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Review

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Emerging Chitosan-Based Films for Food Packaging Applications

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ABSTRACT: Recent years have witnessed great developments in biobased polymer packaging films for the serious environmental problems caused by the petroleum-based nonbiodegradable packaging materials. Chitosan is one of the most abundant biopolymers after cellulose. Chitosan-based materials have been widely applied in various fields for their biological and physical properties of biocompatibility, biodegradability, antimicrobial ability, and easy film forming ability. Different chitosan-based films have been fabricated and applied in the field of food packaging. Most of the review papers related to chitosan-based films are focusing on antibacterial food packaging films. Along with the advances in the nanotechnology and polymer science, numerous strategies, for instance direct casting, coating, dipping, layer-by-layer assembly, and extrusion, have been employed to prepare chitosan-based films with multiple functionalities. The emerging food packaging applications of chitosan-based films as antibacterial films, barrier films, and sensing films have achieved great developments. This article comprehensively reviews recent advances in the preparation and application of engineered chitosan-based films in food packaging fields.

KEYWORDS: *chitosan, food packaging, antibacterial, composite film*

INTRODUCTION

Currently, environment problems and food safety have caused many concerns to the public, and green chemistry appeals to many researchers. Chitosan, the derivative of chitin after deacetylation, is a linear amino polysaccharide with D-glucosamine and N-acetyl-D-glucosamine units. Chitosan has been applied in many fields, such as medicine, agriculture, food, textile, environment, and bioengineering, due to its excellent properties of antimicrobial activity, nontoxicity, biocompatibility, biodegradability, chelating capability, etc.

Chitosan has certain solubility in acetic acid and hydrochloric acid, which leads to the film-forming ability. Many researchers have fabricated chitosan-based films by methods, including casting, coating, layer-by-layer assembly, etc., and modified the characteristics, such as antimicrobial activity, barrier property, antioxidant activity, mechanical property, optical property, sensing/indicating capacity, and thermal stability. Moreover, they added other functional materials into chitosan to fabricate composite films to enlarge the combinational advantages of the obtained films. The obtained films have been applied to different foods, e.g., meat, fruit, and vegetables, with excellent preservative effects displaying the potential as an alternative means food packaging.

Chitosan has made important progress in food packaging with the development of science and technology. Many reviews focused on the literatures regarding overall application (before the year 2000),[1] antibacterial packaging films,[2−9] active packaging films,[10] or the practical food application.[11−14] In this article, we comprehensively reviewed the recent advances in the strategies to fabricate chitosan-based films, including direct casting, coating, dipping, layer-by-layer assembly, and extrusion. Recent advances in the applications of engineered chitosan-based films in food packaging, such as antibacterial films, barrier films, and sensing films, have also been discussed. The aim of this article is to review the latest trends of materials and methods, highlight the potential of chitosan in food packaging, and provide perspectives in the modern packaging technology.

DIFFERENT CHITOSAN-BASED FILMS

Chitosan films have been researched for years because of their excellent performance, especially in food industry, in relation with the reduction of environmental impacts.[8,15,16] Chitosan-based films can be used as food packaging materials and extend the shelf life of food,[4,10,12] in the form of pure chitosan films, chitosan/biopolymer films, chitosan/synthetic polymer films, chitosan derivative films, etc.

PURE CHITOSAN FILMS

Chitosan can be dissolved in dilute acid solutions (e.g., acetic acid and hydrochloric acid), and fabricated into different products, like edible films.[17−21] Various foods have been preserved by chitosan films. The involved foods include banana, pomegranate, carrot, mango, tomato, fish, papaya, wolfberry, etc., with the improved storage stability after treatment. Moreover, these pure chitosan films have been proven to be able to delay the qualitative and nutraceutical traits changes, prevent the growth of microbial, keep antioxidant activity, and prolong the shelf life.

The films based on conventional chitosan and submicron chitosan dispersions with diameter of 600 nm demonstrated better preservation on food than that with submicron chitosan dispersions of 1000 nm.[22] In addition, small amount of plasticizers, like glycerol and sorbitol, could be added to improve the strength, extendibility, flexibility, and chain mobility.[23−26] Also, emulsifiers or surfactant, such as Tween-80, Tween 20, Brij 56, and Span 20, could also be added to chitosan solution to develop films for improvement of

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properties. Vacuum packaging was often used to combine with pure chitosan films for preserving the food, such as swordfish, hake, sea bass, and rainbow trout.[27−29] Though these films demonstrated overall great characteristics, some films have high advantages in some aspects but low disadvantages in other aspects like weight loss, and requires special conditions like ultrasound, which may be not beneficial for the practical mass application to food.[30]

■ CHITOSAN/BIOPOLYMER-BASED FILMS

Due to the characteristics, such as biodegradability, nontoxicity, biocompatibility, etc., the naturally derived biopolymers are appropriate to combine with chitosan for fabricating chitosan/biopolymer films. These obtained chitosan/biopolymer films, with combinational properties, were widely researched for application in food. These biopolymers include polysaccharides, proteins, extracts, organic acids, etc.

■ CHITOSAN/POLYSACCHARIDES-BASED FILMS

Polysaccharides have been reported to blend with chitosan for the development of functional films. Starch, with low cost, wide availability, and biodegradability, is one of the most important renewable polysaccharides derived from plants. Both chitosan and starch have good film-forming capacities, which contribute to the formation of the composite film.[31] These obtained films exhibited reduced bacterial adhesion on the packaging, great antioxidant activity, and improved water vapor barrier property, which proved to be promising for active packaging film.[32,33]

Cellulose has been explored by many researchers to prepare chitosan/cellulose films with improved mechanical property.[34] Hydrogen bonds between nanocellulose and chitosan are the driving forces for development of films. These obtained films showed excellent optical property, gas barrier property, antimicrobial property, sustainability, and bioactivity (in Figure 1).[35−38] The chitosan/carboxymethyl cellulose film prepared via electrostatic interactions proved to increase the shelf life of cheese and wheat bread.[39,40] Other cellulose materials can also be blended with chitosan to develop composite films, such as hydroxypropyl methylcellulose,[24] quaternized hemicelluloses,[41] methylcellulose, and micro fibrillated cellulose.[42] These films possessed proper properties, such as high resistance, elasticity, uniformity, and transparency, which were suitable for application in food packaging.

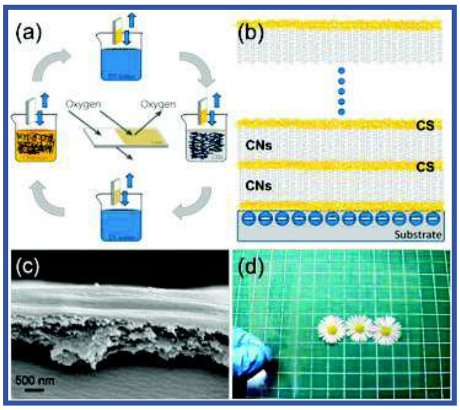

Figure 1. (a) Illustrations of fabrication process, (b) the nanostructure constructed by the alternate adsorption of chitosan (CS, orange) and cellulose nanocrystals (CNs, gray) onto a substrate, (c) scanning electron microscopy image of the multilayer cross section with average thickness of the multilayer about 800 nm, (d) optical property of coated A-PET. Reprinted with permission from ref 37. Copyright 2012 Elsevier.

Alginate, a natural linear and anionic polysaccharide, is an attractive biopolymer for the favorable properties, such as low toxicity and chemical versatility. The stable complex film based on chitosan/alginate were developed via electrostatic deposition of opposite charges. These charges on the chitosan/alginate film had a significant influence on properties, such as contact angle, microstructure, and thermal performances.[43] The chitosan/alginate films showed excellent gas-exchange performance and water vapor permeability property,[44] which provided the treated foods with attractive succulent appearance and high microbiological and physicochemical quality.[45] Overall, chitosan/alginate films displayed great potential for food packaging.[42,46]

Pectin is a structural polysaccharide obtained from plants.[47] Positively charged chitosan and negatively charged pectin promoted the strong intermolecular interaction between each other, which greatly contributed to the stable and uniform film.[48] The treated fresh-cut cantaloupe possessed high physicochemical and sensory values.[49] Overall, the composite films demonstrated desirable characteristics and permitted the practical application as an alternative to conventional food packaging film.[50] Cyclodextrin has been reported to increase the tensile strength of chitosan film.[51] After the incorporation of active materials or photoactive agent in chitosan/cyclodextrin films, the enhanced antimicrobial activities and release properties promoted the composite film to be used as bioactive food-packaging material.[51−53] Many polysaccharides, including glucose, xylan, fucose, and konjac glucomannan, were also studied in combination with chitosan for food packaging. For example, the chitosan/glucose films, with enhanced antioxidant property, effectively delayed the declines of total soluble solids, decreased decay and weight loss, suppressed respiration rate, and ensured better berry texture and higher sensory scores of food.[54,55] These obtained biodegradable chitosan/polysaccharides films, with enhanced properties, could be exploited and applied to food packaging, as a strategy to extend the shelf life of various food.

■ CHITOSAN/PROTEIN-BASED FILMS

Many proteins, obtained from plants, animals, or microorganisms, could be blended with chitosan to form films with different preprogrammed properties. Because of the presence of special groups, these films based on chitosan/protein have abundant functions, which promote the application in food packaging.

Proteins obtained from animals have appealed to many researchers, because of properties like film-forming ability, high nutritive value and biocompatibility. Caseinate, with excellent thermoplastic and film-forming properties, could combine with chitosan to prepare chitosan/caseinate film, through ionic interaction, with the final film properties being improved, like water vapor permeability.[56] Collagen has attracted great interests from researchers as a potential alternative to synthetic polymer. After compositing with chitosan, the developed films obtained high thermal stability, good adhesion, and compatibility.[57] Lysozyme−chitosan films could also enhance the freshness of the egg during storage, improve shell strength, and maintain the internal quality.[58] Gelatin is a purified protein derived from collagen in the bones and skin of animals. Films based on chitosan/gelatin often showed improved properties,

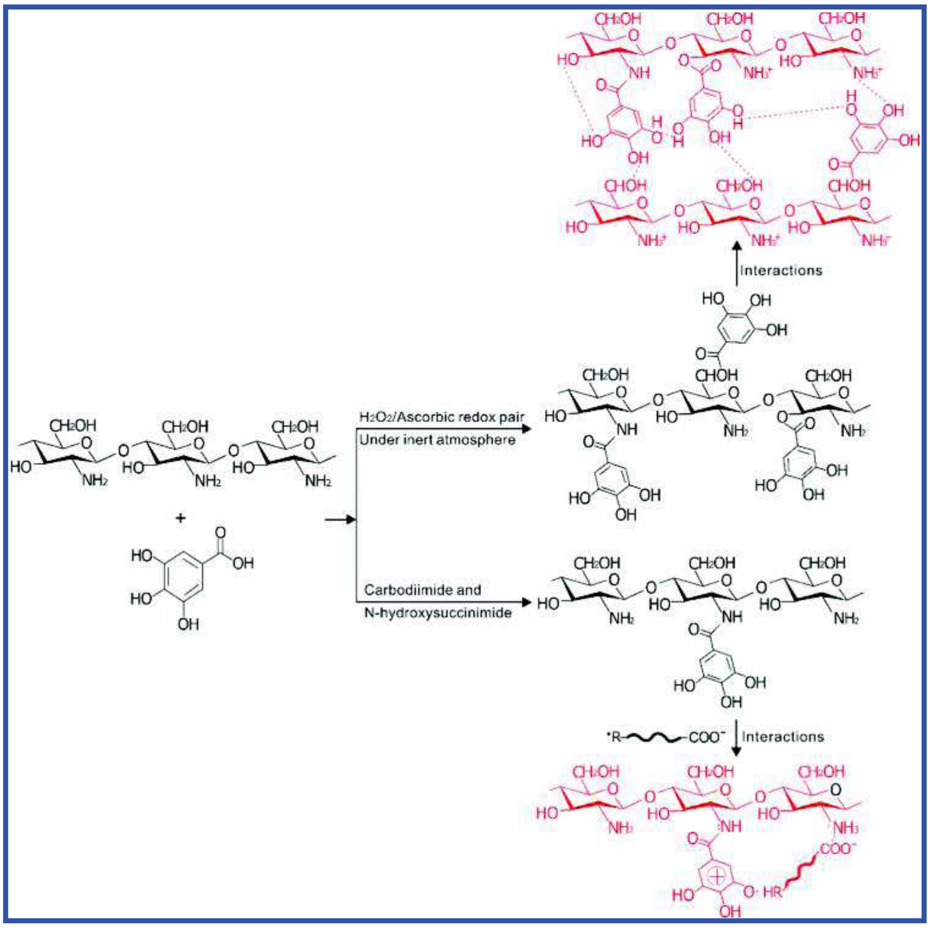

Figure 2. Illustration of grafting gallic acid onto chitosan.

like mechanical properties and barrier properties against water vapor and light (e.g., UV, due to UV absorption of peptide bonds in the polypeptide chains).[59−64] Overall, many foods (e.g., red bell peppers) treated with chitosan−gelatin edible films showed low microbial decay, proper physicochemical and microbiological properties, and longer shelf life.[65]

Proteins, derived from plants, presented great promise in food preservation, due to the rich sources and low cost. Chitosan/kidney bean protein isolate complex produced less rigid and more flexible films, with high surface hydrophobicity and low surface free energy, which were expected to work as antimicrobial packaging for food.[66] The composite film based on chitosan/quinoa protein had the improved properties, such as mechanical and water barrier properties,[67,68] which owned application in food.

Proteins produced from microorganisms could also play an important role in packaging films. Nisin, an amphiphilic cationic peptide, is often obtained from microorganisms like *Lactococcus lactis*. The films based on chitosan and nisin could be favorably used for extending the shelf life of packaged foods.[69] ε-polylysine, naturally biodegradable and nontoxic, is a natural food additive approved by FDA (the United States),[70] National Health and Family Planning Commission of the People's Republic of China (NHFPC),[71] Ministry of Health, Labour and Welfare List of Existing Food Additives (Japan),[72] et al. When the chitosan/ε-polylysine/nisin film was applied to fresh-cut carrots, the carrots showed the inhibited respiration rate, the declined ascorbic acid, the decreased growth of microorganism and the suppressed synthesis of white blush and lignin.[70]

■ CHITOSAN/EXTRACTS-BASED FILMS

Extracts from bee secretions, such as beeswax and propolis, were also blended with chitosan to develop films for food packaging. Beeswax, a complex mixture with antimicrobial activity, is now widely used in the food industry. The incorporation of beeswax into chitosan films was an environmental-friendly alternative to control pathogenic microorganism and to maintain food quality (visual appearance and taste).[73] Overall, after incorporation of extracts from bee secretions, mechanical property, barrier performances, and antioxidant activity of chitosan films were enhanced, though some films demonstrated deep orange color.[74,75]

Extracts from plants, natural and nontoxic, have been used for decades in many fields like food preservation. As for the chitosan film, the addition of extracts from plants proved to significantly modify the film properties, such as antimicrobial activity (including honeysuckle flower extract[76] and citrus extract[77]), antioxidant activity (including clove eugenol[32] and maqui berry extracts[78]), barrier performances (including thyme extract[31]), mechanical property (including tannic acid[79]), thermal stability (including young apple polyphenols[15]), and color property (carvacrol[80]), thus obtaining the synergistic effect of chitosan and plant extracts. Gallic acid, a promising functional material, could be grafted onto chitosan via carbodiimide by free-radical-initiated grafting (in Figure 2).[81,82] Inclusion of gallic acid also significantly increased antioxidant capacity, antimicrobial activity, and tensile strength, and decreased water vapor permeability and oxygen permeability,[82−85] thus exhibiting promise as a good candidate for multifunctional food packaging materials.

Essential oils, aromatic and volatile, are extracted from plant materials. The obtained chitosan films enriched with cinnamon oil exhibited the excellent antimicrobial and showed potential as active food packaging film.[86] Carvacrol incorporated in chitosan films could effectively ensure the food safety, through headspace technique or in combination with gamma irradiation and modified atmosphere packaging.[87−89] Other essential oils, such as olive oil, buriti oil, rosemary essential oil, and oregano essential oil, also proved to improve mechanical properties, barrier properties, and antioxidant activity of chitosan films.[90,91]

These chitosan/biopolymer (including polysaccharides, proteins and extracts) films, exhibit certain advantages, such as the enhanced antioxidant and antimicrobial properties.[34,78] The excellent protection effects on food quality, as indicated in papers,[65,70] demonstrated that these films are holding great promise and deserve further optimization for industrialization in market.

■ CHITOSAN/SYNTHETIC POLYMER-BASED FILMS

Chitosan could blend with synthetic polymers to develop films, with improved properties and characteristics. Poly(vinyl alcohol), with good mechanical property, is a nontoxic and water-soluble synthetic polymer. The intermolecular hydrogen bonds between chitosan and poly(vinyl alcohol) molecules promoted the fabrication of the films.[92] High amounts of poly(vinyl alcohol) could contribute to the plasticization, enhance the elasticity, increase the elongation, raise tensile strength and improve water and oxygen barrier properties of the obtained films, affirming the potential as a universal antimicrobial food packaging material.[92,93] Also, many researchers incorporated or immobilized some bioactive materials to endow the films with special characteristics, such as fire resistance and mechanical property, thus broadening the application of the chitosan/poly(vinyl alcohol) films.[94]

Synthetic acids could also be added into chitosan films. The chitosan/poly(lactic acid) films could be achieved by blending chitosan with poly(lactic acid) or adding lactic acid oligomer-grafted-chitosan as a nanofiller to poly(lactic acid) films.[95,96] Figure 3 shows the composite films with lactic acid oligomer-grafted-chitosan as a nanofiller. The improvement of multiple properties, such as tensile and thermal properties, further verified the promising use of the obtained material in packaging food.[96] The films based on chitosan and synthetic acids (e.g., salicylic acid and fumaric acid), with enhanced properties, proved to alleviate chilling injury and preserve quality of foods, such as cucumber.[97]

Low density polyethylene often blended with chitosan for extruding into chitosan/low density polyethylene films, with promising application in food.[98,99] Poly(ethylene oxide) could greatly influence hydrophobicity and thermal properties of the composite films.[100] The addition of allyl isothiocyanate and polycaprolactone could also synergistically increase the antibacterial effect of chitosan films.[33,101] Moreover, other synthetic polymers, such as lauric arginate ester, poly(butylene adipate-*co*-terephthalate), liquid paraffin and polyethylene terephthalate, could blend with chitosan, allowing a designed flexibility of the final films.

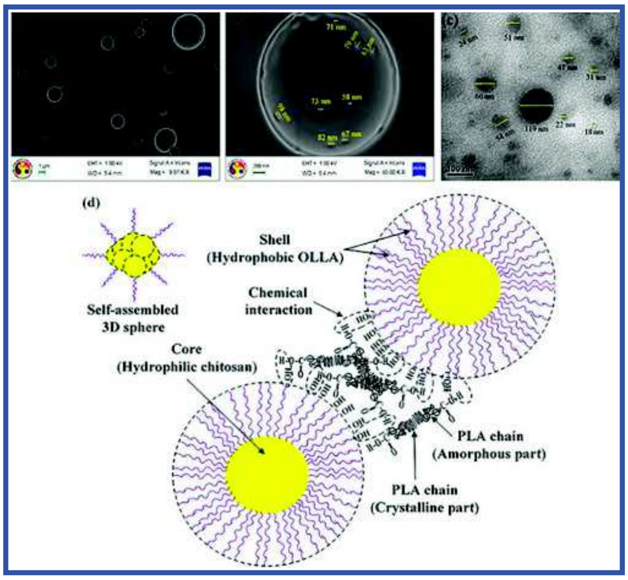

Figure 3. Field emission scanning electron microscopy images of PLA/OLLA-*g*-CH (5%) bionanocomposite film (a) at 8.97 KX, (b) at higher magnification ∼85 KX, (c) transmission electron microscopy topography of PLA/OLLA-*g*-CH (5%) bionanocomposite film, and (d) schematic representation of interaction between matrix and lactic acid oligomer-grafted-chitosan nano filler. PLA, poly(lactic acid). OLLA-*g*-CH, lactic acid oligomer-grafted-chitosan. Reprinted with permission from ref 95. Copyright 2016 American Chemical Society.

Some synthetic polymer films worked as substrates and were coated with chitosan to fabricate the composite films, with polyfunctionality and sustainability.[37,102] Polyethylene films were coated with chitosan to introduce the antibacterial activity, release property, hydrophilic property and chemically reactive ability to the films.[92] The properties of obtained films could be tuned by controlling the electrical charges of biopolymer and volume/concentration of chitosan.[43] Chitosan could be also applied to special synthetic polymer films, such as polypropylene film, polystyrene films, and azopolymer films, mostly by electrostatic interaction.[103−105] These films with properties like antimicrobial activity and optical activity, are promising for food packaging.

It should be noted that some synthetic polymers (e.g., low density polyethylene, poly(ethylene oxide), and polystyrene) are not easy to be degraded in environment and may cause environment problems. Though some research has done the degradation test in soil,[106] many papers have not involved the films' degradation in practical environment.[98−100,102,103] Thus, the environment experiment (e.g., degradation in soil) should be attached with great importance.

■ CHITOSAN/INORGANIC MATERIAL FILMS

Chitosan, with high chelating ability, has been used to prepare different chitosan-inorganic complexes for potential use as films (Figure 4). These films often demonstrated great promises in food packaging.

Silver nanoparticles, with antimicrobial activities against a wide range of pathogenic microorganisms, could be incorporated into chitosan films for active food packaging. Chitosan and silver nanoparticles could be homogeneously distributed in polymer matrix via a green chemistry methodology.[104,107] The enhanced antibacterial activity, hydrophilic property, degradability, biocompatibility, and nontoxicity of the films consisting

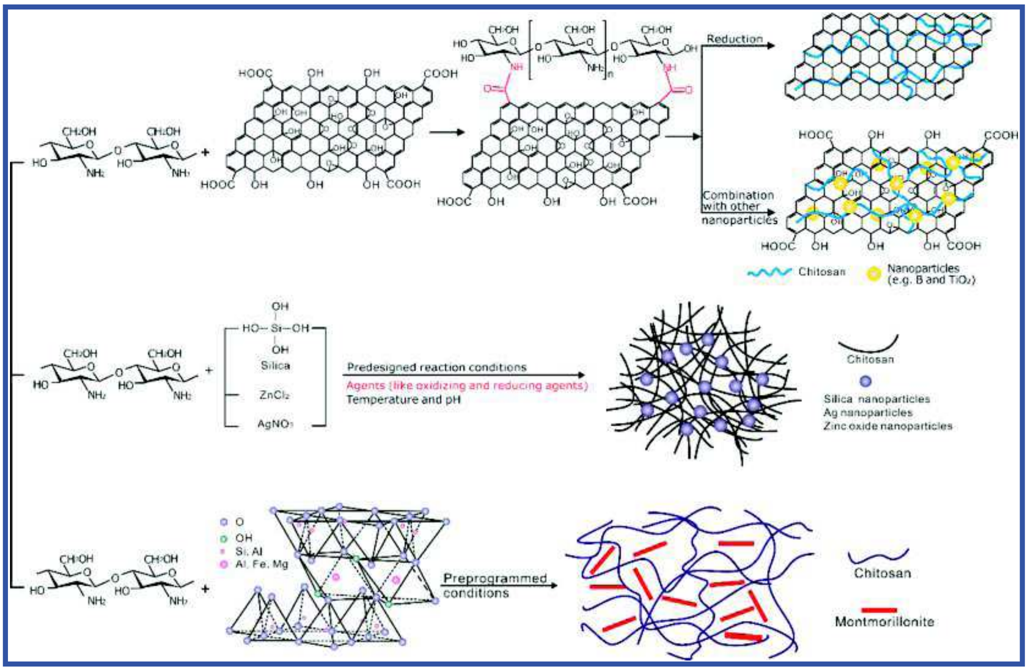

Figure 4. Preparation of chitosan-inorganic complexes.

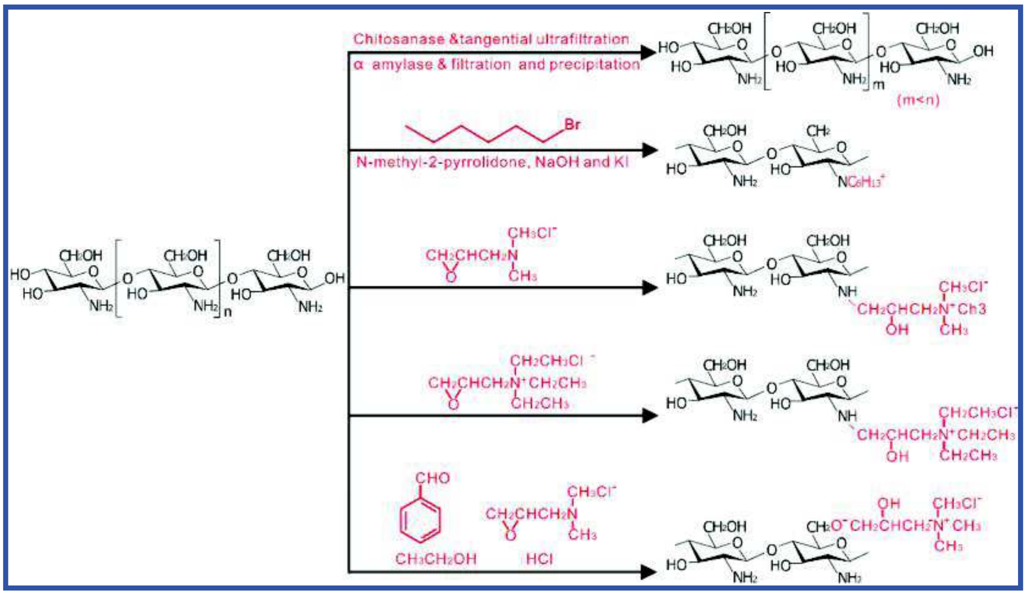

Figure 5. Development of different chitosan derivatives which have been used to fabricate chitosan-based films.

of silver nanoparticles and chitosan could promote the films to be feasibly used for edible food packaging applications.[108,109]

Zinc oxide is another filler which can enhance the physicochemical and biological properties of chitosan films. After incorporation of nano zinc oxide, antimicrobial activity, mechanical properties and transparency of composite films were greatly improved.[110,111] The prevented growth of food pathogens and the increased shelf life of food indicated that the composite films were applicable for food application.[39]

Compared with pristine chitosan, chitosan/graphene oxide films based on chemical cross-linking have the improved mechanical capacity and oxygen barrier property.[112,113] Also graphene oxide and expanded graphite stacks could be added into chitosan to form films. The selectivity and safety demonstrated its potential as antimicrobial films for food storage.[114,115]

Chitosan/montmorillonite composite films has been widely researched, for the improvement of films barrier (oxygen, carbon dioxide, and water vapor).[93,116−118] Some researchers found that the addition of montmorillonite in chitosan films could also enhance mechanical property and improve flame-retardant properties, showing benefits for new types of food packaging.[119−121]

Silicon materials, such as silica and silicon carbide, could be added into the film matrix. There were some reports demonstrating that chitosan/nanosilica films could lower the

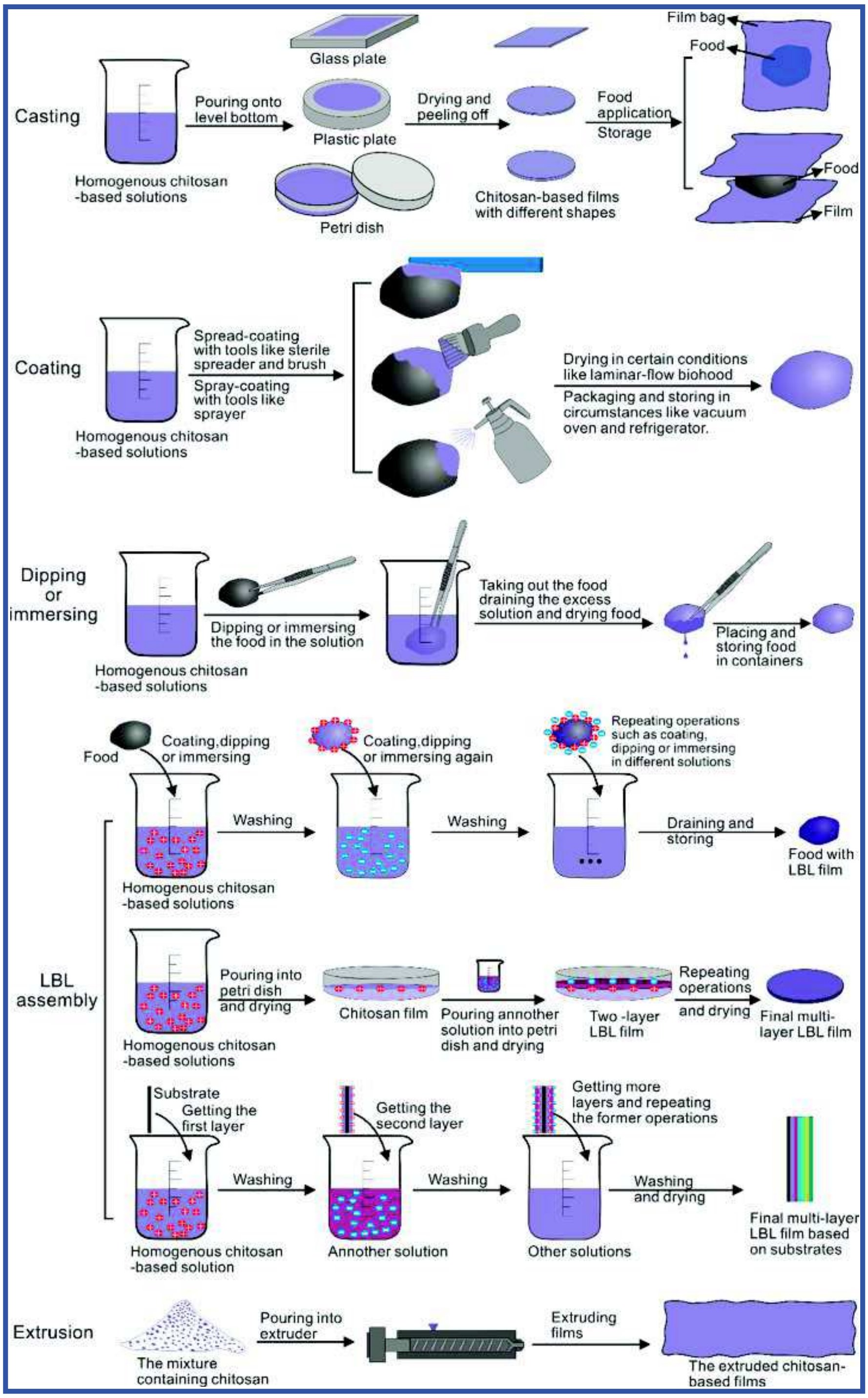

Figure 6. Different methods to fabricate the chitosan-based films.

decay of food by preventing the membrane structure from peroxidation, thus ensuring a longer storage life and offering acceptable external and internal quality.[122,123] What's more, nano silicon carbide incorporated chitosan nanocomposite films could substantially decrease oxygen barrier properties, enhance thermal stability, and strengthen chemical resistance, which indicated the promises in food packaging.[124]

Inorganic materials (including titanium dioxide, cloisite 20A, nanomagnesium oxide,($Mg(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$, $CaCl_2$, $CaCO_3$, zinc(II), and cerium(IV)) proved to reinforce chitosan films,[34,114,125] such as thermal stability and barrier properties.[126−128] These films, with special structure due to the inorganic materials,[129] could even have resistance toward chemical materials like dilute HCl and NaOH,[130] demonstrating as a promising candidate for food packaging application.[131]

When incorporating inorganic materials, it is of vital importance to consider the application objects, even if these inorganic materials have exhibited excellent advantages in

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Table 1. Preparation Tools, Conditions, and Characterization of Chitosan Films[a]

CS-CCT	tools	DC	characterization	refs
1% wt%	Petri dishes	RT	FTIR, TGA, XRD, CIE Lab, CA, MP	23
2% w/v	ceramic plate	25 °C for 48 h	CIE LAB, MP, FTIR	75
0.8% w/w	plastic containers	40 °C for 48 h	CIE LAB, MP	73
2% w/v	plastic Petri plate	60 °C for 24 h	XPS, DSC, SEM, AFM, XRD, UV- VIS, FTIR	53
0.4% w/v	glass plate	50 °C for 12 h	FTIR, TG, DTG, MP	42
0.5% w/v	Teflon sheet	50 °C for 24 h	UV−vis, DLSA, TEM, SEM, XRD, MP, CA	164
2% w/v	glass plate	RT for 72 h	FTIR, XRD, SEM, MP, CIE Lab	141
2% w/w	acrylic plate	45 °C for 72 h	FTIR, XRD.	179
1% w/v	Teflon plate	50 °C overnight	XRD, SEM, SEM-EDS	108
1% w/v	Petri dish	50 °C for 3−4 h	XRD, FTIR, SEM, TGA, MP	120
1 wt%	Petri dish	RT for 72 h	FTIR, TEM, SEM, XRD, EDS, CA	39
0.4% w/v	Petri dish	25 °C for 72 h	SEM, DSC	40
2% w/v	Petri dish	RT	FTIR, SEM, MP	36
1% w/v	glass plate	overnight	TEM, SEM, XRD, FTIR, EDS	35
2 wt%	filter membrane	70 °C for 10 min	MP, TGA, DTG, SEM, AFM, FTIR, UV−VIS	41
0.5% w/w	plastic Petri dish	40 °C for 12 h	FTIR, SEM, TGA, CIE LAB	48
2% w/w	Petri dish	24 h at 25 °C	SEM, ET, TPM, XPS, NMR	184
1% w/v	polystyrene plates	40 °C for 20−24 h	UV−VIS, TA	77
2% w/w	Teflon plate	25 °C for 48 h	SEM, FT-IR, UV−VIS, MP	31
1% w/w	glass plate	23 ± 2 °C	MP, FTIR, SEM	85
2% w/v	silicone resin plate	RT for 12 h	MP, CIE LAB, UV−vis, FTIR, DSC, TGA, SEM	57
2% w/v	plastic Petri dish	25 °C for 18−24 h	CIE LAB, MP, FTIR	181
1.5%; 2.0% w/v	polyethylene plaque	50 °C	TEM, CA, XRD, SEM, MP	68
2% w/v	Petri dishes	25 °C 48 h	SEM, FTIR, NMR, XRD, TA, MP, CIE LAB	15
1.5% w/v	Petri dishes	23−25 °C for 72 h	MP, DSC, FTIR	63
1 wt%	Teflon plates	RT	SEM,	183
2%w/v	glass plates	RT for 4 d	CIE LAB, SEM	175
2%w/v	plastic dish	∼22 °C for ∼5 d	XRD, MP	93
2% w/v	plastic dish	40 °C	FTIR, SEM, MP, CA	174
2.7% w/v	glass plate	RT and VA for 48 h	SEM, FTIR, TGA, XRD, DSC, MP	170
1% w/v	Petri dishes	RT for 72−75 h	SEM	69
2 wt%	glass plate	45 °C for 2 d	TEM, XRD, FTIR, MP, DSC, MCC, SEM, LRS	94
5% w/w	silicon Petri dish	RT for 24 h	UV, XRD, SEM, TEM	107
1.0 wt%	glass plate	RT	XPS, NMR, XRD, TEM, SEM, DMA	113
2% w/v	Petri dish	40 °C for 8 h	FTIR, XRD, SEM	119
1.5% w/w	polystyrene plate	37 °C for 48 h	CIE LAB, DTG, UV−VIS, TEM, XRD	104
1% w/v	glass Petri dishes	50 °C for 4 d	XRD, FE-SEM, TGA, FTIR, UV	126
5% w/v	Teflon pane	50 °C	FTIR, XRD, SEM, TGA	139
1% w/v	Petri dish	20 °C for 48 h	SEM, CIE LAB, MP	180
2% w/v	multiwall plate	45 °C	FTIR, DSC, SEM, XRD	135

[a] Abbreviation: chitosan concentration, CS-CCT; drying conditions, DC; room temperature, RT; mechanical properties, MP; differential scanning calorimetry, DSC; microscale combustion colorimeter, MCC; scanning electron microscope, SEM; laser Raman spectroscopy, LRS; contact angle, CA; thermogravimetric, TG; derivative thermogravimetric, DTG; dynamic light scattering analysis, DLSA; two-photon microscopy, TPM; color measurement, CIE Lab; thermal properties, TP; vacuum, VA; microscale combustion colorimeter, MCC.

packaging. Inorganic materials may be beneficial to one object but unsuitable for other objects. For example, Cu-chitosan coating films could enhance seedling growth in maize by mobilizing reserved food,[132] but copper-free chitosan films demonstrated better results in terms of overall flavor and appearance of fruit in comparison with the copper-loaded films.[133]

■ CHITOSAN DERIVATIVES OR CHITOSAN/CHITOSAN DERIVATIVES-BASED FILMS

With large amounts of amino and hydroxyl groups, chitosan could be modified into chitosan derivatives (Figure 5). These chitosan derivatives not only have the properties of chitosan, but also have additional characteristics due to the modification.[134] What's more, chitosan could be blended with chitosan derivatives for fabricating edible films.

Chitooligosaccharides have appealed to many researchers. Some researchers developed chitosan/chitooligosaccharide-based films and found that chitooligosaccharide could increase the inhibitory effect against microorganisms.[135] On the other hand, the water vapor permeability had not been significantly affected, which demonstrated the possible method to obtain a more insoluble chitosan film with high antimicrobial activity. Wu et al. also prepared the composite films to store white shrimp.[136] The white shrimp showed lower metamorphism, high sensory scores, and long shelf life during storage.

Quaternization of chitosan could improve antibacterial activity.[137] Some authors coated quaternized chitosan onto poly(vinyl fluoride) and metal substrates through electrostatic interaction.[138] The films were noncytotoxic with high killing efficacy against microbial, demonstrating great potential for developing large-scale, stable coating films. Hu et al. fabricated quaternized chitosan (2-*N*-Hydroxypropyl-3- trimethylammonium chloride chitosan)/carboxymethyl cellulose blend film, with improved tensile strength, thermostability, and water resistance.[139] The treated bananas showed low decay and excellent sensory quality. Wan et al. developed three types quaternized chitosans, i.e., N-(2-hydroxyl) propyl-3-trimethylammonium chitosan chloride, N-(2-hydroxyl) propyl-3-triethylammonium chitosan chloride, and O-(2-hydroxyl) propyl-3-trimethylammonium chitosan chloride.[18] The films based on the three types of chitosan showed excellent antioxidant potency and displayed the application possibility in food field.

Chitin, with film-forming ability, could blend with chitosan to form films with special properties like lower oxygen permeability.[140] Jafari et al. added the chitin nanofiber into chitosan films based on affinity interaction.[141] The mechanical and barrier properties of the obtained films were significantly enhanced.

At present, the types of chitosan derivatives applied to food are not much, and more chitosan derivatives with special functions should be explored. Though chitosan derivatives have been produced and applied to film, the production process should be further simplified and the byproducts should be minimized.[18] Also, toxicity test should be considered, which is a paramount process before applying to practical market.[18,139]

■ STRATEGIES TO FABRICATE CHITOSAN-BASED FILMS

Many methods were studied to prepare chitosan-based films to meet the needs of food applications.[17,97,129] In terms of operation, the current fabrication technologies include direct casting, coating, dipping, layer-by-layer assembly, extrusion, etc., (Figure 6) which greatly promote the development of chitosan-based films in food packaging industry.

■ DIRECT CASTING

Casting is often used for preparing the chitosan-based films due to its simplicity. The films were prepared in different conditions and characterized for various properties, such as microstructure, chemical bonds, crystallinity, color, and mechanical performance. Table 1 displays the preparation tools, drying conditions, and characterization of chitosan films. The commonly used instruments for casting solutions are Petri dishes, glass plates, plastic plates, aluminum plates, silicon supports, etc., which usually decide the thickness of the uniform films.

The preparation often has several steps: (1) dissolving chitosan in acid solution with planned pH; (2) blending, compositing, or cross-linking with other functional materials at different volume or mass ratio; (3) stirring for obtaining homogeneous viscous solution; (4) solution filtration, sonication, or centrifugation for removing any remaining insoluble particles and air bubbles; (5) pouring onto level bottom (e.g., flat polystyrene tray) with different sizes; (6) drying under programmed temperature, relative humidity, and time; (7) peeling off, specially treating (e.g., NaOH), and storing.[23,75,141] Though some films need special equipment (e.g., desiccator cabinet, hot-air oven, vacuum oven, convection oven, and ventilated climatic chamber) for drying and require long drying time, the drying conditions are relatively mild and the process needs little complicated operation.

Two-step casting technique was also efficient in preparing the films.[142] After fucose-rich exopolysaccharide solution was cast and dried with adhesive surface, the chitosan solution was cast on the top of it. The excellent properties, especially barrier to gases, imparted the dense and homogeneous films the potential in packaging low-moisture products. Also, some researchers prepared green and biodegradable composite films with novel antimicrobial performance by casting and immersing.[143] The process includes: (1) cellulose solution was cast on a glass plate; (2) the obtained films were then immersed into coagulation bath containing 5% (w/v) H_2SO_4 to regenerate for 10 min and was immersed into 5 wt% Na_5IO_6 solution in succession for different time; (3) the films were then immersed into 2.5 wt% chitosan solution to form the composite films. The composite films had better preservation effect than traditional polyethylene wraps.

Overall, these cast films with programmed formulations often showed the enhanced properties. The application to food also showed that the obtained films held promise as a packaging film for ensuring the safety of the food, maintaining the quality and prolonging the shelf life. In addition to the excellent properties, some cast chitosan-based films had defects and disadvantages. Though the cast films demonstrated some excellent properties, the addition of the special materials could lead to the decrease in Young's modulus for cast films with several layers.[38,39,53] Thus, the film formulations should be designed properly, and combined methods should be carried out to improve the comprehensive properties.

■ COATING

Coating is often applied to prepare the chitosan-based thin films on the surface of objects or immobilizing functional polymers on the surfaces to achieve protection purposes or special properties.[56,138,144,145] The obtained biobased films, with environment friendly nature, have advantages of low cost and biodegradation.[7,22,146,147] The films were even proven to be an attractive alternatives to synthetic materials used in food packaging.[146] This technology, including spread-coating and spray-coating, holds great promises in food preservation.[88,148,149]

■ SPREAD-COATING

Spread-coating is often used to produce chitosan films with the help of tools, like brush and spatula. It contains direct coating (on the surface of food including vegetables, fruit, and meat) and indirect coating (on the surface of packaging materials).

The direct coating is an effective way to limit the growth of microorganisms and maintain the quality of food. The direct coating process may involve several steps: (1) developing chitosan-based solutions that may contains antioxidants, antimicrobials, strengthening agents, etc.; (2) preparing samples with treatment such as screening, washing, cutting, irradiating, heating and steam flash pasteurizing; (3) spreading chitosan-based solutions onto food to form even films by sterile spreader, brush, spatula, etc.; (4) drying in certain conditions, such as laminar-flow biohood under ventilation and drying tunnel; (5) packaging and storing in circumstances, including vacuum oven and refrigerator. The coatings that contact the food surface can influence gas permeability coefficient and the antimicrobials can gradually migrate from the films onto the food surface, thus offering concentrated protection from external environmental factors.

The indirect coating on the surface of packaging materials is needed for the storage of final products, though the direct coating of chitosan-based solutions on food surfaces can lower the number of pathogens and spoilage microorganisms. Some chitosan solutions, based on their binding or adhering capacity, were coated onto plastic films by methods like brushing, thus obtaining multiple-layer functional films for food packaging.[148,149] The coating significantly promoted antibacterial property of the plastic films. Though chitosan layer on coated paper did not have significant influence on the mechanical properties, it greatly reduced the water vapor permeability of the paper.[56] The spin-coating was also used for production of chitosan-based multilayer films.[129] Compared with pristine substrate, the multilayer films had better gas barrier properties.

SPRAY-COATING

Spray-coating is usually achieved on food through tools, such as compressed air-assisted sprayer, knapsack sprayer, and copper backpack. Combination of spray-coating with other treatment shows many advantages. The combined treatment of spraying coating, gamma irradiation, and modified atmosphere packaging could integrate the excellent characteristics of the three treatments, cause the decrease of microbial population and guarantee the food safety of green beans.[88] Also, combination of spray coating of chitosan and heat treatment proved to effectively improve postharvest quality and own higher acceptability of wolfberries.[150] Preharvest spraying coating of oligochitosan proved to stimulate the resistance of navel oranges to anthracnose.[151] Though chitosan film did not alter the ripening and the alcoholic fermentation, it had a great effect on the composition (such as phenolic acids, flavanols, and nitrogenous) of berries and wines.[152]

Above all, the process of coating is easy and does not need complicated equipment. It also shows advantages to protect the food from spoilage and maintain food quality. In some cases, compared with the cast films, coating films performed better in terms of reducing lipid oxidation of food.[153]

DIPPING OR IMMERSING

Dipping or immersing food into the chitosan-based solutions has been adopted to develop uniform films on the surface of food. The success of film formation depends highly on the effective wetting capacity of the surface, processing time, and draining time.

The dipping or immersing steps included: (1) developing chitosan solutions and adjusting the pH; (2) preparing food samples, such as selecting (shapes, maturity, sizes, and health), cutting, cleaning, drying, and weighing; (3) dipping or immersing the food in the solution for designed time, usually around 30 s to 30 min; (4) taking out the food, draining excess solutions, and drying the food (e.g., under or in fans and plastic sieve, forced-air dryer, biosafety cabinet, and food dehydrator) or drying the food with tissue paper for 30 s to 24 h; (5) randomly placing the food onto trays or plastic support; (6) storing the food in plastic boxes, plastic film, cardboard-corrugated boxes, polyethylene terephthalate clamshell containers, biochemical oxygen demand chambers, etc., with definite temperature, relative humidity, and even exposure to certain light. After dipping and drying food, including guavas, blueberries, mushrooms, plums, carrots, salmon fillets, etc., the uniform films on the surface were achieved.[70,144,154] The films could alleviate chilling injury, lower color variation, maintain better quality, and delay the decay, thus significantly extending the shelf life.[17,97]

Several-dipping procedures or combination with other methods were also used to form films with several layers for food preservation with high overall acceptance.[58,136] However, in some reports, double-dipping was more recommended than three-dipping.[155] Cheeses with double-dipping procedures had the best evaluated aroma and flavor, while the aroma and flavor of three-dipped cheeses were negatively affected.

The method of dipping or immersing is easy with simple procedures, without large equipment. Also, the preservation performances on food have been proven to be of high efficacy.[70,144,154]

LAYER-BY-LAYER ASSEMBLY

The layer-by-layer (LBL) electrostatic deposition technique has been extensively explored in biomaterial films and it aims at efficiently controlling the material properties and functionality. It is a versatile technique for the fabrication of multicomponent films.[34,37] It does not need any sophisticated instruments and the formed films are independent of substrate shape.

The pH is an important factor that affects the formation of LBL films. The electrical charge could be changed by pH, which significantly affected the deposition amount of the polymers, because more biopolymer molecules were required to neutralize the previous layer.[43] The structure and properties of the multilayer films could also be greatly influenced by pH.[105] When the pH decreased and the layer number increased, the thickness, roughness, and elastic modulus of the prepared films would increase. Moreover, the high level of photo-orientation was achieved as the pH decreased and the layer number increased. Some authors found that the films with the best barrier performance were based on chitosan (pH 5.5)/poly(acrylic acid) (pH 3)/chitosan (pH 5.5)/graphene oxide (48 nm). At this pH, chitosan was highly ionized by the poly(acrylic acid) counterion and could attract more graphene oxide into the bulk film. The multilayer films proved to have the combinational properties of the components, and demonstrated that its inhibition of *E. coli* and antioxidant activity increased with the increase of bilayer number.[102,156]

LBL assembly technique is often combined with immersing method. The oppositely charged materials are usually used to prepare the films, i.e., polycation chitosan and polyanion materials.[44] The objects were immersed into different solutions for several times.[45,49] The investigation of texture, color, moisture, pH, sensory analysis, microbial quality, and growth indicated that the obtained films could prolong the shelf life of the treated food.

This LBL assembly, often combined with other methods like immersing, is simple and offers a distinct shortcut to fabricate functional materials. It is also reported to produce films that could effectively retain the quality of the food and extend the shelf life. Some films even show great barrier/separation properties under high humid conditions.[112]

EXTRUSION

Melt extrusion has also been developed widely to fabricate biodegradable chitosan-based active packaging. The steps include: (1) preparing material formulations using different compositions; (2) blending materials in a mixer; (3) blending the mixture in a twin-screw extruder under designed conditions; (4) cutting extrudates into pellets through the pelletizer; (5) drying pellets in a hot-air oven; (6) extruding the pellets into sheets through the twin-screw extruder that was attached to a flat die; (7) or blowing the mixed resins into a film by a blown film extruder by an annular die. Extruding process often provides the films with acceptable mechanical properties and good thermal stability.[99] During the extrusion (Figure 7), low density polyethylene worked as a matrix polymer and ethylene-acrylic acid copolymer served as an adhesive promoting the adhesion in the interphase of the immiscible polymers.

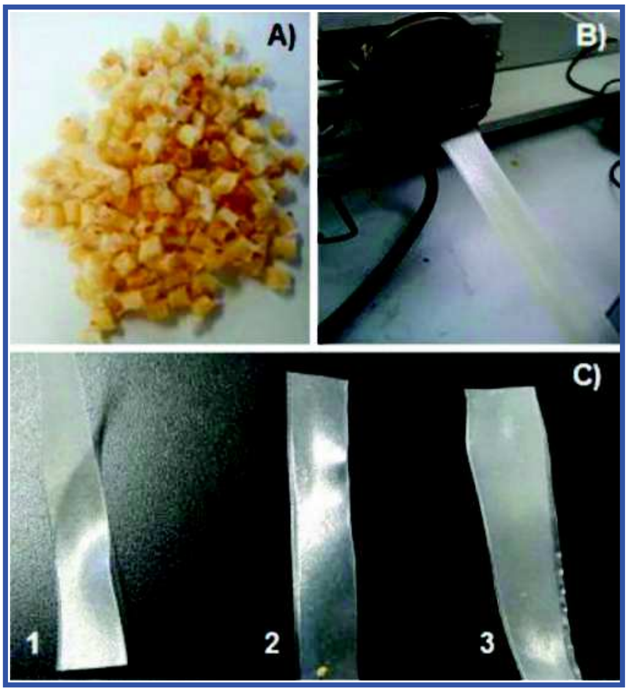

Figure 7. Extrusion of blends containing chitosan. (A) pellets of chitosan/LDPE/adhesive composite blend; (B) laminated film by extrusion of chitosan composite blend pellets; (C) extruded films containing chitosan with different formulations. Low density polyethylene: LDPE. Reprinted with permission from ref 99. Copyright 2012 Elsevier.

Two-step melt-compounding process was also popular for the blown films.[98] When the chitosan content increased, the breaking strength and elongation decreased, and the water vapor permeability was enhanced. Another film based on polyethylene glycol chitosan and low density polyethylene was fabricated by compression molding.[157] The thermal stability of the obtained film mainly depended on low density polyethylene. Though the films had excellent transparency, the addition of polyethylene glycol lowered the Young modulus.

Three-steps extrusion processing could be realized by coextrusion device and could extrude films without degradation:[33] (1) starch or flour powder plasticization by twin-screw extrusion; (2) extrusion of thermoplasticized starches or thermoplasticized flour granulates with polycaprolactone; and (3) coextrusion with polycaprolactone/chitosan. Poly(lactic acid)/starch/chitosan blended matrix was also extruded into antimicrobial film with thickness of the obtained films ranging from 0.15 mm to 0.18 mm,[96] which was suitable for protecting the foods with high water activity, such as fresh meat. Some researchers compared the films fabricated by casting, extrusion, and coating.[158] They found that the coating films were excellent with satisfactory storage effect of beefsteak, while the presence of chitosan exerted a negative influence on mechanical properties of the extruded films probably due to the poor interaction between the polyamide matrix and the chitosan. The poor affinity or lack of miscibility led to the poor mechanical properties and the brittle failure.

Extrusion demonstrates to be an effective way to fabricate films with good properties, such as mechanical properties, thermal stability, and antimicrobial activity. Some extruded film was an exception with the decreased mechanical property and oxygen barrier property.[32] To make full use of materials and achieve the best performance with degradation, the temperature should be tailored to different materials.[32,33,159] Also, the poor interactions between polymers requires attention, because it may cause a negative effect on mechanical properties and lead to brittle failure.[158]

These methods have different advantages in film production. Also, new methods or technologies are still required to meet different packaging applications and market needs.

■ APPLICATIONS OF CHITOSAN-BASED FILMS

The obtained chitosan-based films have different properties, which result in different applications. Overall, there are antimicrobial films, barrier films, and sensing films, which are mostly researched at present.

■ ANTIMICROBIAL FILMS

Chitosan, with polycationic characterization, naturally shows excellent antimicrobial activity.[66,70,160] Therefore, chitosan-based films exhibit great potential for food packaging applications, protecting food from microorganism, and ensuring food safety.

Many factors could influence the antimicrobial activity, though chitosan showed a wide spectrum of antimicrobial activity. The antimicrobial activity of chitosan-based films were contingent on organic acid,[26] temperature,[23,161] molecular weight,[162] heat treatment,[13] concentration,[163] films sizes,[52] additives,[68] type of microbial,[38] etc. In some cases, chitosan film did not show inhibition of the tested bacteria unless the addition of other materials, such as propolis extract and silver nanoparticles.[75,164] What's more, modifications to chitosan, such as chitosan derivatives and Schiff-base, were reported to be influential on the antimicrobial activity, probably due to the structure and groups affecting its interaction with surface groups of microorganisms.[163]

As for Gram-negative bacteria, the antimicrobial activity differs from Gram-positive bacteria. Chitosan-based film was reported to have higher antibacterial performance against Gram-negative bacteria than Gram-positive bacteria,[143] while some other studies reported the reverse antibacterial effect.[82,85] The reasons may be attributed to the chitosan content and the different structure of the cell membrane. Also, some researches put forward that antimicrobial action against Gram-positive bacteria was enhanced with the increase of molecular weight of chitosan because of the formed film inhibiting nutrient entrance into bacteria cell. However, antimicrobial effect against Gram-negative bacteria was improved with the decrease of molecular weight of chitosan due to the easy entrance of low molecular chitosan into microbial cell and the accompanying destruction

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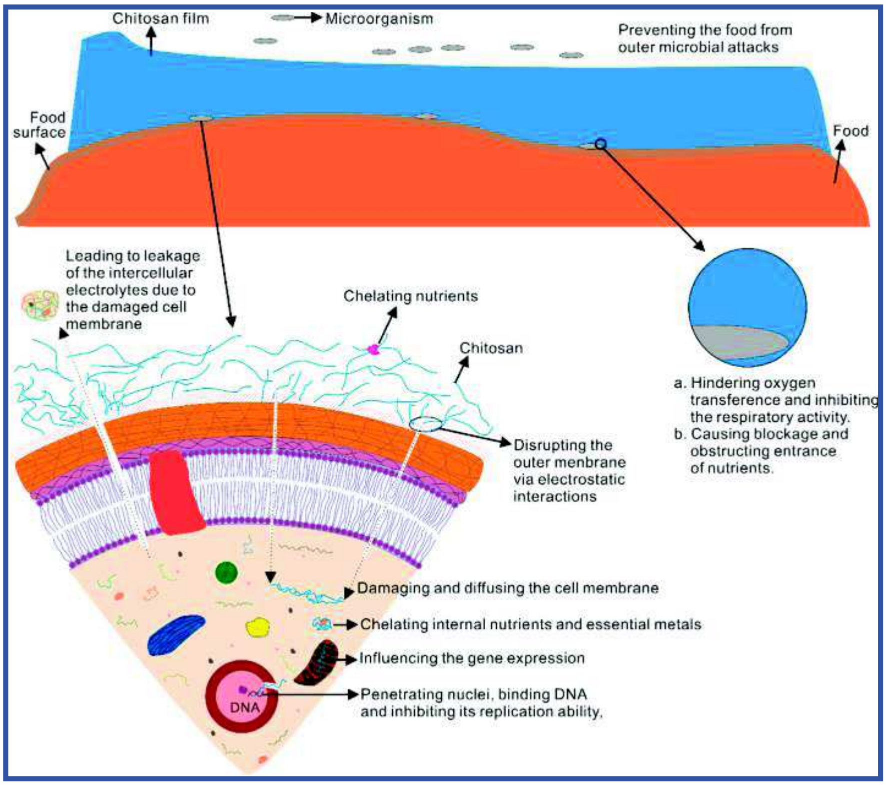

Figure 8. Antimicrobial mechanism of chitosan films.

to metabolism.[165] However, there is also report indicating that as for Gram-positive bacteria, the antibacterial performance differs as bacteria types.[38] For example, *Staphylococcus aureus* was found to be less susceptible to chitosan-based films than *Enterococcus faecalis* and *Listeria monocytogenes*, due to the different structures of the outer membrane. Overall, the obtained films proved to exhibit a remarkable antibacterial activity against poisoning microorganism, including Gram-positive bacteria (e.g., S. aureus,[166] lactic acid bacteria,[27] and *Listeria innocua*,[77,149]), Gram-negative bacteria (e.g., *E. coli*,[102,110,121] Pseudomonas spp,[68,70,78] and Salmonella spp[75,88,111]), and fungus (e.g., yeast and mold,[26,162,167] *Aspergillus niger*,[125] and *Candida albicans*[125]).

There are also some differences between bacteria and fungus regarding antimicrobial activity. Some research pointed out that chitosan's bacteriostasis was higher than its fungistasis at low temperature.[168] The reason may be that mold spores were more resistant to low temperature than bacteria, and mold spore germination kept growing, causing low fungistasis. Even though the differences existed, chitosan films could also effectively protect the food from fungus.[40]

Overall, antimicrobial mechanisms of hypotheses on food are raised from outside to inside as follows. Figure 8 illustrates the antimicrobial mechanism of chitosan films.

Outside:

(1) Chitosan-based films serve as cellophane-like structure on the food surface, thus effectively building a protective layer and preventing the food from the attacks of the outer microbial.[169]

(2) Chitosan-based film can act as an oxygen barrier and hinder the transference of oxygen, which can inhibit the respiratory activity and the growth of bacteria in food.[162]

(3) Chitosan, a polycation biopolymer, can be absorbed on the surface of the microbial, and form a polymer membrane and cause blockage. The membrane can not only chelate some nutrients outside the microorganisms, but also prevent nutrient and necessary elements from entering the microbial cell and influence the physiological activity of the microbes, causing the microbes to death.[111,170]

Inside:

(4) NH_3^+ groups of chitosan can disturb the negatively charged phosphoryl groups on the cell membrane of the bacterial and cause distortion and deformation.[102,171] Also, different bacteria showed different sensitivity to chitosan's NH_3^+ groups.[172]

(5) The chitosan can diffuse the cell wall, disrupt the cytoplasmic membrane of bacteria, and affect the integrity, leading to leakage of the intercellular electrolytes and cell death.[39,173]

(6) Chitosan can penetrate nuclei, bind DNA, and inhibit its replication ability, thus suppressing synthesis of the RNA and the protein.[109]

(7) Chitosan can also chelate internal nutrients and essential metals that are important for microbes. These materials may lose activity and the chelation complex could not be utilized by microbes, restraining the growth of microbial.[174,175]

(8) Chitosan may induce the synthesis of Chitinase in fruit by increasing the gene expression of the Chitinase (in Figure 9), which indirectly degrades the cell walls of the microbial.[167,176] The treated wheat seeds with chitosan proved to induce resistance to *Fusarium graminearum* by

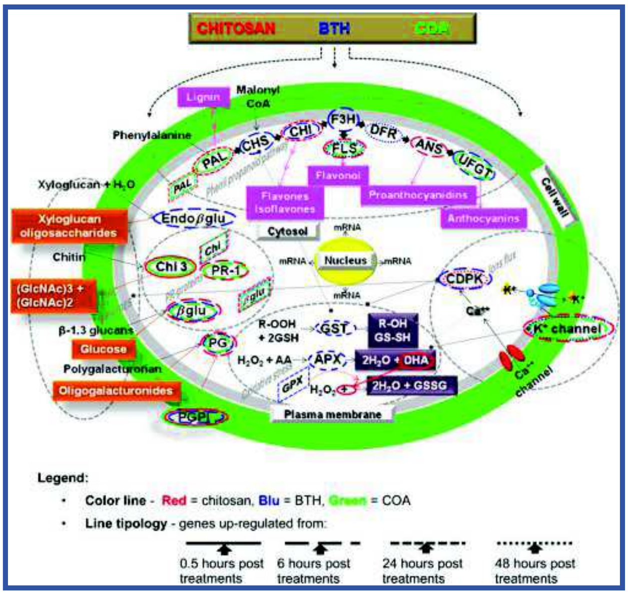

Figure 9. Gene expression and enzyme activity involved in resistance induced by chitosan and other materials. Glutathione S-transferase: GST; calcium-dependent protein kinase: CDPK; ascorbate peroxidase: APX; phenylalanine ammonia-lyase: PAL; chalcone synthase (CHS); chalcone isomerase: CHI; flavano 3-hydroxylase: F3H; dihydroflavonol 4-reductase:DFR; flavonol synthase: FLS; anthocyanidin synthase: ANS; flavonoid 3-O-glucosyltransferase:UFGT; endo-β-1,4-glucanase: endoβGlu; polygalacturonase: PG; polygalacturonase-inhibiting protein: PGIP; β-1,3-glucanase: βGlu; class III Chitinase: Chi3; guaiacol peroxidase (GPX). Reprinted with permission from ref 176. Copyright 2014 American Chemical Society.

stimulating the accumulation of phenolics and lignin and to improve the seed quality.[177]

BARRIER FILMS

Barrier properties are necessary to be characterized for application in stringent food packaging.[98,159] Currently, the detailed barrier properties against water, oxygen, carbon dioxide, nitrogen, UV light, etc. have been widely researched.

WATER VAPOR BARRIER FILMS

One of the main functions of food packaging is to prevent or lower the moisture transfer between food and surrounding environment. Water vapor barrier property, the important property of films for food packaging, indicating the barrier to water vapor, has direct influence on the shelf life of food products.[38,142] Many standards are involved in the measurement, such as ASTM E 96/E 96M,[41] ASTM E96-95,[31,66,85] ASTM D1653-93 and DIN 52615 standard,[68] ASTM E96-05,[60,61] and AFNOR NF H00-030.[56] To retard food deterioration, the water vapor permeability value should be kept as low as reasonably achievable.[41] Many operation conditions were studied to change the water vapor permeability of chitosan-based films, such as functional materials, pH, etc.

Functional materials have a significant decreasing effect on the water vapor permeability. Many organic materials (e.g., polyphenols) may build the interactions with chitosan via bonding, thus limiting the interactions between hydrophilic groups of chitosan and water molecules.[15] This competitive binding effect resulted in the decreased water vapor permeability. Nanoparticles, with three-dimensional networks, can disperse well in the film matrix, fill the empty spaces in the microstructure and thus prevent the migration of water molecule.[60] In addition, orderly dispersed nanoparticles compelled the water vapor to go through a tortuous path through the polymer network, lengthening the path length and hindering the passage of water molecule.[68,110,164] However, high concentration of glycerol caused a poor barrier to water vapor.[178] The phenomenon could be attributed to the glycerol properties that could modify the polymer network and give rise to mobile regions along with larger interchain distances, promoting the water molecules to pass through the film.

The effect of pH on water vapor permeability is attributed to the number of “available” −OH. At low pH, chitosan protonation is enhanced. Hydrogen bonds interaction between chitosan and pullulan molecules was improved, resulting in the decreased number of available −OH groups and the impeded exchange of water vapor.[179] Also the increased intermolecular bonds leaded to a polymeric matrix with reduced free volume and then the lower water vapor permeability.

OXYGEN BARRIER FILMS

Oxygen could lower the quality and reduce the shelf life of food. Oxygen permeability, an important parameter of film in food storage, demonstrates the ease of oxygen molecules transporting through the film and characterizes the film’s possibility for food packaging applications. Though chitosan can inhibit the entrance of gases into the obtained film because of the tightly packed hydrogen-bonded structure, oxygen barrier property of chitosan-based films is being widely studied and improved for practical packaging industries.[130]

The process of gas passing through the film involves four stages: (1) gas is adsorbed on the external atmosphere−film interface; (2) gas is dissolved in polymer matrix via interactions; (3) gas diffuses inside the films and crosses the film; (4) gas is desorbed from the film interface and released into the internal atmosphere.[95] The second and third steps are the rate-determining steps and are of vital importance due to the capacity of controlling the rate of oxygen permeability. During the two stages, many factors can effectively exert great effect on oxygen permeability, such as crystalline, chemical interactions, amorphous zones, fillers compatibility, chain mobility, and hydrophilic−hydrophobic ratio, tortuosity of diffusion path, etc.[26,32,142,159,179]

Chemical interactions act as a major role in the barrier properties of the obtained films. The cross-linking between oxidized products and chitosan was reported to result in tighter matrix, thus reducing oxygen permeability.[180] Films with ordered hydrogen bonded matrix structure and a more compact construction, have been demonstrated to be good oxygen barriers.[41,181] The formation of the cross-linking network developed by chemical reaction between borate ions and −OH of chitosan was also found to enhance the oxygen barrier property of the films.[113]

Environmental conditions matter in barrier property of films. Polar biopolymers including chitosan have good barrier property in dry environment. Relative humidity (RH) could influence oxygen barrier property greatly, because plasticization with water may lead to changes in the diffusivity and the solubility of oxygen molecules in the film matrix. RH from 0 to 50% did not significantly change the permeability.[182] At 50% RH, there are two opposite effects: (1) the occupation of free volume by water molecules (instead of oxygen); (2) the favorable diffusion of the increased segmental motion. Some

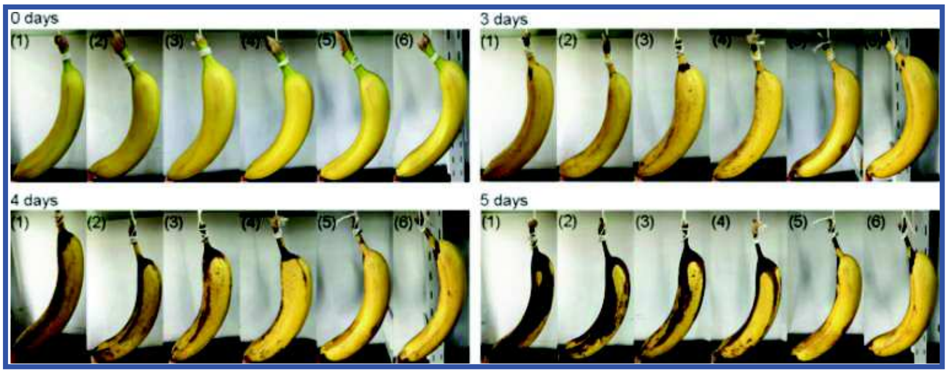

Figure 10. Comparative test of uncoated bananas (1), coated bananas by using CMC100 film (2), HTCC40/CMC60 film (3), HTCC70/CMC30 film (4), HTCC90/CMC10 film (5), and HTCC100 film (6). Carboxymethyl cellulose, CMC. 2-*N*-Hydroxypropyl-3-trimethylammonium chloride chitosan, HTCC. Reprinted with permission from ref 139. Copyright 2015 Elsevier.

researcher simulated the films at low 15% and 95% RH to offer atomistic-level mechanisms and found that oxygen permeability increased with the increase of humidity.[140] The increase in temperature also could result in higher oxygen permeability due to the increased mobility of molecular chains.[183]

This mechanism of oxygen barrier by the nanomaterials is due to (1) the adequate nanomaterial distribution in the films possibly reduces the free spaces and thus increases the difficulty for oxygen to pass through the film; (2) the strong interactions between nanomaterials and polymer result in the chain immobilization; (3) nanomaterials increase the crystallinity degree of the film matrix.[164,170] The oxygen permeability of chitosan-based films with nanomaterials was even lowered by three folds in comparison with the pure chitosan films.[124] Some hydroxide platelets and clays could also result in intercalated structures in the matrix that formed a tortuous path delaying or inhibiting the passage of oxygen.[93,129]

Side effects of the oxygen barrier could be obtained with the addition of some functional materials into chitosan. Carboxymethyl cellulose was reported to increase oxygen permeability of the chitosan-based film.[139] It may be attributed to the formation of carboxymethyl cellulose crystals that disrupted the homogeneous, continuous structure crystals of 2-*N*-hydroxypropyl-3-trimethylammonium chloride chitosan in the films. The treated bananas showed higher delayed decay when chitosan content was high (Figure 10). The addition of some materials, like lignin, may destabilize the chitosan network, thus influencing oxygen permeability.[184] Also, polarity of the material had a great influence on the oxygen permeability because oxygen molecules could dissolve better in less polar polymers. Poly(vinyl alcohol), a nonpolar material, was found to increase the oxygen permeability of chitosan-based films.[92] The explanation was that the polarity of film matrix was lowered due to the decrease of NH_2 and OH groups.

■ SENSING OR INDICATING FILMS

Food safety has been increasingly drawing the concern of consumers. During storage, pH and microbial population rise with the deterioration and spoilage of food. Natural and nontoxic technologies are needed to detect the quality of the food. Chitosan could combine with other biomaterials to develop sensing films, which could be sensitive to pH, microbial enzyme, microbial metabolism, etc. These films own many advantages, such as small size, lightweight, safety, sensitivity reversibility, and low cost, which demonstrate the capacity in intelligent food packaging.

Colorimetric sensor is popular currently. Methylene blue could be immobilized to the modified film via electrostatic interaction for indicating food condition, which was placed into the most inner layer.[103] Methylene blue could display a blue color under certain content of oxygen dissolved, and could show white color when oxygen was depleted by the metabolism of microorganism and the generation of reducing substance. A small window of the sensor on the inner face of the packaging film with reference colors around could thus indicate the food quality. Colorimetric pH sensor also provides potential for the indication of food quality, safety, and freshness. The indicator, based on chitosan, pectin, and anthocyanin, could indicate variation of pH by visual observation in color.[48] The variations of color were related to chemical structures of anthocyanin molecules that were sensitive to pH, and the color was restorable by adjusting the pH. Another study also reported the chitosan/anthocyanin based colorimetric pH sensing film.[185] The color from red to green matched with pH from 2.2–9.0, helping the sensor monitor the freshness of pork and fish (Figure 11). Highly sensitive and reversibility of the pH sensing film demonstrated the latent capacity as intelligent label to detect the spoilage of food.

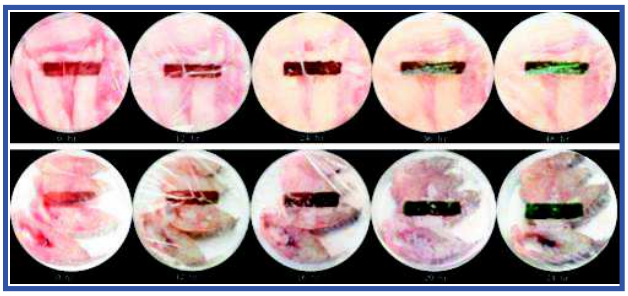

Figure 11. Application of sensing film as a sticker sensor for pork and fish freshness. Reprinted with permission from ref 185. Copyright 2014 Elsevier.

Microbial sensor also shows great promises. Microbial growth increases the threat to food safety, so systems that can report microbial infection are needed. Some authors reported chitosan hydrogel films with a self-reporting function for β-glucuronidase secreted by *E. coli* strains.[186] The hydrogel film sensor, based on covalent coupling of 4-methylumbelli-

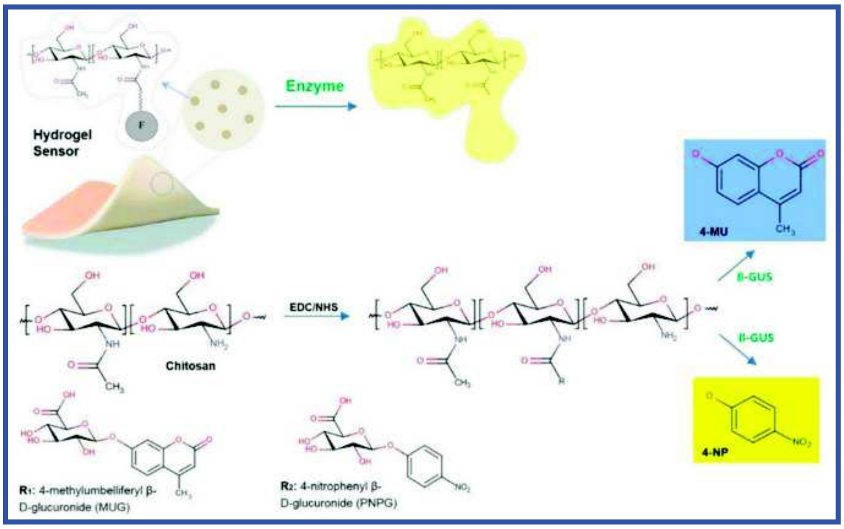

Figure 12. Schematic of the enzyme-sensing hydrogel platform and details of the modification of chitosan hydrogel. Reprinted with permission from ref 186. Copyright 2015 American Chemical Society.

feryl-β-D-glucuronide or 4-nitrophenyl-β-D-glucuronide, could report β-glucuronidase with detection limit <1 nM (Figure 12). The former is based on selective enzymatic reactions of β-glucuronidase. Enzymatic reaction resulted in hydrolysis of 4-methylumbelliferyl-β-D-glucuronide and the cleavage of 4-methylumbelliferone from the glucuronide unit. The deprotonation in the hydrogel medium could dramatically change the fluorescence emission and promote the deprotonated free 4-methylumbelliferone to be detected at certain emission wavelength. The later enzymatic cleavage is the process of β-glucuronidase liberating 4-nitrophenol from the glucuronide. The color from colorless to yellow observed by naked eye is attributed to deprotonation of 4-nitrophenol. The self-reporting chitosan-hydrogel-based film is promising in food packaging.

■ PERSPECTIVES

The biobased polymeric materials possess great potentials in the field of packaging for the severe environmental and human health threat of the petroleum-based packaging materials. Advances in the technology are enabling the preparations of chitosan-based films with multiple functionalities which are promising to be used as packaging materials. Packaging applications, for instance antibacterial films, barrier films, and sensing films, are the most involved areas of chitosan-based films in that chitosan is biocompatible, biodegradeable, antibacterial, and has low cytotoxicity. However, many efforts are needed to develop the chitosan-based films which can meet the practical criteria and compete with the petroleum-based packaging films. For instance some strategies need to be taken to enhance the mechanical strength of chitosan-based films to meet various packaging applications.

Future developments in chitosan-based films should be considered in the following aspects: (1) More chitosan derivatives and functional materials are needed to be explored and produced to meet special requirement. (2) These existing technologies could be optimized or combined with other advantageous technologies for getting closer to industrial production. Also, new technologies are still required for the facilely mass production of the chitosan-based films with desired properties to meet different packaging applications. (3) Thorough toxicity studies of the chitosan-based films need to be performed when the film is contacted with the food, for further practical application in market. (4) More studies need to be carried out to reveal the degradation and environmental impact of the films in a real environment. Though the chitosan-based films face many challenges to realize the practical usage, the films should have a bright future in different packaging applications.

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Notes

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