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CELLULOSE BIOFILMS AS A HIGH-PERFORMANCE ALTERNATIVE IN FOOD PACKAGING, FROM BARRIER PROPERTIES TO BIODEGRADABILITY.

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Lo importante es no dejar de hacerse preguntas.

Albert Einstein

Quiero agradecer, en primer lugar, a mis padres, por todo: por la educación que me han dado, por cómo son, y especialmente por haberme dado la oportunidad de venir a Barcelona para poder regresar como ingeniero químico. Estoy tan agradecido por esta oportunidad que me resulta imposible expresarlo con palabras, a pesar del alto precio que supuso separarme de ellos durante años.

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SUMMARY

Nowadays, there is a growing awareness of the problem of pollution, especially with regard to the generation of plastics, a sector widely in demand due to its versatility in various applications. The polymers commonly used in the food packaging industry represent a significant problem, since they come from a non-renewable source such as petroleum and are not biodegradable. This Final Degree Project is a bibliographic study about the bioplastics derived from cellulose, highlighting two key advantages: their origin from biomass and their biodegradability, which makes them a highly relevant resource for the future. The study focuses mainly on cellulose bioplastics due to their availability, the low cost of the raw material and their wide range of applications, derived from their properties. In addition, they present compatibility with different compounds that allow modifying these properties. However, one of the main drawbacks of these materials is their production cost compared to non-biodegradable plastics.

In the field of food packaging, the most commonly used cellulose biofilms that will be analyzed are cellulose acetate and cellulose propionate. The production methods, characterization and properties of these materials derived of cellulose acetate and cellulose acetate propionate will be studied. In addition, the comparison between different catalysts used in the production will be analyzed, observing the current trend to use heterogeneus catalysts, in concret acidic ion exchange resins due to their lower environmental impact.

Finally, a comparison of the usual production of conventional plastics will be made, evaluating how the innovation and development sector is working in the search for competitive and sustainable solutions to this problem.

Keywords: Food packaging, bioplastics, cellulose biofilms, cellulose acetate, propionate cellulose acetate, biodegradability.

RESUM

En la actualidad, existe una creciente conciencia sobre el problema de la contaminación, especialmente en lo que respecta a la generación de plásticos, un sector ampliamente demandado debido a su versatilidad en diversas aplicaciones. Los polímeros comúnmente utilizados en la industria del empaquetado alimenticio, representan un problema significativo, ya que provienen de una fuente no renovable como el petróleo y no son biodegradables. Este Trabajo de Fin de Grado es un estudio bibliográfico sobre los bioplásticos derivados de la celulosa, destacando dos ventajas clave: su origen a partir de biomasa y su biodegradabilidad, lo que los convierte en un recurso de gran relevancia para el futuro. El estudio se centra principalmente en los bioplásticos de celulosa debido a su disponibilidad, el bajo coste de la materia prima y su amplio rango de aplicaciones, derivado de sus propiedades. Además, presentan compatibilidad con distintos compuestos que permiten modificar dichas propiedades. Sin embargo, uno de los principales inconvenientes de estos materiales es su coste de producción en comparación con los plásticos no biodegradables.

En el ámbito del empaquetado alimenticio, los biofilms de celulosa más utilizados y objeto de análisis parten acetato de celulosa. Se estudiarán los métodos de producción, caracterización y propiedades de estos materiales derivados del acetato de celulosa y del acetate propionate de celulosa. Además, se analizará la comparación entre diferentes catalizadores utilizados en la producción, observando la tendencia actual a emplear catalizadores heterogeneous, en concreto resinas de intercambio iónico ácidas, debido a su menor impacto ambiental.

Finalmente, se realizará una comparación los metodos de producción de los plásticos convencionales, evaluando cómo el sector de innovación y desarrollo trabaja en la búsqueda de soluciones competitivas y sostenibles para esta problemática.

Paraules clau: Empaquetado alimenticio, bioplásticos, biofilms de celulosa, acetato de celulosa, acetate propionato de celulosa, biodegradabilidad.

SUSTAINABLE DEVELOPMENT GOALS

This Final Degree Project is closely linked to several United Nations Sustainable Development Goals (SDGs) by addressing key aspects of environmental sustainability, advancements in material science, and responsible manufacturing practices. The research conducted promotes a more sustainable approach by developing biodegradable biofilms for food packaging, reducing dependency on petroleum-based plastics, and lowering overall environmental impact. The primary SDGs relevant to this study include:

1. SDG 9 – Industry, Innovation, and Infrastructure. This research fosters sustainable industrial innovation by creating biodegradable packaging solutions derived from cellulose. The exploration of solid acid catalysts improves production efficiency, allowing for a more controlled and consistent synthesis process. Furthermore, the adaptability of biofilms to various manufacturing techniques contributes to the progress of sustainable material science, driving eco-friendly advancements in the packaging sector.

2. SDG 12 – Responsible Consumption and Production. A fundamental contribution of this study lies in promoting responsible manufacturing methods. By incorporating biodegradable cellulose-based biofilms, this work presents a viable alternative to conventional plastic packaging, which is a major contributor to global waste. The use of solid catalysts minimizes chemical waste and enhances material reusability, aligning with the principles of a circular economy. This research supports sustainable resource management, encouraging more eco-conscious and efficient production techniques.

3. SDG 13 – Climate Action Plastic. Pollution is a significant factor in environmental degradation and greenhouse gas emissions. By substituting petroleum-based plastics with biodegradable biofilms, this study supports a reduction in carbon footprint related to plastic production and disposal. Additionally, the application of solid-state catalysis helps mitigate harmful byproducts, contributing to a more sustainable and environmentally responsible process.

4. SDG 14 – Life Below Water & SDG 15 – Life on Land. One of the most pressing global issues is plastic pollution, which severely impacts marine and terrestrial ecosystems. The development of biodegradable biofilms plays a direct role in reducing microplastic contamination in water bodies and soil. Since these biofilms decompose naturally without leaving persistent pollutants, they serve as a safer alternative for ecosystems, helping to preserve biodiversity and mitigate environmental damage.

This TFG contributes to multiple SDGs by driving sustainable advancements in material science, reducing ecological impact, and enhancing industrial innovation. The development of cellulose-based biofilms, in combination with solid catalysts for efficient processing, aligns with global sustainability initiatives by curbing plastic pollution, optimizing material efficiency, and supporting a transition towards circular economy models. These findings establish a strong foundation for future research and industrial applications, emphasizing the crucial role of biodegradable materials in achieving global sustainability targets.

1. INTRODUCTION.

The environmental impact of the materials currently in use constitutes a crucial issue, given the increasing concerns regarding sustainability and climate change. The materials employed in daily life —including plastics, metals, textiles, and construction products— present a significant ecological footprint that must be taken into account. This footprint encompasses the extraction and production processes, as well as disposal methods, many of which generate pollution and waste.

The production and incineration of various materials, particularly conventional plastics, involve considerable energy and natural resource consumption, further contributing to greenhouse gas emissions. Moreover, the non-biodegradable nature of conventional plastics leads to the generation of plastic waste that requires extensive periods to decompose, thereby exacerbating environmental pollution, which remains a serious issue.

Analyses of global plastic waste production have indicated that approximately 269,000 tons of post-consumer plastic waste end up in waterways and oceans. Projections suggest that by 2050, the quantity of plastic particles in the ocean will surpass the number of fish [1].

1.1. THE PLASTIC SECTOR, CIRCULAR ECONOMY AND PRODUCTION.

The plastics sector is currently undergoing a transformation, driven by increasing environmental awareness and a push for sustainable practices. While traditional petroleum-derived plastics like polyethylene and polypropylene continue to play a vital role in various industries such as packaging, construction, and automotive manufacturing, the industry is evolving.

Bioplastics have emerged as a potential eco-friendly alternative, attracting interest despite their current small market share. Their rapid growth is fueled by consumer preferences and governmental policies favoring more environmentally responsible products. Central to this shift is the concept of a circular economy, which emphasizes recycling, reusing, and repairing materials and products instead of disposing of them after use. This model aims to minimize waste generation while optimizing resource utilization. Single-use, non-degradable plastics have been heavily targeted by governmental decision-makers around the world because of their immense contribution to environmental pollution. As a result, many governments and policymakers have recently prohibited the sale and distribution of certain single-use plastics. For instance, the state of Victoria in Australia has banned the use of problematic single-use plastics, such as straws, cutlery, plates, and containers, starting in February 2023 [2].

In a circular economy, new plastics are produced through a closed-loop recycling process (Figure 1).

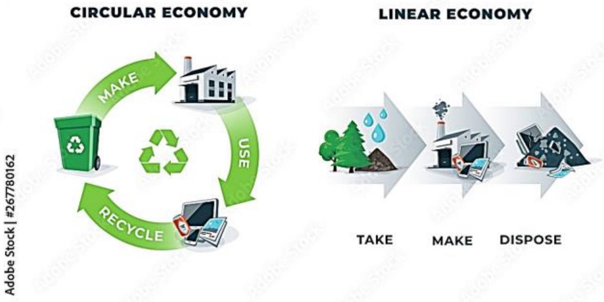

Figure 1 *Difference between circular and linear economy [3].*

The image represents the difference between open-loop linear economy and closed-loop circular economy. In a linear economy, the oil-based raw materials are processed into a product that is thrown away after use. However, the circular model illustrates a cyclical process. After consumption, products are not simply thrown away. Instead, they are either reused in their current form or recycled into new materials.

Firstly, recycling plastic waste from healthcare, which is often contaminated with biological substances, presents significant challenges and is sometimes not feasible [3]. Secondly, recycling is a labor-intensive and time-consuming process that can increase a product's carbon footprint, making it less ideal for achieving carbon neutrality. Thirdly, recycled plastics often have inferior or compromised physical properties compared to new plastics. Due to these core issues, recycling, while helpful in mitigating the problem, is not a complete solution and needs to be complemented by other practices.

The global plastics production hit an impressive 400.3 million metric tons in 2022, representing a 1.6 percent rise from the year before. Since the 1950s, the production of plastics has skyrocketed. The remarkable adaptability of these materials explains their consistent annual production increase. Alongside this increase, the market value of plastics has also been steadily rising. In 2023, global bioplastics production reached 2.02 million metric tons. 50.9% of this amount was produced in Asia, while just over 20% came from North America. [4].

The figure 2 shows that the 50% of the plastics produced, are destined for the field of packaging. This industry has gained significant importance in global economy, every product must be packed to fulfil with the commerce standards [5].

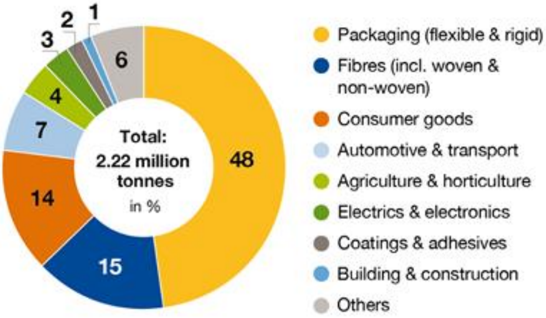

Figure 2 *Plastic global production [6]*

The key properties for selecting an effective packaging material can be organized as follows [7]:

- Polymer Morphology: The crystallinity of a polymer significantly influences its mechanical properties. As crystallinity increases, the polymer's density and tensile strength also increase, but its impact strength and toughness decrease.
- Barrier Properties: In applications such as food packaging (FP), the ability to isolate the product from gases like oxygen or carbon dioxide is crucial for extending the product's shelf life. These characteristics are measured by the material’s gas permeability.
- Thermal Properties: Given that polymers are generally unsuitable for high temperatures, understanding thermal parameters like glass transition temperature

and melting temperature is essential for designing packaging that performs adequately under specific conditions.

- Mechanical Properties: Packaging must withstand mechanical stresses to protect its contents. Critical attributes include tensile strength, tear strength, and impact strength.
- Optical Properties: Packaging needs to be clear and transparent when packaging materials similar to glass. However, for products sensitive to light, the packaging should be completely opaque.

In the specific context of food packaging, particular attention is given to the mechanical and barrier properties of the materials used, as well as to their antioxidant and antimicrobial capabilities. Additionally, thermal properties within a defined range and exhibiting a required behavior are also sought.

1.2. POLYMERS

A polymer is essentially a collection of identical molecules connected through covalent bonds into chains, the length of which determines its applications. As shown in Table 1, increasing the count of monomers (-CH2-) in polyethylene chains alters the material’s characteristics.

Table 1. Properties/applications of chains of monomers depend on the number of them [8]

Number of Carbons in chain	State and Properties of Material	Applications
1-4	Simple gas	Bottled gas for cooking
5-11	Simple liquid	Gasoline
9-16	Medium-viscosity liquid	Kerosene
16-25	High-viscosity liquid	Oil and grease
25-50	Crystalline solid	Paraffin wax candles
50-1000	Semicristalline solid	Adhesives and coatings
1000-5000	Tough plastic solid	Bottles and containers
$3\text{-}6 \times 10^6$	Fibers	Surgical gloves, bullet-proof vests

There are two different ways for synthesizing polymers, which are:

Free Radical Polymerization: Initially, oxygen disrupts the chain, creating a free radical. The initiation phase typically involves adding the first monomer molecule, where the free radical attacks and attaches to the monomer. Following the initiation, numerous monomer molecules are quickly added, possibly within a fraction of a second. With each addition of a monomer, the free radical transfers to the end of the chain. During the termination phase, free radicals react with one another, concluding typically through a combination process [8].

Condensation polymerization is a step-growth chemical reaction in which two or more monomers (small molecules) combine, forming a by-product each time two monomers join. In many cases, this by-product is water or another simple substance. For polycondensation to be successful, the formed monomers must have a minimum functionality level of 2 (they can react 2 times); otherwise, the chain of forming monomers would cease to grow, and the polymer would not form. At each union of two monomers, a small molecule, such as water, is lost. When discussing polymers, one refers not to a singular chain length but to mixtures of chains of varying lengths. To determine a polymer's molecular weight and degree of polymerization (DP), averages of these parameters are calculated across the entire set. These distributions vary depending on the kinetics of the polymerization and the conditions applied. To better understand the behavior and characteristics of polymers, it is crucial to examine the spatial distribution of its molecules: the chains might form simple bonds with each other or cross-link depending on their functional groups. When the chains organize neatly into structures called lamellae, the polymer is described as crystalline. Conversely, when the chain organization is haphazard with a random spatial arrangement, it is classified as an amorphous polymer.

The proportion of molecules arranged in a crystalline structure is known as the degree of crystallinity, and it is influenced by the duration of the polymer's crystallization process. The more time the molecules have to settle into their lowest energy positions (more ordered), the slower the crystallization process, resulting in higher crystallinity. Crystalline areas add rigidity and compactness, thereby increasing the density, while the amorphous areas lend elasticity, as the bonds between the chains in these regions are easier to break and reform [9].

Polymers can be categorized based on their properties into three main types:

- Thermoplastics: These polymers become rubbery as temperature increases and solidify upon cooling, a reversible process. If heated further, they undergo thermal degradation, breaking bonds irreversibly, leading to a loss of original properties. Common examples include polyethylene and polystyrene, which typically have a linear structure.

- Thermosetting: These are predominantly cross-linked polymers that do not soften upon heating due to covalent bonds between the chains, which increase rigidity but make them more brittle compared to thermoplastics. Examples include epoxy and phenolic resins.
- Elastomers: Characterized by their completely amorphous structure, these polymers are highly elastic and lightweight but have a limited stress capacity. Examples include silicone, neoprene, rubber, and polyurethane.

It is important to consider that both bioplastics and biopolymers can exhibit materials with properties corresponding to any of the three previously mentioned categories (thermoplastics, thermosetting, and elastomers). This makes them a competitive and sustainable alternative to conventional polymers.

1.3. SUSTAINABLE POLYMERS

Sustainable polymers are materials derived partially or entirely from biomass—organic matter from plants or animals—and are designed to reduce environmental impact. Unlike conventional plastics, these polymers can be biodegradable, compostable, or easier to recycle. Their link to biomass, a renewable energy source, highlights their role in promoting a circular economy and lowering the ecological footprint of materials used, for example, in food packaging.

Biomass can come from a variety of sources. Farm by-products include plant residues such as corn stalks, sugarcane remains, and wheat straw left after harvest. The forestry industry also contributes biomass through waste generated during logging, including branches, leaves, and other unused wood materials. In addition, certain crops—like sugarcane, corn, or grasses such as miscanthus—are specifically cultivated for energy purposes. Other sources include livestock waste (mainly manure), urban organic waste (like discarded food and paper), and organic by-products from food and paper manufacturing.

The advantages of biomass include its renewability, as organic matter naturally regenerates; its contribution to waste reduction by utilizing residues from agriculture, forestry, and industry; and its relatively low carbon impact, since the CO_2 emitted during combustion is balanced by the CO_2

absorbed during plant growth. Biomass also enhances energy diversification by reducing reliance on fossil fuels.

However, there are also drawbacks. The expansion of land use for energy crops can cause deforestation and biodiversity loss if not properly managed. Although biomass burns cleaner than fossil fuels, it still emits pollutants such as particulate matter. Additionally, its energy conversion efficiency is often lower, requiring advanced technologies to optimize output. The initial costs of biomass facilities and conversion technologies can also be significant. Lastly, dedicating land and water to energy crops may lead to competition with food production, potentially driving up food prices.

An important concept when discussing sustainable materials is compostability, which refers to the ability of a material to biodegrade under specific environmental conditions. Within this context, bioplastics have gained attention as alternatives to conventional plastics. These materials can be classified into three main categories, as shown in Figure 3: (1) biobased and biodegradable; (2) biobased but non-biodegradable; and (3) fossil-based (non-biobased) but biodegradable.

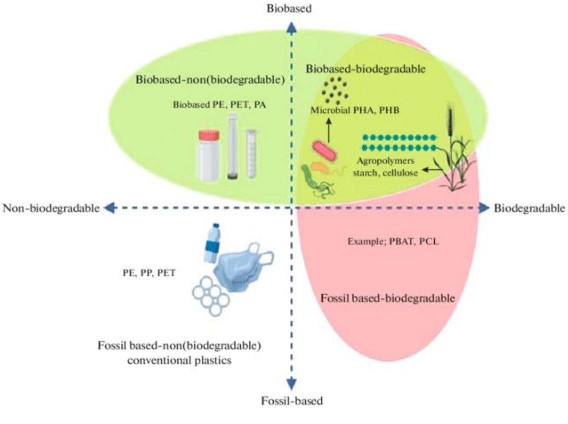

Figure 3 *Main categories of bioplastics [10]*

Among bioplastics, particular attention is given to cellulose-based materials. Derived from the cell walls of plants and thus from biomass, cellulose qualifies both as a bioplastic and a biopolymer. It is compostable, biodegradable, and widely available, making it a cost-effective and environmentally friendly raw material. Cellulose is also the most abundant biopolymer on Earth and can be digested by many microorganisms, further reinforcing its biodegradability [11].

One significant derivative is cellulose acetate (CA), which is used in various applications, including film production, due to its favorable mechanical and processing properties. The sustainable nature of these biopolymers, combined with environmentally friendly synthesis methods, positions them as promising candidates not only for packaging but also for fields such as tissue engineering and drug delivery [12].

2. CELLULOSE

Cellulose, the most widely available biopolymer globally, is used in a variety of industries, including food and pharmaceutical packaging, antimicrobial and transparent films, selective membranes, drug delivery systems, reinforcing fillers for polymer composites, fibers and textiles, batteries, and more. Additionally, advancements in nanotechnology have heightened the interest in nanoscale cellulosic materials. The ability to reduce cellulose to the nanoscale has broadened its potential applications across diverse fields such as materials science, electronics, medicine, and cosmetics.

Cellulose, with its abundant hydroxyl groups and strong hydrogen bonding, possesses high tensile strength, making it ideal for applications where durability is crucial, such as in paper, textiles, and composites. However, its mechanical properties are anisotropic, meaning they vary depending on the direction of the applied force. Additionally, cellulosic materials are rigid, providing resistance to deformation under external pressure, which is vital for applications requiring stiffness, like building materials and structural composites. Its relatively low density contributes to its lightweight nature, making cellulose attractive for use in lightweight structures and products. One significant challenge with cellulosic materials is their tendency to absorb water, which can alter their mechanical properties. While this moisture retention can be beneficial in certain contexts, such as tissue engineering, it can also lead to dimensional changes and reduced strength under specific conditions [13].

Given the broad advantages of cellulosic materials, attention to them is increasing year by year. The wide application of cellulose and cellulose-based materials is more and more attractive; such a tendency can be noticed by analyzing the number of scientific publications including investigations and studies related to the chosen uses of cellulose.

2.1. CHEMICAL STRUCTURE

The chemical formula of cellulose is $(C_6H_{10}O_5)_n$ where n is equal to 1 000 – 30 000, frequently a dozen thousands, but it depends on the source of cellulose. Figure 4 shows the molecular structure of cellulose. The repeating unit of cellulose contains two segments of simple carbohydrate, which are linked with a 1,4-glycosidic bond to stabilize the structure of the polymer. The presence of an oxygen atom within the closed rings of D-glucose is responsible for the formation of intermolecular hydrogen bonds, a crucial interaction that helps keep cellulose molecules stable. There is a second hydrogen bond between hydroxyl hydrogen and hydroxyl oxygen within one molecule.

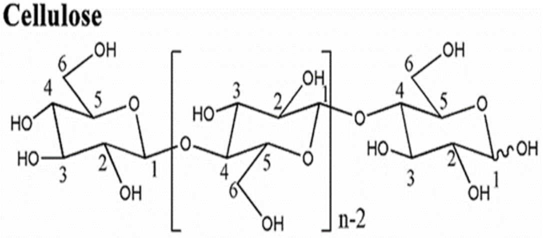

***Figure 4** Structure of cellulose*

Furthermore, hydrogen bonds form between the hydroxyl-hydrogen and hydroxyl oxygen of two distinct molecules, which stabilizes the linear arrangement and prevents the individual polymer chains from separating. The strong and linear configuration of cellulose encourages the development of fibrillar structures [14].

Cellulose fibrils consist of both highly ordered (crystalline) and less ordered (amorphous) regions. After undergoing acidic hydrolysis, the crystalline regions yield cellulose nanocrystals (CNC), while mechanical splitting along the fibrils' longitudinal axis produces cellulose nanofibers (CNF). Both CNC and CNF offer numerous benefits, including high modulus and tensile strength, low density, and sustainability [15]. Nanocellulose is noted for its exceptional stiffness, reaching up to 220 GPa, and a tensile strength as high as 10 GPa [16]. The primary mechanical robustness of nanocellulose films stems from the hydrogen bonds that form among the nanocellulose fibers during the drying process. Additionally, the high aspect ratio of nanocellulose aids in fiber entanglement within composites, enhancing their mechanical traits. Variations in the mechanical properties between the two types of nanocellulose are attributed to their differing proportions of crystalline and amorphous regions, with the crystalline areas providing better alignment and higher modulus. In contrast, the amorphous sections in CNF allow for greater elongation of these materials. Depending on the chemical treatment applied to cellulose raw materials, other forms of cellulose such as hairy cellulose nanocrystalloids (HCNC) or electrosterically stabilized nanocrystalline cellulose (ENCC) can also be derived [17].

2.1.1. AGGREGATION STRUCTURE

Cellulose consists of linear, unbranched molecules that group into rope-like bundles, each containing 100–200 cellulose macromolecular chains aligned parallelly and bonded by hydrogen bonds to form microfibrils. These microfibrils cluster together into larger structures known as fibrils. Within these structures, regular sequences create small crystalline regions (approximately 85%), while irregular sequences form amorphous regions (about 15%). Natural plant fibers are structured in complex, multi-level arrangements where a fiber comprises several of these cellulose microfibrils, and each microfibril consists of numerous cellulose molecular chains. A plethora of intramolecular and intermolecular hydrogen bonds, along with van der Waals forces, stabilizes the self-assembled macromolecular structure in the form of fibrils. Strong acids, alkalis, enzymes, and mechanical forces can cause these fibers to fibrillate, breaking down into microfibers and removing amorphous domains to extract cellulose whiskers and nanocrystals [18].

Cellulose molecules, which are rich in hydroxyl groups, form strong intermolecular and intramolecular interactions, tightly bonding the macromolecules together. Due to the abundance of hydrogen bonds, these interactions are robust and difficult to disrupt, which also applies to the cellulose chains themselves. Moreover, interactions between cellulose and water molecules occur, primarily involving the hydroxyl groups of cellulose, the oxygen bridge O4 of cellulose, and the oxygen O5 of the pyran ring of a glucose residue. The highly regular molecular structure of cellulose facilitates crystallization, with the unique structure of 85% crystalline domains and 15% amorphous domains introducing voids in low-density areas. A cellulose molecule may traverse several microcrystalline and amorphous domains, with the crystalline domains interconnected by the molecular binding forces in the crystals. Notably, the crystalline domains are interspersed with loosely arranged, chaotic amorphous domains, creating alternating dense and loose phases that contribute to the overall bulk structure of cellulose [19].

2.1.2. SWELLING AND DISSOLUTION OF CELLULOSE

A significant scientific topic are the solvents and dissolution processes of cellulose, both in theoretical research and industrial applications. Prior to the 1950s, the primary solvent used for dissolving cellulose was a copper ammonia solution. In 2003, Lina Zhang [20] developed a new solvent system based on an alkali/urea aqueous solution that efficiently dissolves cellulose at low temperatures, marking a new advancement in cellulose technology.

From the perspective of organic chemistry, cellulose solvents are categorized into derivatized and nonderivatized solvents, each differing in dissolution rate and effectiveness. Nonderivatized solvents dissolve cellulose through intermolecular forces, typically viewed as acid-base interactions between the solvent and cellulose [21]. Importantly, strong interactions exist between aqueous transition metal complexes and cellulose without forming covalent bonds, classifying them as nonderivatized solvents. Conversely, derivatized solvents dissolve cellulose by forming covalent bonds with it to create ethers, esters, and acetals. In these solvents, cellulose derivatives can be broken down into regenerated cellulose by altering the solution's composition or pH [22].

In order to facilitate the comparison of different systems for dissolving cellulose, Table 2 is presented below. This table provides a description of each medium along with its respective advantages and disadvantages

Table 2. Comparison of the different types for the dissolution

SOLVENT	DESCRIPTION	ADVANTAGES	DISADVANTAGES	REF
Inorganic compound/organic amine mixture (DMSO)	Organic solvents mixed with simple inorganic compounds, effective in dissolving cellulose	Effective but with high environmental impact, strong dissolution capabilities	Toxic, strong corrosiveness, not suitable for green chemistry	[23]
Amine oxide System (NNMO)	A powerful nonderivatizing solvent, widely used in cellulose fiber production.	High solubility, used in industrial cellulose fiber production	Expensive and requires complex processing	[24]
N,N-dimethylacetamide/lithium chloride (DMAc/LiC)	A well-known solvent system for dissolving high molecular weight cellulose without degradation.	No cellulose degradation, suitable for high molecular weight polysaccharide	Requires preactivation, challenging preparation	[25]
Ionic liquids ([Bmim]Cl)	Organic liquids with high polarity, used for dissolving various cellulose derivatives.	Nonvolatile, nonflammable, dissolves cellulose at higher rate	Sensitive to moisture, high cost	[25]
Transition metal/amine complexes (Cuoxam)	Used for analyzing cellulose structures, efficient in dissolving highly polymerized cellulose	High solubility, useful for cellulose analysis and depolymerization	Limited commercial use, environmental concerns	[25]
Alkali metal hidroxide (LiOH/urea)	Non-derivatized solvents, used as swelling agents for cellulose processing and dissolution	Efficient dissolution at low temperatures, used in cellulose swelling and processing	Highly exothermic reactions, complex to handle at large scales	[26] [27] [28]
Derivatization solvents (CF3COOH)	Dissolves cellulose by forming covalent bonds, producing ethers, esters, and acetals	Well-understood processes.	Unclear role of hydrogen bonds in the process requires specific conditions for regeneration	[27]

3. CELLULOSE DERIVED PLASTICS IN FOOD PACKAGING

The food service sector represents one of the largest markets for food packaging. As of 2021, the global market for food service packaging was estimated at 118 billion U.S. dollars, with expectations to increase by over 57 percent by 2030 [29]. Dairy and meat products are significant segments within the global food packaging industry. Tetra Pak, a Swiss company, specializes in sustainable and safe food packaging solutions, operating in over 160 countries. In 2022, Tetra Pak's net sales reached approximately 12.5 billion U.S. dollars. In the overall food system, packaging contributes around one billion metric tons of greenhouse gas emissions annually. While other stages of the food supply chain, such as agricultural production and land use, emit considerably more greenhouse gases, there is a growing interest in more sustainable packaging solutions to help minimize waste [29].

3.1. WHY CELLULOSE DERIVED PLASTICS IN FOOD PACKAGING WORLD?

Cellulose is the most prevalent biopolymer in nature and has many beneficial characteristics, such as being biodegradable, highly crystalline, non-toxic, resistant to oxygen, and hydrophilic, which makes it well-suited for manufacturing films and membranes. Cellulose-based biopolymers offer a sustainable alternative to petroleum-based plastics, reducing the environmental impact associated with their production, use, and disposal. Besides, these biopolymers help maintain food safety and quality by preserving and protecting food from external contaminants and spoilage, while remaining environmentally friendly. As society faces the growing challenges of plastic pollution and seeks more sustainable solutions, cellulose-based biopolymers emerge as a promising path to revolutionize the food packaging industry.

In addition, the sustainable production of cellulose biopolymers for advanced smart food packaging involves sourcing cellulose from various materials, each contributing unique structural characteristics and properties [30]. Cellulose from wood and non-wood plants like cotton and hemp typically has high degrees of polymerization and crystallinity, giving it strong mechanical properties suitable for rigid packaging [31]. Agricultural residues, such as straw and husks, are cost-effective and environmentally friendly but often have shorter cellulose chains and more impurities, resulting in lower mechanical strength and crystallinity [32]. These differences highlight the need to choose the right cellulose sources to optimize the performance and sustainability of smart food packaging solutions.

3.2. CELLULOSE DERIVATIVES FOR FOOD PACKAGING

This section presents different types of cellulose derivatives with applications in food packaging. A comparative overview of these materials is provided in Table 3.

Table 3. Cellulose derivatives for food packaging

Type	Source	Solubility	Transparency	Barrier properties	Other properties	Use	Ref
Celllulose Acetate	Acetylation	Insoluble in water	High	Moisture, oxygen	Non-toxic, heat resistant, strong mechanical stability	FIlms, container, coatings	[33] [34]
Cellulose Nitrate	Nitration	Insoluble in water	High	Moisture, oxygen	Explosive, flammable, antioxidant	Films with antioxidant properties	[33] [35]
Ethyl cellulose	Ethylation	Soluble in organic solvents	Moderate	Water resistant	Strong cost effective, retains strength at ambient	Film former, used with blends	[36] [37]
Nanocellulose	Cellulose fibers reduced to nanoscale	Insoluble in water but it can form gels	High	Moisture, oxygen,anticontaminants	High mechanical strength, surface area	Films, coatings	[38]
Bacterial cellulose	Synthesized by bacteria, highly pure form	Insoluble, retains high water content	High	UV radiation, oxygen	Highly pure, retains water, UV shield	Films, coatings	[39] [40]

3.3. PROPERTIES NEEDED IN FOOD PACKAGING

The many hydroxyl groups in cellulose's molecular structure facilitate the formation of hydrogen bonds, which encourage the molecules to stack tightly and form dense cellulose microfibrils [41]. Additionally, cellulose exhibits greater thermal stability and the capacity to carry antioxidant and antibacterial agents. However, three main challenges hinder the widespread use of cellulose. The first issue is solubility. Due to its complex hydrogen bonding and the presence of partially crystalline regions, cellulose does not easily dissolve in conventional solvents. Solubilizing cellulose is essential for its conversion into useful products. Another significant challenge is its higher hydrophobicity and lack of inherent antibacterial properties, which are currently being addressed. Green solvents are being used to disrupt the hydrogen bond structure of cellulose. The properties of cellulose-based films have been enhanced through the integration of polymers, which reduces hydrophobicity and improves antibacterial properties. Additionally, research is ongoing on the integration of cellulose with bioplastics in composite films [42].

3.3.1. MECHANICAL AND BARRIER PROPERTIES

The mechanical properties of materials significantly influence their range of use and longevity in practical settings. For packaging, the mechanical characteristics of films are particularly vital. Cellulose-based materials are often used to make laminated films, with cellulose enhancing the blending of polymers and boosting the films' mechanical traits. Commonly assessed mechanical properties of packaging materials include stress, strain, Young's modulus, and tensile strength. Ternary composite films made from natural rubber, cellulose microfibers, and carboxymethylcellulose display excellent mechanical properties, biodegradability, and chemical resistance. Carboxymethylcellulose enhances the interaction between cellulose microfibers and natural rubber. These composite films exhibit improved mechanical properties, high water absorption capacity, solvent resistance, biodegradability, and good water vapor permeability [43].

Films developed from saccharin and cellulose residues of the Araliaceae family showed that higher cellulose purity improves the elastic modulus and elongation (3% to 5%), as well as the visual quality of the films. Studies have also investigated the effects of varying nanocellulose (NC) concentrations (3%, 6%, 9%) on mechanical strength. Adding 2% hydroxypropyl methylcellulose (HPMC) to films with a 9% NC concentration increased the fracture rate. Research by Li et al [44], examined how different proportions of unmodified microcrystalline cellulose (MCC) (0%, 5%, 10%, 15%, 20%, 25%) affect the mechanical properties of MCC/polylactic acid (PLA) bio-composite films, finding that higher MCC content lowers both tensile strength and elongation.

The treatment temperature also impacts film strength. As the temperature rises from room temperature to 175°C, film strength decreases due to the breakdown of the amorphous cellulose polymer network and increased crystallinity, which leads to greater brittleness. Additionally, water acts as a plasticizing agent, enhancing the tensile strength of the material. However, when water retained in the film's pores is removed, the plasticizing effect diminishes, causing the films to lose strength and become brittle [45].

The use of oxygen barrier materials is increasingly prevalent in the food packaging industry. Oxidation of packaged meats, fruits, and vegetables can result in nutrient degradation, color changes, the formation of undesirable odors, and most critically, the promotion of microbial growth. Classifying materials by their oxygen permeability would greatly facilitate their appropriate application. Efforts have been made to establish such a classification, proposing that materials with an oxygen permeability under 75 $cm^3 \cdot m/(m^2 \cdot day \cdot atm)$ at 25°C and 50% relative humidity (RH) are considered to have a "strong oxygen barrier." In dry conditions, nanocelluloses (NCs) show exceptional oxygen barrier properties, comparable to ethylene vinyl alcohol (EVOH) [46]. NCs can form hydrogen bonds with other co-biopolymers, leading to the formation of long rod-like or particle-like structures. These structures interconnect through hydrogen bonds to create a dense, laminar network. Moreover, the crystalline regions of NCs, which are more impermeable to gases, contribute to their effective oxygen barrier properties. Due to their robust barrier characteristics, cellulose nanoparticles are employed in coatings for films with inherently poor oxygen barriers. Films made from cellulose nanofibrils (CNF), cellulose nanocrystals (CNC), and bacterial cellulose (BC) are thick, smooth-surfaced, and are produced through various methods such as suspension drying, shear coating, hot pressing, vacuum filtration, and spin coating [47]. It has been observed that the amorphous nature of CNF and the presence of surface hydroxyl groups lead to decreased oxygen barrier effectiveness as RH increases.

In one study, CNF permeability increased a thousandfold when relative humidity was raised from 0% to 65%, and the oxygen transfer rate (OTR) in CNF films was about 17 mL/m^2. A CNF film produced using a LiOH/urea/H2O solution exhibited an OTR of 3.34 mL/m^2/day·atm at 0% RH [48]. Films with a high concentration of CNCs are more resistant to humidity than CNF films but offer weaker oxygen barriers because CNCs, being highly crystalline, are more brittle and less likely to engage in hydrogen bonding, thus diminishing their oxygen barrier properties.

Tyagi, Lucia, Hubbe, and Pal [49] observed that paper coated with a double layer of CNF/CNC showed a reduction in air permeability by about 300 times, OTR by about 260 times, and water vapor transmission rate (WVTR) by 30%. Additionally, blending other polymers can enhance the oxygen barrier properties of cellulose films. For example, a study showed that a composite coating made by combining chitosan with CNF significantly increased the film's oxygen-blocking capabilities as the CNF content was raised [50].

The exchange of water vapor between food and its environment significantly affects its shelf life. It is crucial to prevent water loss in fresh foods like vegetables and meats, while moisture exposure should be avoided for dry foods such as bread and puffed foods [51]. In a notable experiment [52], gelatin and NCs were utilized to create a film. Due to the glassy state of gelatin and the extended diffusion path created by NCs, the oxygen transmission rate (OTR) values of gelatin decrease with the incorporation of NCs, particularly at 5% and 10% weight percentages. The water contact angle significantly indicates the hydrophilicity of the film's surface; cellulose-based films with contact angles below 90 degrees are deemed hydrophilic, whereas those above 90 degrees are considered hydrophobic. The contact angle is influenced by the size, pore size, and roughness of the film's surface. Shabanpour [53] showed that the high surface roughness of BC films enhances their hydrophilicity. While cellulose is not water soluble, it features numerous polar groups on its surface that effectively interact with water molecules through hydrogen bonding. Water Consequently, cellulosic materials gradually absorb or release water from the environment during storage and use until they reach an equilibrium moisture content (EMC), depending on environmental conditions [54]. The film's solubility is also impacted by hydrogen bonding among.

Cellulose chains, where bonds break due to water molecules absorbed, causing the cellulose chains to loosen and swell, which leads to plasticization. This not only changes the shape of the film material but also inevitably affects the quality of food products. Additionally, the water vapor permeability (WVP) of the film directly influences the film's oxygen permeability.

3.3.2. ANTI-OXIDANT AND ANTICROBIAL PROPERTIES

While certain antioxidants can directly bind to foods, their physicochemical properties might change the sensory characteristics of the foods. Consequently, a controlled release mechanism in packaging is necessary to manage the dispersal of these antioxidants. Although some antioxidants on the packaging surface can neutralize free radicals in the package's headspace, the core concept of antioxidant packaging relies on the diffusion of antioxidants from within the packaging material to the enclosed food [55]. For antioxidants that are non-volatile or have minimal volatility, such as tocopherol and ascorbic acid, their application is ideal in direct-contact food forms like liquids and semi-solids, which absorb antioxidants released by migrating agents. Effective antioxidant packaging must be proximal to the food and capable of protecting porous solid foods through the migration of volatile active substances included in the packaging systems [56]. Lipid oxidation is a prevalent reaction in foods that can lead to rancidity, and antioxidant agents can delay this process. Examples of synthetic and natural compounds with robust antioxidant properties include essential oils, polypyrrole, coffee leaves, and berry polyphenols. Films incorporating tannins and cellulose have recently been developed, showcasing substantial antioxidant, UV-blocking, and mechanical properties, making them highly suitable for food packaging [57].

Additionally, CNF tannin-gelatin films with elevated antioxidant capabilities have been produced based on this approach. Microbial activity in the environment affects food freshness and quality. Thus, antimicrobial food packaging materials can help prevent food spoilage by bacteria. Films made from cellulose and thiazolidine composites demonstrated exceptionally high UV blocking (99.8%) and enhanced antibacterial activity. Studies showed that cellulose-based films containing lysozyme effectively inhibited common foodborne pathogens [58]. Furthermore, cellulose-based composite films incorporating blackcurrant anthocyanin and konjac glucomannan have also proven effective against foodborne pathogens.

Another investigation [59] crafted polyvinyl alcohol (PVOH) and cellulose-based films improved by cross linking cellulose with amino acids, showing that L-histidine cross-linked PVA/cellulose films possess antibacterial qualities suitable for food packaging applications. These antibacterial composite films hold extensive potential for developing novel packaging materials.

3.3.3. THERMAL STABILITY

The thermal stability of cellulose-based composite films is influenced by the cellulose content Bian et al, [60] studied how different acid-base and cellulose extraction methods affect the thermal stability of regenerated films. It was determined that films produced from cellulose obtained through specific extraction processes exhibit superior thermal stability. The method of cellulose extraction and the presence of certain chemical compounds significantly impact film thermal stability, with enhanced integrated program decomposition temperature (IPDT) values indicating greater thermal resilience in cellulose/iron oxide films compared to pure cellulose films [61]. Additionally, Suwanprateep et al [62] developed films by integrating cellulose fibers with rice starch substrates. Maintaining a 2% rice starch content, varying cellulose fiber mass fractions at 4%, 6%, and 8% demonstrated that increased cellulose content enhances thermal stability, with the film containing 8% cellulose fibers achieving the highest thermal stability.

4. ANALYSIS OF THE FOOD PACKAGING MARKET

Global Food Packaging Market size was valued at USD 361.4 Billion in 2022 and is expected to grow from USD 382 Billion in 2023 to reach USD 595.2 Billion by 2031 [63]. Food packaging provides several important advantages, including preventing food contamination and enhancing storage efficiency, which are anticipated to drive growth in the food packaging industry.

In 2022, the flexible packaging segment led the food packaging market, capturing 43.0% of the total market share by revenue [63]. The transition from rigid to flexible packaging is anticipated to drive market growth. The efficiency and convenience of retortable packaging are projected to see increased demand throughout the forecast period. Rigid packaging is the fastest-growing segment in the market, as it is extensively used for its ability to protect food from oxygen, light, and moisture, thereby preventing spoilage.

Sustainability is increasingly important in the food packaging market. Companies are focusing more on investing in biodegradable, recyclable, and compostable materials to satisfy consumer demand for eco-friendly packaging. Advances like plant-based plastics, minimized packaging, and green policies are steering the market towards sustainable practices, with the goal of reducing environmental impact and addressing growing regulatory pressures. Enhancing the sustainability and circularity of plastics is a top priority for the food packaging industry. Currently, the primary use of bioplastics is in packaging (both flexible and rigid), followed by applications in textiles, consumer goods, agriculture/horticulture, automotive and transport items, coatings, adhesives, construction, and consumer electronics, as well as other areas like plastic toys. The packaging sector presents significant opportunities for utilizing bioplastics to safeguard nearly every type of product. Among these, food packaging is likely one of the fastest growing markets for plastic. Conventional plastic food packaging is not sustainable, and bioplastics, which offer numerous competitive benefits, are expected to drive global market demand. Given current trends, food packaging is and will likely remain one of the foremost sectors for bioplastics.

As reflected in Table 4, biodegradable plastic is generally more expensive than traditional plastic. This is because the production process for biodegradable plastic is more complex and requires more costly materials. Biodegradable plastic is made from plant-based materials, which are more expensive than the petroleum-derived materials used in traditional plastic. In our studied case, such as cellulose-derived plastics, we observe that they are clearly more expensive, yet they offer an improved solution to pollution and possess specific properties that make them increasingly competitive in the market. Additionally, the production process for biodegradable plastic requires more energy and resources, which also increases the cost. Therefore, intensive research is currently underway into the production of sustainable plastics, as a reduction in production costs could lead to a surge in production by many companies.

Therefore, intensive research is currently underway into the production of sustainable plastics, as a reduction in production costs could lead to a surge in production by many companies.

***Table 4**. Comparison of main plastics used in food packaging [63]*

Type	Approximate $/kilo	Biodegradable
Bio-Based polyethylene	1.6	No
Polylactic acid	3.1	Yes, in industrial compost
PVC	1.8	No
Cellulose acetate	4.1	Yes
Cellophane	6	Yes

5. PRODUCTION METHODS OF CELLULOSE-BASED FILMS.

This section examines various methods for extracting cellulose from different sources, its isolation from other components, chemical modifications—including reactions, conditions, and catalysts—and the subsequent production and characterization of cellulose-based films.

5.1. EXTRACTION AND PURIFICATION METHODS FOR CELLULOSE.

Production method involves since the efficient extraction and purification of cellulose from natural sources until the modification and the preparation of the film, all the steps are critical for its application in various industries. Cellulose isolation and purification methods must effectively remove contaminants like lignin and hemicellulose while maintaining the polymer's integrity and desired properties. This process involves a range of chemical, physical, and enzymatic techniques, each tailored to enhance the efficiency and quality of the final product. The selection of a suitable method depends on the cellulose source, the required purity level, and the sustainability of the process.

5.1.1. EXTRACTION METHODS.

The extractions methods more used are summarized in Table 5, where it shows the extraction method and the intermediate steps to achieve them.

Table 5. *Main extraction methods*

Extraction method	Steps	References
Cellulose from Sugarcane Bagasse (SCB)	Delignification, Filtering, Rinsing, Bleaching, Acid Hydrolysis, Nanocellulose extraction	[64], [65], [66], [67], [68]
Cellulose from Sisal Fibers	Preconditioning, Chopping, Dewaxing, Alkaline treatment, Oxidative treatment, Washing and drying	[69] [70]
Cellulose from Coffee Husk	Alkali treatment, Bleaching, Acid hydrolysis	[71]
Cellulose from Banana Peel	Drying, Grinding, Maceration, Bleaching, NaOH treatment, Washing	[72]
Cellulose from Wood Pulp	Kraft pulping, Delignification, Caustic soda addition	[73]
Cellulose from Rice Husk	Dewaxing, Delignification, Ultrasound treatment, Bleaching, High-pressure homogenization (HPH) cycles	[74]

5.1.2. ISOLATION METHODS

The next step, once cellulose is extracted from various sources, is the isolation of cellulose, which separates it from other components such as lignin. Although some extraction methods include this step, it is important to highlight the most used methods for isolation, as shown in Table 6.

Table 6. *Main isolation methods for cellulose*

Isolation Method	Steps	Advantages	Disadvantages	Ref
Alkaline Procedure	Digestion at 80°C with 4% NaOH, bleaching with sodium chlorite and acetic acid, Washing and neutralization, Optional Fast Prep system for purification	Effective in removing lignin and hemicellulose, improves cellulose purity, relatively low cost.	Generates alkaline waste requiring treatment, may partially degrade cellulose, reducing yield	[75]
Ultrasound Treatment	Alkaline peroxide treatment at 55°C, Sequential alkali treatment with NaOH and H_2O_2, Filtration, washing until neutral, and drying at 60°C	Enhances extraction efficiency, reduces processing time, less aggressive to cellulose	Requires specialized equipment, may be less effective in removing impurities	[76]
Enzyme Technology	Bio-treatment with fungal culture, Incubation, Mechanical processing, Cryocrushing using liquid nitrogen, Fiber dispersion and filtration	Environmentally friendly, preserves cellulose structure, low chemical waste	High cost due to enzyme requirements, slower process compared to chemical methods.	[77]
Dilute Acid Pretreatment	Material soaking, Filtration, Heating to 160°C in a mini reactor, Cooling, Post treatment filtration and drying, Yield of 75-85%, Increased digestibility	Effectively removes hemicellulose, improves biomass digestibility, relatively fast process.	May generate unwanted by products, risk of cellulose degradation at high temperatures, requires corrosion resistant materials.	[78] [79]

5.2. MECHANISM OF MODIFICATION OF CELLULOSE

The following section addresses the main mechanisms for cellulose modification, specifically the chemical substitution of functional groups through various reactions. The discussion will first focus on the chemical reactions themselves, and subsequently examine patents related to cellulose acetate and cellulose propionate production, which will be the central focus of this final study.

5.2.1. SUBSTITUTIONS REACTIONS OF CELLULOSE

The D-glucopyranose unit (AGU) of cellulose contains three active hydroxyl groups: one primary hydroxyl group at the C-6 position and two secondary hydroxyl groups at the C-2 and C-3 positions. This allows for various derivatization reactions to occur theoretically, such as oxidation, crosslinking, etherification, esterification, and graft copolymerization, among others, leading to the production of different cellulose derivatives [80]. Table 7 lists these derivatives, along with their functional groups (substitutional groups), degree of substitution (DS), and solubility. Derivatizing cellulose enhances its solubility, introduces new functions, and broadens its applications in industries such as food, medicine, chemicals, construction, environmental protection, and petrochemicals. It is a crucial approach to addressing the challenges of cellulose melting and dissolution.

Table 7. *Main parameters for the reaction of substitutions [80]*

Derivative	Functional group	DS	Solubility
Cellulose Acetate	$-COCH_3$	0.6-0.9 1.2-1.8 2.2-2.7	H_2O Ethyl Alcohol Acetone
Cellulose acetate propionate	$-COCH_3-C(O)CH_2CH_3$	2.4/0.2	Acetone,Ethyl acetate
Carboxymethylcellulose	$- CH_3COONa$	0.1-3.0	H_2O

In the field of food packaging, cellulose derivatives have proven to be key materials in the development of sustainable bioplastics. Cellulose acetate is used in the production of biodegradable films and coatings for food packaging, providing moisture barrier properties and mechanical resistance. Cellulose acetate propionate (CAP), due to its higher thermal stability and moisture resistance, is applied in flexible and rigid packaging that requires greater durability without compromising its biodegradability. Its use in laminates and protective films helps extend the shelf life of food products. Meanwhile, carboxymethyl cellulose (CMC) is utilized in edible coatings and active packaging, enhancing the structural and functional stability of bioplastics in food contact applications. Its thickening and gelling properties optimize the barrier against moisture and oxygen, improving food preservation.

Beyond its application in food packaging, these compounds have multiple uses in other industries. Cellulose acetate is widely used in the production of textile fibers, optical lenses, and industrial filters. CAP is employed in transparent plastics for eyewear frames, automotive components, and cosmetic packaging. Finally, CMC finds applications in the food industry as a thickening agent, in pharmaceuticals as an excipient in medications, and in personal care products.

5.2.1.1. Esterification of cellulose

Cellulose esterification involves the reaction of the hydroxyl groups in cellulose with acids, acid anhydrides, or acid halides. This is considered one of the earliest areas of research and production in cellulose chemistry [81]. The hydroxyl groups in cellulose are polar and can be replaced by nucleophilic groups or nucleophilic compounds in a strong acid solution through a nucleophilic substitution reaction, producing cellulose esters. Figure 5 illustrates three primary mechanisms of cellulose esterification.

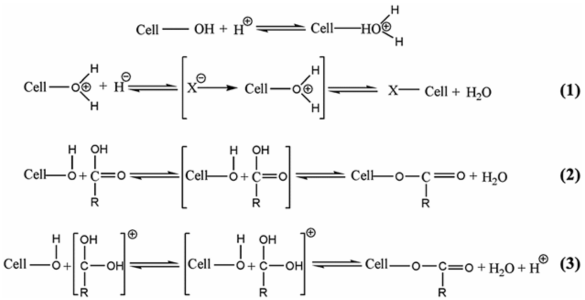

***Figure 5** Mechanism for esterification of cellulose [81]*

First, as shown in equation (1), hydronium ions are formed and then substituted, which occurs when cellulose reacts with inorganic acids. Second, the interaction between cellulose and organic acids takes place through a nucleophilic addition reaction, as seen in equation (2). According to equation (3), acid catalysis can accelerate the esterification of cellulose by adding a proton to the oxygen atom of the carboxyl group, creating positively charged carbon atoms. This promotes the reactivity of nucleophilic alcohol molecules, leading to the formation of water (H2O).

All these reactions are reversible, showing that cellulose esterification is typically in equilibrium. Theoretically, cellulose can react with both inorganic and organic acids to form mono-, di-, and tri substituted cellulose esters.

After addressing the general esterification process of cellulose, attention now turns to two main categories of cellulose esters: inorganic acid esters and organic acid esters. These derivatives differ in their chemical structure and properties, and both offer specific functionalities relevant to industrial and material applications.

Cellulose inorganic acid ester produced by the reactions between cellulose and nitric acid, sulfuric acid, phosphoric acid, xanthate, etc. The main inorganic acid esters are cellulose nitrate and xanthate (an important intermediate for producing regenerated cellulose).

Among these compounds are cellulose nitrate, previously discussed, and cellulose sulfate. Cellulose nitrate is synthesized through the nitration of cellulose using a mixture of nitric and sulfuric acids, with sulfuric acid functioning as a dehydrating agent. However, the use of sulfuric acid may lead to cellulose degradation and pose safety risks, including spontaneous combustion [82].

On the other hand, cellulose sulfate is a water-soluble ester obtained by introducing sulfate groups into the cellulose structure. This modification disrupts hydrogen bonding, thereby enhancing water solubility. When the degree of substitution (DS) exceeds 1.0, cellulose sulfate exhibits anti-enzymatic properties.

Cellulose organic esters can be prepared by reaction between cellulose and organic acids, acid anhydrides, and acid chlorides respectively. The more important products are cellulose acetate and its mixed esters.

Although cellulose acetate has already been discussed, a brief overview of its synthesis is now provided as a preliminary step before introducing the related patents and a more in-depth analysis of its properties. This is due to its high potential as a film-forming material for food packaging applications. This section will also address one of its main derivatives, cellulose acetate propionate (CAP).

Cellulose Acetate, derived from cellulose through acetylation, often from cotton or wood fibres [83]. The most commonly utilized form is cellulose diacetate, with a degree of substitution (between 2 and 3, as indicated in Table 7. The acetylation of cellulose using acetic anhydride was first achieved by Schützenberger in 1864, marking the beginning of cellulose acetate production, which features prominently in numerous patents. Inert diluents such as benzene, toluene, and pyridine are frequently used to partially substitute acetic acid during the acetylation process. Throughout this reaction, cellulose retains its fibrous structure. Perchloric acid is often employed as a catalyst due to its strong catalytic efficiency and its minimal interaction with cellulose, preventing the formation of unwanted acid esters.

Additionally, heterogeneous fibrous cellulose can be acetylated using acetic acid vapor, with zinc chloride serving as a catalyst—ethyl acetate is one such suitable medium for this process. Except for fibrous triacetate, most cellulose acetates are synthesized via solution-phase acetylation, typically involving acetic acid, sulfuric acid, and liver vinegar acting respectively as solvent, catalyst, and esterifying agent.

The acetylation reaction initiated by sulfuric acid begins in the amorphous regions of cellulose and subsequently progresses to its crystalline regions. As the reaction proceeds, the cellulose structure transitions from a heterogeneous to a quasi-homogeneous phase through successive layer-by-layer reactions. Due to the poor solubility of cellulose triacetate in acetone, it is frequently partially hydrolyzed to decrease the degree of esterification, thereby yielding cellulose diacetate [84].

Now, Cellulose Acetate Propionate is produced by activating cellulose with acid and using sulfuric acid as a catalyst. Sulfate esters are formed initially but are replaced by acetyl and propionyl groups to form CAP, used in coatings and thermoplastics [85].

5.2.1.2. Etherification of cellulose

Although the final part of this work focuses on demonstrating that cellulose-based biofilms—specifically cellulose acetate and cellulose acetate propionate—represent a competitive alternative to conventional plastics, the process of etherification will also be addressed. This inclusion is intended to provide a flexible and comprehensive guide that can support future research.

Cellulose ethers are produced through the reaction of the hydroxyl groups in cellulose with etherification reagents and represent an important class of cellulose derivatives. In 1905, Suida [86] successfully prepared methylcellulose using dimethyl sulfate and cellulose. Later, in the 1920s, carboxymethylcellulose was industrially produced for the first time.

One key advantage of cellulose ethers compared to cellulose itself is their improved solubility, which can be controlled by the type of substituent and the degree of substitution. Hydrophilic substituents (such as hydroxyethyl or quaternary ammonium groups) and polar substituents provide cellulose ethers with water solubility, even with a low degree of substitution. Conversely, hydrophobic substituents (such as methyl or ethyl) limit the solubility of cellulose ethers to swelling or dissolving in dilute alkali solutions. As the degree of substitution increases, they can dissolve in both water and organic solvents [87].

Mechanisms of cellulose etherification [88] are:

- Williamson Etherification In this reaction, cellulose hydroxyl groups (Cell–OH) react with an alkyl halide (RX) and sodium hydroxide (NaOH) to form cellulose ether (Cell–OR), sodium halide (NaX), and water. This mechanism is used to produce methylcellulose, ethylcellulose, and carboxymethylcellulose.
- Ring-Opening Addition Reaction of Alkoxy This base-catalyzed reaction involves the ring-opening addition of alkoxy groups (R), producing cellulose ethers such as hydroxyethyl cellulose and propyl cellulose. To effectively suspend and disperse the cellulose during this process, large amounts of organic diluents are often added.
- Alkali-Catalyzed Michael Addition Reaction In this mechanism, cellulose hydroxyl groups undergo an addition reaction with an activated vinyl group, where Y is an electron-withdrawing group. This reaction is commonly used to synthesize cyanoethyl cellulose from acrylic resins and alkali cellulose. It is temperature-sensitive and typically carried out under mild conditions, with low concentrations of

> alkali (1–6%) at around 30°C. Since cellulose is insoluble in water and most common solvents, etherification reactions are usually performed in a heterogeneous system.

The abundance of hydroxyl groups in cellulose molecules forms numerous intramolecular and intermolecular hydrogen bonds, leading to a crystalline fibril structure in the solid state. These hydroxyl groups are often blocked within the crystalline regions, making it difficult for etherifying agents to access them and limiting the efficiency of the etherification reactions. To overcome this challenge and enhance the activity of the hydroxyl groups before etherification, pretreatment methods such as alkali swelling, high-energy electron radiation, microwave treatment, or steam explosion are often used. Among these methods, NaOH is the most effective and widely used pretreatment agent, and it also serves as a catalyst in cellulose derivatization reactions.

Within the cellulose ether derivatives resulting from this reaction, two main groups can be distinguished: alkyl cellulose ethers and anionic cellulose ethers.

In the first group, alkyl cellulose ethers, the most representative compounds include methyl cellulose (MC) and ethyl cellulose (EC). MC is a nonionic cellulose ether produced by methylating the hydroxyl groups of the cellulose anhydroglucose units. Its properties depend on the degree of substitution. Methyl cellulose is known for its heat resistance, salt tolerance, and thermally reversible gelation, forming gels at elevated temperatures and returning to a liquid state upon cooling [89][90].

Ethyl cellulose, a partially ethylated cellulose ether, is more hydrophobic than MC. Its solubility also depends on the degree of substitution: it is soluble in water when the DS ranges from 0.7 to 1.7, and in organic solvents when the DS exceeds 1.5. EC provides excellent mechanical strength, flexibility, and low flammability. These properties make it suitable for applications in plastics, inks, films, and adhesives. Additionally, it reduces surface adhesion, facilitating plastic molding processes [91].

In the second group, anionic cellulose ethers, the most widely used is carboxymethyl cellulose, typically found in its sodium salt form due to the poor solubility of its acidic form. CMC is non-toxic, water-soluble, and forms films with good adhesion, emulsifying capacity, and viscosity. The quality of CMC depends largely on its DS and viscosity. It serves as a thickener, binder, emulsifier, and stabilizer across various industries [92]. Moreover, CMC is used in coating formulations as a replacement for hydroxyethyl cellulose (HEC), offering advantages such as antibacterial activity, stable viscosity, lower cost, and excellent film formation, flow, leveling, and biological stability. Due to its biocompatibility and ability to carry active compounds, CMC also plays a valuable role in drug delivery systems [93]

5.2.2. PATENTS OF CELLULOSE ACETATE AND CELLULOSE ACETATE PROPIONATE.

Table 8 presents various published patents related to cellulose acetate, information can be obtained regarding the synthesis methods, temperature ranges employed, and catalysts used. This study, focused on the development of biofilms for food packaging, acknowledges the environmental concerns associated with conventional plastic alternatives and chemical processes.

A clear pattern emerges in the frequent use of homogeneous catalysts, particularly sulfuric acid. While effective, sulfuric acid is known to degrade hemicellulose, potentially altering the molecular weight and viscosity of the resulting polymer. Additionally, its use presents significant environmental hazards due to its corrosive nature, toxicity, and the generation of hazardous waste. High temperatures reported in the patents are often applied to reduce the concentration of sulfuric acid and mitigate these negative effects.

In contrast, solid (heterogeneous) catalysts offer notable advantages. Their reusability contributes to lower environmental impact, and when optimized for high performance under suitable conditions, they can provide a competitive and more sustainable alternative. These catalysts not only reduce waste and simplify separation processes but may also lower production costs in the long term, despite their initially higher price. The experimental data and patent comparisons confirm that heterogeneous catalysis maintains reaction efficiency and desirable material properties, reinforcing its potential for future applications in sustainable biofilm production.

Table 8. *Patents to produce cellulose acetate*

Patent/Source	Method	Temperature	Catalysts
European Patent Application No. 0638 244 A1 [94]	Acetylation using sulfuric acid and N,N-dimethylacetamide in acetic acid as a solvent	10°C to 90°C	Sulfuric acid and N,Ndimethylacetamide
U.S. Patent No. 2,923,706 [95]	Esterification of cellulose using sulfuric acid with a special pretreatment	Above 50°C	Sulfuric acid
U.S. Patent No. 3,767,642 [96]	Production of secondary cellulose acetate from wood pulp using high temperature hydrolysis	125°C to 170°C	Sulfuric acid
European Patent Application No. 0626.391 A1 [94]	Selective depolymerization of impurities in low alpha-cellulose materials followed by acetylation and hydrolysis	50°C to 175°C	Sulfuric acid
U.S. Patent No. 2,585,516 [94]	Impregnation of cellulose with carboxylic acid derivatives and sulfoxy compounds, followed by esterification	Above 90°C	Carboxylic acid derivatives and inorganic sulfoxy compounds
Takahashi and Takahashi (1970) [97]	Acetylation of cotton linters using acetic acid and metallic/ammonium sulfates	98°C	Metallic or ammonium sulfates

The following section analyzes patents related to cellulose acetate propionate. As this compound is a derivative of cellulose acetate, fewer patents are available in comparison. Among those reviewed in Table 9, it is observed that more recent patents have begun to incorporate heterogeneous catalysis. These catalysts contribute to reducing environmental damage and allow for the recycling of wastewater. Given this trend, further investigation into these catalytic systems is considered relevant in order to propose solutions with lower environmental impact. As will be discussed in detail later, this approach not only offers improved sustainability but also enhances the competitiveness of cellulose-based materials as viable alternatives to conventional plastics.

Table 9. Patents of cellulose acetate propionate

Patent	Description	Temperature	Catalyst
US5977347A [98]	Synthesized through an esterification process involving cellulose, acetic acid, and propionic acid or their corresponding anhydride	10-120ºC	Sulfuric acid
Patent CN102127169B [99]	This method involves activating microcrystalline cellulose with a mixture of acetic anhydride and propionic anhydride. The esterification is catalyzed by a solid superacid catalyst, such as SO_4^{2-}/ZrO_2 or SbF_5/Al_2O_3	20-100ºC	Solid superacid catalysts, specifically SO_4^{2-}/ZrO_2 or SbF_5/Al_2O
Patent US2322575A [100]	This method involves esterifying pretreated cellulose in a closed reaction vessel with a bath containing acetic acid, an excess of propionic anhydride, sulfuric acid as a catalyst, and acetaldehyde.	10-70ºC	Sulfuric acid

Beyond the scope of patents, additional references have been considered to support the study of cellulose acetate production. Table 10 presents a series of examples illustrating various synthesis approaches. These include the use of different raw materials and reactor types, all aiming to achieve efficient production processes adaptable to specific industrial applications. The analysis also highlights the use of diverse catalysts, each of which exerts distinct effects on the final properties of the product such as:

Imidazolium Salts: Provide high efficiency in cellulose breakdown and esterification, leading to high yields and minimal polymer degradation.

Bisulfates: Offer a gentler catalytic process than sulfuric acid, preserving the polymer's molecular integrity and thermal stability.

DMSO: Enhances reaction conditions by improving solubility and ensuring efficient product formation with higher purity and better structural qualities.

These catalysts reduce the harshness of traditional methods (like those involving sulfuric acid) and improve the overall quality of the cellulose acetate produced, by preserving its molecular structure and optimizing yields.

Table 10. *Examples of the production of cellulose acetate*

Raw material	Reactor	Catalysts	Temperature Range	Results	Ref
Sulfite pulp	Kneading type acetylator and autoclave	Sulfuric acid acetic anhydride	40-150ºC	An increase in hydrolysis temperature enhances filtration efficiency; however, it also leads to a yellowish coloration in the product	[95]
Wood Pulp	Three-necked round bottom flask	Bisulfate compounds	65-120ºC	Reduction of sulfuric acid, better thermal stability	[94]
Oil palm empty fruit bunches	Batch reactors	Sulfuric acid	40-105 ºC	The low water content influences the acetylation process because water's –OH groups react more readily with anhydrous reagents than those in cellulose	[101]
Avicel PH-101 Lignocellulosic biomass	ILs-based reactor	EmimOAc	80°C	The chemical structure of Im-ILs had little impact on catalytic activity. DMSO as a cosolvent accelerated the reaction	[102]
Rice straw	Batch reactor (round-bottom flask)	Amberlyst 15 (Ion Exchange Resin)	40-80 ºC	Cellulose acetate was successfully synthesized using a modified literature method. Recyclable catalyst	[103]
Musa paradisiaca	Water bath	HCl	60 ºC	CA product for a competitive biofilm	[104]

If the same analysis is conducted for the production of cellulose acetate propionate, Table 11 is obtained, from which several key points can be identified.

The first is the predominant use of microcrystalline cellulose commonly as the raw material for the production of cellulose acetate propionate. This is mainly attributed to its high purity, ease of dissolution in acid-based solutions, and market availability, making it a technically and economically favorable option for esterification processes, although the table shows other alternatives.

Secondly, as already suggested in the patent analysis, the most commonly used catalyst has been sulfuric acid. However, a growing trend can be observed toward the use of solid superacid catalysts, which provide a more sustainable and less corrosive alternative, reducing both waste generation and equipment degradation. Besides this are the reasons why CAP can be synthesized without a catalyst when using ionic líquids [105]:

- Efficient dissolution of cellulose: Ionic liquids disrupt hydrogen bonding in cellulose, enabling homogeneous dissolution and exposing hydroxyl groups for reaction.
- Intrinsic activation by the ionic liquid: Some ionic liquids act as weak acids or bases, promoting esterification without the need for external catalysts

Lastly, little variations are observed in the operating temperature range, which generally remains between 20 °C and 90 °C. Although the types of reactors used or catalysts employed., This variations does not significantly impact in the required temperature, since the esterification reaction between cellulose and acetic and propionic anhydrides is thermodynamically favorable and does not require high temperatures to proceed.

This clearly indicates a technical and operational advantage, as a more environmentally friendly solution (the use of solid catalysts) can be implemented without the need to modify operating conditions, thereby facilitating the transition toward more sustainable processes in the cellulose derivatives.

Table 11 Example of reaction conditions for obtaining CAP

Raw Material	Reactor	Catalyzer	Temperature	Results	Ref
Purified cotton linters	Closed reaction vessel	Concentrated sulfuric acid	15ºC - 70ºC	The product is a partially esterified cellulose acetate propionate containing 1.13 acetyl and 1.71 propyonyl groups per C_6 unit of the cellulose	[99]
Melt of cellulose acetate	Not defined	Concentrated sulfuric acid	20ºC-90ºC	Low degree of crystallinity. Therefore, a film made of the known cellulose acetate propionate is Soft and has a low mechanical Strength.	[98]
Microcrystalline cellulose	Not specified	SO_4^{2-}/ZrO_2	20ºC - 90 ºC	Excellent toughness, thermal stability and compatibility, and has been widely used.	[99]
Sugarcane bagasse	Stirring tank	Absence	20-100ªC	Preparation of CAP using AmimCl ionic liquid as solvent, in the absence of any catalyst.	[106]
Cotton cellulose pulp	Flask equipped with mechanical stirrer	Abscence	25ºC - 80ºC	Synthesis of CAP with controllable structures and properties were successfully accomplished without external catalysts under mild conditions through a newly developed cellulose dissolution platform of DBU/CO2/DMSO.	[107]

5.3. FABRICATION AND CHARACTERIZATION OF BIOFILMS.

Established the fundamental reaction mechanisms for the synthesis of cellulose acetate and cellulose acetate propionate, the focus now shifts to film fabrication. This includes manufacturing strategies, the influence of plasticizers on the material properties, and the methodologies used for the characterization of cellulose-based biofilms.

5.3.1. STRATEGIES OF FABRICATION.

For the production of biodegradable food packaging, the most common methods used are reflected in Table 12

Table 12. *Main strategies for the fabrication of films [108]*

Method	Description
Layer-by-Layer (LbL)	Versatile method for film and coating preparation with minimal equipment; enhances functional and physiochemical properties
Extrusion	Industrial process for shaping polymers by pressing through a die; used for tubular cellulose films
Hydrogel	Polymeric hydrogels based on cellulose; high water retention, biocompatibility, and encapsulation potential for bioactive compounds
Direct Coating	Coatings applied directly to food surfaces; provides moisture barriers, antibacterial properties, and extends shelf life
Solution Casting	Mixing solutions and casting on surfaces, used for polymer films and liquid crystal displays.
Electro-Spinning	Technique to produce biopolymer fibers using electrical potential.
Spray Drying	Spray-coating polymers to generate films; versatile and efficient for Nanocellulose film preparation.
Nanoemulsions	Nano-sized emulsions stabilize bioactive compounds; enhance nutritional and preservation properties in food products.

5.3.2. INFLUENCE OF PLASTYFIERS

Plasticizers are chemical compounds added to polymeric materials, such as cellulose, to improve their flexibility and ease of processing. In the development of cellulose-based biopolymer films, the presence of plasticizers plays a crucial role in modifying their mechanical and functional characteristics [109]. Besides its impact on the material, the compatibility must also be taken into account, as shown in the experiment [110]. The most common plasticizers are:

Glycerol is a widely used plasticizer with strong affinity for cellulose, enhancing film flexibility by disrupting intermolecular bonding. Excess amounts increase moisture absorption, causing tackiness. Compatibility with cellulose is high, though water interaction can affect stability.

Sorbitol improves tensile strength and elongation in cellulose biofilms. It reduces brittleness while decreasing water solubility. Compatibility is moderate to high, but precise formulation is needed to avoid phase separation.

Polyethylene Glycol (PEG) adjusts flexibility and permeability in cellulose films by lowering crystallinity. Higher molecular weight PEGs enhance durability; lower weights increase plasticization. Compatibility is generally high, depending on PEG type.

A study compared the effects of sorbitol and glycerol on the mechanical properties of cellulose, finding that tensile strength decreased with increasing plasticizer concentration—from 89.36 MPa without plasticizer to 46.42–81.70 MPa with glycerol and 31.42–91.91 MPa with sorbitol—due to weakened hydrogen bonding. Conversely, elongation increased with higher plasticizer content, reaching up to 15.15%, although brittleness was observed in films with high glycerol levels. This behavior is attributed to enhanced polymer chain mobility, which improves elasticity. [111-113]

In summary, plasticizer concentration directly influences tensile strength and elongation. Proper plasticizer selection and dosage are key to optimizing the mechanical, thermal, and barrier properties of cellulose biopolymer films for industrial and biomedical applications.

5.3.3. CHARACTERIZATION OF THE FILMS

The characterization of a cellulose-based biofilm is essential for assessing its physical and chemical properties, which directly influences its suitability for applications in biodegradable materials. This study aimed [104] to determine key parameters such as moisture content, water absorption, water and alcohol solubility, structural composition, and biodegradability.

Understanding how each of these properties affects the material is crucial for evaluating its performance and potential uses. Therefore, before describing the procedures used in film characterization, a brief explanation is provided for each property to highlight its relevance.

- **Moisture Content**: Moisture influences in the flexibility, mechanical strength, and lifespan of the film. To determine this, the sample was initially weighed (W1), then dried in an oven at 85 °C for 24 hours and reweighed (W2). The difference allowed for calculating the moisture content.
- **Water Absorption**: This property affects structural stability and durability in humid conditions. The sample was dried at room temperature for 24 hours, weighed (W1), submerged in 50 mL of distilled water at room temperature for 24 hours, then filtered and reweighed (W2) to assess water absorption.
- **Water Solubility**: Solubility in water indicates the material's stability under wet conditions—high solubility implies reduced resistance. The sample was oven-dried at 85 °C for 24 hours (W1), then immersed in 50 mL of distilled water for 24 hours. The residue was filtered, dried, and weighed (W2) to calculate water solubility.
- **Alcohol Solubility**: This test evaluates chemical stability against organic solvents. It followed a similar method to the water solubility test, using 3 mL of ethanol in capped test tubes at room temperature for 24 hours. After filtering, drying, and weighing (W2), the solubility in alcohol was determined.
- **Fourier-Transform Infrared Spectroscopy (FTIR)**: FTIR analysis was performed to identify the functional groups in the bioplastic. Measurements were taken in the wavenumber range of 4000–650 cm^{-1} with a 2 cm^{-1} resolution, using a Germanium-coated KBr beam splitter for mid-IR spectra.
- **Biodegradability**: This property verifies the film's ability to decompose naturally. Samples were weighed (W1), buried 2 cm deep in various soil types (e.g., garden soil, vermicompost, cow dung) inside Styrofoam cups, and kept at room temperature with moisture maintained for 9 days. Afterward, the samples were retrieved, cleaned, dried at room temperature for 24 hours, and reweighed (W2) to determine the degree of biodegradation.

Overall, the study provided comprehensive data on the physical and chemical characteristics of cellulose-based biodegradable films, offering valuable insights for their development and application [104].

6. WHY IT IS A COMPETITIVE SOLUTION?

This section provides a detailed explanation of the fabrication process of CA and CAP biofilms from the initial stage, starting with renewable raw materials. It also examines the various modifications that can be introduced during the process to tailor and optimize the mechanical, thermal, and functional properties of the material according to its intended application. Furthermore, it demonstrates why this solution is competitive compared to conventional synthetic alternatives, with particular emphasis on its enhanced environmental sustainability. This advantage is largely achieved through the use of **solid heterogeneous catalysts**, which enable cleaner, more efficient, and recyclable reactions in line with the principles of green chemistry.

6.1 CA-FILMS and modifications as a competitive solution

The casting method is a commonly used technique, as it was commented before, for producing bioplastic films due to its simplicity and effectiveness in creating uniform, thin layers. Now with a new example of biofilm fabrication [114], final characteristics are analyzed. Plasticized cellulose films were produced by dissolving varying amounts of cellulose in a mixture of trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) at 50°C for 45 minutes. After achieving a uniform solution, 30% glycerol by weight was added and thoroughly mixed, as this amount of glycerol is known to enhance the mechanical properties of cellulose for food packaging applications. The resulting solutions were then cast onto glass Petri dishes and left to dry overnight, resulting in freestanding films approximately 70 µm thick, this films then were characterized by adding beeswax solutions (1 wt%) to the cellulose-glycerol solutions.

Another study [115] involved the preparation of a cellulose acetate (CA) film using the casting method. The film was modified by incorporating sodium alginate and carrageenan derived from different types of seaweed.

In table 13 shows a comparison of both experiments commented, there are the characteristics of the film without the addition and the modificated film.

The incorporation of polysaccharides, such as sodium alginate and carrageenan, improved the tensile strength and thermal stability of the films. Antibacterial evaluations demonstrated their ability to inhibit the growth of *E. coli, S. aureus, and P. syringae*, while biodegradation assessments confirmed their eco-friendly nature. These findings highlight the potential of these films as an alternative to cellulose-based biofilms, emphasizing cellulose's adaptability and compatibility across various applications. Additionally, the inclusion of beeswax enhanced water and oil resistance, antioxidant properties, and biodegradability by modifying the hydrogen-bond network, all while preserving mechanical properties comparable to petroleum-derived plastics.

The film with 5% of beeswax, maintained the freshness of cut pears, achieving similar results to LDPE, while also demonstrating superior bacterial retention and excellent oxygen barrier properties, surpassing LDPE in performance. This study reinforces the viability of sustainable packaging solutions with improved stability and protective capabilities.

Table 13. Modification of CA-films by sodium alginate, carrageenan and beeswax [113] [114].

Property	CA-film [115]	CA-film 5% beeswax [115]	CA-film 20% beeswax [115]	CA-film [114]	CA-film sodium alginate[114]	CA-film carrageenan[114]
Morphology [SEM]	Continuous and smooth surface	Homogeneous wax plate distribution	Homogeneous wax plate distribution	Porous and cracked surface	Smooth, non-porous surface	Smooth, non-porous surface
Crystallinity [XRD]	Amorphous	Crystalline	Crystalline	Amorphous	Crystalline	Crystalline
Elongation at break [%]	31	20	8	31	> 31	> 31
Young’s Modulus [MPa]	963	673	481	963	> 963	> 963
Weight loss	After 30 days 60%	After 30 days 35%	After 30 days 30%	After 60 days 65 %	After 60 days 55%	After 60 days 50%
Antibacterial activity	Low	Medium	High	Low	High	High

As shown in Table 10 of the corresponding section of patents of cellulose acetate (5.2.2), more sustainable production methods is receiving interest for the development of more sustainable solutions. In this context, the study [103] stands out for its focus on the heterogeneous catalysis of cellulose acetate production using the ion-exchange resin Amberlyst 15.

In this study, the direct acetylation of cellulose to obtain cellulose diacetate was developed using the sulfonated polymer Amberlyst 15 as a catalyst with optimized conditions of 45ºC and 10 hours.

The results characterized by Fourier-transform infrared spectroscopy, thermogravimetric analysis, and differential scanning calorimetry, demonstrated that Amberlyst 15 exhibits acceptable catalytic activity, considering the degree of substitution values and the yields obtained in the production of cellulose acetate, thus offering a promising pathway for the fabrication of biofilms from this material.

Moreover, one of the main advantages of the process is that the catalyst can be reused without further treatment, with no significant differences observed in DS values or yields after four reaction cycles, as shown in the following table 14.

Table 14. Reused catalytic performance of catalyst Amberlyst 15 [103]

Recycle	DS	Yield [%]
1	2.27	43.9
2	2.21	41.5
3	2.19	42.3
4	2.13	42.2

The study by L. J. Konwar, P. Mäki-Arvela, A. J. Thakur, N. Kumar, and J.-P. Mikkola [116], in which mesoporous sulfonated carbons (AC500S, FeCS, among others), functionalized with -SO_3H and -$PhSO_3H$ groups are used, stands out. Although these materials do not correspond to classical ion exchange resins, they present equivalent functions in terms of acidity, heterogeneity and reusability The research confirmed that acetylated cellulose derivatives could be efficiently synthesized with degrees of substitution (DS) ranging from 1.6 to 2.94, achieving high isolated yields between 48% and 77% through a one-pot, solvent-free process. Notably, the process enabled the selective production of commercially relevant, soluble cellulose acetate (DS between 2.0 and 2.7) in yields of approximately 70%, using microcrystalline cellulose and the highly active mesoporous sulfonated catalyst AC500S under optimized reaction conditions.

Based on all this information, two key conclusions can be drawn: first, the versatility of cellulose acetate biofilms, as demonstrated by the ability to modify their properties through the addition of components such as beeswax or sodium alginate; and second, the feasibility of using heterogeneous catalysis like Amberlyst 15 or sulfonated carbons, for the production of cellulose acetate, which not only yields competitive results in terms of performance and degree of substitution, but also offers the added advantage of catalyst recyclability, contributing to a more sustainable process.

6.2 CAP films and heterogeneous catalysis as a competitive solution

As shown in Table 15, or as previously discussed in Section 5.2, the competitiveness of these sustainable approaches has been demonstrated to some extent. This is evident not only from the choice of raw materials used at the initial stages of the process, but also from the adoption of more sustainable and competitive alternatives—such as the replacement of traditional catalysts with lower-impact options, or the use of alternative methods for obtaining CAP or CA. These strategies, while environmentally advantageous, also yield promising results. However, their cost remains a significant drawback. At this point, solid catalysts—or their analogues—come into play. As it will be discussed in the following section, these catalysts not only offer a competitive solution with a lower environmental impact, but also have the advantage of being reusable, which could further reduce overall production costs.

An interesting study [117] on a cellulose-derived biofilm, in the form of cellulose acetate propionate (CAP), is discussed. This material was synthesized using a sustainable approach through the use of a novel solid acid catalyst, PS@PMA-ZrO_2-PW_{12} (PS = polystyrene, PMA = poly(methyl acrylate), PW_{12} = $H_3PW_{12}O_{40}\cdot xH_2O$), which features a core–shell structure. Various solid acid catalysts containing Keggin-type heteropolyacids (HPAs) were evaluated. Among them, the **PS@PMA-ZrO_2-PW_{12} catalyst exhibited the highest catalytic performance.**

The resulting product showed a degree of substitution (DS) of 2.73, a viscosity of 320 mPa·s, and a molecular weight (Mw) of 100,644. Several catalysts were tested, but the core–shell structured PS@PMA-ZrO_2-PW_{12} catalyst outperformed free phosphotungstic acid (PW_{12}), sulfuric acid (H_2SO_4), and Amberlyst-15. Notably, this catalyst maintained both DS and viscosity after five reuse cycles. Moreover, the system allowed for the production of films without the need for plasticizers, presenting optical and mechanical properties suitable for sustainable biofilm production.

Table 15. Comparison of heterogeneous catalysts

Catalyst	Conditions	Reusability	DS max	References
PS@PMA-ZrO_2-PW_{12}	45ºC 3 hours	5 cycles	2.73	[117]
Amberlyst-15	45ºC 10 hours	4 cycles	2.38	[103],[117]
H_2SO_4	40ºC 3 hours	0 cycles	2.78	[117]
PW_{12}	Not defined	0 cycles	2.62	[117]

Compared to commercial catalysts such as sulfuric acid, or other catalyst as Amberlyst-15, the PS@PMA-ZrO_2-PW_{12} catalyst demonstrated enhanced catalytic performance, due to several factors [118][119]:

- The core–shell structure improves substrate accessibility to active catalytic sites [120].
- Higher Brønsted acidity enhances cellulose conversion efficiency [121].
- Greater catalyst stability under reaction conditions.

This study identifies PS@PMA-ZrO_2-PW_{12} as a highly efficient and sustainable catalyst for cellulose esterification, enabling the production of CAP with improved characteristics compared to those obtained with conventional catalysts. The resulting biofilm exhibited high transparency, thermal stability, and mechanical flexibility, making it an excellent candidate for food packaging applications, as shown in Table 16. Additionally, the recyclability and stability of the catalyst further support its potential as a green and cost-effective alternative in polymer processing.

Table 16. Properties of CAP biofilm obtained with PS@PMA-ZrO_2-PW_{12}. [117]

Film thickness	Optical transparency	Structure (SEM)	Thermal stability	Flexibility
200	92.1 %	Highly dense and homogeneous	Thermally stable below 300º C	Elongation at break 32.67 %

Another key factor, as shown in Table 11 in the section of CAP Patents (5.2.2), is the production of cellulose acetate propionate (CAP) without the need for a catalyst when cellulose is dissolved in the specified ionic liquids. This approach has a lower environmental impact by eliminating the use of sulfuric acid, thereby reducing hazardous waste generation and improving process safety. Moreover, ionic liquids act simultaneously as solvents and reaction media, simplifying the procedure, reducing the number of steps, and enabling a cleaner and more efficient synthesis. This alternative represents a significant advancement toward more sustainable and environmentally friendly bioplastic production processes.

The main findings from this section are critical with respect to the general objectives of this work, particularly identifying a sustainable and competitive alternative for the production of biofilms. The following conclusions can be drawn from the analysis:

- Ionic liquids act simultaneously as solvents and reaction media, simplifying the procedure of the production of CAP.
- Advanced solid catalysts, such as core–shell materials (PS@PMA-ZrO_2-PW_{12}) and sulfonated carbons, significantly improve process control, catalyst reusability, and final material properties for CAP biofilms.
- All these heterogeneous alternatives to conventional ion-exchange resins rely on Brønsted acid catalysis, but offer notable advantages such as greater thermal stability, better control over the degree of substitution (DS), and the potential for more sustainable processes thanks to reduced solvent use and catalyst recyclability..

7. CONCLUSIONS

First of all, the essential properties of cellulose have been characterized, which has allowed us to understand how and why its structure is modified for its application in bioplastics. One of the most relevant aspects is the great versatility of these modifications, since cellulose, despite having a common origin, can adopt different forms depending on the processing method used. Among these, cellulose acetate and cellulose propionate have proven to be viable options for food packaging applications. It has been shown that, regardless of the initial form of cellulose, similar properties can be achieved after formulation, and there is scope for adjustment to optimize performance according to the specific requirements of the final material. This is evidenced by the comparative data obtained in relation to the viscosity, flexibility and transparency of the films produced.

In order to ensure that the process is truly sustainable, the use of solid acid catalysts has been further developed, which allow not only to reduce waste generation, but also recover and reuse the catalyst, thus optimizing the production process.

This study has provided a comprehensive overview of the potential of cellulose and its derivatives—particularly cellulose acetate (CA) and cellulose acetate propionate (CAP)—as sustainable materials for the production of biofilms intended for food packaging. Through the analysis of both the structural properties of cellulose and the performance of different catalytic systems, several key conclusions can be drawn regarding the technical, environmental, and industrial relevance of these materials.

Based on the analysis, two main conclusions can be drawn regarding cellulose acetate CA the first is the versatility of CA biofilms which show great adaptability as their properties such as flexibility transparency and mechanical resistance can be fine-tuned through the incorporation of natural additives like beeswax or sodium alginate making them suitable for various packaging applications the second is the feasibility of heterogeneous catalysis since the use of Amberlyst-15 and sulfonated carbons has proven to be an effective and sustainable alternative for CA production these catalysts achieve competitive performance and suitable degrees of substitution allow for catalyst recovery and reuse reducing environmental impact and waste and support the development of more sustainable and cost-effective production processes these findings reinforce the potential of CA as a key material in the transition toward biodegradable and eco-friendly packaging solutions

The results obtained for CAP confirm the viability of a more efficient and sustainable production pathway for cellulose acetate propionate biofilms highlighting first that ionic liquids play a dual role as solvent and reaction medium which simplifies the overall synthesis process and second that the use of advanced heterogeneous catalysts such as core–shell structures like PS@PMA-ZrO_2-PW_{12} and mesoporous sulfonated carbons enables improved process control enhanced catalyst reusability and better performance of the final CAP materials altogether this research confirms the potential for producing high-performance plasticizer-free cellulose biofilms through heterogeneous catalysis in alignment with industrial and environmental demands furthermore it lays the groundwork for future developments involving the integration of natural additives such as beeswax sodium alginate or carrageenans further enhancing the functionality and sustainability of cellulose-based packaging materials thus this work represents a significant contribution to the advancement of innovative and environmentally friendly packaging tecnologies.

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ACRONYMS

AGU: Anhydroglucose unit
AmimCl: 1-allyl-3-methylimidazolium chloride
BC: Bacterial Cellulose
BmimCl: 1-butyl-3-methylimidazolium chloride
CAP: Cellulose acetate propionate
CA: Cellulose acetate
CMC: Carboxymethylcellulose
CNC: Cellulose nanocrystals
CNF: Cellulose nanofibers
DBU: Diazabicyclo[5.4.0]undec-7-ene
DMSO: Dimethyl sulfoxide
DP: Degree of polymerization
DS: Degree of substitution
EC: Ethylcellulose
EmimOAc: 1-ethyl-3-methylimidazolium acetate
EMC: Equilibrium moisture content
ENCC: Electrosterically stabilized nanocrystalline cellulose
EVOH: Ethylene vinyl alcohol
FP: Food packaging
HCNC: Hairy cellulose nanocrystalloids
HEC: Hydroxyethyl cellulose
HPAs: Heteropolyacids
HPMC: Hydroxypropyl methylcellulose
LPDE: Low-Density Polyethylene
MC: Methylcellulose
Mw: Molecular weight
NC: Nanocellulose
OTR: Oxygen transfer rate
PLA: Polylactic acid
PMA: Poly(methyl acrilate)
PS: Polystyrene
PVC: Polyvinyl Chloride
PW_{12}: Phosphotungstic acid
RH: Relative humidity
SCB: Sugarcane Bagasse from cellulose
SEM: Scanning Electron Microscopy
TFA: Trifluoroacetic acid
TFAA: Trifluoroacetic anhydride
TGA: Thermo gravimetric analysis