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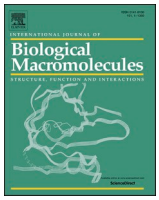

Review

Biopolymer-polyphenol conjugates: Novel multifunctional materials for active packaging

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ABSTRACT

The development of natural active packaging materials and coatings presents a promising alternative to petroleum-based packaging solutions. These materials are engineered by incorporating functional ingredients with preservative capabilities. Concurrently, research has highlighted the diverse physicochemical, functional, and health-promoting properties of protein-polyphenol, polysaccharide-polyphenol, and protein-polysaccharide-polyphenol conjugates within various food formulations. However, a critical gap exists regarding the exploration of these biopolymers as active packaging materials. In contrast to conventional approaches for developing active packaging materials, this review presents a novel perspective by focusing on biopolymer-polyphenol conjugates. In this work, we delve into the realm of active packaging materials and coatings constructed from these conjugates, highlighting their potential as multifunctional active components in food packaging and preservation. This review comprehensively investigates the physicochemical properties, functionalities, and health-promoting activities associated with biopolymer-polyphenol conjugates. Their emulsification, antioxidant, and antimicrobial activities, coupled with enhancements in mechanical strength and permeability properties, contribute to their multifunctional nature. Furthermore, we explore the potential advantages and limitations of utilizing these conjugates in active packaging applications. Finally, the review concludes by proposing crucial research avenues for further exploration of biopolymer-polyphenol conjugates within the domain of active food packaging.

1. Introduction

The wieldy exploitation of non-biodegradable, petroleum-derived materials in food packaging systems has been reported to influence the human health and environment negatively. The migration of plastic compounds into packaged food products, as well as the spread of microplastics in the environment, are the major impacts. These microplastics may be suspended in water, penetrate plant and animal tissues, which are human's food, and ultimately affect human health [1]. While recycling may be a practical solution, its implementation on a global scale is challenging. Design of recyclable and safe materials, development of efficient collection procedures, and economic viability of transporting and processing packaging waste are regarded as major challenges [2]. Therefore, scientists have shifted their focus to biodegradable packaging materials as a solution. Food scientists are conducting studies on the development of hybrid blends that combine plastic and biodegradable polymers, as well as fully biodegradable biopolymers. These biopolymers can be proteins, polysaccharides, or a combination of both. The goal of these explorations is to develop biodegradable materials that can mimic the characteristics of plastic. One of the viable approaches is the modification of biopolymers to enhance their mechanical strength and physicochemical properties. This can be achieved through physical modification processes such as cold plasma treatment [3], radiation [4], enzymatic modification [5], and chemical modifications via cross-linking [6] and grafting [7].

Moreover, the potential health risks linked to certain synthetic preservatives have prompted scientists to investigate alternative methods. One such method involves the creation of active packaging materials. This promising field concentrates on integrating functionalities beyond the conventional barrier properties typically provided by packaging. These functionalities may include antimicrobial and antioxidant properties, which can prolong shelf-life and potentially improve food safety. The integration of natural preservatives such as essential oils [8], polyphenols [9], immobilized enzymes [10], and some organic acids

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[11] in the form of free or encapsulated is also explored as another approach to producing active packaging materials. In addition, the application of inorganic nanoparticles [12], such as silver, could bestow antimicrobial properties and reinforcing effects within the matrix. This is another method that has been extensively researched.

The development and utilization of biopolymer-polyphenol conjugates have been an emerging area of research in food science in the past decade. These structures include protein-polyphenol, polysaccharide-polyphenol, and even protein-polysaccharide-polyphenol conjugates. The term "conjugation" or "grafting" indicates covalent bonds between biopolymers and polyphenols, while complexes refer to the compounds formed through non-covalent bonds between biopolymers [13]. Similarly, the binding of polyphenols to biopolymers can be achieved through enzymatic or chemical techniques. Enzymes such as laccase or tyrosinase, which are types of polyphenol oxidase, are utilized in the enzymatic approach to create biopolymer-polyphenol conjugates. Conversely, chemical techniques are centered around the oxidation-reduction reaction, which serves as a catalyst to form covalent bonds between biopolymers and polyphenols [14]. The concept of these reactions involves the radicalization of either a polyphenol or a biopolymer, making them reactive to the host molecule (Fig. 1). In chemical reactions such as esterification using N,N′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as coupling agents. These coupling agents trigger the carboxyl groups in proteins or polysaccharides and hydroxyl groups of polyphenols, making them a suitable puzzle to react with each other (Fig. 1A) [15]. Other chemical methods include using redox solutions, which could produce free radicals in the reaction environment. Generally, Ascorbic acid and hydroperoxide are regarded as safe redox systems in the conjugation of polyphenols to biopolymers. In this method, the reaction of ascorbic acid and hydrogen peroxide produces hydroxyl and ascorbate radicals, which can attack the biopolymers and product biopolymer radicals. These biopolymer radicals are then a suitable host for the reaction of polyphenols (Fig. 1 B) [16]. In detail, enzymes, including laccase, tyrosinase, peroxidase, and chloroperoxidase, trigger the formation of o-quinones from polyphenols in the presence of molecular oxygen. O-quinones are highly-reactive molecules with an affinity to nucleophilic amine groups in chitosan or proteins, where the reaction might have occurred through Schiff-base or Michael-type reactions (Fig. 1C) [17]. The purpose of using such conjugates may be different. For example, these conjugates may be used as antioxidant [18] or antimicrobial [19] agents, emulsifiers [20], and delivery systems for bioactive compounds for incorporation into food formulations [21]. The process of conjugating polyphenols to biopolymers not only imparts the aforementioned additional functionalities, but may also provide health-enhancing effects associated with polyphenols. These effects can include anti-cancer, anti-diabetic, anti-inflammatory, and antioxidant properties.

Several studies have explored the conjugation of different phenolic compounds with different proteins. For example, in a study by Shang et al. [22], rosmarinic acid was conjugated to ovalbumin to reduce ovalbumin's allergenicity. Both free radical grafting and enzymatic methods were utilized to prepare these conjugates. ELISA analysis revealed a significant reduction in ovalbumin's binding capacity to immunoglobulins G (IgG) following conjugation with rosmarinic acid. Beyond the functionalities of biopolymer-polyphenol conjugates, their inherent physicochemical properties, and bioactivity position them as a promising strategy for the development of multifunctional active packaging materials and coatings. In another study by Wang et al. [18] rosmarinic acid was conjugated to β-Lactoglobulin using free radical grafting and alkaline methods. They reported that the structure of conjugates formed through the alkaline method was more compact, while the free radical grafted conjugates exhibited a more extended structure. The secondary structure analysis indicated an increase in the α-helix and β-sheet content after conjugation, leading to a thermally more stable structure. The conjugation of rosmarinic acid resulted in a significant enhancement in the emulsification capacity and antioxidant activity.

Different polyphenols, including catechin, epigallocatechin gallate, gallic acid, caffeic acid, and ferulic acid, have been conjugated to chitooligosaccharide extracted from shrimp shells, and the antimicrobial activities of the conjugates against *Listeria monocytogenes* were studied [19]. The epigallocatechin gallate conjugate demonstrated superior antibacterial activity against both environmental and clinical strains of *Listeria monocytogenes*. This conjugate could inhibit the production of extracellular polysaccharides, restricting the mobility of the bacteria by 85.7–94.3 %. It was suggested that the primary mechanism of bactericidal activity of these conjugates might be the penetration into the bacterial cells and binding with the DNA backbone.

Chlorogenic acid or tannic acid was conjugated to lesser mealworm (*Alphitobius diaperinus*) by Ballon et al. [20] through an alkaline method. The total polyphenol content analysis showed a higher binding affinity of tannic acid to the protein compared to chlorogenic acid. Chlorogenic acid did not significantly affect the secondary structure of these proteins, while the β-sheet content decreased and random coils increased after the conjugation of tannic acid. Tannic acid could increase the interfacial tension without significantly changing the emulsification capacity of the proteins. The use of the conjugates as emulsifiers in flaxseed oil-in-water emulsions resulted in higher physical stability and a lower oxidation rate compared to the native lesser mealworm proteins.

Emulsion-based delivery systems based on egg white protein-catechin conjugates were developed for β-carotene [23]. The emulsion stabilized by the conjugates or egg white protein alone exhibited the same behavior throughout the simulated gastrointestinal tract model. The results demonstrated that β-carotene was more stable against chemical transformation in the emulsions stabilized by conjugates during the digestion process. The cell-based antioxidant assay showed that the emulsion stabilized by egg white protein-catechin conjugate exhibited a higher cellular antioxidant activity than the emulsions stabilized by native egg proteins. Therefore, the results indicated the potential application of such conjugates as delivery systems in food formulations.

According to the literature, the application of biopolymer-polyphenol conjugates focuses on developing functional ingredients that offer both health benefits and techno-functional properties. The increasing interest in the utilization of such modified biopolymers in food formulations arises from the health-promoting effects of polyphenols, their hydrophobicity in some cases, and the technological properties of biopolymers such as thickening ability, gel-forming ability, and hydrophilicity. However, the application of such biopolymer-polyphenol conjugates in active food packaging systems has yet to be studied comprehensively. The film-forming ability of biopolymers, combined with the antioxidant and antimicrobial activities and, in some cases, the hydrophobicity of polyphenols, could open an opportunity-rich avenue of study on active packaging and coatings for food scientists. As such, the current review focuses on the existing literature revolving around the application of biopolymer-polyphenol conjugates as active packaging materials and coatings, rather than their use as ingredients in food formulations. This study discusses their multifunctionality, which encompasses their potential functionality and possibly improved properties as active packaging materials. In the following sections, recent advancements in the development of active packaging and the evolution of this field of research are first discussed. The discussion is then developed to the functionality and applications of biopolymer-polyphenol conjugates, followed by a comprehensive examination of their use as active packaging materials and coatings. The remaining challenges and proposed future research directions are also addressed in this study.

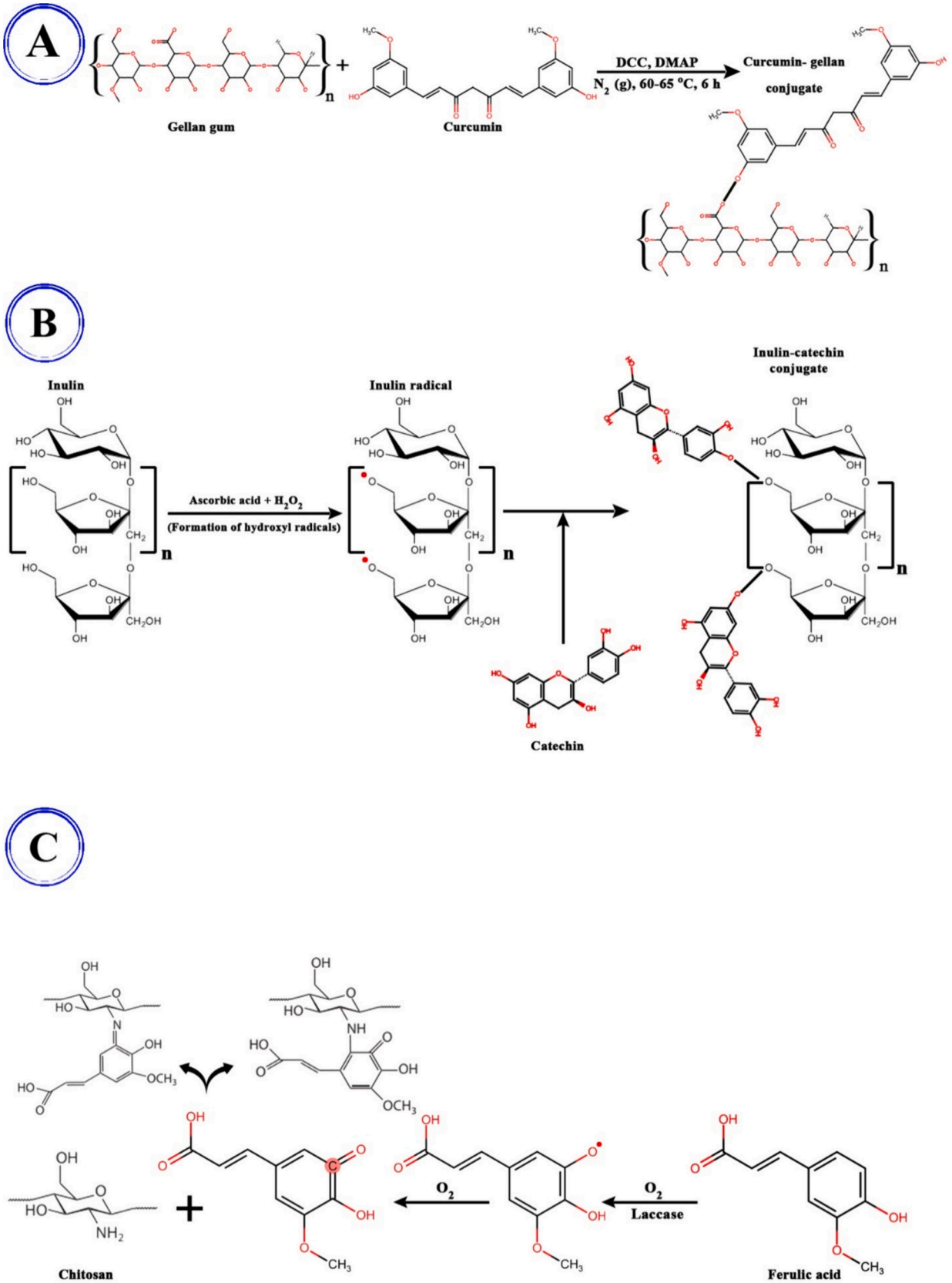

Fig. 1. Development scheme of biopolymer-polyphenol conjugates. Oxidation of gellan gum (biopolymer) using DCC and DMAP (A); conjugation of inulin and catechin via a redox system (B); oxidation of ferulic acid (polyphenol) to produce o-quinone radicals, followed by conjugation with chitosan through a laccase-catalyzed reaction (C).

2. Recent approaches for preparing active packaging materials

2.1. Incorporation of bioactive compounds

Bioactive compounds that occur naturally are substances that not only provide nutritional benefits but also have a proven effect on biological processes within the body, thus enhancing human health. Bioactive peptides, essential oils, polyphenols, carotenoids, sterols, and vitamins are well-documented examples of these bioactive compounds. These are naturally present in a diverse range of food and beverage products [24]. There are numerous techniques for incorporating bioactive compounds into biomaterials to form active packaging systems; e.g., direct addition, encapsulation, and complexation [25,26]. The process of integrating bioactive compounds is often described as the formation of physical bonds with bioactives, rather than establishing a covalent bond with the film matrix (Fig. 2A). For instance, an extract from Pitanga leaves was encapsulated using double emulsions and subsequently blended into a gelatin matrix to create active composite films. These films serve a dual purpose: they act as a packaging material and a delivery system for bioactive substances, thereby enhancing their bioaccessibility [27].

Barış Kavur & Yemenicioğlu [28] utilized the direct addition of eugenol through chickpea protein as an emulsifier in the production of their chitosan film, resulting in active composite films. These composite films demonstrated superior anti-sprouting properties and a more potent antimicrobial nature compared to standard chitosan films. The addition of extra constituents and the application of sonication ensured the mechanical properties were enhanced while simultaneously improving the materials' resistance to moisture. Furthermore, active chitosan coatings were found to be more effective at inhibiting sprouting in onions compared to regular chitosan coatings. The results suggest that the integration of bioactive substances into composite films gives them preservative properties, leading to the development of active packaging materials.

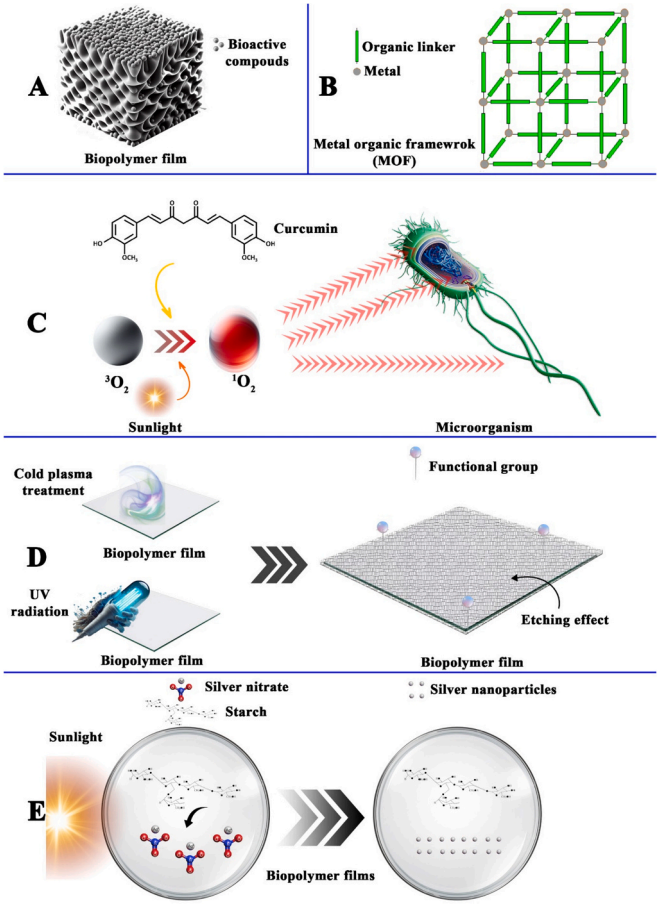

Fig. 2. Recent advances in the preparation of active film materials and coatings.

2.2. Incorporation of inorganic nanoparticles

Most researchers have been investigating a variety of inorganic materials, such as zinc oxide, titanium dioxide, sodium montmorillonite, silica, silver, copper oxide, and clay, primarily in their nanostructured forms [29–32]. The inclusion of these nanostructured particles is expected to significantly enhance the physical properties of biopolymer-based films. This enhancement is observed in both permeability properties, including oxygen and water vapor permeability, and mechanical properties, such as tensile strength and elongation at break. Additionally, these particles can impart functional properties to the films, including antimicrobial and/or antioxidant activities [31]. For instance, composite films of carboxymethyl cellulose-chitosan-oleic acid were developed with various concentrations of zinc oxide nanoparticles. The literature indicates that this incorporation resulted in increased elongation at the break of the films, improved antifungal activity, and enhanced UV radiation protection properties of the films [30].

Metal-organic frameworks (MOFs) represent a versatile class of crystalline, porous materials. The structure of MOFs is the result of self-assembly from metal ions or clusters and inorganic moieties coordinated with organic linker molecules (Fig. 2B) [33]. These linkers essentially act as molecular bridges, defining the pore size, shape, and overall network topology of the MOF. Notably, MOFs possess significantly larger specific surface areas compared to conventional porous materials. The choice of metal centers is crucial for MOF stability; hence, several transition metals, including aluminum, iron, zirconium, titanium, copper, and zinc, have been utilized in the synthesis of robust MOF structures [33]. For example, Khan et al. [32] explored the preparation of active composite films by incorporating a carbon dot-doped titanium-based metal-organic framework into a hybrid matrix of carboxymethyl cellulose/chitosan. The synthesized metal-organic framework exhibited high antioxidant activity and combined well with effective antimicrobial efficacy. The inclusion of the metal-organic framework enhanced the UV barrier properties of the films. These active composite films extended the shelf-life of cherry tomatoes, demonstrating their applicability in food packaging.

2.3. Photoactivation

The underlying principle of photoactivation involves the activation of a photoactive molecule, referred to as a photosensitizer (see Fig. 2C). This process leads to the generation of reactive oxygen species, such as singlet oxygen ($1O_2$), hydroxyl radical (·OH), and hydrogen peroxide (H_2O_2), in the presence of oxygen and light. It is worth noting that most microorganisms are susceptible to these reactive molecules [34]. Curcumin, chlorophyllin, vitamin K_3 (menadione), sunset yellow FCF dye, methylene blue, phthalocyanine, bacteriochlorins, benzoporphyrins, anthraquinone, and benzophenone derivatives are examples of photosensitizers [34–36]. However, there are limitations regarding their use due to their health-related issues in some countries.

In a recent research [34], strawberries were treated with a coating of either alginate or pectin film, which contained curcumin. These strawberries were then stored in darkness or exposed to blue light-emitting diodes (LEDs). The samples exposed to blue light exhibited a significant reduction in fungal contamination, suggesting successful photoactivation of curcumin, leading to antifungal activity. This method resulted in a notable extension of the strawberries' shelf-life. In another study, Islam et al. [37] introduced vitamin K3 into an ethylene-co-vinyl acetate film matrix. The researchers demonstrated that incorporating a certain percentage of vitamin K3 increased the capacity for generating

reactive oxygen species by a factor of a thousand. This innovation led to a new light-activated effect on microbes under daylight conditions. The biocidal properties of this approach showed remarkable, long-lasting activity and could be recharged with repeated light exposure. These findings suggest that films incorporating vitamin K3 present a promising alternative to current packaging materials.

2.4. Surface modification

Surface modification serves as an additional strategy for the development of active packaging materials. This strategy aims to introduce or enhance functionality on the surface of a coating or packaging substrate. This functionality can be achieved through physical modification and grafting or conjugation. Physical modifications involve treating packaging materials with UV radiation, cold plasma processing, or laminating an active film onto an inert substrate such as polyethylene, polyethylene terephthalate (PET), cellulose, or starch. Fig. 2D illustrates surface modification through physical approaches, including cold plasma treatment and UV radiation. These treatments introduce functional groups onto the surface of biopolymers and create an etching effect that increases surface roughness, thereby enhancing printability. For instance, chitosan, which has demonstrated antimicrobial properties, is a suitable candidate for use as a biodegradable active coating. In this method, an inert packaging material, such as PET, is immersed in an active coating solution, such as chitosan (pH = 4), and agitated on a platform shaker to remove excess coating material [38]. A previous study demonstrated that cold plasma treatment of coatings and packaging materials could successfully improve their printability, antimicrobial activities, water vapor permeability, and hydrophobicity [3]. Surface grafting is another technique for modifying the surfaces of packaging materials. In this approach, functional groups or compounds are covalently bonded to the surface of the packaging materials. Examples of this technique include cold plasma treatment and UV polymerization of chitosan and poly(N-isopropylacrylamide) [39].

2.5. In-situ generation of active components

This method involves the generation of active substances directly within the packaging matrix or on the surface of the coating during its formation. The term 'in-situ generation' refers to the creation of active components during the processing or application of the coating or packaging material, as opposed to incorporating pre-synthesized active agents. This can be accomplished through a variety of chemical reactions, such as polymerization, precursor decomposition, and redox reactions. The latter technique has been commonly employed by food scientists [40,41]. For instance, Mathew et al. [41] used boiled rice starch as a reducing agent to synthesize silver nanoparticles from silver nitrate ($AgNO_3$) under sunlight exposure (Fig. 2E). This transformation not only enhanced the hydrophobicity and UV protective properties of the material but also increased its antimicrobial efficacy against *Salmonella typhimurium* and *Staphylococcus aureus*, and decreased its water solubility.

3. Biopolymer-polyphenol conjugates: introduction and applications

To facilitate comprehension, biopolymer-polyphenol conjugates in food science are typically divided into three categories: polysaccharide-polyphenol, protein-polyphenol, and the more intricate protein-polysaccharide–polyphenol, also referred to as a tertiary conjugate. As illustrated in Fig. 3, these conjugates can be produced through a variety of processes, such as the action of polyphenol oxidase enzymes, free radical grafting, esterification with N,N′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as coupling agents, and the application of epichlorohydrin [13].

Various enzymes have been employed by researchers for the synthesis of polyphenol conjugates, including laccase, tyrosinase, horseradish peroxidase, and chloroperoxidase. These enzymes belong to the class of enzymes known as polyphenol oxidases [17]. These enzymes catalyze the oxidation of the hydroxyl groups of the polyphenol to their corresponding o-quinones, which exhibit a strong affinity for nucleophilic amine groups. This reaction, also known as the redox system, is essential for free radical grafting. This approach is cost-effective, non-toxic, and environmentally friendly. During the oxidation of ascorbic acid and hydrogen peroxide, hydroxyl and ascorbate radicals are generated. These radicals extract hydrogen atoms from the biopolymer, resulting in the formation of biopolymer radicals. Ultimately, the polyphenols situated close to the polysaccharide radicals serve as electron acceptors, leading to the creation of the final conjugates [42]. The esterification technique utilizes DCC/DMAP as a coupling agent to activate the carboxyl groups of biopolymers and the hydroxyl groups of polyphenols. This activation enables nucleophilic substitution, culminating in the formation of the desired biopolymer and polyphenol conjugates [43].

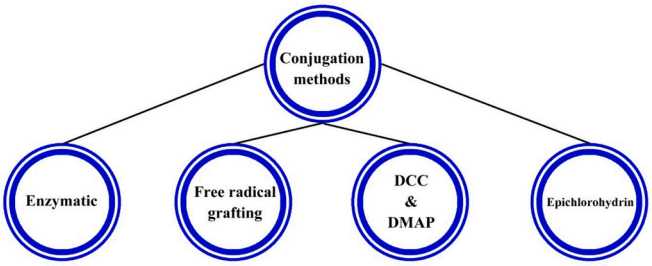

Fig. 3. The conjugation techniques for the development of biopolymer-polyphenol conjugates.

3.1. Protein-polyphenol

Protein-polyphenol conjugates constitute a notable category of biopolymer-polyphenol conjugates that have attracted considerable attention in the realm of food science, owing to their varied functionalities. These conjugates have been tactically utilized to increase the bioavailability of polyphenols, and to enhance their emulsifying, antioxidant, and antimicrobial properties [14]. In the following sections, the applications of protein-polyphenol conjugates are discussed.

3.1.1. Antioxidant properties

Recently, Shi et al. [44] explored the conjugation of ferulic acid, gallic acid, and tannic acid with rice proteins. They compared the properties of protein-polyphenol structures bound both covalently (conjugates) and non-covalently (complexes). The researchers found that the resulting protein-polyphenol conjugates exhibited increased emulsification capacity, water solubility, and antioxidant activity. These results indicate the potential of these conjugates as dual-purpose emulsifiers and antioxidants, with the ability to inhibit oxidation within emulsion systems. Notably, the conjugates with ferulic acid demonstrated the highest solubility. Digestion analysis showed a significant improvement in the stability of the conjugates compared to their corresponding non-covalent complexes under simulated intestinal conditions. In a separate study, Wu et al. [45] investigated the enzymatic conjugation of para-hydroxybenzoic acid, protocatechuic acid, epigallocatechin gallate (EGCG), and gallic acid to Inca peanut albumin. Among these conjugates, the EGCG-protein conjugate showed the highest reaction efficiency. The study found a positive correlation between the number of hydroxyl groups in the polyphenols and both the emulsification capacity and emulsion stability. Additionally, they observed a relationship between higher conjugate reaction efficiency and enhanced antioxidant activity, likely due to the increased polyphenol content in more reactive conjugates. The antimicrobial activities

of protein-polyphenol conjugates have been reported, although more attention has been given to the other functional properties of these conjugates. Li et al. [46] reported that the conjugation of epigallocatechin-3-gallate to pea protein isolate could significantly inhibit the growth of *Escherichia coli* and *Staphylococcus aureus*.

3.1.2. Emulsification activity

Protein-polyphenol conjugates are emerging as potential novel emulsifiers, showing effectiveness in stabilizing emulsions in a variety of food formulations. A recent study by Nimaming et al. [47] examined the use of quercetin-potato protein conjugates as nano-stabilizers for Pickering emulsions. The process of conjugation was observed to increase the particle size of the protein, leading to larger emulsion droplets. Interestingly, this was accompanied by a more negative zeta potential, a factor known to enhance emulsion stability. The study notably demonstrated that these emulsions maintained their stability for an impressive duration of six months.

The incorporation of hydrophobic polyphenols through conjugation can augment the surface hydrophobicity of proteins. This increased hydrophobicity is thought to prevent creaming at the protein's isoelectric point by promoting electrostatic repulsion due to the presence of conjugated polyphenols. As a result, these combined effects contribute to improved emulsification properties [14]. While the conjugation of tannic acid to ovalbumin resulted in a decrease in the protein's surface activity, which could be a negative factor for emulsion stabilization, the presence of tannic acid also led to a reduction in particle size and interfacial tension. This facilitated increased electrostatic repulsions between particles, preventing aggregation and ultimately contributing to enhanced emulsion stability, particularly at the isoelectric point of ovalbumin [48].

3.1.3. Health-beneficial properties

Zhang et al. [49] investigated the potential of conjugates formed from epigallocatechin gallate and β-lactoglobulin for allergy management. The study unveiled a promising mechanism: the conjugate reduced the ability of β-lactoglobulin to bind to antibodies that trigger allergies, suggesting its potential use for desensitization. Another study examined the impact of conjugating epigallocatechin gallate to lactoferrin. The conjugation was achieved through various methods, including enzymatic processes (using laccase and tyrosinase), free radical grafting, and alkali treatment. The findings indicated that the enzymatic method was the most effective for conjugating epigallocatechin gallate to lactoferrin. Furthermore, enzyme-linked immunosorbent assay (ELISA) and western blot analyses revealed a decreased binding capacity of lactoferrin to immunoglobulin E (IgE) and immunoglobulin G (IgG) upon EGCG conjugation. This suggests a potential reduction in allergenicity [50].

3.2. Polysaccharide-polyphenol

In recent years, polysaccharides have gained attention as promising host molecules for polyphenol conjugation. This strategy shows significant potential for the creation of functional polysaccharides that can be applied in a variety of food formulations. Food scientists are actively investigating polysaccharide-polyphenol conjugates to achieve several important goals. These include enhancing the bioavailability of hydrophobic polyphenols, bestowing emulsifying properties upon polysaccharides, improving their foam-forming capabilities, and developing innovative encapsulation and delivery systems [51]. While various natural polysaccharide-polyphenol conjugates exist within plants, as documented by Pawlaczyk-Graja et al. [52], these conjugates can also be synthesized using the methods previously mentioned for protein-polyphenol conjugation. Notably, chitosan, starch, inulin, and pectin have been recognized as the preferred polysaccharides used as hosts for conjugation [53].

3.2.1. Antioxidant properties

In a previous investigation, catechin was successfully conjugated to chitosan through the free radical grafting method [54]. Studies have shown that catechin-grafted chitosan (catechin-g-chitosan) exhibits significantly enhanced antioxidant activity compared to chitosan alone. For instance, at a concentration of 1 mg/ml, catechin-g-chitosan demonstrates a reducing power of 0.51, hydroxyl radical-scavenging activity of 46.81 %, and DPPH radical scavenging activity of 67.08 %. These values were substantially higher than those observed for chitosan. Zeng et al. [55] investigated the conjugation of banana condensed tannins to inulin via free radical grafting to enhance the antioxidant properties of inulin. The antioxidant activities of the conjugates were evaluated using various assays, including ABTS (2,2-azino-bis-3-ethylbenzothiazoline-6-sulphonic acid), 2,2-diphenyl-1-picrylhydrazyl (DPPH), cupric ion reducing antioxidant capacity (CUPRAC), and ferric reducing antioxidant power (FRAP). Their findings demonstrated that conjugation with polyphenols is a promising strategy to improve the antioxidant capacity of inulin. Notably, the study also determined a 1:1 mass ratio of BCT to inulin to be optimal for the preparation of the tannin-inulin conjugates.

3.2.2. Antimicrobial activities

In addition to their antioxidant effects, research suggests these conjugates may exhibit antimicrobial properties. Carboxymethyl chitosan-quercetin conjugates, synthesized through a one-step imine-bond formation via Schiff base chemistry, serve as a prime example [56]. This study demonstrated a fourfold increase in the antioxidant activity of the conjugates compared to unmodified chitosan. Notably, the antifungal activity could also display a twofold enhancement. Several investigations delved into the antimicrobial activities of chitosan-polyphenols conjugates. Chitosan-caffeic acid, chitosan- ferulic and chitosan-sinapic acids exhibited significant antimicrobial activity against 15 clinical strains including *Staphylococcus aureus* strains and food-borne pathogens [51]. The conjugation of polyphenols to the chitosan leads to superior antimicrobial activities of chitosan films [51,57]. In addition to chitosan, the conjugation of polyphenols to other polysaccharides could emerge antimicrobial activities in the conjugates. For example, the conjugation of quercetin to starch aldehyde could significantly inhibit the growth of *Staphylococcus aureus* and *Listeria monocytogenes* as Gram-positive bacteria and *Escherichia coli* and *Salmonella* as Gram-negative bacteria [58].

3.2.3. Emulsification properties

The inherent hydrophilicity of polysaccharides and the contrasting hydrophobicity of various polyphenols offer a strategic approach to endow polysaccharides with emulsification properties. Building upon the aforementioned presence of polysaccharide-polyphenol conjugates in plants, recent research by Li et al. [59] exemplifies this concept. Their investigation successfully isolated three distinct conjugates from *Camellia sinensis* (Chin brick tea) exhibiting varying molecular weights (204, 955, and 1355 kDa). Notably, all three conjugates displayed antioxidant and emulsification properties. However, the authors observed a potency gradient within these functionalities. Specifically, the conjugate possessing the lowest molecular weight (204 kDa) demonstrated the most robust emulsification activity. Vuillemin et al. [60] investigated the conjugation of ferulic acid to gum Arabic via an oxidation process applied to the gum. This modification resulted in conjugates exhibiting enhanced amphiphilicity, a property characterized by the presence of both hydrophilic and hydrophobic regions within the molecule. Consequently, the surface and interfacial tensions decreased, facilitating a more efficient emulsification process compared to native gum Arabic.

3.2.4. Health-beneficial properties

The exploration of health-promoting functionalities is another key area of research surrounding polysaccharide-polyphenol conjugates. Studies suggest these conjugates may offer a diverse range of health

benefits, including anticancer properties, cellular-level antioxidant activity, anti-tumor activity, and potential for Alzheimer's disease prevention [13]. It is noteworthy that hydrophobic polyphenols exhibit limited bioavailability, consequently hindering their biological activity due to poor solubility and absorption rates. Conjugation with hydrophilic biopolymers, such as polysaccharides, has emerged as a successful strategy to address this challenge [13]. To improve the biological activity of hydrophobic polyphenols, Mundlia et al. [15] employed gellan gum as a host for curcumin and naringenin conjugation. The researchers employed the MTT assay, a colorimetric method for evaluating cellular metabolic activity, to assess the anticancer potential of the conjugates against NIH: OVCAR-5 cancer cells. Notably, an increase in the polyphenol content of the conjugates corresponded with enhanced cytotoxicity towards the cancer cell line. Interestingly, curcumin conjugates exhibited a more pronounced anticancer effect compared to their naringenin counterparts. Similarly, Sarika et al. [61] investigated curcumin conjugated with gum Arabic. This approach yielded a remarkable 900-fold increase in curcumin's solubility. Furthermore, the conjugates displayed enhanced cytotoxicity specifically towards HepG2 cells compared to MCF-7 cells.

3.3. Protein-polysaccharide- polyphenol

The development of protein-polysaccharide-polyphenol conjugates has gained significant traction among scientists. Researchers are actively exploring the potential of these ternary conjugates for diverse applications across various fields, including cosmetics, pharmaceuticals, and food formulations [62]. The production methods for protein-polysaccharide-polyphenol conjugates share similarities with those employed for binary protein-polyphenol and polysaccharide-polyphenol conjugates. However, the order of conjugation can be strategically manipulated. One approach involves the initial conjugation of protein and polysaccharide via the Maillard reaction, followed by the attachment of the polyphenol to the resulting protein-polysaccharide conjugate. Alternatively, the polyphenol can be first conjugated with either the protein or polysaccharide, subsequently linked to the remaining biopolymer [62,63]. It is not unexpected that the intrinsic properties such as the nature of proteins, polysaccharide, and polyphenols could result in different ternary conjugates. Notably, the production approach and the sequence of these reactions can influence the final physicochemical properties of the conjugates [13].

3.3.1. Antioxidant properties

Geng et al. [64] highlighted the potential of these conjugates by investigating the antioxidant properties of soy protein isolate conjugated with maltose via the Maillard reaction. This was followed by the attachment of epigallocatechin gallate to the resulting biopolymer. Interestingly, the ternary conjugate exhibited superior antioxidant activity compared to both unconjugated soy protein isolates and binary protein-polysaccharide conjugates. This enhanced functionality can be attributed to the introduction of maltose units and the increased degree of glycation during the Maillard reaction. This process facilitates the formation of a greater abundance of atom donors, including pyrazine, melanoidin, and reductones, all recognized for their potent free radical scavenging abilities through hydrogen atom donation. In another study, Gu et al. [65] prepared catechin-dextran-egg white protein conjugates. The researchers adopted a two-step approach for conjugate formation. Initially, catechin was grafted onto dextran via a free radical mechanism. Subsequently, the dextran-catechin conjugate was attached to egg white proteins through the Maillard reaction. This strategy successfully imparted robust antioxidant activity to the resulting ternary conjugate due to the presence of the polyphenol component. Notably, the reducing power and free radical scavenging capacity against DPPH and ABTS radicals of the ternary conjugates surpassed those of the protein and protein-polysaccharide conjugates by more than two-fold. Additional investigations have demonstrated a consistent trend of enhanced antioxidant activity in ternary conjugates compared to their binary counterparts or individual biopolymers alone [66–68].

3.3.2. Antimicrobial activities

The presence of protein, polysaccharide, and polyphenol constituents in the ternary conjugates is beneficial, as each component can contribute its unique functional properties, enhancing both the technological and health aspects of food formulations. Additionally, certain proteins, such as lysozyme [69] or lactoferrin [70], and polysaccharides like chitosan [71] and fucoidan [72], possess antimicrobial activities that can further boost the antimicrobial properties of the polyphenols within the conjugates. For example, tea polyphenols, *Bletilla striata* polysaccharides, and modified gelatin were conjugated and used to prepare hydrogels. The hydrogels could successfully inhibit the growth of *Escherichia coli* and *Staphylococcus aureus* as Gram-negative and Gram-positive bacteria, respectively [73]. In another study, Zhang et al. [68] reported that common foodborne pathogens, including *Staphylococcus aureus* and *Escherichia coli*, were significantly susceptible to ternary complexes composed of whey protein concentrate and high-methoxyl pectin as biopolymers, along with phenolic acids such as chlorogenic acid and rosmarinic acid as polyphenol constituents.

3.3.3. Emulsification properties

To explore the impact of polysaccharide selection on functionality, Huang et al. (2022) grafted ovalbumin-ferulic acid conjugates to various polysaccharides, including sodium alginate, kappa-carrageenan, hyaluronic acid, and agar. This investigation revealed that polysaccharide conjugation significantly enhanced the emulsification capacity and stability of emulsions formulated using the ternary conjugates compared to the binary protein-polyphenol conjugate alone. Interestingly, some variations were observed among the conjugates. Notably, agar-containing conjugates displayed a lower degree of emulsion stability compared to their counterparts.

Tao et al. [74] investigated the potential of whey protein isolate (WPI)/short-chain inulin (SCI)/cyanidin-3-glucoside (C3G) conjugates as Pickering emulsion stabilizers. Their findings indicated that the presence of polysaccharide moieties within the conjugate structure hindered emulsion creaming by inhibiting droplet aggregation. The study also revealed a trend in particle size and size distribution for emulsions stabilized by the various conjugates, with the order being: WPI > WPI/C3G > WPI/SCI > WPI/SCI/C3G. Corroborating these findings, other studies have documented the successful enhancement of emulsification properties achieved through the use of ternary conjugates compared to their corresponding binary counterparts or individual biopolymers [64,65]. A critical review of the literature revealed no prior investigations into the health benefits associated with ternary conjugates. This observation underscores the intriguing potential of protein-polysaccharide-polyphenol conjugates as a subject for further research, particularly regarding their health-promoting properties. Table 1 summarizes recent studies on biopolymer-polyphenol conjugates and their aims to enhance functionality or bioactivity.

4. Multifunctional packaging materials

4.1. Polysaccharide- polyphenol

Research has shown that several polysaccharides possess functional properties such as antimicrobial and antioxidant activities, and immune-protective properties [75,76]. Additionally, due to their unique physicochemical properties, especially their ability to increase viscosity and form gels, polysaccharides are extensively used in the food industry as thickening agents, gelling agents, and film formers [75]. Given these synergistic properties, food scientists are actively investigating the combined application of polysaccharides and polyphenols for various food product functionalities, including as emulsifiers, preservatives, and active packaging materials [76]. This section discusses the application of

Table 1
Recent studies on the development of biopolymer-polyphenol conjugates to enhance the functionality and bioactivity of biopolymers and polyphenols.

Biopolymer-polyphenol conjugate	Aim of study	Enhanced properties	Reference
β-Lactoglobulin-rosmarinic acid	Improvement of Structure and functionality	• Thermal stability • Interfacial wettability • Emulsification capacity • Antioxidant activity	[18]
β-Lactoglobulin-rosmarinic acid-pectin	Stabilization of Pickering oil-in-water emulsions	• Wettability • Molecular flexibility • Emulsifying properties • Viscoelasticity of interface layer • Electrostatic repulsion	[104]
Potato protein- quercetin	Stabilization of Pickering oil-in-water emulsions	• Stability of Pickering emulsion	[47]
Ovalbumin-gallic acid	Using cold plasma as conjugator	• Antioxidant activity • Emulsifying properties	[105]
• Rice protein-ferulic acid • Rice protein-gallic acid • Rice protein-tannin acid	Comparison between covalent binding and non-covalent binding	• Emulsifying properties • Solubility • Antioxidant activity • Intestinal digestion	[44]
Egg lysozyme-theaflavins	Investigation on the structure and related functions of lysozyme	• Surface hydrophobicity • Thermal stability • Antioxidant properties	[106]
Rice bran globulin-chitooligosaccharide-quercetin-resveratrol	Investigation on the functionality of rice bran globulin	• Solubility • Emulsifying properties • Foaming properties	[107]
• Pea albumin- cyanidin-3-O-glucoside quinone • Pea vicilin-cyanidin-3-O-glucoside quinone • Pea legumin-cyanidin-3-O-glucoside quinone	Characterization the structure and functionality	• Antioxidant activity • Orderliness • Molecular flexibility • Thermal stability	[108]
Soybean protein isolate-curcumin	Functionalization of protein	• Antioxidant properties • Inhibition of digestive enzymes	[109]
Soy protein isolate-rutin	• Stabilization of emulsion gel • Comparison between covalent binding and non-covalent binding	• Interfacial properties • Environmental stability • Digestibility • Thermodynamical stability	[110]
• Myofibrillar protein-dextran-epigallocatechin-3-gallate • Myofibrillar protein-dextran-catechin • Myofibrillar protein- dextran-gallic acid	Stabilization of flaxseed oil emulsion	• Creaming index • Apparent viscosity • Oxidation stability • Emulsion uniformity • Emulsion stability	[111]
• Walnut protein-epigallocatechin gallate • Walnut protein-quercetin • Walnut protein-trans-ferulic acid • Walnut protein-resveratrol	• Reducing the sensitization of walnut protein • Comparison between covalent binding and non-covalent binding	• IgE binding capacity • Allergenicity • Intestinal barrier damage	[112]
Bovine lactoferrin-chlorogenic acid	• Functionalization of proteins • Comparison between covalent binding and non-covalent binding	• Protein active sites • Antioxidant activity • Solubility • Thermal stability • Foaming properties • Emulsifying properties	[113]
Peptide-gallic acid Peptide-sinapinic acid Peptide-coumaric acid	Examination of kinase-binding domain of EphB4 and EphB2 receptors	• Lipophilicity • MDCK[a] permeability • Binding with the EphB4[b] receptor • Minimal binding to EphB2[c] receptor • Inhibitory activity against EphB4	[114]

[a] MDCK: A transfected cell line overexpressing human P-glycoprotein (Multidrug resistance).
[b] EphB4 receptor: A protein that in humans is encoded by the EPHB4 gene.
[c] EphB2 receptor: A protein that in humans is encoded by the EPHB2 gene.

polysaccharide-polyphenol conjugates as active and intelligent packaging materials. A diverse range of polysaccharides are viable candidates for the development of edible packaging materials, including cellulose, chitosan, starch, and alginates. Table 2 summarizes all existing studies focused on biopolymer-polyphenol conjugates as active packaging materials and coatings.

Within the polysaccharide domain, chitosan has attracted significant interest from food scientists for the development of polysaccharide-polyphenol conjugates as active film and coating materials. This preference is likely due to chitosan's inherent low water solubility and superior antioxidant and antimicrobial activities compared to many other polysaccharides. For instance, the literature suggests the possibility of synthesizing carboxymethyl chitosan-quercetin conjugates via heterogeneous carboxylation, providing an alternative to radical grafting and coupling agent methods (Fig. 4) [56]. In the method proposed by Sela et al. [56], an aqueous solution of carboxymethyl chitosan was heated at 80 °C quercetin dihydrate is added to the solution gradually. The mixture was mixed under acidic conditions for a predetermined time followed by the separation of conjugates using ethanol. They reported that the conjugate exhibits antioxidant properties and antifungal activities against *Botrytis cynerea*, a plant pathogen. The use of carboxymethyl chitosan-quercetin conjugate as a coating material for fresh-cut apples proved to be a promising strategy, resulting in extended shelf-life with enhanced firmness and reduced microbial load after five days of storage at 20 °C. Another study explored the conjugation of various flavonols, including myricetin, quercetin, and kaempferol, to chitosan oligosaccharides, through an enzymatic reaction using horseradish peroxidase [77]. The conjugates were then incorporated with gelatin to form active

Table 2
Existing documents on the application of biopolymer-polyphenol conjugates as active packaging materials and coatings.

Biopolymer-polyphenol conjugate (film or coating)	Functionality of active material	Physical properties of active material	Reference
Carboxymethyl chitosan-quercetin (Coating)	↑ Antioxidant activity ↑ Antifungal activity ↓ Browning of fresh-cut apple	↓ *Molecular weight ↓ Particle size ↑ Amphiphilic properties ↑ Hydrophobicity ↑ Young's modulus ↓ Elongation at break ↓ Tensile stress ↓ Water vapor permeability	[56]
• Chitosan oligosaccharide-myricetin • Chitosan oligosaccharide-quercetin • Chitosan oligosaccharide-kaempferol (Coating)	↑ Antioxidant activity ↓ Fish fillet spoilage and oxidation	↑ Water solubility ↑ Surface roughness ↓ Crystallinity	[94]
Chitosan-epigallocatechin gallate (Film)	↑ Antioxidant activity ↑ Antimicrobial activity	↑ Thickness ↑ Color difference (ΔE) ↑ UV barrier properties ↑ Thermal stability ↓ Elongation at break ↓ Tensile strength	[78]
Chitosan-gallic acid (Film)	↑ Antioxidant activity ↓ Peroxide value	↑ Yellowness — Water vapor permeability	[79]
Chitosan-gallic acid (Film)	↓ Weight loss of mushrooms ↓ Firmness loss in mushrooms ↓ Respiration rate ↓ Browning of mushrooms ↓ Oxidation in mushrooms ↓ Reactive oxygen species production ↓ Activity of polyphenol oxidases in mushrooms ↑ Activity of superoxide dismutase and catalase	↓ Water vapor permeability	[80]
Chitosan-protocatechuic acid	↑ Antioxidant activity	↑ Yellowness — Thickness ↓ Moisture content ↑ Water solubility ↓ Water vapor permeability ↓ Lightness ↑ Color difference ↑ Surface roughness	[81]
Aminated starch-gallic acid • Aminated starch-syringic acid • Aminated starch-vanillic acid (Film)	↑ Antioxidant activity ↑ Antibacterial activity	↑ Surface roughness ↑ Thermal stability ↑ Hydrophobicity ↓ Water vapor permeability	[82]
Cationic oxidized starch-tea polyphenols (Film)	↑ Antibacterial activity	↓ Swelling capacity — Moisture content ↑ Thickness ↑ Tensile strength ↓ Elongation at break ↑ Young's modulus ↑ Thermal stability ↑ Hydrophobicity ↑ Tensile strength ↑ Elongation at break ↓ Brittleness	[83]
Starch aldehyde-catechin (Film)	↑ Antibacterial activity ↑ Oxidation of peanut oil	↓ Uniformity — Crystallinity ↑ Thickness ↓ Lightness and whiteness index ↑ Water vapor permeability ↓ Oxygen permeability — Mechanical properties ↑ Thermal stability	[85]
Starch aldehyde-quercetin (Film)	↑ Stability of quercetin ↓ Cytotoxicity ↑ Antioxidant activity ↑ Antibacterial activity ↑ Shelf-life of citrus ↓ Wrinkling of citrus ↓ Flesh dehydration of citrus — Internal color — Rough texture — Aroma	— Surface roughness ↑ Hydrophobicity ↑ Crystallinity ↑ Thermal stability ↑ Thickness ↑ Tensile strength ↓ Elongation at break ↑ Color difference, a*, b* ↑ Light barrier properties ↓ Lightness ↓ Swelling power ↓ Water vapor permeability	[86]
• Soy protein isolate-curcumin • Soy protein isolate-naringenin • Soy protein isolate-catechin (Film)	↑ Antioxidant activity ↑ Antibacterial activity ↑ Emulsifying properties ↓ Peroxide values of emulsions ↑ Shelf-life of cherry tomatoes	↑ Surface hydrophobicity ↓ Particle size ↓ Lightness ↓ Thickness ↓ Transparency ↓ Water vapor permeability ↑ Tensile strength ↑ Elongation at break ↑ Uniformity and compactness	[87]
Gelatin-chlorogenic acid (Film)	↑ Antioxidant activity ↑ Antibacterial activity ↓ Lipid oxidation	ND**	[90]
• Gelatin-apple polyphenol • Gelatin-pectin-apple polyphenol	↑ Antioxidant activity	↓ Uniformity (for gelatin-apple polyphenol) ↑ Uniformity (for gelatin-pectin-apple polyphenol)	[92]
Chitosan-epicatechin gallate (Film)	↑ Antioxidant activity	↓ Crystallinity ↓ Compactness ↓ Water vapor permeability ↓ Oxygen permeability	[112]

(continued on next page)

Table 2 (*continued*)

Biopolymer-polyphenol conjugate (film or coating)	Functionality of active material	Physical properties of active material	Reference
		↓ Lightness ↓ UV–vis light transmittance ↑ Redness and yellowness ↑ Color difference ↑ Tensile strength ↑ Elongation at break ↑ Water solubility ↑ Surface hydrophobicity	
Soy protein isolate-dialdehyde starch-tannic acid (Film)	↑ Antioxidant activity ↑ Antibacterial activity	↑ Particle size ↑ Transparency ↑ Tensile strength ↓ Elongation at break	[115]

* The symbols ↑, ↓, and — indicate an increase, decrease, and no change in the aforementioned factors, respectively.

** ND indicates the functionality or physical properties of the prepared active materials were not determined in the study.

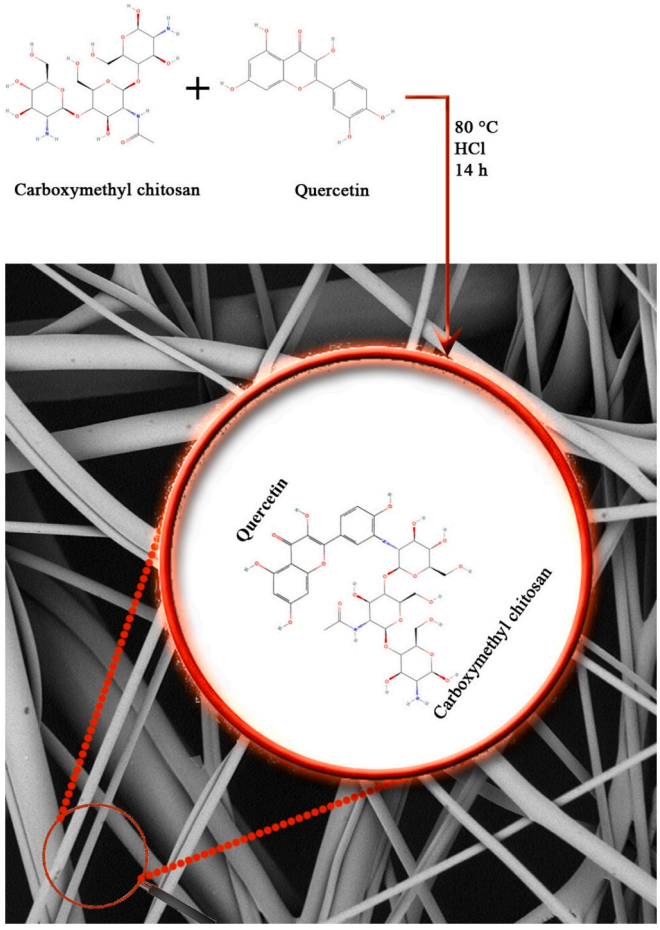

Fig. 4. A schematic of the chitosan-ferulic acid as polysaccharide-polyphenol conjugate fibers at molecular level.

coatings for fish fillets. Beyond demonstrating superior antioxidant activity compared to their individual polyphenol counterparts, the fabricated composite films notably extended the refrigerated shelf-life of largemouth bass (*Micropterus salmoides*) fillets. Compared to the uncoated and gelatin-coated controls, these films achieved a shelf-life extension of 2–3 days, with fillets remaining viable for 7–8 days [77]. Mittal et al. [78] conjugated EGCG onto chitosan through a free radical grafting method. Chitosan-epigallocatechin gallate films exhibited superior light barrier properties compared to pure chitosan films, as evidenced by their lower lightness values. This effect can be attributed to the presence of epigallocatechin gallate. Moreover, the enhanced antioxidant and antimicrobial activities observed in the conjugate coatings suggest their promising potential for extending the shelf-life of food products. Schreiber et al. [79] prepared chitosan-gallic acid through coupling agents. They found that under simulated stress conditions (50 °C, 20–30 % RH) during storage, both chitosan and conjugates films significantly reduced the extent of oxidation reactions in ground peanuts. Notably, the conjugates exhibited superior performance compared to polyethylene and chitosan bags, as evidenced by a significant decrease in the formation of thiobarbituric acid reactive substances, peroxides, and conjugated trienes. In a similar study, active films formulated with chitosan-gallic acid conjugates significantly suppressed respiration rate, browning degree, malondialdehyde content, electrolyte leakage rate, superoxide anion production rate, and hydrogen peroxide content in button mushrooms (Agaricus bisporus) compared to control films of chitosan alone and commercially available polyethylene [80]. Liu et al. [81] conjugated protocatechuic acid onto chitosan to prepare a novel active packaging film. Chitosan-protocatechuic acid conjugate films exhibited a reduction in moisture content, water vapor permeability, and UV protectivity, while simultaneously demonstrating enhanced tensile strength compared to pristine chitosan films. Furthermore, the conjugate films displayed dose-dependent and time-dependent antioxidant activity.

Starch has also emerged as a promising biopolymer for developing edible films and coatings in the food industry. These starch-based materials offer a sustainable alternative to traditional petroleum-derived plastic packaging, addressing growing concerns about environmental pollution and waste management. Starch-based films and coatings offer a compelling combination of environmental and functional benefits for food packaging. Unlike traditional plastics, they are biodegradable, minimizing their environmental footprint. Furthermore, their edible nature eliminates the need for separate packaging, reducing waste. Starch films can be tailored to specific food needs. By adjusting processing methods and incorporating additives, scientists can control the film's strength, flexibility, and gas and moisture permeability. Recently, researchers found that conjugating polyphenols to the structure of starch may offer a novel approach to manipulating its physicochemical properties. For instance, various phenolic acids, such as gallic acid, syringic acid, and vanillic acid, were enzymatically conjugated to aminated starch. These conjugates were subsequently incorporated into the starch film matrix. This integration resulted in enhanced thermal stability, hydrophobicity, antioxidant activity, antimicrobial properties, and increased film thickness. Notably, the mechanical properties exhibited variation dependent on the specific conjugate. For instance, vanillic acid conjugates demonstrated an increase in tensile strength, whereas syringic acid conjugates displayed a decrease in tensile strength [82]. Another study by Li et al. [83] investigated the fabrication of active films through the conjugation of tea polyphenols with oxidized starch and AEM5700, a trifunctional monomer polymerizable under acidic conditions exceeding 100 °C. Chemically represented as 3-(Trimethoxy silyl)-propyldimethyloctadecyl ammonium chloride, AEM5700 facilitates crosslinking within the film matrix. This conjugation process demonstrably enhanced the thermodynamic stability and hydrophobicity of the starch-based films. Furthermore, mechanical properties were positively affected, with increased tensile strength and elongation at break, alongside a reduction in brittleness. The incorporation of tea polyphenols also yielded improved antimicrobial activity. It has been reported that the stability of catechin could improve after conjugation to starch aldehyde [84].

Expanding on their previous research, Hu et al. [85] conducted

further studies on the effects of integrating aldehyde starch-catechin conjugates into quaternary ammonium chitosan/polyvinyl alcohol films. Their analysis indicated a reduction in oxygen permeability, while both tensile strength and elongation at break increased. Notably, the films containing starch aldehyde-catechin conjugates exhibited significantly lower peroxide value and thiobarbituric acid reactive substance levels in peanut oil samples packaged within glass tubes capped with these films, compared to films without the conjugates. These findings suggest that the inclusion of aldehyde starch-catechin conjugates presents a promising strategy for enhancing the barrier and preservation properties of packaging films. Recently, Sun et al. [86] explored the application of starch aldehyde-quercetin conjugate film for fruit packaging. The edible film demonstrated non-toxicity, along with strong antioxidant and antibacterial activities against *Staphylococcus aureus*. It also displayed improved functional properties, including reduced water vapor permeability, decreased light transmittance, and enhanced thermal stability. Sweet oranges packaged using these conjugates and stored at 20 °C and 70 % RH, showed a lower respiratory rate, delayed weight loss, and maintained firmness for a longer duration. Additionally, the conjugates helped to preserve the overall appearance of the oranges.

The current body of research underscores the significant potential of polysaccharide-polyphenol conjugates within the field of packaging materials. However, a critical knowledge gap remains regarding their application as active packaging, warranting further investigation. Notably, existing studies highlight the substantial influence of polysaccharide sources on film-forming ability and final film characteristics in starch-based materials. This knowledge can be leveraged to strategically design and modify starches with tailored physicochemical properties. Such tailored modifications hold promise for enhancing their functional and biological activities, ultimately paving the way for their use as bioactive edible packaging and coating materials. Pectin, for instance, emerges as a compelling candidate for bio-based polymer packaging materials due to its unique film-forming ability and high degree of flexibility. The strategic conjugation of polyphenols with pectin presents a novel avenue for exploring a diverse array of bioactive and preservative functionalities within pectin-based packaging materials. Conjugating polyphenols with polysaccharides presents a potentially more environmentally friendly approach compared to traditional chemical modification methods for imparting physicochemical properties to these biopolymers. This strategy, particularly applicable to edible coatings, holds promise for the development of multifunctional coating formulations. These biopolymers could offer not only preservative characteristics but also health-promoting properties, thereby contributing to a more holistic approach to food preservation and potentially enhancing consumer well-being.

4.2. Protein-polyphenol

Protein-based films have garnered significant interest as a viable alternative to conventional packaging materials, owing to their biodegradability, renewability, and eco-friendly attributes. However, their inherently poor water vapor barrier properties, due to the hydrophilic nature of proteins and the commonly used hydrophilic plasticizers in film formation, present a significant challenge to their widespread adoption [14]. Various strategies have been proposed to overcome this hurdle. One such approach involves the integration of hydrophobic substances like fats and oils into the film-forming solution. While this method can enhance water vapor barrier properties, it carries the risk of lipid oxidation, which could potentially lead to off-odors and discoloration in the final product. Recent research suggests a promising alternative: the development of active composite films based on protein-polyphenol conjugates. Polyphenols offer a unique advantage. They can not only modify the film-forming characteristics of proteins, potentially improving water vapor barrier properties, but also endow the films with additional functionalities and potential health benefits [87]. While the current focus is on protein-polyphenol conjugates as packaging materials themselves, the incorporation of these conjugates into other packaging materials presents a promising avenue for future exploration. For instance, whey protein was conjugated with either proanthocyanidins or curcumin and subsequently incorporated into carboxymethyl cellulose films. This approach demonstrably enhanced the vapor barrier property, tensile strength, and hydrophobicity of the resulting films. Moreover, the incorporation of these conjugates yielded additional functionalities: improved pH sensitivity, enhanced antimicrobial activity, and the ability to impede fat oxidation when the films were employed for beef preservation [88].

Xue et al. [87] explored the use of protein-polyphenol conjugates as a platform for the incorporation of rose essential oil. Their study involved the separate conjugation of various polyphenols, including curcumin, naringenin, and catechin, with soy protein isolate to generate a range of protein-polyphenol conjugates. The compact matrix structure of the conjugate film yielded enhanced oxygen barrier properties and improved water vapor permeability, particularly for films containing curcumin conjugates. In vitro studies confirmed the antioxidant and antimicrobial activities of the active film. Furthermore, its practical application as a coating for cherry tomatoes stored at 25 °C for 15 days proved successful. Beyond plant-based proteins, animal proteins have also emerged as promising candidates for bio-based packaging materials. The study conducted by Chen et al. [89] explored the enzymatic conjugation of various polyphenols, including epigallocatechin-3-gallate, gallic acid, and tannic acid, with casein. In this method, polyphenols were mixed with sodium caseinate in aqueous solution at pH 6.5. The tyrosinase was added to the mixture in the absence of light while the oxygen penetration was not inhibited in order to be involved in the reaction. The reaction was carried out overnight, followed by the thermal deactivation of the enzyme and separation of conjugates using a dialysis bag (Fig. 5). Notably, epigallocatechin-3-gallate exhibited a higher conjugation efficiency compared to the other polyphenols. This enhanced conjugation translated to superior mechanical strength and barrier properties within the films. Furthermore, compared to the non-covalent incorporation of these polyphenols into the film formulation, protein-polyphenol conjugate films displayed demonstrably lower porosity and increased mechanical strength.

Fu et al. [90] further investigated the properties of chlorogenic acid-gelatin conjugate films. Employing various antioxidant and antimicrobial assays, they demonstrated that the conjugates exhibited significantly enhanced antioxidant activity and antimicrobial efficacy against *Escherichia coli*, *Pseudomonas aeruginosa*, *Listeria monocytogenes*, and *Staphylococcus aureus*, compared to native gelatin films. In a previous study, fish gelatin and phenolic acids, including caffeic acid and ferulic acid were conjugated through an alkaline reaction [91]. Gelatin-caffeic acid conjugate films exhibited the lowest levels of solubility, oxygen permeability, and water vapor permeability among the samples analyzed. This finding suggests that caffeic acid may be a more effective phenolic compound compared to ferulic acid for enhancing the safety and functionality of biodegradable packaging materials. Its incorporation demonstrably improves the barrier and physicochemical properties of the films.

Protein-polysaccharide biocomposites represent a novel class of materials for active packaging applications. By strategically combining the functional properties of proteins and polysaccharides, these biocomposites offer enhanced characteristics compared to traditional packaging materials. They are designed to actively interact with the packaged food or other substances, extending functionalities beyond those of passive packaging. Protein-polysaccharide biocomposites for active packaging frequently incorporate additional active components, such as polyphenols, antimicrobial agents, or natural extracts. These components endow the biocomposites with functionalities like antimicrobial activity, antioxidant properties, and the ability to extend shelf life. Consequently, protein-polysaccharide biocomposites hold promise for a wide range of active packaging applications in the food and pharmaceutical industries. However, a critical knowledge gap remains

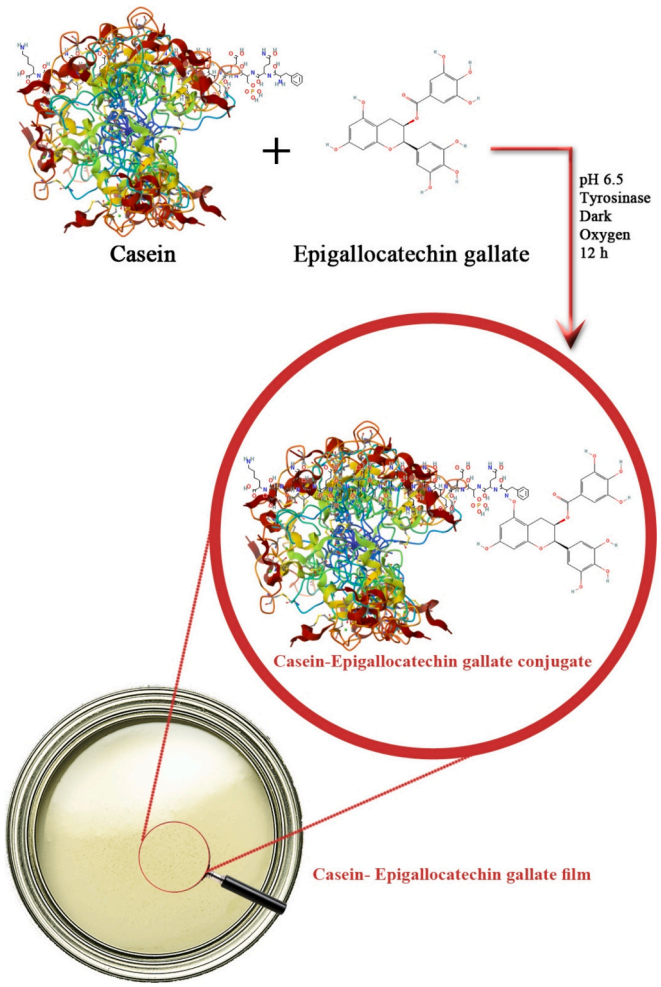

Fig. 5. A schematic of the casein-epigallocatechin gallate as protein-polyphenol conjugate film at molecular level.

regarding the application of protein-polysaccharide-polyphenol conjugates as active packaging materials and their associated bioactivity, which warrants further investigation.

A critical review of the existing literature reveals a scarcity of research exploring the application of protein-polysaccharide-polyphenol conjugates as packaging materials. While some studies have investigated the non-covalent complex forms of these compounds, a comprehensive understanding of ternary conjugates remains elusive. For example, Lin et al. [92] compared apple polyphenol-gelatin conjugate films with polyphenol-gelatin-pectin conjugate films. The study revealed that both binary and ternary complexes exhibited excellent antioxidant properties. Notably, the incorporation of pectin resulted in an increase in the quantity of hydroxyl groups within the complexes, which demonstrably enhanced their overall antioxidant capacity. Furthermore, the inherent polyhydroxy structure of apple polyphenols facilitates their strong binding affinity with macromolecules like gelatin and pectin. These characteristics pave the way for the utilization of polyphenols as natural and innocuous cross-linking agents for macromolecules.

5. Environmental aspects: biodegradability

Biodegradability is a major property of fabricated active packaging materials, making them viable alternatives to petroleum-based packaging. Many scientists assess the biodegradability of composite films by measuring their weight loss after burying them in natural soil at a specific depth, temperature, and relative humidity for a predetermined period [93,94]. However, other researchers prefer composting tests, where vegetable waste is mixed with natural soil, and the relative humidity of the mixture is maintained at a specific level, to evaluate the biodegradability of packaging materials for a predetermined period [95,96]. It should be noted that the abovementioned procedures comply with the structure and the concept of the reference method known as ASTM D 5988, by which the aerobic biodegradation of plastic materials can be assessed [97]. Since such multifunctional packaging materials are emerging in the packaging systems and research is ongoing, there are limited studies focused on the biodegradability of biopolymer-polyphenol conjugate films. Yuan et al. [98] reported that the chitosan-based films and chitosan films incorporated with chitooligosaccharide-caffeic acid conjugates underwent color significant changes in their color and surface after 15 days, decreasing 25 % of their weight, while polyethylene plastic showed no significant changes. It was found that the degradation rate of conjugate-containing composite films was slightly higher than the chitosan films alone. The presence of the catechol group in caffeic acid might trigger the activity of microorganisms in the soil and result in a higher degradation rate. The effect of the incorporation of apple polyphenols on composite films based on pea starch and pulp cellulose nanofibers was investigated by Li et al. [99]. They have found that the incorporation of apple polyphenols into the composite films could enhance biodegradability so that the highest polyphenol content in films resulted in the highest biodegradability rates. It has been reported that the hydrophilic nature of composite films led to a higher rate of biodegradability due to the higher interaction of water with the film matrix, leading to higher microbial penetration and enzymatical activity [99]. Additionally, the presence of highly polymerized structures in the film matrix could negatively affect biodegradability due to the lower penetration of microorganisms into the film matrix [100]. It can be deduced that higher hydrophobicity, polymerization, density, or incorporation of matrix reinforcing agents could reduce the biodegradability of active packaging materials [99–101].

6. Conjugates as active polymers: advantages and challenges

6.1. Advantages

Protein-polyphenol, polysaccharide-polyphenol, and protein-polysaccharide-polyphenol conjugates are emerging as a new category of biomaterials for active packaging and coatings. Owing to their antioxidant and antimicrobial activities, the incorporation of polyphenols into the biopolymer equips the film or coating matrix with these functionalities. By grafting these antioxidants directly onto the packaging material, the conjugates actively combat free radical damage, thereby preserving the freshness and nutritional value of food products over extended periods.

The inherent antioxidant properties of the conjugates are particularly beneficial for packaging foods rich in oils and fats, as they prevent oxidation and the onset of rancidity. This ultimately enhances product quality and prolongs shelf life. They can be easily incorporated into films or coatings for meat and poultry products, effectively fighting both microbial growth and oxidative processes, ultimately extending shelf-life and potentially substituting the use of traditional chemical preservatives.

Active packaging that utilizes these bio-conjugates can significantly reduce spoilage in fruits and vegetables by mitigating oxidative damage and inhibiting fungal growth. This approach holds the potential to significantly decrease food waste and enhance the overall availability of fresh produce. In a study by Sela et al. [56] the fresh-cut apple pieces were coated with carboxymethyl chitosan-quercetin conjugate followed by storing in polyethylene terephthalate (PET) containers at 20 °C for 5 days. The presence of quercetin as an antioxidant could successfully limit the color change and browning in fresh-cut apples. After 5 days of storage, fresh-cut apples coated with conjugates exhibited a total

aerobic count below the acceptable threshold level of 7 log $CFUg^{-1}$. Yong et al. [77] reported that largemouth bass fillets coated with chitosan oligosaccharides-polyphenol conjugates were stored in sealed plastic boxes at 4 °C for 10 days. Fillets coated with native chitosan oligosaccharides reached the limit level of thiobarbituric acid reactive substances content, which is 0.6 mg malondialdehyde per kg, while fillets coated with biopolymer-polyphenol conjugates reached the limit level in 7–8 days. These studies suggest that biopolymer-polyphenol conjugates have the potential to extend the shelf-life of food products and fresh produce due to their antioxidant and antimicrobial activities.

Conjugating hydrophobic polyphenols to the biopolymer can enhance the hydrophobicity of the film matrix. Increased hydrophobicity in active packaging materials reduces their solubility in water. For example, the conjugation of vanillic acid with aminated starch was reported to be able to significantly increase the hydrophobicity of starch-based active films [82]. Furthermore, these bio-conjugates address key sustainability concerns. Unlike traditional petroleum-based packaging materials, they are derived from renewable resources and exhibit excellent biodegradability. This characteristic minimizes their environmental footprint and aligns perfectly with the growing demand for sustainable packaging solutions. The versatility of these bio-conjugates extends to diverse food products.

6.2. Challenges

While the conjugation of polyphenols with biopolymers may offer a range of functional benefits to active film materials, it may also present technical challenges that impact the films' or coatings' efficiency. For instance, integrating antioxidant and antimicrobial activities into the film matrix could occasionally lead to increased water vapor permeability or solubility. It has been reported that the conjugation of protocatechuic acid to chitosan increased the water solubility of the conjugate-based films compared to native chitosan films [81]. An & Fu, [82] reported that the conjugation of gallic acid to aminated starch significantly increased the water vapor permeability of the films, potentially due to the presence of pores on the film matrix's surface.

In addition to the challenges in optimizing biopolymer-conjugate active packaging films and coatings, there may also be industrial and environmental challenges. Like other biodegradable active packaging films and materials, scalability for large-scale production presents a significant challenge. Translating current synthesis methods, which rely on enzymatic or chemical techniques, to an industrial scale can be complex. These approaches may not be readily adaptable to large-scale operations due to intricate reaction conditions and potential limitations in reaction vessel size. For instance, using enzymes in the development of biopolymer-polyphenol conjugates might be costly and necessitates controlling several parameters simultaneously, making the reaction more complex to conduct.

Conventional extraction methods for proteins, polysaccharides, and polyphenols often involve the use of harsh chemical solutions or specialized equipment, significantly impacting cost-effectiveness. Scaling up these processes requires not only substantial investments in infrastructure and expertise but also the development of robust protocols that maintain consistent quality control and desired material properties. Conventional techniques for polyphenol extraction include percolation, decoction, heat reflux extraction, Soxhlet extraction, and maceration. In contrast, advanced techniques include ultrasound-assisted extraction, microwave-assisted extraction, supercritical fluid extraction, high-voltage electric discharge, pulse electric field extraction, and enzyme-assisted extraction. It has been reported that the average rate of polyphenol extraction using advanced methods consumes 15 times less energy than conventional techniques and is 32–36 % more efficient [102]. Additionally, the use of certain chemicals in the chemical extraction of polyphenols raises concerns about potential human health and environmental risks associated with residual byproducts or incomplete reactions [103]. Moving forward, addressing these scalability and production challenges will be crucial for the successful commercialization of these conjugates.

7. Future directions

Addressing the limitations that were discussed in this research requires a multi-faceted approach that emphasizes sustainable production, user-friendliness, and economic viability. One crucial area for progress involves the development of environmentally friendly and straightforward extraction methods for proteins, polysaccharides, and polyphenols. This could entail the exploration of innovative techniques, which offer numerous benefits, including reduced dependence on harsh chemicals, decreased energy consumption, and potentially higher yields of targeted biomolecules. Moreover, research efforts should be steered towards the development of green and simple synthesis pathways for biopolymer-polyphenol conjugates.

Investigating enzymatic cross-linking approaches using food-grade enzymes is promising due to their high specificity, mild reaction conditions, and minimal environmental impact. Additionally, exploring alternative methods such as Maillard reactions or physical cross-linking through the manipulation of processing parameters could provide simpler and more scalable approaches. Streamlining these processes not only reduces production costs but also enables easier integration into existing manufacturing lines, enhancing user-friendliness and paving the way for broader adoption by food manufacturers.

The future of biopolymer-polyphenol conjugates in food packaging holds immense potential. Fascinating research is exploring the possibility of leveraging the color-changing properties of certain polyphenols as a built-in spoilage indicator. As the conjugate degrades or the food product spoils, the color of the packaging could change, providing a visual cue to consumers. This innovation aligns perfectly with the concept of intelligent packaging, offering real-time information about food quality and enhancing consumer trust. Finally, achieving economic viability is paramount for the widespread adoption of these conjugates. Interestingly, due to the presence of some polyphenols, the use of biopolymer-polyphenol conjugates in intelligent packaging systems allows them to detect spoilage markers or dynamically change color in response to temperature fluctuations or microbial growth. This opens up exciting avenues for future developments in active intelligent packaging technology.

Optimizing extraction and synthesis processes, along with exploring alternative bio-based sources, can significantly reduce production costs. Furthermore, life cycle assessments comparing the environmental impact of biopolymer-polyphenol conjugates versus conventional packaging materials can demonstrate their sustainability advantage, potentially attracting investment and fostering market acceptance. By prioritizing these future directions, researchers and industry leaders can overcome current limitations and usher in a new era of sustainable, user-friendly, and cost-effective active food packaging with these conjugates leading the way.

8. Conclusions

Taken together, active packaging materials and coatings based on biopolymers have the potential to extend shelf-life and enhance environmental sustainability in food packaging. While existing research has explored various possibilities for active packaging development, the use of biopolymer-polyphenol conjugates remains largely unexplored. The process of conjugating polyphenols with biopolymers offers an exciting potential for enhancing both functional and physicochemical properties related to emulsification, antioxidant, and antimicrobial activities. This could lead to improved food preservation and potential health benefits for consumers. Despite the promising value of biopolymer-polyphenol conjugates in active packaging, our understanding of their development, characterization, and practical application is still limited. Future research is needed to fully explore this concept for viable industrial-scale

applications. In particular, further studies are required to address potential limitations related to environmentally friendly and cost-effective extraction methods for biopolymers and polyphenols, as well as the economic feasibility of their large-scale production process. A life cycle assessment of these materials will be crucial to ensure overall environmental sustainability. In the biopolymer-polyphenol conjugate system, addressing these knowledge gaps and limitations could transform the food packaging industry and meet the growing demand for environmental responsibility and innovative ways to enhance food safety and quality.

CRediT authorship contribution statement

Shahriyar Sahraeian: Writing – original draft, Visualization, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Behrokh Abdollahi:** Writing – original draft, Software, Methodology, Investigation. **Ali Rashidinejad:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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