Food Engineering Reviews (2023) 15:360–379
https://doi.org/10.1007/s12393-023-09342-6

Hydrophobic Biopolymer-Based Films: Strategies, Properties, and Food Applications

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Received: 17 October 2022 / Accepted: 11 March 2023 / Published online: 4 April 2023

Abstract

Food packaging materials are crucial to maintaining food quality, as they play an important role in preventing food deterioration, dehydration, and oxidation. Unlike synthetic polymers, natural biopolymers, such as polysaccharides and proteins, are abundant and widespread resources that are nontoxic, biocompatible, and biodegradable. In food packaging, contact between packaging materials and moist foods can frequently degrade the performance of the materials. This has increased research into the development of hydrophobic biopolymer-based films. Here, we summarize the effective preparation strategies, mechanical and barrier properties, pH responsiveness, self-cleaning performance, and antibacterial and antioxidant functions of hydrophobic biopolymer-based films. The most effective methods for preparing hydrophobic biopolymer-based films are electrospinning with hydrophobically modified biopolymers, adding micro/nanofillers and hydrophobic compounds to the films, and hydrophobically modifying the films. These methods can even generate superhydrophobic films with excellent barrier properties. We also discuss the current opportunities and challenges presented by hydrophobic biopolymer-based films.

Keywords Hydrophobic · Biopolymer-based film · Water contact angle · Food packaging

Introduction

Petroleum-based plastic packaging is widely used in all kinds of foods, medicines, and daily necessities, mainly for its low cost and superior performance. However, the most commonly used synthetic plastic packaging materials, such as polyethylene, polyethylene terephthalate, and polyvinylchloride, do not degrade after disposal and have severe adverse impacts on the environment and wildlife [1]. An urgent need therefore exists for biodegradable biopolymer-based food packaging films.

Natural biopolymers, such as polysaccharides and proteins, readily degrade in nature and are therefore logical starting materials for biodegradable films. They are also major biomass resources and abundant worldwide [2–4], and their use as thermoplastic materials is becoming increasingly popular because of their biodegradability, renewability, and low cost [5]. The excellent film-forming capabilities of polysaccharides and proteins amenable to the preparation of biopolymer-based films have attracted research interest in the preparation, properties, and applications of natural biopolymer-based films [4]. However, polysaccharides and many proteins are hydrophilic substances; therefore, composite films made with these substances are typically highly sensitive to water.

When hydrophilic films come into contact with water, their mechanical properties worsen, and the films themselves can even disintegrate. This is due to decreases in the cohesion and adhesion between molecules with increasing film water content, and results in poor film mechanical properties [6]. In addition, water molecules form hydrogen bonds with hydrophilic groups in the biomacromolecules, causing the biopolymer-based films to swell and their cross-linking

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density to decrease. Therefore, the hydrophobicity of natural biopolymer-based films must be increased to expand their fields of application.

A film's hydrophobicity is usually reflected by its water contact angle (WCA) (i.e., the angle formed between a water droplet and the film). Hydrophobic films have WCA values greater than 90° [7, 8], but films with a surface WCA greater than 65° are also considered hydrophobic [9]. Hydrophobicity can be enhanced by reducing the surface energy or by first increasing the surface roughness and then reducing the surface energy. Based on these principles, many methods are available for preparing hydrophobic biopolymer-based films to expand their range of applications.

Information about the preparation, performance, and application of hydrophilic polysaccharides [10] and protein-based films [11] has recently been summarized. However, changes in the physical and chemical properties of bio-based films have only been reported for films modified with specific hydrophobic compounds, such as carnauba wax [12] and Pickering emulsions [13]. The aim of the present review was to summarize the strategies available for preparing and utilizing hydrophobic composite films derived from natural polysaccharide and protein biopolymers. The mechanical properties, barrier properties, and antimicrobial and antioxidant properties of these films are comprehensively reviewed, and the applications of hydrophobic biopolymer-based films in food packaging, in the delivery of active substances, as wound dressings, and in sewage treatment are discussed.

Natural Biopolymer-Based Films

Natural Polysaccharide-Based Films

Polysaccharides are abundant naturally occurring biopolymers, and their use as raw materials for biopolymer films has been widely studied (Fig. 1). However, natural polysaccharides have many side groups, including polyhydroxy, amino, or carboxyl hydrophilic groups, which can lead to poor water resistance of films made from them and limit their usefulness in food and biomedicine applications. The compositions and hydrophobic properties of several biopolymer-based films are listed in Table 1.

Pure corn starch films demonstrated a low WCA value (38.2°) within 5 s, and the WCA dropped to 35.3° by 30 s [14]. Neat cellulose nanocrystal films prepared by spin-coating showed a WCA of 23.7° following the application of 20 µL distilled water to the film surface [15]. Similar low WCAs have been reported for other natural polysaccharide films, such as pure chitosan film, which showed a WCA of 38.3° after the application of 5 µL water [16]. A WCA of 59.11° was reported for an agar/sodium alginate (mass ratio of 1:1) film after application of 7 µL to the film surface [17]. Investigation of the hydrophobicity of kappa-carrageenan/xanthan gum/gellan gum films at ratios from 1:0.5:0.25 to 0.25:0.5:1 revealed poor WCAs (32–65.8°) and high water vapor permeability (WVP) ($1.80–2.41 \times 10^{-9}$ g Pa^{-1} m^{-1} s^{-1}) [18].

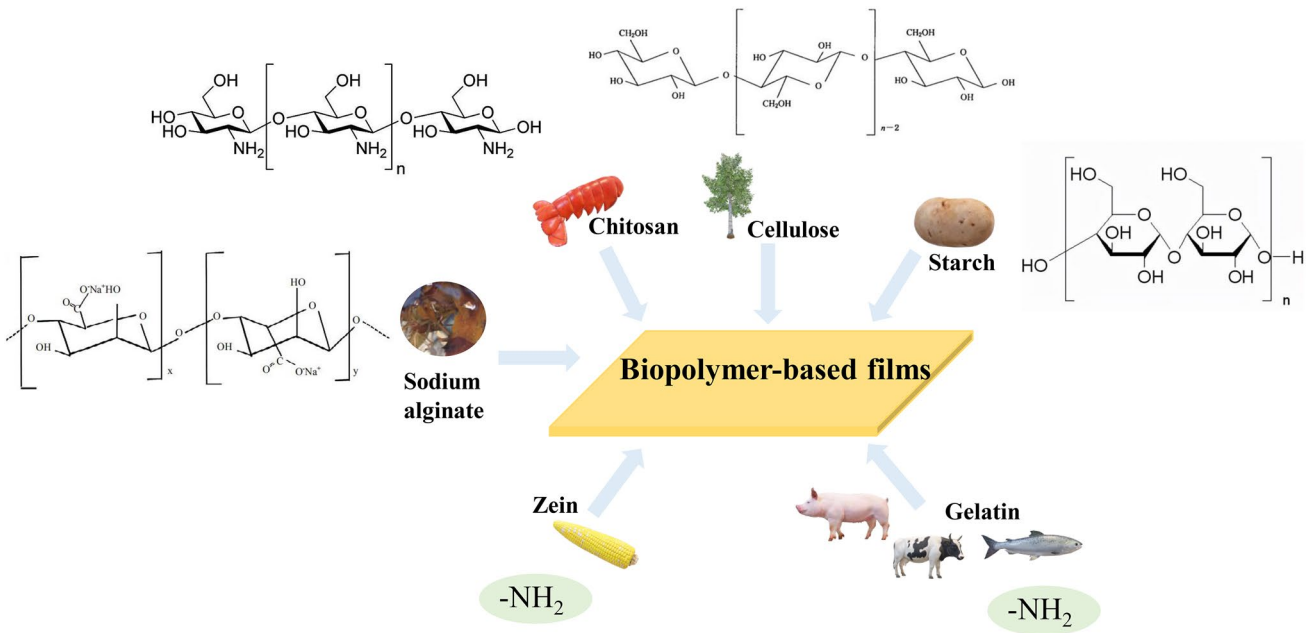

Fig. 1 Raw materials and hydrophilic groups for preparing biopolymer-based films

Table 1 Compositions and hydrophobic properties of biopolymer-based films

Film compositions	WCA (°)	WVP ($\times 10^{-10}$ g/m s Pa)	References
Pure corn starch film	38.2	ND	[14]
Neat cellulose nanocrystal films	23.7	ND	[15]
Pure chitosan film	38.3	2.23 ± 0.07	[16]
Agar/sodium alginate (mass ratio of 1:1) film	59.11	0.872 ± 0.077	[17]
Kappa-carrageenan/xanthan gum/gellan gum film at ratios from 1/0.5/0.25 to 0.25/0.5/1	32–65.8	18.0–24.1	[18]
Zein film	54	420	[22]
Pure whey protein film	ND	14.1	[23]
Neat gelatin film	82	ND	[24]
Wheat gluten protein film	36.9	12.9	[26]

ND no data

In general, most studies have reported WCA values of less than 90°, regardless of the water droplet volume, measuring time, or other test conditions used to investigate natural polysaccharide films. The high WVP values also indicate that the polysaccharide films are hydrophilic. Therefore, expansion of their application range will require modification of polysaccharide films to increase their hydrophobicity.

Natural Protein-Based Films

Most proteins encountered in bulk quantities in nature can be classified as plant proteins (zein, soy protein isolate, wheat gluten, etc.) or animal proteins (whey protein, gelatin, etc.). For example, zein, a byproduct of corn processing, is an environmentally friendly material with unique hydrophobic properties. Alpha zein accounts for 70–85% of the whole zein isolate, and it can be solubilized in 70–95% ethanol [19]. Zein exhibits excellent film-forming performance and can be used to prepare films with good hydrophobic properties through solvent evaporation and agglomeration [20]. However, the WCAs of zein films prepared by the casting method are lower than 60° [21], indicating that hydrophobic films cannot be prepared using zein alone. Nevertheless, pure zein films show swelling of only 30.69%, whereas films of pure rye prolamin swell by 418.54%. This difference is due to the higher content of hydrophobic amino acids in zein (36.2–37.4% mol) than in rye prolamin (29.19% mol).

The hydrophobicity of protein films can be improved by adding nanoparticles. Compared to a control zein film, a nanocomposite film containing 5% w/w silicate nanoparticles (Laponite®) showed an increase in WCA from 54° to 64.77 ± 1.76° [22]. Similarly, the inclusion of 10% Laponite® decreased the WVP of a nanocomposite film by about 40% compared to the control zein film. This effect was due to the distribution of the Laponite® platelets within the zein polymer matrix, which increased the diffusion path length of the water molecules.

Whey protein is a globular animal protein with a hydrophobicity and sulfhydryl group availability that depend on the globular structure. Previous work [23] determined that the WVP of pure whey protein films increased from 1.41×10^{-9} to 1.57×10^{-9} g m^{-1} s^{-1} Pa^{-1} after the addition of 0.1% w/w locust bean gum. The reason for the increase in the WVP value may be a greater movement of water vapor along the film through the highly hydrophilic domains of the larger pores formed in the composite film.

Neat gelatin films also show WCAs of less than 90° [24, 25]. Gelatin films have hydrophobic properties, which may reflect the reorientation of the hydrophobic component of the gelatin molecules at the air–film interface.

Mixed-protein films can also show improved hydrophobic properties compared to single-protein films. Dong et al. [26] reported increases in the WCA of a wheat gluten protein film from 36.9 to 62.2° with the addition of 1.0% egg white protein. This finding revealed that the exposure of greater numbers of hydrophobic groups in the protein molecular structure increases the film surface hydrophobicity. The WVP value was also higher for the complex protein film, at 17.07 g mm/m^2 d kPa, than for the pure wheat gluten protein film, at 11.17 g mm/m^2 d kPa. One possible explanation is that the wheat gluten protein and egg white protein cross-linked to form a sparse grid structure, allowing easier passage of water molecules.

In summary, films prepared from protein alone are not hydrophobic. The hydrophilicity and the low water vapor barrier properties of protein-based films are due to the high content of polar amino groups in natural proteins [27].

Strategies for Preparing Hydrophobic Biopolymer-Based Composite Films

The preparation of biopolymers into hydrophobic films has been widely reported in recent years. The preparation methods have been based on different design principles, which can generally be divided into four strategies (Fig. 2): (1) electrospinning to prepare hydrophobic biopolymer-based films; (2) modification of hydrophilic biopolymers to enhance hydrophobicity; (3) addition of hydrophobic compounds and micro/nanofillers to hydrophilic polymer films to enhance their hydrophobicity; and (4) modification of hydrophilic film surfaces by vapor deposition, self-assembly, and layer-by-layer deposition. The final hydrophobicity of the resulting biopolymer-based films is usually determined by WCA, swelling, and WVP tests.

Electrospinning

Biopolymer-based films are typically obtained by a solvent-casting method, in which a polymer solution is poured into a mold and the solvent is then removed, leaving a film. However, solvent-casted films often have undesirable properties, such as poor surface stability, compact structure, and low thermal stability [28]. For this reason, electrospinning has been adopted to produce nanofibrous films with improved hydrophobic properties.

Electrospinning is a simple yet versatile process for producing hydrophobic biopolymer-based films. One important requirement of this method is that the solvent used must be conductive, so that the film material forms in the deposition area. Electrospinning can result in the formation of biopolymer-based nanofiber films with high porosity, a high surface-to-volume ratio, and a small pore size. In essence, an electrospun fiber film can be regarded as having hydrophobicity determined by its surface roughness and hydrophilicity determined by the permeability afforded by its porous structure [29]. Due to their micro- and nanoscale roughness and low surface energy, electrospun films generally have high hydrophobicity [30]. The biopolymers used to electrospin continuous nanofiber films have included proteins (gelatin, soy zein, gliadin, marine source proteins) and polysaccharides (chitosan, starch, alginate, cellulose, and cellulose derivatives) [31]. Table 2 lists the preparation methods, hydrophobicity, mechanical properties, and applications of hydrophobic biopolymer-based films.

Deng et al. [32] found a higher WCA for the surface of gelatin/zein (1:1 w/w) nanofibrous films produced by electrospinning (118.0°) than by solvent casting (53.5°). Another study reported a much higher WCA (155.5 ± 1.4°) for films of zein fibers (10% w/w) prepared by electrospinning than for films formed by solvent casting [7].

Polysaccharide and protein mixtures can also be used to prepare films by electrospinning. For example, Liu et al. [33] compared ethyl cellulose/gelatin (1:1 w/w) composite films prepared by electrospinning and by solvent casting. The WCA was higher for the electrospun composite films (113.8°) than for the cast composite films (67.5°). The reason for this difference was attributed to differences in the mechanisms of film formation between the surface-mediated evaporation during electrospinning and solvent-cast drying. In the process of electrospinning, the maximum biopolymer concentration is located at the gas–liquid interface. During solvent evaporation, the gas–liquid interface moves inward, to the center of the droplet [32], meaning that the biopolymer solidifies from the outside to the inside of the droplet. At the same time, the relatively nonpolar outside forces the hydrophobic portions of the protein molecules to face outward, leading to the formation of a hydrophobic surface.

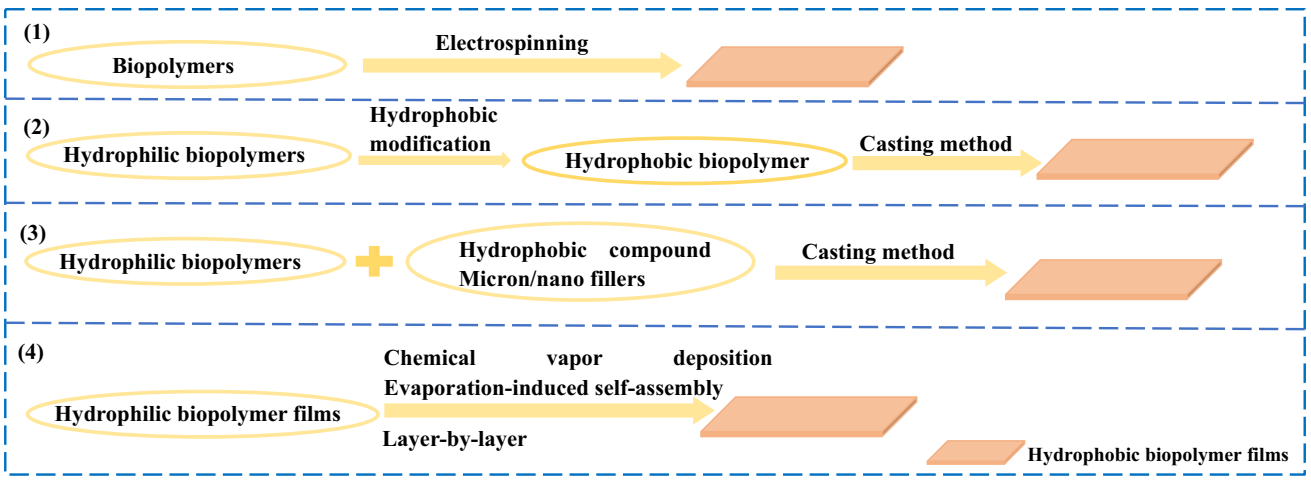

Fig. 2 Four preparation strategies of hydrophobic biopolymer-based films

Table 2 Preparation methods, hydrophobic performance, mechanical properties, and applications of biopolymer-based hydrophobic films

Biopolymers	Additive content	Prepared methods	WCA (°)	WVP ($\times 10^{-10}$ g/m s Pa)	Mechanical properties	Applications	References
Gelatin	Lecithin (0.5% w/w) and thymol (0.5%w/w)	Casting method	106.6	0.719	Tensile strength (TS): 5.22 ± 0.08 MPa Elongation at break (EAB): 104.05 ± 0.93%	Packaging materials	[25]
Gelatin	Zein nanofibrous (50% w/w)	Electrospinning technology	118	ND	ND	Bioactive delivery or controlled release in food	[32]
Ethylcellulose	Gelatin (50% w/w)	Electrospinning technology	113.8	ND	ND	Delivery or controlled release of water-unstable bioactive materials	[33]
Pea protein isolate	Pullulan (50% w/w)	Electrospinning technology	89.8	ND	ND	Delivery system	[34]
Plasma-modified corn starch (containing 30% amylose)	Glycerol (30% w/w)	Casting method	ND	1.0	TS: 7.6 MPa Young´s modulus (YM): 400 MPa EBA: 35%	Packaging materials	[38]
Acylation modified Cellulose nanofibrils	ND	Vacuum filtration	101 ± 2	33.96	TS: 47 MPa EBA: 6.1% Tensile modulus: 2000 MPa	Packaging applications	[39]
Pullulan butylate	ND	Casting	93.5	7.92	TS: 12 MPa EBA: 1.5%	Food packaging	[41]
Modified soy protein by the grafting reaction of methyl methacrylate	ND	Heat compression	ND	94	TS: 19 ± 3.3 MPa YM: 3826 ± 379 MPa EBA: 25.8 ± 3.1%	Food packaging	[43]
Succinylated rapeseed protein isolate (5%)	ND	Casting method	108.68	0.89	TS: 5.02 ± 0.12 MPa EBA: 123.6 ± 4.90%	Food packaging	[44]
Zein	Licorice essential oil (30 wt%)	Casting method	112.50 ± 3.48	0.317	TS: 5.31 ± 0.62 MPa YM: 257.97 ± 31.80 MPa EBA: 2.21 ± 0.38%	Food packaging	[45]
Konjac glucomannan/poly (methyl methacrylate)	Chlorogenic acid (10% w/w, based on konjac glucomannan powder)	Microfluidic spinning technology	89.2	0.041	TS: 14.94 ± 3.86 MPa EBA: 4.88 ± 1.34%	Food packaging	[47]
Gelation	Zein (5% to 40% w/w)	Casting method	60.3–78.3	0.50–1.00	ND	Food packaging	[48]
Fish gelatin	Palm wax (15% w/w)	Casting	116.38 ± 1.14	1.02	TS: 12.58 ± 0.76 MPa YM: 16.64 ± 0.82 MPa EBA: 72.86 ± 2.76%	Food packaging	[50]
Chitosan	Carnauba wax (50% w/w)	Casting	83	2.10	ND	Packaging	[51]
Chitosan	Zein particles (8%)	Casting method	95	ND	TS: 22 MPa EBA: 50%	ND	[53]
Starch	ZnO nanoparticles (5%)	Casting method	117.93	ND	ND	Food Packaging	[54]

Table 2 (continued)

Biopolymers	Additive content	Prepared methods	WCA (°)	WVP ($\times 10^{-10}$ g/m s Pa)	Mechanical properties	Applications	References
Cassava starch	Stealic acid-modified microcrystalline cellulose (2 wt%)	Casting method	75.5	ND	TS: 3.8 MPa Elasticity modulus: 25 MPa	Preservative package materials	[55]
Cassava starch/chitosan/gallic acid	Cellulose nanofibers (cellulose nanofibers/starch ratio 0.1 g/g)	Casting method	95.01	0.64	TS: 10.51 ± 0.13 MPa EBA: 34.04 ± 3.62%	Food packaging	[56]
Artemisia sphaerocephala Krasch. gum	Anionic cellulose nanofiber (mass ratio of *Artemisia sphaerocephala* Krasch. gum and anionic cellulose nanofiber were 19:1)	Casting method	102	~ 3.6	TS: ~ 44 MPa EBA: ~ 56%	Intelligent packaging and gas-sensing label	[57]
Regenerated cellulose	Graphene oxide modified by grafting octadecylamine (2 wt%)	Hot-pressure drying	125.8	1.35	ND	Area of encapsulation package	[58]
Soy protein isolate/oxidized sodium alginate@AgNPs	Aminoclay (8 wt% based on soy protein isolate content)	Casting method	103.3 ± 2.0	ND	TS: 10.9 ± 0.4 MPa Toughness: 12.9 ± 0.3 MJ m^{-3}	Packaging	[59]
Maize starch	Stearic acid (5%), sodium carboxymethyl cellulose (5%)	Casting	ND	1.9–2.5	TS: 5.1–11 MPa EBA: 20%–51%	ND	[68]
Microfibrillated cellulose	Chitosan (3%)	Casting, coated with polypyrrole	122	ND	TS: 21 MPa YM: 1.7 MPa EBA: 1.9%	Food packaging	[69]
Cellulose nanofibrils	Halloysite nanotubes-zinc oxide (1–20 wt%)	Vacuum filtered	155–159	ND	ND	Packaging	[72]
Alginate	Submicron linseed oil	Coating	89.9	3.38	TS: 30.7 ± 4.4 MPa YM: 11.2 ± 2.1 MPa EBA: 26.6 ± 2.3%	Food packaging	[73]
Gelatin	Nisin montmorillonite (3%) and dialdehyde xanthan gum (15%)	Casting	92.7	4.39	TS: 38.7 ± 2.66 MPa YM: 992.82 ± 12.58 MPa EBA: 15.05 ± 2.32%	Food packaging	[74]
Chitosan	Negatively charged graphitic carbon nitride (30%)	Casting	102.38	18.2	TS: 450 MPa EBA: 37%	Antibacterial activity food packaging	[75]
Fish gelatin	Nanoclay (Cloisite Na^+) (5%) and glycerol (0%–20%)	Casting	ND	21.1	TS: 1.7–77.1 MPa EBA: 2.4%–48.5%	Active packaging	[76]
κ-carrageenan and hydroxypropyl methylcellulose	Extract of *Prunus maackii* pomace (8 wt%)	Casting	ND	207	EBA: 43.20 ± 2.07%	Indicating the freshness change of protein-rich foods	[78]

Table 2 (continued)

Biopolymers	Additive content	Prepared methods	WCA (°)	WVP ($\times 10^{-10}$ g/m s Pa)	Mechanical properties	Applications	References
Chitosan	Alizarin (1 wt%)	Casting	70.1	23	TS: 29.1 ± 3.6 MPa Elastic modulus: 1.53 ± 0.5 GPa EBA: 54.4 ± 2.2%	Intelligent packaging	[80]
Cellulose nanofibers	Shikonin (1 wt%)	Casting	73.4	14	TS: 79.4 ± 3.3 MPa	Monitor fish freshness	[82]
Cellulose	Myristic acid (10% w/v)	Solvent-vaporized	130	ND	TS: 188.7 MPa Toughness: 34.4 MJ m^{-3}	Biodegradable packaging materials	[85]
Agar	Clove essential oil (0.5%)	Casting	ND	0.94	TS: 10.16 ± 1.02 MPa EBA: 3.93 ± 0.15%	Food packaging	[98]
2266-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidized bacterial cellulose	Thymol (0.1%)	Vacuum filtration	ND	31.0	TS: 83.92 ± 0.13 MPa EBA: 2.65 ± 0.47%	Commercial shrimp packaging	[99]
Zein/gelatin	Tea polyphenol (7.5 wt%)	Casting	113.70	2.55	TS: 4.61 ± 0.73 MPa YM: 120.57 ± 11.34 MPa EBA: 9.89 ± 1.75%	Fresh fruit and vegetable packaging	[100]
Whey protein	Essential oils (2% w/w)	Casting	73.59	ND	TS: 0.133 ± 0.016 MPa EBA: 1.111 ± 0.011%	Food packaging	[101]
Soy protein isolate	Ferulic acid (4.0 g L^{-1})	Casting	ND	5.34	ND	Extending the shelf life of fresh-cut apples	[102]
Chitosan	Poly(allylamine hydrochloride) (10 wt%)	Casting	115	ND	ND	Drug delivery systems	[103]
Gelatin	Ethylcellulose (25% w/v)	Electrospinning technology	134.7	ND	TS: 0.25 MPa YM: 120.57 ± 11.34 MPa Elastic modulus: 8 MPa	Bioactive encapsulation and controlled release	[105]
Dextran	Zein (25% w/v)	Electrospinning	125.7	ND	TS: 0.4 MPa EBA: 3.49% Elastic modulus: 23.01 MPa	Controlled release of curcumin	[106]
Zein	ND	Electrospinning technology	155.5 ± 1.4	ND	ND	Scaffold in tissue engineering to support cell growth and tissue regeneration	[109]

WCA water contact angle, *WVP* water vapor permeability, *ND* no data

By contrast, in the drying process associated with solvent casting, the relatively nonpolar side forces the hydrophobic compartment of biopolymer molecules to face inward, resulting in a hydrophilic film surface [33]. Therefore, compared with the solvent-casting method, the electrospinning method significantly improves the hydrophobicity of the films.

The hydrophobicity of electrospun biopolymer-based films has also been enhanced by post-treatment of the films. For example, the hydrophobicity of pea protein isolate/pullulan (1:1 w/w) composite nanofiber films was improved by a thermal cross-linking method [34]. The WCAs of the cross-linked films also increased from 38.0 to 89.8°.

Electrospinning is therefore used as a tool for the conversion of natural polysaccharide and protein polymers into hydrophobic nanofiber films. The resulting hydrophobic nanofibers formed by electrospinning are suitable for use in food packaging.

Preparation of Hydrophobic Films Using Hydrophobic-Modified Biopolymers

Biopolymer-based films prepared with hydrophilic polymers generally do not have hydrophobic properties. However, hydrophobic modification of hydrophilic polymer molecules can result in prepared films that clearly exhibit hydrophobic properties.

Hydrophobic Modification of Polysaccharide-Based Films

The preparation of starch-based films using starch hydrophobically modified by acylation or plasma modification is one way to improve the hydrophobicity of starch-based films. Acetylation modification has been widely used because of its strong enhancement of the hydrophobicity of starch and starch-based films. Compared to native rice starch films, the weight loss of acetylated native rice starch films was reduced from 16 to 9% during 2 weeks of incubation [35], largely due to the hydrophobicity and steric bulkiness imparted by the acetyl groups to the rice starch.

Hexamethyldisiloxane is a popular acetylating compound, as it is sufficiently volatile at near room temperature, relatively nontoxic, inexpensive, and commercially available. Films that are plasma polymerized with hexamethyldisiloxane can be used in different fields for many applications, such as barrier films for food and drug packaging and coatings for biocompatible materials [36, 37]. Hexamethyldisiloxane plasma treatment has been used to form a layer of hexamethyldisiloxane on starch granules to improve the hydrophobic property of starch-based films. Compared to native corn starch films, starch films prepared by plasma-modified corn starch show WVP decreases of about 50%, from 2.6 to 1.2 g/m s Pa [38]. This difference indicates that the presence of hydrogen bonds caused by starch oxidation and the higher helical order after the plasma treatment could restrict the migration of water molecules. It also suggests that the starch obtained after plasma treatment differed in its amylose content and could be used to develop soft or rigid packaging materials with good hydrophobicity.

The development of hydrophobically modified cellulose-based films has also received increasing attention. Cellulose fibers have excellent hydrophilic properties, but their hydrophilicity can be reduced by chemical modification with hydrophobic compounds. The preparation of hydrophobic films using hydrophobically modified cellulose is a simple strategy. Currently, cellulose acetate films have been commercialized for food packaging because they can maintain superior oxygen permeability and keep stored foods fresh. Li et al. [39] obtained hydrophobic cellulose nanofibril films by attaching 10-undecylenoyl chloride to cellulose nanofibrils. They found that the WVP value was 62.4% lower for the modified cellulose nanofibril films than for pristine cellulose nanofibril films. This difference could reflect the low surface energy of the nonpolar long aliphatic chains, which would give the modified cellulose film superior hydrophobicity, making them promising materials for packaging applications.

Cellulose-based films with enhanced hydrophobicity have also been prepared using cellulose modified with epoxidized soybean oil [40], resulting in increases in the WCA from 27.9 to 137.5° as the concentration of epoxidized oil increased from 0% (w/w) to 40% (w/w). This modification replaces a cellulose hydroxyl group with a long-chain hydrophobic alkane from the epoxidized soybean oil, thereby reducing the surface polarity and improving the film hydrophobicity.

Generally, the hydrophobic properties of pullulan-based films are improved by pullulan esterification. Niu et al. [41] used pullulan butylate casting to obtain novel hydrophobic films for fruit preservation. The WCA was higher for the pullulan butylate films (93.5°) than for pure pullulan films (32.1°) because esterification replaced the hydroxyl groups in the pullulan polysaccharide molecules with hydrophobic alkenyl groups. In short, polysaccharide-based films exhibit excellent hydrophobicity when hydrophobic groups are grafted onto the polysaccharide molecules.

Hydrophobic Modification of Protein-Based Films

Protein-based films have received considerable attention due to their excellent film-forming ability, low cost, and good barrier properties. However, most natural protein-produced films are brittle and hydrophilic. Therefore, many studies have explored ways to improve the hydrophobicity of protein-based films by modifying the proteins by different processes, including esterification, succinylation, and

grafting. For example, zein was modified by esterification with a small amount of *para*-toluene sulfonic acid at 55 °C to replace amide and carboxylic acid functional groups with methyl esters [42]. Films prepared from the esterified zein did not become soft, and their color did not change after soaking in water for 12 h, whereas non-modified zein films became completely opaque and soft. This result showed that the zein esterification modification could improve the water repellency of zein-based films.

González and Alvarez Igarzabal [43] modified soy protein by grafting methyl methacrylate with a grafting degree of 27.04%, followed by film preparation by heat compression. The WVP decreased from $19.9 \pm 0.7 \times 10^{-11}$ for unmodified soy protein films to $9.4 \pm 1.3 \times 10^{-11}$ kg m Pa^{-1} s^{-1} m^{-2} for the grafted films, with significant reductions observed in the swelling and water solubility of the soy protein-grafted methyl methacrylate films ($p < 0.05$). The enhanced hydrophobic character of the grafted films was directly attributed to the presence of poly(methyl methacrylate). He et al. [44] prepared a succinylated rapeseed protein isolate using 5% w/w succinic anhydride and used it to form protein films. Succinylation decreased the WVP value of the films from 0.77 to 0.32 g mm/(h m^2 kPa) and increased the WCA from 77.66 to 108.68° compared to the control rapeseed protein film. Therefore, succinylation is an effective method for improving the hydrophobicity of natural biopolymer films. The hydrophobic modification strategy is effective for improving film hydrophobicity, but the safety of using hydrophobically modified hydrophobic films for food packaging still requires further study.

Preparation of Biopolymer Films by Adding Hydrophobic Compounds and Micro/Nanofillers

Generally, the hydrophobicity of biopolymer-based films is enhanced by adding hydrophobic substances (e.g., essential oils, polyphenols, and waxes) or micro/nanofillers.

Adding Natural Essential Oils

Luís et al. [45] dissolved zein in 80% ethanol and obtained zein films by the casting method. They then added licorice essential oil (30% g essential oil/g dry zein powder) to the zein films to generate a layered surface morphology similar to that of a lotus leaf, and they found an increase in the WCA from 81.95 ± 8.74° for unmodified zein films to 112.50 ± 3.48° for the zein-based films treated with essential oil. Similarly, the WVP of a gellan gum/citrus pectin composite film was decreased from $8.72 \pm 0.19 \times 10^{-11}$ to $4.78 \pm 0.35 \times 10^{-11}$ g m^{-1} s^{-1} Pa^{-1} by adding 0.03% v/v clove essential oil and 0.1% v/v Tween 80, while Young's modulus decreased from 640.8 ± 76.8 to 500 ± 60.6 MPa [46]. The addition of thymol nanoemulsions to gelatin films increased the WCA of the films from 74.2 to 106.6° [25]. Many studies have found that incorporating essential oil emulsions into biopolymer-based films can also improve the stability and activity of the essential oil components.

Adding Naturally Occurring Hydrophobic Compounds

Natural compounds, such as polyphenols, can be added to biopolymer-based films to increase their hydrophobicity. For instance, the WVP value was lower for a konjac glucomannan/poly(methyl methacrylate) food packaging film containing chlorogenic acid, fabricated by microfluidic spinning ($1.47 \times 10^{-5} \pm 0.11$ g/(m h kPa)) than for an unmodified control film ($1.66 \times 10^{-5} \pm 0.15$ g/(m h kPa)) [47].

Zein, as a hydrophobic alcohol-soluble protein, is widely used in the preparation of hydrophobic biopolymer-based films, as it can be directly prepared into films (see "Natural Protein-Based Films" section). Zein can also be added to other biopolymer-based films to improve their hydrophobicity. Ahammed et al. [48] found that zein enhanced the hydrophobicity of gelatin films, while decreasing their solubility in water from 100 to 30% for films with a zein content of 40%. The addition of 10% corn zein to cellulose nanocrystal films also improved the water vapor barrier property of the films [49], decreasing the WVP from 70 to 30 g/m^2·day.

Waxes, such as palm and carnauba waxes, tend to reduce the WVP and solubility when added to biopolymer-based films. Increasing concentrations of palm wax (0–60%) were shown to promote significant decreases in the swelling of gelatin/palm wax films from 430.41 ± 14.89% to 201.07 ± 5.44% ($p < 0.05$) [50]. Similarly, the inclusion of carnauba wax (40%) in a chitosan film decreased the WVP from 2.73 to 0.77 g mm/h kPa m^2 [51]. This is because the solid lipid component caused substantially greater perturbations in the biopolymer-based film matrix and created voids at the biopolymer–wax interface [52].

Adding Micro/Nanofillers

In recent years, the excellent reinforcing effect of nanoparticles and micro/nanofibers when used as fillers in hydrophobic biopolymer-based films has drawn much attention. Zein nanoparticles (500–800 nm) have been blended with biopolymers like chitosan to fabricate hydrophobic composite films. The WCA increased from 75° for pure chitosan films to 95° for chitosan-based films containing 8% zein particles [53]. Chitosan films containing both 4% palygorskite nanoclay and 8% zein particles showed WCAs greater than 100°, indicating a synergistic enhancement of the hydrophobicity of the composite films by the two fillers.

ZnO nanoparticles have been widely applied to produce highly hydrophobic or superhydrophobic biopolymer-based films because of the high specific surface area of these

nanoparticles. Ni et al. [54] added ZnO nanoparticles (2.0 wt%) to a starch solution used to cast hydrophobic starch-based films and found that the WCA increased from 85.73° for neat starch films to 121.45° for films containing ZnO nanoparticles.

Chen et al. [55] added stearic acid-modified microcrystalline cellulose and cellulose nanofibers as hydrophobic materials to polysaccharide-based films to increase their hydrophobicity. As the concentration of stearic acid-modified microcrystalline cellulose increased from 0% w/w to 2.0% w/w, the WCA of the composite cassava starch films increased from 44.9 to 75.5°. This increase in WCA was essentially ascribed to the addition of the modified microcrystalline cellulose. Zhao et al. [56] added cellulose nanofibers (10% w/w) to cassava starch/chitosan/gallic acid bioactive films to improve the moisture resistance of the films. The WCA of the films increased from 68.23° for the films without nanofibers to 94.94° for the films with added cellulose nanofibers. Liang and Wang [57] reduced the water sensitivity of a gum-based film by adding anionic cellulose nanofibers and demonstrated a WCA of the composite films of up to 102°. They attributed this change to the hydrophobicity of the anionic cellulose nanofibers.

Modified nanosheets and nanoclays can also be added to biopolymer-based films to improve their hydrophobicity. Xu et al. [58] added octadecylamine-grafted hydrophobic graphene oxide nanosheets to regenerated cellulose nanocomposite films to enhance their water vapor barrier performance. The WVP decreased from 1.71×10^{-12} for the pure regenerated cellulose films to 1.35×10^{-12} g cm cm^{-2} s^{-1} Pa^{-1} for the regenerated cellulose nanocomposite films loaded with the nanosheets. The results indicated that the hydrophobically modified graphene oxide nanosheets effectively restricted water vapor diffusion.

The addition of plate-like aminoclay (8% w/w) to soy protein isolate/oxidized sodium alginate/silver nanoparticle films to produce hydrophobic films [59] also significantly increased the WCA from 65° for the control films to 103.3° ± 2.0° for the aminoclay modified films. This addition of aminoclay was a simple way to improve the hydrophobicity of natural polymer films by adding hydrophobic compounds and micro-nano fillers. However, the migration and safety of added hydrophobic additives in natural biopolymer-based films used as food packaging must be confirmed.

Hydrophobic Modification of Biopolymer-Based Films

Chemical Modification of Biopolymer-Based Film Surfaces

Table 3 lists the WCA values and modification methods used to prepare hydrophobic biopolymer-based films. The feasibility of improving the hydrophobicity of biopolymer-based films by chemical grafting has been confirmed in practice. Chemical grafting onto the surface of biopolymer-based films improves their hydrophobicity while also retaining the inherent advantages of the films. Qiao et al. [60] grafted alcohols of different chain lengths (hexanol, dodecanol, and stearyl alcohol) onto the surfaces of starch-based films and found greater improvements in the film surface hydrophobicity with increasing alkyl chain length. Specifically, the surface hydrophobicity improved from 55.7° for the control films to 92.7° for starch films grafted with stearyl alcohol.

Zhang et al. [61] prepared starch/tea polyphenol nanofibrous films using a temperature-assisted electrospinning method, followed by glutaraldehyde gas-phase cross-linking to increase the film hydrophobicity. A reaction between the hydroxyl group of the starch molecules on the surface of the films and the aldehyde group in glutaraldehyde promoted the formation of multiple ether bond/acetal ring-bridged cross-linked networks. The WCA increased from approximately 17.5° for the uncross-linked films to approximately 87.2° for the cross-linked films.

Physical Modification of Biopolymer-Based Film Surfaces

The most common methods used to impart hydrophobicity to biopolymer-based films are chemical vapor deposition, evaporation-induced self-assembly, layer-by-layer deposition, and ultrasonic treatment. All these methods essentially construct a hydrophobic coating on the hydrophilic surface of the biopolymer-based films.

Table 3 Methods for hydrophobically modifying films and water contact angle (WCA) of the films

Biopolymer-based films	Modification	WCA (°)	References
Starch-based film	Alkanol surface grafting	92.7	[60]
Starch/tea polyphenols nanofibrous films	Glutaraldehyde gas-phase cross-linking method	~87.2	[61]
Hydrophobicity sodium alginate/poly(vinyl alcohol)/palygorskite nanorods film	An in-situ surface coating with methyltrichlorosilane	111.8	[63]
Bacterial cellulose-zein composite nanofiber films	Evaporation-induced self-assembly of adsorbed zein	110.5	[65]
Gellan gum/amino-functionalized tannin derivative)/anionic iota-carrageenan film	Layer-by-layer deposition	127 ± 18	[66]
Cellulose nanofibers/cationic poly-l-lysine/anionic carnauba wax particles film	Layer-by-layer deposition	138	[67]

A hydrophobic coating can be constructed on a biopolymer-based film by adjusting the film surface chemistry. One simple, economical, and effective method for creating a hydrophobic surface is chemical vapor deposition, which can achieve the desired modification without significantly affecting the performance of the film [62]. Ding et al. [63] prepared hydrophobic sodium alginate/poly(vinyl alcohol)/palygorskite nanorod films by coating the film surface with methyltrichlorosilane by a vapor deposition–surface polycondensation reaction. The WCA was significantly higher in the film with the hydrophobically modified surface (111.8°) than in the control film (72.7°). The alginate-based film used for the modification step has potential for use as food packaging; however, the safety of the methyltrichlorosilane modifier has not been evaluated.

The microstructure formed by the self-assembly method is also generated on the surface of biopolymer-based films to increase the surface roughness, thereby increasing the film's surface hydrophobicity. Zein, which is soluble in an ethanol–water mixture, forms a variety of microstructures, such as spheres, when the solvent evaporates [64]. Therefore, the hydrophobicity of the surface of the film can be improved by modulating the evaporation-induced self-assembly of zein. Wan et al. [65] prepared bacterial cellulose-zein composite nanofiber films with high hydrophobicity by the evaporation-induced self-assembly of adsorbed zein. The WCA was higher for the bacterial cellulose-zein composite nanofiber films (110.5° at 0.5% w/w zein) than for bacterial cellulose films (below 30°). The evaporation-induced self-assembly method also increased the film's hydrophobicity without changing its internal structure or mechanical properties.

The layer-by-layer deposition method is a low-cost, controllable, and versatile choice for the surface modification of biopolymer-based films, including surface hydrophobicity. Layer-by-layer deposition has also been widely used to construct multilayer polyelectrolytes, and nanoparticles have also been incorporated into the coating for the construction of multilayer films. For example, Rufato et al. [66] alternately deposited a natural polycationic polymer (an amino-functionalized tannin derivative) and an anionic iota-carrageenan on a gellan gum film. They found that the WCA increased from 94° for the pure gellan gum films to 127° for the polyelectrolyte multilayer films. Similarly, Forsman et al. [67] deposited cationic poly-lysine and anionic carnauba wax particles, layer by layer, onto the surface of cellulose nanofiber films. The result was the creation of superhydrophobic films that showed increases in WCA from 34° for single cellulose nanofiber films to 138° for the 2-layer films.

Ultrasonic treatment can also enhance the hydrophobic properties of biopolymer-based films. Liu et al. [68] used ultrasonic treatment to improve the moisture barrier properties of maize starch/stearic acid/sodium carboxymethyl cellulose composite films. The WVP value declined from 2.50×10^{-12} g cm cm^{-2} s^{-1} Pa^{-1} for the control sample (without sonication) to 1.90×10^{-12} g cm cm^{-2} s^{-1} Pa^{-1} for the ultrasonically treated composite films.

Properties of Hydrophobic Biopolymer-Based Films

In addition to their hydrophobic properties, hydrophobic biopolymer-based films may also have other useful characteristics, such as barrier functions against oxygen and ultraviolet rays, consistent mechanical properties, pH responsiveness, self-cleaning capability, and antimicrobial and antioxidant activities. These other characteristics also make hydrophobic biopolymer-based films highly useful in food packaging, as carriers of active ingredients, and in biomedicine (Fig. 3).

Barrier Properties

The aim of food packaging is to extend the shelf life of foods; therefore, biopolymer-based films used as food packaging materials must have good barrier properties to block out water vapor, oxygen, and ultraviolet (UV) rays.

Gao et al. [69] used microfibrillated cellulose, chitosan, and polypyrrole to prepare bioactive films that could block oxygen and water vapor. The WCA increased from 90° (pure microfibrillated cellulose films) to 122° for the microfibrillated cellulose/chitosan/polypyrrole films. Moreover, the oxygen transmission rate measured at 23.1 °C and

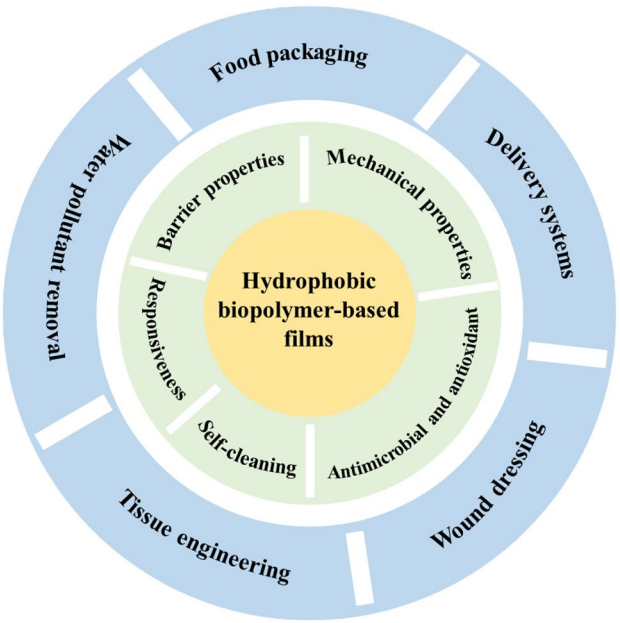

Fig. 3 Functional characteristics and applications of hydrophobic biopolymer-based films

55% relative humidity (RH) decreased from 566.76 cm^3 (m^{-2} day^{-1}) for the microfibrillated cellulose/chitosan films to 32.38 cm^3 (m^{-2} day^{-1}) for the microfibrillated cellulose/chitosan/polypyrrole films, suggesting that the oxygen barrier property of the composite films was improved after adding chitosan and further improved by adding polypyrrole. Similarly, an inorganic–organic copolymer coating on cellulose nanofiber films significantly increased the oxygen barrier properties and hydrophobic properties of the films. The oxygen transmission rate at 80% RH decreased from 107 cc/m^2/day for the uncoated cellulose nanofibril films to 51 cc/m^2/day for glyceryldimethacrylate silane-coated cellulose nanofibril films. The water vapor transmission rates at 23 °C and 50% RH decreased from 990 g/m^2/day for the uncoated film to 230 g/m^2/day for the coated cellulose nanofibril films [70].

Erdem and Kaya [71] prepared soybean protein isolate films containing sunflower oil by a freeze-drying method. They found that the WVP at 75% RH and 24 °C decreased from 1.69 g mm m^{-2} h^{-1} kPa^{-1} for the control film to 1.17 g mm m^{-2} h^{-1} kPa^{-1} for the film containing 0.15% w/v sunflower oil. The oxygen permeability at 25 °C decreased from 0.7 cm^3 mm m^{-2} h^{-1} atm^{-1} for the control film to 0.53 cm^3 mm m^{-2} h^{-1} atm^{-1} for the composite film. These results confirmed that the addition of oil improved the hydrophobicity and barrier performance of protein-based films. In summary, hydrophobic films have been shown to be very effective at blocking water vapor and oxygen when used in food packaging.

UV rays can cause oxidation and deteriorative chemical reactions that can destroy the quality of foods; therefore, an essential feature of packaging films is that they block UV rays. Hu et al. [72] developed cellulose nanofibril/halloysite nanotube-zinc oxide hybrid hydrophobic films that achieved high UV-blocking efficiency for UV-A (95.7%), UV-B (98.7%), and UV-C (99.8%) wavelengths. The uniform dispersion of zinc oxide in the polymer matrix and the strong interfacial bonding between zinc oxide and the matrix were the key factors that improved the ultraviolet ray shielding effect of zinc oxide. In addition, the excellent ultraviolet ray shielding performance is also attributed to the hydrogen-bonding interaction between cellulose nanofibril and halloysite nanotube-zinc oxide.

Alginate-based films prepared with a coating of drying submicron linseed oil showed enhanced water vapor barrier properties and UV absorption [73]. The WVP decreased from 2.86 g/mm/m^2/day/kPa for uncoated films to 2.14 ± 0.10 g/mm/m^2/day/kPa for films coated with a submicron thickness of linseed oil. The pure alginate films absorbed UV below a wavelength of 230 nm, whereas the coated films demonstrated strong UV absorption below about 320 nm. This characteristic of alginate film is attributed to the strong connection between phenolic compounds and alginate, which can maintain the UV absorption capacity of alginate for prolonged periods.

Ge et al. [74] developed UV-absorbing gelatin-based films by adding nisin, montmorillonite, and dialdehyde xanthan gum (as the cross-linking agent) and found a broadening of the wavelength range of light from 200–238 nm (films not cross-linked) to 200–345 nm (films cross-linked using dialdehyde xanthan gum). This broadening was due to the C = N bond produced by the Schiff base reaction between gelatin and dialdehyde xanthan gum.

All these UV-absorbing films have potential applications in food packaging, as they can protect foods from UV damage.

Mechanical Properties

The application of natural biopolymer-based films in food packaging is limited by their poor mechanical properties. Therefore, natural extracts and micro/nanofillers have been added to biopolymer-based films, both to improve the film hydrophobicity and to enhance the mechanical properties. Zhang et al. [61] added tea polyphenols to starch to fabricate electrospun nanofibrous starch films with improved mechanical properties. The tensile strength of the films increased from 0.67 to 1.45 MPa as the tea polyphenol concentration increased from 0 to 10 wt%. Table 2 lists the hydrophobicity, preparation methods, and potential applications of several biopolymer-based films with excellent mechanical properties.

A chitosan/negatively charged graphitic carbon nitride bionanocomposite was fabricated by Ni et al. [75], who showed that the negatively charged graphitic carbon nitride improved the mechanical properties of chitosan films. The tensile stress of the bionanocomposite films increased from ~ 180 kPa for neat chitosan films to ~ 450 kPa for films made from a composite in which 30% of the chitosan weight was negatively charged graphitic carbon nitride. The increased tensile stress could reflect the electrostatic interactions between the negatively charged graphitic carbon nitride and the positively charged chitosan.

The addition of aminoclay to soy protein isolate-based films was shown to improve the hydrophobic properties of the films while also enhancing their mechanical properties [59]. The results of mechanical tests showed that the tensile strength of the films was increased from 5.0 MPa for the soy protein isolate/oxidized sodium alginate@AgNPs films to 10.9 MPa for films containing 8 wt% aminoclay (based on soy protein isolate content). This improvement was attributed to the cross-linking and hydrogen-bonding interactions between the soy protein isolate, oxidized

sodium alginate, and aminoclay. Incorporating nanoclays into gelatin films appears to be another promising modification that improves their hydrophobic properties and mechanical strength [76].

pH Responsiveness

In our previous summary, we introduced details about using the pH responsiveness of starch-based films to monitor changes in food quality [77]. Of course, films prepared using biopolymers other than starch, such as sodium alginate, chitosan, pectin, and gelatin, also exhibit pH responsiveness. Natural biopolymer-based films with pH responsiveness often change color in response to pH changes. This capacity for change is usually introduced by the addition of a natural pigment to hydrophobic biopolymer-based films.

Anthocyanins are common byproducts derived from extracts of food waste. Anthocyanins added to films can serve as pH indicators while also improving film hydrophobicity. For example, a composite containing κ-carrageenan, hydroxypropyl methylcellulose, and an extract of *Prunus maackii* pomace has been used to prepare pH-responsive films [78]. The WVP was reduced from 2.60 g m^{-1} s^{-1} $Pa^{-1} \times 10^{-12}$ in the control films to 2.07 g m^{-1} s^{-1} $Pa^{-1} \times 10^{-12}$ in films containing 8% *P. maackii* pomace extract. These pH-responsive films demonstrated the potential to indicate changes in the freshness of protein-rich foods. When the pH value changed from 2 to 12, the color of the composite film changed from peach to grayish-green. The aromatic rings in the anthocyanins also blocked the penetration of water molecules into the biopolymer-based films [79].

Alizarin has recently been used as a new option for monitoring pH changes and for improving the hydrophobic performance and functional properties of biopolymer-based films. For example, Ezati and Rhim [80] used alizarin to develop pH-sensitive chitosan films. They showed that the color of the chitosan-based films changed from slightly yellow to purple in response to a pH change in the range of 4–10. The addition of alizarin also improved the hydrophobicity of the chitosan-based films and increased their WCA from 64.3 to 70.1°.

Shikonin is a widely used alcohol-soluble pigment that is recognized as a powerful substance used in herbal medicine [81]. The naphthazarin moieties of shikonin have high chemical reactivity with acids and bases, turning red at low pH and blue at high pH, making shikonin useful as a pH indicator. Cellulose nanofiber-based films containing shikonin (1 wt%) were pH-responsive and had enhanced surface hydrophobicity [82]. The films were reddish-pink at a pH below 7 and turned reddish-purple, purple, and light blue as the pH increased from 7 to 12. The WCA increased from 59.3° for neat cellulose nanofiber films to 73.4° for the pH-responsive films.

Self-cleaning Performance and Easy Package Emptying Properties

For many years, the self-cleaning function of the lotus leaf, that is, the fact that dust and dirt on the leaf surface are washed away by the leaf itself—the lotus effect—has been of interest to researchers around the world. The recognition that this lotus leaf effect is caused by micro- and nanostructures on the leaf surface [83] has led to the fabrication of superhydrophobic natural biological polymer films based on the lotus leaf effect, and the versatility of these films has expanded. Although the main function of food packaging is to contain and protect foods, the food remaining on the packaging after emptying may lead to food waste [84]. Therefore, package emptying properties are important for food packaging.

Chen et al. [85] showed that cellulose/myristic acid composite films fabricated by a solvent-vaporization method had high hydrophobicity (WCA = 132°) and outstanding self-cleaning and easy package emptying properties. Specifically, dust attached to the films could be washed away with water, and the WCAs for cola, mango juice, yogurt, milk, soy sauce, and vinegar were 128 ± 1°, 130 ± 1°, 123 ± 1.3°, 123.4 ± 1.2°, and 117.1 ± 2°, respectively. These properties were consequences of the synergistic effects of the gap between the low surface energy of the myristic acid crystals, the interstitial space between microplates, and the micro-nano-binary film structure. Cai et al. [86] demonstrated that stearic acid self-assembled starch nanofibrous films had excellent self-cleaning capability. Their wettability measurement results suggested that starch nanofibrous films coated with stearic acid were hydrophobic, with a high WCA of ~134.7°. Their simulated hydrophobicity tests showed that the water beads freely scrolled in various directions along the films—a crucial parameter for self-cleaning packaging.

Huang et al. [87] manufactured galactomannan/graphene oxide films with superior gas barrier and self-cleaning properties for food packaging. The WVP and oxygen permeability decreased from 5.82 g·mm·m^{-2}·day^{-1}·kPa^{-1} and 0.39 mL·μm·m^{-2}·day^{-1}·kPa^{-1}, respectively, for the control films to 3.33 g·mm·m^{-2}·day^{-1}·kPa^{-1} and 0.11 mL·μm·m^{-2}·day^{-1}·kPa^{-1}, respectively, for films with 5% w/w graphene oxide. Apjok et al. [88] prepared a cellulose-chitosan-Ag/TiO_2 nanocomposite film with self-cleaning and easy package emptying properties for use as a butter packaging material. The WVP was 0.63×10^{-10} for the cellulose-chitosan-TiO_2 film and 0.68×10^{-10} g/m s Pa for the cellulose-chitosan-Ag/TiO_2 nanocomposite film. After storage for 6 months, the appearance of the cellulose-chitosan-Ag/TiO_2 nanocomposite film packaging was clean, while the cellulose-chitosan film and cellulose-chitosan-TiO_2 film had oil spots.

The self-cleaning property of films is improved by the use of superhydrophobic coatings, which in turn improves the safety and hygiene of packaged food [89]. A starch nanoparticle/polydimethylsiloxane composite coating exhibited superhydrophobicity (WCA > 152.0°) and self-cleaning properties [90] due to the hierarchical micro and nanostructures formed by coralloid starch nanoparticle aggregates combined with the low surface energy of the polydimethylsiloxane covering. Coffee and milk powder on film-coated glass substrates were quickly removed by rolling water droplets. In addition, the oil–water separation efficiency remained above 99.8% after 25 separation cycles.

Highly hydrophobic natural biopolymer films with easy package emptying properties are essential for use in various food packaging scenarios to avoid the waste of packaged foods. However, only a few biopolymer-based films with the desired superhydrophobicity and self-cleaning functions have been reported. Therefore, more research on self-cleaning biopolymer-based films is needed to expand their potential applications in food packaging, electronics, wound dressings, and other areas where waterproofing and antifouling are required [91].

Antimicrobial and Antioxidant Properties

Biopolymer-based films that are used in food packaging, in active substance delivery, and as wound dressings require antibacterial and antioxidant properties in addition to hydrophobicity. These properties can often be improved by the incorporation of hydrophobic compounds into biopolymer films. The compositions, preparation methods, and WCA values of the antimicrobial and antioxidant films mentioned in this section are listed in Table 2. These biopolymer-based films have hydrophobic, antibacterial, and antioxidant properties.

The addition of chitosan and polypyrrole, which have antioxidant properties, to microfibrillated cellulose films enhanced the oxidation resistance of the films [69]. Pure microfibrillated cellulose films inhibited oxidation, as determined by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay, by 3%, whereas the microfibrillated cellulose/chitosan/polypyrrole films inhibited the oxidation of DPPH by 54%. Luís et al. [45] fabricated zein-based functional films with good antioxidant and antibacterial activities by incorporating licorice essential oil into the films. The results of a β-carotene bleaching test indicated higher percentages of inhibition for the films containing licorice essential oil (22.36%) than for the zein films alone (5.91%). The antibacterial activity, demonstrated by the diameters of the inhibition zones for *Listeria monocytogenes* LMG 16,779, was increased from 6.64 mm for the control film to 8.64 mm for the film containing licorice essential oil. The zein-based films containing licorice essential oil can inhibit both lipid peroxidation and the growth of foodborne pathogens, making them useful as alternative food packaging systems, especially in foods with high lipid content. Licorice essential oil also showed selective effects on *Enterococcus faecalis* and *L. monocytogenes*. The film containing licorice essential oil had the potential to prevent biofilm formation, which may reflect the inhibition of growth and suppression of bacterial cell adhesion to the film surface [92].

Cinnamon essential oil improved the hydrophobicity and antibacterial activity of cellulose nanofiber films. The addition of 3% cinnamon oil increased the hydrophobicity of the film, as indicated by a WCA of 92.36° [93]. The formation of strong glycosidic bonds and intramolecular and intermolecular hydrogen bonds between *Euchema cottoni* seaweed, cellulose nanofibers, and cinnamon oil extract following the incorporation of cinnamon oil extract into the matrix network resulted in the formation of an antibacterial film.

Essential oils with phenolics as the main compounds have the highest activity against microorganisms and the broadest spectrum of activity [94]. Therefore, cinnamon oil, with cinnamaldehyde as its main component, has excellent antibacterial activity. Biopolymer films containing cinnamon oil showed good inhibitory activity against *Staphylococcus aureus* and *Escherichia coli*, giving inhibitory zone diameters of 26.94 ± 9.4 mm and 30.28 ± 0.46 mm, respectively. Cinnamon oil and its phenolic compounds have demonstrated the potential to inhibit the initial biofilm formation of *L. monocytogenes* and other pathogens [95]. Therefore, films with antibacterial and antioxidant activities have the potential to serve as packaging specifically for foods with high lipid contents.

Applications of Hydrophobic Biopolymer-Based Films

Hydrophobic biopolymer-based films with excellent mechanical properties, barrier properties, antibacterial properties, and antioxidant properties have tremendous potential for use as active food packaging materials, as functional ingredient delivery carriers, in tissue engineering, and as wound dressings [96].

Active Food Packaging Materials

Recently, hydrophobic biopolymer-based films have received increasing attention as active food packaging materials for many foods, including fruits, vegetables, seasoning, fish fillets, shrimp, salami, and cakes. As defined in European Regulation (EC) No. 450/2009, active packaging materials are intended to extend the shelf life or to improve the condition of packaged food (European Commission 2009). Hydrophobic bioactive packaging materials can achieve this

due to their antibacterial, antioxidant, and pH-responsive properties. Hydrophobic biopolymer-based films reduce the water loss of fresh fruits and vegetables, but can also prolong their shelf life. The hydrophobic characteristics of several of these films are summarized in Table 2.

Niu et al. [41] showed that pullulan butylate films can function as effective edible films that can extend the shelf life of strawberries and delay their ripening and senescence. These films had low WVP (0.792×10^{-11} g/m s Pa) and low oxygen permeability (0.625×10^{-3} g/m^2 s) properties. In their study, strawberries in the control group rotted by the eighth day, while the pullulan ester film-coated strawberries maintained good hardness.

Chitosan is a biopolymer known for its antibacterial and antifungal properties, and it can also be widely applied in fruit packaging as chitosan-based films that form a protective layer on fruits and vegetables. In one study, the addition of glycerol (30% w/w) increased the WCA of chitosan film from 50 to nearly 120°, indicating a substantial increase in film hydrophobicity. Strawberries coated with the chitosan/glycerol films showed resistance against gray fungus attacks [97]. Similarly, microfibrillated cellulose/chitosan/polypyrrole films showed improved antioxidant properties, antibacterial properties, and oxygen barrier properties, and increased WCA of up to 122° [69]. These hydrophobic composite films were used for the active packaging of fresh cherry tomatoes (10 days), effectively extending their shelf life and delaying their ripening.

Seafood products, such as fish and shrimp, are common perishable foods, and some biopolymer-based films have been developed for the active packaging of these products to reduce microbial reproduction. Agar films with incorporated clove essential oil were prepared by Rocha et al. [98] to improve the shelf life of flounder fillets. The addition of clove essential oil improved the hydrophobicity of the films. Fillets produced lower volatile bases when covered with films containing clove essential oil (25.39 mg total volatile basic nitrogen/100 g) than with the control film (33.97 mg total volatile basic nitrogen/100 g, pH 7.11), and showed stable pH values (pH 6.76) until day 10.

Bacterial cellulose films oxidized with 2,2,6,6-tetramethylpiperidine-1-oxyl radical and containing thymol and anthocyanin-rich purple potato extract were prepared by Wen et al. [99] to extend the shelf life of shrimp. The composite films exhibited excellent antibacterial and antioxidant properties. The bacterial counts for the shrimp coated with control film (2,2,6,6-tetramethylpiperidine-1-oxyl radical-oxidized bacterial cellulose/anthocyanin-rich purple potato extract film lacking thymol) reached 7.8 log CFU/g after 24 h, whereas the log CFU/g value for films containing thymol was 6.5 after 40 h of storage.

Protein-based films have also been used in food packaging to suppress the rapid browning of fresh fruits and weight loss of vegetables, salami, and cakes. For example, Xia et al. [100] prepared multilayer zein/gelatin films containing tea polyphenols for application to freshly cut fruits. The maximum WCA of the composite films at 60 s was 105.23°. The gelatin side of the multilayer films presented a nonporous and tight surface, which strengthened the water resistance of the film surface. The results suggested that these multilayer films could control oxidative discoloration and enhance the color stability of fresh avocados.

Whey protein active films incorporated with essential oils have also shown potential applications in reducing lipid oxidation [101]. Among them, the films containing 1% w/w and 2% w/w essential oils had the strongest hydrophobicity and the lowest water solubility. The hexanal content of salami after 180 days of storage decreased from 1200 µg/100 g when packaged with control film to 100 µg/100 g when packaged with whey protein films containing a 5% essential oil blend.

Alves et al. [102] used soy protein isolate and ferulic acid to prepare edible films and to extend the shelf life of fresh-cut apples. After 7 days of storage at 10 °C and 50% RH, the weight loss of uncoated fresh-cut apples was 26.5%, while the weight loss of fresh-cut apples coated with soy protein isolate and ferulic acid films was only 9.5%.

Erdem and Kaya [103] found better textural results for cakes wrapped with composite films made from soy protein isolate and sunflower oil and freeze-dried than for uncoated cakes. Therefore, the application of hydrophobic biopolymer-based films to fruits, vegetables, and cakes has been demonstrated to be considerably effective at reducing moisture loss and preserving the structure of food during storage.

Controlled Release of Functional Ingredients

Recent drug research on bioactive ingredients and their applications has frequently used delivery systems based on natural biological macromolecules. These potential carriers can deliver bioactive compounds to specific cells and tissues while eliciting only minimal immune responses. Films prepared with natural polymers can be used as carriers of active substances and drugs, and can provide a slow release of their payloads. Hydrophobic biopolymer-based films repel water; therefore, they will show reduced swelling in aqueous environments, leading to the controlled release of active substances and drugs.

Chitosan/poly(allylamine hydrochloride) composite films fabricated by Sarwar et al. [104] as smart drug (ciprofloxacin hydrochloride monohydrate) delivery matrices showed a relatively reduced drug release (85%, 50 min) in simulated gastric fluid (pH = 1.2) and a maximum drug release (98%, 120 min) in phosphate-buffered saline (pH = 7.4). This result indicated that blended films have excellent potential for use as unstable drug sustained-release systems.

Wang et al. [105] fabricated a multilayer film with ethylcellulose nanofibers and curcumin-loaded gelatin nanofibers by sequential electrospinning. They found a continuous release of curcumin from the multilayer films for 96 h, whereas the drug was released immediately from gelatin films within 30 min. The results indicated that multilayer nanofibrous films have potential applications in bioactive encapsulation and controlled release. Encapsulation of curcumin in dextran/zein electrospun fiber films also provided controlled release in in vitro investigations [106]. The drug release rate differed according to the release medium, as about 13.5% of the curcumin was released into a phosphate-buffered saline/ethanol solution (7:3) from the 15% zein film fibers. Changing the phosphate-buffered saline/ethanol ratio of the medium to 3:7 increased the curcumin release to 33.4%. Overall, these results indicate that these biopolymer-based composite films have considerable potential for use as bioactive intelligent delivery systems for various biomedical applications.

Other Applications

Recent research trends in wound dressings, tissue engineering, and water pollutant removal using hydrophobic biopolymer-based films have been of increasing interest to researchers.

Natural biopolymers have desirable characteristics, such as nontoxicity, biodegradability, and biocompatibility, which make hydrophobic biopolymer-based films attractive biomaterials for use as wound dressings and in tissue engineering. The low swelling degree and low water vapor transmittance are of particular value in wound-dressing and tissue engineering applications. Sodium carboxymethylcellulose-based films containing Tween 80, fabricated for wound-healing applications by Ali et al. [107], showed good fluid adsorption, low erosion, and high tensile strength (21.04 MPa) due to the formation of "folds" on the film surface. Therefore, these complex films were deemed useful as antibacterial materials for wound-dressing applications.

Mohebali and Abdouss [108] prepared a promising wound dressing made from halloysite nanotube composites and fabricated with both poly(lactic-co-glycolic acid) and chitosan for the targeted and controlled drug delivery of minocycline. The amount of water vapor transmission rate decreased from 2481 to 1860 g/m^2 per day with increasing halloysite nanotube content (from 20 to 80%) in the prepared films. The composite films absorbed wound secretions and penetrated the wounds correctly during treatment. Compared to sterile polyvinyl alcohol films, the composite films showed faster healing of burn wounds in rats. Therefore, the use of surfactants and nanoparticles to improve the hydrophobicity of the films also benefits the use of these films as wound dressings.

Hydrophobic biopolymer-based films also play an important role in biomedical engineering, especially in tissue engineering. For example, Dong et al. [109] found that a greater number of cells attached to and grew on zein nanofibrous networks than on conventional zein casting films. The results indicated that electrospun zein nanofibrous networks have great potential in tissue engineering to support cell growth and tissue regeneration.

Hydrophobic biopolymer-based films are also useful for water decontamination because of their advantages in terms of cost competitiveness and environmental acceptance. For example, Das and Mukherjee [110] reported that a hydrophobic guar gum benzoate film fabricated for soluble pollutant sorption and the reduction of microbial loads in a water environment adsorbed a large number of organic molecules from sewage. The maximum sorption by the guar gum benzoate films under the test conditions was 612.02 μg g^{-1} for bisphenol A and 864.55 μg g^{-1} for 2-naphthol.

Membrane separation is also viewed as an effective method for the treatment of oily wastewater [111]. The WCA values for PVA and agar/PVA membranes coated with methyltrichlorosilane were 148.1° and 150.1°, respectively [112]. Coated PVA and agar/PVA membranes also exhibited a good separation (≥ 97.5%) of water-in-oil/organic solvent emulsions (water-in-toluene, water-in-chloroform, and water-in-diesel). Therefore, hydrophobic biopolymer films have the potential to separate oily wastewater.

Conclusion

The current evidence indicates that natural biopolymers (polysaccharides and proteins) can be used to fabricate useful hydrophobic films. At present, four common methods are used to prepare hydrophobic biopolymer-based films: (1) electrospinning, (2) hydrophobic modification of the biopolymers, (3) addition of hydrophobic compounds or micro/nanofillers to the films, and (4) hydrophobic modification of biopolymer-based films. The WCA of hydrophobic biopolymer-based films prepared by any of these four methods is typically greater than 90°, indicating that the films attain good hydrophobicity. In addition, the hydrophobic biopolymer-based films also provide strong barriers against oxygen and UV irradiation, stable mechanical properties, self-cleaning capabilities, antibacterial and antioxidant activities, and pH responsiveness. Because of their excellent performance, hydrophobic biopolymer-based films are now being widely used as food packaging materials, as active substance carriers, as wound dressings, and in tissue engineering.

Hydrophobic biopolymer-based film products are still in the preliminary development stage and require improvement before they are presented to consumers. Moreover, hydrophobic biopolymer-based films destined for use as

food packaging materials need to be evaluated for possible impacts of their components (hydrophobic compounds and nanofillers) on food safety. At present, few studies have reported the use of superhydrophobic biopolymer-based films, and developing these films remains a challenge. Superhydrophobicity can expand the applications of biopolymer-based films in liquid food packaging, biomedicine, and waterproof materials. Therefore, carrying out more research and developing new hydrophobic biopolymer-based films would be useful in the future.

Funding The study was supported by the National Natural Science Foundation of China [No. 31972028], National Natural Science Foundation of China (No. 32272349), Natural Science Foundation of Shandong Province (ZR2020KC010), Key R&D Plan of Shandong Province (No. 2022CXGC010604), Qingdao Municipal Science and Technology Benefit People Project (No. 20–3-4–34-nsh), Science & Technology Specific Projects in Agricultural High-tech Industrial Demonstration Area of the Yellow River Delta (No. 2022SZX27), and Foreign Expert Project (No. G2022025008L).

Declarations

Conflict of Interest The authors declare no competing interests.

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