
<td>Neat PLA</td>
<td>9.85±1.42&lt;sup&gt;f&lt;/sup&gt;</td>
<td>90.75±1.47&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
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<td>81.2±0.5&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>PLA/Flax&lt;sup&gt;5&lt;/sup&gt;</td>
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<td>73.98±1.7&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
<td>PLA/Flax&lt;sup&gt;10&lt;/sup&gt;</td>
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</tr>
<tr>
<td>PLA/Flax&lt;sup&gt;20&lt;/sup&gt;</td>
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<td>60.43±0.46&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>PLA/Flax&lt;sup&gt;30&lt;/sup&gt;</td>
<td>47.8±0.32&lt;sup&gt;a&lt;/sup&gt;</td>
<td>51.62±0.3&lt;sup&gt;f&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

Figure 4.9: Colour of PLA/Hemp films (a) Neat PLA (b) PLA/Hemp<sup>2.5</sup> (c) PLA/Hemp<sup>5</sup> (d) PLA/Hemp<sup>10</sup> (e) PLA/Hemp<sup>20</sup> (f) PLA/Hemp<sup>30</sup>
Table 4.3: Colour Results of PLA/Hemp films (particle size < 75 µm)

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<tbody>
<tr>
<td></td>
<td>ΔE</td>
<td>WI</td>
</tr>
<tr>
<td>Neat PLA</td>
<td>9.85±1.42f</td>
<td>90.75±1.47a</td>
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<tr>
<td>PLA/Hemp²</td>
<td>22.68±1.39e</td>
<td>76.74±1.46b</td>
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<tr>
<td>PLA/Hemp⁵</td>
<td>31.77±1.04d</td>
<td>67.67±1.14c</td>
</tr>
<tr>
<td>PLA/Hemp¹⁰</td>
<td>39.4±0.4c</td>
<td>59.97±0.39d</td>
</tr>
<tr>
<td>PLA/Hemp²⁰</td>
<td>46.01±1.47b</td>
<td>53.52±1.52c</td>
</tr>
<tr>
<td>PLA/Hemp³⁰</td>
<td>60.32±0.55a</td>
<td>39.33±0.57a</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)
*Data are means ± SD

Table 4.4: Colour Results of PLA/Hemp films (particle size 149-210 µm)

<table>
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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔE</td>
<td>WI</td>
</tr>
<tr>
<td>Neat PLA</td>
<td>9.85±1.42f</td>
<td>90.75±1.47a</td>
</tr>
<tr>
<td>PLA/Hemp²</td>
<td>19.94±0.14e</td>
<td>79.75±0.21b</td>
</tr>
<tr>
<td>PLA/Hemp⁵</td>
<td>25.33±1.94d</td>
<td>74.11±1.92c</td>
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<tr>
<td>PLA/Hemp¹⁰</td>
<td>38.35±2.2c</td>
<td>61.03±2.24d</td>
</tr>
<tr>
<td>PLA/Hemp²⁰</td>
<td>43.17±1.64b</td>
<td>56.25±1.68e</td>
</tr>
<tr>
<td>PLA/Hemp³⁰</td>
<td>49.39±0.07a</td>
<td>50.09±0.07f</td>
</tr>
</tbody>
</table>

‡ Means within each column with the same letters are not significantly different (P<0.05)
*Data are means ± SD

These findings suggest that the addition of fillers may not be desirable if the goal is to maintain the original color and whiteness of the PLA film. However, there may be certain applications where the use of flax filler could be advantageous, such as in packaging materials or in products where a natural, earthy look is desired. It is important to consider the color properties of the material when selecting the appropriate filler for a particular application. In order to mask the
color of the filler material and maintain the original color and whiteness of the PLA film, one possibility is to add colorants to the mixture. By incorporating colorants, the desired color can be achieved, effectively hiding the natural color of the flax and hemp fillers. This approach can be particularly useful in applications where a specific color or a consistent appearance is desired, such as in certain consumer products or industrial applications.

4.5 Mechanical characteristics of composite films

To ensure that packaging materials maintain their quality from the time of production to consumption, it is important to evaluate their mechanical properties because they may undergo various levels of external stress during this period. Based on the findings presented, it can be concluded that both flax and hemp fillers have the potential to improve the mechanical properties of polylactic acid (PLA) bioplastic. However, the effects of filler particle size, surface treatment, and loading must be carefully considered to achieve optimal results. Alkali treatment can improve the mechanical properties of both flax and hemp bioplastics by enhancing surface chemistry and interfacial bonding between the filler particles and the PLA matrix. For flax bioplastic, the addition of untreated filler did not improve tensile strength and elongation at break, and Young's modulus decreased with increasing filler loading. In contrast, alkali-treated bioplastics showed an improvement in tensile strength for 2.5 and 5 wt% loading. Acetylation treatment improved elongation at break at lower loading percentages but became less effective as the percentage of filler loading increased. The addition of flax fillers of size range 149-210 µm to a polymer matrix, whether untreated or alkali-treated, resulted in a decrease in both tensile strength and Young's modulus. However, at filler loadings of 2.5% and 5%, the addition of both untreated and alkali-treated fillers led to an increase in the elongation at break of the films. The larger particle size of acetylated flax fillers in the range of 149-210 µm decreased all three mechanical properties: Tensile strength, elongation at break, and Young's modulus. For hemp bioplastic, the tensile strength initially decreases at low filler loadings due to insufficient reinforcement caused by low surface area of the filler particles in contact with the polymer matrix. However, as filler loading is increased to 5%, better adhesion between the filler particles and the polymer matrix results in increased tensile strength. Alkali treatment improves tensile strength at lower filler loadings (2.5% to 5%) due to enhanced surface chemistry, resulting in better adhesion and interfacial bonding. In contrast, the addition of filler particles reduces the mobility of the polymer chains, making the material more rigid and less able to stretch before failure, leading to a decrease in elongation at break at all filler loadings.
loadings for particle size < 75 µm. Alkali treatment improves interfacial adhesion and increases elongation at break up to 5%, but at higher loadings, agglomeration once again leads to defects and decreased elongation at break. Additionally, higher Young's modulus values at low to moderate filler loadings are due to improved adhesion between the filler particles and the polymer matrix, resulting in better load transfer and reinforcement of the polymer. However, at higher filler loadings, agglomeration of excess filler particles leads to a decrease in Young's modulus. Acetylation treatment can improve the tensile strength of the composite material. However, excessive filler loading can lead to agglomeration, resulting in decreased mechanical properties. The Young's modulus increases with increasing filler loading for smaller particle sizes, while it decreases for larger particle sizes. The mechanical characteristics of PLA/flax films are illustrated in Figure 4.10. Detailed information about the mechanical characteristics can be found in Tables A.1, A.2, B.1, and B.2 in Appendix A and B.

The three-way ANOVA results showed that all three factors, as well as their interactions, have a statistically significant impact on the tensile strength (TS), elongation at break (EB), and Young's modulus (YM) of the films. Specifically, for flax bioplastic, the analysis revealed a statistically significant effect of particle size, treatment, and loading on TS, with the interaction between treatment and loading being significant for the filler of particle size <75 µm. However, the impact of the interaction between treatment and loading on TS was found to be insignificant for particle size 149-210 µm. For EB and YM, a significant effect of particle size, treatment, loading, and their interaction was found. The size of the flax filler particles can have a significant impact on the Young's modulus of the composite material when untreated. However, when the particles are acetylated, their size does not seem to have a significant impact.
For hemp bioplastic, as shown in Figure 4.11 and depicted in Tables A.3, A.4, B.3, and B.4 in Appendix A and B, the tensile strength initially decreases at low filler loadings due to insufficient reinforcement caused by low surface area of the filler particles in contact with the polymer matrix. However, as filler loading is increased to 5%, better adhesion between the filler particles and the polymer matrix results in increased tensile strength. Alkali treatment improves tensile strength at lower filler loadings (2.5% to 5%) due to enhanced surface
chemistry, resulting in better adhesion and interfacial bonding. In contrast, the addition of filler particles reduces the mobility of the polymer chains, making the material more rigid and less able to stretch before failure, leading to a decrease in elongation at break at all filler loadings for particle size < 75 µm. Alkali treatment improves interfacial adhesion and increases elongation at break up to 5%, but at higher loadings, agglomeration once again leads to defects and decreased elongation at break. Additionally, higher Young's modulus values at low to moderate filler loadings are due to improved adhesion between the filler particles and the polymer matrix, resulting in better load transfer and reinforcement of the polymer. However, at higher filler loadings, agglomeration of excess filler particles leads to a decrease in Young's modulus. For Hemp bioplastic, all three factors, as well as their interactions, were found to have a statistically significant impact on TS, EB, and YM. In addition, the study found that the particle size, loading of the fillers, and their interaction with each other have a significant impact on the EB of the films. The impact of treatment on EB was found to be statistically significant for fillers with a particle size of less than 75 µm but insignificant for fillers with a size of 149-210 µm.

In summary, the choice of filler particle size and surface treatment are critical factors in achieving optimal mechanical properties in polymer composites, and the observed trends in tensile strength, elongation at break, and Young's modulus can be explained by a combination of factors, including changes in crystallinity, interfacial adhesion, and the presence of defects.
Figure 4.11: Mechanical Characteristics of PLA/Hemp Films: Particle Size 75 µm (a) Tensile Strength (b) Elongation at Break (c) Young’s Modulus; Particle Size 149-210 µm (d) Tensile Strength (e) Elongation at Break (f) Young’s Modulus

4.6 Moisture absorption behaviour of composite films

The moisture absorption plays a crucial role in determining the performance and durability of bioplastics over an extended period. Moisture absorption properties of PLA bioplastics with
flax and hemp fillers were investigated for two different particle sizes (<75 µm and 149-210 µm). There was an increase in the moisture absorption with filler content for both untreated and alkali-treated bioplastics, with the rise being more accentuated for the untreated bioplastics. The findings are summarized in Tables A.5 and A.6 which provide detailed breakdown of moisture absorption behavior of alkali treated bioplastics. The increase in moisture absorption can be attributed to the addition of filler particles. These particles make the material more porous and easier for moisture to get in the matrix. At low filler loadings, moisture absorption was mainly due to surface adsorption of water molecules on the exposed surfaces of polymer chains. However, at higher loadings, clustering of filler particles resulted in voids and gaps between particles, allowing moisture to penetrate and be absorbed by the plastic matrix. It can be said that the interplay between the moisture absorption, loading percentage, and filler particles is intricate and multi-faceted. At higher loadings, the clustering of filler particles happens, creating voids and gaps between the particles that can allow moisture to penetrate and be absorbed by the plastic matrix. In contrast, the presence of both filler particles with a size range of 149-210 µm, irrespective of the filler loading and alkali treatment, resulted in an increase in moisture absorption due to the creation of a porous polymer matrix structure with voids and gaps providing additional pathways for moisture ingress. The agglomeration of the particles at higher filler loadings further increased the moisture absorption. Neat PLA film had lower moisture absorption than untreated and alkali-treated bioplastics at all loading percentages, making it less porous and less susceptible to moisture absorption. Tables B.5 and B.6 in the appendix offer a comprehensive overview of the moisture absorption behavior of acetylation treated bioplastics. Films with acetylated hemp fillers of particle size 149-210 µm had reduced moisture absorption at 2.5%, 5%, and 10%, with a minimum at 10%, followed by an increase at 20% and 30%.

As shown in Figure 4.12 and Figure 4.13, both alkali and acetylation treatment reduced the moisture absorption of bioplastics as compared to untreated bioplastics at all loading percentages. This reduction in moisture absorption was due to the improved interfacial bonding between the filler and the matrix material resulting from the removal of impurities and defects through these treatments. Both treatments reduced the impact of loading percentage on moisture absorption, as observed by the less pronounced effect of loading percentage on treated bioplastics as compared to untreated bioplastics. Therefore, it is essential to consider the impact of filler loading and treatment on moisture absorption while developing bioplastic materials to ensure their long-term stability and performance.
The three-way ANOVA results indicate a statistically significant effect of particle size, treatment, and loading on the moisture absorption (MA) of both flax and hemp bioplastics. In the case of flax bioplastic, the interaction between particle size and loading was found to be significant for untreated filler, while it was insignificant for treated ones. For hemp bioplastic, the interaction between particle size and loading significantly affected the MA in untreated films, while this interaction was not significant in films with alkali-treated fillers. The results
suggest that the method of treatment used on the fillers can have an influence on how the particle size and loading interact with each other, which ultimately affects the MA of the resulting films. These findings highlight the importance of considering multiple factors, such as particle size, treatment, and loading, when predicting the MA of polymer composites. The results of this statistical analysis can be used to develop effective strategies for mitigating moisture-induced degradation in bioplastics by optimizing the particle size, treatment, and loading of fillers.

4.7 Water vapor permeability of composite films

Water vapor permeability (WVP) is an important property to consider when designing bioplastics for packaging applications. The effect of filler loading and particle size on WVP was studied for both flax bioplastic and hemp bioplastic. The findings are summarized in Tables A.7, A.8, B.7 and B.8 which provide detailed breakdown of WVP properties of these bioplastics. Both untreated and alkali-treated flax and hemp fillers showed an increase in WVP with increasing loading percentage of filler. The increase in WVP with the addition of fillers to PLA films can be attributed to several factors. The presence of voids and gaps between the filler and the matrix can create pathways for water molecules to penetrate into the film, leading to an increase in WVP. The hydrophilic nature of the natural fillers can attract water molecules and create localized regions of high-water concentration, further increasing the WVP. Additionally, the particle size of the filler can play a role in determining the WVP of the resulting film. Smaller particle sizes (<75 µm) lead to more interactions with water molecules and higher WVP, while larger particle sizes (149-210 µm) can create larger voids between the particles and the matrix, resulting in a higher WVP. Acetylation of flax fillers initially decreased WVP for particle size <75 µm, but at higher loadings, the increased flax filler content created a more porous structure, leading to higher WVP values. For acetylated hemp fillers, WVP reduced until 5% and then started to rise at higher loadings (10, 20 and 30%). The reduction in WVP could be due to improved adhesion between the filler and matrix resulting from the treatments, reducing the number of voids and gaps between the filler and the matrix. However, alkali and acetylation treatment reduced the impact of loading percentage on WVP. The observed trend in WVP values as shown in Figure 4.14 and Figure 4.15 for different particle sizes and filler loadings suggests the clustering of filler particles is occurring at higher loadings, which can create voids or channels in the composite material that allow water vapor to pass through more easily.
Overall, the increase in WVP with the addition of fillers to bioplastics should be taken into consideration when designing packaging applications where water vapor barrier properties are important. The balance between the ability of the filler particles to fill the gaps between the polymer chains and the formation of a more porous structure as the loading percentage increases should be carefully considered when selecting composite materials for specific applications.

Figure 4.14: Water vapor permeability of PLA/Flax Films (a) Particle Size 75 μm (b) Particle Size 149-210 μm

Figure 4.15: WVP of PLA/Hemp Films (a) Particle Size 75 μm (b) Particle Size 149-210 μm
The results of the statistical analysis showed that each factor, as well as the interaction between treatment and loading, had a significant effect on the WVP of the flax bioplastic films. This indicates that these factors individually or in combination affect the WVP values of the films. Additionally, the significant interaction between loading and treatment implies that the effect of loading on WVP is dependent on the treatment applied to the filler. On the other hand, the interaction between particle size and treatment, and particle size and loading were not significant, indicating that the impact of particle size on WVP is independent of treatment or loading, and vice versa. Similarly, the results of the analysis for the hemp bioplastic films indicated that each factor had a significant impact on the WVP of the films, and the interaction between these factors was also found to be significant. This suggests that the combined effect of particle size, loading, and treatment was greater than the effect of each factor individually. Overall, these findings suggest that the WVP of bioplastic films can be manipulated by adjusting particle size, loading, and treatment, and a careful selection of these factors can be used to tailor the WVP of the films to meet specific requirements for different applications.

### 4.8 Surface wettability analysis of composite films

The impact of fillers on the water contact angle of PLA-based films was investigated in both flax and hemp bioplastics. The appendix contains Tables A.9, A.10, B.9, and B.10, which provide a comprehensive summary of the water contact angle of these bioplastics, encompassing the main findings. For particle sizes smaller than 75 µm and between 149-210 µm, the water contact angle decreased. This suggests that the plastic became more hydrophilic. This was attributed to the increased availability of the filler particles on the surface of the films, providing more sites for water molecules to interact with and reducing the contact angle. Additionally, it was observed that the surface of the films became rougher when larger filler particles were added. This increased the amount of surface area for water molecules to interact with, which ultimately resulted in a further decrease in the water contact angle. The reduction was more prominent in untreated ones than that of alkali and acetylation treated ones as shown in Figure 4.16 and Figure 4.17. This behavior can be explained by the improved interfacial bonding between the filler and the matrix material due to the removal of impurities and defects through treatments.
For flax-based bioplastic, the interaction between particle size and loading was also found to be statistically significant for untreated films. This suggests that the effect of loading on WC depends on the particle size of the filler. However, the interaction was statistically insignificant for alkali-treated films, implying that the alkali treatment reduced the dependency of WC on particle size and loading. The treatment made the surface of the filler more uniform and hydrophilic, thereby reducing the variation in WC caused by the size and loading of the filler.

For hemp-based bioplastic, the statistical analysis indicated that all three factors (particle size, loading, and treatment) had a statistically significant effect on the WC. Additionally, the interaction between treatment and loading was found to be statistically significant for the 149-210 µm particle size. This means that the effect of treatment on the WC was different depending on the weight percentage loading of the filler. However, for the 75 µm particle size, the interaction between treatment and loading was found to be statistically insignificant. This implies that the effect of treatment on the WC was similar across different weight percentage loadings of the filler.
Overall, these findings suggest that both particle size and surface treatment of fillers can significantly affect the water contact angle of PLA-based films. Further studies are needed to investigate the effect of other factors, such as filler concentration and processing conditions, on the water contact angle of PLA-based films.

4.9 Material chart

Experimental measurements are used to compare the Young's modulus and tensile strength of various materials, including flax and hemp-based PLA composite films. This comparison is visualized through "Ashby plots," where each region corresponds to a specific material class such as metals, ceramics, or wood. These plots help categorize and analyze the properties of different material systems based on empirical data. The purpose of this chart is to provide guidelines for identifying materials that exhibit high storage of elastic energy per unit volume and are suitable for use as elastic hinges. The highlighted samples in this thesis, denoted by stars, correspond to the specific objectives of the study. This Ashby plot depicted in Figure 4.18 provides a valuable tool for evaluating materials suitable for high-stiffness and high-strength applications while minimizing weight (Babaeighazvini 2023). This assessment is particularly...
relevant in industries like automotive and aerospace, where lightweight yet robust materials are crucial. The Ashby plot illustrates that PLA films incorporating 2.5% alkali-treated flax and hemp outperformed other blends in terms of mechanical properties. Notably, these formulations fall within the polymer region, highlighting their potential for developing composites with elevated Young's modulus and strength.

Figure 4.18: Ashby plot (Babaeighazvini 2023)
CHAPTER FIVE
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, this study highlights the significance of comprehending the intricate interplay of several factors that affect the properties of bioplastic films. The following bullet points outline the key results and highlight the implications of our study.

(A) Alkali treated bioplastics.

(a) For flax bioplastic, the addition of untreated filler did not improve tensile strength and elongation at break, and Young's modulus decreased with increasing filler loading. In contrast, alkali-treated bioplastics showed an improvement in tensile strength for 2.5 and 5 % loading. The addition of flax fillers of size range 149-210 µm to a polymer matrix, whether untreated or alkali-treated, resulted in a decrease in both tensile strength and Young's modulus. However, at filler loadings of 2.5% and 5%, the addition of both untreated and alkali-treated fillers led to an increase in the elongation at break of the films. For hemp filler of particle size <75 µm, tensile strength and elongation at break decreased with increase in filler content, however, Young’s modulus increased till 10% loading and then started decreasing. For hemp filler of particle size 149-210 µm, tensile strength and young’s modulus decreased at all filler loadings, however elongation at break increased till 5% loading and started reducing. The trends observed in tensile strength, elongation at break, and Young's modulus can be attributed to several factors, including changes in crystallinity, interfacial adhesion, and the presence of defects.

(b) The addition of fillers to bioplastics resulted in an increase in moisture absorption and WVP with effects being more pronounced in untreated ones compared to the treated ones.

(c) Water Contact Angle of films reduced with increasing filler content for both particle sizes. However, the decrease in water contact angle absorption was more prominent in case of untreated fillers.
(B) Acetylation Treated Bioplastics

(a) The results indicated that for particle sizes less than 75 µm, untreated flax filler reduced the elongation at break of the bioplastic, while acetylation treatment improved elongation at break at lower loading percentages but became less effective as the percentage of filler loading increased. The larger particle size of fillers in the range of 149-210 µm decreased all three mechanical properties: Tensile Strength, Elongation at Break, and Young’s Modulus. For hemp bioplastic, the results indicate that smaller filler particle sizes (< 75 µm) and acetylation treatment can improve the tensile strength of the composite material. However, excessive filler loading can lead to agglomeration, resulting in decreased mechanical properties. The Young's modulus increases with increasing filler loading for smaller particle sizes, while it decreases for larger particle sizes.

(b) With increasing filler content, the moisture absorption of the films increased. The acetylation treatment reduced the impact of loading percentage on moisture absorption, as observed by the less pronounced effect of loading percentage on acetylated bioplastics compared to untreated bioplastics.

(c) Acetylation initially reduced the WVP of the films for smaller particle size but at higher loadings, the increased flax filler content created a more porous structure, leading to higher WVP values. WVP increased at all loadings of flax filler of particle size 149-210 µm. For both particle sizes of untreated hemp fillers, WVP increased at all loadings, while for acetylated hemp fillers, WVP reduced till 5% and then started to rise at higher loadings (10, 20 and 30%).

(d) Water Contact angle reduced with addition of fillers.

The balance between the ability of the filler particles to fill gaps between polymer chains and the formation of a more porous structure as loading percentage increases should be carefully considered when selecting bioplastics for specific applications. Therefore, it is essential to consider various factors such as particle size, treatment, and loading of the filler and their interaction while designing bioplastics with tailored properties for various applications.
5.2 Recommendations for future work

(1) As the field of bioplastics continues to advance, there are several avenues of research that hold promise for further development and improvement. The following recommendations outline key areas for future work, including exploring alternative processing techniques, assessing biodegradability, developing multilayer films, investigating other lignocellulosic biomass options, conducting techno-economic and life cycle analyses, and evaluating long-term durability. These research directions aim to enhance the functionality, sustainability, and commercial viability of bioplastics, paving the way for their broader adoption in various industries. Investigation of other processing techniques: It is crucial to explore other plastics manufacturing techniques such as extrusion and 3D printing for producing the bioplastics. These manufacturing strategies offer several benefits in terms of process efficiency, scalability, and to produce complex shapes and structures.

(2) Biodegradability: Future studies should focus on the biodegradability of such bioplastics. It is quite important to assess the biodegradability rate, conditions, and mechanism of these developed bioplastics under different ambient conditions.

(3) Development of Multilayer films: The development of multilayer films using PLA/agricultural biomass and their feasibility should be explored. This approach offers the possible improvements in mechanical, barrier, and other functional characteristics of the bioplastics. Moreover, the adhesion between different layers should be studied.

(4) Other lignocellulosic biomass: Comprehensive studies should be conducted to assess the functionality and feasibility of using other lignocellulosic biomass as fillers for producing bioplastics specially, canola biomass which is anticipated to substantially increase in Saskatchewan because of canola farming.

(5) Techno-economic and Life cycle analysis: Technoeconomic analysis should be conducted to understand the economic feasibility of large-scale production. Identification of possible cost reduction areas will contribute significantly to the commercial viability of the bioplastics.

(6) Long term durability: Behaviour of bioplastics under real world conditions should be explored to assess their durability. The effect of temperature changes, sunlight on the characteristics of the bioplastics should critically studied to assess the long-term durability and stability of the bioplastics.
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APPENDIX A

Supplementary Information for Alkali Treated Bioplastics

Table A.1: Mechanical Characteristic of PLA/Flax films (particle size < 75 µm)

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<td>Tensile Strength (MPa)</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

Table A.2: Mechanical Characteristic of PLA/Flax films (particle size 149-210 µm)

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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD
### Table A.3: Mechanical Characteristic of PLA/Hemp films (particle size < 75 µm)

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<td>8.42±1.92&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>PLA/Hemp&lt;sub&gt;20&lt;/sub&gt;</td>
<td>21.93±0.49&lt;sup&gt;c&lt;/sup&gt;</td>
<td>9.8±1.19&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>24.61±3.13&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.18±1.77&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>PLA/Hemp&lt;sub&gt;30&lt;/sub&gt;</td>
<td>15.84±1.09&lt;sup&gt;d&lt;/sup&gt;</td>
<td>8.6±0.43&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>15.72±1.08&lt;sup&gt;d&lt;/sup&gt;</td>
<td>7.55±0.68&lt;sup&gt;e&lt;/sup&gt;</td>
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† Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

### Table A.4: Mechanical Characteristic of PLA/Hemp films (particle size 149-210 µm)

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<tbody>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>Elongation at Break (%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neat PLA</td>
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<td>19.67±4.25&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>548.69±38.65&lt;sup&gt;c&lt;/sup&gt;</td>
<td>548.69±38.65&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>PLA/Hemp&lt;sub&gt;2.5&lt;/sub&gt;</td>
<td>18.06±3.09&lt;sup&gt;b&lt;/sup&gt;</td>
<td>24.45±2.22&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>30.44±1.10&lt;sup&gt;b&lt;/sup&gt;</td>
<td>11.45±1.28&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>23.29±2.29&lt;sup&gt;b&lt;/sup&gt;</td>
<td>32.78±0.97&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>PLA/Hemp&lt;sub&gt;10&lt;/sub&gt;</td>
<td>16.48±1.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.56±1.35&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>12.51±0.88&lt;sup&gt;e&lt;/sup&gt;</td>
<td>28.23±2.06&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>21.81±0.41&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>7.82±0.43&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>17.33±0.39&lt;sup&gt;d&lt;/sup&gt;</td>
<td>7.06±0.75&lt;sup&gt;de&lt;/sup&gt;</td>
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† Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD
Table A.5: Moisture Absorption (%) of PLA/Flax films

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<td>Untreated</td>
<td>Alkali Treated</td>
</tr>
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<td>0.61±0.17&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>0.67±0.28&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>PLA/Flax&lt;sup&gt;5&lt;/sup&gt;</td>
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<td>0.67±0.14&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>PLA/Flax&lt;sup&gt;10&lt;/sup&gt;</td>
<td>1.09±0.16&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>1.78±0.26&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.42±0.07&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>PLA/Flax&lt;sup&gt;30&lt;/sup&gt;</td>
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<td>1.91±0.25&lt;sup&gt;a&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

Table A.6: Moisture Absorption (%) of PLA/Hemp films

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<td>Untreated</td>
<td>Alkali Treated</td>
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<td>Neat PLA</td>
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<td>0.61±0.17&lt;sup&gt;d&lt;/sup&gt;</td>
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<tr>
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<td>0.52±0.17&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>PLA/Hemp&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1.07±0.08&lt;sup&gt;d&lt;/sup&gt;</td>
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<tr>
<td>PLA/Hemp&lt;sup&gt;20&lt;/sup&gt;</td>
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<td>1.85±0.03&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>PLA/Hemp&lt;sup&gt;30&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD
Table A.7: WVP ($\times 10^{-7}$ g·m/m²·Pa·s) of PLA/Flax films

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<td>Alkali Treated</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

Table A.8: WVP ($\times 10^{-7}$ g·m/m²·Pa·s) of PLA/Hemp films

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<td>Untreated</td>
<td>Alkali Treated</td>
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<td>1.42±0.43${}^c$</td>
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<td>1.55±0.31${}^c$</td>
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<td>3.85±0.37${}^b$</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD
Table A.9: WC of PLA/Flax films

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<td>82±1.09&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>PLA/Flax&lt;sup&gt;5&lt;/sup&gt;</td>
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<td>69.15±0.94&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>61.1±0.94&lt;sup&gt;f&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

Table A.10: WC of PLA/Hemp films

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<td>Neat PLA</td>
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<td>85.31±0.95&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>PLA/Hemp&lt;sup&gt;2.5&lt;/sup&gt;</td>
<td>78.6±0.71&lt;sup&gt;b&lt;/sup&gt;</td>
<td>81.15±1.12&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>PLA/Hemp&lt;sup&gt;5&lt;/sup&gt;</td>
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<td>76.97±0.96&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>61.06±1.75&lt;sup&gt;f&lt;/sup&gt;</td>
<td>64.98±2.07&lt;sup&gt;e&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD
APPENDIX B

Supplementary Information for Acetylation Treated Bioplastics

Table B.1: Mechanical Characteristics of PLA/Flax Films (Particle Size <75 µm)

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<td>Elongation at Break (%)</td>
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<td>19.67±4.25&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>10.46±0.51&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>PLA/Flax&lt;sub&gt;10&lt;/sub&gt;</td>
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<td>14.83±1.74&lt;sup&gt;bc&lt;/sup&gt;</td>
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<td>15.86±0.94&lt;sup&gt;ab&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

Table B.2: Mechanical Characteristics of PLA/Flax Films (Particle Size 149-210 µm)

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<td>Tensile Strength (MPa)</td>
<td>Elongation at Break (%)</td>
</tr>
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<td>Neat PLA</td>
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<td>19.67±4.25&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
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<td>23.71±1.79&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>22.45±4.05&lt;sup&gt;ab&lt;/sup&gt;</td>
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<td>PLA/Flax&lt;sub&gt;10&lt;/sub&gt;</td>
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<td>17.49±1.15&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>8.75±0.73&lt;sup&gt;c&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD
Table B.3: Mechanical Characteristics of PLA/Hemp films (particle size < 75 µm)

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<td>Elongation at Break (%)</td>
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<tr>
<td>Neat PLA</td>
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<td>19.67±4.25&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>9.96±0.66&lt;sup&gt;b&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

Table B.4: Mechanical Characteristics of PLA/Hemp films (particle size 149-210 µm)

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<td>Tensile Strength (MPa)</td>
<td>Elongation at Break (%)</td>
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<td>Neat PLA</td>
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</tr>
<tr>
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</tr>
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<td>14.56±1.35&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
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<td>7.82±0.43&lt;sup&gt;d&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD
Table B.5: Moisture Absorption of PLA/Flax films

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<tr>
<td>Neat PLA</td>
<td>0.61±0.17&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.61±0.17&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.61±0.17&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>1.18±0.11&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.94±0.07&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>1.01±0.17&lt;sup&gt;bc&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

Table B.6: Moisture Absorption of PLA/Hemp films

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<td>PLA/Hemp&lt;sup&gt;5&lt;/sup&gt;</td>
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<td>0.72±0.09&lt;sup&gt;bcd&lt;/sup&gt;</td>
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<td>1.16±0.0.09&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>2.59±0.31&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.2±0.29&lt;sup&gt;a&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD
Table B.7: WVP of PLA/Flax films

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<td>Treated</td>
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<td>1.94±0.52&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>0.67±0.15&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>23.97±9.25&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.95±1.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>16.98±7.25&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17.73±5.8&lt;sup&gt;a&lt;/sup&gt;</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)
*Data are means ± SD

Table B.8: WVP of PLA/Hemp films

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<td>Untreated</td>
<td>Treated</td>
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‡ Means within each column with the same letters are not significantly different (P<0.05)
*Data are means ± SD
### Table B.9: Water Contact Angle of PLA/Flax films

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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD

### Table B.10: Water Contact Angle of PLA/Hemp films

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‡ Means within each column with the same letters are not significantly different (P<0.05)

*Data are means ± SD