

Review

An Overview of Starch-Based Materials for Sustainable Food Packaging: Recent Advances, Limitations, and Perspectives

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Abstract: As the global plastic pollution crisis intensifies, the development of sustainable food packaging materials has become a priority. Starch-based films present a viable, biodegradable alternative to petroleum-derived plastics but face challenges such as poor moisture resistance and mechanical fragility. This review comprehensively examines state-of-the-art advancements in starch-based packaging, including polymer modifications, bio-nanocomposite incorporation, and innovative processing techniques that enhance functionality. Furthermore, the role of advanced analytical tools in elucidating the structure–performance relationships of starch films is highlighted. In particular, we provide an in-depth exploration of advanced characterization techniques, not only to assess starch-based food packaging but also to monitor starch retrogradation, including Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and iodine binding (Blue Value). We also explore cutting-edge developments in active and intelligent packaging, where starch films are functionalized with bioactive compounds for antimicrobial protection and freshness monitoring. While substantial progress has been made, critical challenges remain in upscaling these technologies for industrial production. This review provides a roadmap for future research and the industrial adoption of starch-derived packaging solutions.

Keywords: starch-based materials; starch retrogradation; food packaging; biodegradable materials; sustainable packaging; nanocomposites; biopolymer modification; smart packaging



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1. Introduction

Due to the aim of minimizing the environmental impacts caused by the improper disposal of fossil-derived plastics, increased interest in alternative strategies such as reuse, recycling, and the employment of bio-based polymers has arisen [1]. The former includes the exploration of polymers obtained from renewable sources and/or possessing a biodegradable behavior. The most abundant biodegradable polymers are derived from biomass, mainly polypeptides and polysaccharides [2].

Among the examples of bio-based polymers, starch has been considered as one of the most promising candidates for use in future materials. It is the second most abundant

natural polysaccharide after cellulose [3], and possesses several advantages, such as good compatibility with other materials, good processability, and moderate to good barriers against oxygen and carbon dioxide [4,5]. Furthermore, starch is considered a safe and low-cost renewable resource with broad availability, as it can be obtained from various agricultural and industrial by-products [6,7].

As one of the most abundant biopolymers that is currently available, starch has been extensively studied by the scientific community to provide alternatives to petroleum-derived plastics that pose environmental risks. Starch-based materials offer good alternatives to conventional polymers due to their intrinsic biodegradability and biocompatibility, and are even used as edible coatings in the food packaging industry [8]. Furthermore, starch can be isolated from various botanical sources with different proportions and molecular weights of its main components, amylose and amylopectin, which affect its physical and chemical properties, processing, and potential applications [9–12]. Nonetheless, the structure of starch presents several challenges to its potential industrial application as a substitute for conventional plastics, such as, for example, the three hydroxyl groups per D-glycosylic unit, resulting in starch-based films with high hydrophilicity degree [13]. Furthermore, the brittleness of starch films is a significant weakness, as their mechanical properties are usually inadequate to maintain the film's structural integrity and resist deformation and damage during subsequent processing [14].

In this sense, great advances have been made in the last years towards improving the applicability of starch-based materials as packaging substitutes, overcoming the limitations faced for this polysaccharide. Therefore, in this review, we summarize the recent progress supported by the “state-of-the-art” information concerning the usage of starch-based materials, surveying the main challenges that are still faced and the prospects for their application as bio-based food packaging alternatives. In addition, advances in functionalization and characterization techniques are also overviewed, providing a concise exploration of starch polymeric films and their potentialities.

2. Insights into Native Starch Chemistry and Film-Formation Properties

Produced by most green plants as an energy storage molecule, starch mainly consists of two macromolecules: amylose and amylopectin. Together, they correspond to 98–99% of starch's dry mass and are structurally packed into concentric rings that form semi-crystalline and amorphous layers [15] (Figure 1). In fact, most native starches evidence crystallinity indexes of about 20–45% [16]. Amylose corresponds to ca. 20–25% of the composition of starch and is an essentially linear macromolecule with a helical structure formed by ca. 1000 α -D-glucopyranosyl units linked via α -D-(1–4) bonds. On the other hand, amylopectin (ca. 75–80% of starch's composition) possesses a highly branched structure containing approximately 4000 glucose units which are interlinked by multiple α -D-(1 $\rightarrow$ 6) branching points [17]. The amylopectin molecules present A, B, and C side chains that varies in the degree of their polymerization (DP): the A chain is the outer side chain without branches (DP 6–12); the B chain (DP 12–60) comprehends the inner side chain of the branch, acting as the mediator connecting the A and C chains, and can be further subdivided into the B1 chain (DP 13–24), which carries only one branch connected to the A chain, and the B2 (DP 25–36) and B3 (DP > 36) chains; and the C chain, characterized as the main chain of amylopectin, is directly linked to both A and B chains. Each amylopectin molecule contains only one C chain, which has a non-reducing end group at one end and a unique reducing end group at the other end [18].

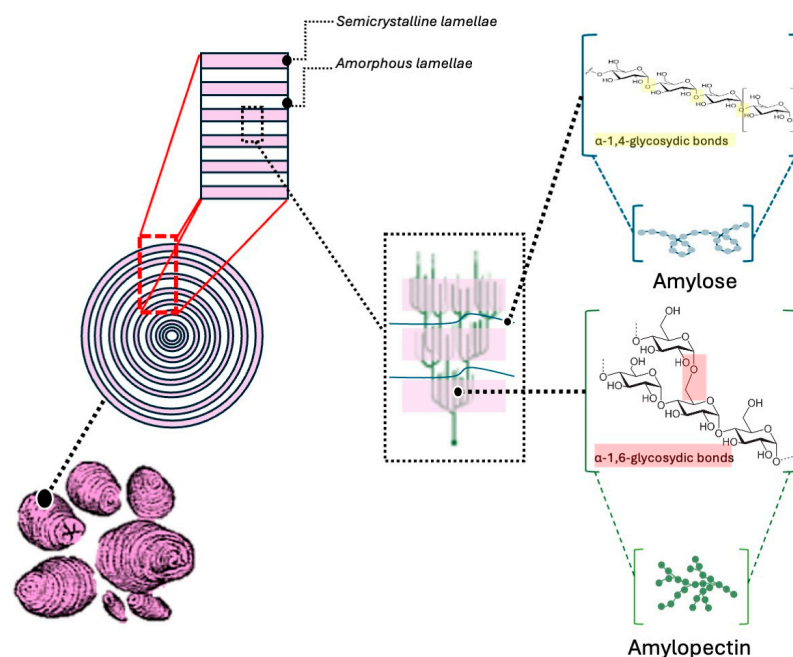


Figure 1. Schematic representation of starch granule structures.

Several factors can impact the starch granule structure and its consequent properties, including the sources and botanical species as well as the different growing conditions of the plant [15]. The molecular weight, DP, chain length distribution (CLD), branching degree, and amylose–amylopectin ratios are crucial indicators of starch’s molecular properties [19]. Due to their intrinsic structural differences, amylose is mainly responsible for the amorphous phase of starch granules, while amylopectin contributes predominantly to the peripheral crystalline organization [20]. Therefore, the proportion of amylose to amylopectin is an important factor that dictates the physicochemical and functional characteristics of starch from different sources and compositions, such as its gelatinization properties, *in vitro* digestion behavior, paste characteristics, degradation behavior, flow characteristics, thermal and mechanical performances, and retrogradation profile [21–23]. Furthermore, the amylose–amylopectin relation in the granule can also affect the solubility of starch in water, as the crystallinity of the granule affects the amount of energy that must be delivered to starch gelatinization (gelatinization enthalpy ΔH and temperature), possibly also affecting the viscosity of the initial slurry [3].

Native starch is not characterized as a thermoplastic polymer, since pyrolysis occurs before the melting point of the crystalline regions in starch is reached. Consequently, starch cannot be melt-processed via conventional extrusion equipment without the incorporation of additives such as plasticizers [13]. In fact, even though native starches have a hydrophilic nature, they are poorly or not soluble in water at room temperature due to the presence of strong inter- and intra-molecular hydrogen bonds between the hydroxyl groups in the starch granules. Therefore, their rupture must occur in a heated aqueous medium: First, the granule swells because of water absorption in the amorphous zone when the temperature remains under the gelatinization point (T_{gel}). One important factor is that, once the temperature exceeds T_{gel} , the semi-crystalline structure starts to collapse irreversibly. Thus, water molecules can easily diffuse into the semi-crystalline amylopectin clusters, breaking the hydrogen bonds and making both solubilizing both the amylose and amylopectin. These events are followed by the entanglement of the amylose and amylopectin in a continuous phase to form the so-called starch gel [17,24]. In this sense, for the obtention of starch-based polymeric films, two technological processes can be employed: a “wet” process based on

starch gelatinization from a film-forming dispersion or an emulsion (e.g., through casting techniques), and a “dry” one based on the thermoplastic properties of this biopolymer at low concentrations of water and/or other plasticizers [13]. The processing techniques applicable to the obtention of starch films are better discussed in the following section (Section 3).

Starch-based films with a greater amylose composition generally have better film characteristics, such as better elongation, mechanical strength, and gas barrier properties for usage as food packaging materials [25]. The reason behind this fact is related to the amylose linear molecular structure that facilitates faster water migration rates and requires less space for rearrangement and relocation, playing a dominant role in the early stages of gel formation. During retrogradation, the amylose promotes crystallization, which leads to a compact and ordered network that enhances the gel strength [26–28]. In contrast, the highly branched structure of amylopectin complicates reorganization, resulting in disordered starch chains after gelatinization [27,28]. Therefore, amylopectin retrogrades more slowly than amylose [25]. In other words, while amylose is primarily responsible for short-term retrogradation, amylopectin can also retrograde, albeit over a longer timescale [29]. So why is the retrogradation so important in dictating the properties of starch-based films?

Upon heating and subsequent cooling in an aqueous medium, starch undergoes a thermodynamically driven reorganization known as retrogradation [30]. This phenomenon involves the progressive re-association of its amylose and amylopectin chains into ordered structures, significantly impacting the rheological and physicochemical properties of starch-based matrices [31]. Retrogradation manifests through increased viscosity, gel rigidity, turbidity, and syneresis—where water is expelled due to molecular realignment [31,32].

Considering the two major components of starch, the amylose rapidly recrystallizes, contributing to the initial gel firmness, whereas the amylopectin undergoes a slower, more gradual realignment, influencing the material’s long-term stability [30]. Consequently, the initial phase of retrogradation, occurring within a time frame from the first few hours to several tens of hours, is largely attributed to the rearrangement of amylose, whereas the long-term retrogradation is governed by the gradual realignment of amylopectin [29,33]. Notably, amylopectin retrogradation is believed to involve two distinct processes: the inter-chain repolymerization of double helices and the subsequent packing of these helices within starch chains. Furthermore, Li et al. [34] showed that the short-term retrogradation of rice starches is positively correlated with the proportion of amylose short-medium chains, while it is negatively correlated with the amylose molecular size.

Starch primarily exists in two distinct polymorphic forms, A-type and B-type, with a third form, C-type, representing a combination of both [34,35]. These crystalline structures differ in their molecular packing, hydration levels, and structural stability, which directly influence the physicochemical behavior of starch, particularly in applications such as packaging films [29]. A-type crystallites, predominant in cereal starches (e.g., wheat, maize, and rice), feature a monoclinic unit cell arrangement with tightly packed double helices and minimal hydration, and which typically contains around eight water molecules per unit cell [29,36]. This compact organization enhances the mechanical strength, reduces the water permeability, and increases the resistance to environmental moisture of the starch, making A-type starch ideal for applications requiring structural integrity and moisture barrier properties.

In contrast, B-type starch, commonly found in tuber and root starches (e.g., potato and banana) [37], features a hexagonal unit cell with a more open packing configuration and a significantly higher water retention capacity, accommodating up to 36 water molecules per unit cell [29,38]. This increased hydration enhances the swelling behavior and flexibility of the starch but also reduces its mechanical strength and increases its susceptibility to

moisture-induced degradation. Recent studies suggest that post-harvest hydration can induce a transformation from A-type to B-type crystallinity, as the water molecules infiltrate monoclinic structures and facilitate their rearrangement into hexagonal networks [39]. This dynamic conversion between crystalline forms offers a pathway for modifying the functional properties of starch-based materials.

These crystalline polymorphs significantly influence the design of starch-based packaging films, where mechanical robustness and controlled water vapor permeability are desired. Due to their dense crystalline arrangement, A-type starch films exhibit superior tensile strength and reduced moisture sensitivity, making them advantageous for use in rigid and moisture-resistant packaging applications [40,41]. Conversely, B-type starch films demonstrate greater flexibility and higher permeability, which can be beneficial for applications requiring stretchability and controlled degradation rates [41]. However, their susceptibility to moisture uptake can lead to premature weakening, necessitating modifications such as blending or cross-linking to enhance their stability.

By precisely controlling the ratio of A-type/B-type crystallinity, the functional properties of starch-based films can be tailored for specific applications. In the presence of an appropriate ligand, amylose can adopt a single helical conformation, known as a V-type starch [42]. Integrating V-type and C-type crystalline structures into starch-based films further enhances their functional performance. V-type crystallinity forms when amylose single helices, with hydrophilic outer surfaces and hydrophobic inner cavities [43,44], assemble into a crystalline structure that is capable of incorporating hydrophobic functional compounds such as fatty acids [43]. This structure is particularly advantageous in bio-based packaging, where improved barrier properties are essential. The hydrophobic nature of V-type complexes significantly reduces their moisture permeability, enhancing the water resistance and storage stability of the resulting material.

In regard to the discussion of the native structure of starch and its properties, the large number of hydrophilic hydroxyl groups on the surfaces of starch molecules means that starch films have poor mechanical properties, high water permeability, and high sensitivity to moisture, which restricts their widespread application as replacements of conventional plastic materials. Therefore, several techniques have been consistently explored as alternatives in starch-based packaging development, including the chemical, physical, and enzymatic modification of native starch [45]. Additionally, blending starches with different crystalline characteristics or inducing partial retrogradation allows for the fine-tuning of films' mechanical, permeability, and biodegradability features, enabling the development of customized bio-based packaging solutions.

One well-established technique for tailoring the properties of starch consists in cross-linking methodologies. The cross-linking of starch is induced by the formation of covalent bonds within or between starch molecules. It can significantly alter the properties of the material, including an increase in its hydrophobicity. Common chemicals used to cross-link starch include glyoxal, epichlorohydrin, and sodium tri-metaphosphate, but most of these substances are either toxic, expensive, or inefficient, which limits their application in food [45]. Therefore, alternative substances have been investigated for starch cross-linking, including citric acid [46] and urea [47].

Other chemical modifications of starch include the following: esterification, which involves the conversion of hydroxyl groups into alkyl or aryl derivatives, which can weaken the intermolecular bonding holding the starch granules together, reducing their water absorption capacity and altering the size, shape, and other functional properties of the starch granules; etherification, which involves the substitution of hydroxyl groups on the glucose units by carboxyl methyl groups, hydroxypropyl groups, and/or other modified groups, leading to significant improvements in the properties of the starch, such as reduced

aggregation and altered physical properties (e.g., more resistant to acid hydrolysis, alkaline hydrolysis, and oxidizing agents); and grafting, which involves attaching polymers onto the starch backbone using covalent bonds and can be achieved by directly attaching polymers (i.e., synthetic or natural) or by attaching monomers that grow into polymers [45]. Interested readers are referred to a review by Lin et al. on the updated techniques for the modification of starch-based films [45].

3. Strategies for the Production of Starch-Based Films

The thermal degradation of starch occurs at ca. 275 °C, when a significant loss of macromolecules begins to occur, characterizing it as a material with good thermal resistance. This enables the application of starch in technologies that require thermal stability and the preservation of structural properties, such as the manufacturing of films and other innovative materials [48]. For example, the casting method is a “wet” technique, widely used in the production of starch-based films, where the starch is gelatinized in an aqueous medium under heating and stirring, which is essential for the formation of a cohesive and homogeneous polymeric matrix, and then poured onto a flat surface and subjected to drying to obtain the film [49].

The casting temperature has a limited impact on the properties of starch-based films, since the variation in crystallinity in the process is minimal, and generally results in insignificant damage to the structure of the starch [50]. On the other hand, the botanical origin of the starch is a more decisive factor, as it influences the molecular organization, the interaction between the polymeric chains, and the formation of the film’s final structure, which can significantly alter its structural properties and performance [51]. One of the advantages of this method is the possibility of incorporating additives that are compatible with the polymer matrix [52]. In the specific case of starch-based films, additive incorporation improves the interaction between the components, eliminating irregularities and improving their mechanical and structural properties, which are essential to the flexibility and integrity of the material [53]. However, the production of starch films using the casting method has some limitations, especially regarding upscaling, since the process is predominantly laboratory-based and requires lengthy drying stages, restricting its industrial application [54].

On the other hand, the extrusion processing (“dry”) method stands out for its efficiency and industrial viability, as it allows starch to be plasticized in the presence of moisture and/or plasticizers, subjected to high temperatures, and sheared within an extruder, promoting homogeneous melting of the material and ensuring a continuous and controlled process [55]. Temperature control in starch extrusion is essential to preventing its thermal degradation, as high temperatures can break the chemical bonds of natural polymers, compromising their structural and mechanical properties. Furthermore, precise control ensures that the starch reaches the ideal viscosity for processing, with adequate performance for industrial applications [56].

Although extrusion offers advantages such as greater efficiency and process control when compared to casting, it can present some limitations in obtaining extremely homogeneous and transparent films, since the high shear can cause polymer alignment or air retention in the matrix, affecting the uniformity of the final material [57].

In this context, the electrospinning technique has emerged as a promising alternative for obtaining nanofibrous starch films, as it allows greater control over the morphology of the fibers, favoring the formation of more uniform structures. In electrospinning processing, the polymer solution is subjected to a high-voltage electric field that allows the polymer jet to form and stretch until the fibers solidify on the surface of the substrate [58]. The concentration of starch plays a key role in the process. Increased concentrations can result

in high viscosity, promoting dense entanglement of the molecular chains, which can hinder the formation of a stable jet and influence the morphology of the fibers [59].

Another important factor in this technique is the voltage applied during the procedure, since it represents a critical parameter in electrospinning. The study by Zhu et al. showed that higher voltages favor uniform and smooth fibers, improving the quality of the resulting material [60]. However, this parameter must be adjusted according to the specific application, considering the particularities of each system.

The thermal behavior of starch nanofibers is influenced by their amorphous structure and the intermolecular interactions formed during the electrospinning process. Initially, moisture loss occurs, followed by thermal decomposition of the carboxyl and hydroxyl groups, and, at higher temperatures, a degradation of the starch polymer chains occurs, resulting in a significant mass reduction [61]. These results indicate that the thermal stability of starch nanofibers is directly related to their structural organization and the type of modification applied to the polysaccharide, influencing their degradation and possible applications in high-temperature conditions.

Given the influence of structure composition and possible intermolecular interactions on the thermal stability of starch nanofibers, the choice of processing technique becomes a determining factor in obtaining materials with optimized properties. In this context, compression molding has also emerged as an effective alternative, allowing starch to be formed into cohesive and homogeneous films through the application of controlled heat and pressure.

The production of starch films involves the preparation of the polymer mixture, which is initially subjected to an increased temperature, promoting partial melting and reorganization of the polymer chains, followed by final cold compression molding, favoring the structural stabilization of the film, which is further removed and conditioned at a controlled temperature and humidity for at least 48 h, ensuring uniformity [55].

Compression molding makes it possible to control the thickness and density of polymeric films, ensuring structural uniformity and consistent mechanical properties. The application of uniform pressure during the process reduces dimensional variations and minimizes the occurrence of defects such as bubbles or cracks, resulting in more homogeneous materials that are suitable for various industrial applications [62].

After discussing the different techniques used to process starch films, it is important to consider the specific applications of each method. Table 1 presents the main advantages and challenges of different processing methods for starch-based films, along with some applications for which the obtained films are used.

Each processing strategy for starch-based films has advantages and challenges, and the ideal method depends on the desired application. A promising alternative for improving the performance of these films is the blending of starch with other polymers. This technique can be performed through extrusion or casting, which allow the properties of the resulting material to be modulated according to the desired application. Starch blends have gained prominence in scientific research and industrial environments, being formulated with biopolymers or synthetic polymers to form materials that are more resistant, flexible, and suitable for applications such as innovative packaging [63].

Table 1. Main advantages, challenges, and applications of starch-based films.

Processes	Advantages	Challenges	Applications	References
Extrusion	Continuous; Scalability; Compatibility with additives; Thickness control	Heat sensitivity; Transparency; Homogeneity	Active packaging for meat; Active packaging for bread	[64–66]

Table 1. Cont.

Processes	Advantages	Challenges	Applications	References
Casting	Simplicity; Homogeneity; Compatibility with additives	Moisture sensitivity; Scalability; Production time	Active packaging for fresh fruits; Active packaging for grapes	[67,68]
Electrospinning	Nanometric structure; Morphology control; Compatibility with additives	Precise parameters; Moisture sensitivity	Nanofiber mats; Active packaging	[69,70]
Compression molding	Fast process; Good mechanical strength; Compatibility with additives	Moisture sensitivity; Transparency; Heat sensitivity; Homogeneity	Edible fish gelatin film; Active packaging for pork	[71,72]

It is also important to highlight the limitation in the miscibility of starch with hydrophobic polymers due to their highly hydrophilic nature, compromising the obtention of homogeneous polymeric blends; however, structural modifications, the incorporation of additives, and the appropriate choice of starch and complementary polymer concentrations can minimize this drawback, promoting improved dispersion and the material's compatibility [73].

4. Advanced Functionalization for Application as a Food Packaging Material

The growing interest in sustainable materials has driven the search for biodegradable polymers of renewable origin, among which starch stands out as a promising alternative. Its functionalization is an effective strategy for modifying its physicochemical and mechanical properties, expanding its applications in active packaging, smart packaging, and edible films [74,75].

To overcome the shortcomings of starch, various modification techniques—encompassing both physical and chemical processes—have been employed to enhance its functional properties while maintaining its biodegradability and sustainability. These modifications yield starches with improved characteristics, including enhanced thermal stability, increased mechanical strength, reduced water solubility, and a greater capacity for interaction with other compounds [76].

Among the physical modifications that are used, one of the best known is gelatinization, which occurs when starch is heated in the presence of water, causing the granules to absorb liquid, swell, and lose their crystalline structure, resulting in a viscous paste [77]. This process results in more uniform starch films and favors interaction between the polymer chains, contributing to greater flexibility [78].

Further, to further improve the properties of starch and expand its applications, chemical modifications such as esterification can be employed. This process consists of introducing ester groups into the starch structure, modifying its properties by making it more hydrophobic [79].

In addition to esterification, another widely used chemical modification is cross-linking (as discussed in Section 2), in which the starch molecules are interconnected using cross-linking agents, forming a more stable three-dimensional network [80]. In the study by Xu et al. [81], as the concentration of the cross-linking agent increased, the pore structure became progressively more compact, resulting, at higher concentrations, in smoother surfaces and practically no empty microstructures. This effect is associated with the strong interaction between the cross-linking agent ions and the starch polymer chains, which promotes the formation of a denser and more resistant network.

In addition to the well-established techniques, novel starch modification approaches have been gaining attention. A great part of these emerging processing technologies involves the physical modification of starch, in agreement with the recent tendencies of consumers and their demand for “natural and health products”, with cleaner and more environmentally friendly processes that reduce chemical usage while achieving similar results being favored. These alternative processes are also claimed to be sustainable since they can reduce the carbon footprint of the product regardless of whether their application needs to be optimized [82]. One example is the usage of cold plasma, which involves supplying gas to an electric field at a constant or alternating amplitude. Consequently, the kinetic energy of the electrons is enhanced, which results in more collisions in the gas and the production of cold plasma species. Cold plasma contains numerous reactive substances, including electrons, ions, free radicals, excited states, and bound neutral molecules [83]. This technology induces alterations in the polymeric matrix that are based on the specific type of plasma that is applied and the characteristics of the starch. These modifications can occur through four identified processes, cross-linking, depolymerization, cold plasma erosion, and the introduction of new functional groups, and can consequently be applied to enhance and refine the attributes of starch granules, improving their performance as a packaging material [83,84].

The main aspects of starch that are affected by cold plasma include the following: (i) the molecular properties (e.g., cleavage of hydrogen bonds and degradation of the polymeric starch chain into its component glucose units), (ii) granule morphology (e.g., promotion of fissures and shape changes in starch granules), (iii) crystallinity (e.g., decrease in the crystallinity of starch-based materials due to the reorganization of the double helices into a less perfect crystalline structure), (iv) gelatinization (e.g., modifications in the thermal properties, with a decrease in the gelatinization parameters), (v) pasting properties (e.g., decreasing the temperature at which starches paste), and (vi) rheology (e.g., decreasing the onset of retrogradation, resulting in starches that form softer gels) of the starch. Further changes can also be observed in starch-based films, such as modifications in their solubility, mechanical properties, hydrophilicity, barrier capacity, and thermal stability. However, it is important to emphasize that the ability of cold plasma to induce any modifications in the overall properties of starches will essentially be determined by the botanical starch type, the source of cold plasma, the gas/gases employed, the power, the pressure of the operating system, and the treatment time [85].

For example, cold plasma was applied at 100, 200, and 300 Hz for 0, 10, and 20 min for three different groups of starch-based films: a film produced with plasma-treated starch, a film produced by subjecting the film-forming solution to plasma treatment, and a plasma-treated film produced with untreated starch [84]. The results indicated that the cold plasma induces significant differences in the physical-chemical and morphological properties of the tested materials, with the highest chemical modifications being observed in the starch subjected to plasma prior to film formation, while the films produced with the untreated starch presented physical changes. Furthermore, the authors identified that the plasma-treated films presented reduced solubility and higher hydrophobicity.

Other emerging techniques used for starch modification include high-pressure processing, ultrasound, and pulsed electric field techniques. Among these, ultrasound technology has the highest potential for modifying starch-based films, which occurs through the employment of cavitation and radical attack mechanisms. The cavitation results from the energy released from the bursting bubbles and shatters the network of starch polymer chains, modifying the physicochemical and structural characteristics of the starch. As a result, starch-based films may exhibit improved mechanical, barrier, and thermal properties [82,86].

On the other hand, the pulsed electric field technique is a low-temperature treatment that can be employed in the development of composites, as it can alter biomacromolecular interactions, such as the polarization of biomacromolecules and electrochemical reactions that produce free radicals to enhance cross-linking and bioconjugation (i.e., intermolecular interactions). It has been suggested that pulsed electric field-induced biomacromolecule depolymerization and ion migration can promote the formation of networks, leading to enhanced cross-linking, bioconjugation, and intermolecular interactions. Furthermore, this technology can help shorten the duration of the starch gelatinization procedure and its energy consumption [82,87].

High-pressure processing is a technique that involves exposure to a pressure between 100 and 1000 MPa for a predetermined amount of time at a specific temperature and can be applied for both liquids and solids. It promotes a disruption at the network of starch polymer chains, leading to modifications in the physicochemical and structural features of the starch. Nevertheless, this emerging technique can cause macromolecular alterations, such as the denaturation of proteins or the gelatinization of starches, which might affect the packaging characteristics of biopolymer-based films [82].

Efforts have been directed toward addressing the limitations of starch-based packaging, due to its low barrier efficiency against external factors and insufficient mechanical strength, which often restrict its use in food packaging applications. The barrier properties of packaging are fundamental to its performance, especially in the context of preserving food and other sensitive products, making it necessary to develop strategies to improve the resistance and functionality of starch [88,89]. Some attempts have been made to improve the mechanical and barrier performances of starch-based materials, including the manufacture of nanocomposites within the incorporation of nanocellulose products.

Composites are mixtures prepared to reconcile the distinct properties of pure components, seeking favorable interactions that lead to better characteristics and performance of the resulting materials [90–92]. In the area of nanocomposites, nanometric-sized plant fibers have been explored as reinforcement materials due to their high specific surface area per unit mass ($>100 \text{ m}^2/\text{g}$), which allows them to interact more effectively with the composite's continuous phase compared to micrometric-sized fibers [93]. In this sense, some components can be incorporated to modify starch's structure and further performance as packaging materials, including its use in combination with nanocellulose materials.

According to the technique employed and the synthesis conditions, dimensions, composition, and properties of the cellulose, nanocellulose products are known as cellulose nanofibers (CNFs), cellulose nanocrystals (CNCs), or bacterial cellulose (BC). CNCs and CNFs are formulated by disintegrating cellulose fibers into nanoparticles and are typically 50 nm–0.5 μm and 50 nm–3 μm in length with a diameter of 3–15 nm and 5–50 nm. BC, on the other hand, is prepared by bacteria inoculation and exhibits a length of 200 nm–3 μm [94].

As with all composite materials, the properties of nanocomposites depend on the individual properties of each component (matrix and reinforcement), the composition of each component (volume fraction of constituents), the morphology of each phase (spatial arrangement, dimensions, crystallinity), and the interface properties [95]. According to Samir et al. (2005) [96], essential parameters that define the mechanical properties of nanocomposites reinforced with nanocellulose include the following: (i) the aspect ratio (L/d) of the nanocomponents, which depends on the source material and the extraction method—higher ratios generally lead to improved reinforcement effects; (ii) the method of preparation of the nanocomposites, which may involve solvent evaporation (i.e., water, in the case of starch films obtained through casting) or melt processing techniques such as extrusion and injection molding; and (iii) the interactions between the polymer matrix and

the nanoparticles. Optimizing these parameters is crucial for obtaining nanocomposites with superior mechanical properties.

The usage of agro-industrial by-products as a source of nanofillers for nanocomposite development is another potential strategy that can be employed for starch-based films. For instance, pineapple leaf waste can be used as a novel raw material to synthesize carbon dots through a simple hydrothermal method [97]. Kuchaiyaphum et al. (2024) [97] introduced this type of carbon dots (2.36 ± 0.33 nm) into pineapple stem starch-based active food packaging films, which led to notable enhancements in both the mechanical strength and UV-barrier properties, alongside improved antioxidant and antimicrobial properties, of the film, thereby extending the shelf-life of fresh pork.

Other nanocomponents can be added into starch-based matrices to provide improved performance and/or bioactive properties. For example, Dhiman et al. (2025) [98] investigated the manufacturing of biodegradable starch-based nanocomposite films with the incorporation of zinc oxide nanoparticles. The zinc oxide nanoparticles were added at 1%, 2%, and 3% within a starch matrix and the authors verified that the obtained films showed improved mechanical, antibacterial, and UV barrier qualities. Furthermore, the water vapor barrier increased significantly from $1.16 \text{ g mm/m}^2 \text{ day kPa}$ (pure starch film) to $2.25 \text{ g mm/m}^2 \text{ day kPa}$ upon the addition of the nanoparticles.

Despite the challenges, starch continues to stand out as a sustainable and promising alternative in the formulation of edible films, which consist of a thin layer of material that can be consumed alongside the food, providing additional protection [99]. Its structure, rich in amylose, favors the formation of cohesive and transparent films, making it a viable option for industrial applications [100].

Other interesting applications of starch-functionalized polymers include the manufacturing of active packaging materials. The main strategies for making starch packaging active include the incorporation of antioxidants and antimicrobial agents, which can be added directly to the film matrix or encapsulated for controlled release, and which makes it possible to create materials that delay lipid oxidation, inhibit pathogenic microorganisms, and preserve the sensory characteristics of food [100,101].

Smart packaging has revolutionized food protection by allowing monitoring of its quality and interaction with the consumer. Starch is a promising biopolymer due to its abundance, biodegradability, and versatility, and can be functionalized with natural pigments and from particles on nano and macro scales [102,103].

Among the main applications of starch-based smart packaging are freshness indicators, which change their color in response to the release of metabolites resulting from food degradation, such as volatile amines that are present in meat [104]. In addition, pH-based colorimetric sensors can be incorporated into starch-based films to indicate the deterioration of food products [105].

For example, a recent study introduced a starch-based composite film integrated with quaternary ammonium chitosan and *Lycium ruthenicum* anthocyanins via a facile casting method, which could be applied in intelligent food packaging [106]. The results obtained by the authors included that the film exhibited pH-responsive color changes from pink to green across a pH range of 2–12, alongside excellent UV-blocking and antibacterial properties. Furthermore, the film was tested for shrimp preservation, and the findings revealed a 16 h shelf-life extension, coupled with real-time freshness monitoring.

Another study investigated the functionalization of corn starch-based composite films with *Rosa roxburghii* Tratt fruit pomace via extrusion compression molding for active food packaging. The films were produced by employing different concentrations of Tratt fruit pomace (0–30% *w/w*, based on corn starch) and the results indicated that this additive can remarkably improve the barrier, mechanical, and antioxidant properties of the obtained

films compared to pure corn starch film, especially the water and oxygen barrier performances. The films also evidenced enhanced antioxidant activity *in vitro*, a property that was further evaluated during a shelf-life trial with mushrooms. The mushrooms packaged in the film containing the highest concentration of Tratt fruit pomace (30% *w/w*) maintained optimal appearance and freshness after 12 days at 4 °C.

5. Advanced Analytical Techniques for Characterization of Starch-Based Films

The ratio of crystalline to amorphous material in starch can change after processing steps such as annealing, extrusion, and enzymatic digestion [107–110]. Compact and dense structures of the starch crystalline regions can resist enzymatic digestion, slowing down starch digestion, and this type of structure can also be called resistant starch [111]. The characterization of and changes in the structure of starch can be detected through different advanced analytical techniques such as X-ray diffraction, nuclear magnetic resonance, infrared spectroscopy, differential scanning calorimetry, and atomic force microscopy (Figure 2), which are well discussed in the following sections.

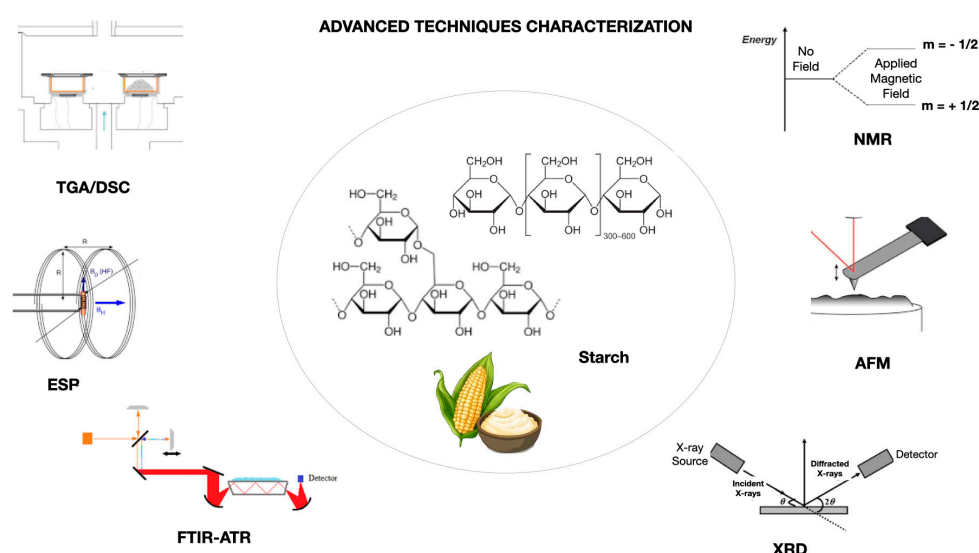


Figure 2. Schematic representation of the analytical techniques applicable for screening starch-based materials.

5.1. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) analysis is one of the most powerful nondestructive technologies utilized to explain the position of atoms, their arrangement, unit cell size, preferred crystalline orientation, phases, and structure, and the structural parameters of materials like their crystal defects, strain, grain size, and crystallinity, facilitating a better understanding of the analyte's microstructure [112]. X-rays are a part of the electromagnetic spectrum, with energy levels from 100 to 100 kV [113,114]. Using the X-ray technique, the long-range crystalline order of starch in relation to the arrangement of its double helices can be determined, allowing for the identifying of patterns of amorphous, semi-crystalline, or crystalline structures, and this technique is used to classify starch into types A, B, C, and V [115]. Type A crystallinity starch shows two strong diffraction peaks between 15° and 23°, and a doublet at 17° and 18°; type B crystallinity produces a strong diffraction peak at 17°, and low-intensity peaks between 15° and 24°; and type C is a mixture of A and B [116].

An atom's 3D array is visualized as imaginary points in a 2D plane called a crystal lattice, and its basic 3D repetitive unit in real space is defined by three axial lengths (*a*, *b*, and *c*) and three interaxial angles (α , β , and γ) called the unit cell [117]. The A-type unit cell

assembly has 12 glucosyl units that are arranged as a monoclinic space group ($a = 2.124$ nm, $b = 1.172$ nm, $c = 1.069$ nm, and $\gamma = 123.5^\circ$) and four molecules of water, which are left-hand oriented and parallel-stranded with double helical arrangements [118]. Similarly, the double helices of B-type starch are also left-hand oriented and connected through hydrogen bonding within hexagonal arrangements of six double helices ($a = b = 1.85$ nm, and $c = 1.04$ nm). Another single-helical V-type starch structure, essentially an amylose–lipid complex, has been identified as forming during the cooking process. The V pattern was retained at the 2θ position of 20, and it was shown that V-type crystallites help enhance the resistant starch content in rice [119,120].

5.2. Nuclear Magnetic Resonance (NMR)

Another helpful technique, nuclear magnetic resonance (NMR), has been widely used to identify the chemical structure and composition of materials through solution-state high-resolution NMR [121,122], to determine the molecular and supramolecular structures of materials through solid-state high-field NMR, and to monitor the molecular dynamics of materials through time domain NMR [123]. NMR phenomena have origins within the nucleus of individual atoms that have a net “nuclear” spin, whose effects can be noted in a magnetic field and involve the exchange of energy between two levels at least (resonance) [124]. For one sample, different nuclei, such as ^1H , ^{13}C , and ^{31}P , can be chosen to study the aspects of sample and to extract the relevant information under natural/industrial conditions [125,126].

^{13}C solid state cross polarization/magic angle spinning NMR (^{13}C CP/MAS NMR) has been used to quantify the molecular order of granular starch; to study chemical and double helix content changes in starch [116,127]—e.g., a chemical shift of ca. 100 ppm has a triplet feature for A-type starch while it is a duplet for B-type starches, which is attributed to the specific arrangement of the crystals in the granules [128,129]; and to determine the hydration level of starch through the peak sharpness, as moisture content of starch increases [110] depending on the polymorph type and starch composition [130]. Further, the spectral decomposition of the C-1 peak of the ^{13}C CP/MAS NMR spectrum under ^1H decoupling revealed five types of α -(1,4) linkages in starch [131], while the glass transition temperatures of amorphous waxy maize starches have been measured by pulsed (through rigid lattice limit) and solid-state ^{13}C CP/MAS NMR [132]. Similarly, ^1H NMR has been used to determine the amylose content in starch or to assess the anomeric protons involved in its α -(1,4) and α -(1,6) linkages [133]. Therefore, changes in and the features of starch can be understood.

5.3. Fourier-Transform Infrared Spectrometry (FTIR)

Regarding changes in starch components, Fourier-transform infrared spectrometry (FTIR) has been widely used in starch chemistry to determine the short-range structural alterations in starch [110], to identify the new functional groups after starch chemical modification [134], and to detect solid and gas component changes in starch during thermal degradation [135]. The attenuated total reflection (ATR) model, a FTIR mode, is normally used to determine the short-range structural changes in starch and the surface properties of starch film, and is even used as an “infrared crystalline phase index” [136–138]. The FTIR spectra of starch typically contain bands at $2900\text{--}3000\text{ cm}^{-1}$ (C-H stretching), $1100\text{--}1150\text{ cm}^{-1}$ (C-O and C-O-H stretching), and $1100\text{--}900\text{ cm}^{-1}$ (C-O-H bending). The bands in the region of $1100\text{--}900\text{ cm}^{-1}$ have been shown to be sensitive to changes in starch structure, including retrograded starches [139], mixtures of starch and amorphous maltodextrin [138], enzyme hydrolyzed starches [137], and acid hydrolysis residues (“lintners”) [136]. From these studies, it can be seen that the band at 1022 cm^{-1} seems to increase

in more amorphous samples, while the bands at 1000 cm^{-1} and 1047 cm^{-1} become more defined in more crystalline samples. However, Capron et al. (2007) found the absorbance at 1047 cm^{-1} to be essentially independent of the degree of structure in the starch [136]. On the other hand, the intensity ratio of the bands at 1022 cm^{-1} and 1000 cm^{-1} proved a useful tool to monitor the loss of structure associated with the hydration sensitivity of starches that results from nematic–smectic transition, but a detailed appraisal of the spectra suggested greater complexity, with an apparent peak position shift during gelatinization. Furthermore, FTIR can be a useful tool in monitoring starch retrogradation.

FTIR, combined with the Avrami equation, provides a powerful approach to quantifying the retrogradation degree (RD) of starch by examining structural transformations over time. The FTIR spectra of starch reveal changes in its ratio of absorbance from 1047 cm^{-1} (crystalline regions) to 1022 cm^{-1} (amorphous regions), denoted as $R_{1047/1022}$ [140]. This ratio increases with the storage time, indicating progressive starch retrogradation due to the formation of double helices and crystalline structures, which can be quantified by the Avrami equation (Equation (1)).

$$X(t) = 1 - \exp(-kt^n) \quad (1)$$

In the above equation, $X(t)$ represents the RD at time t , k is the crystallization rate constant, and n is the Avrami exponent, describing the nucleation and growth characteristics of the crystalline regions. The RD can be determined using the FTIR-derived $R_{1047/1022}$ values through Equation (2).

$$RT(t) = \frac{R_{1047/1022}(t) - R_{1047/1022}(0)}{R_{1047/1022}(\infty) - R_{1047/1022}(0)} \times 100\% \quad (2)$$

In the above equation, $R_{1047/1022}(t)$ is the measured FTIR ratio at time t , $R_{1047/1022}(0)$ is the initial ratio before retrogradation, and $R_{1047/1022}(\infty)$ is the maximum value after full retrogradation. By fitting the experimentally determined RD values into the Avrami model, the recrystallization kinetics of starch retrogradation can be accurately described [140]. This approach demonstrates that FTIR, when coupled with the Avrami equation, serves as a reliable, rapid, and non-destructive method for evaluating the structural evolution of retrograded starch, offering practical value for predicting the shelf-life and tailoring the material formulations of starch-based films for packaging applications.

5.4. Thermal Analyses: Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

Differential scanning calorimetry (DSC) is a thermal analysis method in which the occurrence of a temperature difference between the sample and the reference due to a thermal event within the sample is the primary effect [141]. DSC has been widely used to characterize the phase transition of starch, e.g., gelatinization [142], retrogradation [143], and glass transition [144]. DSC measures the enthalpy change, which involves the disruption of ordered regions in the granule and is predominantly the result of crystallite melting, with contributions to the overall enthalpy change also coming from the swelling, hydration, and disruption of the short-range double helix structure. Moreover, gelatinization is a kinetic event that is dependent on both the heating rate and water content [107,145,146]. Enthalpy is also related to the shape, size, and presence of phosphate esters in starch granules [147–149]. The gelatinization process depends on the composition, crystallinity, botanical source, and processing of starch, which can present an initial temperature (T_0) around $55\text{--}60\text{ }^{\circ}\text{C}$ and a final temperature (T_f) around $70\text{--}90\text{ }^{\circ}\text{C}$, with the enthalpy of gelatinization (ΔH) being about $10\text{--}19\text{ J/g}$ [147,150]. Moreover, an endothermic peak can be observed at $95\text{--}115\text{ }^{\circ}\text{C}$ which is attributed to the dissociation of the amylose–lipid com-

plex [115,151], which is a reversible process, contrary to the phase transition of amylopectin. Therefore, the DSC technique is important to understanding the transitions that occur in the starches.

Complementary to DSC, thermogravimetric analysis (TGA) has been widely used to evaluate the microstructure, multiphase transitions, thermal stability, and decomposition of starch during thermal processing. The derivative thermogravimetric (DTG) technique, the first derivative of TGA, is a sensitive measurement and supplies information on the relative rates of volatilization and decomposition in a material. Sometimes, the further manipulation or deconvolution of overlapping peaks is needed in some complex processes [152]. Dehydration and decomposition have generally been considered as the two major processes associated with the degradation mechanisms of starch in an open system [143]. Two or three events can be observed in the thermograms of starch. The first one represents the evaporation/dehydration that starts around 70–100 °C, and the weight loss in this stage is dependent on the moisture content in the starch samples. This event can be affected by a chemical modification that involves the introduction of functional groups into the starch molecule, which has been used to improve the physical and chemical properties of starch; however, this modification can change the thermal stability of the starch. The condensation reaction is reduced with the substitution of the hydroxyl group by the acetyl group, which increases the thermal stability of the starch. The dehydration of neighboring hydroxyl groups in the glucose ring can occur, resulting in the formation of C-C bonds, the breakdown of the glucose ring, and the formation of aldehyde as end groups when the glucose ring is fractured. Aromatic rings, such as substituted benzene and furan structures with either $-\text{CH}_2-$ or $-\text{CH}_2-\text{O}-\text{CH}_2-$ as the main linkages between the aromatic groups can be generated with increasing temperatures. The second and third weight-loss steps correspond to thermal decomposition, which commences at about 320 °C [135]. The last stage of carbonization reactions at temperatures above 500 °C increases the relative intensity of aromatic carbon resonances while decreasing the intensities of aliphatic carbons. Relatively large conjugated aromatic structures are formed at temperatures above 600 °C, and further heating generates amorphous carbon structures [141].

5.5. Atomic Force Microscopy (AFM)

Representing a different approach, atomic force microscopy (AFM) has been used to observe the structure of starch granules from different botanical sources. In AFM, the contrast is due to differences in topography on the surface of the sample and/or differences in the elastic modulus of different parts of the section [153]. The use of rapid-setting Araldite, a non-penetrating resin, allows the ultra-structure of the granules to be viewed without the necessity of pre-treatment (linearization or enzymatic degradation) steps. A black hole in the middle of the granule (hilum) is commonly observed in maize starch and represents an air pocket, and the surface of the sectioned granule will have a textured appearance with spheroidal objects that are typically 50–80 nm in size. The proportions of the oblong nodules' diameter, the inter-lamellar distances, and the dimensions of the structural elements in the crystalline region of starch granules obtained by AFM can fit or be compared with the previously mentioned techniques [154].

5.6. Other Analyses

Similar to FTIR due to targeting changes in starch components, electron paramagnetic resonance (EPR) or electron spin resonance spectroscopy (ESR) can be used for studying chemical species that have one or more unpaired electron, such as organic and inorganic free radicals or inorganic complexes that possess a transition metal ion. Radicals have been generated in starch during thermal processing, such as conventional heating [155],

microwave heating [156], extrusion [157], and irradiation [158], as well as during mechano-chemical process and ionizing irradiation [155]. Thermally generated starch radicals are very stable, and originate from the homolytic cleavage of the C–H, C–OH, and CO–H bonds, in which the unpaired electron is localized on the carbon and/or oxygen atom [159]. The EPR spectra, in the Q-band at constant microwave power for starch samples that have been previously heated at 483 K for 30 min in an oven, have two components and contain two kinds of radicals [155]. The hydrogen atom is abstracted from the carbon C1 of the glucose in the starch and a type I radical is produced. Subsequently, due to the dehydration at the C2 and C3 carbons, a type II radical is produced. It has also been noted that the number of radicals generated decreases with time [156], highlighting the importance of the technique for obtaining cooked starches.

The employment of advanced techniques in order to characterize and comprehend differences and changes among the kinds of starches and their processing methods is pertinent, helping to choose the best source for each application.

5.7. Monitoring Starch Retrogradation: A Multi-Technique Analytical Approach

Starch retrogradation is a complex reorganization of gelatinized starch molecules into more ordered structures upon cooling and storage. This process impacts the texture of food, its shelf-life, and its nutritional properties. No single analytical method can fully capture the multi-scale structural changes of retrogradation, so a combination of techniques is often employed. Table 2 summarizes the key analytical methods used to study starch retrogradation, detailing the measured properties, advantages, limitations, and typical applications of each method in conducting retrogradation studies.

Table 2. Analytical techniques for multi-scale characterization of starch retrogradation.

Method	Type of Analysis	Measured Properties	Advantages	Limitations	Measurement Purpose
Differential Scanning Calorimetry (DSC)	Thermal	Melting temperature, enthalpy of recrystallization	Highly sensitive; quantitative	Requires controlled moisture; only detects crystalline phase	Quantifies retrogradation by measuring energy changes in stored starch gels
Thermogravimetric Analysis (TGA)	Thermal	Moisture loss, decomposition profile	Simple; real-time measurement	Limited sensitivity to structural changes	Evaluates water retention and stability of retrograded starch
Rapid Visco Analyzer (RVA)	Rheological	Setback viscosity, pasting profile	Fast; mimics food processing	Shear disrupts structure; limited to short-term retrogradation	Ranks starches by retrogradation tendency via setback viscosity
Texture Profile Analysis (TPA)	Mechanical	Gel hardness, adhesiveness, cohesiveness	Directly relates to texture	End-point measurement; sample-dependent	Assesses firmness increase in starch gels during storage
Fourier Transform Infrared Spectroscopy (FTIR)	Spectroscopic	Molecular order (1047/1022 cm ^{−1} ratio), hydrogen bonding	Non-destructive; rapid	Water interference; qualitative without calibration	Tracks short-range order changes in retrograded starch
Raman Spectroscopy	Spectroscopic	Backbone conformation, glycosidic bonds	Water has minimal interference	Weaker signals; fluorescence issues	Complements FTIR to analyse starch molecular changes
Nuclear Magnetic Resonance (NMR)	Spectroscopic	Water mobility (T ₂ relaxation), molecular conformation	In situ monitoring; differentiates bound vs. free water	Requires specialized equipment; complex interpretation	Monitors retrogradation kinetics via water dynamics and starch crystallization
X-Ray Diffraction (XRD)	Structural	Crystallinity, polymorphic transitions (A, B, V)	Identifies crystal forms; quantifies order	Requires dried samples; low sensitivity to amorphous regions	Confirms amylopectin retrogradation by detecting B-type crystals
Small-Angle X-ray Scattering (SAXS)	Structural	Lamellar structure (5–20 nm scale)	Sensitive to nanoscale ordering	Requires advanced modelling; not routine	Analyses amylopectin rearrangement during retrogradation

Table 2. *Cont.*

Method	Type of Analysis	Measured Properties	Advantages	Limitations	Measurement Purpose
Scanning Electron Microscopy (SEM)	Microscopy	Gel morphology, phase separation, granule remnants	High resolution; visual confirmation	Sample preparation can introduce artifacts	Examines gel structure changes due to retrogradation
Turbidity Measurement	Physical	Light transmittance loss (paste cloudiness)	Simple, fast	Non-specific; requires consistency	Monitors aggregation of retrograded starch in pastes
Syneresis Test	Physical	Water separation from gels	Directly relevant to food stability	Destructive; semi-quantitative	Measures water expulsion due to retrogradation
Iodine Binding (Blue Value)	Chemical	Amylose retrogradation (iodine complex formation)	Quick, inexpensive	Affects amylose only; influenced by branching	Estimates extent of amylose retrogradation
Resistant Starch (Enzymatic Digestibility Test)	Chemical	Resistance of starch to enzymatic hydrolysis	Nutritional relevance	Multi-step procedure; indirect measurement	Determines digestibility reduction due to retrogradation

5.8. Starch Retrogradation Impact on Practical Applications in Packaging

The structural rearrangement of starch by retrogradation directly influences its key material properties and the packaging features of starch-based films, such as its mechanical behavior, compatibility with other biopolymers, and biodegradability. Given that retrogradation refers to the gradual reassociation of gelatinized starch chains—primarily amylose and, over longer periods, amylopectin—into more ordered crystalline structures, this process alters the physico-chemical and functional characteristics of starch-based materials and has significant implications for their performance in biodegradable packaging systems.

From a mechanical perspective, retrogradation increases the crystallinity of starch-based materials, leading to enhanced tensile strength and stiffness due to the formation of inter-chain hydrogen bonding networks. While this improved rigidity can be beneficial for structural packaging applications, excessive retrogradation often results in brittleness and a marked reduction in elongation at break, limiting the flexibility of the resulting material. Furthermore, the retrogradation process continues over time—particularly for materials with a high amylopectin content—causing gradual changes in the mechanical properties of the material, commonly referred to as aging, which compromises the material's stability.

Retrogradation also affects the compatibility of starch with other biopolymers that are commonly used in packaging formulations. The formation of crystalline domains during retrogradation restricts polymer chain mobility, which can hinder the miscibility of starch and lead to phase separation in blends with polymers. Thus, the sequence and timing of processing steps are crucial, since blending starch before extensive retrogradation occurs allows better polymer entanglement and obtaining more homogeneous materials.

In terms of biodegradability, retrogradation has a generally inhibitory effect. The crystalline regions that are formed are more resistant to enzymatic hydrolysis and microbial degradation than amorphous regions. As a result, highly retrograded starch materials degrade more slowly in soil or composting environments. This reduced biodegradability stems from limited water uptake, restricted enzyme diffusion, and lower microbial accessibility. Nevertheless, in some packaging contexts—particularly where material stability during storage is critical—this slower degradation rate may be advantageous.

The practical implications of starch retrogradation in packaging applications depend on the specific requirements of the end use. For short-term packaging items, e.g., single-use films and food wraps, minimal retrogradation is preferred to maintain flexibility and facilitate rapid environmental degradation. In contrast, packaging applications that demand structural integrity, such as trays or rigid containers, may benefit from controlled retrogradation to enhance their mechanical strength and dimensional stability. Addition-

ally, retrogradation improves the moisture barrier properties of starch films by reducing their water vapor permeability, which can be valuable for packaging moisture-sensitive products. However, this benefit must be balanced against the potential for embrittlement and reduced degradability.

In summary, starch retrogradation presents both challenges and opportunities in the development of starch-based packaging materials. Controlling the extent and kinetics of retrogradation through the use of formulation strategies, altering the plasticizer content, and selecting appropriate processing conditions is essential for tailoring the performance of the obtained material to the intended application.

6. Challenges and Limitations

The environmental burden of plastic waste has intensified the search for sustainable packaging alternatives. Food packaging alone represents the largest use of plastics, and the accumulation of non-biodegradable packaging waste is a critical concern. Starch-based films have emerged as promising candidates to replace conventional plastics due to their renewable source, low cost, and inherent biodegradability. Starch is a naturally abundant polysaccharide (e.g., from corn, potato, cassava) that is FDA-approved for contact with food and even used in edible coatings and pharmaceutical capsules [160]. However, native starch films suffer from poor mechanical strength and water sensitivity, limiting their direct application as packaging. They are often brittle (especially under dry conditions due to the retrogradation of starch polymers) and show low resistance to moisture and gases [8]. These challenges have spurred extensive research into material innovations—from chemical modifications and the formation of nanocomposites to the use of multilayer designs—to enhance the performance of starch film [161]. In parallel, efforts are underway to scale up the production of these bio-based films and ensure that they can be manufactured economically and meet food-contact standards. Below, we discuss recent advancements in starch-based films for food and intelligent packaging, focusing on material science innovations and the outlook for commercial scalability.

6.1. Intrinsic Limitations of Starch Films

Starch-based films, in their unmodified form, have notable shortcomings in the context of food packaging. The hydrophilic nature of starch leads to high water vapor permeability and weak moisture resistance. This means that, in humid or wet conditions, starch films tend to swell or even dissolve, and their mechanical integrity deteriorates. Moreover, without additives, starch films are brittle and prone to cracking under stress. In terms of barrier properties, pure starch films have only moderate oxygen barrier capabilities, and, in the presence of moisture, their barrier performance degrades substantially [20,162]. These inherent issues necessitate material science strategies to enhance the mechanical strength, water resistance, and gas barrier properties of starch films.

One of the most critical limitations of starch films is starch retrogradation, a process in which amylose and amylopectin molecules in the starch undergo reassociation after gelatinization [30], leading to phase separation [163], increased relative crystallinity [29], and film brittleness over time [164]. This phenomenon results in mechanical deterioration, reduced transparency, and compromised barrier properties [162], limiting the functional lifespan of the films [20,30]. For instance, a higher concentration of amylose accelerates starch retrogradation, promoting the formation of B-type crystallites and increasing gel hardness [165]. The molecular arrangement of starch components significantly influences their retrogradation behavior, where linear amylose molecules tend to reassociate more readily than branched amylopectin, leading to enhanced crystallinity and reduced flexibility in the obtained films. Additionally, the presence of hydroxyl groups in starch polymers

facilitates intermolecular hydrogen bonding, further reinforcing the crystalline regions and exacerbating the brittleness of the film [8]. The degree of polymerization and molecular weight distribution also affect the film performance, as shorter chains can realign and crystallize faster, resulting in stiffer and less elastic structures [166,167].

Regarding visual film characteristics, blooming and blushing are common optical defects arising from these structural instabilities [164]. These defects occur when low-molecular-weight plasticizers migrate to the surface due to overplasticization—when the plasticizer concentration exceeds the polymer's capacity—leading to phase segregation (exudation) and the physical exclusion of compounds such as glycerol or sorbitol [167,168]. This phase separation results in a whitish or hazy appearance. Additionally, moisture absorption, particularly from hygroscopic substances, e.g., CaCl_2 , SiO_2 , and glycerol, induces a plasticization effect, reducing the mechanical properties of the film and its opacity by enhancing light scattering [169,170]. These phenomena can be intensified by environmental humidity and temperature fluctuations and may be reversible upon drying. To mitigate these issues, strategies, e.g., optimizing the plasticizer content (while avoiding highly hygroscopic plasticizers), incorporating compatible polymer blends, chemically modifying the starch, and controlling the storage conditions, can mitigate undesired optical changes.

Various modification techniques, including esterification (e.g., acetylation) [171,172], oxidation [173,174], cross-linking [175,176], and grafting [177–179], have been explored to mitigate retrogradation and enhance the physicochemical properties of starch films [161]. For instance, esterifying starch with organic acids or anhydrides introduces hydrophobic acetyl or long-chain groups. The resulting starch esters exhibit increased hydrophobicity and reduced intermolecular hydrogen bonding, which translates into lower water absorption and improved thermoplasticity. Furthermore, acetylated starch films show significantly less retrogradation and enhanced flexibility and strength compared to native starch films [180,181]. Similarly, etherified starch (e.g., hydroxypropyl starch) tends to be more amorphous and stable, which can improve the clarity and flexibility of the film [14,182].

Traditional plasticizers such as glycerol and sorbitol function by disrupting intermolecular hydrogen bonding within starch, thereby enhancing the flexibility of the film [164,183]. However, their tendency to migrate within the polymer matrix often accelerates the retrogradation over time, compromising the film's stability and mechanical integrity [162]. In contrast, natural deep eutectic solvents (NADESs) have emerged as promising alternative plasticizers, offering enhanced starch dissolution, improved resistance to retrogradation, and superior processability under extrusion conditions [184–186]. Despite these advantages, their application in starch-based packaging remains largely unexplored. Future research should prioritize the systematic investigation of NADESs in combination with diverse starch sources, optimizing formulations to balance functional performance and environmental sustainability, with a particular emphasis on facilitating large-scale production. Equally important is the need for comprehensive toxicological assessments and regulatory scrutiny to ensure that NADESs meet the safety standards for food-contact applications.

Beyond chemical means, physical modifications can also enhance starch films. Techniques such as annealing [187,188], and heat–moisture treatment (exposing starch to controlled heat and limited moisture) can increase starch's crystallinity or reorganize its amylopectin networks, thereby improving the resulting film's tensile properties and reducing its solubility (by reinforcing internal hydrogen bonding) [189,190]. High-shear or ultrasonic treatment during gelatinization can similarly alter the microstructure of starch, yielding films with different textures and strengths [191]. These physical methods do not introduce new chemicals and thus maintain the film's food-safe simplicity, although they may not achieve as large a property boost as chemical modifications. Overall, chemical and physical

modifications expand starch's functionality—from improving its water resistance and mechanical toughness to tuning its gelatinization and thermal stability—creating a toolbox of starch derivatives optimized for packaging needs.

To facilitate a clear comparison between starch-based films and other bio-based polymers for potential use as food packaging, Table 3 presents a concise evaluation of key material properties. This comparative analysis focuses on the biodegradability, mechanical and barrier properties, and food safety of the different films, as well as their suitability for active and intelligent packaging applications. Given the wide range of material behaviors, a qualitative rating system has been applied, using symbols to indicate different levels of suitability. Starch-based films stand out in categories such as biodegradability, edibility, and compatibility with active agents, whereas other bio-based polymers, such as PLA and PHA, offer advantages in mechanical strength and moisture resistance. Protein-based films demonstrate excellent oxygen barrier properties and compatibility with colorimetric indicators, making them valuable in intelligent packaging. This comparison highlights the trade-offs and complementary strengths of different materials, guiding their application in sustainable smart packaging solutions

Table 3. Comparison of bio-based polymers for food packaging and smart applications *.

Properties	Starch-Based Films	Poly (Lactic Acid)	Poly (Hydroxyalkanoates)	Protein-Based Films
Film Transparency Edibility & Food Safety	++ (clear films) ++ (safe, edible, GRAS **)	Fundamental Characteristics ++ (transparent)	± (varies by crystallinity)	++ (glossy, clear)
		+ (safe but not edible)	+ (safe, but not edible)	++ (safe, edible)
		Performance and Processing Features		
Mechanical Strength	- (brittle, weak alone)	++ (strong, durable)	+ (flexible, varies by type)	± (moderate, varies by moisture)
Oxygen Barrier	++ (very low O ₂ permeability)	+ (moderate O ₂ barrier)	+ (good O ₂ barrier)	++ (excellent O ₂ barrier when dry)
Moisture Barrier	-- (high water absorption)	± (moderate resistance)	++ (highly water-resistant)	- (poor, absorbs moisture)
Processability	± (requires blending/modification)	++ (easily extruded/molded)	± (thermal instability in some PHAs)	- (not thermoplastic, solution-cast only)
Biodegradability	++ (fast, all environments)	Environmental and Economic Aspects		
		± (only industrial composting)	++ (biodegrades everywhere)	++ (fast, edible)
Scalability & Cost	++ (low cost, abundant)	++ (commercially established)	- (expensive)	- (more costly, variable availability)
Antimicrobial Suitability	++ (high compatibility with bioactives)	Active and Smart Packaging Features		
		+ (can hold antimicrobials)	+ (less explored, but promising)	++ (strong binding to antimicrobials)
		± (requires additives)	± (not widely studied)	± (requires additives)
Oxygen Scavenging	+ (can host O ₂ absorbers)	- (difficult for hydrophilic dyes)	- (limited research)	++ (works well with pH dyes)
pH-Indicator Use	++ (excellent for color changes)	- (not suited for moisture control)	++ (best for wet conditions)	± (moisture-sensitive, needs coating)
Moisture Regulation	+ (can absorb/release moisture)	++ (commercially established)	- (expensive)	- (more costly, variable availability)
Scalability & Cost	++ (low cost, abundant)			

* The rating system follows the scale: (++) excellent—highly suitable with superior performance; (+) good—effective with minor limitations; (±) moderate—functional but with trade-offs; (-) poor—limited suitability, requiring enhancement; (--) very poor/not suitable—not recommended for this application. Ratings reflect intrinsic polymer properties, although modifications (e.g., blending, cross-linking, nanocomposites) may enhance weaker attributes. ** GRAS: generally recognized as safe.

6.2. Starch for Food Packaging Features and Smart Applications

The most critical challenge regarding starch-based films, as standalone packaging, is their pronounced water sensitivity, which significantly compromises their barrier properties. Owing to the high density of hydroxyl groups in starch's molecular architecture, these films exhibit inherent hydrophilicity, making them highly susceptible to moisture uptake. This excessive water absorption not only disrupts their structural integrity but also limits their efficacy in applications that demand low permeability, particularly in high-humidity conditions or aqueous food-contact systems. Strategies to enhance the water

resistance of these films have involved blending the starch with hydrophobic polymers, e.g., poly (lactic acid) (PLA) [192,193] and poly (caprolactone) (PCL) [194,195], and incorporating nano-fillers, e.g., cellulose nanocrystals [94], montmorillonite clay [196], or graphene oxide, to create nanocomposite films with improved moisture barrier properties. Additionally, cross-linking starch molecules through physical and chemical methods has demonstrated potential in reducing its water solubility while maintaining its mechanical integrity [177,197,198]. However, achieving optimal compatibility between starch and hydrophobic additives remains a challenge, requiring further research into interfacial interactions and processing methodologies.

In addition to passive protection, starch-based films are being engineered for active and intelligent packaging functionalities. Active packaging refers to imparting the film with the ability to interact with the food or the environment, e.g., releasing antimicrobial agents [199], scavenging oxygen [200], or absorbing moisture [201]. Intelligent packaging involves sensing and indicating some quality attribute, e.g., freshness [202], pH sensitivity [203], gas levels [204], to the consumer.

Starch films lend themselves to these roles by serving as an edible or at least non-toxic carrier for various natural additives. A prominent example is the incorporation of natural pH indicators into starch films to create color-changing freshness sensors. Anthocyanins, the pigments found in berries [204], red cabbage [205], and açai [206], are a well-studied choice for this purpose. These pigments change color in response to pH shifts—for instance, turning from reddish to purple to green as their conditions go from acidic to alkaline [207]. In a typical intelligent packaging application, a starch film is infused with anthocyanin extracts; as food spoilage occurs (e.g., fish or meat releasing alkaline amines), the local pH increase triggers a visible color change in the film from, say, purple to blue-green, alerting the consumer to degradation. Other natural colorimetric indicators like curcumin (which changes color from yellow to red in base) have also been incorporated into starch-based matrices for smart packaging [208,209].

One of the main challenges in intelligent packaging is ensuring the long-term stability of these natural dyes, as anthocyanins and curcumin are photosensitive and susceptible to hydrolysis. Another significant hurdle is the mismatch in color-change timing, with many intelligent packaging solutions altering their color either prematurely or long after food spoilage has occurred. To address these issues, Silva et al. (2024) successfully enhanced the longevity of intelligent packaging by incorporating salt into polysaccharide films. This approach extended the functional lifespan of the packaging to up to 60 days [210]. Furthermore, the sensitivity of ammonia (NH_3) gas detection was fine-tuned by modulating the ionic strength of the added salts before drying the intelligent film [169,210].

The mechanism behind this extended shelf-life relies on anthocyanin co-pigmentation, which is facilitated by ion-dipole interactions between metal ions and phenolic compounds [210]. Meanwhile, the color modulation effect is attributed to the hygroscopic nature of salts such as CaCl_2 and MgCl_2 . These salts absorb environmental moisture, shifting their Le Chatelier equilibrium toward reaction products where more basic gaseous species are present, and thereby enhancing the conversion of anthocyanin species into hemiacetal and cis-chalcone forms (manifesting as yellow and brown hues) [210].

These discoveries have significantly advanced the commercialization of intelligent packaging, although further research is needed to fully comprehend the interactions between starch components (amylose and amylopectin) and their structural rearrangements. The continued optimization of starch film formulations holds the potential to enhance their efficacy and scalability.

Regarding antimicrobial active packaging, starch films containing essential oils or nanoparticle antimicrobials (e.g., nano-silver or zinc oxide) can actively reduce the microbial

growth on surfaces of food [211,212]. Starch can serve as a carrier for essential oils, e.g., garlic oil, by being formulated to release them slowly over time for direct consumption in meat and bread [213–215]. Furthermore, starch-based materials can be made edible, allowing possibilities like dissolvable sachets or films that consumers can safely ingest along with the product, which is particularly interesting for spice or flavor packets and also ensures that no packaging waste remains [214]. In summary, the most promising method regarding starch-based films is the integration of bioactive compounds and smart indicators, through which future starch-based packaging can go beyond passive containment to actively extending the shelf-life of food and providing real-time information on food quality—aligning with the concept of intelligent packaging systems.

6.3. Commercial Scalability and Industrial Feasibility

Translating starch-based film technology from the lab to the factory floor involves several challenges. One primary hurdle is that native starch is not thermoplastic on its own—it does not melt and flow like polyethylene—so, initially, it could not be processed on standard plastic equipment (extruders, injection molders) without prior modification. This is due to the strong intermolecular hydrogen bonds in starch granules, which cause thermal degradation before flow. The solution that was developed is to produce thermoplastic starch (TPS) by mixing starch with plasticizers (water, glycerol, sorbitol, etc.) under heat and shear, turning TPS processability similar to the synthetic plastics [216,217]. However, the high plasticizer content required for TPS development, averaging ca. 35% and reaching up to 50% [216], poses challenges due to the hygroscopic nature of plasticizers, which leads to increased water absorption and a significant reduction in the mechanical properties of the material. This presents a trade-off between high processability and mechanical performance. Furthermore, ensuring consistent quality in large-scale production requires precise control of the moisture content, temperature, and shear to prevent starch degradation or uneven gelatinization.

On an industrial scale, extrusion has proven to be a viable method to continuously produce starch-based films. In a twin-screw extruder, starch and additives are compounded under high pressure, converting granular starch into a molten TPS melt that can be cast or blown into films [216]. When extrusion is used instead of solvent casting processing, not only is the method scalable, but it can also improve the properties of starch film through in-situ modification (e.g., reactive extrusion that simultaneously acetylates or grafts starch while processing) [218–220]. TPS can also be processed via injection molding and thermoforming, processes that are typically used to produce cutlery and food service implements [221,222]. However, these high-temperature methods have a narrow processing window, as excessive heat or shear can degrade starch. Further, mitigating the degradation of starch requires careful screw design and the addition of heat stabilizers such as antioxidants or polyols.

One of the biggest challenges regarding plastic products based on TPS is reproducibility—a scale-related issue. Starch sourced from different crops or harvests can vary in its amylose content and moisture, which affects its processing behavior and film properties. Industrial producers must either tightly specify the type that they use (e.g., high-amylose corn starch vs. potato starch) or pre-treat it to ensure consistency (e.g., by blending or adding minor synthetic polymers to compensate for variability).

In summary, while the large-scale production of starch films demands careful process optimization, advances in thermoplastic starch technology and equipment modification have largely addressed this fundamental incompatibility, allowing starch packaging to be produced with techniques (extrusion, molding, lamination) familiar to the plastics industry. However, beyond technical feasibility, a key consideration is economic viability, i.e., how

starch-based packaging compares to both conventional plastics and other bio-based materials in terms of its cost and scalability. On the cost side, starch has an advantage: it is an abundant agricultural product (often a side stream of food processing) and is therefore inexpensive compared to biopolymers made via fermentation or chemical synthesis. In fact, raw starch is several times cheaper per kilogram than PLA or PHA. This low cost and wide availability make starch an attractive filler or base material for bioplastics.

Processing starch can require a relatively low amount of energy if done via extrusion (since water/plasticizer can facilitate melting at moderate temperatures). However, to achieve the required performance, starch films often need additives (plasticizers, stabilizers, fillers) or blending with higher-cost polymers, which raises the material cost. There is a careful balance between cost and performance: using more of an expensive polyester like PLA in a blend will improve its strength and water resistance but also drive up its price; using mostly starch keeps costs low but may sacrifice functionality.

Scale economies are another factor—starch-based polymers are not yet produced at polyethylene's scale, so current prices reflect smaller volume operations. As demand grows, economies of scale could lower costs, narrowing the gap with conventional plastics. Starch competes with PLA, cellulose-derived, and protein-based films. PLA offers strength and clarity but is costly and brittle; starch is cheaper and more flexible (when plasticized) but requires water resistance enhancements [223]. Some blends combine starch with PLA for cost-effectiveness and performance. Cellulose films provide excellent oxygen barriers and biodegradability but can be expensive and have limited heat-sealability [223,224]. In contrast, properly formulated starch is thermoplastic and heat-sealable. Regulatory pressures also drive starch packaging adoption: as taxes and bans on single-use plastics increase compliance costs, biodegradable alternatives become more competitive.

Still, a challenge remains in convincing the industry to switch: the new materials must offer not only environmental benefits but also reliable performance and supply. Ongoing improvements in the durability and shelf-life stability of starch film are thus crucial for industry adoption. As these materials approach parity with plastics in function (and if oil prices or environmental penalties increase), starch-based packaging is likely to become economically favorable for many applications.

Finally, any new packaging material intended for food must navigate a complex regulatory landscape to ensure its safety and compliance. Starch itself, being edible, is generally recognized as safe. However, the modifiers and additives used in starch-based films (plasticizers, nanoparticles, cross-linkers, etc.) require scrutiny. Regulations like the European Union's Plastics Food Contact Regulation (EU) No. 10/2011 set strict migration limits on substances that leach from packaging into food. For a starch film to be approved, it must not release chemicals above these overall migration limits (60 mg of total substances per kg of food) and must meet specific migration limits for any given additive. Besides migration, food contact approvals often require the toxicological evaluation of all components. For instance, if a starch film is cross-linked with citric acid, that is fine, as citric acid is food safe; however, if it used with something like epichlorohydrin, the residual must be below limits due to its toxicity.

6.4. Scaling up Starch Films: Practical Barriers and Feasibility for Food Packaging

Starch-based films offer a renewable alternative to conventional plastics in food packaging, but their industrial adoption depends on scalable processing techniques and the ability to incorporate functional additives without compromising the film's safety or performance. This section discusses the feasibility of key manufacturing routes, highlighting the regulatory, economic, and technical challenges of integrating active agents into starch-based food contact materials.

Although extrusion equipment involves higher energy and capital costs, and the intense shear can slightly reduce film homogeneity (e.g., inducing polymer alignment or air entrapment), it has nonetheless been successfully used at scale—for instance, starch-based Mater-Bi® blends are extruded into compostable bags on standard plastic film machines. Emerging techniques like electrospinning offer nanofibrous starch mats with precise morphology control, but they currently suffer from low throughput and require exacting, high-voltage process control, making them less economical for mass production. Compression molding is another viable route; it rapidly presses gelatinized starch into films under heat and pressure, yielding consistent thicknesses and good mechanical strength in short cycle times.

The traditional solvent casting method produces uniform, additive-rich films but is inherently slow and difficult to scale due to its batch nature and reliance on prolonged water evaporation. As a result, it remains primarily a laboratory or pilot-scale technique. To address this limitation, continuous casting systems have emerged as a promising alternative, in which the film-forming solution is deposited onto a moving belt or roller system, followed by controlled drying through heated tunnels or infrared systems. This setup significantly reduces the drying time and allows for uninterrupted film formation, improving the productivity and reproducibility of starch-films manufacturing. While continuous casting maintains the formulation flexibility and structural uniformity of traditional casting, its implementation at the industrial scale requires careful optimization of the drying parameters, e.g., belt speed, and solution viscosity to ensure film homogeneity and prevent defects such as cracking or curling. Nevertheless, it represents a feasible bridge between laboratory casting and full industrial production, particularly for starch-based films that require the incorporation of thermally sensitive additives or bioactives that are not easily processed by extrusion.

Incorporating active additives (essential oils, natural antimicrobials, pigments, or nano-enhancers) into starch-based films can impart valuable functionalities, but several practical factors govern their use in food packaging. Cost is a major concern: many of these additives (e.g., essential oils or nanosilver) are expensive, and embedding them uniformly often requires extra processing (e.g., emulsification or encapsulation), driving up manufacturing costs. Because packaging is typically a low-margin, high-volume business, even modest cost increases can deter industrial adoption. Migration and safety are equally critical—any compound that can leach into food must comply with strict food contact regulations. In the EU, for example, plastics regulation 10/2011 sets specific migration limits to ensure no harmful or organoleptic effects on food. Volatile essential oils can alter a food's aroma or taste if they migrate excessively, and regulators would require evidence that the residual levels stay below toxicity thresholds. Many plant extracts are GRAS (generally recognized as safe) under FDA rules, but they still must be used such that dietary exposure remains safe and within allowed limits. Nanomaterials require additional regulatory scrutiny: while substances like zinc oxide or silver have antimicrobial efficacy, authorities need to be assured that the nanoparticle migration is negligible and that the particles will not accumulate in the food.

Stability is another practical limitation—bioactive additives can degrade or volatilize during processing and storage. Natural dyes like anthocyanins or curcumin which are used as freshness indicators can fade or decompose upon light, pH, or temperature exposure, which shortens the sensor film's useful shelf-life. Essential oils may gradually evaporate or lose their potency over time, meaning that the packaging might have diminished activity by the time it reaches consumers. To mitigate this, techniques such as the nano-encapsulation of oils have been used to enable the slow release of additives and protect their activity, although this can introduce complexity and cost. Lastly, any additive must not compromise

the film's base properties: high loadings of oils or fillers could weaken the film or make it opaque, meaning that formulations must be optimized. These economic and regulatory realities mean that, while many starch-based active packaging concepts show promise in the lab (e.g., antimicrobial starch films for bread, produce, or meat have been demonstrated), scaling them up for commercial food industry use requires careful compliance testing, shelf-life validation, and cost-benefit analysis. Only when an additive delivers clear value (e.g., extending food shelf-life or providing safety indicators) and meets safety standards at an acceptable cost will food manufacturers integrate it into starch packaging on a large scale.

7. Conclusions

The global needs supported by consumer demands have dictated the movement of plastic production towards the usage of biopolymers, although a long journey still needs to be faced between the scientific advancements detailed herein and the upscaling process and industrial application of these materials. Starch-based materials have demonstrated outstanding advantages for employment as a biomaterial for packaging production, such as obtention from renewable and widely available sources, relatively low cost, biodegradability, and non-toxicity. However, despite the recent advances in the development of biodegradable starch-based films, several fundamental issues still need to be addressed before most of them become commercially viable, including the increased hydrophilicity of native starch and the consequent low water barrier properties. In this sense, the latest attempts to improve the applicability of starch-based films include attempts to improve their functionalization in order to improve their mechanical and barrier performance. The optimization of the types of starches, the temperature and time required for film formation, the usage of plasticizers, the employment of co-biopolymers, the usage of and nanocomposite manufacturing strategies can produce starch-based films with good properties, meeting requirements for food packaging features and further smart applications.

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