

Nanocellulose in Bioplastics for Sustainable Packaging

by
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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Packaging has become a critical concern due to the prevalence of single-use plastics from petrochemicals, leading to environmental issues. To address this, interest in bio-based materials for packaging has grown, offering biodegradability and a lower carbon footprint. However, bioplastics have limitations like weak mechanical properties and high permeability. To overcome these issues, there is a need for chemical compositions and processing methods that improve the barrier properties. One effective approach is incorporating nanomaterials, such as cellulose nanofibers, to enhance bioplastics' properties and contribute to sustainable development.

One prominent bioplastic that has garnered significant attention is thermoplastic starch (TPS). Furthermore, the preparation of blends comprising polybutylene succinate (PBS) and TPS (at a ratio of 30%) has been explored as a means of producing cost-effective composite materials with desirable performance characteristics. The TPS and PBS blends were prepared through extrusion and hot pressing, and their morphological, mechanical, and barrier properties were assessed. The findings revealed that the presence of fibers in the composite acted as reinforcement within the matrix, thereby improving the mechanical properties and, to some extent, the barrier properties. Notably, the incorporation of citric acid as a compatibilizer further enhanced the composite's performance.

The primary objective of this project is producing cellulose nanofibers (CNF) from industrial hemp and develop biodegradable nanocomposite films with excellent barrier properties for packaging applications. PBS is known for its favorable transparency, mechanical properties, and water resistance, but it is expensive and lacks adequate oxygen resistance. Hence, in this study, PBS was blended with CNF to increase the biobased content and reduce costs. The nanocomposites, comprising CNF and PBS, were prepared using an extruder and hot press. The microstructure, barrier properties, and mechanical properties of the nanocomposites were investigated.

Scanning electron microscopy (SEM) analysis revealed that lower CNF contents (less than 15%) exhibited better dispersion of nanoparticles within the polymer matrix, while higher contents (30 and 50% wt) resulted in agglomeration of CNF, making the nanocomposites more brittle. The water vapor permeability (WVP) tests showed that the incorporation of nanofibers had no significant impact on film permeability. However, there was a notable improvement in oxygen permeability. The transparency of all the films was found to be satisfactory, particularly when the CNF content was below 15%.

Other aspects of the research involved comparing CNF with and without bleaching processes, as well as utilizing different chemicals to enhance CNF dispersion in PBS and improve the properties. The effect of these chemicals on atomized droplet size and hydrogen bond retardation between CNFs was examined by analyzing product morphology, particle size distribution, and dispersion stability in aqueous systems. The results indicated that CNF suspensions treated with Sodium chloride (NaCl) could be atomized into smaller droplets during spray drying, leading to the production of CNF powder with reduced particle sizes. Therefore, drying with NaCl was considered a cost-effective and environmentally friendly method for obtaining highly dispersible dried CNFs suitable for large-scale industrial applications in composite industries. Additionally, NaCl salts are relatively inexpensive, and the process does not involve the use of organic solvents or hazardous chemicals. The intriguing aspect of this section pertained to the varying coloration observed between the CNF and the final film. The films incorporating bleached CNF exhibited a transparent and white appearance, while those created solely through mechanical means exhibited a slight yellowish hue while maintaining good transparency. Furthermore, all films demonstrated a consistent and homogeneous appearance without any surface particles.

Overall, the PBS/CNF nanocomposites demonstrated favorable properties for sustainable packaging, depending on the specific application requirements. However, further research and development are necessary to enhance and optimize the final properties of these materials.

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Dedication

I would like to express my dedication of this thesis to all the students in my home country, Iran, who are unable to be present here today due to the imposed sanctions and political circumstances.

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List of Abbreviations

%	Percentage
BC	Bacterial cellulose
CH ₄	Methane
cm	Centimeter
CNC	Cellulose nanocrystal
CNF	Cellulose nanofiber
CNW	Cellulose nano whiskers
CO ₂	Carbon dioxide
CTAB	Cetyltrimethylammonium bromide
FTIR	Fourier Transform Infrared Spectroscopy
g	Gram
H ₂ O ₂	Hydrogen peroxide
HCl	Hydrochloric acid
HNT	Halloysite nanotube
KCl	Potassium chloride
KPa	Kilopascal
Nm	Nanometer
M	Meter
Mm	Millimetre
MFC	Micro fibrillated cellulose
M _a	Moisture absorption
M _c	Moisture content
NaCl	Sodium chloride
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxides
NaSiO ₃	Sodium metasilicate
NFC	Nano fibrillated cellulose
O ₂	Oxygen
OP	Oxygen Permeability
OTR	Oxygen Transmission Rate
Pas	Pascal

Pas	Polyester amides
PA	phthalic anhydride
PBS	Polybutylene succinate
PCL	Polycaprolactone
PE	Bio-based polyethylene
PEO	Polyethylene oxide
PET	Polyethylene terephthalate
PLA	Polylactic acid
PP	Polypropylene
PS	Polystyrene
PVA	Poly vinyl alcohol
SDS	Sodium dodecyl sulfate
SEM	Scanning Electron Microscopy
ST	Starch
T_g	Glass transition temperature
THC	Tetrahydrocannabinol
TPS	Thermoplastic starch
W_a	Water absorption
W_s	Water Solubility
WVP	Water vapor permeability
WVTR	Water vapor transmission rate
wt-%	Weight Percent

Chapter 1 Introduction

1. Introduction

In this chapter, an overview of the research topic is covered, including significance, problem, objective, research goal and outline.

1.1. The Problem and Motivation

Global warming and climate change are two important problems that exist in today world. A great reason for these two issues and environment's pollution is plastic [1]. Conservation of the environment from some kind of polymers that produced from exhaustible resources has become one of the controversial topics these days [2]. Many social changes have been created by COVID-19. Since the pandemic began, there has been a surge in the use of personal protective equipment including gloves, masks, and face shields. As a result, the packaging sector has been forced to look for low-cost, renewable materials to help reduce contamination of the air, land, and water [3]. China ranks among the top plastic producers globally, with one of the largest outputs of plastic materials. Figure 1.1 shows the global plastic production in different countries.

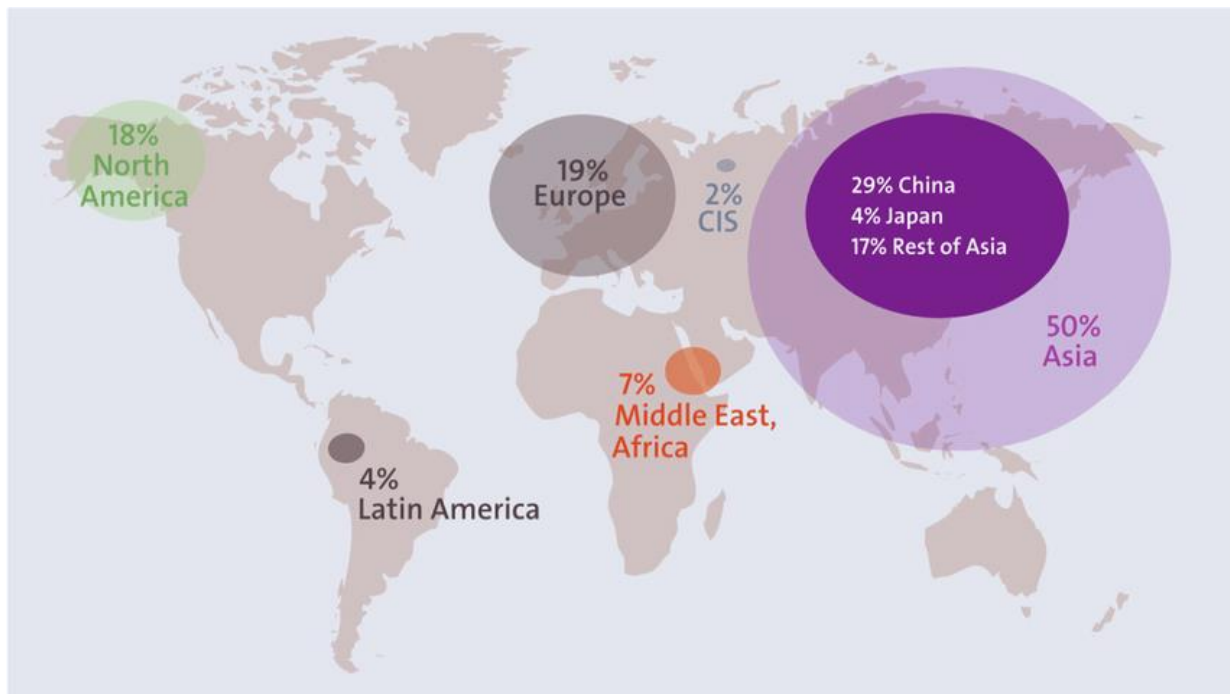


Figure 1.1 The global use of plastic, adapted from [1], under the Springer Nature and Copyright Clearance Centre.

The extensive utilization of conventional plastics has led to a significant environmental problem on a global scale, as these materials require hundreds of years to decompose, and disposal poses a significant challenge. Due to their production from renewable resources and ability to biodegrade, bioplastics present a potential solution to this issue. Nevertheless, the production of bioplastics itself has an environmental impact, so there is a pressing need to develop more sustainable alternatives. There are some solutions to solve these problems; making the strict polluting policies and try to clean up more, but these are short-term solutions[4]. As a permanent solution we should move toward biodegradable materials [5]. These environmental concerns and the limitation of petroleum supply sources have increased attention to biodegradable and renewable materials [6]. One promising solution is the use of nanocellulose in bioplastics, particularly for sustainable packaging, as it offers an opportunity to address this issue. The addition of nanocellulose to bioplastics can enhance their performance properties, resulting in improved strength and stiffness, better barrier properties, and reduced toxicity. Furthermore, the use of nanocellulose in bioplastics may contribute to a reduction in plastic waste in the environment, as nanocellulose is biodegradable. The packaging industry is a rapidly growing market, with a significant portion of the market being driven by the food industry [3]. While bioplastics are a more environmentally friendly option than traditional plastics, they still have limitations that need to be addressed. The effectiveness of bioplastics can be limited by their mechanical and barrier properties, which can be problematic in packaging applications that require the materials to endure different types of stress while preserving the quality of the packaged goods. Furthermore, the production of bioplastics still has a considerable environmental impact, particularly when considering the energy and resources required for their creation. Consequently, the development of sustainable packaging materials is crucial to ensure that the necessary mechanical and barrier properties are maintained while also reducing the environmental impact of packaging waste [7].

1.2. Research Objectives

The main purpose of this thesis is to explore the potential of using nanocellulose as a reinforcement agent in bioplastics for sustainable packaging applications, specifically focusing on polybutylene succinate (PBS). The aim is to develop an environmentally friendly packaging material that can meet the required mechanical and barrier properties while reducing the environmental impact of packaging waste. The research will investigate the effect of nanocellulose on the mechanical and barrier properties of bioplastics, assess their biodegradability, and evaluate their suitability for packaging applications. The use of PBS, a

transparent biobased polymer, in combination with starch and nanocellulose will be employed to enhance the material's properties while maintaining high levels of renewable content. The project's most significant contribution is the utilization of industrial hemp-derived nanocellulose produced in the lab. The overall objective is to develop a sustainable and environmentally friendly packaging material that can replace conventional plastics and minimize plastic waste.

1.3. Project Outline

This thesis is composed of 7 chapters as described below:

Chapter one provides information regarding the current problem also it covers motivation, objectives, and outline. The second chapter provides background and literature review of relevant studies related to materials, process, techniques, testing methods and goal of this project. The next chapter lists materials used with their properties, preparation methods and testing methods. Chapters 4 to 6 address specific research objectives individually, providing experimental findings and discussions. Chapter 4 explores the influence of CNF and citric acid as a compatibilizer in PBS and starch blends. Chapter 5 compares the properties of treated and untreated CNF in PBS, while Chapter 6 investigates the impact of various chemicals on the dispersibility of untreated CNF and their effect on the final properties of PBS. Finally, the last chapter presents the overall thesis conclusions and recommends some future works.

The layout for this project is shown in Figure 1.2.

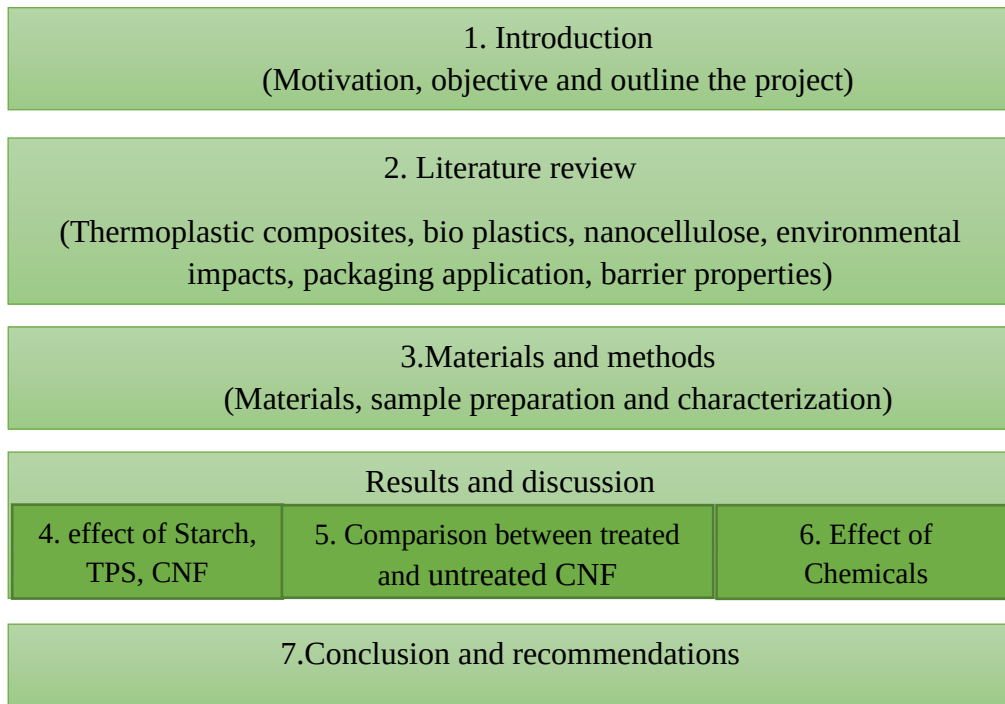


Figure 1.2 Project outline.

1.4. Experimental Plan

Figure 1.3 presents the summary of the experimental plans including materials, processing and characterization procedure.

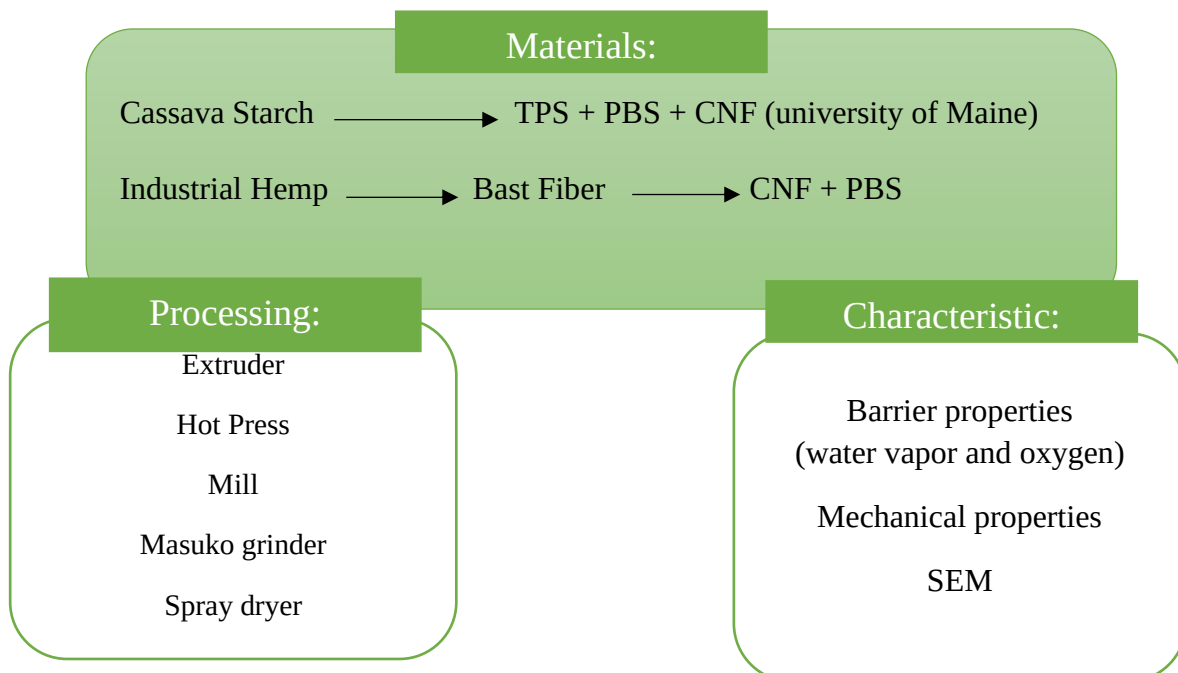


Figure 1.3 Experimental plan.

Chapter 2 Literature Review

2.1. Nanotechnology

Nanotechnology is a complex science which including physics, maths, and chemistry to produce materials with nano dimensions (10^{-9} m) [4]. Briefly, manufacture, characterization, organization, and consumption of nanomaterials for different applications are part of nanotechnology [8]. Nanomaterials, which range in size from 1 to 100 nm, can help increasing the surface to volume ratio. Nanotechnology has lots of application in different fields, such as environment, medical, agriculture and food industry. Incorporating nanocomposites into packaging films can enhance their thermal, mechanical, barrier, and antimicrobial properties [7]. Making a film consisting of nanoparticles can help lower the amount of harmful gases like carbon dioxide (CO_2) and oxygen (O_2) that reduce food's shelf life. It can also act as a barrier film against microbes to prevent food from deteriorating [9]. The application of nanotechnology in the food industry can be divided into two categories, as can be seen in Figure 2.1:

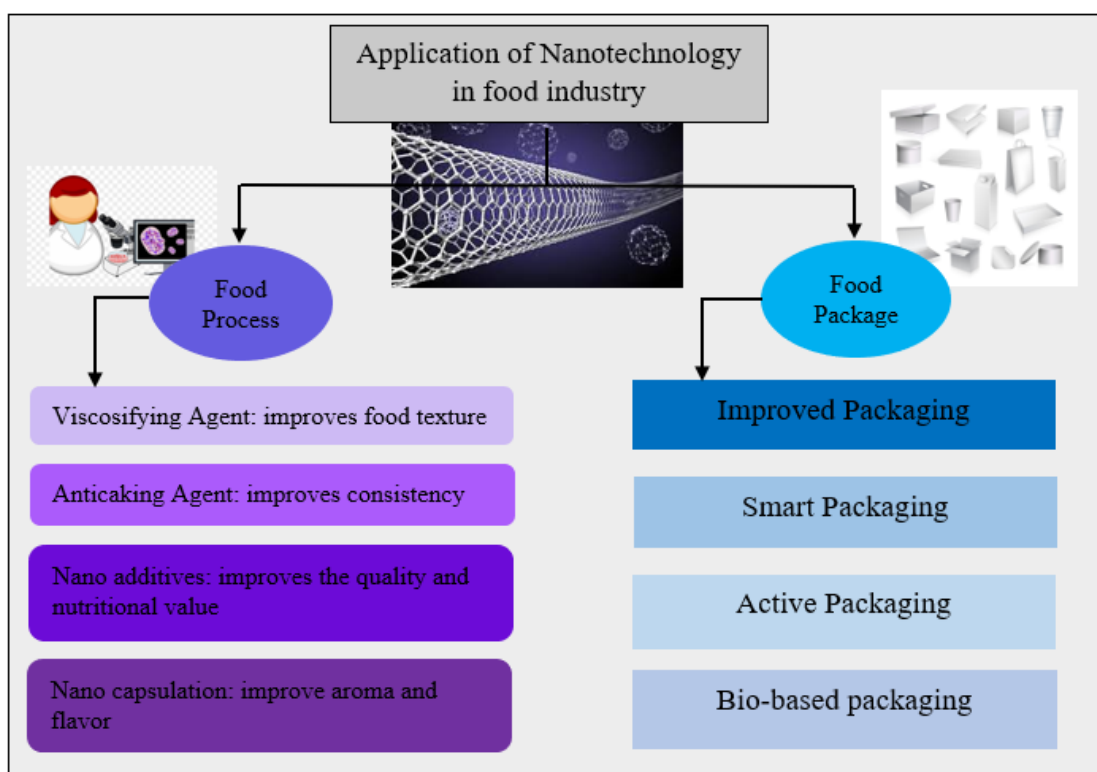


Figure 2.1 Application of nanotechnology in different fields of the food industry [9]; Image by author.

2.2. Food Packaging

Packaging is used to offer hygienic safety and preserve the quality of food for people. It also helps in handling, marketing, storing, and transporting, preserving food, beverages, cosmetics, and healthcare from chemical, biological, and physical damage [10].

Most packaging, almost 85%, is used in food packaging. Since the distant past, glass, aluminum, tin, and petroleum-based plastics have been used. Currently, some polymers have been used in the food industry as gas barrier materials, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) because of their excellent properties like low cost, safety, flexibility, and good mechanical properties. The only problem with them is that these materials are non biodegradable. These types of materials are produced from synthetic polymers, but currently, due to environmental issues, renewable resources are being considered as an alternative. These materials should provide a satisfaction of shelf life, good mechanical properties, sufficient barrier to bacteria, light, water, oxygen, and other contaminants simultaneously to keep food safe [11].

Plastic packaging plays a crucial role in the food, pharmaceutical, and biomedical industries by helping to preserve their products. The effectiveness of plastic packaging is directly related to the barrier properties of the polymer used in the packaging, which determines its ability to prevent the permeation and dissolution of moisture and oxygen gases. To meet the strict protective standards in food packaging, a plastic material must have high barrier attributes if it is to be used as a barrier film, wrap, or coating. While traditional polymers used in food packaging have well-established barrier properties, newer bioplastics often have inferior properties that require further optimization and development. Figure 2.2 provides a summary of the comparison between the packaging requirements and the barrier properties of single-component biodegradable and bio-resourced materials. It includes normal ranges for moisture and oxygen permeability for specific foods that exist in standard packaging [12].

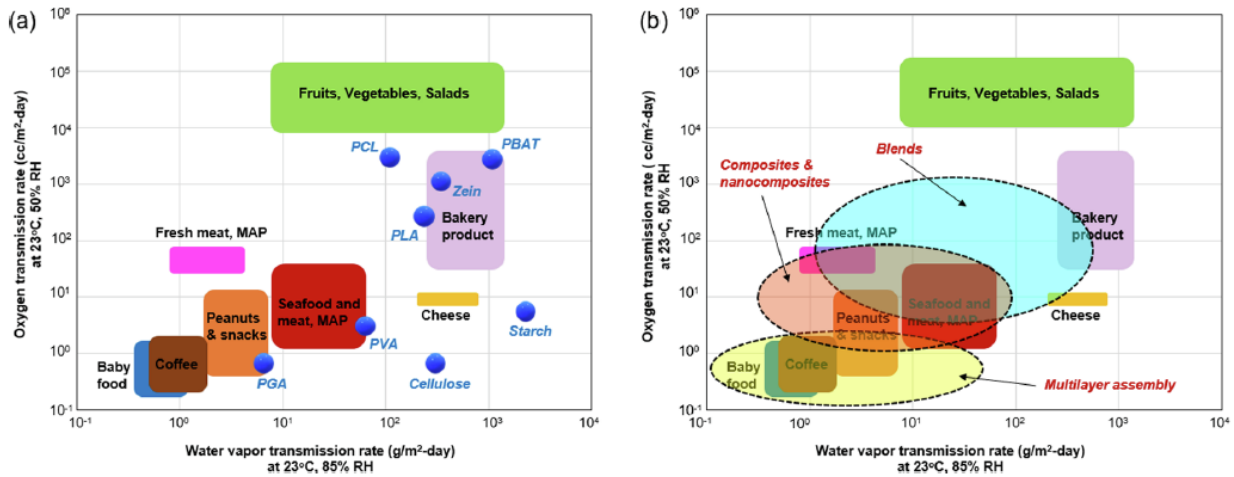


Figure 2.2 the water vapor and oxygen transmission rate for different food packaging a) polymers b) polymer blends, Adapted from [12], .Under the Elsevier and Copyright Clearance Centre.

Packaging can be classified into four categories according to the packaging methods and materials involved: improved, active, smart, and bio-based packaging. Figure 2.3 presents a summary of the four different packaging groups.

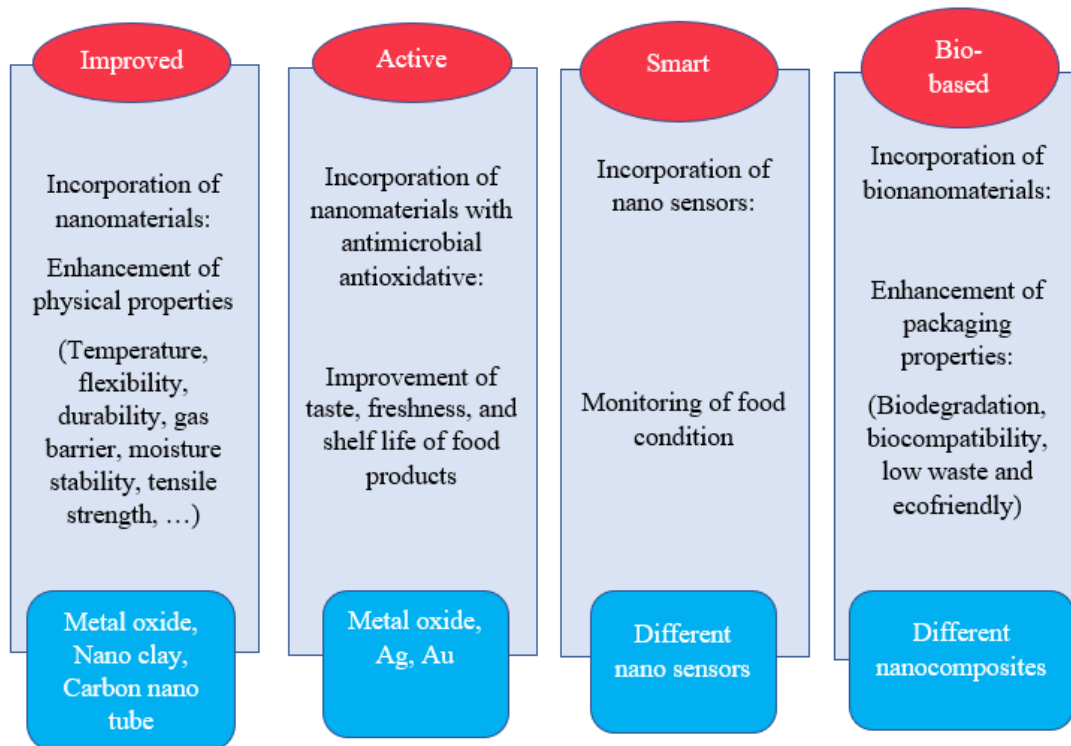


Figure 2.3 Different type of packaging in food industry [9], image by author.

In improved packaging, by incorporating nanomaterials into packaging, the physical and mechanical properties of the polymeric matrix can be improved, such as flexibility, barrier properties, resistance to temperature, humidity, and pH [7], [9].

Active packaging is a type of packaging that incorporates active agents to improve or maintain the quality and safety of the product inside the package. These agents can modify the environment inside the package to enhance or preserve the sensory properties and shelf life of the food. Examples of active agents include antimicrobial agents, oxygen scavengers, UV absorbers, and moisture absorbers. Antimicrobial agents are used to prevent the growth of microorganisms and increase the shelf life of the food, while oxygen scavengers remove oxygen from the package to slow down the oxidation process and preserve the freshness of the food. UV absorbers are used to protect the food from UV radiation, which can cause degradation and discoloration. Moisture absorbers are used to prevent moisture from entering the package and causing spoilage. Overall, active packaging can improve the shelf life and quality of food products by protecting them from spoilage and degradation. [7].

Intelligent or smart packaging is a packaging method that has the capability to sense and adapt to variations in the product's surrounding environment. Using nano sensors, it is feasible to detect and track several variables including moisture, temperature, gas, and nearby atmosphere without any impact on the food inside or its surroundings. The data obtained by these sensors can then be utilized to make alterations in the packaging, such as dispensing antimicrobial substances or adjusting the temperature, to prolong the product's shelf life and uphold its quality. Intelligent packaging has the potential to significantly impact the food industry by decreasing waste and enhancing safety and quality management. [7], [9].

The final group of packaging is bio-based packaging. Bio-based packaging has become a popular choice in the food packaging industry as it offers an alternative to petroleum-based polymers which are non-biodegradable. This category involves using biodegradable and biocompatible materials such as fats, polysaccharides, and proteins. In the coming years, it is expected that the market for bioplastics, such as poly lactic acid (PLA), bio-polyethylene terephthalate (PET), and poly butylene succinate (PBS), will continue to increase and expand. [9].

2.3. Biopolymers

Biopolymers are a type of polymer that can either be derived from renewable resources or non-renewable sources, and may be either biodegradable or non-biodegradable, Figure 2.4 [13].

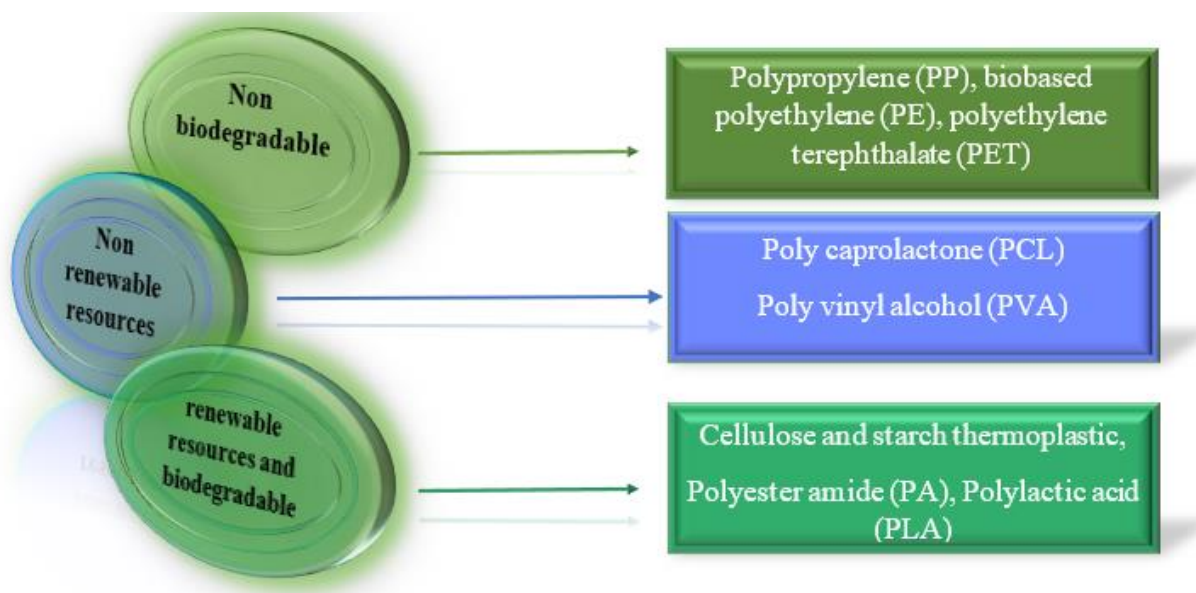


Figure 2.4 Types of biopolymers based on biodegradability [9]; image by author.

Nowadays, renewable biopolymers are at the centre of attention [11]. The use of biopolymers offers several environmental benefits, as they are derived from renewable resources and are biodegradable, thus making them an eco-friendly alternative. Upon disposal, these materials can break down into water, biomass, and CO₂, resulting in minimal harm to the environment. Furthermore, the production of biopolymers requires less energy compared to traditional polymers, as they are derived from renewable sources, thereby contributing to the conservation of non-renewable resources [9]. Biopolymers can be categorized based on their origin, which includes polymers made from biomass, polymers obtained from microorganisms, and polymers produced from bio-monomers or from a combination of biomass and petrochemicals, figure 2.5 [9]. Biopolymers such as starch, chitosan, and cellulose are becoming increasingly popular due to their renewable and cost-effective nature. They can be produced from various sources including agricultural and marine sources [13].

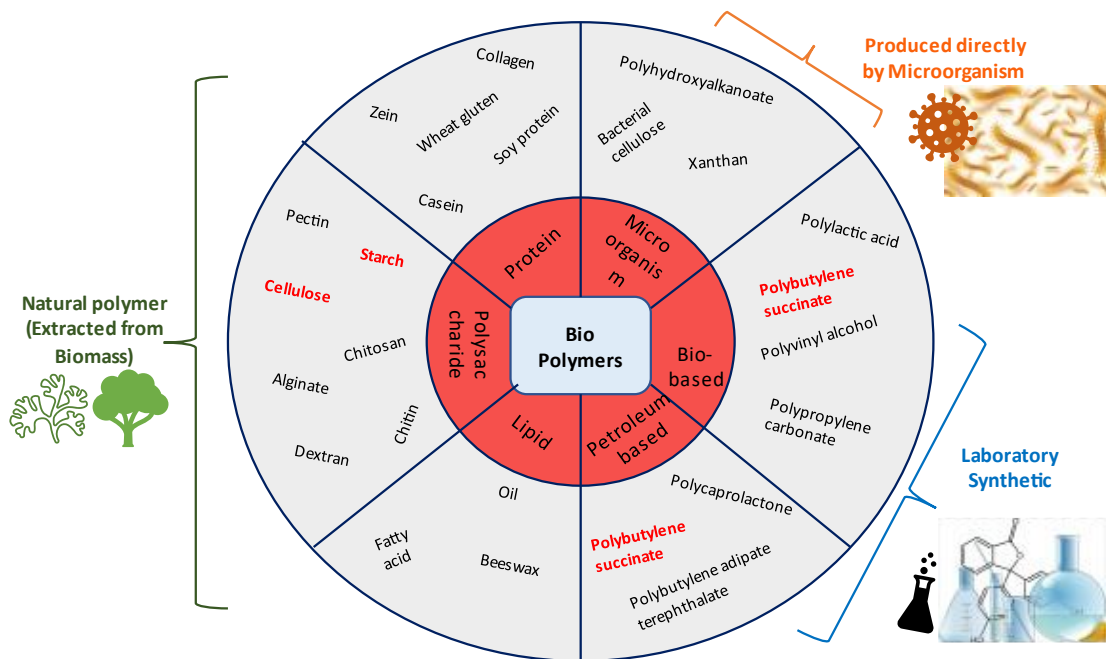


Figure 2.5 The classification of biopolymer [7], [10]; image by author.

Biodegradable plastics are used especially in disposable packaging as an alternative to plastics to decrease the plastic waste pollution [14]. Bioplastics such as poly butylene succinate (PBS), poly lactic acid (PLA), and thermoplastic starch (TPS) have caught much attention. Bioplastics can solve some problems regarding to cost, recycling process, sustainability, and energy consumption. While they have poor stability during processing, mechanical and barrier properties in comparison with synthetic plastics. For improvement in their properties, some methods like adding plasticizer, gamma irradiation, adding nano particles, blending with other biopolymer and chemical modification of polymer have been introduced [15]. To produce bioplastics, biomaterial is used in the form of bio composites [16]. One of the most efficient methods is adding nanomaterials like cellulose nanofibers [15]. In general, the addition of starch and fibers to polyesters such as poly butylene succinate (PBS) is a common practice to reduce the cost of the final product, improve the gas barrier properties, and maintain or enhance its biodegradability [17].

2.4. Starch

Starch is a bio-based polymer that has lots of application in construction, automotive, medical, and packaging. Starch is a large macromolecule consist of glucose monomers with crystalline and amorphous domains that form large starch granules as shown in figure 2.6.

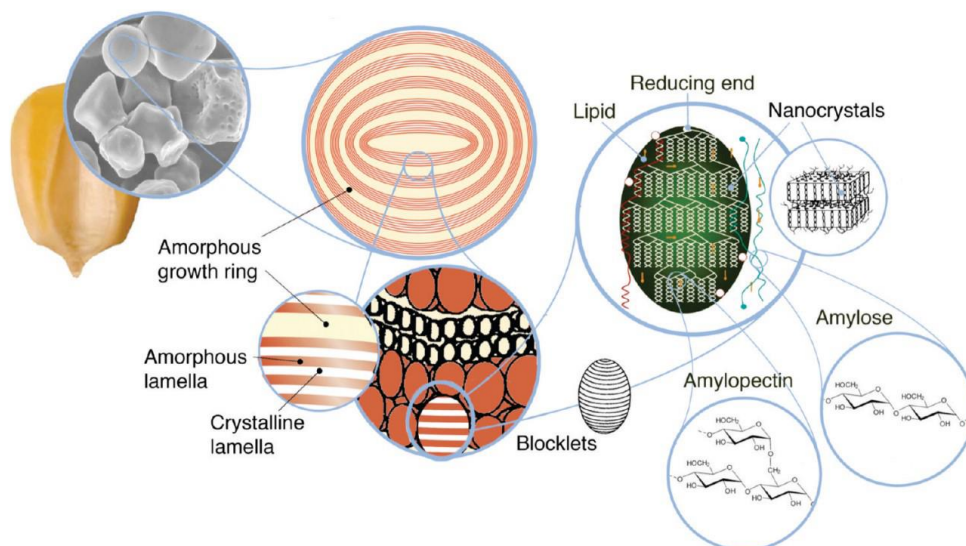


Figure 2.6 Starch structure, Adapted from [18], Under the terms of the Creative Commons Attribution 3.0 License.

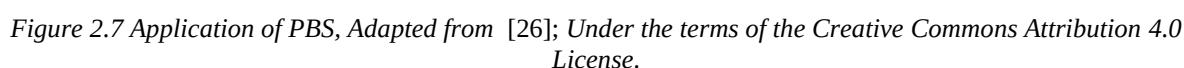
Starch is biodegradable, renewable, affordable, and abundant [16]. Despite the benefits of using starch in biopolymers, its hydrophilic nature and lack of antioxidant ability are drawbacks that need to be addressed. To address these issues, modified starches have been developed, which are considered more environmentally friendly materials. Modified starches are commonly used as stabilizers, viscosifying agents, coatings, and thickeners, and they offer improved properties over unmodified starches [19]. The starch plasticization method involves the use of various techniques such as heat, shear, and plasticizers, including glycerol, sorbitol, water, formamide alcohols, and fatty acids, to improve the processability of starch. This is achieved by breaking the strong inter and intra-molecular hydrogen bonds, resulting in the formation of a material known as Thermoplastic Starch (TPS). The TPS obtained from this process has improved properties such as flexibility, water resistance, and biodegradability, making it an attractive alternative to traditional plastics in various applications [16], [20]. Starch-based bioplastics offer a promising alternative to petroleum-based plastics. However, TPS is vulnerable to moisture, which can result in structural reorientation during storage. This characteristic can lead to a reduction in shelf life, surface stickiness, and undesirable physical properties [14]. Researchers have employed various

methods to improve the mechanical properties and water resistance of TPS, such as modifying the starch structure, blending it with other biodegradable polymers, adding compatibilizers, and reinforcing it with fibers. These approaches have been shown to enhance the overall performance and durability of TPS-based bioplastics [6]. Cassava is the fifth most popular and abundant starch in the world [17]. Blending TPS with synthetic biodegradable polymers is carried out for various reasons, including reducing costs, accelerating the rate of biodegradation, maintaining biocompatibility and renewability, and achieving satisfactory levels of physical and mechanical properties [21]. The mixture of these two types of polymers results in a synergistic effect [20].

At present, it is common to mix starch with PBS to create sustainable film materials that can be used for packaging and flushable hygiene products, which results in cost savings and improved biodegradability. However, blending TPS and PBS can be challenging due to their different viscosity and interfacial tension, which causes them to be immiscible. Several methods have been developed and studied to improve the compatibility between TPS and polyester mixtures, including carboxylic acid-based systems, maleic anhydride-based systems, glycidyl methacrylate-based systems, and binary/ternary blend formulations. Carboxylic acid-based systems use carboxylic acids to create a bond between TPS and polyester, while maleic anhydride and glycidyl methacrylate-based systems form graft copolymers between the two materials. Binary/ternary blend formulations involve the addition of other polymers or additives to improve interfacial adhesion. The choice of strategy depends on the specific application and desired properties of the final product [21].

For example, Yin et al. [20] utilized maleic anhydride grafted PBS (MA-g-PBS) as an interfacial compatibilizing agent to produce biodegradable blends of TPS/PBS. Although the mechanical properties of TPS-rich blends were not notably affected by the compatibilization, the addition of the compatibilizer improved the tensile strength, elongation at break, adhesion, and even dispersion of starch particles in the blend. Furthermore, incorporating hydrophobic PBS reduced water absorption and sensitivity, making the blends more water-resistant. The authors concluded that the resulting TPS/PBS blends with MA-g-PBS had the potential to be utilized as packaging materials due to their biodegradability, high strength, and water resistance [22].

Succinic acid and butanediol are polycondensed to form the polymer known as polybutylene succinate (PBS). PBS has several advantageous properties, including high toughness, high heat distortion temperature, melt processability, and biodegradability [23]. Polybutylene succinate (PBS) can undergo biodegradation and be effectively disposed of in diverse environments, including compost, moist soil, fresh water (with the assistance of activated sludge), or seawater. When exposed to aerobic conditions, microorganisms can compost PBS into carbon dioxide (CO_2), water (H_2O), and inorganic products, whereas under anaerobic conditions, it can be converted into methane (CH_4) and carbon dioxide. The biodegradability of PBS is chiefly determined by its chemical structure, specifically the hydrolysable ester bond in the main chain, which is susceptible to breakdown by microbial activity. [24]. PBS possesses high thermal stability, flexibility, and a low glass transition temperature (T_g), making it home compostable. Additionally, it has a high degree of crystallinity ranging from 40-60% [14]. Its biodegradability and combustibility, along with its non-toxic by products during incineration, make it an attractive and eco-friendly option. PBS shares similarities with polyethylene, such as ductility, elongation, and low melting point, making it compatible with conventional processing techniques. However, the high cost of production and the need for enhancement in mechanical properties and melt viscosity are limiting factors for its widespread use [25]. It is common to mix PBS with other biopolymers, such as cellulose, starch, soy protein, and other plant fibers, to reduce costs and improve its applications. Blending PBS with natural polymers does not have a negative effect on biodegradability and can help enhance overall mechanical and water barrier properties [26].



2.6. Cellulose

Cellulose is a linear, homopolymer polysaccharide composed of repeating β -D-glucopyranose units connected by β -(1-4) glycosidic bonds. It is the primary structural component of plant cell walls and is also found in microorganisms such as bacteria, algae, and fungi. Cellulose is the most abundant and sustainable natural polymer (figure 2.8) [27].

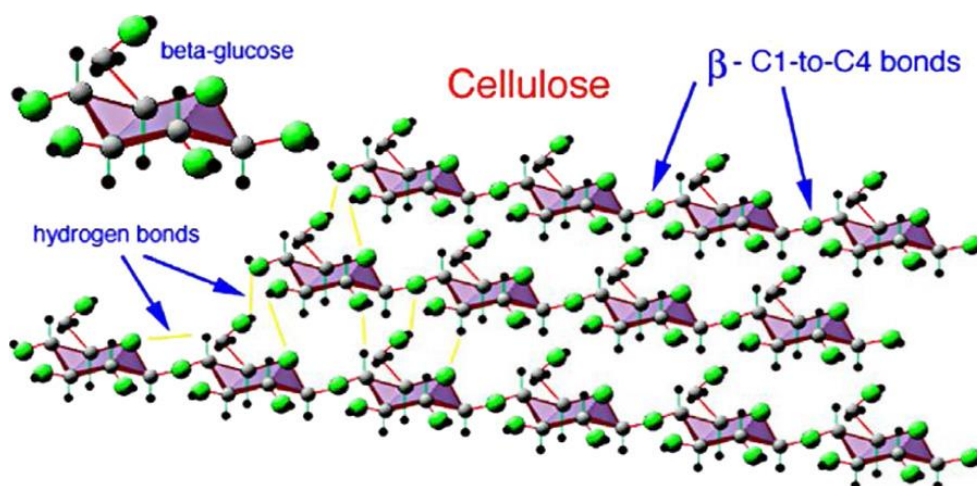


Figure 2.8 Cellulose structure, Adapted from [28], Under the Elsevier and Copyright Clearance Center.

Cellulose has many properties like non-toxicity, inexpensive, excellent mechanical properties, low density, and flexibility [29]. Nanocellulose is a type of cellulose with a one-dimensional scale ranging from 1 to 100 nanometers. It shares the fundamental characteristics of cellulose, such as renewability, biodegradability, and ease of chemical modification. Additionally, it exhibits unique nanoscale properties, including high tensile strength and elastic modulus, high specific surface area, and low density [30]. The use of cellulose-based materials in the packaging industry is widespread, with applications ranging from wrapping materials and containers to flexible and rigid packaging for both primary and secondary packages. The advantages of using cellulose in packaging include its low cost, sustainability, and lightweight properties. However, these materials have some limitations, such as a low barrier ability against water, water vapor, oxygen, and oil, which must be addressed through improvement measures [31].

Cellulose is produced from different wood and non-wood sources, bacteria, algae, fungi, marine animals, and invertebrates. Apart from woody sources, non-wood fibers like bagasse and bamboo, agricultural straws and bast fibers like jute, hemp, flax, and ramie are gaining much

attention these days, because they are abundant, affordable, and containing less lignin. So, the extraction process is easy and consume less energy [32], [33].

Hemp fiber is one of the most sustainable sources among others. Industrial hemp, a non-psychoactive type of *Cannabis sativa* L., is widely used to produce industrial products. Hemp consists of two main parts, the inner core of woody component known as hurd or shive, and the outer layer containing fiber bunches, referred to as bast. Hurd fibers account for almost 70% of the total hemp and are commonly used as animal bedding due to their high absorption capability. On the other hand, bast fibers are utilized for making canvas, rope, netting, and bio composites [32].

Nanocellulose presents a promising potential for substituting plastics as a barrier for humidity, grease, and oxygen [13]. Nanocellulose has used in lots of applications such as paints and coatings [34], biomedical materials [28], electronic devices [35], sensors [36], and energy storage materials [37].



Figure 2.9 Applications of nanocellulose [27], image by author.

2.6.1. Plant Cell Wall

Cellulose fibers consist of individual fibers that are connected by a middle lamella, which is mainly composed of lignin (90%, w/w) and does not contain cellulose. The cell wall of cellulose fibers consists of a primary and secondary wall. The primary cell wall comprises 9-25% cellulose microfibrils, 25-50% hemicellulose, and 10-35% pectin. The secondary wall is made up of three layers, designated as S₁, S₂, and S₃ [6][33]. However, the secondary wall has a higher proportion of cellulose, ranging from 40-80%, along with 10-40% hemicellulose and 5-25% lignin. Notably, the highest concentration of cellulose is found in the S₂ layer of the secondary cell wall [33].

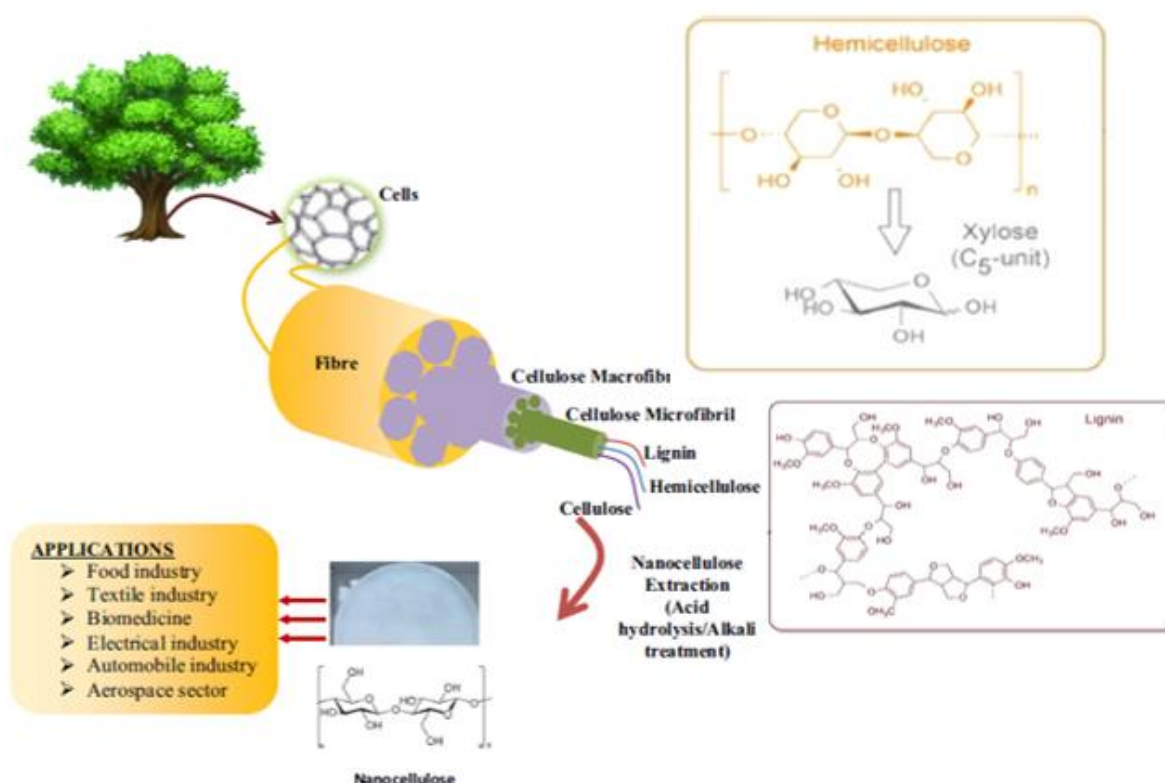


Figure 2.10 Plant cell wall structure, Adapted from [28], [38], Under the Springer Nature and Elsevier and Copyright Clearance Center.

Lignocellulosic biomass is a complex structure, as illustrated in Figure 2.10, which consists of various components such as cellulose, hemicellulose, lignin, ash, and other extractives. The proportions of these components vary depending on the source of the biomass [4].

Lignin is a three-dimensional polymer comprised of propyl-phenol groups linked by C-C bonds and ether groups. Its main function is to protect cellulose from biological degradation by acting as an adhesive and stiffening agent for the cellulose fibers [4].

Hemicellulose is a low molecular weight, heterogeneous, and amorphous polysaccharide composed of xyloglucans, xylenes, mannans, and glucomannans. It acts as a compatibilizing agent, forming an interface between the hydrophobic lignin and hydrophilic cellulose. In general, lignin and hemicellulose make up 15-25% and 20-30 wt.% respectively of the total composition of cellulose [4].

2.6.2. Cellulose from Hemp

Industrial hemp is a type of *Cannabis sativa* that is cultivated for its fiber, seeds, and other non-psychoactive derivatives. Unlike marijuana, it contains very little Tetrahydrocannabinol (THC), which is the compound that produces the high associated with marijuana use. Industrial hemp is utilized for various purposes such as producing textiles, paper, plastics, fuel, food, and supplements, unlike its counterpart marijuana which is used primarily for recreational or medicinal purposes. The cultivation of industrial hemp is permitted in numerous countries, but it is also subject to regulations and limitations [39]. About 76% of the hemp's bast fibers are composed of cellulose, 14% of them of hemicellulose, 5% of lignin, 1% of pectin, and 6% of other components. As their popularity grows, these natural fibers offer a viable alternative to synthetic fibers [40]. Cellulose nanofibers have a promising future in various fields, including composites, coatings, and packaging, and can be obtained from hemp, a plant with robust and lengthy fibers that can be chemically and mechanically processed to obtain nanofibers. This project will examine the process of creating cellulose nanofibers from hemp, utilizing mechanical and chemical treatments.

There are two main ways of producing cellulose nanofibers from hemp: mechanical and chemical processing. In mechanical processing, high shear forces like grinding or high-pressure homogenization are used to break down the hemp fibers into smaller fragments until nanofibers are produced. Chemical processing, on the other hand, involves treating the hemp fibers with chemicals such as sodium hydroxide or hydrogen peroxide to eliminate impurities and break down the fibers into nanofibers [41].

A popular mechanical processing method for producing cellulose nanofibers is refining, where a Masuko grinder can be used. This type of high-speed mill uses centrifugal force to break down the fibers by rapidly rotating them and impacting them with a series of blades or pins. This energy-intensive process reduces the fibers into smaller fragments, including nanofibers.

The use of hemp fiber as a source of cellulose nanofibers has both advantages and disadvantages. One of the benefits of hemp is its strength, durability, and availability. Additionally, hemp is

considered a sustainable option as it requires less water and fertilizer compared to other crops. However, impurities such as lignin and hemicellulose can be present in hemp fibers, affecting the quality and purity of the resulting nanofibers. Furthermore, regulations and competition with other uses of hemp can present challenges to its use in nanofiber production [42].

2.6.3. Classification, Preparation, and Performance of Nanocellulose

In different types of food packaging like dry, frozen, and liquid or even some kind of fresh foods, cellulosic fibers have been used as a paper or cupboard [11]. In general, nanocellulose can be divided in three types in terms of their morphology, size, sources, and preparation techniques:

- 1- Cellulose nanocrystals (CNCs), also known as cellulose nano whiskers (CNWs) or nanocrystalline cellulose, are rod-shaped particles with a rigid structure, having a diameter of 10-30 nm and a length of 500 nm. [27]. CNCs are produced by hydrolyzing cellulose with a strong inorganic acid or enzyme. During this process, the amorphous region of cellulose is broken down into sugars, leaving behind the crystalline portion in the form of rigid rod-like particles resembling whiskers [43]. CNCs that exhibit a high degree of crystallinity and thermal stability are well-suited for use as nanofillers to reinforce nanocomposites [27].
- 2- Cellulose nanofibrils (CNFs), also known as nano fibrillated cellulose (NFCs) or microfibrillated cellulose (MFC), are composed of both elementary fibers and aggregated fibrils. The elementary fibril has a diameter of 3-5 nm and length of 500-1000 nm, while the diameter of the aggregated part is 20-50 nm. Residual biomass can be utilized to produce CNFs through mechanical treatment, chemical and mechanical treatment, or enzymatic processes. CNFs are a promising type of cellulose material with excellent mechanical and barrier properties that are desirable for packaging applications [44]. The biodegradable and renewable nature of CNF, along with its unique characteristics, has garnered significant attention as a sustainable substitute in coatings, films, composites, and packaging materials. Its large specific surface area, resulting from its small width and high aspect ratio, makes it an interesting material for these applications [45]. There are both crystalline and amorphous region in CNF [27]. MFC-based films have a disadvantage of poor water barrier properties as they are produced from purified cellulose fibers with lower lignin content, which makes them more hydrophilic [11].
- 3- Bacterial cellulose (BC) is produced by *Acetobacter* with biotechnological process using low molecular weight carbon sources. It is kind of cellulose with high degree of

crystallization without lignin and hemicellulose. The diameter of this kind of cellulose is in the range of 20-100 nm and a length of several microns [46].

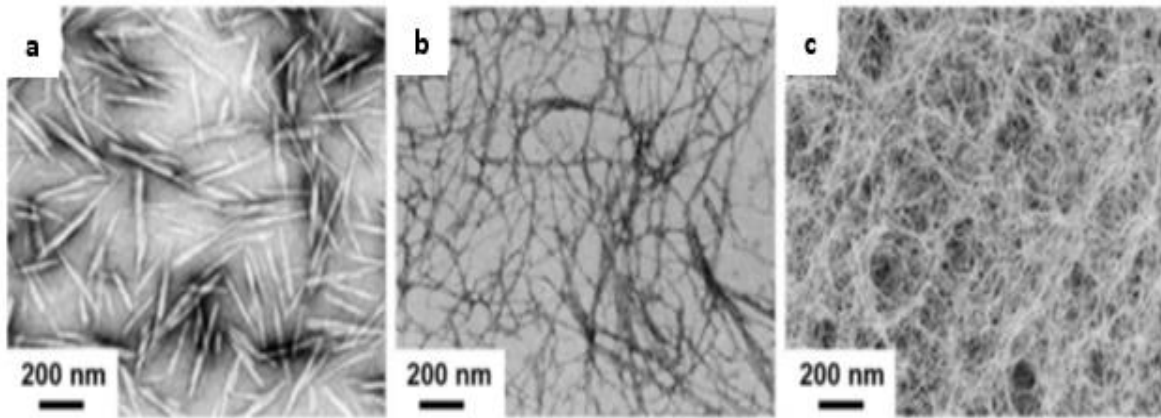


Figure 2.11 (a)TEM image of CNCs, (b)TEM image of CNFs, (c) SEM image of BC, Adapted from [27], Under the Springer Nature.

2.6.4. Production of Nanocellulose Fiber

The process of isolating nanocellulose from biomass involves two main steps: first, cellulose is obtained by breaking down the lignocellulosic materials, and second, the cellulose is treated to obtain nanocellulose [13]. Acid hydrolysis and mechanical processes are currently the most widely used methods for producing nanocellulose [2].

Some reasons for pre-treatments:

- Removing hemicellulose and lignin
- Increasing the efficiency
- Making purified nanocellulose
- Changing the hydrophilic surface to hydrophobic
- Decreasing the size to prevent agglomerate
- Reducing the energy that need for mechanical extraction

Cellulosic materials require some form of pre-treatment before mechanical treatment to make fibrillation easier. The chemical procedure consists of using alkali to remove lignin and dissolving the cellulosic material with acetic acid, aqueous methanol, ethanol, acid hydrolysis, or ionic liquids can be used to alter the cellulose structure and increase the surface area, which leads to better fibrillation [41]. The chemical process also involves bleaching colored materials through oxidation with hydrogen peroxide (H_2O_2) or sodium hypochlorite (NaOCl). Enzymatic

pre-treatment can also be used to break down hemicellulose and lignin, which can make the cellulose more accessible for mechanical fibrillation. These pre-treatments are necessary to facilitate the mechanical defibrillation process and obtain high-quality nanocellulose materials [47]. Enzymatic treatments are typically expensive and time consuming.

There are some mechanical methods for producing nanocellulose from cellulosic fibers. A brief overview of each:

- Homogenizing: involves passing the cellulose fibers through a narrow gap, which results in shear forces that defibrillate the fibers into smaller sizes.
- Micro fluidization: uses high-pressure fluid streams to defibrillate the cellulose fibers, resulting in smaller particle sizes.
- Grinding: involves using mechanical force to break down the cellulose fibers into smaller particles.
- Cryocrushing: uses liquid nitrogen to freeze the cellulose fibers, followed by crushing them into smaller particles.
- High-intensity ultrasonication: uses high-frequency sound waves to break down the cellulose fibers into smaller sizes.

Each method has its own set of benefits and drawbacks regarding energy consumption, yield, and the quality of nanocellulose produced [33].

Tyagi et al. [32] developed a sustainable and environmentally friendly alternative to synthetic polymer-based barrier coatings and films, by using a waste product of the hemp industry to produce high-performance material. First, the hemp hurd was subjected to a hydrothermal treatment, which involved heating it in water under high pressure. This treatment caused the lignin and hemicellulose in the hemp hurd to break down, leaving behind cellulose nanofibers. The researchers then used mechanical methods to further break down the cellulose nanofibers into smaller fibers. A high shear mixer was used to mechanically treat the hydrothermally treated hemp. This process helped to separate the cellulose fibers and create a uniform dispersion of the nanofibers. Once the nanofibers were prepared, they were used to produce barrier coatings and films. The researchers found that the resulting coatings and films had excellent barrier properties against gases and liquids.

2.6.5. Produce Cellulose Nanofiber with Masuko

Grinding is a supplementary approach employed to convert cellulose into fibers on the nanoscale level. The procedure entails the passage of pulp through two stones where one stone remains stationary while the other rotates, thereby exerting shear forces that break down the hydrogen bonds and cell wall structure of the fibers and convert the pulp into nanoscale fibers. Friction generated by the stones produces heat during the fibrillation process, resulting in the evaporation of water content and an increase in solid content. The characterization of the resulting CNF is influenced by the number of cycles used in the grinding process. To create CNF of uniform size, grinding typically requires ten cycles [33].

2.6.6. Nanocellulose Properties

Reducing the dimensions of cellulose from micro to nano scale is expected to lead to changes in several properties. Some of the most significant properties that are affected include:

Specific Surface Area:

The reduction in particle size leads to an increase in specific surface area, which is the surface area per unit mass. Cellulose nanoparticles have a high specific surface area, ranging from greater than 100 m²/g to several hundreds of m²/g. This increased surface area facilitates hydrogen bonding between the filler and polymer matrix, promoting greater surface reactivity and chain mobility of the polymer. As a result, the properties of nanocomposites are improved. However, due to their high surface area, these nanoparticles tend to aggregate, resulting in poor properties of the final products. [13]. But it depends on the desired properties. The large specific surface area helps to form inter and intra molecular hydrogen bond then they make a strong network, so water and oxygen cannot pass through easily [3].

Aspect Ratio:

The aspect ratio, defined as the ratio of length to width, is a critical parameter for nanocellulose. Nanocomposites with higher aspect ratios can exhibit improved properties due to the percolation behavior of their nanostructure [13].

Morphology:

The physical dimensions and shapes of nanoparticles play a significant role in determining the properties of nanomaterials. The characteristics of nanocellulose, such as its dimensions and crystallinity, vary depending on the source material used to produce it. Therefore, selecting the most suitable nanocellulose sample based on cost, application, and availability requires an understanding of the distribution of these characteristics. For instance, tunicate, ramie, algae,

banana, coconut husk, and bacterial cellulose nanocrystals have a higher aspect ratio compared to others, which may explain their exceptional mechanical properties. Conversely, microfibrillated cellulose, which is limited by mechanical treatment, has larger diameters [13].

Table 2.1 Morphological properties of nanocellulose [10]

Type	Extraction method	Length (nm)	Width (nm)	Crystallinity (%)
Banana	Fermentation	>1000	50	71
Cassava	Sulfuric acid	1150	15	54.1
Hemp	Hydrochloric acid	148 ± 3	5.8 ± 0.1	73
Softwood	Sulfuric acid	2500	25	-
Kenaf Bast	Sulfuric acid	100- 20	10- 20	75- 82
Bacterial Cellulose	Hydrochloric acid	88 ± 5	6.5 ± 0.2	70

Mechanical Properties:

The mechanical properties of fillers are essential in determining the overall properties of composites. Nanocellulose, for instance, relies on its crystalline portion to provide high stiffness and strength to the polymer matrix. As each type of nanocellulose has a unique level of crystallinity, the mechanical properties of each type will also vary [13]. Cellulose Nano Fiber (CNF) reinforced composites are recognized for their exceptional mechanical properties when compared to other natural fiber additives. The performance of the composite is heavily reliant on the uniform distribution of the fibers within the polymer and the interfacial interaction between them. CNFs possess key attributes that make them an effective reinforcing agent, including high specific rigidity and aspect ratio. These properties facilitate the efficient transfer of loads from the continuous polymer phase to the discontinuous fiber phase [48].

Thermal Properties:

Cellulose-based materials exhibit high thermal stability due to the strong intermolecular hydrogen bonding between cellulose chains. Cellulose with a high degree of crystallinity is particularly resistant to thermal degradation because of the robust and stable structure of its hydrogen bonding network, which is difficult to disrupt even at elevated temperatures. As a result, cellulose-based materials are often preferred for applications that require high thermal resistance [13].

Beside of the good properties mentioned before about nanocellulose, using cellulose in some applications is still restricted due to the poor barrier, mechanical properties, and water absorption ability. A solution for this problem is using cellulose as nanofiller in the composite material or blend it with other biopolymers [13].

2.6.7. Barrier Properties of Nanocellulose Film

To comprehend the function of nanocellulose in packaging, it is important to understand how molecules diffuse through the material. The diffusion of molecules between two adjacent areas separated by a thin film of solid polymer or membrane involves three stages. The first stage involves the diffusing molecule adhering to the surface of the sample, followed by the molecule moving through the film or membrane in the second stage. The final stage involves the molecule being released from the film or membrane surface on the other side. Generally, it is assumed that the absorption and release stages occur rapidly compared to the diffusion through the film. The three-stage process implies that the permeability of gas molecules through a film will be determined by the rate of gas dissolution and diffusion in the film [49]. The permeability of gas molecules in different types of materials, such as thin films, can be expressed using the following formula:

$$P = D \times S$$

The permeability coefficient (P) is determined by the diffusion coefficient (D) and the solubility coefficient (S).

The formula for calculating the permeability coefficient is derived from applying Henry's law of solubility to Fick's law of diffusion, so the above equation converts to this:

$$P = D \times S = \frac{q \times L}{A \times t \times \Delta P}$$

The amount of material that passes through the film is represented by "q". The flow length or thickness is represented by "L", while the cross-sectional area is represented by "A". Time is represented by "t", and the pressure difference between the two sides of the film is represented by " Δp " [31].

Before the process of diffusion can occur, gas molecules must be dissolved within the membrane or film. While the impact of the film surface on the permeation of gas molecules is commonly recognized, the rate of molecule diffusion within the membrane or film is the most significant factor in molecular migration, which is also referred to as bulk flow. Bulk flow describes the

movement of molecules from high to low concentration areas. The dense network structure formed by nanofibrils in nanocellulose provides strong barrier properties against oxygen [49]. The high density of nanocrystalline cellulose is attributed to the small and uniform particle sizes, while the flexible nature of wet material enhances the densification of nano fibrillated cellulose. Despite the presence of pores within the films, oxygen molecules can permeate through them. NFC can create a denser film due to its inherent flexibility, effectively sealing most of the spaces between the fibrils, even down to a molecular scale. On the other hand, CNC particles are rigid, resulting in a lower density of packing and higher porosity in a film composed solely of CNC. The barrier properties of NFC films are superior to those of CNC films. Both NFC and CNC exhibit similar solubility. However, NFC films have a more organized and entangled structure, which creates a denser and tortuous diffusion path that hinders oxygen molecules from passing through, resulting in slower penetration [31], [49].

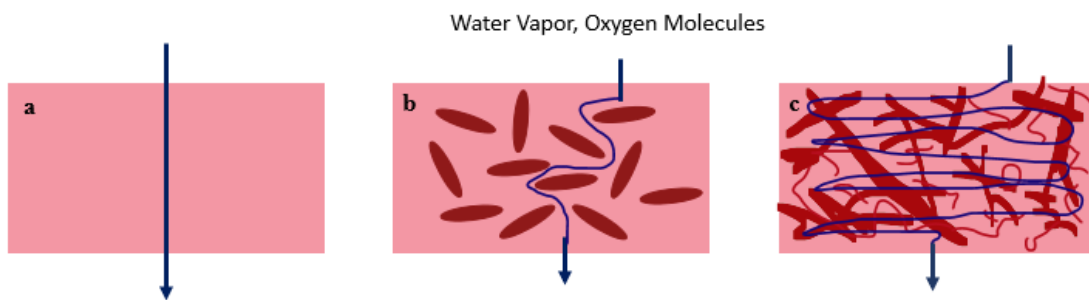


Figure 2.12 Schematic representation of increased diffusion path in the film a) without nano, b) with CNC, c) with CNF [50]; image by author.

When nanocellulose is utilized as a reinforcing material in a polymer matrix, its effect on gas permeability may differ from its use in a film. Further research is necessary to determine the extent to which the tortuosity of nanocellulose-containing polymer films can reduce permeability. The amount of nanocellulose added to the polymer matrix is typically low, ranging from 0.5-20%. Previous research has suggested that the addition of nanocellulose to the polymer matrix can improve film uniformity, toughness, and reduce defects, which may contribute to reduced permeability. However, due to the fibrillar or columnar shape of nanocellulose, it is not expected to effectively block diffusion paths when present in low concentrations in a polymer matrix [31].

In summary, nanocellulose exhibits high oxygen barrier properties but low water vapor barrier properties due to the affinity of water for nanocellulose fibrils. However, nanocellulose fibrils have a stronger impact on reducing water vapor barrier compared to cellulose fibers due to their size and swelling limitations. Under high humidity conditions, the barrier properties for both oxygen and water vapor can be compromised as the structure of nanocellulose fibrils may be damaged by excessive swelling [31], [49].

In contrast to its high oxygen barrier properties, unmodified nanocellulose has lower water vapor barrier properties due to its high hydrophilicity. However, the density of the film can also play a role, and nanocellulose films tend to have higher density, resulting in less water penetration. The presence of lignin in cellulosic sources can affect the properties of nanocellulose films. While delignification is typically required, it is possible to skip this step using mechanical shearing. However, the presence of lignin can make films more hydrophobic, resulting in higher water contact angles but lower water vapor barrier properties. This is because lignin can hinder the formation of hydrogen bonds, creating more hydrophobic pores that allow for easier water vapor transmission. Further research is needed to fully understand the impact of lignin on nanocellulose film properties [31].

2.6.8. Different Ways of Drying Cellulose Nanofiber

The dewatering and drying process presents a significant challenge to the commercialization of nanocellulose. This process is necessary for the efficient transportation of nanocellulose to manufacturing facilities and its blending in nonpolar mediums. However, producing dried nanocellulose materials that retain their nanoscale properties and can be fully redispersed is difficult. CNCs and CNFs, with their high surface area and hydrophilic nature, present similar challenges in dewatering, drying, and redispersion. Conventional drying methods can cause irreversible particle agglomeration, and fibril surfaces may lose their desired properties. Therefore, effective processes for concentrating and drying nanocellulose are necessary to meet the demands of end-use applications. Dewatering nanocellulose involves removing free water from the suspension, and drying refers to removing all water to obtain fully dried materials [51][52].

Nanocellulose suspensions are known to exhibit high viscosity at approximately 3% (CNF) and 10% (CNC) solid concentrations, which poses challenges for both pumping and dewatering. Various strategies have been proposed for dewatering nanocellulose, including centrifugation, filtration, shear stress-assisted dewatering, pressing, and solvent evaporation [53].

After completing the dewatering process, the next crucial step is to fully dry the nanocellulose material. Various drying technologies are utilized for nanocellulose suspensions, such as oven drying, spray-drying, freeze-drying, and supercritical CO₂ drying. Sometimes, these techniques are combined, for example, spray freeze-drying and supercritical CO₂ spray-drying. Among these techniques, freeze-drying and spray-drying are the most used for larger-scale production as they prevent reaggregation and enable easy redispersion of nanocellulose solids in aqueous suspensions. However, freeze-drying is a time-consuming and energy-intensive process, and supercritical drying requires high installation and maintenance costs. Oven drying is the quickest and most cost-effective method, but it tends to produce aggregated masses of material that are difficult to redisperse in aqueous media or polymer matrices. [53]. You can see the summary of these methods in table 2-2.

Table 2.2 Advantages and disadvantages of drying methods

Method	Advantage	Disadvantage	Application
Oven Drying	-Quick process -Most economical method -Good production scalability	-Agglomeration -Loss of the nanoscale -Poorly dispersible	Reinforcement filler
Spray Drying	-Low cost -Short time -Re-dispersible -Large scale production	-May form clusters -Micro-nanosized particles -High maintenance costs - for some material clogging happens	Reinforcement filler
Freeze Drying	-Large scale production -Stable process -preventing aggregation -Porous structure - Re-dispersible	-Slow process -High energy consumption -Unfrozen water desorption process influences the dried product	Laboratory research Reinforcement filler
Supercritical CO₂	-Low surface tension -Used mainly for drying CNF -Good efficient drying -Excellent mechanical properties	-Hight equipment cost -Complex process -not used for CNC -Solvent exchange is needed	Water oil separation Biomedical application Foam and aerogel

2.6.8.1. Oven Drying

Oven drying is a widely used method to eliminate water from nanocellulose suspensions or gels. The effectiveness of drying is dependent on various factors such as temperature, airflow, agitation, and surface area. During the process, the nanocellulose fibrils are mobile within the suspension or gel and can diffuse and reconfigure into lower-energy arrangements. The drying process has three stages: the constant rate-drying period, the first falling rate-drying period, and the second falling rate-drying period. However, oven drying frequently results in nanocellulose films that are challenging to disperse in water or other solvents, which makes them less ideal for applications that require nanoscale properties. To enhance the dispersibility of dried nanocellulose materials, additives or pretreatments can be utilized alongside oven drying [54].

2.6.8.2. Spray Drying

Spray drying is a commonly used technique for producing powders from liquid or semi-solid materials. In this process, a liquid or semi-solid feed is atomized into small droplets, which are then dried rapidly by contact with hot air. The resulting dried particles are typically spherical in shape and have a narrow size distribution. The mechanism of spray drying involves several stages, including atomization, evaporation, and particle formation. In the atomization stage, the feed is broken up into small droplets by a nozzle or other atomization device. In the evaporation stage, the droplets are exposed to hot air, causing the water or solvent to evaporate, and leaving behind solid particles. In the particle formation stage, the solid particles agglomerate and form spherical particles as they travel through the drying chamber. The resulting powders can have a wide range of properties and applications, depending on the feed material and process conditions [53], [55].

Zimmermann et al. [56] studying the drying process of CNCs verified that the drying process using spray drying was similar to the process using oven, resulting in the formation of spherical particles with rough surfaces. However, for CNFs, two different types of droplets were observed based on the length of the fibrils. The first type of droplets had CNF fibrils with no protrusions, while the second type had partially protruding fibrils.

Furtado et al. [57] examined the properties of CNF particles that had been produced using a spray-drying technique. They found that the spray-drying process resulted in spherical CNF particles with a smooth surface, and that these particles had a size range of 100-500 nm. They found that the reconstituted CNF suspension showed good stability and exhibited pseudoplastic behavior, which means that the viscosity of the suspension decreased with increasing shear rate.

Spray-drying is a faster and more efficient drying method compared to direct evaporation and can be scaled up for industrial use. However, spray-drying can lead to the formation of agglomerates of nanocellulose fibrils that may not disperse easily, resulting in the loss of nanoscale properties. Moreover, the high viscosity of nanocellulose solutions at higher concentrations necessitates low solids concentrations during spray-drying, leading to high energy consumption, production costs, and greenhouse gas emissions. Therefore, if small nanocellulose agglomerates are acceptable for a specific application, then spray-drying may suffice. But if redispersion of nanocellulose in water is required, then an additive will be needed to prevent strong hydrogen bonding between different fibrils [53].

Fairman [58], discussed the challenge of preventing the aggregation of nanocellulose during the drying and rehydration process, which can impact its properties and potential applications. Different strategies were explored to prevent aggregation, including the use of surfactants and salt solutions, as well as varying the drying and rehydration conditions. Addition of the positively charged cetyltrimethylammonium bromide (CTAB) surfactant aided in the redispersion of the nanocellulose. When the nanocellulose was subsequently dried, CTAB was also effective in creating particle size distributions that were comparable to, but not quite as small as, those of the initial suspension. The research also examined the influence of varying mixing energies and revealed that low concentrations of CTAB brought about a significant enhancement, although this effect was reduced at high concentrations of CTAB.

In another study, Yang [59] investigated the impact of using two different salts, sodium chloride (NaCl) and potassium chloride (KCl), on the spray drying and redispersion of cellulose nanofibers suspension. The results suggest that both NaCl and KCl can improve the spray drying process and the redispersion of cellulose nanofibers after drying. However, the study found that KCl was more effective than NaCl at reducing particle

aggregation and improving the stability of the cellulose nanofiber suspension during spray drying.

Beck et al. [60], created a dry form of nanocrystalline cellulose (M-NCC), such as a solid film, with controlled water dispersibility. Once fully dried, nanocrystalline cellulose suspensions produced by sulfuric acid hydrolysis are not soluble or dispersible in water or other aqueous solvents. When the positively charged hydrogen ions in the dried nanocrystalline cellulose are replaced with positively charged monovalent ions, the resulting M-NCC form can disperse in water without requiring sonication treatment. So, for this study they tried some salts like sodium chloride, potassium chloride, and calcium chloride.

2.6.8.3. Freeze Drying

Freeze-drying, also known as lyophilization, is a commonly utilized technique for drying food and pharmaceuticals. To dry nanocellulose suspensions using this method, two steps are involved: first, the suspension is frozen to form ice crystals, and second, the sample is dried through the sublimation of ice molecules. The nanocellulose suspension is frozen to a temperature below the triple point, and then the pressure is reduced below the solvent's vapor pressure, which causes the solid solvent to easily break up into fine particles with minimal shear. It is important to note that nanocellulose can form bonds between ice crystals, which is highly dependent on the concentration of the suspension. Some of the disadvantages of this method include the need for dilute solutions to prevent bonding, the requirement for flash freezing in liquid nitrogen to avoid ice crystals forcing nanocellulose particles together, long batch times, and scalability limitations. As a result, freeze-drying is primarily used for higher-value, small-volume, specialized nanocellulose applications [56], [61].

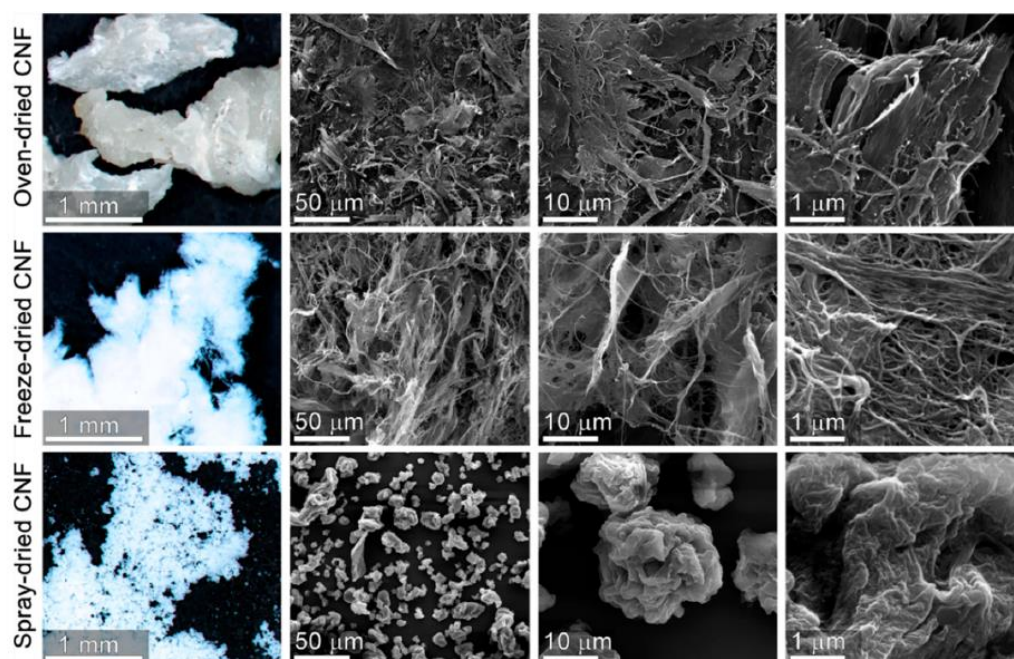


Figure 2.13 Light microscopy and SEM images of dried CNF by various methods, adapted from [53], Under the ACS sustainable Chemistry &Engineering.

2.6.8.4. Supercritical CO₂ Spray-drying

The fourth technique for drying nanocellulose is known as critical point drying, which utilizes CO₂ to preserve the delicate structures of the suspended solids. This method involves the use of a fluid in its supercritical state, which possesses properties of both gases and liquids. To prevent the liquid-gas interface transition, this process is performed above the critical point of the suspending liquid. Water, which has a critical point of 374°C and 229 bar, would damage a cellulose sample, whereas CO₂, with a critical point of 31°C and 74 bar, is harmless to cellulose. However, a nonsolvent that can mix with both water and CO₂ is necessary because water and CO₂ do not mix. Ethanol is used as an exchange fluid to replace water with CO₂ at high pressure. The pressure is then reduced to allow the CO₂ to exit the nanocellulose as a gas, without crossing the liquid-gas interface curve on the phase diagram for CO₂. [61], [62].

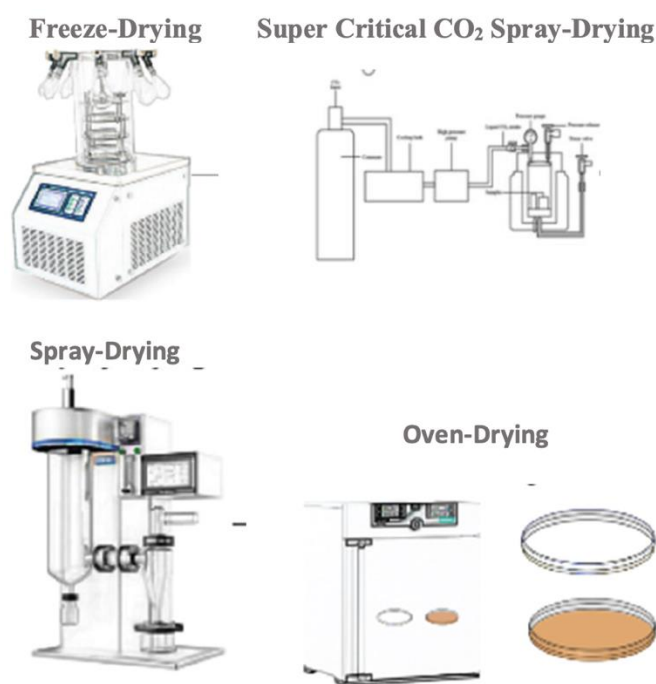


Figure 2.14 Drying techniques used for removing of water from cellulose suspensions, Adapted from [52], [61], Under the Journal of Natural Fibers and Springer Nature Copyright Clearance Center.

2.6.9. Nanocellulose in Food Packaging

Packaging is widely used to safeguard consumable items such as food, beverages, healthcare products, and other goods from various types of damage. To effectively serve their purpose, packaging materials must offer strong barriers against factors like water vapor, oxygen, microorganisms, and grease. As concerns about sustainability and waste disposal grow, there is an increasing need for alternative, renewable materials to replace traditional packaging solutions [63]. Cellulose is a natural polymer that constitutes around 40% of lignocellulosic biomass, and it has the potential to be used for producing sustainable, low-cost, and lightweight paper-based packaging. However, conventional paper made from lignocelluloses lacks adequate barriers against oil, oxygen, and water. Currently, paper-based packaging containers are often manufactured using unsustainable wax, plastic, or aluminum coatings. Cellulosic materials have been widely used in the packaging industry for various purposes, such as container and wrapping materials, primary and secondary packaging, and rigid and flexible packaging. Due to the ability of nanocellulose to form robust hydrogen bonds, it can create a strong and dense network, which makes it difficult for other molecules to penetrate. Typically, the amount of nanocellulose within the polymer matrix is quite small in these composite structures, ranging from 0.5 to 20%. In packaging, cellulose fibers have traditionally been utilized for various food products, including

fresh food, beverages, frozen, liquid, and dry foods. The demand for renewable-resource materials to replace traditional packaging is increasing due to concerns regarding environmental sustainability and waste management [38].

2.7. Nanocomposite

A nanocomposite is a material that consists of two phases, where the continuous phase contains a dispersed phase at the nanometer level [64]. Polymer nanocomposites have gained global interest due to their numerous benefits such as enhanced mechanical and thermal properties, surface properties, barrier properties, transparency, and recyclability [65]. Nanocomposites are preferred due to their superior barrier properties, which can be attributed to their chemical versatility. The high barrier properties of these materials are influenced by two distinct mechanisms. Firstly, the inorganic nanofillers, which are impermeable to gas, liquid, and light, generate a tortuous pathway that molecules must traverse, leading to a longer mean path and greater effective thickness of the film. Secondly, when the polymer and filler exhibit a strong affinity for each other, the interfacial regions of the polymer are affected, and the polymer strands near the fillers become partially immobilized [66]. We should consider the migration rate of nanocomposite material like nanofiller to foodstuff because of safety when we want to use nanocomposite for packaging application [15].

2.7.1. Cellulose Nanocomposites

Cellulose-based composites are attractive due to their low cost, abundance, renewability, and biodegradability. Various methods are used to prepare nanocomposites, including solvent casting, melt intercalation process, in situ polymerization, and coating [13]. The use of nanocellulose as a filler in the bio composite has considered a lot for packaging application to improve mechanical properties [3]. Besides the mechanical properties, they can produce a tortuous and longer diffusion pathway to preventing crossing moisture and gas through the membrane, so the barrier properties improved [3]. There have been very few studies conducted on extrusion methods for producing cellulose nanofiber-reinforced nanocomposites. The hydrophilic nature of cellulose can cause irreversible agglomeration during drying and aggregation in nonpolar matrices due to the formation of additional hydrogen bonds between amorphous parts of the nanoparticles. However, researchers have explored the possibility of dispersing cellulosic nanofibers in nonaqueous media using surfactants or chemical grafting, which presents other options for processing nanocomposites. Cellulose nanoparticles have a

reactive surface covered with hydroxyl groups, offering the potential for extensive chemical modification. While this approach decreases the surface energy and polar character of the nanoparticles, improving their adhesion to nonpolar polymeric matrices, it generally has a detrimental effect on the mechanical performance of the composite [64].

Platnieks et al. [67], explored the use of sustainable materials in polymer composites by incorporating microcrystalline cellulose and cellulose nanofiber into a biobased PBS matrix. A gel-like dispersion of cellulose nanofiber was produced through a mechanical process that involves applying a high shear force. The resulting composites were analyzed for their thermo-mechanical properties and biodegradability. The addition of cellulose fibers improved the tensile strength and Young's modulus of the composites but decreased their elongation at break. The biodegradation of the composites was found to be influenced by the cellulose content, with higher cellulose content resulting in higher degradation rates. Overall, the study demonstrates the potential of using cellulose fibers to enhance the properties of bio-based polymers and promote their sustainable use in various applications.

Liang et al. [68], investigated the physical properties of composites made from PBS reinforced with untreated natural fiber (Kenaf Fiber). The researchers analyzed the impact of different fiber contents on the mechanical and thermal properties of the composite. The findings indicated that the inclusion of Kenaf fiber enhanced the tensile and storage moduli and considerably increased the crystallization rate of PBS. However, an SEM analysis indicated that the interfacial adhesion between PBS and KF requires improvement.

Table 2.3 Recent studies on starch and CNF composites

Polymer	Polymer Ratio	Plasticizer/ filler/ compatibilizer	Description	References
PBS Cassava Starch	60/40 50/50 40/60	Glycerol Maleic anhydride (rPBS)	• rPBS improved the water resistance of the blend • The rPBS improved the strength, elongation at break, and interfacial miscibility	[6]
PBS	90/10 80/20 70/30	Kenaf Fiber	• Tensile strength and modulus were improved • The crystallization rate of PBS is enhanced	[68]
PBS	60/40	CNF MCC	• The young's modulus improved about two-fold • Biodegradation rate got faster • The storage modulus increased	[67]
PBS Thermoplastic cassava starch	75/25 50/50 25/75	CloisiteNa Cloisite30B PBS-g-MA	• Cloisite30B improve the tensile modulus • CloisiteNa enhance thermal stability • Both nano fillers helped to increase the Oxygen and water barrier properties when using with high amount of PBS (75 %)	[23]
TPS	0.1,0.2, 0.3, 0.4, 0.5, 1	CNF	• By adding 0.4% CNF the WVTR decreased by 86% • The OTR decreased by 94% • Tensile strength and tensile Modulus increased • The surface roughness of nanocomposite is decreased	[69]
TPS	5,10,15	CNF from rice strew	• By adding 15% wt CNF tensile strength and tensile modulus increased • the permeability coefficient decreased from for TPS combined with 10 wt% CNF. However, for TPS combined with 15 wt% CNF, this value increased again. • As the content of cellulose nanofiber increased, the light transmittance of the films decreased.	[70]
PLA	1, 3, 5	CNF modified with acetylation process	• uniform distribution observed at lower contents and agglomeration at higher contents. • incorporating acetylated nanofibers did not have a notable impact on the permeability of the films.	[71]

2.8. Outlook and Conclusion

In recent years, the demand for sustainable and environmentally friendly packaging solutions has increased, and biodegradability has become a critical property for packaging materials. Researchers are increasingly interested in working with biopolymers due to environmental concerns surrounding the use of non-sustainable, non-biodegradable, and toxic materials in industrial applications. Biopolymers, such as PBS, Starch and Cellulose, offer a potential solution as they are renewable, biodegradable, and non-toxic. Additionally, biopolymers can offer unique properties and functionality compared to traditional materials, making them attractive for a wide range of applications. Among the biopolymers, Polybutylene succinate (PBS) is a biodegradable polyester composed of repeating units of butylene succinate, characterized by ester bonds that are hydrolysable, leading to its biodegradability. The molecular weight of PBS is adjustable to attain optimal properties for specific applications. PBS presents several advantages, including its biodegradability, mechanical properties comparable to conventional petrochemical-based polymers, and its production from renewable resources. Moreover, PBS is non-toxic, which renders it suitable for biomedical applications. Nonetheless, PBS has certain disadvantages that cannot be ignored, such as its susceptibility to hydrolysis, causing a decline in its mechanical properties over time, limiting its application in specific environments. Furthermore, the cost of producing PBS is still considerably higher than that of traditional petrochemical-based polymers. However, despite its drawbacks, the potential for PBS as a sustainable alternative to traditional petrochemical-based polymers has spurred an increase in interest and research in its development and applications.

Polybutylene succinate (PBS) has emerged as a promising biodegradable polymer for packaging applications due to its acceptable barrier properties.

Packaging materials play a crucial role in protecting and preserving the quality of the packaged product. Among the essential properties of packaging materials, barrier properties against gases, water vapor, and aromas are critical to ensuring the product's safety and shelf life. Mechanical properties such as tensile strength, elongation, and impact resistance are also important to withstand transportation, handling, and storage without damage or rupture. Compatibility between the packaging material and the product is essential to prevent interactions that may alter the product's taste, odor, or color. Optical properties such as transparency enable consumers to view the product and assess its quality. Seal ability is another crucial property to maintain the product's freshness and shelf life.

PBS possesses barrier properties against water vapor, and aroma, but it is not good against Oxygen. In addition, PBS has a low water vapor permeability, which prevents moisture from affecting the quality of packaged products. PBS-based packaging films also can retain the aroma of packaged food, which is particularly important for food products with distinct aromas, such as coffee or spices. The barrier properties of PBS-based packaging films can be further improved by incorporating nanocellulose, a renewable and biodegradable nanomaterial derived from plant cell walls. Nanocellulose has been shown to enhance the barrier properties of PBS-based packaging films against oxygen, water vapor, and aroma. Overall, the barrier properties of PBS and its potential to be enhanced by nanocellulose make it a promising biodegradable polymer for sustainable packaging applications.

2.9. Comparison with Prior Research

In this study, obtaining a CNF from industrial hemp using chemical and mechanical treatment was explored. The CNF was mixed with PBS in the extruder and then a thin film was made using a hot-press. The same process using only mechanical refining (Masuko Grinder) to obtain the CNF was done. Then, the properties of these two methods were compared.

Mechanical processing of bast fiber to produce cellulose nanofibers may be preferred for several reasons. Firstly, it is more environmentally friendly as chemical treatments can generate waste streams and require careful disposal to avoid environmental contamination. On the other hand, mechanical processing can be done with minimal use of chemicals or water. Secondly, it is a simpler and more straightforward method that is easier to scale up for commercial production and requires less specialized equipment. Additionally, mechanical processing may retain more of the natural properties of the fibers, such as their crystallinity or strength, whereas chemical treatments can alter the chemical composition of the fibers and affect the properties of the resulting nanofibers. However, mechanical processing alone may result in lower yields or less consistent quality of the resulting nanofibers. The choice of processing method may depend on various factors, such as the intended application of the resulting nanofibers, the specific properties of the fibers being used, and the availability of resources and expertise for different processing methods.

Most papers discuss obtaining a film using the solution casting method because drying CNF is challenging. In this work, it was tried to dry the CNF using a spray dryer and then the obtained CNF powder was processed with PBS in an extruder.

Since CNF is hydrophilic and has many OH group on the surface, many researchers used some modification during the producing process to change the functional group on its surface. In this work, no modifications were made due to expensive steps, but some chemicals, such as surfactants, were used to help disperse the CNF.

Chapter 3 Materials and Methods

In this chapter a description is made about the materials used for the preparation of the nanocomposite, thermoplastic starch system, and the cellulose samples. The methodology used for this purpose and the methods of characterizing these materials are also described.

3.1. Materials

Biobased PBS FD-92 in the form of pellets were bought from PTT MCC BIO CHEM LIMITED company in Thailand. Cassava starch in form of powder was obtained from Bahiamido in Brazil. The cellulose nanofiber was obtained from University of Maine, USA. To minimize moisture effects and hydrolysis, all materials were dried in an oven at 70 °C for 24 hours prior to use. Meanwhile, Glycerol was used for plasticized the starch, was supplied from Merck.

Industrial hemp (natural bast fiber) was purchased from IND HEMP in the USA.

Other chemicals used in this project are Sodium dodecyl sulfate (SDS), Cetyltrimethylammonium bromide (CTAB), Polyethylene oxide (PEO), Sodium chloride (NaCl), Citric acid and Triton X-100 from Sigma Aldrich and Merck.

Table 3.1 presents the material characteristics.

Table 3.1 The material characteristic

Materials	Characteristic	Supplier
Poly Butylene Succinate (PBS)	Density = 1.24 gr/cm ³ MFR = 4 gr /10min White, No odor Melting Point = 84 °C	PTT
Cassava Starch	Average size = 4-7 µm White, No odor	Bahiamido
CNF	Freeze dried White, Odorless 50 nm in width Surface property=30-33 m ² /gr Density = 1.5 gr/cm ³	University of Maine
Glycerol	Specific gravity = 1.26 kg/lit Boiling point = 290 °C M _w = 92.1 gr/mol	Merck
Industrial hemp		IND HEMP USA
Sodium dodecyl sulfate (SDS)	Anionic surfactant	Sigma Aldrich
Cetyltrimethylammonium bromide (CTAB)	Cationic surfactant	Sigma Aldrich
Polyethylene oxide (PEO)		Sigma Aldrich
Sodium chloride (NaCl)	Salt, Ionic compound	Sigma Aldrich
Citric acid	Organic acid	Sigma Aldrich
Triton X-100	Non-ionic surfactant	Sigma Aldrich

3.2. Methods

3.2.1. Preparation of Plasticized Starch

Thermoplastic starch (TPS) pellet was made with cassava starch. The TPS was made by mixing cassava starch, water, and Glycerol (100 phr starch, 20 phr distilled water, 30 phr glycerol). The blends were mixed for 10 min in mixer then fed into the corotating twin screw extruder (Haake Minilab Extruder). The extruder temperature was 110 °C with a screw speed of 75 rpm. The extruded TPS was cooled in the air and cut in the small size like pellets. The final moisture content of the TPS pellets was approximately 2%.



Figure 3.1 Thermoplastic starch, Image by Author.

3.2.2. The Process of Treatment of Hemp CNF

Pulp production using hemp fibers followed the procedure outlined in the patent of University of Maine [72]. The fibers were cut using a mechanical laboratory mill to the size of 3 mm. The procedure consisted of adding hemp fibers to a conical flask and introducing an alkali solution to extract and eliminate most of the hemicelluloses and minerals, as well as partially eliminating lignin from the plant material. For this, a 10% wt. solution of sodium hydroxide (NaOH) was prepared in 4 L of water and then 100 grams of milled fiber was added. The solution was kept at room temperature for 4 hours with mild agitation. Then, the fibers were washed with water using a sieve to reach pH 6-8. This step increases the surface area of fiber and helps to hydrolysis process.

The second step consisted of treating the fibers with hydrochloric acid (HCl). A 1M HCl solution was made by adding 262.4 mL of HCL (37%) to 3.2 L of water. After homogenizing the solution,

it was divided into four flasks (each containing 800 mL) and then 25 g of washed fiber was added to each flask. The flask was kept at 80 °C for 2 hours in a silicon oil bath with a mild agitation (Reflux is needed). At the end, the fibers were washed again with water to reach PH 6-8. This helps to dissolve the hemicelluloses.

The last step consisted of the chemical treatment of the fibers using a 5% wt. NaOH. 160 g of NaOH were mixed with 3.2 L of water, and after homogenizing the solution, it was divided into four flasks (each containing 800 mL) and then 25 g of washed fiber was added to each flask. The flask was kept at 80 °C in silicon oil bath for 2 hours with mild agitation. At the end, the fibers were washed again with water to reach 6-8 PH. This causes a disturbance in the structure of lignin and separates the connections between carbohydrates and lignin.

For the bleaching process, 24 g of NaOH, 192 ml of H₂O₂ and 96 g of sodium metasilicate (Na₂SiO₃) were mixed in 3200 mL of water for 10 to 15 minutes. Then this solution was divided into the four flasks and 25 g of fiber was added to each flask. The solution was kept at 80°C for 3 hours with reflux. At the end, the samples were washed again with water to remove all chemicals and residues and then the pulp was kept in water (5% suspension) for refining in the Masuko.

To attain comparable nano-scale fiber gel-like consistency, cellulose fibers processed in various ways were subjected to fibrillation with a Masuko grinder for 15 passes.

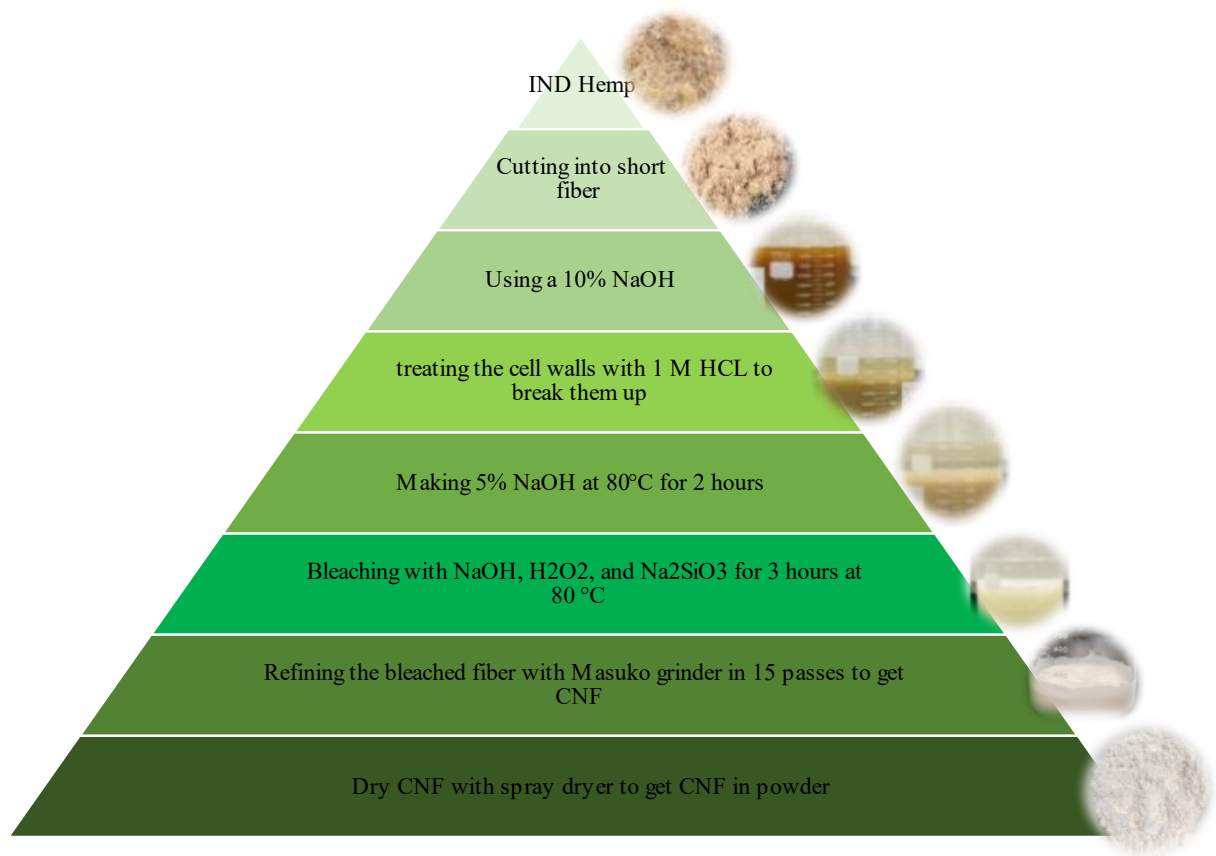


Figure 3.2 Procedure for producing CNF.

3.2.3. Preparation of CNF without Chemical Treatment

The fibers were cut using a mechanical laboratory Mill in the size of 1.5 mm. Then, a suspension with 3% concentration was prepared and refined with Masuko grinder for 15 passes. The experiment started with a gap of 1.4 mm and every two cycles the gap was decreased until it reached 1 mm. The final consistency of the samples was approximately 2.8% and the samples were stored in a refrigerator for future use and drying with spray dryer.



Figure 3.3 Making CNF without chemical treatment.

3.2.4. Drying of CNF with Spray-dryer

The samples were diluted to 0.5 % and mixed for 2-3 hours on the hot plate, then sonicated for 30 minutes to separate the agglomeration of fibers. The chemicals such as, NaCl, SDS, CBAT, PEO added in this step. The sample was kept under agitation at 500 rpm using a stir plate before being fed into the top of the spray dryer. The aspirator was used at 100 %, the nozzle heat set at 180 °C, nitrogen flow rate was 30-40 mm and pump value were 20 %. The dry powder was collected and kept in the refrigerator.

3.2.5. PBS/TPS and PBS/CNF Blends

PBS/TPS blends with different composition were prepared by mixing them in the Extruder at 125 °C with the rotor speed of 75 rpm. The ratio between PBS and starch was 80/20, 60/40, 40/60, 30/70, 20/80. The ratio between PBS and TPS was constant (70/30). The weight of CNF and compatibilizer was considered based on the total weight. After the extrusion process all samples were ground using a mill to obtain a powder. The samples were kept in the oven at 70 °C for 24 h and then a hydraulic compression molding machine was used to make a film with the thickness of 0.18 ± 0.02 mm. The sample was pre-heated at 140 °C for 1 min before molding. The molding was conducted under 8 -12 metric tonnes for 3 min.

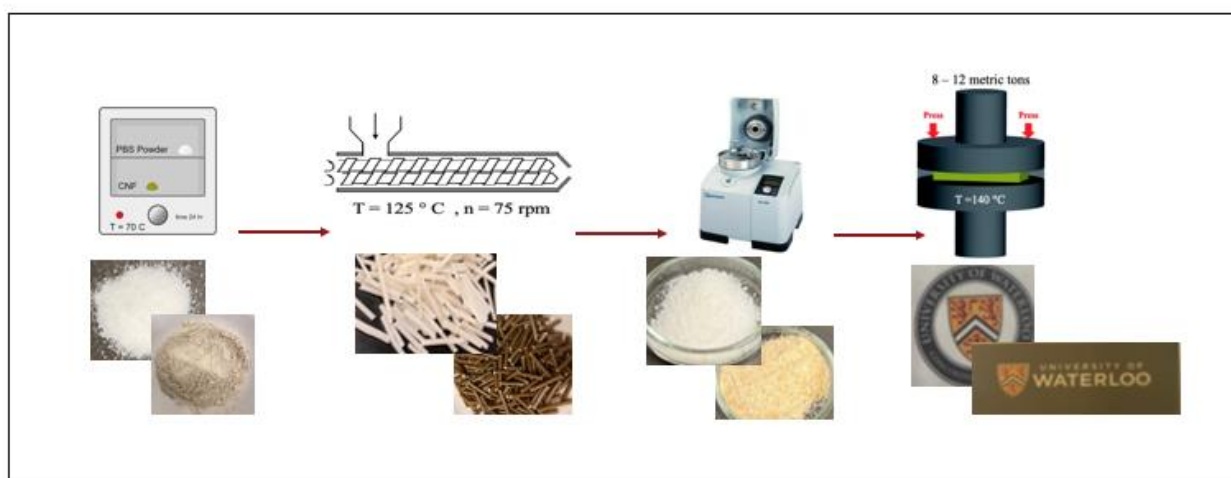


Figure 3.4 A summary of the producing film steps.

3.3. Characterization

3.3.1. Scanning Electron Microscopy (SEM)

The Surface morphology of the cassava Starch, CNF, TPS/PBS blends, PBS/CNF blends and their cross sections were investigated by Quanta FEG ESEM at an accelerating voltage of 20 kV. To obtain the natural fracture surface, the samples were cooled in liquid nitrogen until they fractured. All samples were fixed on aluminum stubs and were sputter coated with a thin layer of gold.

3.3.2. Moisture Content

The test was conducted following the ASTM standard D570-98. First, all samples were kept at a relative humidity 50 % for 24 hr. After that all the samples were weighed (M_t). Then the samples were dried in an oven at 70 °C for 48 hours and weighed again (M_0). To calculate the percentage of moisture loss (M_c), the following formula was used:

$$M_c (\%) = \frac{M_t - M_0}{M_t} \times 100$$

3.3.3. Water Absorption Capacity (W_a)

Tests to measure the water absorption capacity, also known as water uptake, were conducted following the ASTM standard D570-98, but with adjustments made to the sample size and amount of water used. The size and shape of samples are small dumbbell which is used for mechanical test. Beforehand, the specimens were dried in an oven at 50 °C for 24 hours, and subsequently cooled to room temperature inside a desiccator. Weighed the samples as a W_0 .

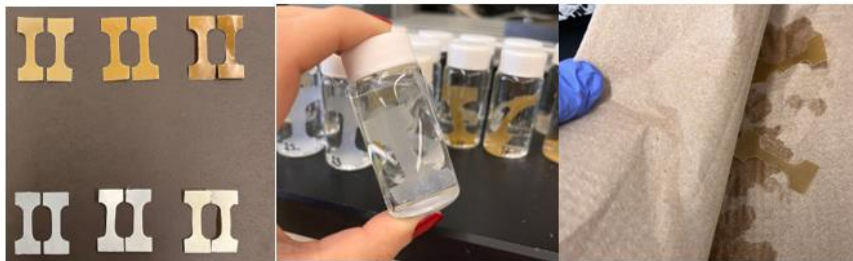


Figure 3.5 The shape and size of samples for water absorption test.

Then all samples were immersed in 20 ml of deionized water and kept for 24 hrs in room temperature. After this time, the water on the surface of the films was removed with paper tissues. The samples were subsequently weighed once more to determine their wet weight after being immersed (W_t). For each batch, three samples were examined and the resulting average data, along with the corresponding standard deviations, were reported. The water absorption capacity (W_a) was computed using the following formula:

$$W_a (\%) = \frac{W_t - W_0}{W_0} \times 100$$

3.3.4. Water Solubility (W_s)

All the expanded samples obtained from the water absorption tests were utilized to determine the water solubility of the materials in accordance with the ASTM standard D570-98. The samples were once again dried in a vacuum oven at 60 °C for 24 hours, and then allowed to cool to room temperature inside a desiccator for around 30 minutes. The dried samples were weighed to obtain the weight after immersion (W_d). The water solubility (W_s) was then calculated using the following formula:

$$W_s (\%) = \frac{W_0 - W_d}{W_0} \times 100$$

3.3.5. UV-Vis Spectra

The measurement of light transmittance and absorbance of the films in the range from 400 to 800 nm was carried out using a UV-Vis spectrophotometer (Jasco, J-815 CD spectrometer, Japon). Rectangular samples of approximately 13 mm × 45 mm in area were cut and placed in cuvettes. The transmittance and absorbance of the samples were determined with air as the standard. The light transmittance (T %) of the film samples, with three specimens per material batch, was determined using a scan rate of 200 nm/min.

$$T \% = 10^{(2 - Absorption)}$$

The transparency index of each sample was calculated using the absorbance obtained, and the below equation:

$$T_r = \frac{A_{600}}{x}$$

where T_r is the Transparency index, A_{600} is the absorbance at 600 nm and x is the thickness (mm) of the film [73].

3.3.6. Mechanical Properties

A universal testing machine (Test Resources 120R,) was employed to determine the mechanical properties of different blends and nanocomposites. The samples were conditioned prior to testing at $23\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ and $50 \pm 5\%$ relative humidity for at least 48h. Suitable dies were used to cut the sheet and prepare dumbbell-shaped specimens according to ASTM D638. The measurement of mechanical properties was carried out at room temperature. The tensile test was carried out at a crosshead speed of 50 mm/min. Each of the samples has a gauge length of 22.5 mm, a width of 4.9 ± 0.3 mm, and a thickness 0.18 ± 0.02 mm. For each sample, a minimum of seven specimens were tested, and subsequently, the average values of Young's modulus, tensile strength at break, and elongation at break were calculated and reported.

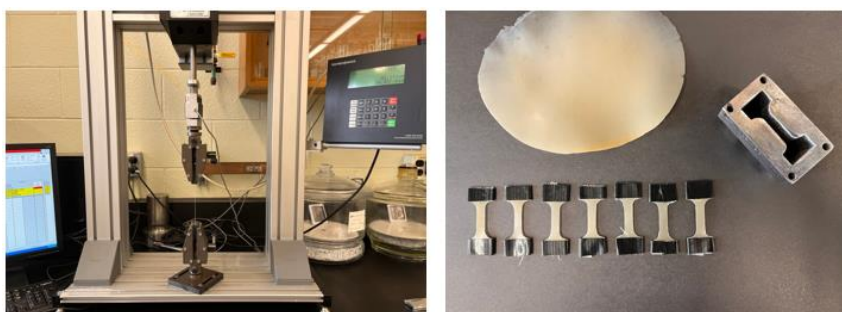


Figure 3.6 The shape of the sample for mechanical test.

3.3.7. Water Vapor Permeability (WVP)

The water vapor permeability (WVP) and water vapor transmission rates (WVTR) of the films were measured in triplicate using the standard cup method (ASTM E96/E96M-12). This involved placing circular films with a 3.5 cm diameter on top of cups that contained deionized water, then sealing them with an O-ring. The cups were then kept in a desiccator with a temperature of $21\text{--}23\text{ }^{\circ}\text{C}$ and relative humidity of 12-15 % for 10 days. The weight of the samples was measured during this time. The WVTR was determined by calculating the slope of the linear weight loss and then deriving the WVP using an equation:

$$\text{WVP} = \frac{\text{WVTR} \times L}{\Delta P}$$

Where L and ΔP are film thickness (mm), and the saturation vapor pressure of water between the surface of the films (KPa). This value can be calculated using the equation $\Delta P = S (R_1 - R_2)$, where S represents the saturation vapor pressure at the experimental temperature, 2.812 KPa, R_1

represents the relative humidity inside the capsule containing water (100 %), and R2 represents the relative humidity outside the capsule. WVTR is the slope of linear weight change ($\text{gr/m}^2\text{day}$).



Figure 3.7 The condition of WVP test.

3.3.8. Oxygen Permeability (OP)

To measure oxygen permeability (OP), a custom-made bubble flowmeter was used. The specimens with a circular shape and a diameter of 4.8 cm were placed in a chamber with one side facing pure oxygen and the other side of the film was attached to the bubble flowmeter system. The time required for the bubble to travel 20 mL through a burette was recorded to calculate the flow rate. The test was conducted under a fixed pressure of 5 psig.

$$OP = \frac{OTR \times L}{\Delta P}$$

Where OTR is the measurement of the amount of oxygen gas that passes through a material with a specific area over a specific period of time ($\text{cm}^3/\text{m}^2.\text{s}$), L is the thickness of the film (μm) and ΔP is the oxygen gas pressure difference between the two sides of the film (pa).

3.3.9. FTIR Analysis

Fourier transform infrared (FTIR) spectroscopy was used to detect the presence of functional groups existing in the PBS films. Infrared spectra were recorded using a FTIR spectrometer (Bruker Tensor 27). The wavenumber was over the range of $400\text{-}4000\text{ cm}^{-1}$ by placing the films on the sample holder and scanning them. The number of accumulated scans and scanning rate were 32 and 4 cm^{-1} , respectively. To standardize and correct the data, vector normalization and baseline correction were performed on each individual spectrum using the OPUS software.

Chapter 4 Results and Discussions: PBS and Starch Blends

The main focus of this chapter was to investigate the properties of blends of PBS and starch, which contained a constant amount of glycerol (20%) and compare them to the properties of blends containing thermoplastic starch. In addition, CNF and citric acid were added to the thermoplastic starch blend as a compatibilizer. Two tables were created to display the composition of the samples that were utilized in this study.

Table 4.1 Formulation of PBS/Starch blends with constant amount of glycerol

	% wt			phr			gr		
	PBS	Starch	Glycerol	PBS	Starch	Glycerol	PBS	Starch	Glycerol
PBS	100	0	0	100	0	0	100	0	0
80/20	64	16	20	100	25	31.25	64	16	20
60/40	48	32	20	100	66.66	41.66	48	32	20
40/60	32	48	20	100	150	62.5	32	48	20
30/70	24	56	20	100	233.33	83.33	24	56	20
20/80	16	64	20	100	400	125	16	64	20

Table 4.2 Formulation of PBS/TPS blends with different amount of CNF (University of Maine)

	% wt			phr			gr		
	PBS	TPS	CNF	PBS	TPS	CNF	PBS	TPS	CNF
PBS	100	0	0	100	0	0	20	0	0
70/30/0	70	30	0	100	42.86	0	14	6	0
70/30/1	69.3	29.7	1	100	42.86	1.443	13.86	5.94	0.2
70/30/5	66.5	28.5	5	100	42.85	7.526	13.3	5.7	1
70/30/10	63	27	10	100	42.85	15.873	12.6	5.4	2

4.1. Morphological Observation

The behavior of polymer blends in different phases is essential to understand their mechanical properties. The morphology of different phases helps to explain the relationship between the microstructure and mechanical properties of the blend. Figure 4.1 shows the SEM micrograph for starch and TPS.

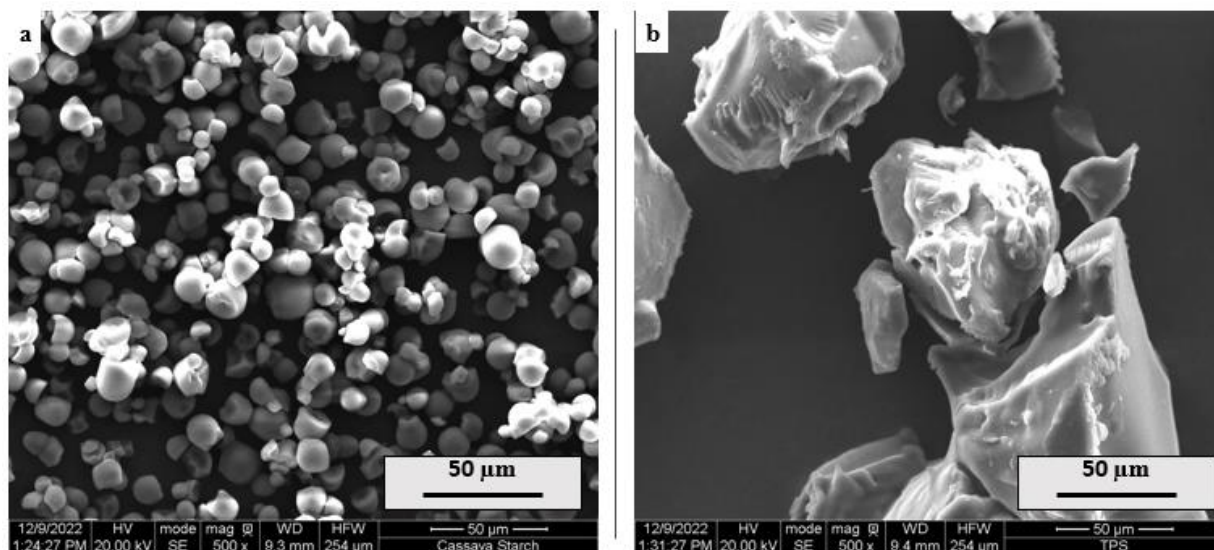


Figure 4.1 SEM micrograph of a) starch and b) TPS.

As mentioned in chapter two, starch possesses numerous hydroxyl groups in its chemical structure, which facilitates the formation of strong hydrogen bonds between molecules, thereby inhibiting the movement of starch molecules. When water and plasticizers such as glycerol are added to starch, their hydroxyl groups can interact with the hydroxyl groups present within the starch molecules, resulting in the formation of hydrogen bonds [16].

Analyzing figure 4.2, starch particles can be seen in the PBS matrix, but when only 5% glycerol is added, it is possible to observe some improvements in the matrix. The detachment of starch granules from the PBS matrix suggests that phase separation occurred. However, the addition of Glycerol resulted in no visible starch granules in Figure 4.2b, so, resulting in smaller phase domains. This is another reason that show starch should be plasticized by glycerol before mixing with other polymers.

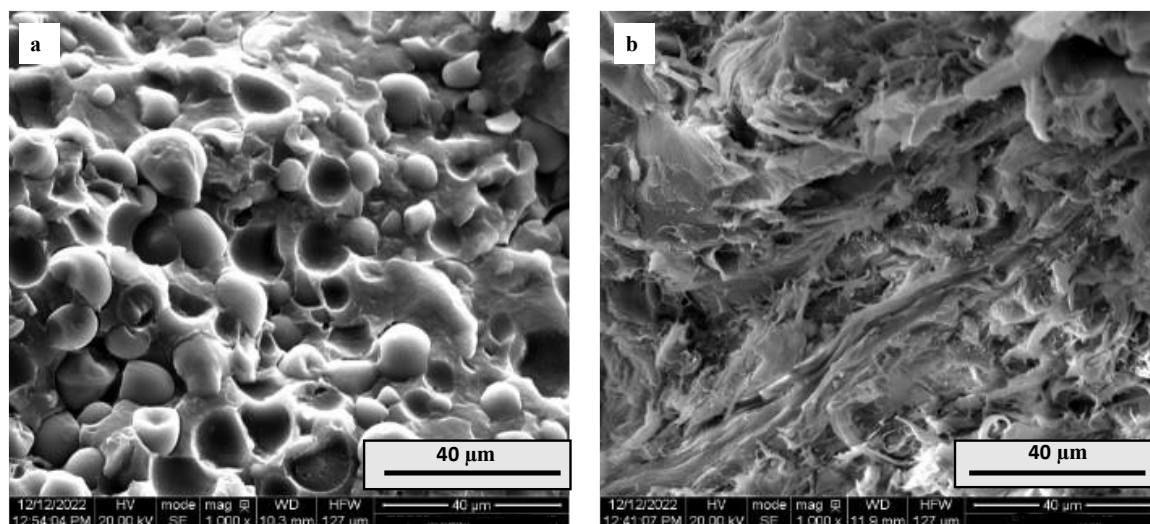


Figure 4.2 SEM micrograph of cross section of a) PBS60/Starch40, b) PBS60/Starch40/Glycerol5.

SEM analysis was conducted to comprehend the structural morphology of cross section of tidy PBS, PBS/ST blends with 20% of Glycerol, and PBS/TPS/CNF nanocomposites, as shown in Figure 4.3 and 4.4 respectively.

As can be seen in figure 4.3a, the PBS film that was completely pure exhibited a sleek appearance, which indicated its relatively sturdy and malleable composition. When PBS is blended with starch, the two polymers form two distinct phases due to their immiscibility. The resulting morphology is typically characterized by a dispersed phase of starch granules in a continuous matrix of PBS. However, the addition of glycerol, as a plasticizer, can modify the morphology of the blend. In figure b-d some miscibility can be seen between PBS and starch due to existing of glycerol and the spherical starch in PBS can also be seen. But in figure b and c, there are some cracks and hole in the interface that can act as a weak point and lowering the mechanical properties. This indicates that 20% glycerol for these compositions that contains more PBS was too much, but the figures d, e, and f indicate that the blends exhibited improved homogeneity, and the adhesion of starch particles to the PBS matrix was enhanced. So, in this case glycerol may act as a surfactant, promoting better interfacial adhesion between the PBS and starch phases. The improved adhesion leads to a more uniform distribution of the starch phase within the PBS matrix and reduced phase separation.

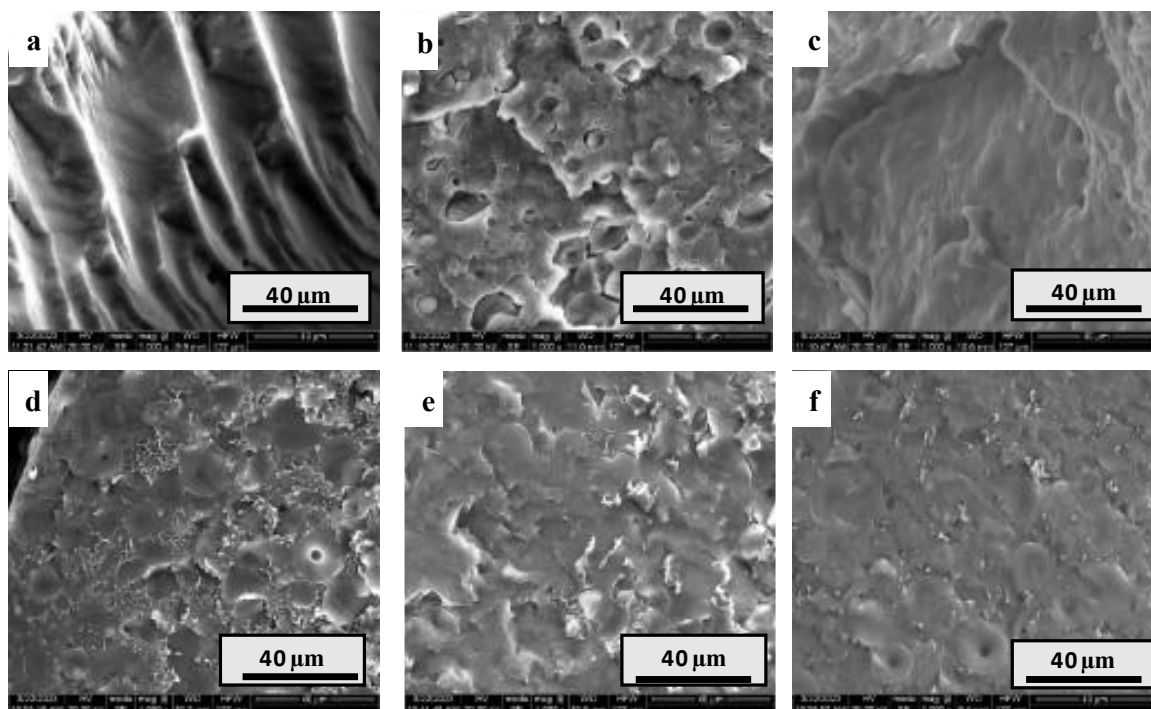


Figure 4.3 SEM micrograph of cross section of a) pure PBS, b) PBS80/Starch20, c) PBS60/Starch40, d) PBS40/Starch60 e) PBS30/Starch70, f) PBS20/Starch80.

Figure 4.4 shows the SEM images for a) pure PBS, b) PBS70/TPS30, c) PBS70/TPS30/CNF1, d) PBS70/TPS30/CNF5, e) PBS70/TPS30/CNF10, f) PBS70/TPS30/CNF1/citricacid0.5, g) PBS70/TPS30/CNF1/citricacid1, h) PBS70/TPS30/CNF5/citricacid2. As mentioned in previous chapters, the relative hydrophobicity of PBS compared to TPS is due to the presence of fewer hydroxyl groups in the repeating units of PBS. This can result in insufficiently strong interfacial adhesion between the two phases, which show phase separation and voids and gaps at the interface. This weak interface acts as a stress concentrator, leading to reduced mechanical properties of the specimens [25], [74].

The morphology structure of blends of PBS and starch undergoes significant changes upon the addition of a compatibilizer. The SEM images demonstrate that the incorporation of CNFs results in a more even distribution of starch within the PBS matrix, with fewer observable gaps and voids at the interface although, the TPS molecules still exist. But the amount of CNF must be considered, for example in figure 4.4 some agglomeration of fibers can be seen in picture e when 10% of CNF was added. Furthermore, the addition of the compatibilizer produces further improvements in the morphology structure, as evidenced by the SEM images. The TPS particles are distributed more uniformly in the PBS matrix, and the interface between the two polymers is

smoother and more continuous also cause to smaller size of TPS phase. This implies that the compatibilizer enhances the interaction between PBS and starch, leading to a stronger interfacial adhesion and improved mechanical properties. In conclusion, the addition of CNFs and compatibilizer leads to a more homogeneous morphology structure and improved interfacial adhesion to some extent, which can ultimately enhance the overall performance of PBS/TPS blends.

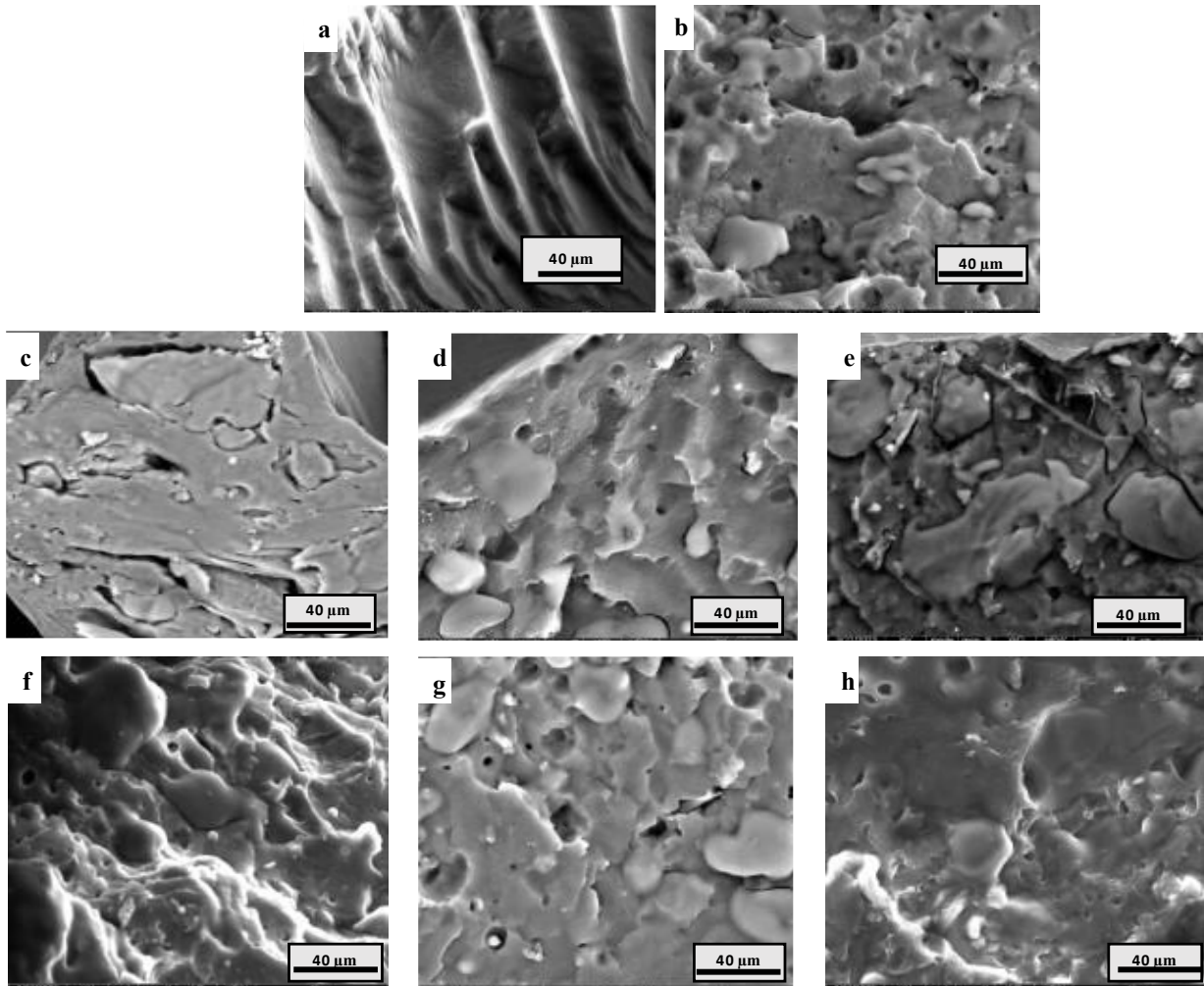


Figure 4.4 SEM micrograph of cross section of a) PBS, b) PBS70/TPS30, c) PBS70/TPS30/CNF1, d) PBS70/TPS30/CNF5, e) PBS70/TPS30/CNF10, f) PBS70/TPS30/CNF5/citric acid0.5, g) PBS70/TPS30/CNF5/citric acid1, h) PBS70/TPS30/CNF5/citric acid2.

4.2. Water Absorption, Solubility and Moisture Content

Starch based materials are well-known to be susceptible to water, hence the importance of investigating their water sensitivity when blended with hydrophobic polymers for efficient packaging applications. As expected, higher starch concentrations led to faster moisture absorption rates. This increase can be attributed to the presence of cracks and voids, as highlighted in the morphological analysis, due to insufficient interfacial bonding between the starch and PBS matrix [19], [20]. Also, starch is hydrophilic so by increasing the concentration of starch in the blend the samples tend to absorb more moisture. Comparing figures 4.5a and b, it is noticed that when TPS was used instead of starch, the moisture absorption is not too much and when CNF and citric acid were added, some improvement can be seen.

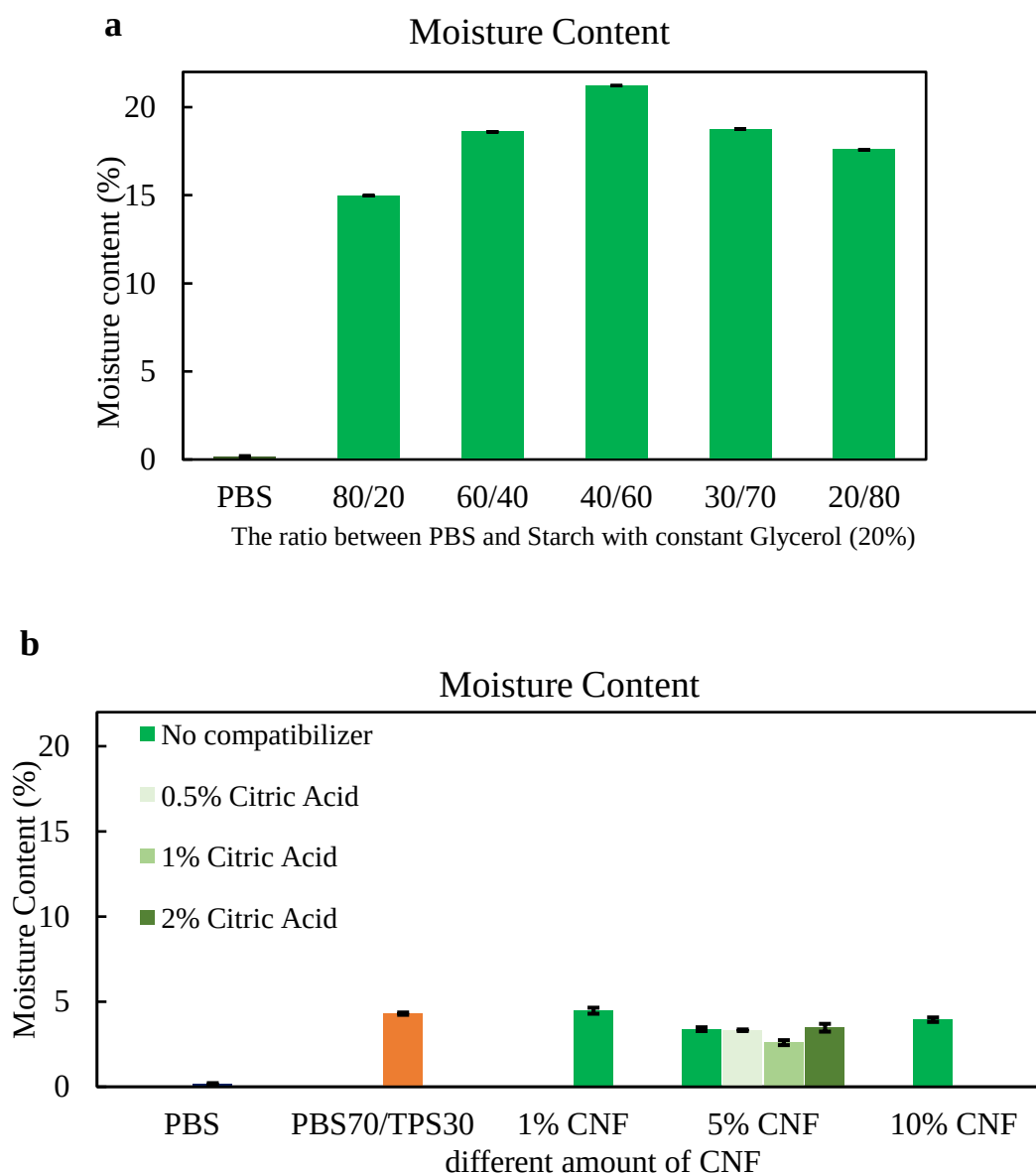


Figure 4.5 The moisture content for a) PBS/Starch/20% glycerol and b) PBS70/TPS30/CNF.

Water absorption behavior is a crucial factor for the performance of biopolymer-based materials in various applications, especially in the field of food packaging. The water absorption behavior of PBS/starch blends in the presence of 20% glycerol was investigated in figure 4.6a. It was found that the water absorption increased with an increase in starch content, which is attributed to the hydrophilicity of starch. The effects of incorporating cellulose nanofiber and a compatibilizer on the water absorption behavior of PBS/TPS blends were investigated in the figure 4.6b. The results showed that the water absorption of the PBS increased with adding TPS due to the hydrophilic nature of TPS. However, the addition of CNF reduced the water absorption of the blends due to the decreased pore size and improved interfacial adhesion between PBS and TPS phases. But if the amount of fiber is increased, due to agglomeration of CNF the water absorption increases again. Moreover, the compatibilizer further reduced the water absorption of the blends by improving the interfacial adhesion and reducing the size of the water-filled pores. The reduced water absorption of the blends indicates their potential for use in food packaging applications where resistance to moisture is crucial.

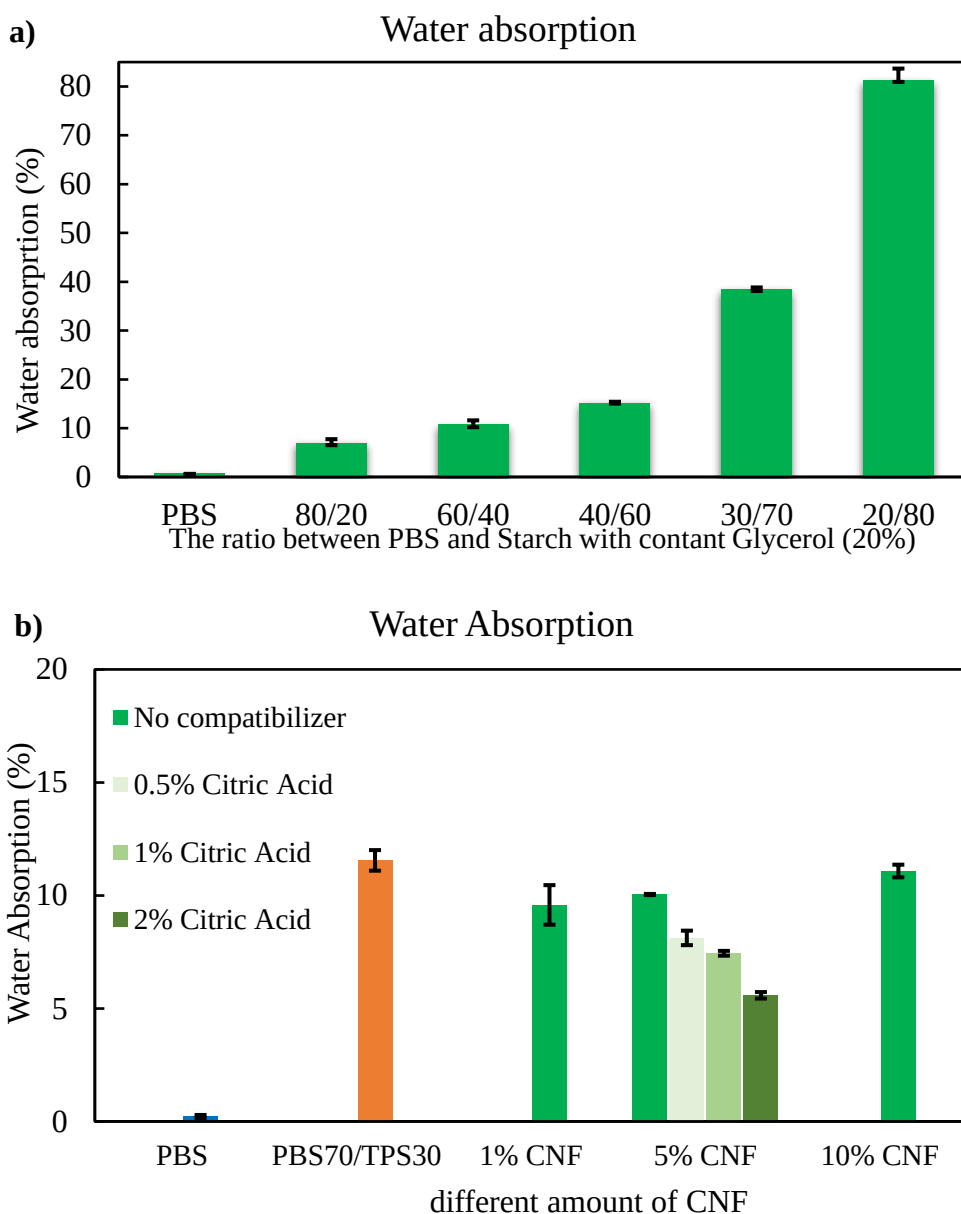


Figure 4.6 The water absorption for a)PBS/Starch/20%glycerol and b)PBS70/TPS30/CNF.

Figure 4.7 demonstrates the water solubility values of neat PBS, PBS/ST blends, and PBS/TPS/CNF nanocomposites. Water solubility is a fundamental aspect to consider in the development of biodegradable packaging materials, and it can be influenced by the composition and processing conditions of the blends. As starch is water-soluble, incorporating it into PBS blends can raise the blend's water solubility. Unlike starch, PBS is a hydrophobic polymer and is not soluble in water (figure 4.7a). Typically, materials with high W_a values are easily dissolved in water due to the absorption of water molecules onto hydroxyl groups through hydrogen bonding, making films easier to dissolve [15]. Thus, despite different magnitudes of parameters,

the W_a and W_s of all film materials exhibited a similar trend. The solubility of PBS and TPS blends in the presence of CNF and a compatibilizer was investigated in figure 4.7b. The high values of W_s were expected since all the constituents, including ST, CNF, and GL, had a hydrophilic nature. The results revealed that the addition of 5% CNF and the compatibilizer led to a decline in the water solubility of the blends. This outcome can be attributed to the enhanced interfacial adhesion between the PBS and TPS phases, which impeded the ingress of water molecules to the starch component of the blend. Moreover, the compatibilizer significantly contributed to reducing the water solubility by enhancing the interfacial bonding between the two polymers.

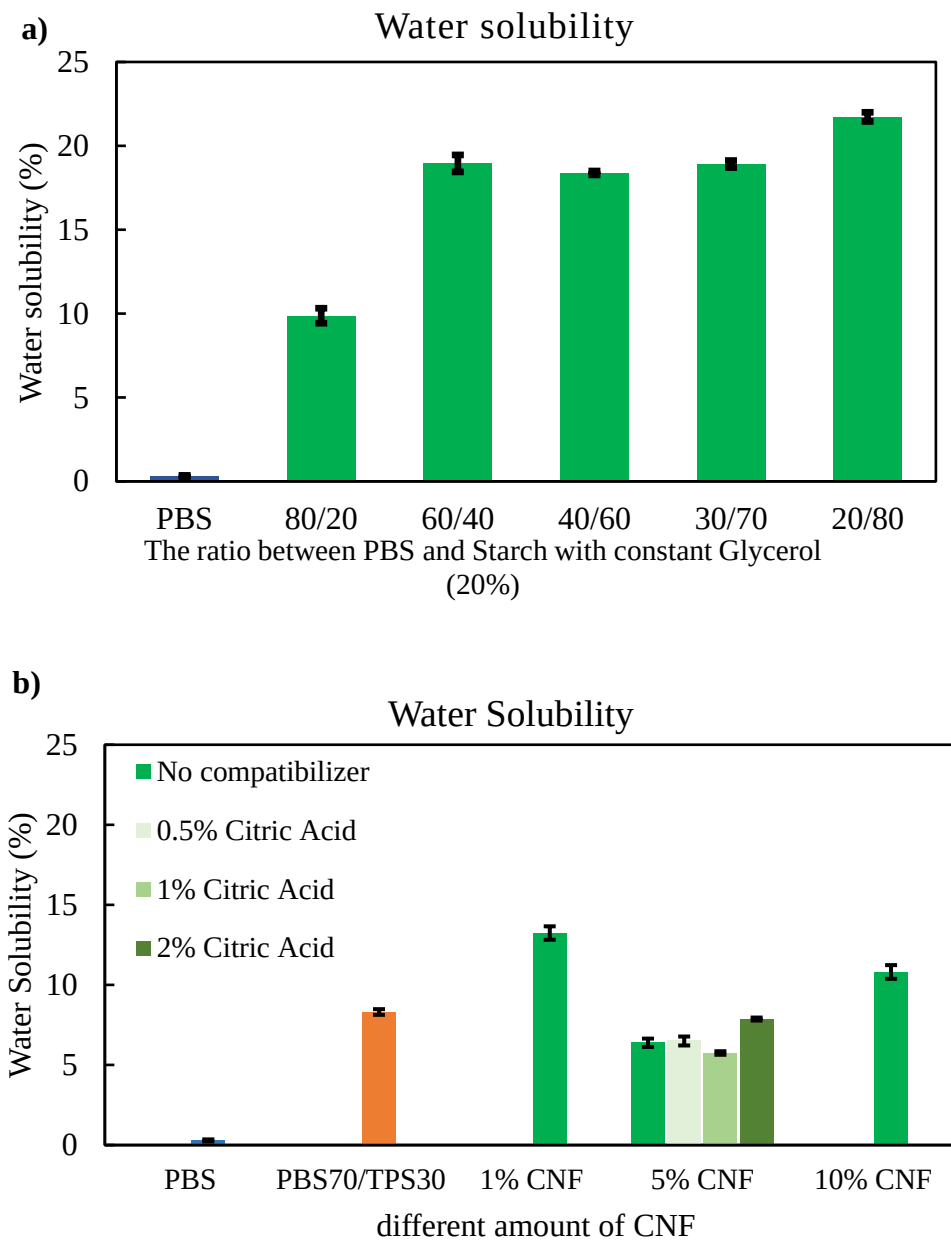


Figure 4.7 The water solubility for a) PBS/Starch/20% glycerol and b) PBS70/TPS30/CNF.

4.3. Water Vapor permeability

WVP is an important property to consider for biodegradable packaging materials because it can impact the shelf life and quality of the packaged product [23]. In the case of PBS and starch blends (figure 4.8a), PBS is a hydrophobic polymer with a low WVP, which means it is relatively resistant to water vapor passing through. However, starch is known to be more hydrophilic, and adding it to the blend can increase the WVP. So, as can be seen by increasing the concentration of starch the WVP increased. The WVP of PBS/TPS films (figure 4.8b) was found to be notably higher than that of PBS films alone. This is likely due to the fact that TPS has a hydrophilic nature, meaning it has an affinity for water molecules and can readily absorb them. This property makes the TPS component of the blend more permeable to water vapor than PBS alone. The high WVP of PBS/TPS films may limit their effectiveness as a barrier material for certain packaging applications, as it may allow for moisture to penetrate the package and affect the quality of the product inside. In addition, a higher WVP was observed by adding CNF. This is due to the hydrophilic nature of CNF that can attract water molecules and facilitate their penetration through the material. Another possibility is that CNF create some agglomerations result in allowing for easier passage of water vapor molecules. Furthermore, by adding citric acid a little improvement was observed in WVP. Citric acid has the potential to the formation of a network structure that can decrease the quantity and size of pores in the film. Consequently, the transportation of water molecules through the film may be restricted. Additionally, the amount of citric acid added may not have been sufficient to cause a noticeable change in the WVP. So, no considerable difference between the samples is seen.

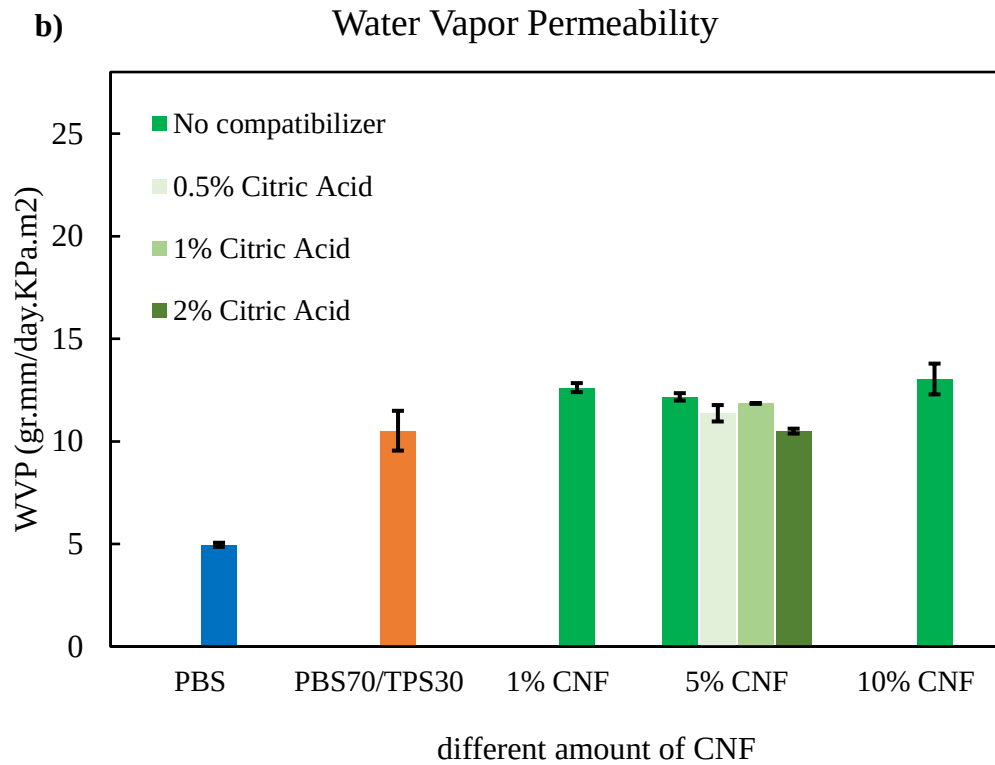
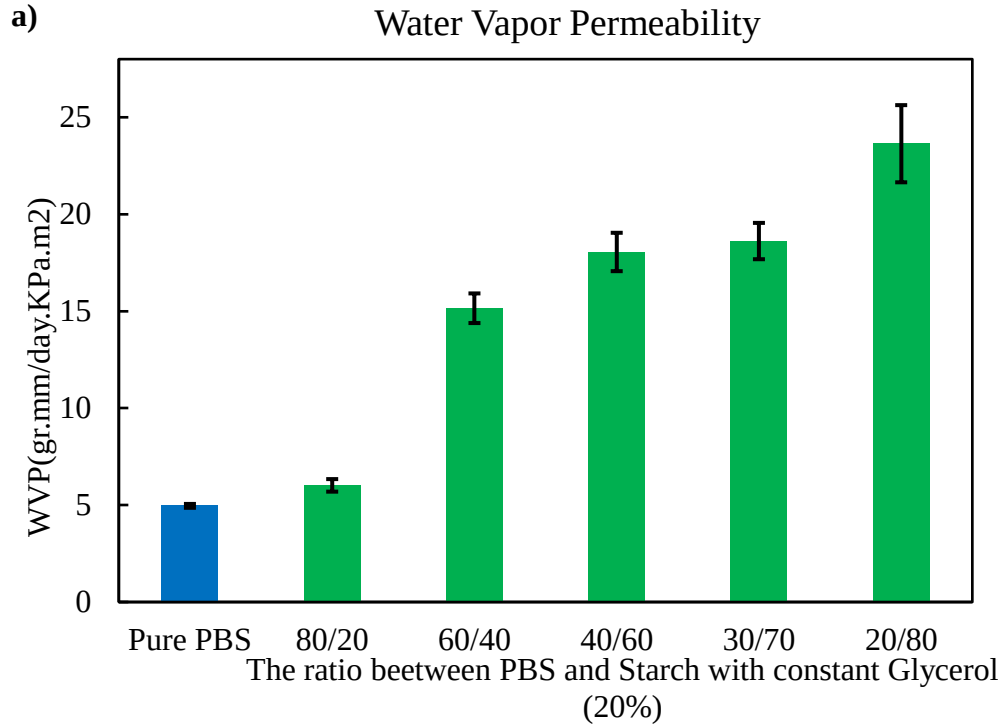


Figure 4.8 The water vapor permeability for a)PBS/Starch/20%glycerol and b)PBS70/TPS30/CNF.

4.4. Mechanical Properties

Figure 4.9 – 4.11 illustrates the mechanical properties of PBS/ST blends and PBS/TPS/CNF composites.

The findings demonstrate a clear relationship between the volume content of starch and the tensile stress and modulus. An increase in starch content resulted in a decrease in tensile stress and modulus (figure 4.9a and 4.10a). This behavior can be attributed to the change in the main phase from the comparatively flexible PBS to the comparatively rigid starch, which provides better rigidity but lower strength and extensibility. Additionally, the poor dispersion of starch in PBS leads to stress concentration spots, which reduce the tensile strength of the blends. The presence of more voids due to increased starch content weakens the structure of the blends and results in poorer interfacial bonding between PBS and starch. So, by increasing the amount of starch the Tensile strength and modulus decrease.

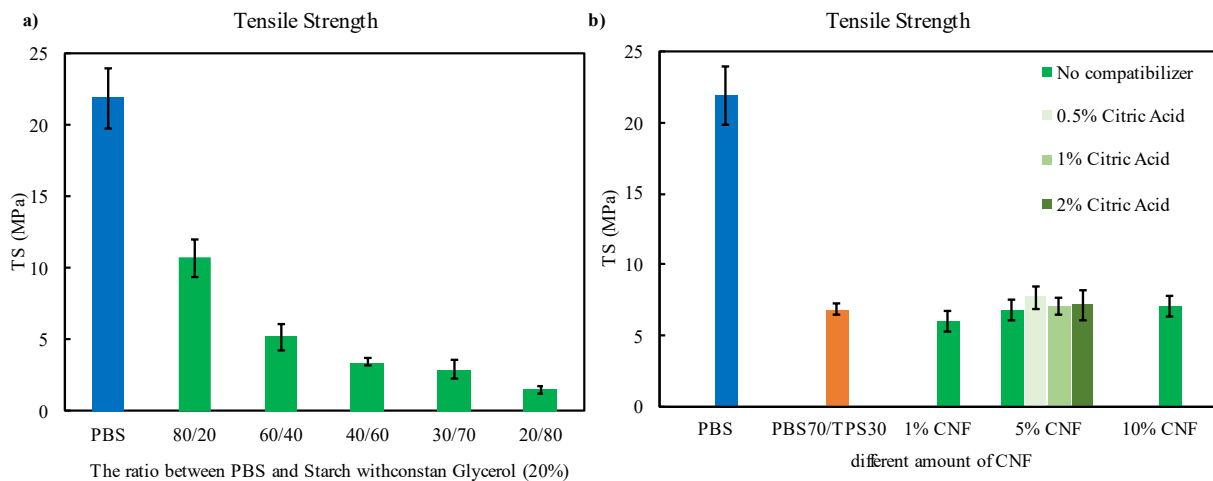


Figure 4.9 The tensile strength of a)PBS/Starch/20%glycerol and b)PBS70/TPS30/CNF.

Figures 4.9b and 4.10b display the tensile strength and tensile modules for blends of PBS and TPS in the presence of CNF and citric acid. The results show a decrease in tensile strength and tensile modulus upon the addition of TPS, which can be attributed to the poor interfacial adhesion between the two phases. The mechanical properties of PBS and TPS blends can be notably altered by the addition of nanocellulose fibers and citric acid. The high aspect ratio, strong hydrogen bonding, and good dispersibility of CNF in the polymer matrix can contribute to the enhancement of the blend's mechanical properties [75]. The incorporation of CNF into the blend can result in improvements in the tensile strength and tensile modulus. This could be due to the

reinforcing effect of CNF as they reinforce the polymer matrix and improve the interfacial bonding between the PBS and TPS phases.

In addition, citric acid has the ability to increase the interactions and entanglements between the polymer chains by creating some physical network and structure, leading to a more compact and denser structure. Consequently, the addition of citric acid can improve the tensile strength, tensile modulus, and elongation at break of the blend as some improvements can be seen in the addition of 1% citric acid to 5% CNF composites.

However, the impact of citric acid on the mechanical properties of the blend varies depending on the concentration. Higher concentrations of citric acid (such as 2%) can cause a decline in the mechanical properties due to the some interaction and network structure are produced. This can ultimately result in brittleness and reduced ductility of the blend.

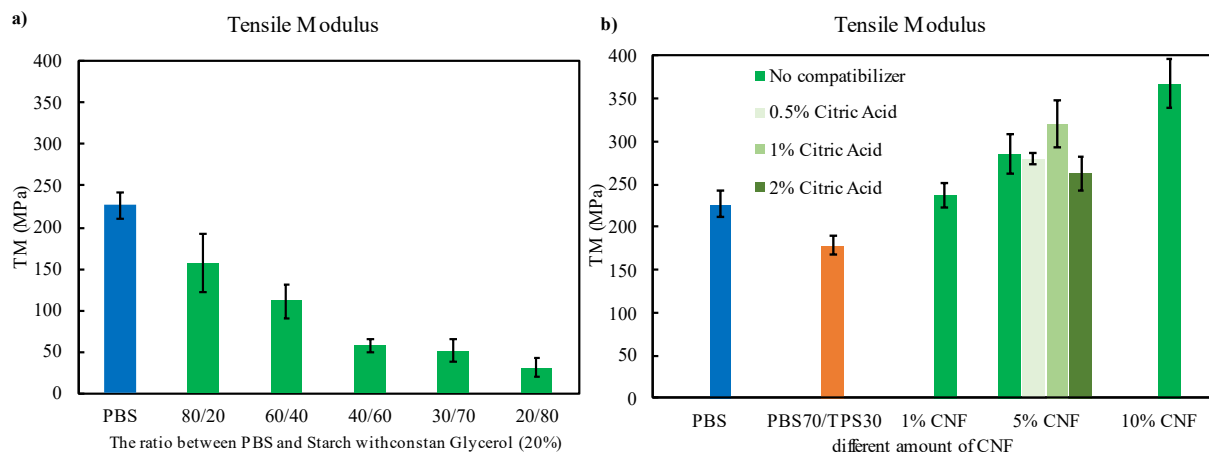


Figure 4.10 The tensile modulus of a)PBS/Starch/20%glycerol and b)PBS70/TPS30/CNF.

Figure 4.11 shows the elongation of different composition of PBS/ST and PBS/TPS with various amount of CNF. The addition of starch and TPS to PBS resulted in a decrease in elongation at break due to the relative rigidity of both starch and TPS compared to PBS. The starch or TPS phase creates a stiff structure in the blend, which constrains the movement of the more flexible PBS phase, causing a reduction in the overall flexibility and stretchability of the blend. Furthermore, the weak interfacial adhesion between the different phases can generate stress concentration spots, leading to localized deformation and, consequently, a reduction in elongation at break [68]. As explained in the previous part by adding CNF and citric acid the elongation improved to some extent due to the reinforcing effect of CNF and compatibilizer.

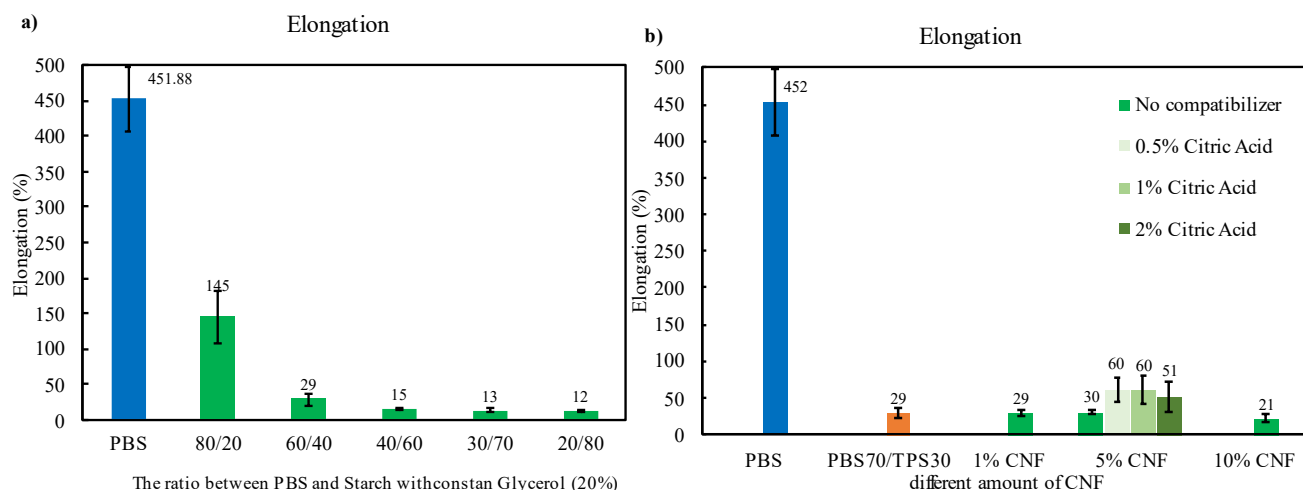


Figure 4.11 The elongation of a) PBS/Starch/20%glycerol and b) PBS70/TPS30/CNF.

Yun et al. [25] conducted a study in which they utilized PBS and corn starch as components in their research. They also incorporated two distinct plasticizers, namely glycerol and ethylene glycol, in their experimental setup. The introduction of TPS in the blends led to a decrease in tensile strength, primarily caused by inadequate interfacial adhesion between the two phases. Furthermore, a comparison between PBS/GTPS and PBS/EGTPS blends revealed that the former exhibited higher tensile strength. This difference can be attributed to the superior plasticizing effect of glycerol compared to ethylene glycol. Additionally, the addition of TPS resulted in a reduction in elongation at break due to poor compatibility between the phases.

4.5. Conclusion

In conclusion, PBS has emerged as a highly regarded synthetic biopolymer due to its desirable properties. To increase its biodegradability, compatibility, and cost considerations, PBS was blended with ST and GL. However, the resultant PBS/TPS blend films displayed suboptimal water resistance attributed to the hydrophilicity of TPS. To overcome this limitation, the incorporation of CNF was employed. Notably, the addition of 5% CNF to the PBS/TPS blend films yielded some enhancements in barrier properties, including reduced water solubility, enhanced water absorption. The introduction of CNF served as a reinforcement mechanism within the blends, resulting in improved tensile modulus. Moreover, all the films exhibited a uniform and homogeneous visual appearance, free from any visible surface particle. Through the incorporation of thermoplastic starch (TPS), polybutylene succinate (PBS), and cellulose nanofibers (CNF), a sustainable and renewable substitute for traditional packaging materials has been successfully developed. However, further investigations are warranted to optimize the desired properties of the composite materials.

Chapter 5 Results and Discussion: CNF with Chemical Treatment and without Chemical Treatment

The goal of this chapter is comparing the characteristic between PBS/CNF films in which CNFs were produced by chemical treatment, bleaching, and refining with Masuko (Treated) and the other one just refining with Masuko (Untreated). The table below displays the composition of the samples that were utilized in this study.

Table 5.1 Formulation of PBS/CNF blends

	%wt		phr		gr	
	PBS	CNF	PBS	CNF	PBS	CNF
PBS	100	0	100	0	20	0
PBS/CNF1	99	1	100	1.01	19.8	0.2
PBS/CNF10	90	10	100	11.11	18	2
PBS/CNF15	85	15	100	17.65	17	3
PBS/CNF30	70	30	100	42.86	14	6
PBS/CNF50	50	50	100	100	10	10

5.1. Chemical Composition of CNFs

In this investigation, Fourier Transform Infrared (FTIR) spectroscopy was employed to compare the chemical composition of CNF produced through chemical treatment with that of CNF produced solely through refining using Masuko (Untreated). FTIR is a widely employed analytical technique for identifying chemical bonds in materials. Figure 5.1 shows the FTIR spectrum of two different CNFs.

Typically, the FTIR spectra of CNF exhibit multiple peaks that correspond to different functional groups present in the cellulose molecules. The peak at 3,400-3,600 cm^{-1} is associated with the OH stretching vibration of hydroxyl (-OH) groups, which is often broad and intense and can be used to determine the degree of hydrogen bonding in the CNF. The peak at around 2,900 cm^{-1} corresponds to the C-H stretching vibration of methylene groups in the cellulose molecule and can be utilized to assess the degree of crystallinity in the CNF. The spectral bands witnessed in the CNFs spectra within the range of 1639-1648 cm^{-1} correspond to the OH bending of adsorbed water. Despite undergoing the same meticulous drying process, these spectra still contain water

adsorbed in the cellulose molecules, which is difficult to eliminate due to the cellulose-water interaction [76]. A decrease in spectral intensity indicates the removal of hemicellulose and lignin fractions during the processing stage. Similarly, the peak at around 1040 cm^{-1} corresponds to the C-O stretching vibration of ether linkages and can be used to determine the degree of esterification in the CNF. Additional peaks detected in the CNFs spectra at around $1410\text{--}1420\text{ cm}^{-1}$ correspond to the CH_2 scissoring motion in cellulose, while those observed at $1368\text{--}1373\text{ cm}^{-1}$ represent CH bending. The peak at around 1048 cm^{-1} corresponds to C-O-C pyranose ring stretching vibration in cellulose. Similarly, the peaks at $1154\text{--}1159\text{ cm}^{-1}$ represent the C-C ring stretching band. However, the prominent peak detected at around 1738 cm^{-1} indicating the existence of the lignin and hemicelluloses [77].

By conducting a comparison of the FTIR spectra of CNF produced using different methods, it is possible to discern differences in the intensity and position of these peaks, thereby providing valuable insights into the chemical composition of the CNF and its potential effects on the properties of the final product.

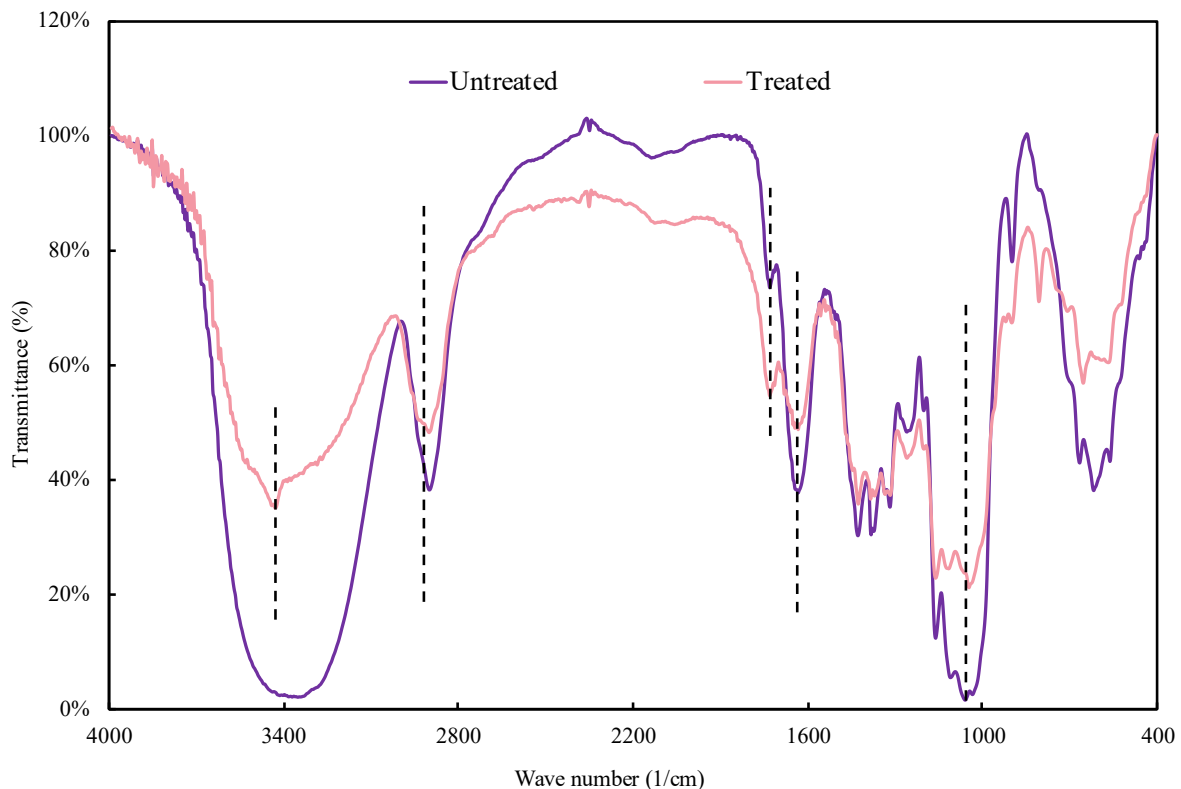


Figure 5.1 FTIR spectra of treated CNF and untreated CNF.

5.2. Size Distribution of Fiber before and after Producing CNF

The diameter of the cellulose nanofibers (CNFs) can be influenced by several factors, including the raw material used, the processing method, and the extent of mechanical and/or chemical treatments. Figure 5.2 presents the size distribution of these CNFs, and also the diameter and length of the initial fibers.

In figure 5.2 and 5.3, it can be observed that the diameter range of both types of fibers is similar, with the main difference between them being their length. Due to the long length of the fibers, it is recommended to cut them into smaller sizes before further processing. To achieve this, the fibers were milled using two different sieves, with a 1.5 mm sieve used for untreated fibers and a 3 mm sieve used for chemically treated fibers. The selection of the 3 mm sieve for the chemical treatment process was based on the need to wash the samples several times during the treatment process. Using a smaller sieve size could result in significant sample loss during washing, which would affect the accuracy and reproducibility of the results.

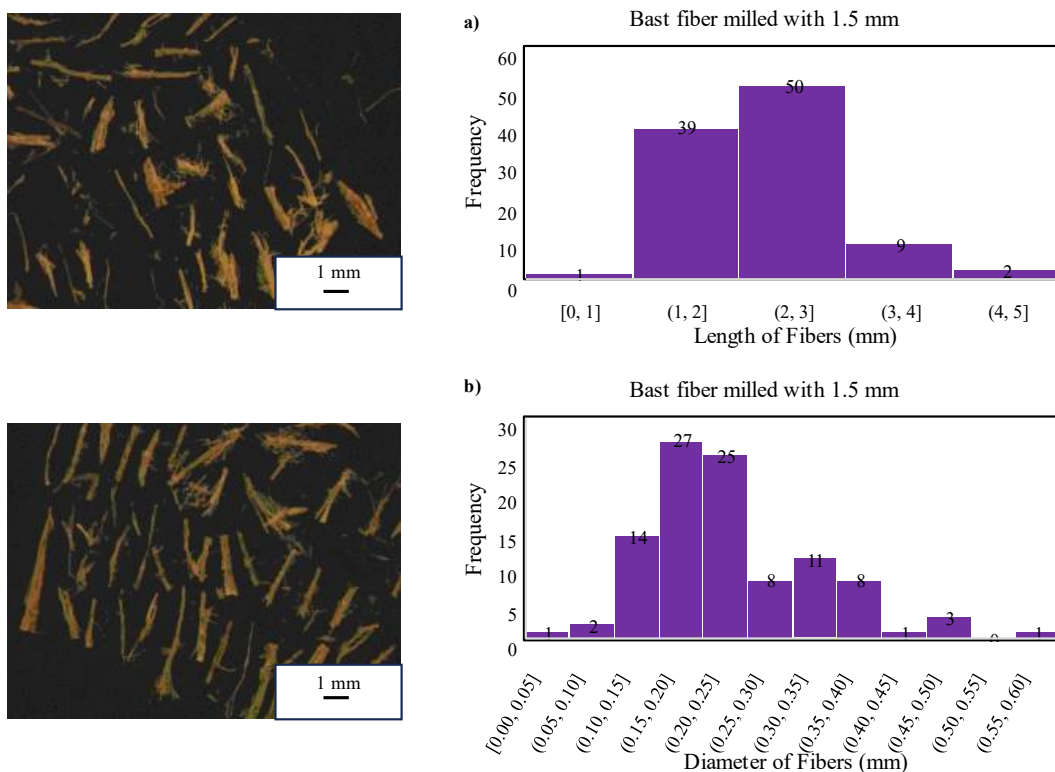


Figure 5.2 Size distribution of hemp fiber before processing analyzed by optical microscope a,b) length and diameter of fiber milled with 1.5 mm.

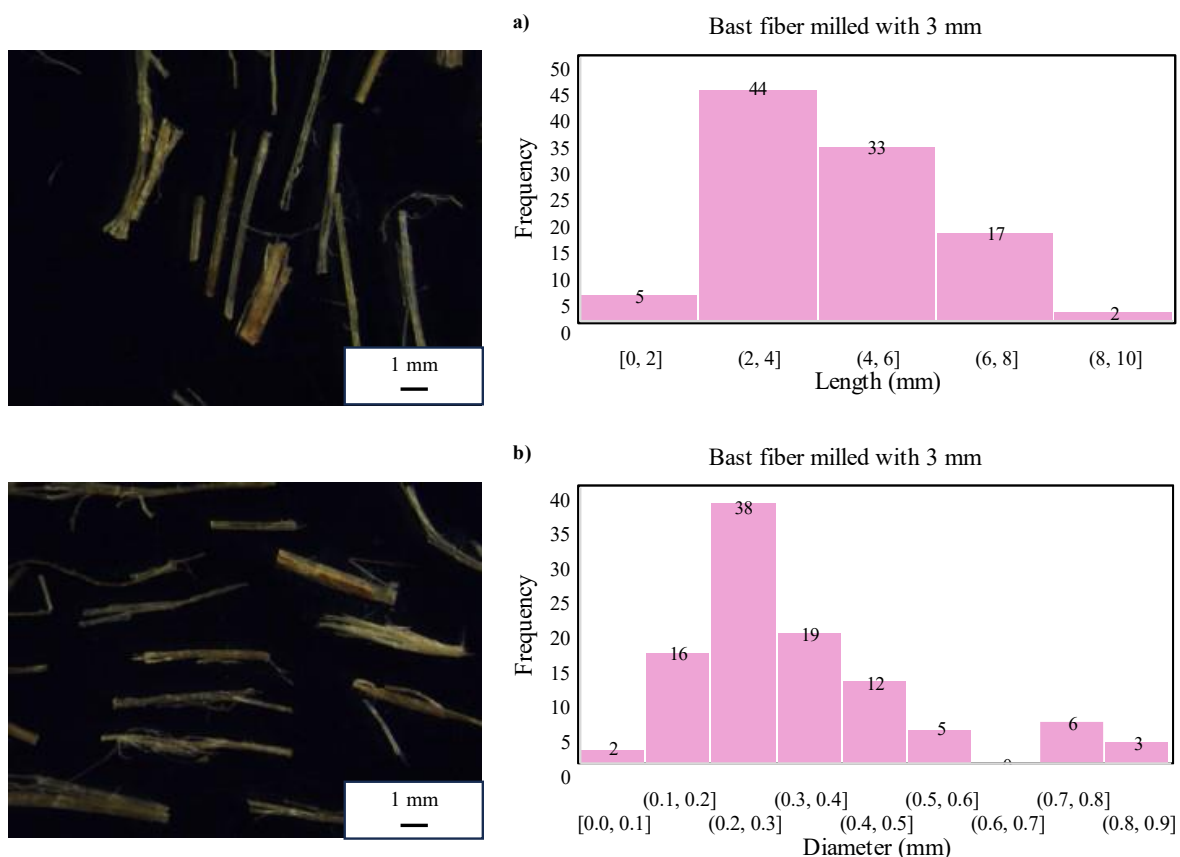


Figure 5.3 Size distribution of hemp fiber before processing analyzed by optical microscope a,b) length and diameter of fiber milled with 3 mm.

Figure 5.4 presents the transmission electron microscopy (TEM) images showing the size of the diameter of two fibers after processing. Image a shows the untreated fiber, while image b shows the fiber after undergoing chemical treatment and bleaching.

The reduction in diameter size can be seen in both pictures. The chemical treatment and bleaching processes could have caused swelling and deformation of the fibers, resulting in an increase in their diameter. The use of chemicals such as sodium hydroxide and hydrogen peroxide can break down the lignin and hemicellulose in the fiber, making it more accessible for mechanical refining. However, this can also cause the cellulose fibers to swell and become more pliable, resulting in an increase in their diameter. The Masuko grinder is a mechanical method of producing CNFs that involves repeated high-pressure shear forces to break down the cellulose fibers into smaller fibrils. This method can also result in CNFs with smaller diameters. Also, it can be deduced that the existence of lignin in nanofibrils decreased the gathering of cellulose fibrils.

The size and morphology of the CNFs can have a significant impact on their properties and potential applications. For example, smaller diameter CNFs may have higher surface area, which can enhance their mechanical properties, increase their reactivity, and improve their dispersion in polymer matrices. However, it is also important to consider other factors such as the aspect ratio and surface chemistry of the CNFs in determining their suitability for specific applications.

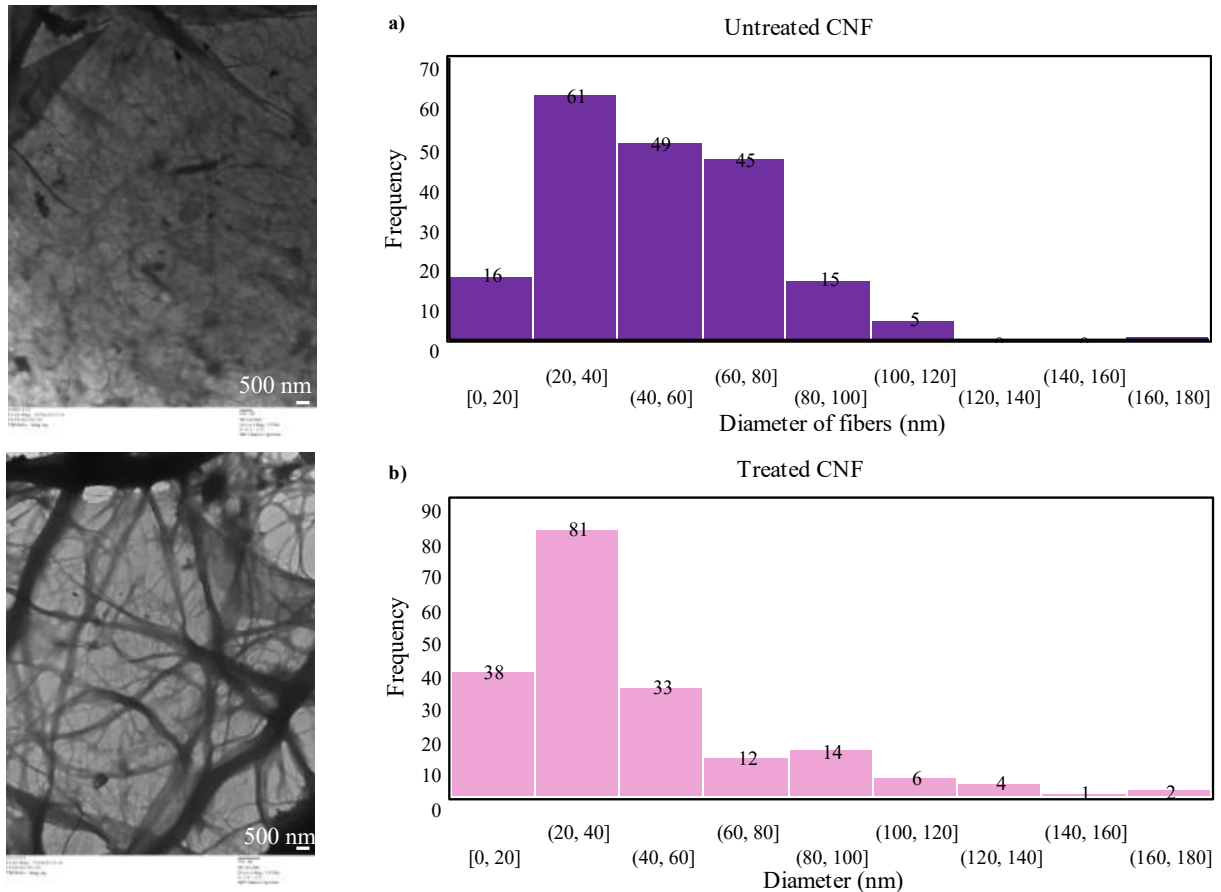


Figure 5.4 Size distribution of fiber after processing analyzed by TEM a) untreated CNF, b) treated CNF.

5.3. Morphological Characterization of CNFs

Figure 5.5 presents a detailed analysis of the two types of CNFs produced from untreated and chemically treated fibers. The images include TEM, SEM, and microscope views, providing a comprehensive examination of the morphology of the fibers after processing. The TEM images (a and d) reveal the size and shape of individual CNFs, while the SEM images (c and f) show the overall morphology of the CNF network. The microscope images (b and e) provide a more macroscopic view of the CNF.

The TEM images of both CNFs (a and d) exhibit a fibrous morphology with a non-uniform structure, where some fibers seem to be twisted and intertwined. The images indicate that CNFs possess a long, slender, and flexible shape, which is characteristic of nanofibers. Furthermore, the intertwined and interconnected fibers appear to form a network-like structure. Due to the tightly packed arrangement of the fibers, their exact diameter is difficult to determine. Nonetheless, the images suggest that the treated fibers are relatively thick and long compared to other CNF types. Moreover, the surface of the chemical-treated CNF appears to be smoother and free of irregularities. In contrast, the individual fibers in the Masuko-ground CNF seem to be shorter and more fragmented.

Upon comparison of the microscope images (b and e), it can be observed that the treated CNF displays a tendency to aggregate, resulting in a cotton-like shape. Conversely, the untreated CNF exhibits a powderier appearance.

SEM images provide a high-resolution surface view of the CNF samples after drying with spray dryer. The SEM results (c and f) indicate that the CNF suspension underwent a significant transformation after undergoing the spray drying process. According to Peng [78], two distinct droplets were formed in the drying chamber during the CNF suspension atomization process due to the size and morphology of the original CNF fibrils in the suspension. The suspension comprised of long and large cell wall sections coexisting with relatively short and skinny CNF fibrils. In the first scenario, the length of the CNF fibril exceeded the diameter of the formed droplet, and the CNF fibril was sufficiently rigid to protrude outside the droplet. In the second scenario, all CNF fibrils were enclosed within the droplet, and some may have been longer than the droplet's diameter. However, these CNF fibrils were too weak to overcome the water's surface tension and folded inside the droplet. When the CNF suspension droplets came in contact with hot gas in the drying chamber, water evaporation occurred. Consequently, the spray-dried CNF suspension formed fibrous and agglomerate particles, consisting of needle-like fibril shapes and large cell wall sections, which were obtained separately in dry form particles. In figure c, the surface of the CNF appears to be relatively smooth and free of irregularities, which may be attributed to the chemical treatment and bleaching process. However, some surface roughness may occur during the drying process of untreated CNF. Finally, the individual fibers are found such as bundled or intertwined, forming a network-like structure.

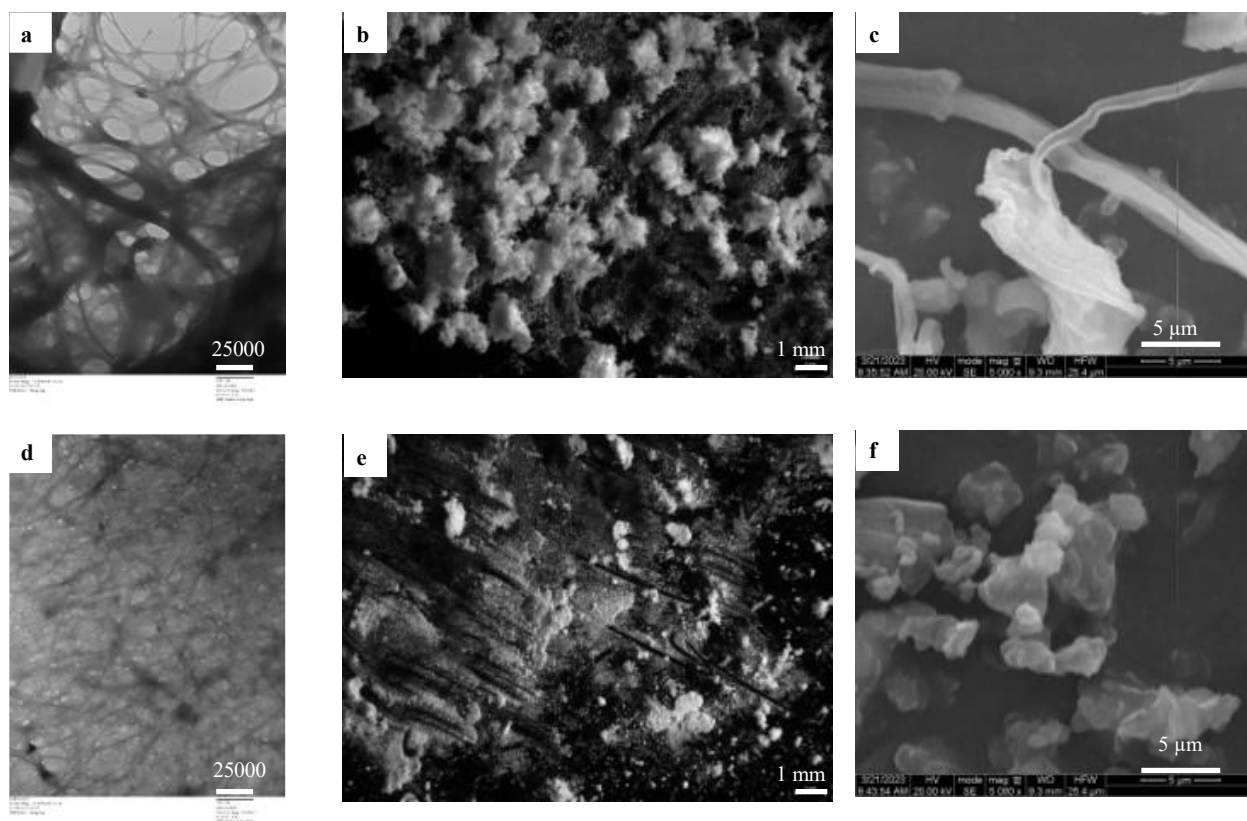


Figure 5.5 TEM, Microscope and SEM images for a, b, c) treated CNFs and d, e, f) untreated CNFs.

5.4. Morphology of Films

In this study, the morphologies of PBS/CNF composite films were analyzed using SEM. The results are presented in figure 5.6, which shows SEM images of the cross section of treated and untreated of three different compositions of PBS/CNF films. Based on the SEM analysis of PBS/CNF composite films, it can be concluded that there is poor dispersion and incompatibility between CNF and the PBS matrix, as evidenced by the pronounced CNF agglomeration. However, there is no cracks or void formation at the interface, indicating that CNF can still be dispersed into the PBS matrix. By comparing the treated and untreated samples, it can be observed that the agglomeration of fibers in the treated samples is less prominent, resulting in a more homogenous structure. In other words, the chemical treatment process has some effects on the dispersion of the fibers in the matrix, leading to a more uniform distribution and a smoother surface.

This statement suggests that the observation of a better dispersion of CNF in the PBS matrix after treatment indicates that there is potential for improvement in the mechanical and barrier properties of the composite material. This is because better dispersion of CNF can lead to better

load transfer between the CNF and the matrix, resulting in enhanced mechanical properties. However, further testing and analysis would be necessary to confirm these expectations.

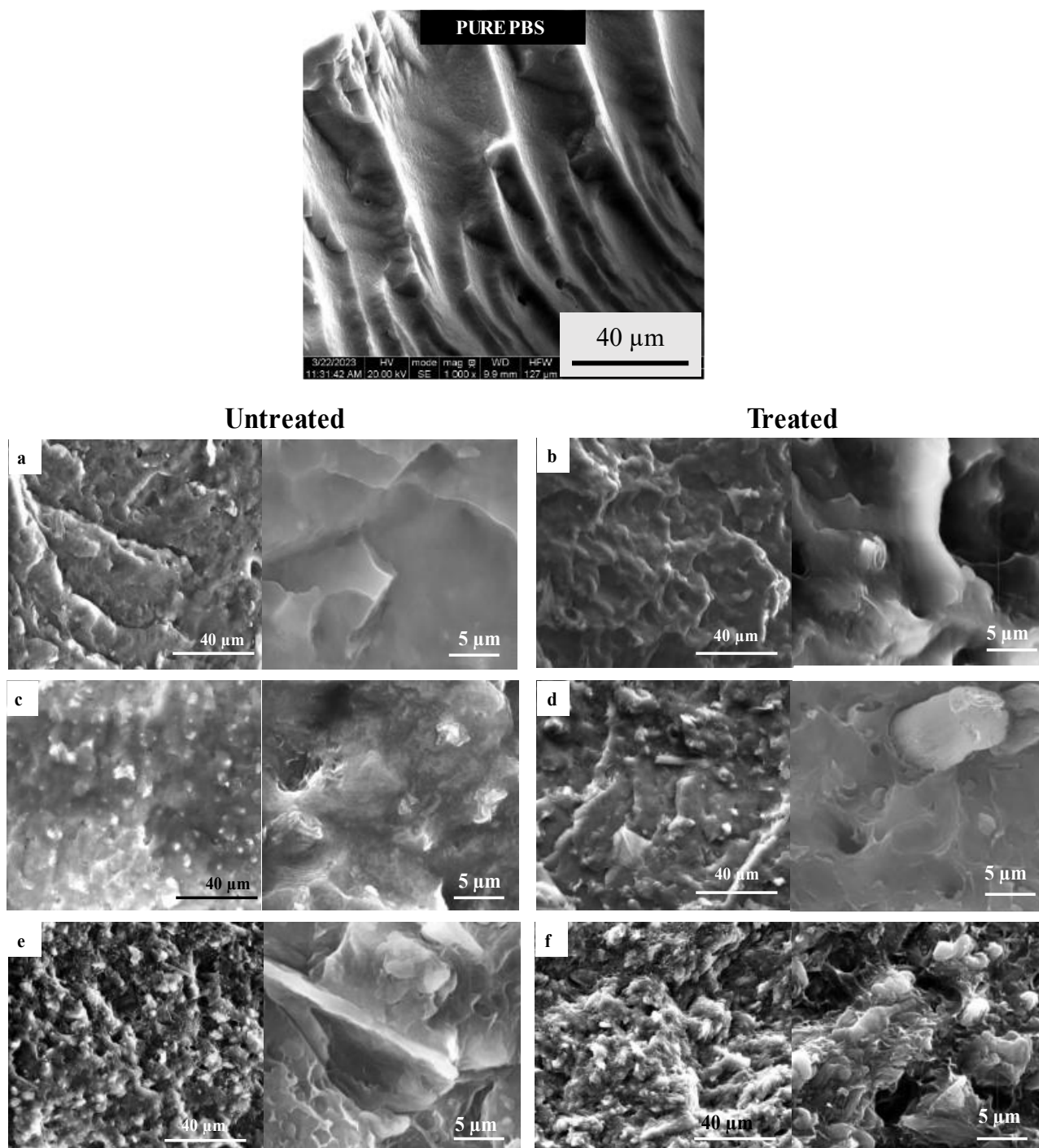


Figure 5.6 SEM images of PBS/CNF films; a, b) 10% CNF, c, d) 15% CNF, e, f) 50% CNF.

In a study conducted by Liang et al. [68], biodegradable polymeric composites were fabricated by blending PBS with kenaf fiber (KF) using a melt mixing technique. The fiber was found to be partially covered by a thin layer of PBS matrix, but there was also observed separation between the fiber and the polymer matrix. In composites with a higher amount of fiber, the fracture surface exhibited irregularities, and fiber pullout was more prominent than fiber fracture. Furthermore, the detachment of the PBS matrix from the fiber was observed.

5.5. Water Absorption, Solubility, and Moisture Content

The water moisture content graphs for all composite films are displayed in figure 5.7. Also, the water sorption values and water solubility of pure PBS, PBS/CNF composites are also shown in the figure 5.8.

The moisture uptake behavior of composites containing different amounts of CNF was investigated, and it was found that increasing the CNF content resulted in a higher level of moisture absorption. This is attributed to the hydrophilic nature of cellulose. The water solubility of these composites is closely related to the degree of water absorption. It is generally observed that materials with high W_a values are more likely to dissolve in water, as water molecules are adsorbed onto the hydroxyl groups of the material through hydrogen bonding. This weakens the film structure, making it more susceptible to dissolution.

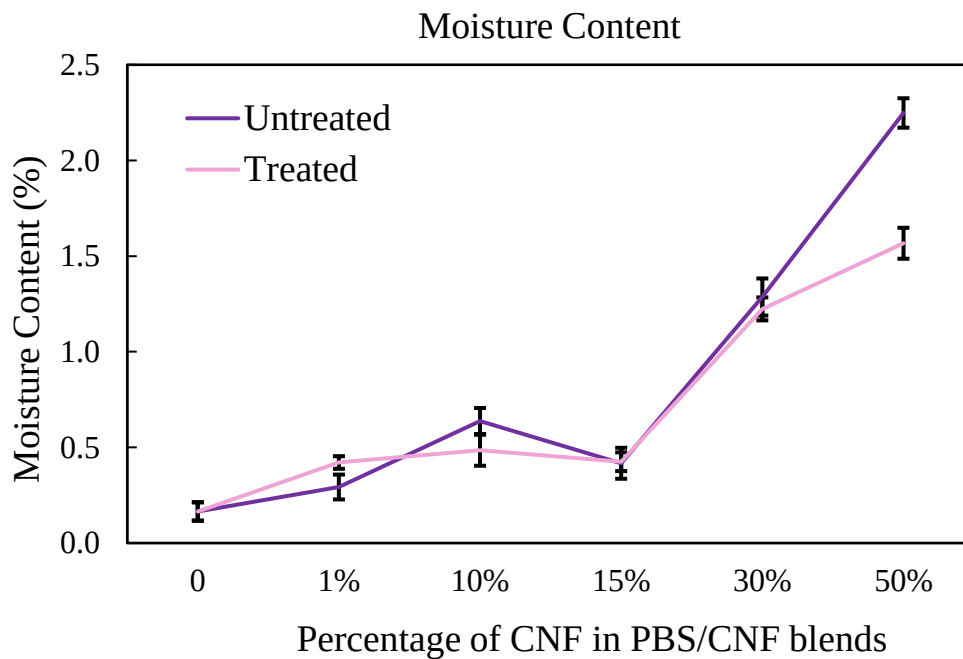


Figure 5.7 The comparison between the moisture content value for treated and untreated composites.

The water uptake rate of pure PBS was found to be the lowest compared to all other samples. This can be attributed to the high hydrophobicity of pure PBS. Based on the data, the composite made with the chemically treated CNF and Masuko-ground CNF exhibited a lower water absorption capacity compared to the composite made with only Masuko-ground CNF. This indicates that the composite made with the chemically treated CNF has better water resistance properties than the composite made with only Masuko-ground CNF.

The water absorption difference observed in the two composites can be attributed to various factors, including the CNF's morphology, dispersion in PBS matrix, and interfacial bonding [15]. Chemical treatment of CNF removes most hemicelluloses and lignin, resulting in a purer and more crystalline cellulose material with lower water absorption capacity. Additionally, the treatment can introduce functional groups on the CNF's surface, improving the compatibility and adhesion with the polymer matrix (PBS), leading to a more stable composite structure with reduced moisture absorption and solubility. Hence, the composite made with chemically treated CNF and Masuko-ground CNF had lower water solubility and moisture content due to the changes in CNF's surface chemistry and physical properties.

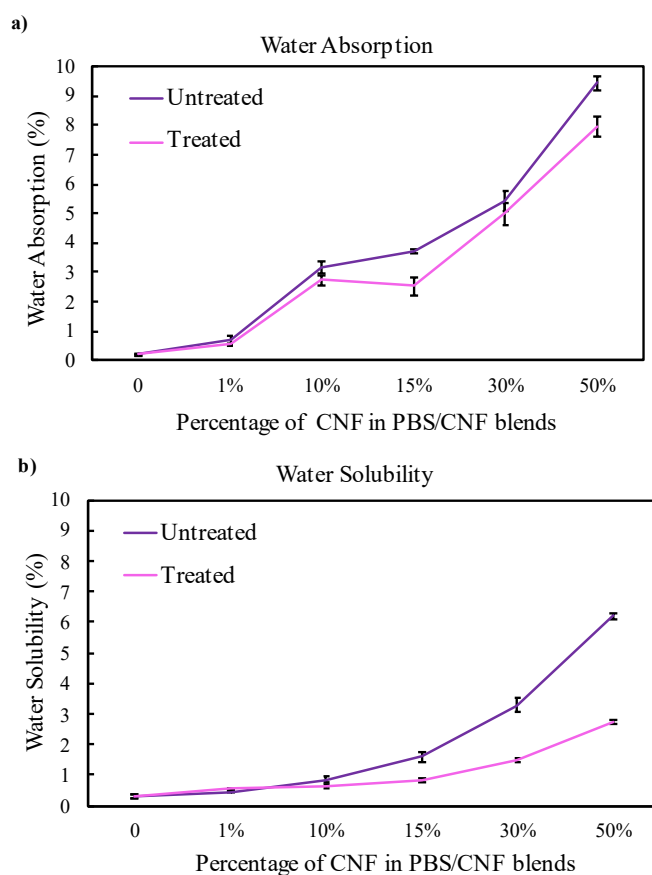


Figure 5.8 Water absorption and solubility for neat PBS and its composites.

5.5. Water Vapor Permeability (WVP)

The measurements of water vapor permeability (WVP) for the samples were conducted and visually represented in Figure 5.9. Until the CNF content reaches 15%, there is no significant difference in the WVP compared to the pure PBS and some improvements can also be seen in some cases. CNF beyond this point may lead to changes in the composite structure, which could result in increased WVP. Water vapor permeability and water absorption depend mainly on the density and internal packing of the films and coatings. The hydrogen bonding between fibrils in films is responsible for their higher density, leading to less water vapor permeability. The chemical treatment of CNF removes hemicelluloses and lignin, resulting in a more ordered structure and fewer pores that obstruct water molecule movement. Additionally, it enhances the compatibility and adhesion between CNF and PBS, leading to a more compact and cohesive composite structure with fewer voids and defects.

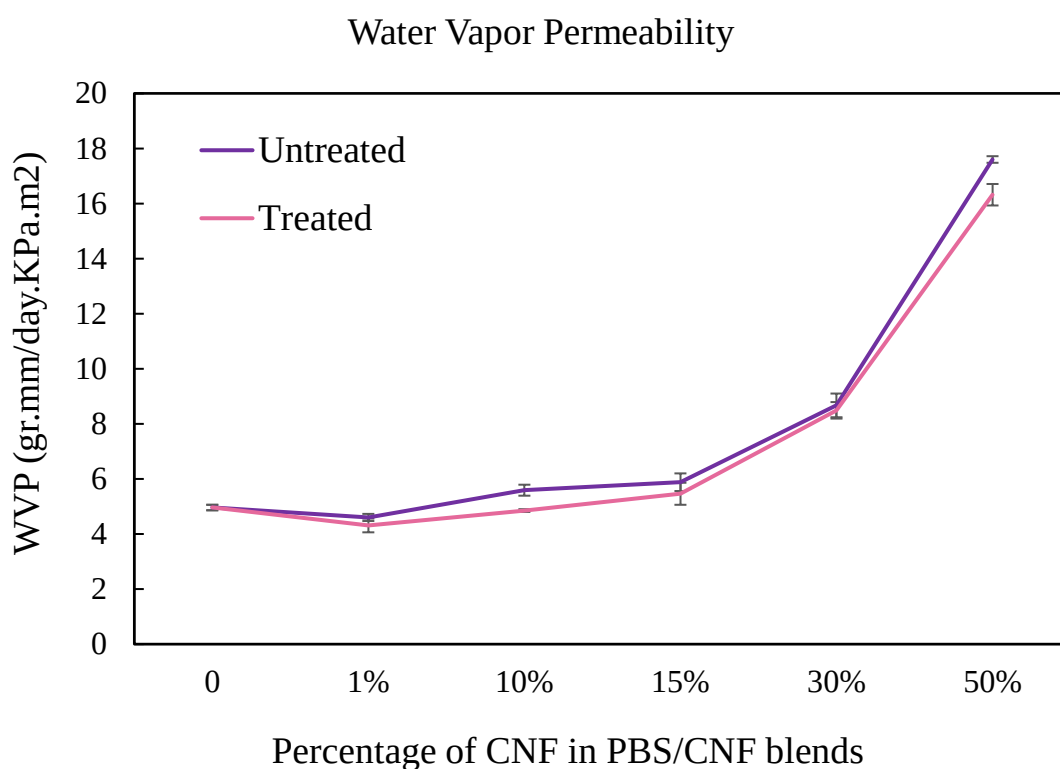


Figure 5.9 Water vapor permeability of different nanocellulose films.

5.6. Oxygen Permeability

Figure 5.10 illustrates the oxygen permeability of pure PBS and different nanocellulose films. As a result, the oxygen permeability of the composite material is reduced compared to that of pure PBS. The addition of CNF to PBS results in a composite material that has a more compact and uniform structure. CNF has a fibrous morphology with a high aspect ratio, which enables it to form a network structure that helps to reduce the size and number of pores in the composite material. This network structure of CNF fibrils also acts as a barrier for gas molecules, such as oxygen, and slows down their diffusion rate through the material. Therefore, the addition of CNF to PBS can improve its gas barrier properties, which is useful for applications where oxygen permeability needs to be minimized, such as in packaging materials for food or pharmaceuticals. Furthermore, the utilization of treated CNF can enhance the oxygen barrier performance when compared to untreated fibers due to the same reasons previously discussed. The chemical treatment process of CNF can improve the purity and crystallinity of the cellulose material while also introducing functional groups on the surface of the CNF, which leads to a more stable composite structure with reduced oxygen permeability.

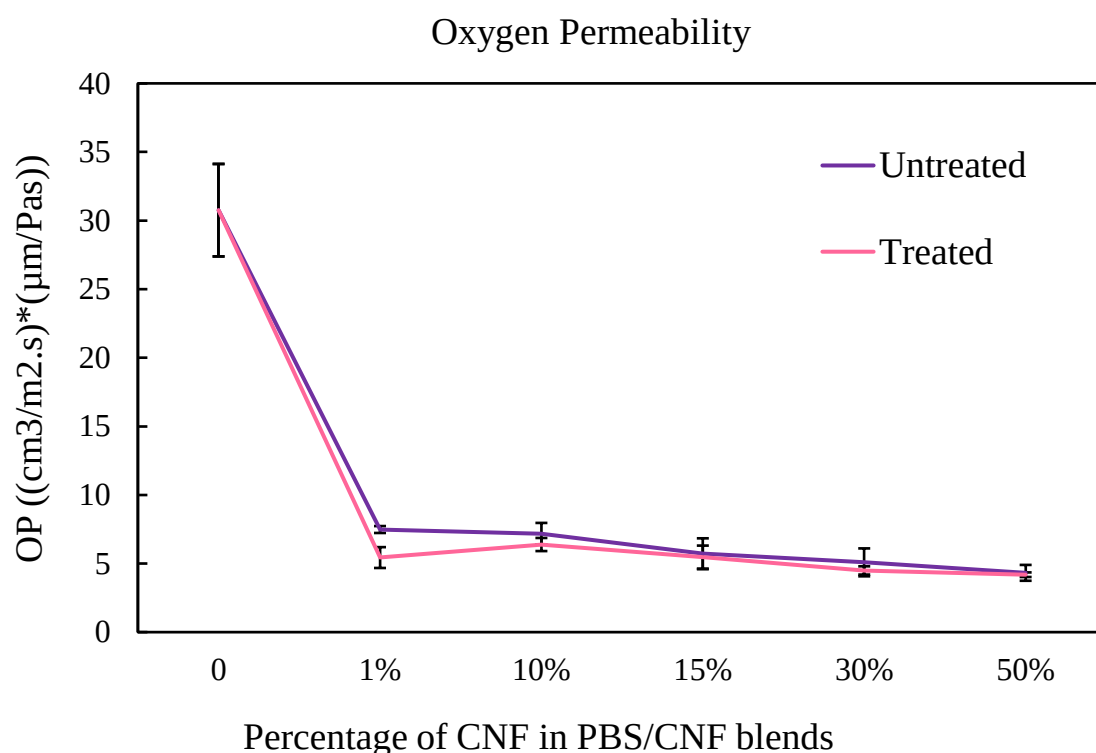


Figure 5.10 Oxygen permeability of PBS and its composites.

5.7. Mechanical Properties

The mechanical characteristics of nanocomposite films are influenced by several factors including the composition, orientation of the filler reinforcements, and the interaction between the filler and matrix [67]. Figure 5.11 illustrates the tensile strengths, tensile modulus, and elongation of the nanocomposite films with CNFs, including both treated and untreated CNFs, in comparison to pure PBS. The pure PBS exhibits a tensile strength of 23 MPa, a modulus of 240 MPa, and a fracture strain of 450%. In figure 5.11, it can be observed that the addition of CNF increases the composite's stiffness, making it more rigid and less prone to deformation under stress. As a result, the tensile modulus increases. This indicates that there is a transfer of stress from the polymer matrix to the stiffer fiber. When compared to neat PBS, the tensile modulus of PBS/CNF composites containing 30 and 50 wt % of CNF increase by 75% and 140%, respectively. Nonetheless, incorporating CNF in the composite material may also lead to the emergence of imperfections and vulnerable regions, such as gaps or clusters of CNF, that result in a reduction of the tensile strength and fracture strain of the composites. This may be attributed to the inadequate adhesion between CNF and PBS, resulting in poor interfacial interaction and debonding of the matrix from the fiber during tensile deformation. Debonding creates voids, which lowers the tensile strength because cracks can easily propagate through regions containing voids. Therefore, the reduction in tensile strength and fracture strain can be attributed to the presence of voids due to debonding caused by poor adhesion between CNF and PBS. A comparison of the two types of CNF revealed that the increase in tensile modulus resulting from the chemical treatment and bleaching of the CNF was greater than that observed with mechanical treatment alone. These findings suggest that the chemical treatment and bleaching of the CNF can alter its surface chemistry and physical properties, which can affect the interaction between CNF and PBS, impart greater reinforcement to the composite material, thereby resulting in a higher tensile modulus.

In general, it is observed that the incorporation of a large amount of fiber in a composite material can cause a reduction in the failure strain. This is due to the fact that all of the elongation in the composite comes from the polymer matrix, as the CNF fiber is comparatively rigid to PBS. When the amount of filler is increased, it leads to a decrease in the amount of polymer available for elongation. Additionally, higher amounts of fiber (30% and 50 %) can result in fiber agglomeration, which can create regions of concentrated stress where less energy is required for crack propagation. During tensile deformation, the inefficient transfer of stress near these stress-concentrated regions may cause the specimens to fail before reaching the yield point.

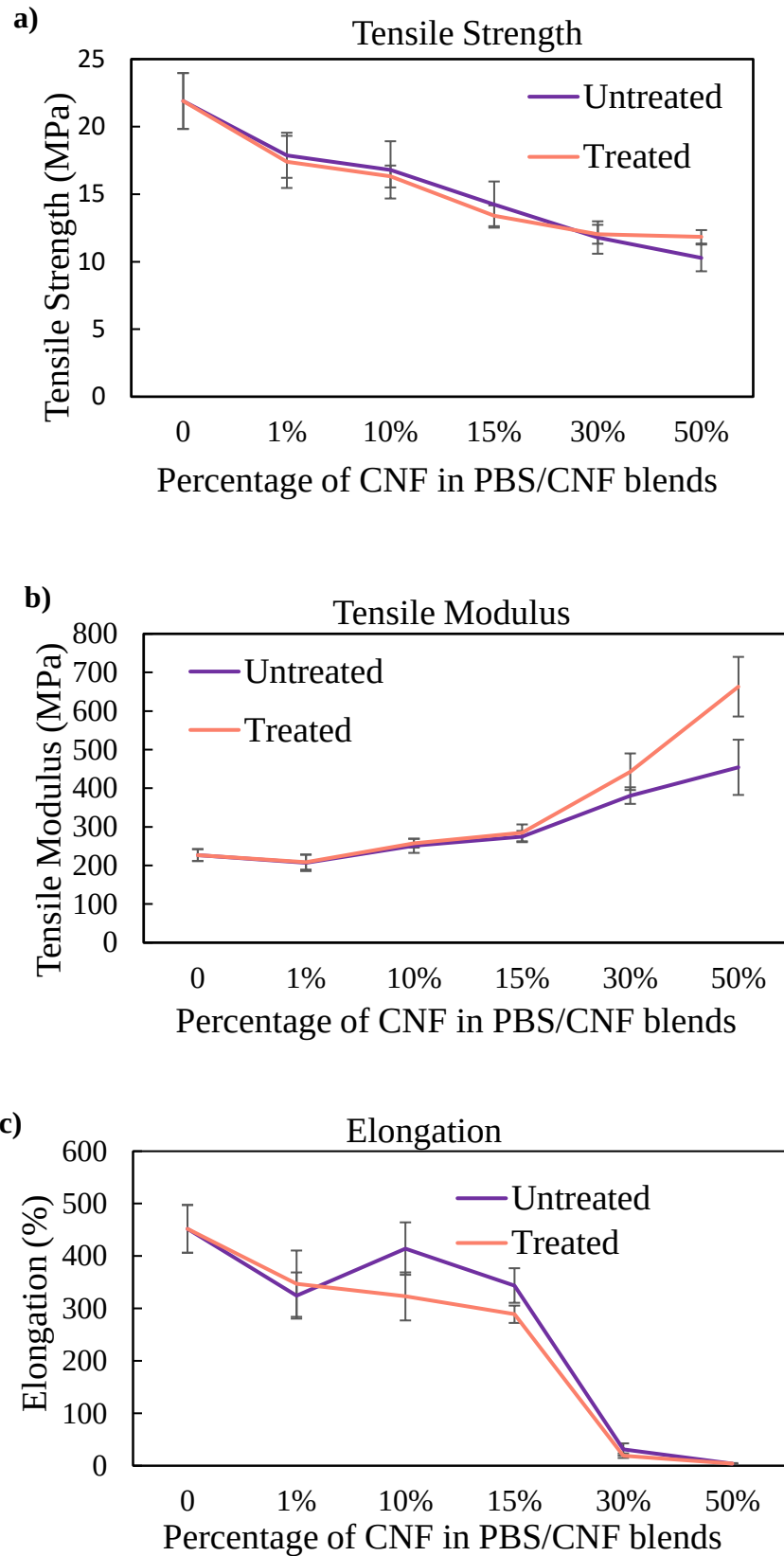


Figure 5.11 Tensile properties of PBS and its composites.

Platineks et al. [67], investigated the use of microcrystalline cellulose (MCC) and nanofibrillated cellulose (NFC) fillers in PBS matrix for wood-like composite applications. They found that adding cellulose fillers led to an increase in Young's modulus, reaching a maximum value of 626 MPa for a 5/5 ratio of MCC/NFC. However, there was a decrease in tensile strength and elongation, indicating weaker interactions between the fillers and matrix. NFC showed poorer mixing with the PBS matrix compared to MCC, possibly due to differences in cellulose structure, surface area, and crystallinity. The decrease in ductility was explained by the increased volume of cellulose at higher loading, restricting polymer chain movements and resulting in reduced elongation. Similar effects have been observed in PBS/plant fiber compositions.

5.8. Optical Transmittance

The examination of the optical characteristics of films is crucial in deciding their suitability for usage in the food industry, as it can determine their potential applications in packaging or coating of food and bioproducts. The film's ability to extend the shelf life of fat-based food products by absorbing UV light and reducing oxidative degradation is significant [63]. The UV-visible spectra of the films are presented in Figure 5.12 and Table 5.2 presents the light transmittance percentage for various films, respectively.

The addition of CNF (both treated and untreated) to the biopolymer matrix resulted in a decrease in film transmittance, which can be attributed to the opaqueness and whiteness of the nanoparticles. This may impede the passage of light through the interior of the biopolymer. The films presented very low light transmittance percentages in the UV range between 200 and 280 nm. This indicates that the films have an excellent ability to block or absorb UV light, which is crucial for protecting food and bioproducts from degradation caused by UV radiation. The low transmittance percentage suggests that these films can provide effective protection against UV light and thus improve the shelf life of food and bioproducts.

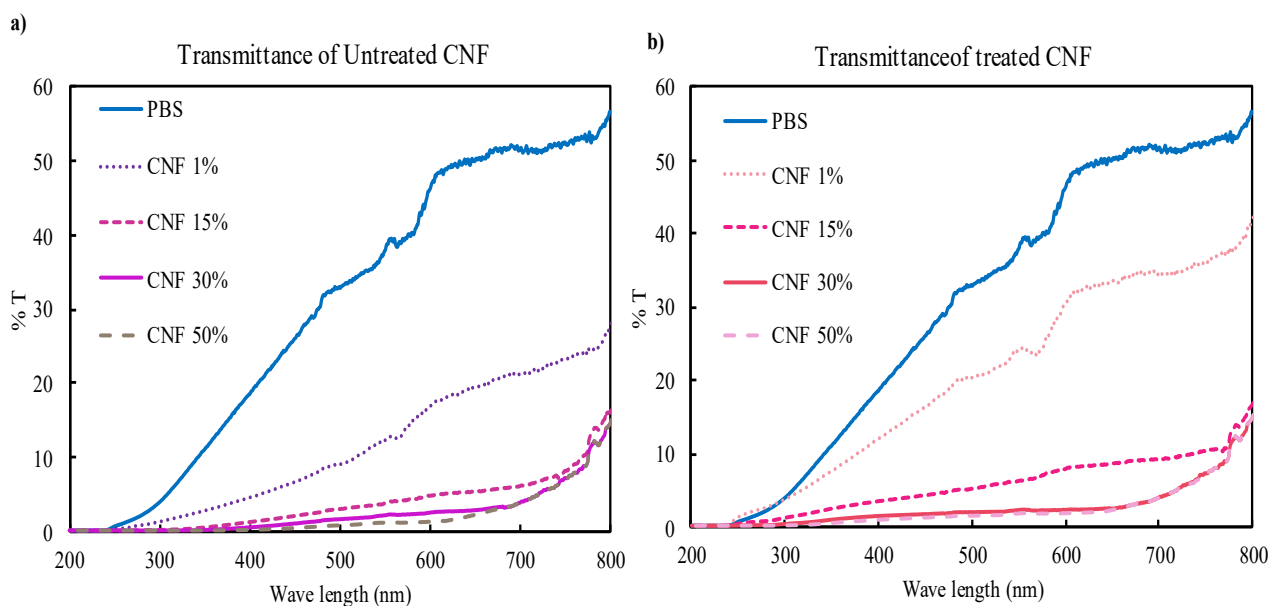


Figure 5.12 Transmittance UV-Vis spectra of PBS/CNF films a) untreated CNF, b) treated CNF.

Table 5.2 Light Transmittance (%) of different films with untreated and treated CNFs

Sample		Light transmittance (%) at various wavelengths (nm)							
		200	280	350	400	500	600	700	800
Untreated CNF	PBS	0.003953	2.0577	10.9861	18.4674	32.8061	46.3832	51.7784	56.5054
	CNF 1%	0.006807	0.7249	2.6617	4.4636	8.9484	16.8220	21.3062	27.9744
	CNF 15%	0.003950	0.0298	0.4179	1.1560	2.9404	4.741	6.1204	16.4295
	CNF 30%	0.003941	0.00187	0.0790	0.4301	1.5483	2.4523	3.9253	15.1678
	CNF 50%	0.003935	0.00076	0.0060	0.0886	0.7118	1.2264	3.9254	15.1463
Treated CNF	CNF 1%	0.003956	2.5083	7.5229	11.8832	20.2597	30.2460	34.7230	42.3065
	CNF 15%	0.003927	0.6461	2.3592	3.3964	5.1104	7.8639	9.2804	17.0153
	CNF 30%	0.003934	0.0820	0.8264	1.3325	1.8507	2.1790	3.9253	15.1529
	CNF 50%	0.003929	0.0130	0.3674	0.8086	1.3668	1.6970	3.9241	15.1458

Table 5.3 displays the numerical values of the transparency index. Transparency index is a numerical value that represents the transparency or clarity of a film. It is calculated by dividing the absorbance at a specific wavelength (often 600 nm) by the thickness of the film. Higher film transparency is represented by lower transparency values. This indicates that more light can pass through the film so, it is more transparent.

Table 5.3 Transparency index of films with treated and untreated CNFs

sample	PBS	CNF 1%	CNF 15%	CNF 30%	CNF 50%
T _r (untreated)	1.517	3.871	8.434	10.665	11.048
T _r (treated)	1.517	2.597	7.079	8.393	8.047

Despite the fact that incorporating CNF in PBS films decreased their transmittance, the resulting nanocomposites maintained acceptable levels of transparency when compared to the control film. This can be observed in figure 5.13, which shows a photograph of the control film (PBS) and the nanocomposites, with readable text beneath each. Films made from PBS as a polymer base are well-known for their colorless and transparent properties, making them ideal for applications in food packaging where visualizing the product is important. The ability of the nanocomposites to maintain their transparency even with the addition of CNF is a desirable characteristic for their potential use in food packaging. As can be seen in the picture, using untreated CNF due to containing impurities or residual lignin shows yellowish color in the resulting film.

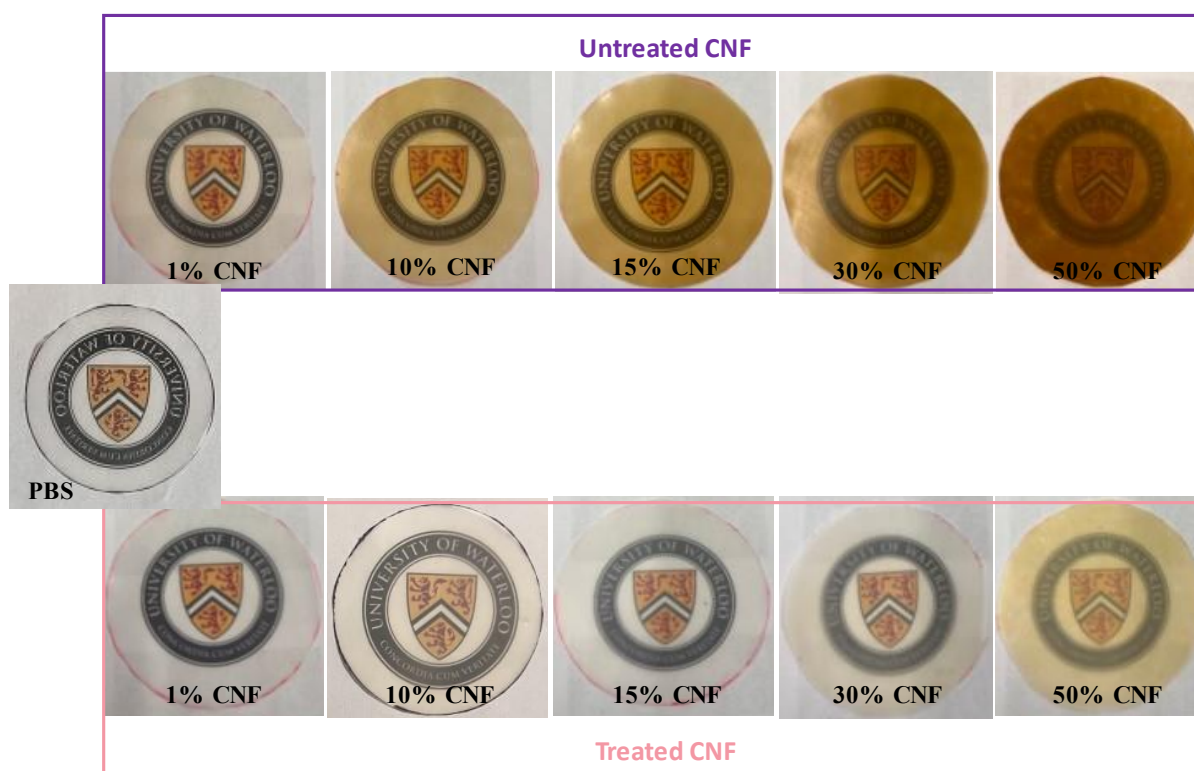


Figure 5.13 The pictures showing the films obtained using various concentrations of CNF.

In Figure 5.14, the diverse colors of each film, as measured by a colorimeter, are presented. The white color represents transparency in the films. During the experiment, white paper was placed underneath each film, and as a result, when light passed through the films, the white paper was visible through them, indicating their transparency.

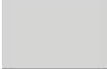
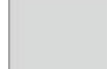
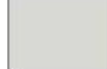
PBS		CNF1%	CNF10%	CNF15%	CNF30%	CNF50%
 sRGB 213,213,210	Untreated CNF	 sRGB 213,209,196	 sRGB 197,177,135	 sRGB 185,158,108	 sRGB 162,126,67	 sRGB 134,94,39
	Treated CNF	 sRGB 213,213,210	 sRGB 216,218,218	 sRGB 217,217,212	 sRGB 216,214,201	 sRGB 214,204,174

Figure 5.14 The different colors of each film, as measured by a colorimeter.

5.9. Conclusion

In conclusion, the successful production of cellulose nanofibers (CNF) from hemp using a series of treatments, including alkaline and acid treatment, bleaching, and refining with the Masuko method, has yielded promising outcomes. The resulting CNF films derived from lignin-containing CNF exhibited a yellowish color, which offers specific advantages for packaging applications, while the films from low-lignin-containing CNF demonstrated enhanced transparency. Interestingly, samples with higher lignin content displayed higher water vapor transmission rates. SEM observations revealed that the incorporation of less than 15% CNF in the film formulation significantly improved barrier performance by mitigating agglomeration and structural defects, leading to enhanced resistance against water vapor permeation.

Chapter 6 Results and Discussion: Effect of Different Chemicals on Dispersion of Untreated CNF

In this chapter, the main focus was on the utilization of untreated CNF which was refined using a Masuko grinder. The aim was to find effective chemicals that could improve the dispersion of CNF in water, thereby reducing agglomeration. These chemicals were added to the CNF suspension in a proportion of 5% wt. of CNF, and the resulting suspension was then subjected to drying using a spray dryer. The chemicals utilized for this purpose included Sodium chloride (NaCl), Sodium dodecyl sulfate (SDS), Cetyltrimethylammonium bromide (CTAB), Polyethylene oxide (PEO), Citric acid, and Triton X-100. After drying, the CNF containing these chemicals was used to fabricate films with a composition of PBS90/CNF10. In the initial part of the study, the impact of these chemicals on the dispersibility and structure of CNFs was examined. The subsequent part of the investigation focused on evaluating any discrepancies in the barrier and mechanical characteristics of the films resulting from the usage of these chemicals.

6.1. Analyzing the Appearance and Dispersibility of CNF Spray-dried

6.1.1. Effect on Chemical Composition

The current study utilized Fourier Transform Infrared (FTIR) spectroscopy to examine and compare the chemical composition of CNF treated with various chemicals. Figure 6.1 displays the FTIR spectrum of the different CNFs examined in the investigation.

Upon comparing the FTIR results of various CNFs, it was observed that there was a consistent trend in the chemical composition of all the CNFs. However, the intensity of certain peaks in the FTIR spectra differed depending on the type of chemical used to disperse the CNFs. This suggests that the addition of chemicals affects the arrangement of chemical bonds in the CNFs, leading to changes in their FTIR spectra. The differences in peak intensities provide information about the extent of chemical interactions between CNFs and the dispersing chemicals.

Based on the FTIR analysis, the most significant changes were observed in the CNFs treated with PEO and citric acid. These two chemicals caused changes in the position and intensity of certain peaks in the spectrum. Some peaks related to C-H stretching (2900 cm^{-1}) and C-O stretching (900 cm^{-1}) showed a little shift towards a lower wavenumber, suggesting the formation

of hydrogen bonds between the functional groups of CNF and PEO. This interaction could lead to improved dispersion and reduced agglomeration of CNF in the composite matrix.

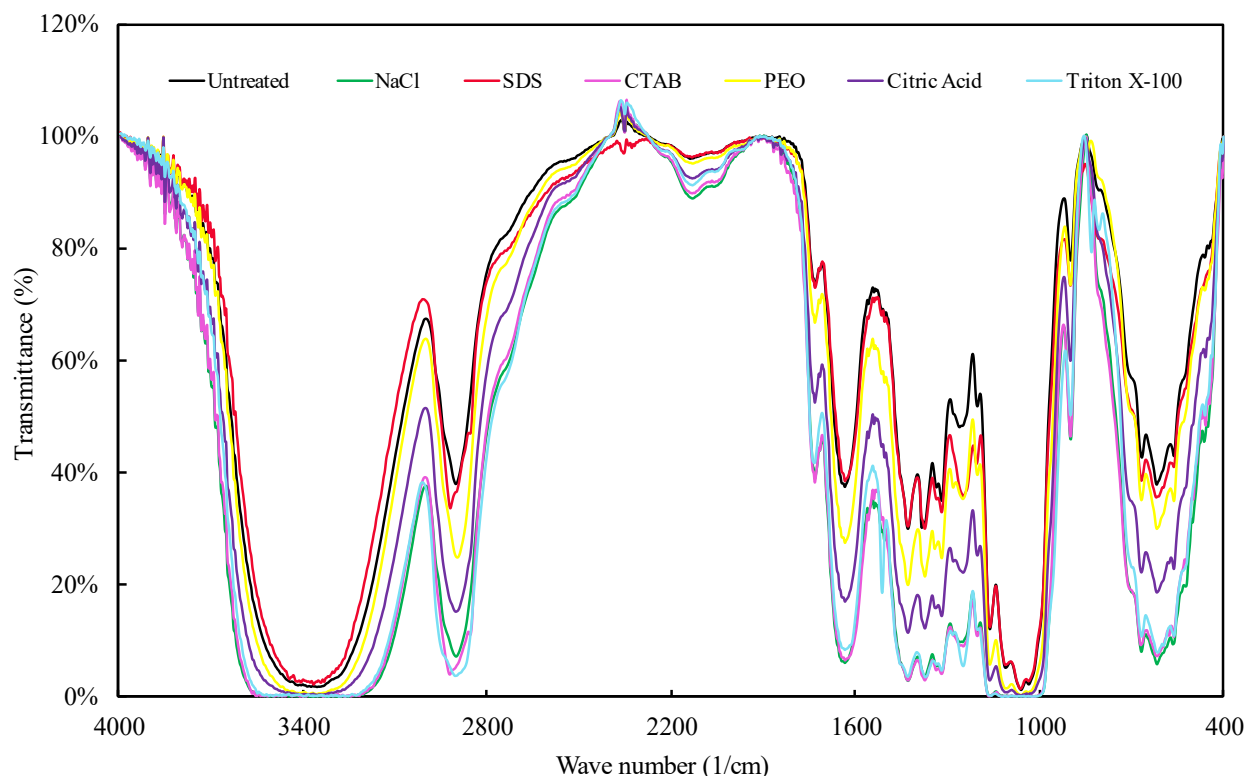


Figure 6.1 FTIR spectra of untreated CNF with different chemicals.

6.1.2. Morphological Characterization of Different CNFs

Through FTIR peak analysis, structural changes were observed in the CNF after the addition of various chemicals. To further investigate, both a microscope and SEM were utilized to examine the CNF samples. Figure 6.2 displays the microscope image on the left and SEM image on the right. The SEM images provided insight into the distribution and morphology of the CNF, highlighting any changes that may have been caused by the added chemicals. The microscope, on the other hand, revealed the overall morphology of the CNF samples and any potential agglomerations or other features that could have arisen from the chemical additions.

Although the microscope images did not reveal any significant differences, the SEM images showed that some chemicals resulted in improved dispersion and less agglomeration, such as NaCl and SDS. On the other hand, Triton X-100, Citric acid, and CTAB led to increased agglomeration. Interestingly, PEO resulted in a different structure and surface of the CNF compared to other chemicals.

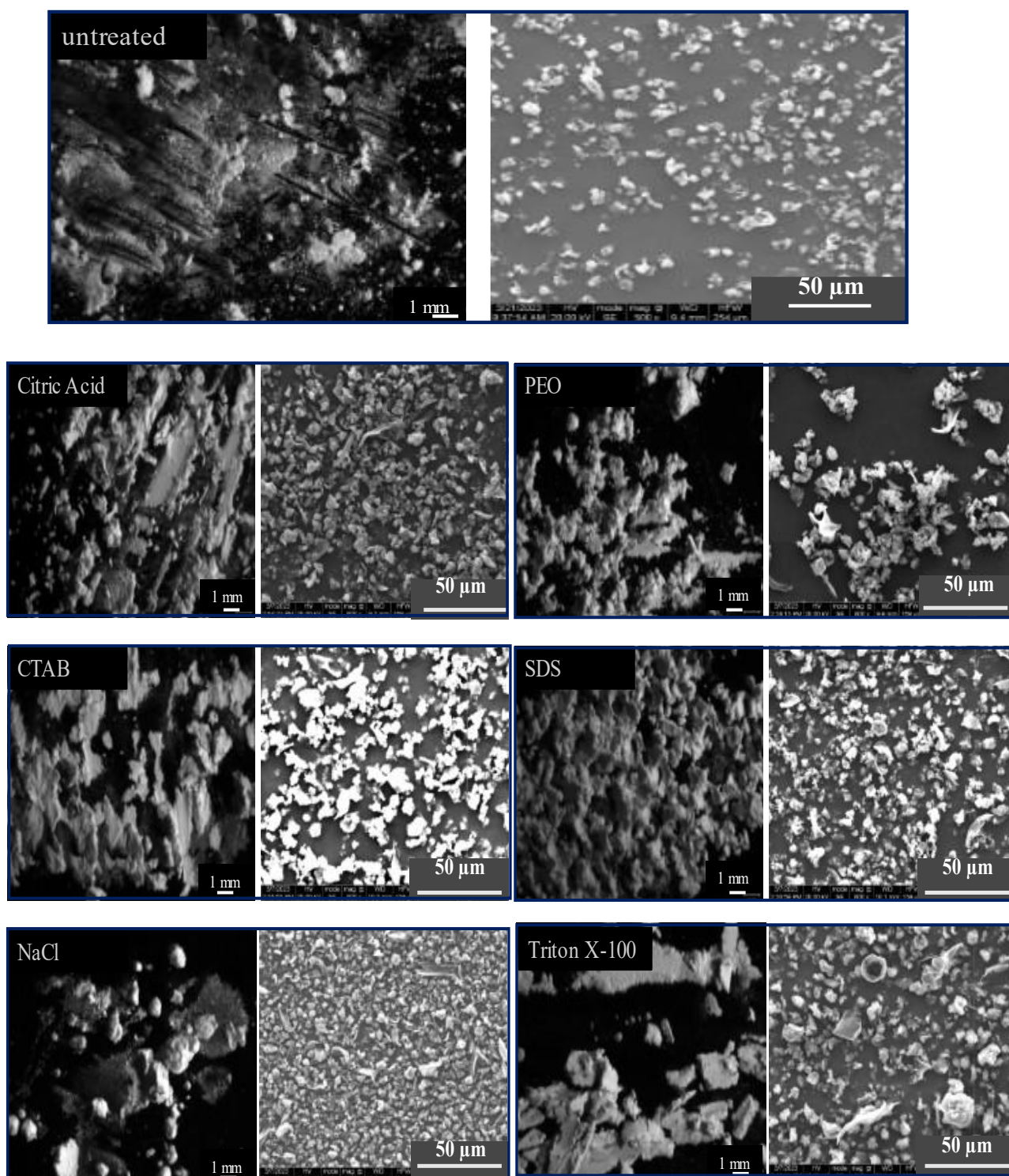


Figure 6.2 Microscope and SEM images for CNFs with different chemicals.

6.1.3 Redispersation of CNFs

In the process of spray drying, CNF tends to agglomerate and form clusters, leading to difficulties in achieving a uniform dispersion in water. Redispersation is the process of breaking down these clusters and achieving a more even distribution of CNF in the water suspension. To enhance the redispersation of CNF, a variety of chemical agents can be added to the suspension during or after the drying process. These agents work by reducing the surface tension of the suspension, preventing the formation of large clusters, and promoting easier dispersion of CNF. However, it is crucial to select the appropriate chemical agents to avoid influencing the properties of CNF and the final product. In this study, the dispersibility of CNF with different chemicals was evaluated using three methods: Redispersation without Mixing, Redispersation with Mechanical Stirring, and Sonication.

6.1.3.1. Redispersation without Mixing

A quantity of 0.1 grams of cellulose nanofiber powders that had undergone spray-drying was added onto the surface of 10 mL of deionized (DI) water. The process of the CNF particles becoming wet, and sinking was recorded on video, and the time it took for the CNF samples to settle was measured and recorded in Table 6.1. The settling time and swollen granule size can provide insight into the aggregation and morphology of the CNF particles, which can have significant implications for their properties and performance in various applications.

As indicated in Table 6.1, it can be observed that upon contact with water, all CNF powders sank rapidly to the bottom of the beaker within approximately 20 seconds. In contrast, CNFs with PEO and NaCl exhibited a delayed sinking and settling. This phenomenon can be attributed to the presence of less dense particles that swelled before eventually sinking.

Table 6.1 Settling time of CNFs with different chemicals

Sample	Untreated CNF	Treated CNF	NaCl	SDS	CTAB	PEO	Citric Acid	Triton X-100
Settling time (sec)	20	5	23	19	19	125	21	20

After a period of five minutes in water, the swollen CNFs settled at the bottom of the vials, as depicted in Figure 6.3. The CNFs did not break down or disintegrate into individual particles when exposed to water. As Esparza [79] mentioned, in the absence of external forces or energy, agglomerates of nanoparticles can only decrease in size up to a certain extent due to the erosion of individual nanoparticles on the granule surface. However, to fully break the interparticle bridges and reduce agglomerate size beyond this point, additional energy input is necessary.

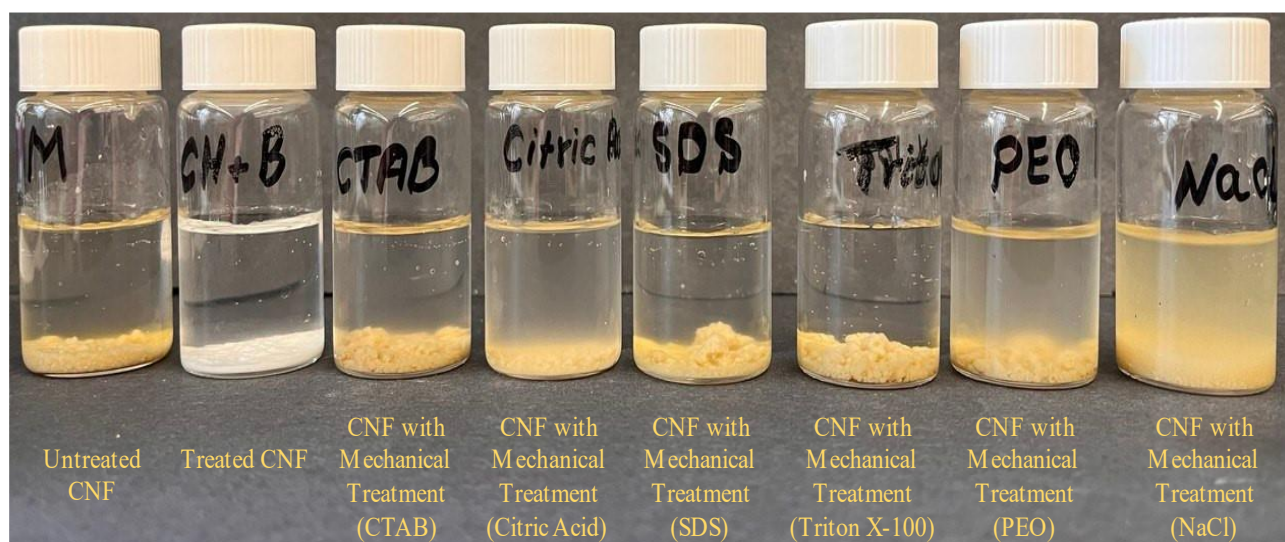


Figure 6.3 CNF powders wettability after 5 minutes.

6.1.3.2. Redispersion with Mechanical Stirring

The previous samples with the concentration of 1 % were stirred with the aid of a magnetic stir bar on a magnetic stirrer plate at 450 rpm for four hours. The visual stability of 1% spray-dried CNF suspensions was evaluated at different intervals after stirring for 4 hours (Figure 6.4). It was observed that most of the suspensions were unstable, with particles settling down soon after mixing. A layer of CNF swelled particles at the bottom of the vials was formed for all samples, except for the ones treated, citric acid and SDS.

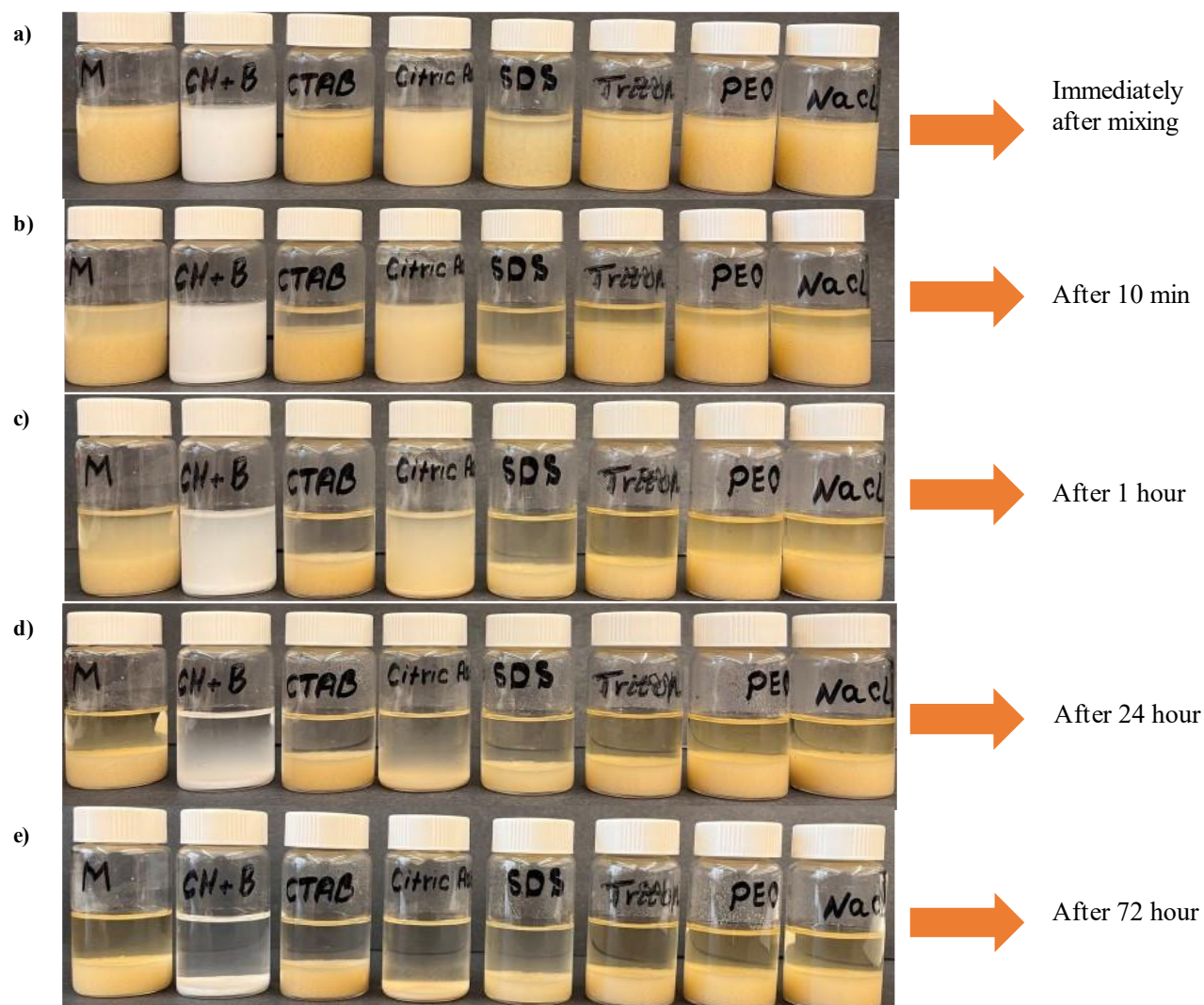


Figure 6.4 Visual stability of 1% spray-dried CNF suspensions.

Table 6.2 displays the measurements of the height of the swelling layer of CNF after 72 hours.

Table 6.2 Swelling height of CNFs with different chemicals

Sample	Untreated CNF	Treated CNF	NaCl	SDS	CTAB	PEO	Citric Acid	Triton X-100
Swelling Height (mm)	9	2	12	6	8	11	2	9

6.1.3.3. Redispersion with Ultrasound

CNFs were dispersed in 10 milliliters of deionized water at three different concentrations: 0.5%, 0.8%, and 1%. Glass vials with the CNF suspensions were subjected to sonication in a water bath sonicator for a duration of 10 minutes. Figure 6.5 displays the CNF suspension immediately after sonication and after 72 hours. The vials on the left, middle, and right correspond to CNF suspensions of 0.5%, 0.8%, and 1%, respectively. Ultrasound has commonly been regarded as a valuable method to improve the re-dispersion of CNFs. As can be seen in the image below, all samples have a good dispersibility and stability.



Figure 6.5 Visual dispersibility after sonication as a function of concentration of CNF.

6.2. Barrier and Mechanical Properties of PBS/CNF Films by Using Chemicals

After conducting an analysis of the morphology and structure of various CNFs in the preceding section, a mixture containing 90% PBS and 10% CNF was prepared in order to compare the mechanical and barrier properties.

6.2.1. Morphological Characterization of PBS90/CNF10

SEM was used to investigate the morphology of phase dispersion in nanocomposites PBS90/CNF10 treated with different chemicals. The fracture surfaces of these nanocomposites were observed in liquid nitrogen and the results are presented in Figure 6.6. When comparing the micrographs taken at 100 micrometers, little information can be obtained regarding the dispersion of CNFs. The morphology of fracture surfaces of composites is affected by the CNF particles, which causes a reduction in micro voids in comparison to the pure matrix. However, by looking at images taken at 5 micrometers, more differences can be observed. For instance, the surface morphology of samples containing NaCl, SDS, and PEO is significantly different from others, and the agglomeration of CNFs is less visible. Based on the micrographs, the presence of small particles in agglomerates of several micrometers can be observed in all samples. The CNF is uniformly dispersed, and fibrils are surrounded by a polymer matrix without any signs of being pulled out or separated from PBS. Some slight agglomeration between nanocellulose fibrils is visible, but no major defects can be observed.

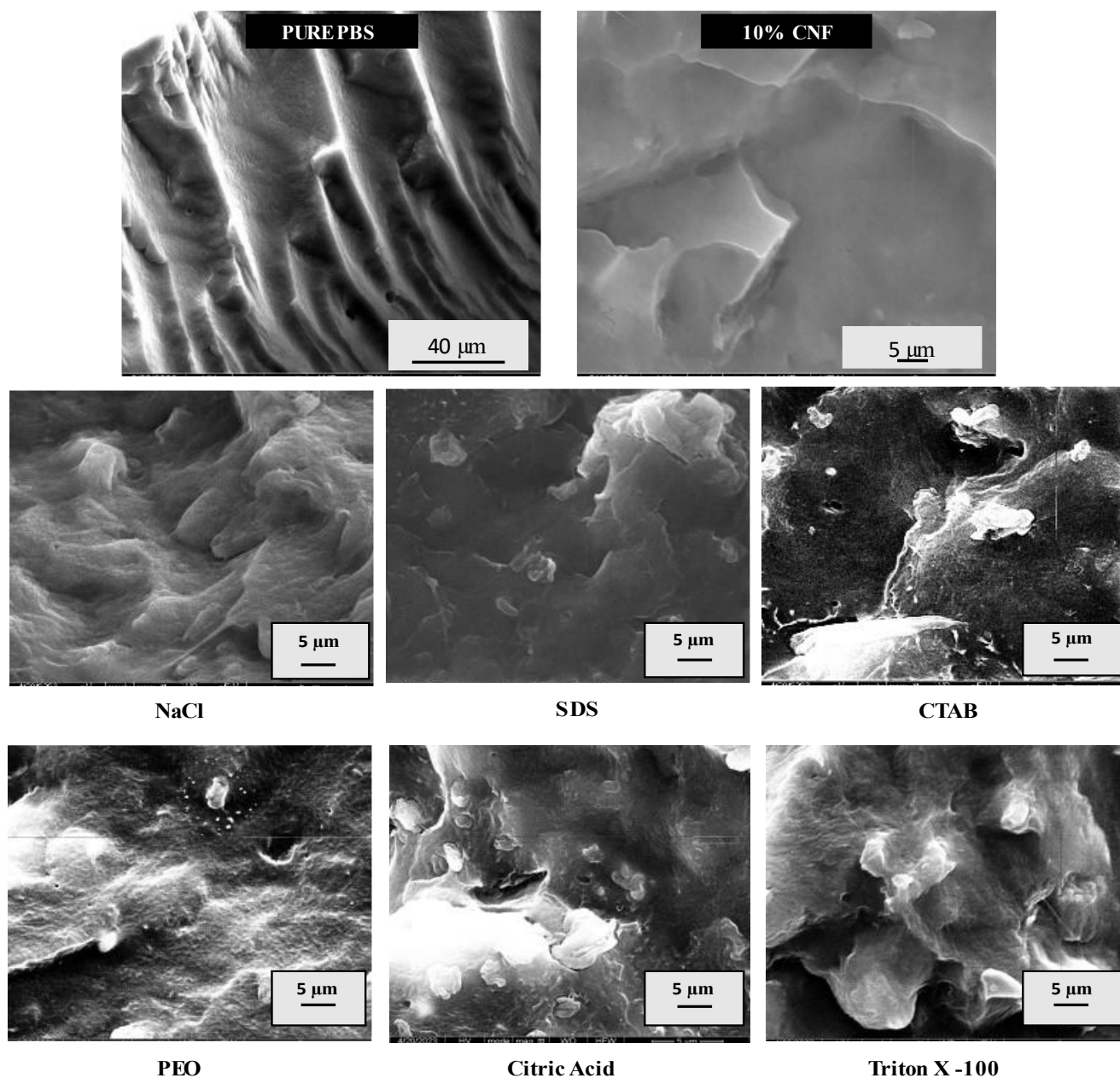


Figure 6.6 Fracture surface of PBS90/CNF10 which dried with different chemicals.

6.2.2. Water Absorption and Solubility

Figure 6.7 presents the water absorption and solubility of PBS90/CNF10. The results showed that the water absorption of CNF treated with chemicals such as NaCl, citric acid, and PEO was lower compared to untreated CNF. This suggests that the chemical treatment can decrease the water absorption capacity of CNF. The reason for the decrease in water absorption of chemically treated CNFs compared to normal CNFs could be that these chemicals create a barrier around the CNFs, reducing their ability to absorb water.

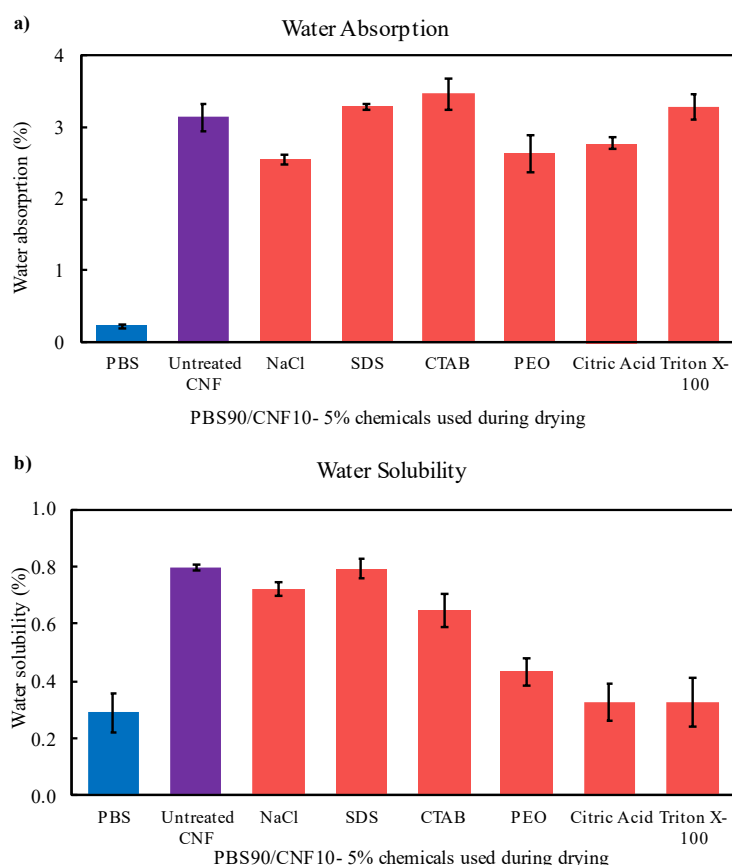


Figure 6.7 a) Water absorption and b) Water solubility of different PBS/CNF films.

6.2.3. Barrier Properties (Water Vapor and Oxygen)

Figure 6.8 a illustrates the oxygen permeability of PBS films and PBS/CNF composites treated with various chemicals. As discussed in earlier sections, the addition of 10% CNF was found to enhance the permeability resistance against oxygen. However, in the current analysis, no significant increase in oxygen permeability was observed. Notably, certain chemicals, such as NaCl, PEO, and SDS, demonstrated a greater reduction in oxygen permeability compared to others.

Figure 6.8.b displays the results of the permeability rate measurements conducted on PBS films and nanocomposites. The water vapor permeability of the neat PBS film was measured to be approximately 5 (gr.mm/day.KPa.m²). Upon incorporating 10%wt CNF into the PBS matrix, the WVP slightly increased to 5.5. The effects of using different chemicals in the CNF drying process on the WVP can be observed in the figure 6.8 b. It is evident that there were minimal changes when these chemicals were used, but the addition of NaCl, SDS, and citric acid resulted in a slight decrease in WVP. The findings from earlier sections demonstrated that the water vapor

permeability of the fabricated layers was significantly affected by multiple factors. These factors include the inherent hydrophilic or hydrophobic properties of the materials used, the specific manufacturing techniques employed, the type, amount, and distribution of additives incorporated, the presence of any voids or cracks, and the overall arrangement within the polymer structure.

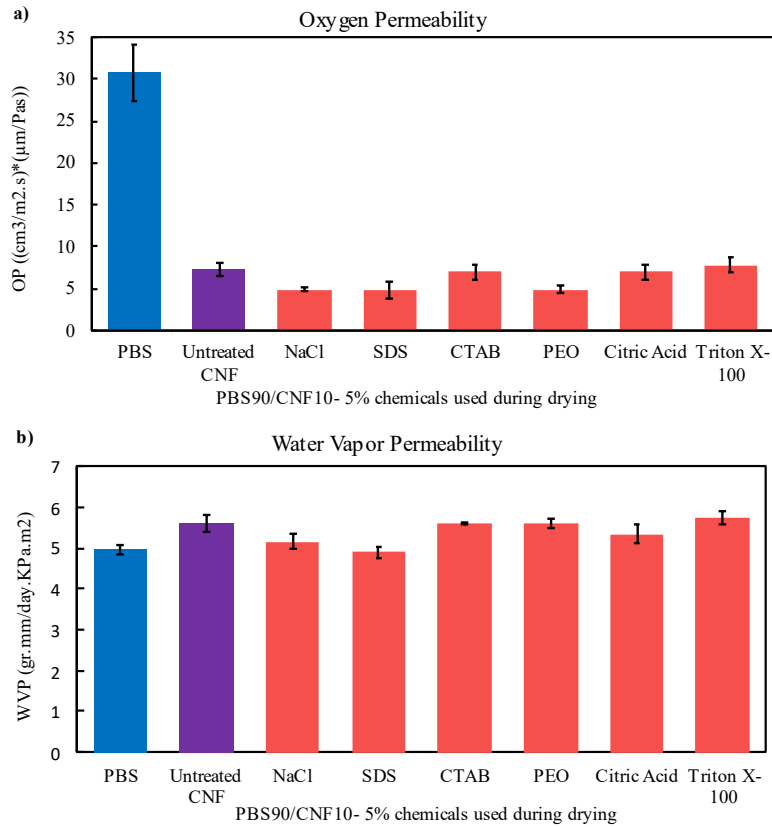


Figure 6.8 a) Oxygen permeability, b) Water vapor permeability of PBS90/CNF10 which dried with different chemicals.

6.2.4. Tensile Properties

Figure 6.9 displays the results of mechanical tests conducted on films made of PBS and its nanocomposites, specifically measuring tensile strength (TS), tensile modulus (TM), and elongation (E). Abdulkhali et al. [80], highlighted the factors that play a crucial role in determining the mechanical properties of composites, particularly nanocomposites. These factors include the adhesion and compatibility between the polymer matrix and additives, the efficiency of stress transfer from additives to the matrix, the volume fraction of additives present, the aspect ratio of the additives (referring to their length-to-diameter ratio), the orientation of the additives within the matrix, and the crystallinity of the matrix itself.

Regarding the specific case of adding various chemicals to CNF in PBS/CNF nanocomposites, it can be observed that these chemical additions do not significantly impact the mechanical

properties of the resulting composites. This suggests that the presence of these chemicals does not significantly alter the adhesion, stress transfer efficiency, volume fraction, aspect ratio, orientation, or crystallinity of the nanocomposite. Therefore, in the context of the study's findings, the mechanical properties of the PBS/CNF nanocomposites remain largely unaffected by the incorporation of these chemicals.

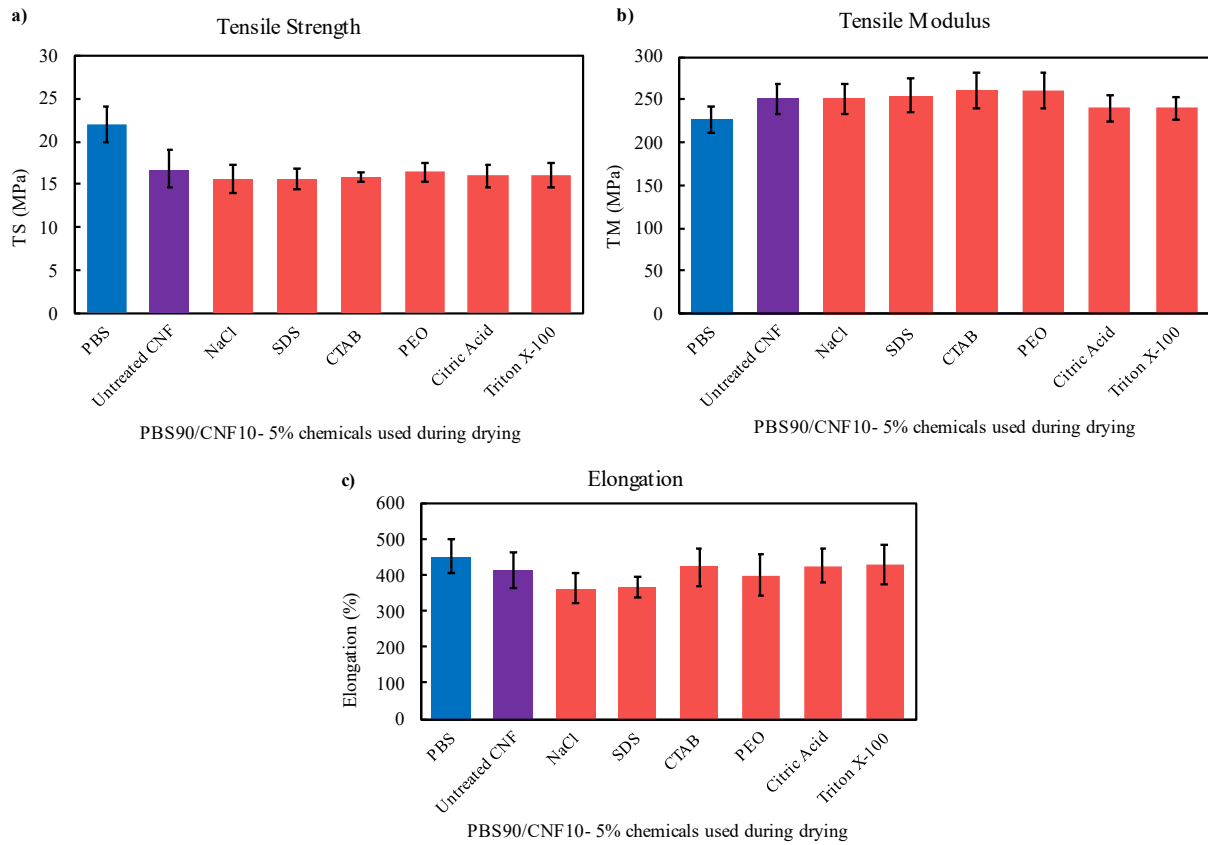


Figure 6.9 a) Tensile strength, b) Tensile modulus, c) Elongation of PBS90/CNF10 with different chemicals.

6.3. Conclusion

In summary, the experimental investigation aimed to incorporate various chemicals into the composite matrix during the drying process and assess their impact on the dispersion of cellulose nanofibers (CNF). SEM, optical microscopy, and stability tests were used to evaluate the morphology, dispersion, and effectiveness of the chemicals. A PBS90/CNF10 blend was prepared using different CNFs, and its properties were analyzed. The results showed that treatments with NaCl, SDS, and PEO improved atomization during spray drying, resulting in smaller droplet sizes. However, the addition of these chemicals did not significantly affect the mechanical strength and barrier performance of the composite compared to the composite without any chemicals. Thus, while the dispersion of CNF was influenced by specific chemical treatments, the overall properties of the composite remained largely unchanged.

Chapter 7 Conclusion and Recommendations

7.1. Conclusion

The primary aim of this research endeavor was to develop a cellulose nanofiber (CNF) composite that exhibits favorable barrier properties suitable for sustainable packaging applications. Throughout this study, extensive efforts were dedicated to exploring and optimizing the composition and characteristics of the CNF composite to enhance its barrier performance.

Chapter 4 : an in-depth analysis was conducted to investigate the properties of thermoplastic starch (TPS)/polybutylene succinate (PBS) blends in the presence of cellulose nanofibers (CNF) obtained from the University of Maine. Additionally, the effect of a compatibilizer on the properties of the blends was examined.

Chapter 5 : focused on the production of CNF from hemp and presented a comprehensive comparison of the properties between treated CNF and untreated CNF.

Chapter 6 : focused on investigating the impact of various chemicals on the dispersion and properties of composites. The study aimed to understand how the addition of different chemicals could enhance the dispersion of fillers and improve the overall performance of the composites.

1. PBS has gained significant attention as a synthetic biopolymer with attractive properties. To enhance its biodegradability, compatibility, and cost-effectiveness, PBS was blended with ST and GL. However, the resulting PBS/TPS blend films exhibited poor water resistance due to the hydrophilic nature of TPS. In order to improve the barrier properties of the films, the addition of CNF was chosen. The incorporation of 5% CNF into the PBS/TPS blend films led to notable improvements in barrier properties such as water solubility (W_s), water absorption (W_a), and water vapor permeability (WVP). The CNF served as a reinforcing agent within the blends, resulting in enhanced tensile strength and modulus. The combination of TPS, PBS, and CNF offers a biodegradable and renewable alternative to conventional packaging materials. This innovative approach contributes to environmental conservation efforts by reducing reliance on non-renewable resources and promoting the use of sustainable materials. The findings of this study demonstrate the potential of PBS-based nanocomposite films as promising candidates for sustainable packaging applications.

2. The production of CNF from hemp involved alkaline and acid treatment, followed by bleaching and refining using the Masuko grinder. A comparison was made between two types of CNF to examine their properties. The utilization of lignin-containing CNF opens up new possibilities for CNF applications and offers potential cost reductions in processing by reducing energy and chemical requirements. The CNF films derived from lignin-containing CNF exhibited a yellowish color, which may be advantageous for certain packaging applications, whereas the films from low-lignin-containing CNF were more transparent. Surprisingly, it was observed that samples with higher lignin content showed higher water vapor transmission rates, contrary to expectations. This suggests that the hydrophilic nature of the material alone is not the sole determining factor for barrier properties. Overall, the SEM observations suggest that incorporating less than 15% CNF in the film formulation leads to improved barrier performance by minimizing agglomeration and structural defects, thereby enhancing the film's resistance to water vapor permeation.
3. The experimental procedure involved incorporating different chemicals, such as NaCl, SDS, PEO, Citric Acid, Triton X-100 and CTAB into the composite matrix during the drying process. The effects of these chemicals on the dispersion of CNF, were thoroughly analyzed. Several characterization techniques were employed to evaluate the dispersion and properties of the composites. SEM and optical microscope were used to examine the morphology and dispersion of the fillers within the matrix. Stability tests in aqueous systems, was performed to assess the effectiveness of the chemicals in promoting dispersion. At the end, a mixture of PBS90/CNF10 was prepared with different CNFs and the properties were analyzed. The findings indicated that the CNF suspensions treated with NaCl, SDS, and PEO exhibited improved atomization and resulted in smaller droplet sizes during spray drying. However, it was observed that the addition of chemicals to the composite did not result in any significant differences in properties such as mechanical strength and barrier performance when compared to the composite without any chemicals.

In conclusion, the PBS/CNF nanocomposites exhibited promising characteristics suitable for sustainable packaging applications, taking into consideration the specific demands of each application. Nonetheless, further investigations and advancements are imperative to improve and optimize the ultimate properties of these materials.

7.2. Recommendations for Future Works

1. *Changing the main polymer*; Instead of PBS, alternative options for the composite matrix include PLA, bioPE, and PBAT.
2. *Surface modification of CNF*; In order to enhance compatibility and dispersibility, it is advisable to employ surface modification techniques on CNF to introduce functional groups, thereby rendering it hydrophobic.
3. *Additives*: To achieve improved dispersibility, various chemicals such as paraffin wax, potassium chloride (KCl), and silane-based compounds could be investigated. Based on previous studies, these chemicals could increase the dispersibility of CNF through interactions with its surface, thus promoting better compatibility within the composite system.
4. *Compatibilizer*; In order to enhance the compatibility between the hydrophobic matrix and hydrophilic CNF, the utilization of compatibilizers such as phthalic anhydride, succinic acid, and other suitable compounds is recommended.
5. *Other test*; As the CNF was produced in our laboratory, further investigation is warranted to explore additional properties of the nanofibers. Parameters such as fiber length, surface area, lignin content, and other relevant characteristics should be thoroughly examined to gain a comprehensive understanding of the CNF material. Additionally, for the final composite, it is advisable to conduct tests to assess its biodegradability and contact angle, among other pertinent evaluations. These analyses will provide valuable insights into the performance and potential applications of the CNF composite.

Chapter 8 SEM Figures

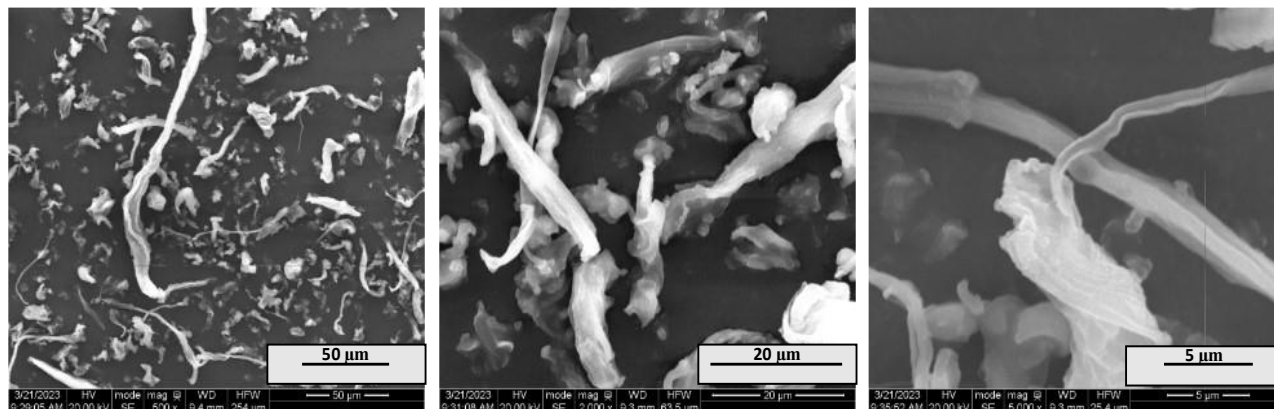


Figure 8.1 SEM images of treated CNF

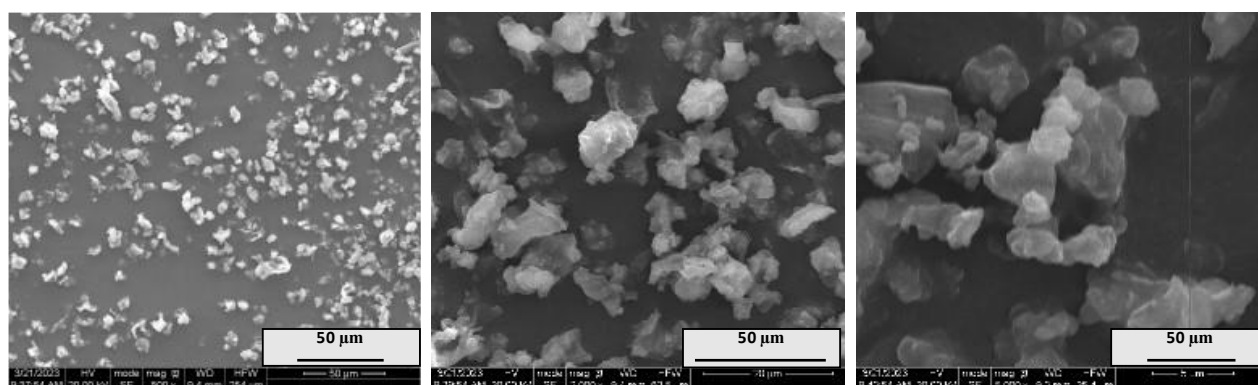


Figure 8.2 SEM images of untreated CNF

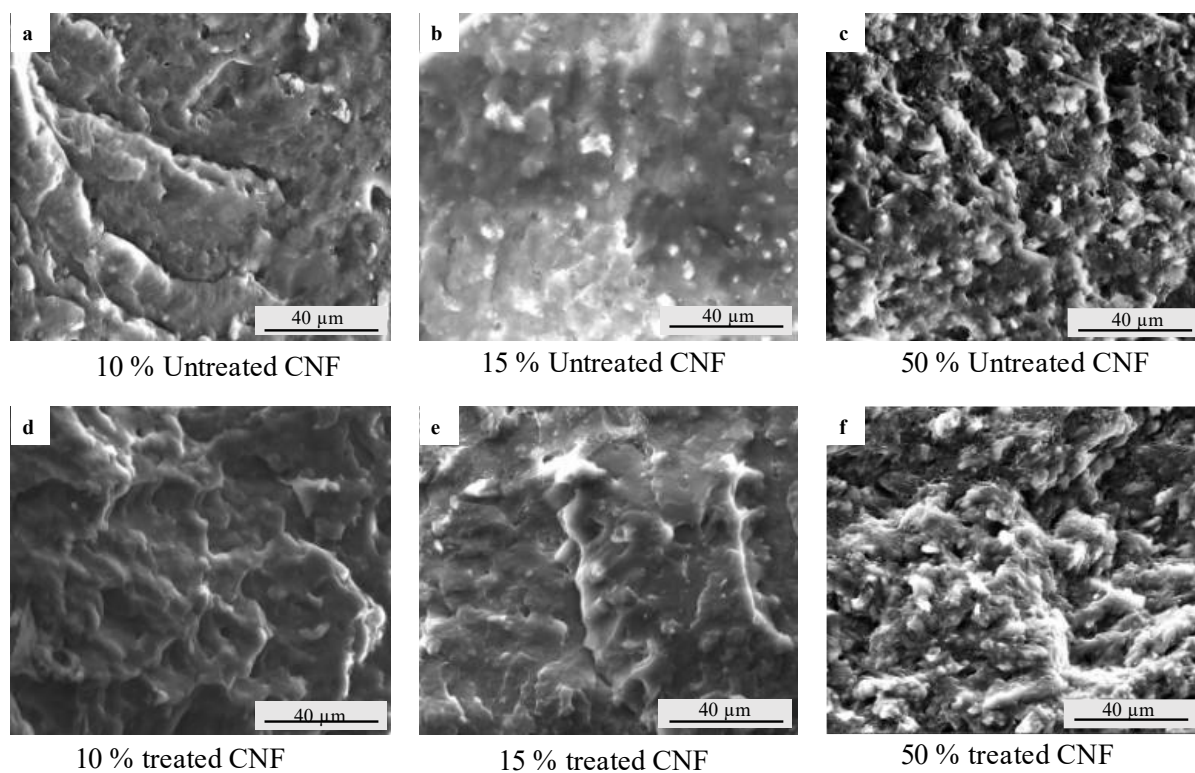


Figure 8.3 SEM images of PBS/CNF with treated and untreated CNF

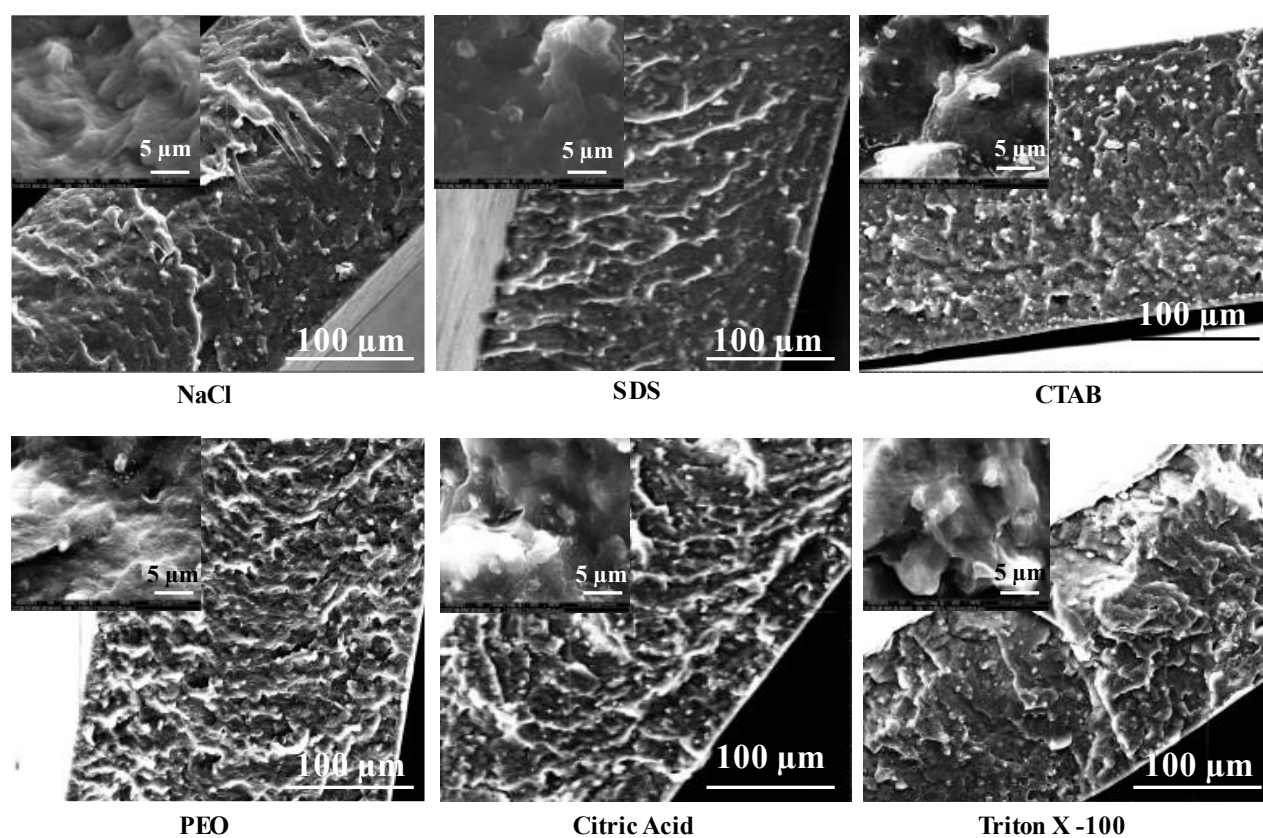


Figure 8.4 SEM images of PBS90/CNF10 in which CNF dried with different chemicals

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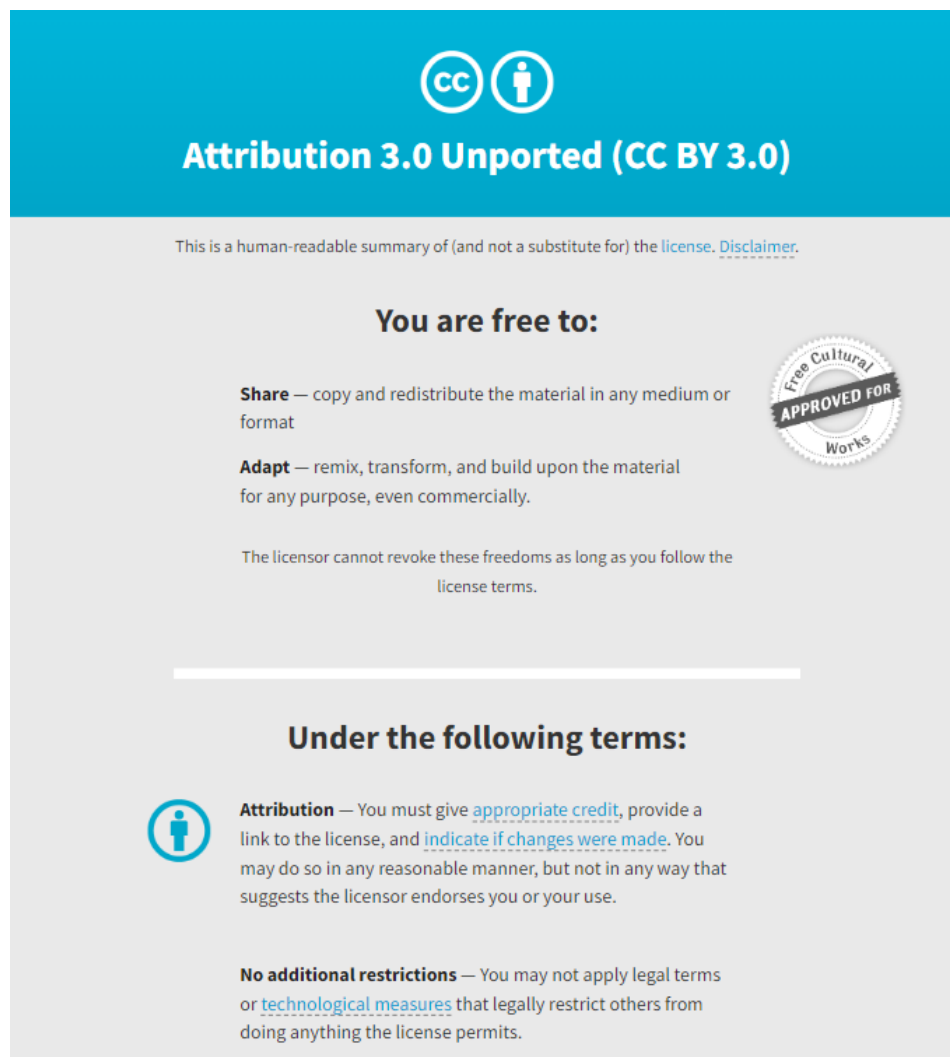


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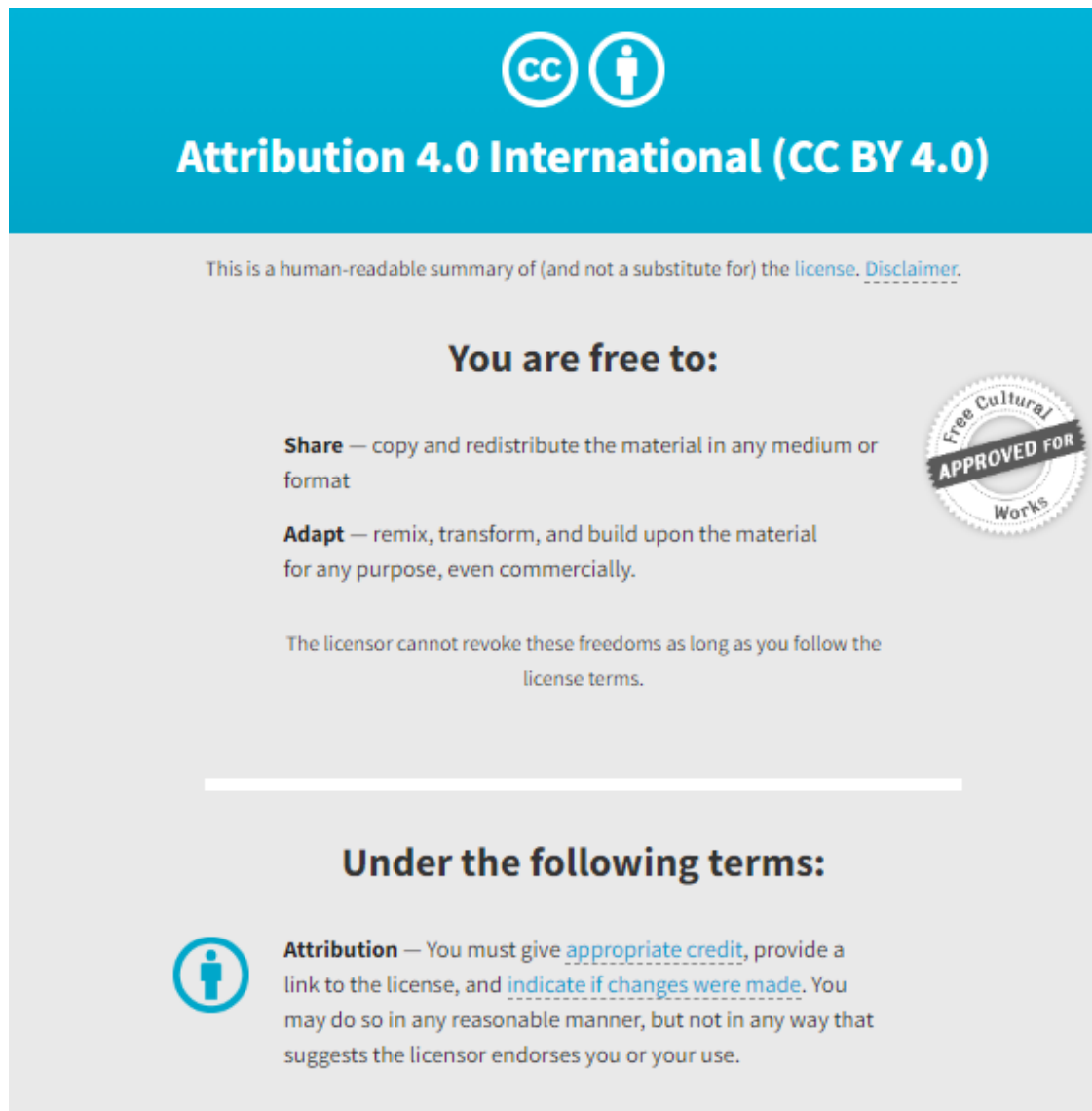


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