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## Chapter

# Advances in Cellulose-Based Packaging Films for Food Products

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## Abstract

Cellulose and its derivatives can be used to manufacture packaging film materials with versatile properties as alternatives to petroleum-based films. This chapter covers the recent trends and advancements in cellulose-based films for food materials. The chapter starts with the introduction of traditional and novel cellulose structures relevant to film-making properties including cellulose fibers, filaments, nano-fibrils, crystalline cellulose, and other traditional cellulose derivatives. The relevant cross-linking methods, such as esterification, etherification, oxidation, and carboxylation will be described in the production of materials such as methylcellulose, cellulose acetate, rayon fabric, carboxymethyl cellulose, cellulose ether, etc. The chapter will relate the properties of the films (e.g., crystallinity, mechanical, optical, barrier, and solubility properties) to the chemical characteristics of the cellulose materials. The chapter will also cover the interactions of cellulose with polymeric composites such as protein, polysaccharides, and other nanoparticles ingredients with a focus on emerging technologies.

**Keywords:** packaging films, cellulose structures, cellulose derivatives, physical modifications, chemical modifications, cellulose crosslinking, cellulose interactions

## 1. Introduction

The packaging film materials are significant contributors to safety, quality, and shelf life of food materials. They are as primary, secondary and tertiary depending on the level of contact with the product. Primary packaging films that are the focus of this chapter directly contact with products. Packaging films are made of a polymer matrix to create cohesive structure providing strength, often with a plasticizer to reduce rigidity and brittleness. They provide protection against physical and biological damage to food, and extend shelf life by limiting the diffusion of moisture, gases, volatile compounds.

Traditional packaging films are manufactured from petroleum-based polymers with tunable properties, but well-known environmental drawbacks. For example, the concentration of microplastics fragmented from synthetic films has been increasing to critical levels and is predicted to further increase in the next decades. The microplastic contamination in aquatic environment and soils considered as dominant environmental plastic pollutants to result in serious health concern for humans and animals [1]. The adoption of biodegradable films, which are known as materials that

can naturally decompose into water, carbon dioxide, methane, or biomass in three to six months, can serve as a viable solution to this problem [2]. These materials can be obtained from biomass, synthesized from bio-derived monomers or produced from microorganisms [3]. Moreover, these materials can be produced from renewable resources (i.e., cellulosic materials and fibers recovered from process waste-streams) supporting sustainable agriculture practices [4]. There is, therefore, a large need for designing biodegradable, safe, and high-performance packaging materials using biopolymer sources, such as cellulose.

Biopolymers are natural macromolecules obtained from living organisms. They can be used to produce packaging films as alternatives to petroleum-based materials. The literature has plethora of examples for such films produced from polysaccharides, proteins, lipids, and their combinations [5]. Some of the biggest challenges for the adoption of biopolymers films are related to their limited film forming abilities, and lower mechanical and gas barrier properties as compared to traditional synthetic materials. The high production cost is another limitation related to the extraction, purification, conversion, and recovery steps involved.

Cellulose is the most abundant natural biopolymer found in cell walls of all plants as well as algae and fungi. It can serve as an ideal material for film manufacturing related to its versatility, chemical stability, non-toxicity, and affordability. The versatility of cellulose is also related to its various derivatives with distinct chemical structures and physicochemical properties used in a wide array of industrial segments as covered in this chapter. For example, cellulose acetate is one of the well-known cellulose derivatives and its commonly used to produce strong and resistant films in addition to distinct applications as frame materials in personal care items and other rigid tools (glasses, combs, screwdriver handles, etc.), imaging and photography films, filters, reservoirs for liquids, synthetic fiber etc. Therefore, it is safe to claim that cellulose and its derivatives are popular in packing applications. This chapter starts with the structures and sources of cellulose relevant to film-forming characteristics; then, continues with chemical and physical approaches to tailor cellulose derivatives. The chapter also highlights various polymeric interactions within cellulose fibrillar network. The chapter adds the use of cellulose in various food film applications with advances in manufacturing cellulose-based packaging films and emerging technologies. To illustrate prior knowledge, four recent review papers were included throughout the chapter [3, 6–8].

## **2. Cellulose structure and sources**

### **2.1 Structure**

The simplest and well-known definition of cellulose considers the polymer as D-glucopyranose subunits linked by  $\beta$ -1,4-glycosidic bond  $(C_6H_{10}O_5)_n$ . The degree of polymerization (n) of native cellulose expresses the number of glucose units that range between 1000 and 30,000 units depending on the source. For example, native wood cellulose of 10,000 glucose units is smaller than cotton cellulose of 15,000 units. Cellulose structure is typically in a linear form, where adjacent glucose units rotate by  $180^\circ$  to create subunits of a repeating cellobiose disaccharide. Larger organization of these subunits forms fibrous structures, commonly referred to as microfibrils or lignocellulosic fibers. Microfibril subunits are organized to generate cellulose fiber structure. The micro-scale interactions of cellulose and associated

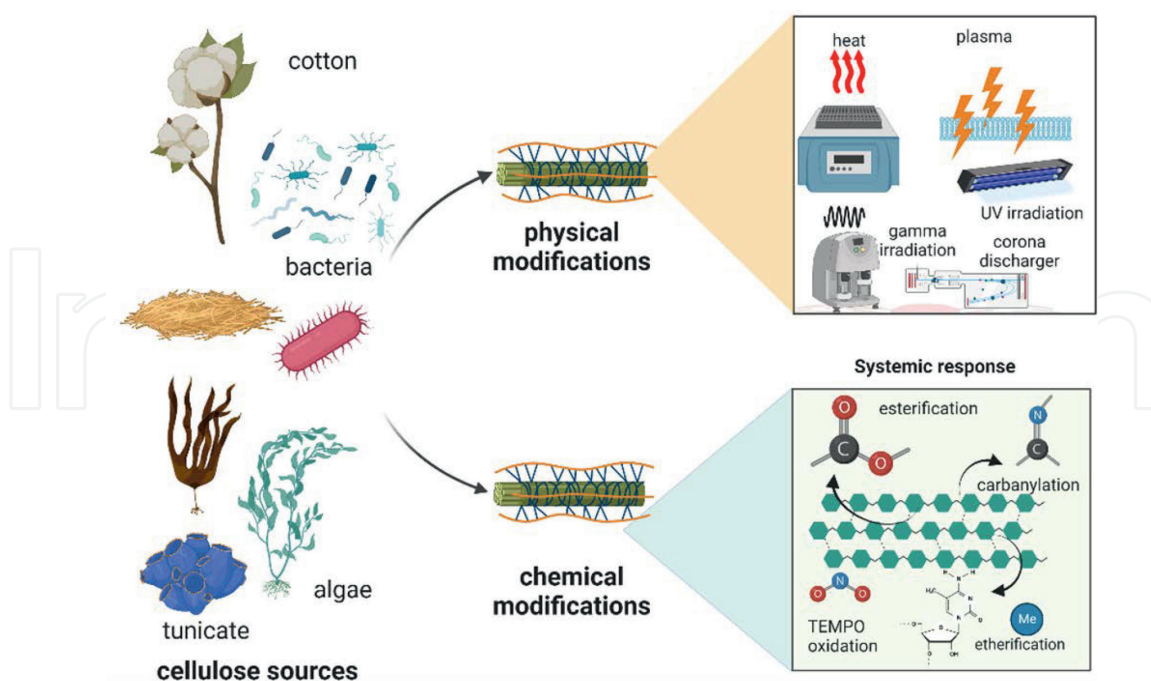
bonds have significant effect on its characteristics and functionality. For example, hydrogen bonds between three hydroxyl groups of the anhydroglucose unit and D-glucopyranose oxygen atom provide rigidity and generate the three-dimensional arrangement of cellulose in their polymer network. Besides, strong hydrogen bonding of the hydroxyl groups is responsible for the reduced solubility, crystallinity, and reactivity of the polymer.

The microfibril regions are composed of crystalline and amorphous regions. The crystalline structure formed by hydrogen bonding between adjacent microfibrils. Crystalline units are found in two different phases, namely,  $\alpha$ -cellulose and  $\beta$ -cellulose. The predominance of crystalline phase is determined by its source (i.e., plant- and animal-based celluloses are predominantly in the  $\beta$ -cellulose form, and the bacteria-based cellulose is in  $\alpha$ -form). The crystalline cellulose appears as rod-shaped particles, which can be extracted using enzymatic, chemical, or mechanical methods. The amorphous cellulose lack a certain shape and order, and formed by randomly ordered microfibrils surrounded by hemicelluloses and. In the amorphous region, the cellulose microfibrils are more available for hydrogen bond and subsequent interactions with water, protein or enzymes. Overall, the composition of crystalline and amorphous regions determine the physicochemical properties (e.g., rigidity, strength, extractability, etc.) of cellulose. For example, crystalline cellulose may display deuteration whereas amorphous cellulose swells in hydrophilic solvent and can penetrate inside the amorphous matrix by disrupting the intermolecular hydrogen bonds [9]. The high crystallinity can increase the rigidity and reduce the elasticity of cellulose-based films. Furthermore, these structures can be modified to obtain derivatives with desired functionalities as explained in Section 3.

## 2.2 Sources

*Plants* are the most common source of cellulose and cellulose derivatives. A schematic diagram of cellulose sources and modification methods is given **Figure 1**. The literature and industry have various examples for the use of various cellulose sources in packaging applications. Following extraction, cellulose is typically purified to eliminate lignin and hemicellulose for the manufacturing of cellulose derivatives. Among plant sources, cotton fibers have the advantage of having relatively low non-cellulosic components with around 90 wt% purity with long chains of crystalline regions (60%). Cellulose fibers from cotton displays twisted morphology with an internal structure of cell wall layers. The strength of cotton fiber increases with moisture. Therefore, cotton-based cellulose are suitable for film applications, where mechanical integrity is required. The second most abundant source of cellulose is wood. It displays not only good mechanical properties but also potential antibacterial characteristics due to the presence of natural phytochemicals [6]. Cellulose extracted from wood includes lignin and other polysaccharide compounds with ca. 50 wt% cellulose content. The presence of hemicellulose aids extraction of wood fibers easily during the pulping process.

*Bacteria-based cellulose or cellobiose* is produced by Gram (–) aerobic bacteria such as *Acetobacter xylinum*, *Gluconacetobacter xylinus*, *Komagataeibacter xylinus*, *Agrobacterium*, *Achromobacter*, *Pseudomonas*, and *Rhizobium*, and Gram (+) bacteria such as *Sarcina spp.* The bacteria-based cellulose is typically of high purity with ribbon-like shaped microfibril structures. Isolation and purification of bacterial cellulose do not require additional chemical treatment unlike plant-based cellulose. The bacteria-based cellulose microfibrils may agglomerate into a gel-like network (i.e.,



**Figure 1.**  
A diagram of common cellulose sources and modification techniques.

microfibril gels) via interfibrillar hydrogen bonds and Van der Waals interactions, ideal for obtaining natural cellulose packaging films [10]. Another related structure is bacterial nanofibrils, which are thinner than microfibrils with higher surface area/volume ratio. This structure is desirable for film manufacturing since it can impart higher elasticity and strength. The microfibril structure can be controlled by altering the bacterial growth conditions. For example, using different carbon sources (e.g., replacing glucose with fructose, galactose, mannitol or xylose) can modify the surface area, porosity and crystallinity index of cellulose fibrils, and subsequently enhance resistance of their cellulose films against the oxygen and water vapor permeabilities [11]. Therefore, bacterial cellulose serves as a suitable source of cellulose with tunable characteristics for film applications.

*Algae* are known as renewable cellulose sources due to their ability to get nutrients from waste streams. Several species of green, gray, red, yellow, or brown algae, such as *Caldophora*, *Micrasterias denticulata*, *Gelidium elegans*, *Micrasterias rotata*, *Valonia*, *Boergesenia* and *Posidonia Oceanica*, were used to obtain cellulose microfibrils from their cell walls. Red algae contain the largest amount of cellulose. In comparison, green algae cellulose shows higher crystallinity (above 70%) than others, and therefore lower moisture adsorption capacity and limited the swelling. The purity of algae cellulose is typically lower than bacterial and plant cellulose. This is related to the presence of cellular proteins in the microfibril isolates. Algae based cellulose was used for biopolymer film applications, but they exhibited poor water vapor permeability and low mechanical strength [12]. Moreover, crystalline cellulose extracted from seaweed species of *Alaria esculenta*, *Saccharina latissima* have higher pure cellulose content as compared to cellulose isolated from *Ascophyllum nodosum* with heterogeneous content with minerals and proteins. Impurities reduces the presence of free hydroxyl group to limit their applications. The researchers showed that films produced from high purity cellulose exhibit better visual appearance and less moisture permeability [13].

*Tunicates* are invertebrate marine animals that can serve as a unique animal source of cellulose. Tunicate has three subclasses: *Ascidiacea*, *Thaliacea* and *Appendicularia*. Tunicate epidermal cells contain many enzyme complexes in epidermis membrane, which are responsible for cellulose production. The tunicate cellulose can be isolated nanofibril form, which are bundled in the outer tissues of tunicates. Tunicate cellulose exhibits higher crystallinity (ca. 95%) and surface area compared to other cellulose types. This provides excellent mechanical and thermal properties for cellulose-based films [14].

### 3. Modification of cellulose and cellulose derivatives

Cellulose is often modified via physical and chemical techniques to increase their functionality responsive to the film application and industry. Physical methods refer to approaches, which do not largely rely on the use of chemical compounds to modify cellulose fibers. The physical modification section covers the use of techniques that utilize mechanical, thermal, electrical, and other high-energetic (e.g., gamma irradiation, UV light) processes. The chemical modifications section covers common techniques to obtain traditional and novel cellulose derivatives including hydrolysis, esterification, acetylation, etherification, silylation, carbamylation, TEMPO oxidation. A summary of the modification methods for obtaining cellulose derivatives is illustrated in **Figure 1**.

#### 3.1 Physical modifications

*Thermal treatment* can be used as a pre-treatment or post-treatment to remove undesired substances, enhance the oxygen-carbon ratio, and improve crystallinity of cellulose fibers. These modifications can improve the gas barrier properties and increase the acidity of the fiber surfaces used to produce films. For example,

heating (up to 145°C) tempo-oxidized cellulose nanofiber films was shown to significantly reduce the water retention and oxygen permeability as compared to original films prepared without post-thermal treatment [15]. Moreover, heating can help in inducing the closure of pores between cellulose nanofibers. This can be explained with the reorientation of amorphous and paracrystalline regions into the crystalline regions [16].

*Plasma surface treatment* can be used to enhance the hydrophilicity to cellulose fibers, and subsequently to provide functional properties to their films, such as better oxygen and air permeability. This technique utilizes electric discharge to generate vacuum-based ionized gas at ambient temperatures. The ionized gas can be generated via low pressure, low temperature, atmospheric glow discharge, atmospheric pressure plasma jet technique. The ionized gas includes a mixture of free radicals, heavy particles, and electrons, which promote the modification cellulose fibers and fiber aggregates as in films. The modifications can be in the form of defibrillation, remove low molecular weight impurities from nanocellulose fibers, and enhance microcrystalline cellulose [17]. Plasma treatment can increase the hydrophilicity of the fibers by generating polar functional groups, which provides good adhesion of cellulose coating layers. Plasma treatment was also shown to increase the crosslinking and entanglements of cellulose nanofibrils, increase the extent of impermeable crystals, which hinders the molecular diffusion of oxygen to increase the oxygen barrier properties of microfibrillar cellulose films [18].

The *corona discharger* process is similar to plasma surface treatment and involves the use of a bundle of charged particles, such as ions and electrons, accelerated through an electric field. The ionization process involves a shade of plasma that occurs at the tip of the particle generator that is named corona. This method has several advantages such as high efficiency, continuous processing and being environmentally friendly [19]. Cellulose fibers exposed to electromagnetic field with high voltage become excited and available for further surface modification via oxygenation. Electric discharge induces oxygenation of ozone into carbonyl groups that brings about crosslinking between fibers and the media to improve the mechanical and thermal properties of cellulose fiber films. The corona treatment process was shown to improve the interfacial adhesion between cellulose fiber and polypropylene in laminated film applications in addition to improved film strength and rigidity [19]. In parallel, corona treatment was also shown to enhance the strength and thermal resistance of cellulose films [20].

*Gamma irradiation* is a non-thermal and environmentally friendly process that modifies the chemical structure of cellulose fibers via high energetic gamma rays. High energy gamma irradiation results in decomposition and crosslinking, thus strengthening the structure of cellulose fibers [21]. Gamma rays typically are generated by using Cobalt-60 or Cesium-137 sources at specific irradiation facilities, which constitute a major limitation for its availability and wide-spread use. The irradiation process has several advantages over traditional treatment methods, such as no need for catalysts, less atmospheric pollution, minimum time for the process and continuous operation. Irradiation may cause initial structure disruption and irreversible bond cleavage, thus fragmentation of the polymers into nanofibrils. The high energetic of the gamma irradiation can result in crosslinking of cellulose nanofibrils into fiber networks and gels without the use of chemical reagents.

The mechanism involves the formation of macro-cellulosic radicals by the removal of hydrogen-hydroxyl and disturbance of carbon-carbon bonds through high energy gamma rays. These radicals are very reactive to facilitate cross-linking between cellulose nanocrystals and result in strong cellulose nanocrystal films with desirable oxygen and water vapor resistance [22].

*UV radiation* treatments is the application of electromagnetic radiation at wavelengths from 100 nm to 400 nm. This method uses ultraviolet laser light source to treat cellulose with enough energy to modify the molecular bonds on the surface layer. Briefly, UV radiation increases the formation of carbonyl groups on cellulose fiber surface and increases the surface polarity. In addition to this, the strength and gas barrier ability of cellulose films and sheets can be increased by promoting crosslinking between fibril units. For example, cellulose sheets undergone through UV radiation showed increased tensile strength since UV radiation enables intercross linking between the neighboring cellulose molecules [23].

*Homogenization and related mechanical processes* including spinning, flow-focusing, microfluidization, and ultrasonication can modify the structure of cellulose fibrils into microfibrils and nanofibrils through mechanical breakdown. Cellulose filaments are typically continuous fibers of random length. Cellulose microfibrils, on the other hand, are smaller fiber agglomerates with diameters ranging from 3.5 nm to 35 nm. Nanofibrils are smaller than microfibrils in width nanometric range and the length of micrometer range. Cellulose microfibrils store three different domains, namely, non-crystalline, paracrystalline and crystalline regions. The former chains include regions without regular packing of cellulose chains. The paracrystalline domain has partial crystal distortion and loose molecular packing. As its name implies, the crystalline region takes shape with highly ordered chains. Furthermore, additional networks

such as hydrogen-bonded bundles or microfibrils can be observed on microfibril surfaces due to hydroxyl groups. Cellulose micro or nanofibril units possess large surface area and strength. Hence, films made from cellulose micro/nano fibrils are known to have low thermal expansion coefficient, high transparency and good mechanical characteristics [24]. Cellulose nanofibril films may even show better oxygen and water vapor barrier ability than some petroleum-based polymers [25]. Furthermore, mechanical properties are important for handling and packaging applications to interpret the durability and sustainability of materials. Cellulose nanofibrils mixed with other polymers can exhibit good mechanical features such as high elasticity and tensile strength [26]. Application of high-shear and high-pressure processes (e.g., homogenization and microfluidization) on cellulose dispersions dates back to couple of decades. These techniques can be used during extraction to obtain microfibers. For example, They can provide sufficient mechanical force to breakdown native cellulose fibers in the pulp into microfibrillated cellulose gels [27]. Another research demonstrated the use of microfluidization in combination with enzyme treatment to obtain nanofibrillated cellulose from palm fruit peels [28, 29]. Extrusion and flow spinning were used in a similar way to modify cellulose fibers in their solution, which is extruded through a spinneret and rotating godets with a certain velocity and pressure. The cellulose solution pushed through the axial direction, generates a highly oriented form. These cellulose filaments contain highly crystalline and dense microfibrillar structure leading to strong and moisture resistant film materials [30].

### **3.2 Chemical modifications**

#### *3.2.1 Hydrolysis*

Hydrolysis involves partial depolymerization of cellulose by using dilute mineral acid. Microcrystalline cellulose (MCC) constitutes the micron scale highly crystalline regions of cellulose microfibrils. MCC can be generated by the hydrolysis of partially depolymerized  $\alpha$ -cellulose using hydrochloric acid. MCC is preferred as a biocomposite in various application areas, such as medicine and pharmacology due to its biodegradability, physicochemical stability, low density, elasticity, and large surface area. MCC was first discovered and commercialized as Avicel<sup>®</sup> since early twentieth century. Commercial production is conventionally from softwood, hardwood, cotton stalks, soybean husks or rice husks. MCC dispersions are decomposed using sulfuric acid to obtain hydrophobic or hydrophilic CNC depending on the solvent polarity. In parallel to MCC, nanocrystalline cellulose (or cellulose nanocrystals, CNC) are rod-shaped highly crystalline units of cellulose microfibrils at nanoscale dimensions. Processes similar to MCC are involved in production of CNC by hydrolysis of native cellulose commonly from algae, bacteria and cotton linter. CNC enjoys optical transparency, light weight, biocompatibility and low thermal expansion for uses in biomedical and packaging applications. There are examples of manufacturing packaging films from CNC using layer by layer deposition or spray drying techniques. The former method is based upon adsorption of the oppositely charged polyelectrolytes to create uniform nanocellulose multilayers [31].

#### *3.2.2 Esterification*

Esterification or acylation process involves the combination of organic acid and alcohol to form an ester and water. Esterification reactions can occur on cellulose



polymer chains or the outer surface of cellulose fibers by aromatic and aliphatic reagents. Cellulose esters can be classified as organic (e.g., cellulose acetate, cellulose acetate butyrate and cellulose acetate propionate) and inorganic (cellulose nitrate, cellulose phosphate, cellulose sulfate, and cellulose xanthate) esters.

*Cellulose acetate* is a well-known and one of the most versatile cellulose derivatives. It can be obtained by the reaction of cellulose with acetic acid, acetic anhydride and sulfuric acid as catalysts. Degree of substitution with the acetate groups is the average number of acetyl groups replacing the hydroxyl groups per glucose unit, and it determines the solubility of cellulose acetate in water. The maximum degree of acetylation is three, when all OH groups are replaced by acetyl groups, which has the highest water solubility. Cellulose acetate has a great commercial appeal due to its versatility related to its solubility in various solvents and toughness for mechanical strength. Therefore, it found applications in distinct industry segments which require either flexible and resistant material as in photography films or rigid and durable materials produced by molding such as in glass frames, combs, tool handles, solvent reservoirs, etc. Therefore, it is not surprising to find packaging applications of cellulose acetate due its high chemical and thermal stabilities, dense and strong structure, and low cost [32]. The versatility of cellulose acetate allows its adoption to different film production technologies [6]. Electrospinning was used a promising and affordable method to manufacture packaging material. This technique relies on the application of an electrical potential to create thin cellulose fibers extruded through a nozzle [33].

*Cellulose sulfate* is an inorganic derivative produced with the addition of sulfuric acid, sulfur trioxide or chlorinated sulfonic acid to cellulose fiber. Esterification can occur via two strategies. Heterogeneous sulfation includes  $\text{SO}_3$  complexes such as DMF as solvent, pyridine as sulfation agent and  $\text{H}_2\text{SO}_4$  as the reactant. The sulfation of cellulose results in chain cleavage and produces cellulose sulfate with a high degree of substitution. Cellulose sulfate produced with heterogeneous method may have non-uniform distribution of crystalline and amorphous regions and limited solubility in water. In contrast, homogeneous sulfation requires  $\text{N}_2\text{O}_4$ -DMF and  $\text{SO}_3$  complexes for the synthesis of cellulose sulfate. It generates even distribution of crystalline and amorphous regions, which results in higher solubility in water and low-chain degradation. When used in packaging manufacturing, cellulose sulfate can represent antimicrobial characteristics. In addition, cellulose sulfate films are recognized as biodegradable and biocompatible, different from cellulose acetate.

*Cellulose phosphate* is an inorganic cellulose derivative generated by phosphorylation of cellulose fibers using phosphor-containing esters such as phosphonites, phosphites, or phosphinates. Similar to sulfation, phosphorylation may take place under heterogeneous or homogeneous conditions. Heterogeneous phosphorylation of cellulose fiber occurs in the presence of solvents such as *N*-methylmorpholine *N*-oxide or DMF. The homogeneous approach results in complete or partial esterification of cellulose fiber to yield a soluble product. Unlike cellulose sulfate, cellulose phosphate is largely water-insoluble due to polymer chain crosslinking. This may result in coagulation in the solution and serves as a limitation for applications that require a free-flowing melt, such as packaging [7].

*Cellulose nitrate* is the poly-nitrate ester of cellulose obtained by replacing hydroxyl groups with nitrates using nitrating acid mixtures. Cellulose nitrate demonstrates odorless and tasteless characteristics and is typically soluble in organic solvents (e.g., alcohols), which allow it to be used in various areas, such as packaging film, membrane filters, pharmaceutical, and optical instruments. The degree of

nitration is an important parameter for cellulose nitrate that shows the volume of nitric oxide release when 1 g of cellulose nitrate is completely decomposed at 0°C and 1 atm. It influences the physicochemical properties of cellulose nitrate such as viscosity, solubility, heat of formation and combustion and thermal stability [34, 35]. Generally, lower degree of nitration (10–11%) is preferred for film manufacturing as it provides thermoplastic behavior and solubility in organic solvents, which are essential for film manufacturing [36].

*Cellulose xanthate* is a sodium hydroxide-soluble cellulose derivative. The control over the process is critical since industrial viscose rayon fabric (known as viscose) and cellophane are formed from xanthate. It is obtained by stepwise xanthation reactions, which involve alkalization using sodium hydroxide, followed by ripening to bring the degree of polymerization to 0.5 (i.e., to adjust the viscosity). After ripening, the solution is passed through a spinneret to create soft filaments [37]. Finally, the soft filaments are exposed to sulfuric acid and zinc, and sodium sulfate to obtain the rayon fiber filaments. Rayon fabric shows good plastic behavior with high mechanical strength, elasticity and strong moisture absorption. Degree of ripening and polymerization determine the strength of rayon fibers: higher DP and DR increased the strength of the films prepared by fiber spinning [38]. The high moisture absorption rate is related to their lower crystallinity that serves as a drawback for packaging films applications. Rayon fabric is commercially produced from wood pulp. The physicochemical features of the rayon fabric are close to fabrics produced from natural cellulose (e.g., cotton or linen). The viscose fibers show high resistance to acid and alkali conditions, and resistant to fabric and film manufacturing conditions [39]. Versatility and affordability allow viscose for its use in large-scale industrial textiles and food packaging, such as sausage casings [40].

### 3.2.3 Etherification

Etherification of cellulose involves homogeneous or heterogeneous reactions with etherifying agents, such as epoxides, halogenated alkanes, alkyl, silyl chlorides, bromides, or vinyl compounds. Cellulose ethers are classified as silyl ethers, ionic alkyl ethers and nonionic alkyl ethers and have alkyl halide structures with hydroxyl groups. They are among the most abundant cellulose derivatives and manufactured on large scales. The commercial forms used in various industries include methylcellulose, carboxymethyl cellulose, ethyl cellulose, hydroxyethyl cellulose, and hydroxypropyl cellulose. Cellulose ethers represent non-toxic, tasteless and non-flammable and water-soluble features. These properties enable them to be used as a thickener, water binder, processing aids in food formulations; as excipients in pharmaceutical formulations; and textile and packaging applications [41]. Their solubility depends on the pH of the solution: soluble in alkaline conditions with decrease in solubility with decreasing pH. They are also thermally stable up to 100°C, and form crosslinking network with slight degradation at 130–150°C [42].

*Methyl cellulose* is the nonionic alkyl ether that is produced with methyl chloride or dimethyl sulfate in an alkaline medium. Methyl cellulose demonstrates high solubility in water and organic solvents, good gelling capabilities and emulsifying power. Therefore, they are common ingredients in sugar-based syrups, oil emulsions, creams, food gels, baked goods, fried foods, and soups. Moreover, methyl cellulose has a potential in food packaging film industry as a plasticizer since they display low cost, transparency, high strength, easy handling and environmentally friendly structure that are important properties for packaging films [43].

*Carboxymethyl cellulose (CMC)* is an anionic cellulose ether derivative obtained by the reaction between alkali cellulose and sodium chloroacetate, where hydroxyl groups are replaced with carboxymethyls at 2nd, 3rd, and 6th carbon of a glucose unit. CMC is another traditional food additive as a thickener, stabilizer, emulsifier, bulking agent, and water binder related to its affordability, water solubility, chemical stability, and non-toxicity. It is a common ingredient in food gels, such as processed meat products, dry pet foods, yoghurt, beverages, ice cream and dessert. In addition to these, CMC can provide control to the viscosity of film-forming solution, and protective barrier when used in food packaging film applications [44].

*Ethyl cellulose* is a nonionic cellulose derivative obtained by the reaction between alkali cellulose and ethyl chloride between 90 and 150°C, where hydroxyl groups are converted into ethyl ether groups. This results in less polarity than CMC and methyl cellulose. Ethyl cellulose is soluble in various organic solvents such as hydrocarbons, alcohols, esters and chlorinated solvents. The physicochemical properties and applicability of ethyl cellulose depend on the degree of etherification. The conversion of hydroxyl groups into ethyl ether units provides water-solubility, adhesive features as well [45].

*Hydroxyethyl cellulose* is a nonionic derivative obtained by the reaction of cellulose with sodium hydroxide and ethylene oxide, where ethyl groups are attached to hydroxyl units. They show non-toxic, compressible, and water-soluble characteristics attractive for tissue engineering and biomedical applications. They are also widely used as a thickening, emulsifying agent and stabilizer in personal care and cosmetic products. It is not permitted to be used in food formulations due to its chemical structure, but it might be an alternative for food packaging films [46].

*Hydroxypropyl cellulose* is an alkali cellulose derivative obtained with the substitution of 2-hydroxypropyl chloride with hydroxyl groups. Similar to methyl cellulose, it shows gelling ability, however, at higher temperatures. Hydroxypropyl cellulose can be used as gelling agent, emulsifier or thickener in salad dressing, sorbet, and confectionary product fillings. Hydroxypropyl cellulose can also contribute to gas barrier properties oil-resistance of packaging films [47, 48].

#### 3.2.4 Silylation

Silylation is based on incorporation of multifunctional silane compounds (i.e., methyltrimethoxysilane, aminopropyltriethoxysilane, methacrylopropyltrimethoxysilane alkoxy silane) into cellulose fibers or micro- and nano-crystals. Silylation provides unique characteristics depending on the specific groups in the glucose unit (i.e., -OH, -CH or -COOH). For example, cellulose nanocrystals can be partially silylated using n-dodecyldimethylchlorosilane as a silylating agent and acetone as the solvent to allow surface modification. The silylation process can effectively enhance crystallinity, crosslinking, and strength of cellulose fibers. For example, partially silylated cellulose nanocrystals exhibited improved degree of crystallinity and tensile strength [49]. Similar to other cellulose derivatives, when used in film formulations, silylation can improve their functional properties, such as water vapor barrier and thermal resistance [50].

#### 3.2.5 Carbamylation

Carbamylation of cellulose occurs by the reaction of hydroxyl group of cellulose with isocyanate. Carbamylation of nanofibers can increase their reactivity and

thermal stability. The carbamylation of cellulose modifies the polarity of cellulose fibers. For example, hydrophobicity of cellulose nanocrystals increased by crosslinking phenyl isocyanate with hydroxyl groups, while crystallinity and other physicochemical characteristics of cellulose nanofibers remained unchanged [51].

A major limitation in food and packaging applications is related to the use of isocyanate that can create toxic byproducts during the carbamylation process.

### 3.2.6 TEMPO oxidation

The free radical TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) is a water soluble and relatively stable nitroxyl radical (i.e., half-life in minutes at room temperature). It can catalyze the oxidation of primary hydroxyl groups of cellulose fibrils to carboxyl form. TEMPO reaction requires oxidizers such as NaClO or NaClO<sub>2</sub> in the presence of NaBr at alkaline conditions. This process can provide electrostatic repulsion between cellulose fibers by preventing hydrogen bonding. TEMPO-oxidized cellulose fibers can be used to produce films with improved network structure, optical features, gas barrier and thermomechanical characteristics. For instance, the films prepared from TEMPO-oxidized wood cellulose nanofibers exhibited improved degree of fibrillation and low oxygen permeability, desirable optical transparency, and high tensile strength and Young's modulus in their films [52]. Similarly, softwood and hardwood celluloses oxidized by TEMPO displayed transparent, flexible and low thermal expansion coefficient with higher crystallinity compared with untreated cellulose nanofiber films [53].

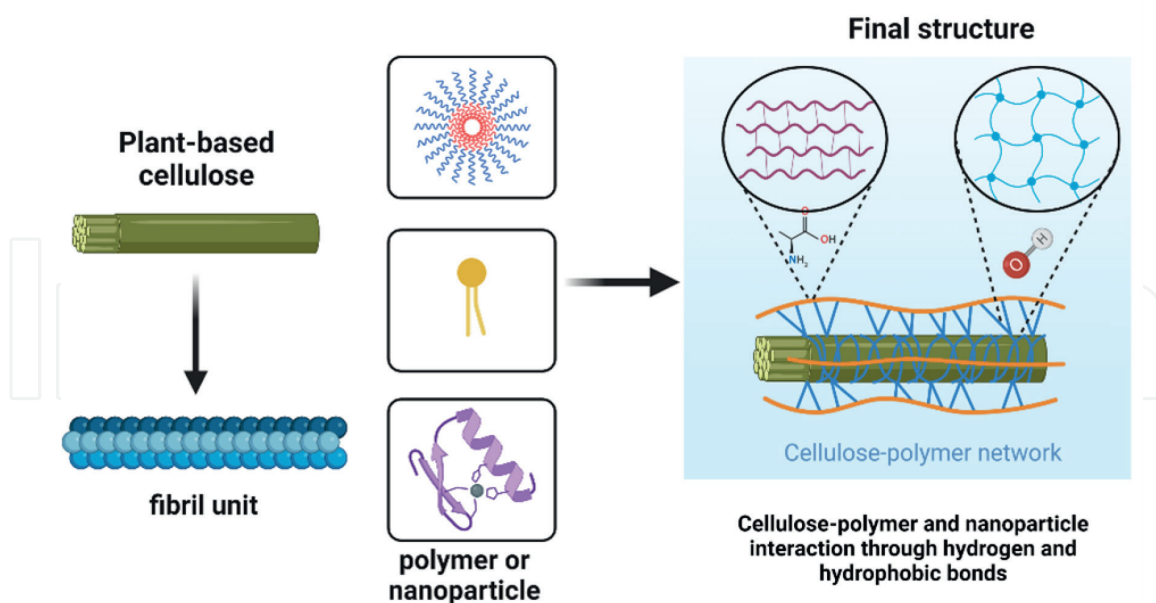
## 4. Cellulose network and cellulose interactions

### 4.1 Cellulose fibrillar network

The cellulose microfibrils and their derivatives are responsible for the formation of a cellulose polymer network as seen in film structures, where they interact with other polymeric materials and doped nanoparticles through electrostatic forces, hydrogen bonds, Van der Waals attraction as illustrated in **Figure 2**. The nature of these interactions influences the strength and morphology of cellulose-based films. For example, the presence of similar charged substitutes on fiber surfaces may create repulsive forces to result in porous structure while opposite charged groups on fibril units might cause dense and smooth film surfaces [54]. In addition to this, high dispersibility of cellulose fibrillar matrices and strong hydrogen bonds with other polar moieties through hydroxyl groups are important for the strength of the cellulose-based films. For example, nanocellulose films with high fibrillar network and extensive hydrogen bonding demonstrate low porosity and high oxygen and moisture barrier [55]. Overall, these interactions support a good film framework important for desirable mechanical and gas barrier features. This section explains and exemplifies the nature and importance of cellulose interactions with a focus on physicochemical and mechanical properties of film materials.

### 4.2 Cellulose-protein interactions

Native cellulose is a nonionic polymer with reduced interaction capacity without pretreatment. Cellulose derivatives can show interfacial activity and electrostatic



**Figure 2.**  
A schematic illustration of cellulose interactions with polymers and nanoparticles.

potential to interact with proteins via electrostatic interaction, hydrogen bonding or hydrophobic attraction. Electrostatic interactions between protein and cellulose derivatives (e.g., negatively charged methylcellulose and carboxymethyl cellulose) can provide advanced control over the characteristics of cellulose films to improve their mechanical and barrier properties. For example, a recent research showed that cellulose nanocrystals from a bacterial source can participate in protein gels to improve mechanical properties (tensile strength) and as well as oxygen and moisture barrier abilities of nanocomposite biodegradable packaging films [56]. Another study showed that the intermolecular interactions between fish gelatin and crystalline regions of cellulose microfibrils significantly increased the tensile strength and reduced the water vapor permeability of biodegradable fish gelatin films [57]. In addition to this, the physicochemical properties (e.g., pH, temperature, ionic strength, concentration, etc.) of solutions of cellulosic polymers and proteins determine the extent of their interactions. Among these parameters, pH played the most critical role since it affects the surface charges, wettability, density and conformational state of dispersed systems [58]. For example, at lower pH (pH 3), soy protein isolate (SPI) and TEMPO oxidized bacterial cellulose interacted via electrostatic attractions and formed a positively charged noncovalent complex that displayed good creaming stability and elastic gel texture. On the other hand, at higher pH (pH 9), cellulose-protein interaction shifted from strong electrostatic attraction to repulsion [59]. Moreover, at pH 4 negatively charged CMC can form a complex with positively charged pea protein to form insoluble complexes. At lower pH values, the interaction between CMC and protein increases with strong electrostatic repulsion, high viscosity, and steric hindrance [60]. In addition, the presence of small molecules, such as salts or sugars, may alter the nature of interactions. For example, ionic liquids, which are molten salts with organic cations and anions, show significant effects on cellulose-protein complexes [61]. Anions may form hydrogen bonds with hydroxyl groups found in cellulose or protein and disrupt the naturally occurring hydrogen bond between these two polymers. Moreover, cations in ionic liquids may interact with ether oxygen atoms or CH groups in native

cellulose or derivatives [62]. It was shown that chloride ion associated with hydroxyl groups in cellulose and resulted in weakening intermolecular hydrogen bonds between protein-cellulose complex extracted from peanut leaf. These interactions reduced the tensile strength of prepared films [63].

### **4.3 Cellulose-polysaccharide interactions**

The interactions between cellulose and polysaccharides, such as starch, glucomannan, pullulan occur between unsubstituted chains via hydrogen bonding. Anionic cellulose derivatives, such as CMC and CNC can interact with charged polysaccharides, such as sodium alginate or chitosan to form hydrogel structures by intermolecular inclusion interaction. These interactions occur via hydrogen bond or ionic crosslinking and enhances mechanical performances. For example, chitosan-carboxymethyl cellulose interaction creates polyelectrolyte multilayer films that includes oppositely charged layers of polyelectrolytes [64]. The electrostatic interaction between these two polymers results in binding of the oppositely charged polymers on the film surface. This brings about improved strength in composite film. Another study showed that intermolecular interaction between konjac glucomannan and pullulan and natural cellulose nanofibrils yields strong crosslinks to improve the flexibility and elasticity of films and reduce the water vapor permeability [65]. Besides, strong hydrogen bonds between hydroxyl groups of cellulose nanofibrils and hydroxyl or carboxyl groups of sodium alginate increased the cohesiveness and water resistance of the biopolymer films [66]. The authors in the reference [67] examined the influence of molecular interactions between microcrystalline cellulose (MCC) and propylene glycol alginate-agar polymeric mixture and their effect on mechanical, physical and barrier properties of microcrystalline cellulose gum edible films. The addition of 4% MCC was sufficient to reduce the water vapor permeability and enhance the tensile strength of the film due to inter and intramolecular hydrogen bonds. Interestingly, incorporation of cellulose resulted in reduced intramolecular interactions between polymers and caused less compact network and hydrophobicity on the film surfaces. A study focused on the effect of electrostatic interactions between cellulose nanofiber and alginate or chitosan in their films [68]. It was highlighted that cellulose-polysaccharide interaction mechanisms led to an increase in tensile strength and water vapor resistance of the polysaccharide films. Another study modified CMC films with xanthan gum, and flaxseed gum to improve the physical and mechanical properties (e.g., water vapor resistance, tensile strength, elasticity), and reduce the weight loss and increase shelf life of mango [69].

### **4.4 Cellulose-nanoparticle interactions**

Packaging films prepared from native cellulose or derivatives, such as cellulose nanocrystals or CMC, can be doped with nanoparticles to provide them strength, stability, ultraviolet barrier, optical or antimicrobial functionality. For example, paramagnetic iron oxide nanoparticles coating to cellulose nanocrystals was shown to improve the thermostability of the films [70]. Another study focused on the preparation of cellulose nanocrystal films incorporated silver (Ag) [71]. The films showed ultraviolet barrier property and reduced water vapor permeation. Furthermore, calcium hydroxide nanoparticles can support the crosslinking between polysaccharide and cellulose nanofiber by diffusing into the matrix and attaching with ionic bonds. This enables to increase in the opacity and thermal stability of multilayer packaging

films. Photocatalytic TiO<sub>2</sub>-Ag nanoparticles can be added to provide antimicrobial and photocatalytic activity to CMC based films. In addition, they also increased the tensile strength of the films related to increased electrostatic attractions between hydroxyl groups and O-Ti-O bonds between CMC and nanoparticles [72]. In another study, ZnO-loaded cellulose acetate film was obtained by ionic interaction between zinc and oxygen atoms in cellulose acetate [73]. These films exhibited antibacterial action against *E. coli* and moisture barrier characteristics. Recently, Amini et al. [74] created nano-composite packaging films using cotton cellulose and hydrophobic polycaprolactone (PCL) dissolved in an ionic liquid containing zinc oxide nanoparticles. The intermolecular hydrogen bond between cellulose fibers, PCL and zinc oxide resulted in promising film properties (i.e., improved oxygen barrier property, good tensile energy absorption, elasticity, and surface smoothness). The authors mentioned that nanocomposite film may serve as a packaging film for peanuts and meat based on physical and mechanical characteristics. An interesting study mentioned that CMC films prepared with the addition of cobalt nanosheets show strong antimicrobial activity against *E. coli* and *S.s aureus* without affecting mechanical properties of the films [75].

## 5. Conclusion and future perspectives

In conclusion, several literature and industrial examples indicate great potential for cellulose and its derivatives to be used in manufacturing of film materials with tailored properties for specific applications and needs. Cellulose and derivatives are potential sources for commercial packaging films due to their good film-forming abilities. There is an increasing trend in cellulose-based biodegradable packaging applications in combination with active ingredients with antioxidant and antimicrobial properties. Cellulose fibers are abundant and can be obtained from affordable and sustainable resources extracted from plants, animals, bacterial or algae-based sources and as well as waste streams of industrial production lines. The research is still ongoing to overcome certain challenges and improve film properties in consideration of environmental sustainability, biodegradability as well as mechanical and gas permeation resistance properties of the film materials. Controlling the micro-scale interactions between cellulose and other polymers as well doped nanoparticles can be used to strengthen the film network and furnish them with new functionalities. As a general trend of following research efforts, development and scaling up the emergent technologies to large scale production and industrial applications remain as one of the biggest challenges. For example, industrial production of films requires specialized instruments where the materials need to be resistant to high temperatures and pressures associated with the extruders. Overall, advances in cellulose modification methods can address practical challenges associated with adoption of their films as future perspectives.

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