polysaccharides

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Review

Improving the Properties of Polysaccharide-Based Films by Incorporation of Polyphenols Through Free Radical Grafting: A Review

Karla Hazel Ozuna-Valencia [1], Francisco Rodríguez-Félix [1], Enrique Márquez-Ríos [1], María Jesús Moreno-Vásquez [2,*], Abril Zoraida Graciano-Verdugo [2], Miguel Ángel Robles-García [3], Santiago Pedro Aubourg-Martínez [4], Idania Emedith Quintero-Reyes [5], Betzabe Ebenhezer López-Corona [1] and José Agustín Tapia-Hernández [1,*]

[1] Departamento de Investigación y Posgrado en Alimentos (DIPA), Universidad de Sonora, Blvd. Luis Encinas y Rosales, S/N, Colonia Centro, Hermosillo 83000, Sonora, Mexico; a215208659@unison.mx (K.H.O.-V.); francisco.rodriguezfelix@unison.mx (F.R.-F.); enrique.marquez@unison.mx (E.M.-R.); betzabe.lopez@unison.mx (B.E.L.-C.)
[2] Departamento de Ciencias Químico Biológicas, Universidad de Sonora, Blvd. Luis Encinas y Rosales, S/N, Colonia Centro, Hermosillo 83000, Sonora, Mexico; abril.graciano@unison.mx
[3] Centro de Investigación en Biotecnología Microbiana y Alimentaria, Departamento de Ciencias Básicas, Centro Universitario de la Ciénega, Universidad de Guadalajara, Av. Universidad 1115, Ocotlán 47810, Jalisco, Mexico; miguel.robles@academicos.udg.mx
[4] Instituto de Investigaciones Marinas, Consejo Superior de Investigaciones Científicas (CSIC), 36208 Vigo, Spain; saubourg@iim.csic.es
[5] Departamento de Ciencias de la Salud (DCS), Universidad de Sonora, Campus Cajeme, Blvd. Bordo Nuevo N/N, Antiguo Ejido Providencia, Ciudad Obregón 85010, Sonora, Mexico; idania.quintero@unison.mx
* Correspondence: mariadejesus.moreno@unison.mx (M.J.M.-V.); joseagustin.tapia@unison.mx (J.A.T.-H.)

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Abstract: The increasing demand for sustainable materials has propelled research into polysaccharide modifications for various applications, particularly in active packaging. This review aims to explore the incorporation of bioactive compounds such as polyphenols into polysaccharides, focusing on chemical modification through free radical grafting techniques. The methods examined include enzymatic, physical, and chemical grafting techniques, highlighting their effectiveness in enhancing the properties of polysaccharide-based films. Recent studies have demonstrated that free radical grafting can significantly improve the mechanical, barrier, and antimicrobial properties of these films, extending their applicability in the food and pharmaceutical industries. However, challenges such as the stability of polyphenols and the understanding of grafting mechanisms remain critical areas for further investigation. This review discusses these advancements and outlines future research directions, emphasizing the potential of polysaccharide modifications to create innovative materials that meet the evolving needs of consumers and industries alike.

Keywords: polysaccharides-based film; polyphenols-grafted-polysaccharide; free radical grafting method; polyphenols-grafted-biofilm; conjugate

1. Introduction

Polymers have been widely utilized in various applications due to their inherent properties, with thin and flexible films emerging as crucial materials in sectors such as food packaging and healthcare [1,2]. Their versatility is rooted in their ability to adapt effectively to various physical and chemical environments, enabling them to meet the specific requirements of diverse applications [3]. Depending on the type of polymer utilized—such as polysaccharides, proteins, or lipids—these films can exhibit a range of characteristics, including transparency, color, and mechanical properties [4,5].

Polysaccharide-based films have garnered significant attention for their vital role in the packaging sector, where they contribute to the protection and preservation of food products [6,7]. These films serve as effective barriers against moisture, oxygen, and other environmental factors, all of which can jeopardize the quality and shelf life of food items [7]. The inherent flexibility and versatile nature of polysaccharides not only enhances their barrier properties but also opens avenues for innovative applications in biodegradable packaging solutions [5]. The rising consumer demand for sustainable packaging options further propels the exploration of polysaccharide-based materials in this field.

Polyphenols, which are secondary metabolites found in plants [8,9], are recognized for their wide-ranging health benefits and have drawn attention for their potential to enhance the functionality of films. Renowned for their antioxidant and antimicrobial activities, polyphenols contribute significantly to the performance of packaging materials [10]. Furthermore, these compounds exhibit multiple health-promoting properties, including anti-inflammatory, cardioprotective, immunological, and anticancer effects, and the potential to lower blood pressure [11]. However, one of the main challenges associated with polyphenols is their inherent instability; these compounds are prone to degradation, leading to alterations in their molecular structure and a consequent reduction in biological efficacy [12]. Consequently, incorporating polyphenols into polymeric matrices through grafting techniques is a compelling strategy to stabilize and preserve their bioactivity [13].

The grafting process entails the chemical modification of the polymer surface, allowing for the formation of active sites that can anchor bioactive compounds [14]. This technique enables modifications to the functional groups within the polymeric chains, thus enhancing the compatibility and interaction between the matrix and the grafted compounds [15]. Various methodologies exist for achieving this modification, including physical, enzymatic, and chemical initiators [16]. This review will specifically examine the process of free radical-induced modification, utilizing agents such as ascorbic acid and hydrogen peroxide (H_2O_2) to facilitate the efficient grafting of bioactive compounds onto polysaccharide films.

There are two predominant strategies for incorporating polyphenols into polysaccharide-based films. The first method (Method-1) emphasizes surface modification of the polymers through free radical reactions. In contrast, the second method (Method-2) involves more extensive film modification techniques that facilitate the enhanced integration of polyphenols throughout the film matrix. While recent research has shown a growing interest in Method-1, Method-2 remains less explored and presents a gap in the current literature. Therefore, this review aims to elucidate the mechanisms underlying free radical grafting of bioactive compounds in polysaccharide-based films and to investigate how this grafting method influences the physicochemical properties and biological activities of the films.

2. Polymeric Films

Biodegradable polysaccharide-based films are thin and flexible sheets derived from renewable sources, which are increasingly being used in food packaging and protective coatings due to their biodegradability and sustainability. These films can be transparent or colored, and their chemical composition varies depending on the type of polysaccharide used. Their environmental friendliness makes them a more sustainable alternative to synthetic, non-biodegradable polymers. They can adapt to different physical and chemical properties according to specific needs, making them an attractive option for diverse applications such as food packaging and protective coatings [17,18].

2.1. Film Composition

2.1.1. Polysaccharides

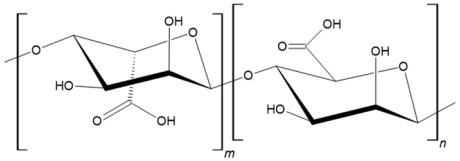
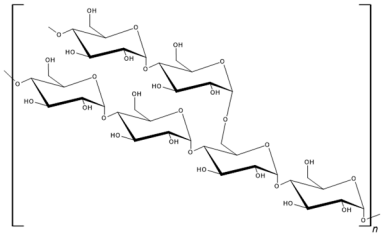
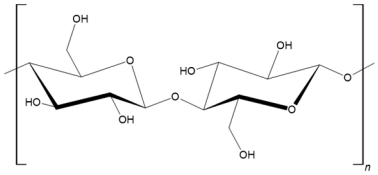
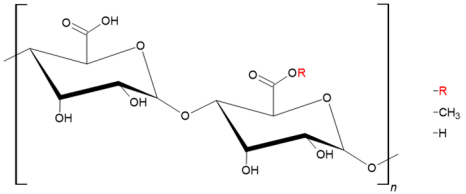
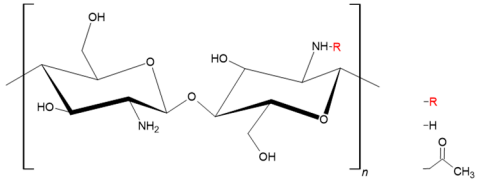
Biopolymers are large macromolecules formed by multiple monomers that are repetitively linked and derived from natural sources [3]. Their application in food packaging is primarily driven by their biodegradability and renewable nature, as they can be extracted from plants or animal sources [19]. Currently, these biopolymers are used in food packaging

as an alternative to synthetic plastics due to their mechanical strength, flexibility, and film-forming properties, mimicking many of the desirable attributes of conventional plastics [3].

Biopolymers, including lipids, proteins, and polysaccharides, have been studied extensively, with polysaccharides being of particular interest due to their abundance, biodegradability, and film-forming properties. Polysaccharides have emerged as ideal candidates to replace petrochemical-based polymers in various applications due to their unique properties [18]. They exhibit a high affinity for paper-based materials, provide effective barriers to gasses and aromas, and possess significant mechanical resistance, making them an attractive option for the development of sustainable and functional packaging [20]. Additionally, polysaccharides are biodegradable, non-toxic, and offer the possibility of including additives with specific functionalities, such as antimicrobial properties [3,20].

Table 1 shows the most used polysaccharides for film production. The table displays the polymer structures and the functional groups they possess. The functional groups in the polysaccharide structures correspond to the binding sites that can be utilized for polysaccharide-polyphenol binding. These topics will be mentioned later in the text.

Table 1. Most used polysaccharide-based films.

Biopolymer	Characteristics	Structure	Functional Groups	Refs
Alginate	Advantages: good film-forming ability due to the formation of cross-linked structures. Disadvantages: films with low water vapor barrier properties.		Carboxyl -COOH Hydroxy -OH	[20,21]
Starch	Advantages: the films have excellent oxygen barrier properties. Disadvantages: they form films with poor mechanical properties.		Hydroxy -OH	[21,22]
Cellulose	Advantages: the films have good mechanical properties. Disadvantages: the formed films can absorb water and affect mechanical properties		Hydroxy -OH	[18,23]
Pectin	Advantages: films with an excellent film-forming capacity. Disadvantages: they do not have microbial properties and may promote fungal growth due to the C content.		Carboxyl -COOH Hydroxy -OH	[21,24]
Chitosan	Advantages: they form films with good mechanical properties and antimicrobial activity. Disadvantages: the films have low water vapor barrier properties.		Amine -NH2 Hydroxy -OH	[21,25]

2.1.2. Use of Plasticizers

Plasticizers employed in film production are low-molecular-weight and non-volatile compounds that help to reduce fragility and improve the flexibility and hardness of films [26]. Molecules such as xylitol, mannitol, propylene glycol, glycerol, sorbitol, polyethylene glycol, triethylene glycol, and ethylene glycol, among others, are plasticizers and are added to the polymers in proportions ranging from 10 to 65% [13]. However, glycerol is the most widely used, as it enhances water vapor permeability in various polymers such as starch, chitosan, and pectin [27].

Polysaccharide-based films exhibit hydrophilic properties and have poor water barrier properties; therefore, plasticizers with similar structures like glycerol, sorbitol, and mannitol are used [26]. In the case of starch film production, the addition of plasticizers reduces hydrogen intramolecular bonds [28]. Plasticizers improve the mechanical properties of chitosan films by increasing their flexibility and reducing brittleness without significantly altering the polymer's chemical structure [18].

2.2. Active Films

Polymeric films, particularly those based on polysaccharides, are used in various applications ranging from food packaging to biomedical materials. In food packaging, these films can function as oxygen barriers, preserving the quality and freshness of products. Moreover, their inherent biodegradability makes them a preferred choice in the development of environmentally friendly packaging solutions. Polysaccharide films are also being explored for use in active packaging systems, where they serve not only as a physical barrier but also as carriers of functional compounds such as antioxidants and antimicrobial agents.

Active packaging is characterized by the incorporation of compounds that release or absorb substances to enhance food preservation and extend shelf life [29]. During their production, biological compounds providing antioxidant and/or antimicrobial properties are integrated [30,31]. However, the efficacy of these packages relies on the interaction of the active compounds with the food product [32]. Active packaging systems are designed to safeguard food from the environment and ensure food safety [33].

In the design process, it is essential to include active components such as organic acids, enzymes, bacteriocins, fungicides, extracts, and even metallic ions [34]. This system encompasses migratory and non-migratory active packages, with classifications depending on the release of the bioactive compound (antioxidant or antimicrobial) from the film into the food [33]. Polyphenols offer both antioxidant and antimicrobial properties, which are crucial for enhancing the shelf lives of food products.

Antioxidant and Antimicrobial Activity

Active films incorporate compounds such as polyphenols, which provide both antioxidant and antimicrobial properties. Polyphenols are natural antioxidants that delay oxidative degradation by neutralizing free radicals [35]. Their activity can be enhanced by coordinating with metallic ions, allowing them to function as free radical acceptors. In the food industry, antioxidant films help to delay oxidation by incorporating high concentrations of these compounds within their matrices [36].

The antimicrobial mechanism of polyphenols involves disrupting the bacterial cell membrane, leading to leakage of cellular contents and subsequent cell death. Polyphenols also interfere with bacterial enzymes and DNA, inhibiting their replication and metabolism, which makes them potent inhibitors of microbial growth [37]. The activity of flavonoids in inhibiting the growth of yeasts and molds, as well as potential mechanisms of action, has also been investigated [38]. This dual action makes polyphenols highly effective in preventing the spoilage of food products.

3. Polyphenols as Bioactive Compounds

Bioactive compounds possess antioxidant and/or antimicrobial activity [39] and are characterized by a hydrophobic chemical structure [40]. The incorporation of bioactive compounds into active films has been well studied [41]. Among these compounds, polyphenols stand out due to their versatile properties.

Polyphenols are bioactive compounds [42] which are the products of the secondary metabolism of plants and can be found in leaves, stems, roots, fruits, and seeds [11,42]. They are characterized by having one or more hydroxy groups attached to one or more benzene rings [11] and can be classified into two major groups: non-flavonoids and flavonoids [14].

Polyphenols are widely recognized for their antioxidant, antimicrobial, and anti-inflammatory properties [43]. Regarding food, they can improve the shelf life of food products by delaying oxidation and the growth of microorganisms. In the field of packaging, the incorporation of polyphenols into packaging materials can enhance protection against oxidation and prolong the freshness of food [44]. In the pharmaceutical industry, polyphenols have shown significant therapeutic potential [45].

Despite their numerous benefits, polyphenols exhibit some instability, which can limit their effectiveness. Factors such as light, oxygen, and pH variations can affect their stability, resulting in a decrease in their biological activity [12]. However, different strategies are being investigated to improve the stability of polyphenols, such as the use of encapsulation or grafting techniques [46–49].

Polyphenols are commonly incorporated into polysaccharides to form complexes that can have synergistic effects on physical, chemical, and functional properties [50]. These complexes can be formed through non-covalent and covalent interactions. Non-covalent interactions, such as hydrogen bonds and hydrophobic interactions, can alter the bioavailability of polyphenols by affecting their solubility and absorption in biological systems, potentially reducing their efficacy [51].

Table 2 describes numerous studies in which polyphenols or polyphenol-rich extracts have been incorporated into films to obtain active packaging. These studies are characterized by forming non-covalent polysaccharide-polyphenol complexes. We can observe that the bioactivity of polyphenols is commonly affected, meaning that, in most cases, a lower antioxidant and/or antimicrobial capacity is observed. Therefore, studies have been conducted in which polyphenols are incorporated through grafting techniques that form covalent bonds between them.

Table 2. Active films based on polysaccharides with polyphenols or polyphenol-rich extracts.

Film		Bioactive Compound	Characteristics	Bioactivity		Application	Ref
Polysaccharide	Blend			Antioxidant	Antimicrobial		
Alginate	-	Extract of gallnut rich in gallic acid and tannin acid	The extract improved mechanical properties, permeability, and barrier.	Evaluated concentration: 50% (p/p de alginate) TPC: 192.66 ± 0.10 mg GAE/g film DPPH: 75.80 ± 0.68%	Evaluated concentration: 50% (p/p de alginate) Inhibition zone *S. aureus*: 22.75 ± 1.06 mm *E. coli*: 17.50 ± 0.70 mm	Active Food Packaging	[52]
	-	Tanic acid	Tannic acid functioned as a crosslinker in the film.	Evaluated concentration: 70:30 alginate–tannic acid DPPH: 50.05 ± 0.94	-	Active Food Packaging	[53]
Chitosan	Bacterial cellulose	Tea polyphenol	At concentrations greater than 10%, polyphenols alter the physicochemical properties of the films.	Evaluated concentration: 10% (p/p) DPPH: 39.34 ± 1.88% ABTS: 76.23 ± 3.87%	Evaluated concentration: 10% (p/p) Inhibition zone *E. coli:* 21.22 ± 0.19 mm *S. aureus*: 26.28 ± 0.63 mm	Active Food Packaging	[54]
	Methylcellulose	Tannins	Tannins affect the physicochemical properties of the films. Bilayer films showed improved barriers and antioxidant properties.	Hydroxy propyl-methyl cellulose bilayer films with white tannins DPPH: 23 ± 3 EC_{50} (g tannins/mol DPPH)	Bacterial population increased from 2.5 to 3 log CFU/cm2 to 8 log CFU/cm2 after 10 days of storage Bacterial strains: *L. innocua* y *E. coli*	Active Food Packaging	[55]
Chitosan	-	Pineapple peel polyphenol	The antioxidant capacity was preserved when incorporating them into the films. The film was not characterized; however, it is promising due to its antioxidant and antibacterial activity.	Evaluation 100 µL methanolic extract (ME) and ethanolic extract (EE) (µmol TE/g) ABTS: 13.60 ± 0.50 (ME) y 49.80 ± 0.10 (EE) DPPH: 5.82 ± 0.28 (ME) y 13.63 ± 3.66 (EE) CUPRAC: 3.45 ± 0.44 (ME) y 6.28 ± 0.40 (EE)	Evaluation of 75 mg/mL methanolic extract (ME) and ethanolic extract (EE) Inhibition zone (mm) *E. coli*: 16 ± 3.4 (ME) y 21 ± 1.0 (EE) *S. typhimurium*: 16 ± 1.5 (ME) y 17 ± 1.0 (EE) *S. aureus*: 12 ± 0.0 (ME) y 15 ± 1.5 (EE) *B. cereus*: 11 ± 1.0 (ME) y 11 ± 1.5 (EE)	Active Food Packaging	[56]
				Evaluated concentration extract (ME and EE) film: 1% (p/v) (µmol TE/g) ABTS: 8.031 ± 0.56 (ME) y 26.40 ± 0.72 (EE) DPPH: 3.36 ± 0.28 (ME) y 6.23 ± 1.52 (EE) CUPRAC: 2.48 ± 0.35 (ME) y 6.23 ± 0.30 (EE)	Evaluated concentration of extract (ME and EE) in film: 1% (p/v) Logarithmic reduction in bacterial growth ME: ≥ 6 log CFU/mL EE: ≥ 5 log CFU/mL Bacterial strains: *E. coli*, *S. typhimurium*, *S. aureus* y *B. cereus*		

Table 2. *Cont.*

Film		Bioactive Compound	Characteristics	Bioactivity		Application	Ref
Polysaccharide	Blend			Antioxidant	Antimicrobial		
Pectin	-	Mulberry leaf extract	Improvements were observed in mechanical and barrier properties.	Evaluated concentration: 10% (*v*/*v*) TPC: 164.87 ± 2.75 mg GAE/g film TFC: 26.93 ± 1.10 µg QUE/g RPA: 0.860 ± 0.005 (DO_{700} 5 mg film) DPPH: 2.67 ± 0.04 IC_{50} (mg/mL)	Evaluated concentration: 10% (*v*/*v*) Inhibition zone diameter (mm) for 6 mm Diameter Film *P. aeruginosa*: 15.78 ± 0.06 *B. cereus*: 18.08 ± 0.01	Packaging or coating from pepper (*C. annum L.*). The films extend the shelf life of the pepper.	[57]
	-	Citrus Junos Pomace and Rambutan (*Nephelium Lappaceum*) Peel Extract	Enhanced elasticity was observed, and it showed the ability to block UV light.	Evaluated concentration: 1% (p/v) TPC: 53.00 mg GAE/g film ABTS: 98.20% DPPH: 90.87% RPA: 41.64 mg ascorbic acid/g film FIC: 35.14%	-	Biodegradable and antioxidant food packaging	[58]
	Goma Tara	Ellagitannins	Improvements in mechanical properties were observed.	Evaluated concentration: proportion 1:1:0.1 FRAP: 0.95 ± 0.02 DPPH: 83.23 ± 0.75%	Evaluated concentration: proportion 1:1:0.1 Inhibition zone *E. coli*: 10.41 ± 0.07 mm *S. aureus*: 13.56 ± 0.61 mm	Edible Food Packaging	[59]
Pectin	-	Green tea extract	Increasing the extract concentration improved tensile strength, elasticity, Tg, crystallinity, and barrier properties.	Evaluated concentration: 5% (p/p de film) DPPH: more than 80%	-	Antioxidant packaging	[60]
Starch	Sodium carboxymethyl cellulose	Apple polyphenols	Adding apple polyphenols resulted in higher film barrier performance and improved thermal stability.	Evaluated concentration: 80 mg/mL DPPH: 53.13 ± 0.855% ABTS: 63.05 ± 0.92%	-	The films were applied to chicken, and the thiobarbituric acid index was determined to analyze lipid oxidation	[61]
	Pectin	Broccoli leaf polyphenols	Films with a maximum of 3% polyphenol exhibited the best mechanical and barrier properties.	Evaluated concentration: 50 µg/mL DPPH: 96.18% RSA: 86.68%	-	Container for storing lamb in refrigeration	[62]
	(porous starch)	Tea polyphenols	Improved tensile strength, UV barrier, and thermal stability were observed.	Evaluated concentration: 0.55 g DPPH: 79%	-	Antioxidant packaging	[63]

Table 2. *Cont.*

Film		Bioactive Compound	Characteristics	Bioactivity		Application	Ref
Polysaccharide	Blend			Antioxidant	Antimicrobial		
Starch	-	Catechin/β-cyclodextrin complex	The complex enhanced thermal stability and tensile strength.	Evaluated concentration: 20% (p/p starch) It was determined for 28 days at 40 °C with 75% RH ABTS: 0.90707 ± 0.00112% DPPH: 0.9828 ± 0.02054%	After 60 h of incubation, all treatments showed an inhibition zone greater than 8.5 mm. Strains: *S. aureus* and *S. mutans.* Evaluated concentration: 20% and 25% (*w*/*w* starch). Inhibition (%): 100.00 ± 0 in *S. mutans*.	Migratory Active Food Packaging	[64]
	-	Tea polyphenols	It improved mechanical properties and water and oxygen vapor barrier.	Evaluated concentration: 7.5% (p/p de starch) ABTS: exceeded 80% inhibition DPPH: exceeded 80% inhibition FRAP: exceeded 1.5 absorbance	-	Fruit packaging	[65]

(-): Information not available; DPPH: 1-diphenyl-2-picrylhydrazyl; ABTS: 2,2′-azinobis-3-ethylbenzthiazoline-6-sulphonateand; FRAP: Ferric Reducing Power Assay; TPC: Total Phenolic Content; TFC: Total Flavonoids Content; RSA: Radical Scavenging Activity; RPA: Reduction Power Assay; FIC: Ferrous-Ion Chelating Ability; CUPRAC: Copper (II) Ion Reducing Antioxidant Capacity; GAE: Gallic Acid Equivalents; QUE: Quercetin Equivalents; Laccase: polyphenol oxidase with high catalytic efficiency.

Polysaccharide-polyphenol complexes using covalent bonds lead to greater stability of the given polyphenol [50]. It has been demonstrated that these complexes exhibit improvements in their physicochemical and bioactive properties, which give them greater applications compared to complexes formed by non-covalent bonds [51]. Therefore, there are various methods to construct these complexes, but enzyme-mediated and free radical grafting methods have been highlighted [50].

3.1. Classification of Polyphenols

3.1.1. Non-Flavonoids

Non-flavonoid compounds constitute a broad group, of which most have small structures [66]. Within this category, compounds such as phenolic carboxylic acids, tannins, lignans, stilbenes, and some other phenolic acids are found [67]. Phenolic acids are small structures that consist of a single phenyl group with a carboxyl group as a substituent that may contain one or more hydroxy groups [66]. These are mainly divided into benzoic and cinnamic acids [68]. Table 3 describes the classification of polyphenols and their sources, as well as the polysaccharides they have been grafted onto.

3.1.2. Flavonoids

Flavonoids are synthesized as secondary metabolites in plants [9,38,69,70]. Chemically, flavonoids are characterized by having a phenylpropanoid chain of a 15-carbon structure, composed of a system of three rings (C6-C3-C6), where the C6 components are aromatic rings linked by a heterocyclic pyran ring [9,38,69]. In terms of their chemical properties, flavonoids exhibit a variety of characteristics depending on their specific structure.

Depending on changes or branching, flavonoids can be classified into seven categories: flavonol, flavanone, isoflavone, flavone, anthocyanidin, and chalcone [9]. Unlike other flavonoids, chalcones are characterized by the absence of cyclization in the C3 portion; similarly, flavanols and anthocyanins are known as condensed tannins because of their complexity [38]. Table 3 summarizes the families of flavonoids and their main characteristics.

Table 3. Polyphenols are used for grafting onto polysaccharides.

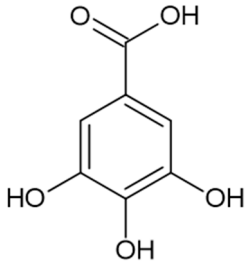
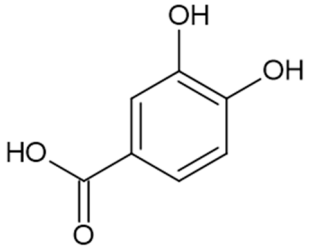
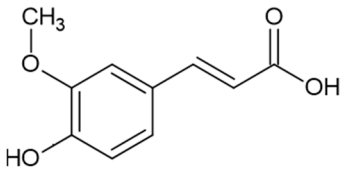
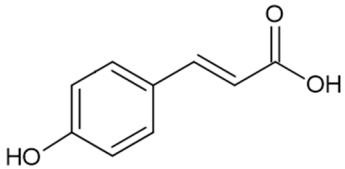
Polyphenol	Characteristics	Structure	Sources	Bioactivities	Grafted on	Refs
Non-Flavonoids						
Gallic acid	It is a phenolic acid, possessing three hydroxy groups in its benzene ring structure		Grapes, strawberries, walnuts, apples, pomegranates, tea leaves, legumes, bananas, lemons, blueberries, mangoes, chard, spinach, coffee, and wine	Antioxidants, anti-inflammatory, antimicrobial, anticancer, gastroprotective, cardioprotective, neuroprotective, antitumor, anti-obesity and anti-myocardial ischemia	Carboxymethyl cellulose, chitosan, gelatin and cellulose	[50,71–79]
Protocatechuic acid	It is a phenolic acid with, possessing two hydroxy groups in its benzene ring structure		Rice, buckwheat, pea, fava beans, hemp, lupine, wheat, lentils, pea, beans, onion, mint, yayla cayi, grossheimii, loquad, kinnow peel, banana, prune, friar plum, peach, currant, currant, grapes, acai, cocoa beans, almonds, walnuts, black cohosh, rattan, echinacea, green tea, barley tea, wine, and olive oil	Anti-inflammatory, antimutagenic, antidiabetic, antiulcer, antiviral, antifibrogenic, anti-allergic, neuroprotective, antibacterial, anticancer, anti-osteoporotic, anti-aging and analgesic properties	Chitosan and carboxymethyl chitosan	[50,76,80–83]
Ferulic acid	It is a phenolic acid, possessing one methoxy group and one hydroxy group. The benzene ring is linked to a carboxyl group through a two-carbon chain		Corn, wheat, rice, oats, oranges, apples, carrots, pineapple, herbs, grains, vegetables, flowers, leaves, beans, seeds, artichoke, peanuts, walnuts, corn, barley, avocado, broccoli, carrot, cauliflower, eggplant, garlic, red cabbage, soybeans, spinach, tomato, banana, grape, and tangerine	Antioxidants, anti-inflammatory, anticancer, antiviral, neuroprotective, anti-aging, antidiabetic, antifibrosis, anti-apoptotic and antiplatelet	Pectin, chitosan and carboxymethyl cellulose	[50,84–86]
Coumaric acid	It is a phenolic acid, possessing a hydroxy group. The benzene ring is linked to a carboxyl group through a two-carbon chain		Wheat, rice, barley, tomato, garlic, cinnamon, rosemary, oregano, thyme, basil, caraway, turmeric, marjoram, pepper, cumin, bay leaf, dried, sage, malissa, mint, nutmeg, parsley, and white pepper	Antioxidant, antimicrobial, anti-inflammatory, anticancer, neuroprotective, cardioprotective, hepatoprotective, antidiabetic, antihyperlipidemic and anti-melanogenic	Chitosan	[87–93]

Table 3. *Cont.*

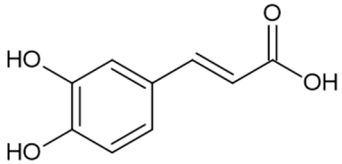
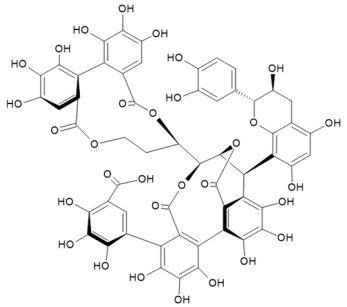
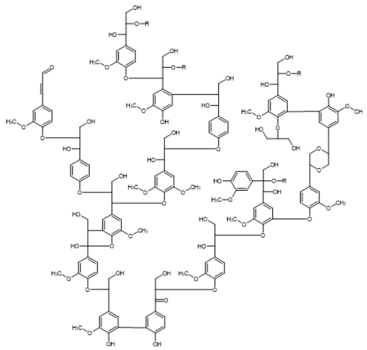
Polyphenol	Characteristics	Structure	Sources	Bioactivities	Grafted on	Refs
Caffeic acid	It is a phenolic acid, possessing two hydroxy groups. The benzene ring is linked to a carboxyl group through a two-carbon chain		Kiwi, blueberry, cherry, apple, blueberry, plum, lettuce, wine, coffee, olive oil, legumes, carrot, eggplant, cabbage, and artichoke	Antioxidant, antimicrobial, antihypertensive, antidiabetic, anticancer, anti-inflammatory, and moderate vasorelaxant	Chitosan and β-lactoglobulin	[66,71,94–97]
Tannins	Are classified into hydrolysable tannins, complex tannins, and phlorotannins		Grape, tea, blueberry, plums, blue mara, apple, peach, apricot, beans, and peanuts	Antioxidant, anticancer, cardiovascular protective, antibacterial, antifungal, antinociceptive, antipyretic, antidiabetic, cardioprotective, antidiarrheal, antiviral, gastro protective, antiproliferative, deworming and wound repair	Porcine plasma protein, gelatin, inulin, zein Modification of tannins to be added to a polymer	[42,50,98–104]
Lignanos	Are low molecular weight polyphenols, consisting of two joined phenylpropanoid units		Straw, walnut shell, almond shell, stems, stubble, cob, jute, hemp, cotton, and wood	Antiviral, antibacterial, antifungal, anticoagulant, anti-emphysema, antitumor, antioxidant, anti-UV, hypopolicemic effect and hypolipidemic effect	Polyurethanes, poly(ε-caprolactone) and resins	[105–108]

Table 3. *Cont.*

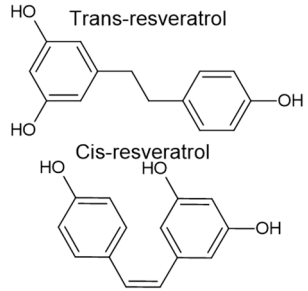
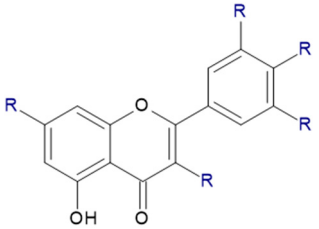
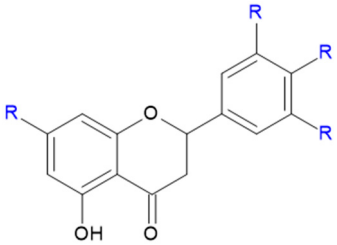
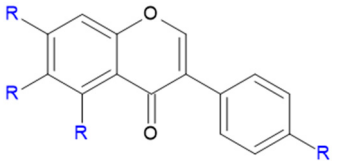
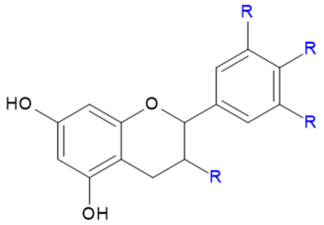
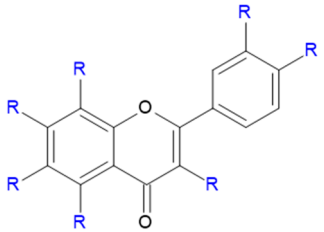
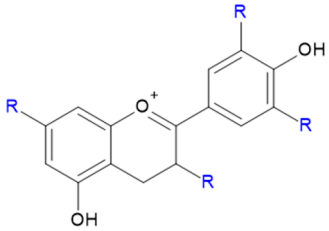
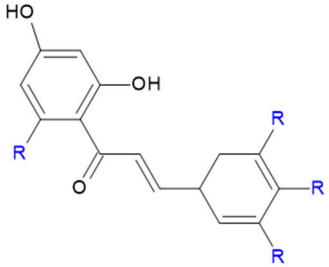
Polyphenol	Characteristics	Structure	Sources	Bioactivities	Grafted on	Refs
Stilbenes	It has two aromatic rings joined by an ethylene bridge, the most common being resveratrol		Grapes, red wine, pistachios, peanuts, blueberries, blueberries, red currants, and blackberries	Antioxidant, antimicrobial, anti-inflammatory, cardiovascular protective, and anti-aging	Zein	[109,110]
Flavonoids						
Flavonol	The most common structures are quercetin, kaempferol, myricetin, rutin, and robinin		Broccoli, onion, asparagus, apple, blueberry, peaches, grapes, red pepper, lettuce, kale, endive, potatoes, tomatoes, nuts, and tea	Antioxidant, cardioprotective, antibacterial, antiviral, anti-inflammatory, anticancer, antidiabetic, anti-obesity, antihyperlipidemic, anti-osteoporotic, anti-allergic, antithrombotic, hepatoprotective and antifungal	Starch and chitosan	[8,9,38,50,70, 111–115]
Flavanone	The most common structures are: hesperetin, naringenin, eriodictyol, pinocembrin and prunin		Orange, lemon, tangerine, lime, and grape	Antioxidant, anti-inflammatory, anticancer, cardioprotective, antidiabetic, anti-obesity, antihyperlipidemic, anti-osteoporotic, anti-allergic, antithrombotic, hepatoprotective, antibacterial, antifungal and antiviral	-	[8,9,38,70,115]
Isoflavonoid	The most common structures are: biochanin A, formononetin, daidzein, genistein and glycitein		Soybeans, lupins, fava beans, chickpeas, kidney beans, kudzu roots, and peanuts	Antioxidants, antiestrogen, anti-inflammatory, anticancer, cardioprotective, antidiabetic, anti-obesity, antihyperlipidemic, anti-osteoporotic, anti-allergic, antithrombotic, hepatoprotective, antibacterial, antifungal and antiviral	-	[8,9,38,70,115]

Table 3. *Cont.*

Polyphenol	Characteristics	Structure	Sources	Bioactivities	Grafted on	Refs
Flavanol	The most common structures are: catechin, epicatechin, epigallocatechin and epigallocatechin galate		Apples, cherries, plums, apricots, tea, cocoa, raisins, red grape, nectarine, peach, mango, pear, and plum	Antioxidant, anti-inflammatory, anticancer, cardioprotective, antidiabetic, anti-obesity, antihyperlipidemic, anti-osteoporotic, anti-allergic, antithrombotic, hepatoprotective, antibacterial, antifungal and antiviral	Chitosan, dextran, arabinoxylan, alginate, CMC, chito oligosaccharides, gelatin, starch, ovalbumin	[8,9,14,38,50,70, 112,116–126]
Flavone	The most common structures are: apigenin, baicalein, diosmetin, luteolin, tangeritin		Celery, tea, red pepper, oranges, green tea, lettuce, broccoli, olive oil, oregano, thyme, rosemary, mint, parsley, and cocoa	Antioxidant, anti-inflammatory, anticancer, cardioprotective, antidiabetic, anti-obesity, antihyperlipidemic, anti-osteoporotic, anti-allergic, antithrombotic, hepatoprotective, antibacterial, antifungal and antiviral	-	[8,9,38,70,115]
Anthocyanidin	The most common structures are: cyanidin, delphinidin, malvidin, petunidin, pelargonidin, and seranin		Blueberries, purple cabbage, tomato, purple sweet potato, eggplant, blueberries, blueberries, raspberries, blueberry, strawberries, blackberries, red cabbage, grapes, cherries, plums, red turnip, black beans, and purple corn	Antioxidant, antidiabetic, anti-obesity, antihyperlipidemic, anti-inflammatory, anti-osteoporotic, anti-allergic, antithrombotic, hepatoprotective, antibacterial, antifungal and antiviral	Chitosan and soy protein	[8,9,38,50,70, 115,127]
Chalcone	The most common structures are: naringenin chacone, eriodictyol chalcone and pinocembrin chalcone		Apples, grapes, blueberries, onions, broccoli, white tea, green tea, oolong tea, black tea, cocoa, kale, tomatoes, and lettuce	Antioxidant, antibacterial, antiviral, antiulcer, antiprotozoal, anticancer, anti-inflammatory, analgesic, anticholinergic, antiplatelet, antimalarial, antileishmania, antidiabetic, immunomodulatory, aldose reductase inhibition, estrogenic, acetylcholinesterase inhibition	-	[8,9,38,128]

3.2. Reactivity and Potential Binding Sites of Polyphenols

Figure 1 displays the chemical structures of some polyphenols, highlighting in red the potential binding sites for the formation of covalent bonds with polysaccharides. Zhang [50] mentions that numerous studies emphasize the essential role of -OH groups in facilitating polyphenol-polysaccharide linkages. Therefore, understanding both the compound structures and their reactivity is crucial for comprehending grafting reactions.

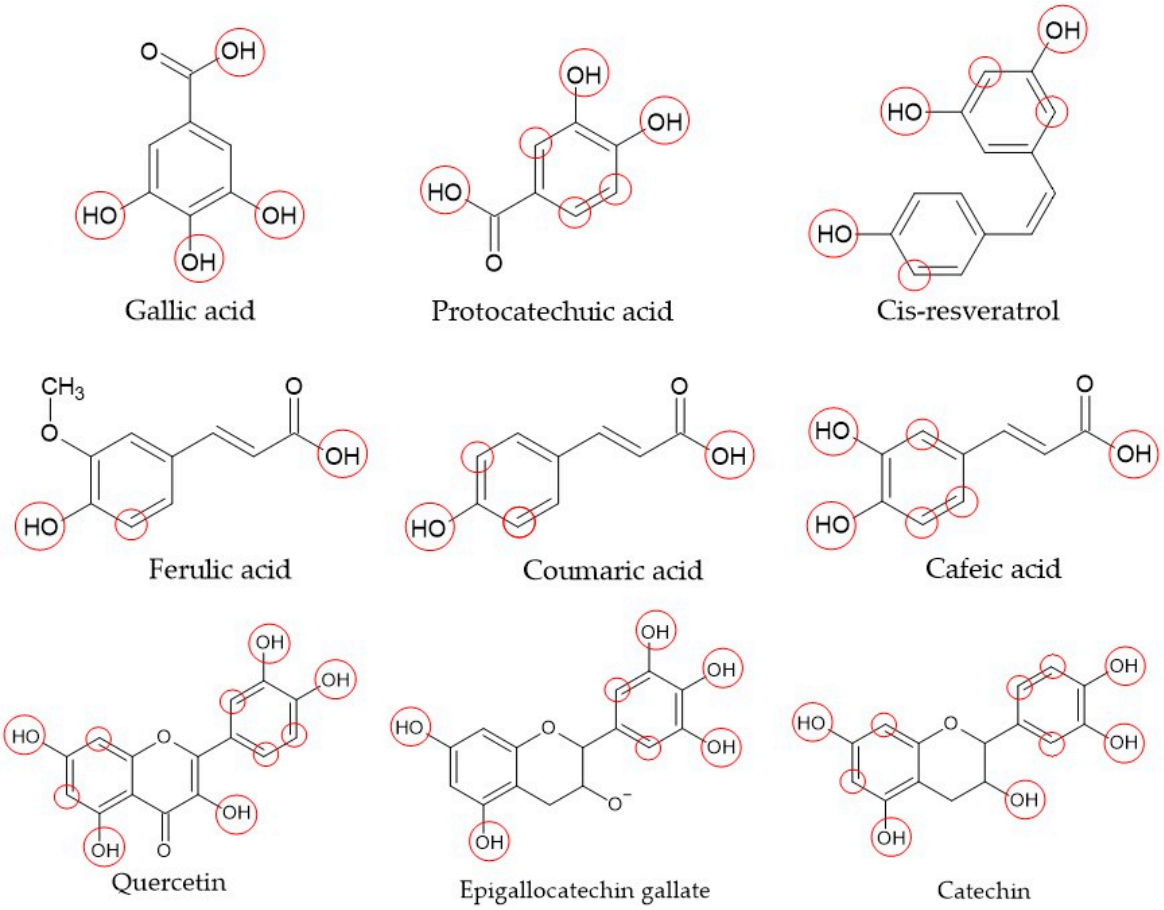


Figure 1. Structures of commonly used phenolic compounds for grafting methods and their potential reactive binding sites.

As previously mentioned, polyphenols consist of benzene structures with one or more -OH groups. Polyphenols tend to bond through -OH groups, although bonding within the benzene ring is also possible. Due to their structure, benzenes are less reactive than alkenes; however, they can undergo substitution and addition reactions under the influence of substituent groups [129].

According to McMurry [130], the -OH groups of benzene exhibit a strong activating effect, enhancing the reactivity of the attached benzene. This is attributed to their ability to donate electrons to the benzene through a mesomeric or resonance effect. During this process, the lone pair of electrons from oxygen can be delocalized towards the ring, increasing electron density and, consequently, reactivity. The bond formation can occur at distinct positions (ortho, meta, or para); -OH groups tend to engage in direct bonding towards the ortho and para positions.

4. Chemical Modification

Grafting is a technique used to modify the surface of polymers [15,131]. This technique enables the alteration of chemical groups in the polymeric chain or the creation of anchoring sites to attach bioactive compounds through covalent bonds [132,133]. There

are various methods available for grafting such as enzymatic (laccases and tyrosinases), physical (irradiation, plasma, and microwaves), and chemical (alkaline, acidic, coupling, and free radicals) [131,134,135].

These techniques involve three distinct systems known as grafting through, grafting to, and grafting from (Figure 2). In the context of "grafting from," this method refers to a process where the polymer is modified by introducing monomers that react with initiators already attached to the polymer chain, leading to the formation of new branches. This process is characterized by the growth of new polymer chains from the existing structure, distinguishing it from polymer-analogous transformations, which primarily involve modifications to the original polymer without creating new chains.

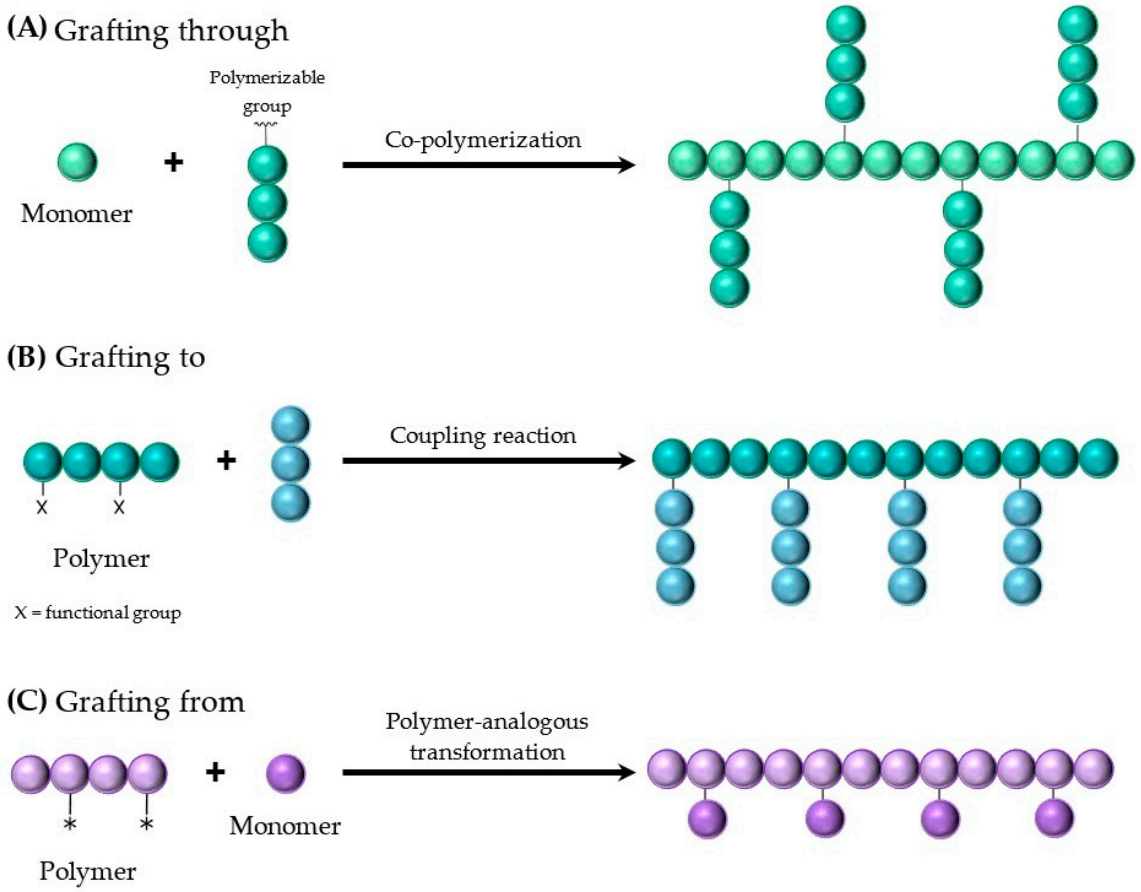


Figure 2. Grafting systems in polymers. (**A**) grafting through; (**B**) grafting to; (**C**) grafting from.

Figure 2 illustrates the differences between these grafting systems. Figure 2A depicts co-polymerization, where monomers are integrated into the polymer matrix, resulting in the formation of copolymers. Figure 2C, on the other hand, shows a polymer-analogous transformation, where the grafted monomer modifies the original polymer backbone rather than contributing to new polymer chain formation. This distinction is crucial for understanding the nature of the modifications being made.

These three grafting systems can be utilized in enzymatic and chemical methods. However, the grafting from system is predominantly associated with physical methods and grafting via free radicals, a chemical method. Minko [136] explains that in the grafting from system, the polymer is first prepared with initiators (azo, peroxide, or photo). Subsequently, a monomer is introduced that can react with the polymer to form the branches or grafts of the copolymer.

4.1. Polymer Modification by Free Radicals (Method 1)

Free radical grafting is an efficient and versatile method for modifying polymers with various functional groups [131]. This technique is favored for its environmentally friendly, safe, and practical nature [50]. Free radical grafting is widely used in polysaccharides [43,45,50,120,122,134,137].

Free radical grafting is commonly mediated by an initiator system with a redox pair composed of ascorbic acid and hydrogen peroxide (H_2O_2) [43,45,50,111,119]. Figure 3A illustrates the mechanism of the radical generation reaction and shows how ascorbic acid reacts with hydrogen peroxide to form the •OH radical and the ascorbate radical (AscH•). This reaction generates free radicals (•OH and AscH•), where the highly reactive •OH radical attacks nearby molecules to stabilize, while the ascorbate radical stabilizes through resonance [111,138].

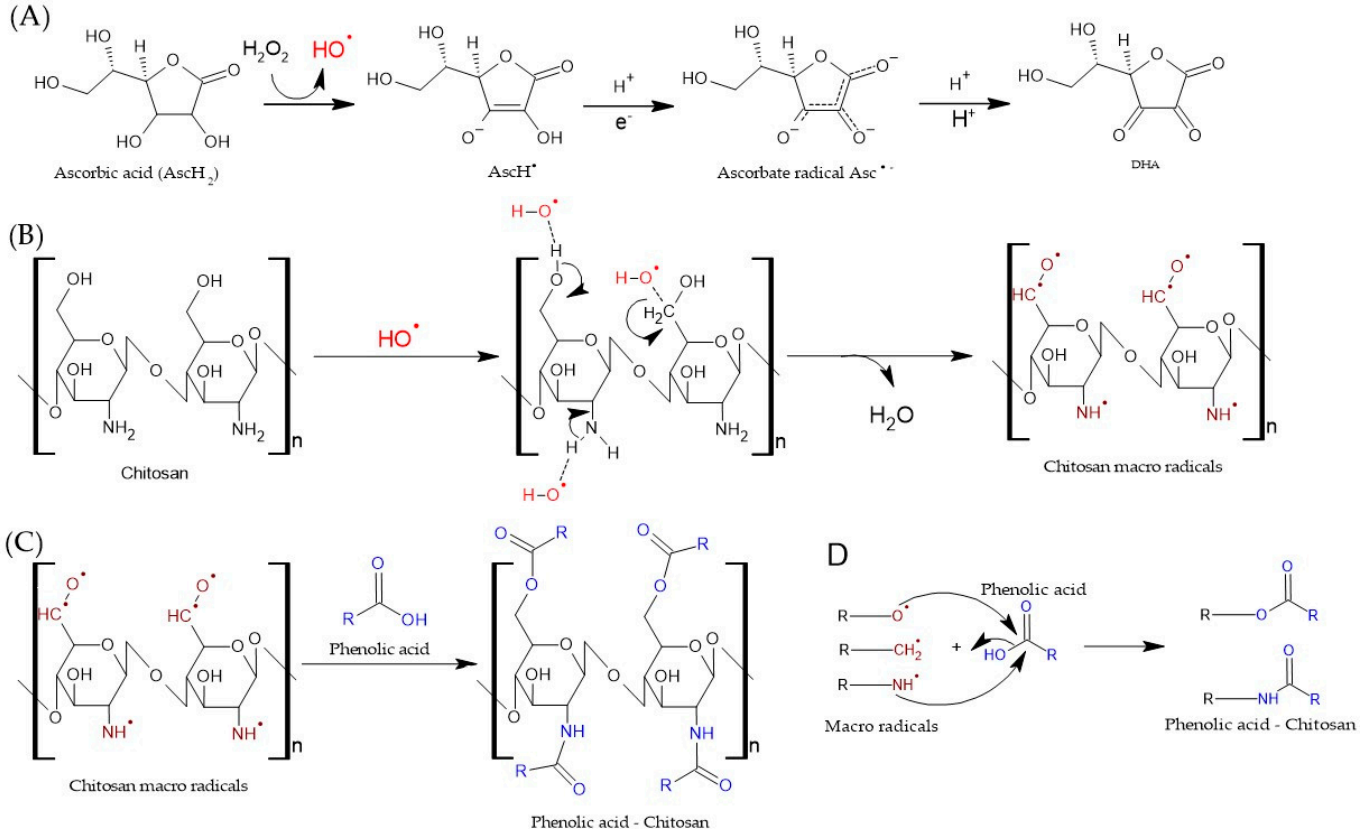


Figure 3. Mechanism of obtaining polyphenol-g-chitosan. (**A**) Generation of the •OH radical, which initiates the radicalization process and stabilizes the ascorbate radical. (**B**) Formation of macro radicals from the reaction of the •OH radical with polysaccharide functional groups, revealing potential anchoring sites for grafting. (**C**) Grafting polyphenols into the polymeric matrix through the reaction with macro radicals. (**D**) Nucleophilic addition illustrates the formation of covalent bonds between the macro radical and polyphenol, establishing stable interactions that enhance the properties of the polysaccharide films.

According to Oliver [48], polysaccharide grafting with polyphenols is conducted in two steps. In the first step, macro radicals are formed by the •OH radical, and in the second step, the macro radicals are stabilized with polyphenols. Figure 3B shows how the highly reactive •OH radical attacks nearby molecules to stabilize. According to Zhang [50], the •OH radical removes the -H from the functional groups of polysaccharides to allow for the formation of macromolecular free radicals (macro radicals).

Curcio [139] states that in chitosan, the •OH radical attacks the H atoms of the functional groups α-methylene (CH_2), hydroxy (OH), and amino (NH_2) to increase reactivity. The NH_2 group, when deprotonated, acts as a nucleophile due to its pKa (6.3), enabling

easy reactivity. To determine anchoring sites in polymers, it is necessary to consider the functional groups and their reaction order, based particularly on the pKa of each group, to understand their reactivity towards the •OH radical.

Polysaccharides contain the following functional groups: carboxylic acids (-COOH), amino (NH_2), and hydroxy (-OH). McMurry [130] describes that carboxylic acids typically have a pKa between 4 and 5 due to the electronegativity of the carbonyl group to which the -OH group is attached, while the hydroxy groups present in polysaccharides have a pKa around 15–16, making them weak acids. Therefore, the reactivity order of functional groups towards the •OH radical would be -COOH, -NH_2, -OH, and -CH_3.

In Figure 3C, it is observed how macro radicals are stabilized with polyphenols. It is worth noting that polyphenols are compounds with antioxidant activity that allow the stabilization of free radicals by donating hydrogen atoms or electrons [9,48,68]. When the macro radicals react with polyphenols, covalent bonds are formed, resulting in the formation of polysaccharide-polyphenol derivatives rather than complexes. This reaction indicates a chemical modification of the polysaccharide, leading to new structures that incorporate the polyphenol components. As shown in Figure 3D, the formation of the polysaccharide-polyphenol derivatives is characterized by the establishment of covalent bonds [132].

4.2. Film Modification by Grafting Techniques (Method 2)

There are numerous studies that graft bioactive compounds onto polymers using free radicals, which, in some cases, are used for film production. However, there are few studies that address the grafting of bioactive compounds onto polymeric films. Research on this topic is based on physical methods such as UV and gamma ray irradiation.

Lacroix [140] conducted grafting of compounds by gamma radiation onto four different films. The first film was made of zein-polyvinyl alcohol (PVA) onto which acrylic acid was grafted, and it was observed that the grafted films showed significant improvements in mechanical properties. The second film was made of methylcellulose (MC), onto which 2-hydroxymethyl methacrylate (HEMA) and silane were grafted, resulting in an increase in the strength and flexibility of the grafted films.

The third film was made with a trilayer of polycaprolactone (PCL) and chitosan, resulting in PCL-chitosan-PCL with silane grafts, showing a significant improvement in strength. The fourth film was made of methylcellulose (MC) reinforced with crystalline nanocellulose (CNC) containing grafts of Trimethylolpropane trimethacrylate (TMPTMA), showing improved mechanical and barrier properties, as well as a significant reduction in water vapor permeability.

Nasef [141] produced a film of polytetrafluoroethylene (PTFE) irradiated with gamma rays with grafted styrene. The film had a thickness of 90 mm, prepared by prior acetone washes and drying in a vacuum oven to a constant weight. For the grafting process, a solution of a known concentration of styrene in three different solvents (methanol, benzene, and dichloromethane) was prepared to investigate if the type of solvent affects the grafting and the efficiency of the process.

For the grafting process, Nasef [141] placed the films in nitrogen-sealed glass ampoules. Subsequently, they were irradiated with gamma rays at different doses. Finally, they were washed with toluene to remove residues and then with methanol before being left to dry in a vacuum oven. These films were modified to prepare ion exchange membranes for potential applications in the chemical industry, water industry, energy industry, and in medicine.

Arrua [142] grafted caffeic acid onto polypropylene (PP) films with UV light. They conducted the reaction by copolymerization, adding hydroxyethyl methacrylate (HEMA) as an initiator in the reaction. For the grafting, caffeoyl chloride was synthesized from caffeic acid, followed by an esterification reaction between the PP-HEMA films and caffeoyl chloride. FTIR analysis was performed on these films, confirming the chemical modification of the films and the grafting of caffeic acid.

The phenol content, antiradical activity, and antioxidant capacity were also determined. The phenol content showed a positive correlation with antiradical activity. The

films exhibited high efficiency in removing DPPH• radicals and were evaluated for their protective capacity against the oxidation of ascorbic acid in orange juice, showing high efficiency. In conclusion, these films have the potential for application as active packaging with antioxidant properties for food products and pharmaceuticals.

Figure 4 illustrates the activation mechanism described by Arrua [142] on modification by UV light. According to the figure, the structure of polypropylene exhibits fewer reactive functional groups (CH_2), which necessitated the use of HEMA as an initiator for the grafting process. While the focus of this review is on polysaccharides, the inclusion of these examples demonstrates that there is evidence that pre-formed films can be chemically modified to graft bioactive compounds. This emphasizes the versatility of grafting techniques, even when applied to synthetic polymers, thereby enriching the discussion on polymer modification methods and their implications for the development of active packaging. Additionally, the structure shown in the figure next to the caption "UV light" represents the activation of HEMA, which subsequently enables the grafting of bioactive compounds to the polypropylene surface. The reference in the figure caption has also been updated to correspond accurately to the text.

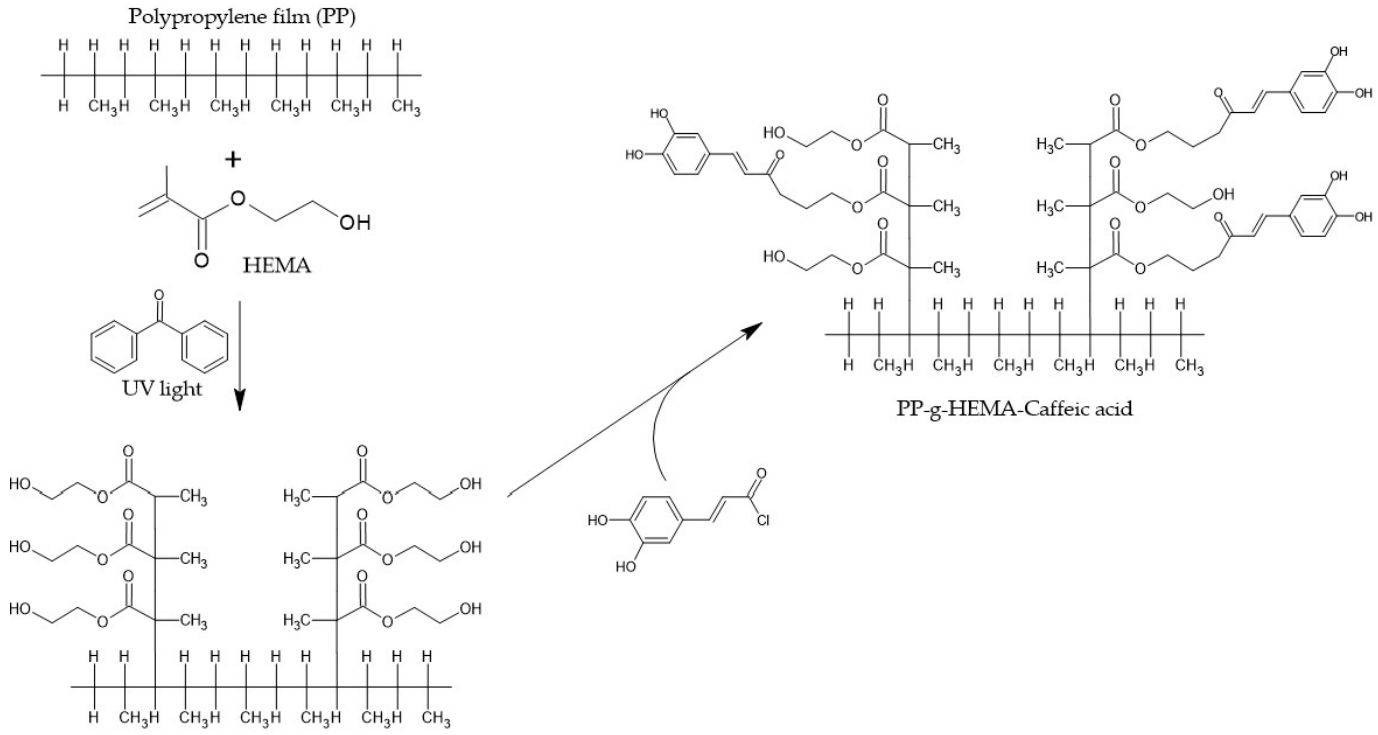


Figure 4. General scheme of the caffeic acid grafting reaction in a polypropylene film. Adapted from [142], with permission from American Chemical Society, 2010.

5. Potential Application of Free Radical Grafting Technique in Films

The chemical modification of polysaccharide-based films using the free radical grafting technique is a promising area of research. This technique requires the presence of functional groups in the polymer that forms the film. Therefore, it is essential to study the polymer's chemical structure, as understanding the functional groups and their availability plays a critical role in the efficiency and outcome of the grafting process. Among these characterization analyses, Fourier Transform Infrared Spectroscopy (FTIR) is a key method for identifying the functional groups present in polysaccharide films.

Potential Application of Free Radical Grafting Technique of Polyphenols in Polysaccharide-Based Films

The chemical modification of polysaccharide-based films using the free radical grafting technique presents a promising area of research. This technique capitalizes on the inherent

functional groups within the polymers, making them suitable for various grafting methods. This review specifically focuses on the application of the free radical technique with ascorbic acid and hydrogen peroxide, suggesting its potential for producing active polysaccharide-polyphenol packaging. The proposed reaction mechanism is adapted from Arrua [142], with the initiators being ascorbic acid and H_2O_2. Although this approach has not yet been extensively evaluated, it opens new avenues for research in the development of active films. This section aims to bridge the discussed methods and emphasize the practical applications of free radical grafting in enhancing polysaccharide films.

6. Future Perspectives

The modification of polysaccharide-based films through free radical grafting is a promising avenue for research and development. This innovative approach, which combines polymer modification by free radicals (Method 1) and film modification through grafting techniques (Method 2) holds substantial potential among different industries. The applications of these techniques can be extended not only to health and pharmacology but also to the food industry, allowing for the development of active and intelligent packaging. Despite being an emerging research field, the potential of these techniques is significant. The modification of polysaccharide-based films through free radical grafting represents a new challenge in materials research with the potential to open new avenues of investigation.

7. Conclusions

The implementation of the free radical technique in polysaccharide-based films presents a new area for packaging development. With ongoing research and development, significant advancements in this field can be expected. However, it is worth noting that there are various challenges that may limit the implementation of this technique, such as the stability of polyphenols and the stability of the films during the reaction. There is also a significant lack of information on the formed conjugates of polyphenols-g-films, as the mechanism by which grafting takes place is not clearly understood, resulting in a low grafting index.

According to the above, it is crucial to continue researching the reactivity of bioactive compounds and how they can interact with the film surface. While the reaction occurs on the surface, steric hindrances may arise due to the size and spatial arrangement of grafted polyphenols, which can limit accessibility to reactive sites on the polysaccharide matrix. Thus, it is suggested that structural analyses be conducted when performing these techniques to better understand the distribution of polyphenols and the conformational changes that may occur in the polymers after the grafting reaction. Finally, there is encouragement to continue studying grafting techniques to obtain new materials with applications in the health and food industries.

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