Advances in Polymer Technology

Polymer-Based Microencapsulation Delivery Systems in the Food Industry

Lead Guest Editor: Li Li
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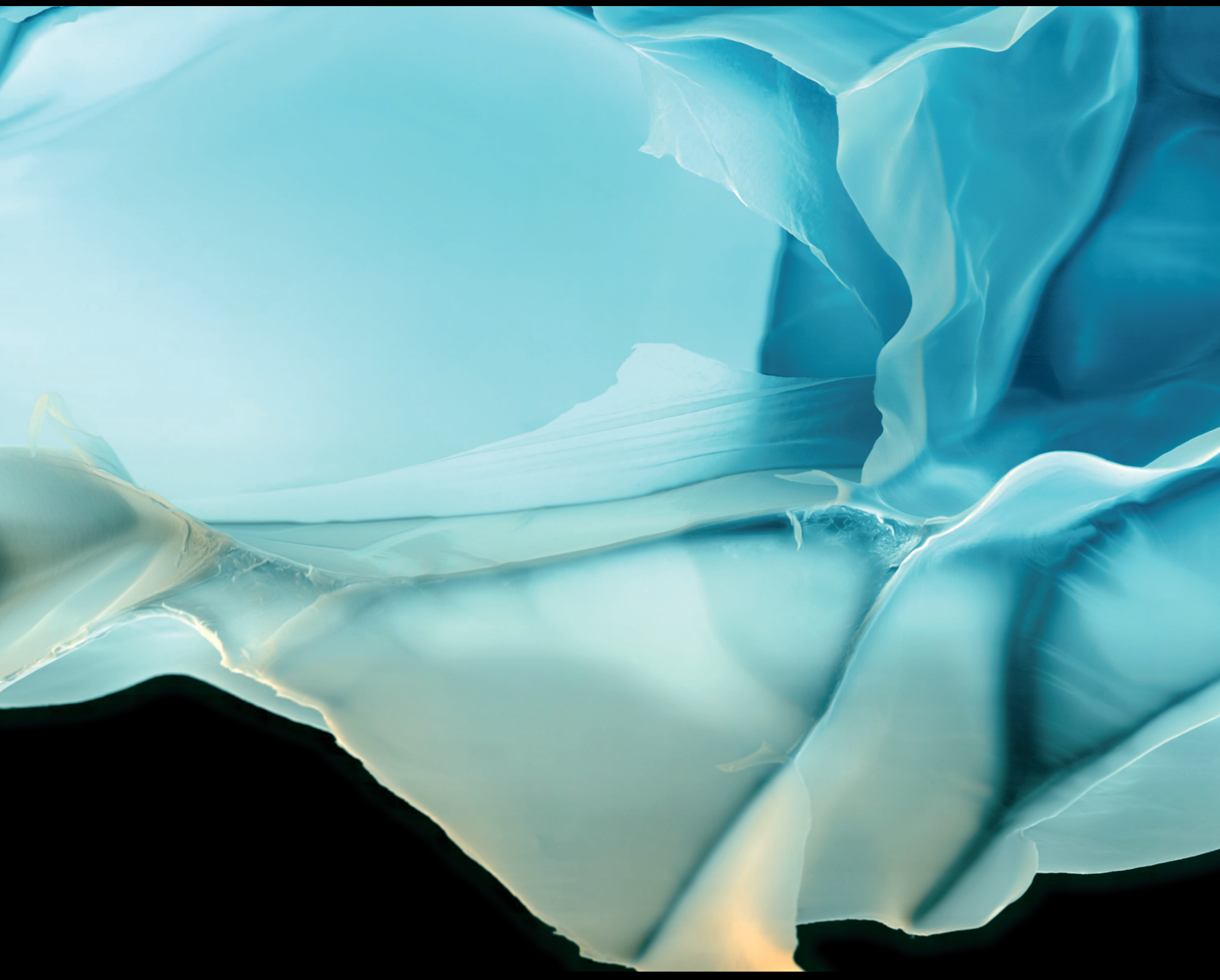

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Review Article

Microencapsulation Delivery System in Food Industry—Challenge and the Way Forward

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Microencapsulation is a promising technique, which provides core materials with protective barrier, good stability, controlled release, and targeting delivery. Compared with the pharmaceutical, cosmetic, and textile industries, food processing has higher requirements for safety and hygiene and calls for quality and nutrition maintenance. This paper reviews the widely used polymers as microcapsule wall materials and the application in different food products, including plant-derived food, animal-derived food, and additives. Also, common preparation technologies (emphasizing advantages and disadvantages), including spray-drying, emulsification, freeze-drying, coacervation, layer-by-layer, extrusion, supercritical, fluidized bed coating, electrospray, solvent evaporation, nanocapsule preparation, and their correlation with selected wall materials in recent 10 years are presented. Personalized design and cheap, efficient, and eco-friendly preparation of microcapsules are urgently required to meet the needs of different processing or storage environments. Moreover, this review may provide a reference for the microencapsulation research interests and development on future exploration.

1. Introduction

Microencapsulation is a physicochemical or mechanical process whereby one substance is embedded in another material, forming particles ranging from a few nanometers to a few millimeters. The global microencapsulation market was expected to expand at a compound annual growth rate of 13.70%, rising to 19.35 billion dollars by 2025 [1]. Microcapsules have been widely used in the drug delivery market. Nowadays, microencapsulation is also highly recommended in food industry because of the benefits provided, such as thermostability enhancement, bioactive compound protection, controlled release, volatiles maintaining, odor shelter, and texture/sense improvement [2]. Figure 1 presents the life of microcapsules, from forming to fading. Core materials are microencapsulated in monolayer or multilayers of wall materials with a variety of molecular interactions, including electrostatic attraction, van der Waals forces, and hydrogen bonding or ionic interaction. The wall materials protect the core material from harsh temperature changes, oxygen, or moisture permeation during processing and storage. Finally, passing through human digestive system, the outer layers of microcapsules might be dissolved in gastric acid at lower pH, then the core substances are released and absorbed in the small intestine. To adapt to different environmental conditions, the wall materials are designed to escort the core to target location.

The preparation of microcapsules requires simple equipment, continuous production, low production cost, and environmental friendliness. In addition, the most important thing for microcapsules applied in the food industry is to ensure that wall and core materials meet food safety

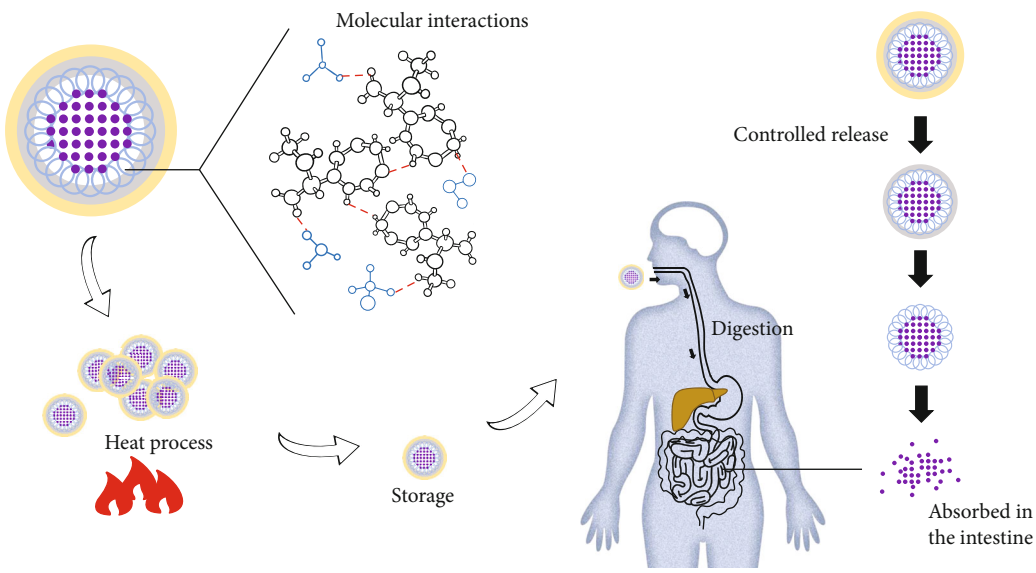

Figure 1: The life of microcapsule, forming to fading.

standards. Thus, strict requirements must be met including food grade raw and auxiliary materials and sanitary conditions of processing equipment. In the past few decades, the microencapsulation process has been constantly innovated to overcome the problems of easy degradation, low stability, and controlled release of functional components of food ingredients [3, 4]. In particular, the modification of particle characteristics was achieved through different equipment, procedures, materials, processing conditions, and other technologies [3–5].

In this review, the polymers commonly used in wall materials such as polysaccharides and proteins and their different properties are discussed. Additionally, the latest update of microencapsulation applied in food industry, including plant-derived food, animal-derived food, and additives, is introduced. Moreover, the advantages and limitations of different embedding technologies, as well as the correlation between the selective biopolymer and microencapsulation process, are presented to offer new insight for further development.

2. Polymers Used in Microencapsulation

The profile of microcapsules with different wall materials and their characteristics is shown in Table 1.

2.1. Cellulose and Its Derivatives. Cellulose is a macromolecular substance composed of glucose and is one of the main components of plant cell wall, the most abundant polysaccharide and widely distributed in nature, accounting for more than 50% of the plant carbon content. In order to improve the solubility, the thermoplasticity, and other properties of products, the hydroxyl group in cellulose polymers is usually artificially esterified or etherified into derivatives, such as methyl cellulose (MC), carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), and hydroxypropyl methyl cellulose (HPMC) [34].

Probiotics *Lactobacillus plantarum* LAB12 was enclosed in alginate-cellulose derivatives, MC, CMC-Na, or HPMC. Results showed that alginate-MC and alginate-HPMC significantly reduced the vitality loss of LAB12 in comparison with alginate alone [10]. Besides, the microencapsulated LAB12 in alginate-MC and alginate-HPMC exhibited the higher survival rate of 91% under simulated gastric environment, with the maximal release of approximately 100% [10]. With the increase of MC and HPMC concentration, their viscosity increased, the stability and strength of the cementing network also increased, and the matrix and gel system became more compact, reducing the free volume of the matrix, thus blocked the release of probiotics during gastric transport [10]. Furthermore, intermolecular interactions in the gel network strengthened the bonding, while at low pH, the gel network was weakened (molecular interactions were broken), leading to the release of probiotics [10]. Moreover, in order to increase the thermostability of probiotics *Bifidobacterium animalis* spp. *lactis* for powdered infant formula (PIF), the double-layered microcapsule with HPMC as an inner layer and HPC as the outer layer was performed to protect it against the high-temperature stress stimuli; and the presence of HPC with higher molecular weight and the thicker coating delayed the bacterial development after exposure to 70°C [35].

Oils, especially those rich in polyunsaturated fatty acids, tend to be oxidized and produce unpleasant odors; thus, oils are often essential to be sheltered in microcapsules. Cellulose derivative microcapsule enhanced the oil stability, and the variance in particle size and the shape affected the mobility, solubility, agglomeration, etc. [11, 13, 14] For instance, Karim et al. [13] optimized the encapsulation conditions of temperature (60°C), pressure (150 bar), and feed emulsion rate (1.36 mL min^{-1}) of the microencapsulated fish oil. Results demonstrated that the higher concentration of HPMC contributed to the increase of particle density, wettability, and powder porosity [13]. In addition to coating effect,

Table 1: Overview of microcapsules with various characteristics and bioactive effects.

Wall material	Core material	Embedding technology	Characteristics	Bioactive effect	Ref.
Algal extract					
Chitosan, alginate, chitosan/alginate, chitosan/inulin	Coriander essential oil	Spray-drying	Swelling degree ↑, Release rate ↑, Resistant to pH and temperature variations ↑, Encapsulation efficiency ↑		[6]
Sodium alginate and calcium chloride	Wine waste	Vibration nozzle	Polyphenol stability ↑		[7]
Sodium alginate/sodium alginate-citric pectin	*Lactobacillus plantarum*	Electrospray	Cell viability ↑, *L. plantarum* BL011 survival ↑		[8]
Sugarcane bagasse and sodium alginate	*Lactobacillus rhamnosus* NRRL 442	Extrusion	Thermotolerance ↑, Cell survivability ↑		[9]
Cellulose					
Alginate with supplementation of cellulose derivatives (methylcellulose, sodium carboxymethyl cellulose or hydroxypropyl methylcellulose	*Lactobacillus plantarum* LAB12	Freeze-drying	The survival of LAB12 ↑	Protective delivery for probiotic strains	[10]
Carboxymethyl cellulose or pullulan	Tuna oil, tuna oil/peppermint oil	Spray-drying	Spherical microcapsules with a smooth surface, Oxidative stability ↑	Higher antioxidant capacity	[11]
Carboxymethyl cellulose sodium and microcrystalline cellulose	Astaxanthin	Spray-drying	Astaxanthin retention value↑, Attractive color	Improved DPPH-scavenging activity	[12]
Hydroxypropyl methyl cellulose	Fish oil	Supercritical fluid collection	Particle flowability ↑, Particle density, wettability, and porosity ↑, Encapsulation efficiency ↑, Oxidative stability ↑		[13]
Yeast cells with hydroxypropyl methyl cellulose	Fish oil	Freeze-drying	External surface of the microcapsules ↓, Oxygen diffusion rate ↓		[14]
Chitosan					
Chitosan and chitosan/k-carrageenan	*Pimenta dioica* essential oil	Complex coacervation	The release rate increases with the chitosan content	Antimicrobial	[15]
Chitosan and inulin	*Lactobacillus casei*	Vibrating nozzle	*L. casei* survival rate ↑		[16]
Chitosan/xanthan and chitosan/pectin	Palm oil	Complex coacervation	Controlled release		[17]
High methoxyl pectin-alginate and chitosan	Kenaf seed oil	Coextrusion	Controlled release	Increased radical scavenging activities and tocopherols content	[18]
Pectin					
Pectin and milk protein–carbohydrate mixture	Fish oil	Spray-drying	Oil leakage ↓		[19]
Whey protein hydrolysate/pectin	Fish oil	Spray-drying	Thickness of the interfacial layer ↑, Encapsulation efficiency ↑	Increased antioxidant activity	[20]
Whey protein isolates and pectin	Anthocyanins	Freeze-drying	Flavonoid entrapment ↑, Thermal stability ↑	Antioxidant	[21]

Table 1: Continued.

Wall material	Core material	Embedding technology	Characteristics	Bioactive effect	Ref.
Starch					
Maltodextrin and modified corn starch	Swiss cheese bioaroma	Spray-drying	Moisture and water activity ↓		[22]
Maltodextrin, gum Arabic, and modified starch	Curcumin	Spray and freeze-drying	Curcumin loss and color change ↓, Curcumin retention and stability ↑		[23]
Porous starch granules from purple sweet potato	Olive oil	Osmosis or diffusion	Adsorption capacity ↑, Oxidative stability ↑		[24]
Resistant starch (Hi-maize)	*Lactobacillus acidophilus*	Spray-drying	Probiotic survival rate ↑		[25]
Protein					
Dairy proteins mixed with vegetable proteins	Sodium caseinate	Spray-drying	Droplet size↓, Thermal stability ↑, Encapsulation efficiency ↑		[26]
Pea protein concentrate, pea protein isolate, maltodextrin and sodium carboxymethyl cellulose	Conjugated linoleic acid	Spray-drying	Solubility ↑, Dispersibility ↑, Glass-transition temperature values ↑		[27]
Whey protein concentrate with mesquite gum	Chia oil	Spray-drying	Kinetic parameters ↓	Antioxidant	[28]
Zein	*Geoffroea decorticans* extract	Electrospray	Water sorption ↑, Release properties ↑	Inhibitory activity on metabolic syndrome enzymes	[29]
Composite materials					
Alginate, pectin and gelatin complexes	*Lactobacillus plantarum* and DHA-rich oil	Freeze-drying	Smoothness and compactness of the particle surface ↑, Thermal stability ↑	Higher survivability of encapsulated probiotics	[30]
Chitosan/sodium tripolyphosphate, chitosan/carboxymethyl cellulose	Carotenoids	Complex coacervation	Controlled release, Encapsulation efficiency ↑		[31]
Gum Arabic and modified starch together with either whey protein concentrate or soy protein isolate	Jussara pulp	Spray-drying	Process yield ↑, Solubility ↑, Total anthocyanin retention ↑, Encapsulation efficiency ↑		[32]
Gum Arabic, maltodextrin, and cellulose nanofibrils	Sweet orange essential oil	Spray-drying	Emulsion viscosity ↑, The droplet size ↓, Release rate ↑, Encapsulation efficiency ↑		[33]

HPMC promoted agglomeration, which reduced the outer surface of microcapsules, and decreased the oxygen diffusion rate [14].

2.2. Chitosan. Chitosan is the second richest biological polysaccharide in nature, inferior to cellulose, mainly distributes in the shell of shrimp and crab or cell wall of algae and fungi and is one of the most commonly used wall materials in the preparation of microencapsulation. The character of containing free amino group makes the chitosan the only basic polysaccharide among natural polysaccharides. And chitosan has many unique properties such as biodegradability, biocompatibility, and osmotic enhancement effects [36]. Chitosan, nontoxic and biodegradable, is a cationic polymer possessing strong antibacterial and antioxidant properties, thus is widely used in fresh fruit and vegetable, food additive, and even cosmetics, medicals, etc. [37].

For instance, chitosan coating improved the survival of probiotic *Lactobacillus casei* (only 2.7-2.9 logs reduction) and long-chain inulin (2.7 log reduction) under simulative gastrointestinal solution and better kept the size of micro particles while that of alginate beads was significantly decreased by 0.2 mm [16]. The protection effect might be explained by the electrostatic interactions between chitosan and alginate beads, which blocked gastric juices [16]. Besides, the addition of chitosan into microencapsulated alginate matrix improved the tolerance of *Lactobacillus reuteri* DSM 17938 against stress conditions during food processing, so

as to better maintain its microcapsule morphology and cell vitality after freeze-drying [38]. Lavinia-Florina et al. [39] reviewed in detail the application of chitosan in probiotic embedding products, focusing on cell survival, protection performance, and application.

Chew et al. [18] investigated the response of antioxidant activities and biological compounds in microencapsulated kenaf seed oil before and after *in vitro* simulated digestion, and results showed that the chitosan-coated microcapsule exhibited significantly higher DPPH (145.1%), ABTS (120.9%) scavenging activity, and vitamin E content (32.1%) than that of the noncoated microcapsule. In addition, chitosan can be hydrolyzed/digested by trypsin and lipase (mainly in the small intestine), contributing to the release of encapsulated substances [18]. Similarly, both enhanced antioxidant capacity and less loss of active ingredients were achieved in chitosan-microencapsulated palm oil, which contained a high content of carotenoid [17, 40]. Furthermore, it was evident that the chitosan microsphere-encapsulated *P. dioica* essential oil presented antibacterial effects against *Bacillus cereus*, *Bacillus subtilis*, and *Candida utilis* due to the antimicrobial activity of chitosan itself [40].

2.3. Alginates. Alginate is a natural polysaccharide and combines with various cations in seawater to form various alginate salts. Alginate is popularly applied in the development of controlled release system and microencapsulation technology due to its great thickening, flocculability, film-forming property, stability, chelation, and biocompatibility, as well as mild reaction conditions, nontoxic and harmless characteristics, simple gelatinization process, and low cost [34].

Sodium alginate is easily soluble in water but forms a gel when meeting the calcium ions, which offers a promising material for microencapsulation. Grape wastes rich in polyphenols were microencapsulated in calcium-alginate beads with optimized vibration nozzle and showed higher stability than nonencapsulated ones [7]. Compared with low molecular weight alginate, microcapsules made of high molecular weight alginate have higher encapsulation efficiency, but they are also bigger in size and release the active constituents much more slowly [7]. Therefore, low molecular weight alginates are more suitable for the occasion when the degradation of active constituents must be avoided, but their rapid release is desirable [7]. Besides, the alginate-based microencapsulated phenolic extracts of *Clitoria ternatea* (CT) petal flower had smooth surface with the maximal encapsulation efficiency of 84% under 1.5% alginate and 3% $CaCl_2$ conditions [41]. Higher polyphenol content was maintained, with the improved antioxidant capacity and thermal stability (at 188°C), as well as the inhibited pancreatic α-amylase activity, in this microcapsule after simulated gastrointestinal digestion [41]. A differential scanning calorimetry (DSC) test found that the interaction between alginate and CT enhanced the thermal stability of CT [41]. In addition, the enhanced tolerance in response to severe environmental conditions was achieved by microencapsulated probiotics *Lactobacillus reuteri* DSM 17938 in freeze-dried skim milk [38], *Lactococcus lactis* subsp. *cremoris* LM0230 in functional food [42] and *Lactobacillus rhamnosus* NRRL 442 exposed to heat stress [9]. A higher concentration of sodium alginate minimized the free volume of the microcapsules, thus reduced the thermal permeability [9].

Fioramonti et al. reported that the emulsion stability was affected by the pH value of solution and the initial sodium alginate concentration due to the electrostatic adsorption between whey protein isolate (charge differently at different pH) and negatively charged sodium alginate [43]. The optimal condition for linseed oil (rich in high unsaturated fatty acids) microencapsulation was 0.25% initial sodium alginate at pH 5.0 where no phase separation and coacervate formation was found [43]. Furthermore, the maximum release rate of spray-dried coriander essential oil embedded in chitosan was at pH 2.5, while that of alginate was at pH 6.5 [6].

2.4. Starch and Its Hydrolysates. A series of starch hydrolysates can be obtained with acid or amylase treatment. Dextrose equivalent (DE) value was reported to demonstrate the degree of hydrolysis or saccharification of starch and affect the viscosity, browning, and oxidation resistance of starch hydrolysates. Maltodextrin and corn syrup are two commonly used microcapsule wall materials, whose DE values are <20 and >20, respectively [44]. Porous starch is a kind of hollow particle (looks like honeycomb), which have great adsorbability and can contain various substances.

Olive oil microencapsulated with the porous starch prepared from purple sweet potato exhibited higher loading rate and oxidative stability than those of free olive oil, and the best adsorption capacity of porous starch was obtained at 45°C and pH 5.0 with reaction for 12 hours [24]. Maltodextrin-microencapsulated saffron and beetroot pigment extracts showed effective heat protection during storage with the average half-life period of 60.03 and 53.03 weeks, respectively [45].

It is widely known that the natural starch is insoluble in cold water, easy to retrogradation and dehydration, and poor in emulsification, while the modified starch improves its properties to widen its application. Curcumin yellow dye was an antioxidant easily degraded in response to light and oxidation stress, but the ternary mixture of maltodextrin, gum Arabic, and modified starch-encapsulated curcumin yellow dye still maintained a high retention rate after spray-drying or freeze-drying and light exposure [23]. In addition, the probiotics *Lactobacillus acidophilus* in microcapsule added with 1% resistant starch (Hi-maize) possessed smaller size (78.49 μm) than that in the sole alginate microcapsule (114.51 μm), while Hi-maize offered better protection for the probiotics exposed to the simulated gastrointestinal juice [25]. It was reported that the iron microcapsule embedded in the mixture of gum Arabic, maltodextrin, and modified starch at the ratio of 4 : 1 : 1 had the optimal encapsulation efficiency of 91.58% and particle stability; also, the significantly higher iron bioavailability *in vitro* was detected in microcapsule than that in the unencapsulated or in iron salt fortified milk [46]. It was reported that 50% modified starch-encapsulated Swiss cheese bioaroma had lower the moisture and water activity, which might be attributed to the reduced water diffusion by increasing viscosity with higher concentration of modified starch.

Also, the concentration of modified starch was positively correlated with the bulk density and average particle diameter [22].

2.5. Pectin. Natural pectin, widely exists in plant roots, stems, leaves, and fruits, is one of the components of the plant cell wall. The main component of pectin is partially methylated α-1,4-D-polygalacturonic acid, whose residual carboxyl units existed in the form of free acids or salts of ammonium, potassium, sodium, and calcium. Pectin has a good gelatinization and emulsification stability, widely applied in the food industry, such as ice cream, jam, and fruit juice gelatinization, and the gelatinization mechanism varies with different degree of esterification of pectin to match various characteristics (pH sugar concentration, etc.) of food gels [47].

Sanguansri et al. [19] reported that both the addition of pectin and heat treatment at pH 3 could reduce the surface oil and free oil of spray-dried fish oil powder and also lessen the oil leakage during powder compression, because a protective layer can be formed around the positively charged oil-water interface by adding the negatively charged pectin to a heated, positively charged stable emulsion. However, additional heat treatment of pectin-free emulsion at low pH resulted in greater loss of eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) in powder, since heating facilitated proteolysis and increased polydispersity [19]. Additionally, by using the layer-by-layer technology, the pectin was attached to the protein monolayer emulsions of fish oil microcapsule through the electrostatic interactions and reinforced the microencapsulation efficiency to 95.2% [20]. Although the addition of pectin increased the thickness of interface layer, the antioxidant effect and stability of the microcapsule was enhanced because of the inhibition of lipid oxidation [20]. Besides, pectin, as the wall material, protected the multicomponent carriers of microencapsulated hydrophobic and hydrophilic active substances from oxidation or degradation by oxygen or water [48]. Stănciuc et al. [21] embedded the grape anthocyanin extract with whey protein isolates and two different polysaccharides (acacia gum and pectin), and the encapsulation efficiency was up to 94%-99% after freeze-drying. The laser confocal scanning microscope observation showed that the addition of pectin contributed to the smaller particles, and the variant Cu pectin retained more flavonoids in microcapsules, leading to higher antioxidant activities; and results of the thermal stability study indicated that the pectin had a better protective effect against the anthocyanin degradation [21].

2.6. Protein. Protein widely holds processing properties such as solubility and emulsification, as well as the physiological activities of oxidation resistance, good biocompatibility and biodegradability. In addition, the susceptibility to pH rendered the protein in a great role in strict pH-controlled release conditions [49]. Therefore, protein is another widely used wall material of microcapsules to meet particular situations.

It was reported that microcapsule with sodium caseinate as wall material had a 13.93% higher retention rate of vitamin A than that with milk protein concentrate, which might be attributed to the excellent emulsification performance and the molecular flexibility of sodium caseinate [26]. Moreover, the combination of sodium caseinate and pea protein isolates as wall materials led to smaller droplet size, better emulsion thermal stability, and the optimal microencapsulation efficiency (96.08%) [26]. Higher denaturation temperature of pea protein isolates (83.8°C) contributed to its great thermal stability, while the denaturation temperatures of whey protein and soy protein were only 70°C and 68-88°C, respectively [26]. Oxidation kinetics and thermodynamic analysis indicated that water within the a_w range of 0.614-0.654 acted as the plasticizer in the polymer matrix, preventing oxygen from passing through the pores, thus delaying the oxidation process to improve the stability of the microcapsule in a whey protein concentrate-polysaccharide matrix and to extend the shelf life [28].

Compared with animal protein, which costs more natural resources, plant protein that is more environmental friendly and meets the needs of vegetarians and people who want to lose weight, gradually enters the market [50]. Studies showed that the application of pea protein, soy protein, zein, or other plant protein well maintained the bioactivities of core materials and improved the solubility, dispersibility, stability, and so on [27, 29]. For example, the microcapsule encapsulated with pea protein isolates exhibited smaller size by preventing droplet aggregation, and higher oxidative stability, which possibly resulted from its antioxidant properties [26]. Besides, the hydrogen bonding between the amino group of protein and the hydroxyl groups of the polyphenolic compounds strengthened the compactness of the wall and the core materials [29].

2.7. Composite Materials. The application of a single material is usually limited to its own nature; therefore, it is necessary to add other ingredients to make composite materials to enhance advantages and weaken disadvantages, so as to satisfy various environmental requirements.

Santana et al. (2016) found that the microcapsule made from the ternary formula of gum Arabic and modified starch, together with either whey protein concentrate or soy protein isolate, exhibited higher process yield, solubility, anthocyanin retention rate, and encapsulation efficiency, as well as lower moisture content than that made from pure or binary formulas [32]. The addition of the ternary mixture of gum Arabic, modified starch, and whey protein concentrate with a high molecular weight increased the glass-transition temperature of the powder and decreased its viscosity, so that fewer solids would paste on the dryer chamber wall, which improved the process yield [32]. In addition, cell survival was increased by nearly 40% in encapsulated microcapsule composite of 1.06% alginate, 0.55% pectin, and 0.39% gelatin, in comparison to the 50.36% survival of free cells [30]. At high pH, the chain repulsion between the negatively charged deprotonated carboxyl groups in alginate and pectin produced osmotic pressure, leading to an increase in the swelling rate [30]. But the strong hydrogen bonding between the protonated amino group in gelatin and deprotonated carboxyl groups in alginate and pectin well balanced the intermolecular forces to avoid destruction [30]. Higher thermal resistance and

crystallinity degree were detected in (ovalbumin, pectin, and xanthan gum) microencapsulated sacha inchi oil, indicating better heat stability and structure organization to protect ω-3 in oil [51].

The composition and proportion of microcapsule materials were adjusted to shape different properties, applying in personalized customization. For example, in the sweet orange essential oil microcapsule, the presence of cellulose nanofibrils helped reduce the droplet size and improve the encapsulation efficiency by increasing the emulsion viscosity, but promoted more essential oils release at 25°C due to its favorable permeability to liquid, in comparison to the formulation without cellulose nanofibrils [33]. Chitosan/carboxymethyl cellulose encapsulated carotenoid microcapsule showed low release in water and gastric juice which avoided degradation, and also low release in intestinal juice (adverse for absorption). In contrast, the microcapsules encapsulated in chitosan/sodium tripolyphosphate exhibited high release rate in water and gastric juice, and intestinal juice [31]. Similar research was performed on the microencapsulation of palm oil and the release curve revealed that the chitosan/xanthan wall material was more suitable for yoghurt system than chitosan/pectin [17].

FTIR spectra is widely used to investigate the characteristics of molecular structure and is also used to determine the intermolecular forces, including the bonds between wall and core materials, or those among composite materials of microcapsule, such as hydrogen and Van der Waals bonds [30], electrostatic interactions [52], and Ca^{2+} complexation [8]. However, the lack of structure-activity relationship studies remains to be a major barrier in microcapsule application. That is why there were lots of research on microencapsulation with composite materials, but much fewer were actually applied in market production. It might be a promising solution to design the microparticles according to corresponding delivery process in desperate need of further study on molecular mechanism. Moreover, it is of great significance to establish a database to sort out and summarize the current researches on microcapsules, including the properties of various materials and the interactions and effects of these materials in different occasions. Then, the researchers can customize the microcapsules according to their use to match the suitable wall material and give full play to the advantages of different ingredients.

2.8. Yeast Cells. Yeast cells, which are light in color and smell, disperse well in water, have strong adaptability to environment, and can be cultured on a large scale. Their natural eukaryotic cell structure makes them potential for material embedding. These characteristics of yeast cells offer advantages that other microcapsule wall materials cannot match: (1) the natural double-layer cyst structure formed from the outer cell wall and inner cell membrane of yeast cells can avoid volatilization loss of aromatic substances and oxidative deterioration from environmental light or oxygen invasion [53]. (2) No requirement of any other additives during the preparation of microcapsules (only yeast cells, core substances to be embedded, and solvents are needed to contact at high frequency) [14]. (3) Easy release of core substances: once meeting the wet mucosa such as tongue or nose mucosa, flavor substances or other active components can be released without breaking the wall. Yeast cells' natural biological adhesion provided a long-term release for flavor substances. (4) The nonthermoelastic cavity structure ensures that the wrapped core material will not be damaged by heat extrusion, roasting, frying, or boiling in the food processing. The β-glucan, which supports the physical strength of the cell wall, is difficult to break down and protects the core substance from pressure heating or freezing treatments [54]. (5) Yeast cells, safe and nontoxic, are easy to culture, thus have become an economical and eco-friendly microcapsule wall material.

For example, two flavors (D-limonene and ethyl hexanoate) in the yeast retained almost 85% after 1 h dry heating at 140°C, and thermogravimetric analysis suggested that the yeast cell wall would not break until a temperature above 260°C [54]. However, flavors were rapidly released once water was added to the powder, because hard β-glucans became soft and soluble under wet conditions and turned into a gelatinized solution [54].

3. Applications in Food Industry

3.1. Applications in Plant-Derived Food. With the improvement of people's living standard and the pursuit of healthy life quality, health-promoting and environmental friendly plant-derived food will have a larger m4arket. At present, there have been a few studies on the application of microcapsules in baking, fruit/vegetable juice, or other plant foods to enhance the nutrition.

Umesha et al. found that the addition of microencapsulated garden cress seed oil protected α-linolenic acid against the oxidation in biscuits to prolong its shelf life [55]. The *Garcinia cowa* fruit extract rich in hydroxycitric acid, which is health-promoting but hygroscopic and thermosensitive, was protected by microencapsulated powder using whey protein concentrate and was incorporated into bread baking [56]. Among three microcapsules with different wall materials (whey protein isolate, maltodextrin, and a composite of both), the whey protein isolate exhibited higher encapsulation efficiency during the baking process. Besides, the bread with whey protein isolate-encapsulated *Garcinia cowa* fruit extract showed softer, lighter-texture, more desirable color and organoleptic properties, and higher free hydroxycitric acid concentration [56]. Furthermore, the pasta with microencapsulated hydroxycitric acid by spray-drying had higher antioxidant ability and sensory characteristics [57].

It was reported that passion fruit juice encapsulated in *n*-octenylsuccinate-derivatised starch retained over 70% of vitamin C after 77 days of storage at 7 or 25°C [58]. Alginate microbeads were effective in reducing the acidification and improving the sensory properties of fruit-based foods during storage [59]. In addition, the microencapsulation of allyl isothiocyanate (resistant to pathogenic fungi but irritating) effectively controlled its release rate to relieve irritation. And its application on fresh tomato significantly reduced the decay rate and weight loss, thus prolonged the shelf life of fresh products [60]. Microencapsulation was also a promising alternative to improve the stability

of polyphenols, pigments, and nutrients in fruit-based food [61–63]. It was evident that the microcapsule of maltodextrin and Arabic gum maintained the anthocyanin content up to 150 mg 100 g^{-1}, over 80% of the initial concentration in juçara fruit pulp [63]. Interestingly, the microencapsulated alginate beads (*Lactobacillus plantarum* HER1325) prevented bacteriophage infections during vegetable fermentation [64].

3.2. Applications in Animal-Derived Food. Compared with plant-derived food, microencapsulation technology is more applied in animal-derived food, especially in antiseptic and antimicrobial properties of meat products and probiotics maintenance in dairy products.

Microencapsulated clove oil might be an alternative preservative with antimicrobial effect, and only 0.070% of addition could reduce the disease index and mold spore variation rate, which made it effective for cooked meat products [65]. Although nisin has antibacterial activity, but no free nisin was available after 28 days of storage at 4°C. It was reported that the nisin microencapsulated in alginate-cellulose beads was evident to maintain half of the initial concentration of nisin (63 μg mL^{-1}), which significantly reduced the number of *Listeria monocytogenes* in ready-to-eat ham and did not change the pH and the color [66]. Furthermore, lower fat content and energy value and higher protein concentration were detected in sausage, partially replaced with microencapsulated fish oil [67]. Besides, better preserved EPA and DHA, oxidation protection, and healthier polyunsaturated/-saturated fat ratio were achieved by microencapsulation which reduced the atherogenicity and thrombogenicity traits [68–70].

Microencapsulation technology was also widely used in dairy products, especially in yogurt, in order to improve the vitality of probiotics in lower pH environment [71], resist gastric juice [72], inhibit postacidification [73], and release microbial cells in the intestinal environment to increase the bioavailability [74, 75]. *Lactobacillus paracasei* subsp. *paracasei* and *Lactobacillus paraplantarum* microencapsulated with whey protein isolate and gum Arabic by complex coacervation exhibited significantly higher viability in simulated gastric juice (from 19% to 73%) and higher survival rate (from 59% to 86%) after 60 days of storage at 4°C than nonencapsulated cells [74]. Results demonstrated that the polyphenol extract microcapsule obtained by freeze-drying method had higher stability than that by spray-drying method, and the pH, titratable acid, viscosity, or other physiochemical properties of the supplemented yogurt were less affected [76]. Penhasi microencapsulated *Bifidobacterium animalis* spp. *lactis* in a double-layer capsule with the smart coating of hydroxypropyl cellulose and hydroxypropyl methyl cellulose for powdered infant formula [35]. The polymer formed a gel structure around the bacterial core to prevent heat and humidity from reaching the core materials and to protect the bacteria [35].

Excitingly, a research confirmed the specific interactions between the bacteria and whey protein, and that the pilus played a crucial role in the localization of bacteria in the microparticles. On the contrary, the encapsulation efficiency of the mutant lacking pili decreased significantly [77]. This discovery provided a new insight into the molecular mechanism of the embedding of probiotics [77].

3.3. Additives. Except for plant-derived food and animal-derived food, microencapsulation is also widely applied in food additives to offer food attractive appearance and fragrance to satisfy market requirement. Aromatic substances (D-limonene and ethyl hexanoate) coated with yeast powder had higher oxidation stability than that coated with maltodextrin [54]. Moreover, the presence of cyclodextrin entrapped volatiles and well maintained the strawberry flavor in response to the environment stress stimuli [78]. Estevinho and his colleagues produced flavor microparticles encapsulated in water-soluble chitosan by spray-drying, and the particle less than 100 μm in size with smooth spherical surface was obtained [79]. The mussel protein hydrolysate had bitter taste because of the hydrophobic amino acids produced during protein hydrolysis, but the bitterness was well covered up by microencapsulation to improve the sensory acceptance [80]. Similarly, unpleasant taste and odor of isoflavone added in the beverages were masked by being microencapsulated in inulin and maltodextrin [81]. Then, the microencapsulated isoflavone was gradually released during simulated digestion [81]. In addition, hibiscus extract rich in anthocyanins was a natural colorant but sensitive to light, heat, and oxygen. Microencapsulation through dripping-extrusion or atomization effectively increased the stability of anthocyanin during food processing and storage [82]. Furthermore, the controlled release achieved by microencapsulation offered a long duration of flavor in chewing gum [83]. Due to the high cost and technical constraints, the application of microcapsule technology in everyday condiments is still under research in the laboratory stage. But microcapsule technology has already commonly appeared in the fortified food market, such as Capsulae (France), Microtek Laboratories, Inc. (U.S.), Aveka, Inc. (U.S.), Taste-Tech Ltd. (U.K.), LycoRed Ltd. (Israel), and Innobio Limited (China), which are top companies in microencapsulation market involved in food industry [84].

4. Microencapsulation Techniques

The publications of commonly used microcapsule embedding technologies from 2010 to the end of 2019 are shown in Figure 2. Apparently, "spray-drying" came first by a landslide, accounting for almost a third of all publications, followed by "emulsification," "freeze-drying," and "coacervation." Next, the advantages and disadvantages of several top published embedding techniques are presented below.

4.1. Spray-Drying Technique. Spray-drying microencapsulation is to atomize the emulsion of wall material and core material in the dry and high-temperature environment, which evaporates the moisture via heat exchange between the droplets and the drying medium and solidifies the shell of droplet quickly to wrap the core material. This coating method, the most widely used embedding technology, is characterized by low cost (30-50 times lower than freeze-drying), simple operation, continuous production, and

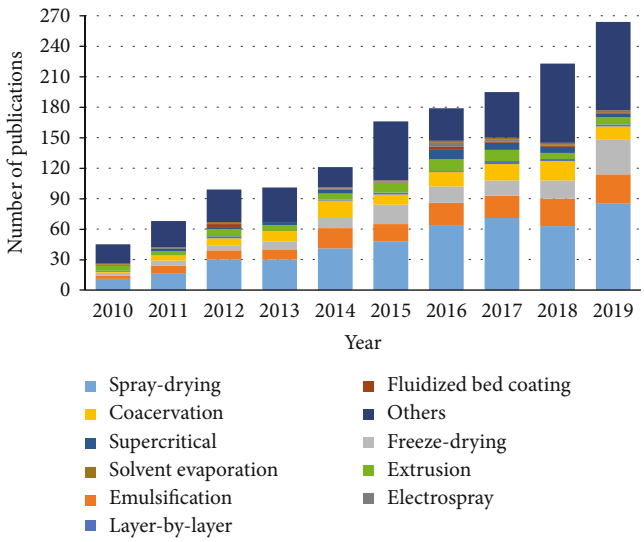

Figure 2: Number of literatures published from 2010 to 2019 regarding microencapsulation technology development on food science and engineering (obtained on Scopus, June, 2020; common keyword: "microencapsulation" and "food").

suitability for mass production [4]. However, during the preparation process, the core material should be in the high-temperature airflow, where the active substances are easy to be inactivated, resulting in lower embedding rate and coating efficiency [4]. Besides, spray-drying method requires that wall materials have good water solubility, low viscosity, and good fluidity, so only few wall materials can be used for spray-drying, such as Arabic gum and modified starch, which limit the application of spray-drying [3]. Moreover, low water evaporation brings about agglomeration or hardening, whereas the excessive water evaporation leads to cracks in the wall material and reduced compactness. Several studies combining spray-drying with vacuum-drying or freeze-drying improved the embedding efficiency of probiotics or other heat-sensitive materials but also increased the production cost [85].

4.2. Emulsification Technique. Emulsification is a chemical embedding method in which the mixture of core material and wall material (dispersed phase) is added into a large number of vegetable oil (continuous phase), containing the emulsifier to form a stable emulsion and microencapsulate under the action of cross-linking agent. Although the high survival rate and simplicity of encapsulated probiotics, the feasible preparation process was achieved by this method, and the production cost was usually very high because of the large amount of vegetable oil required [5].

4.3. Freeze-Drying Technique. Freeze-drying is a method of sublimating the ice into vapor under high-vacuum condition after quick freeze. The ice sublimation removes heat and keeps the whole process cool, which preserves the activity of some biological samples, such as proteins. However, the formation of ice crystals during freezing process and the high osmotic pressure during dehydration might destroy the integrity of the microbial cell membrane; therefore, the hydrophilic substance is usually added into the system as the cryoprotectant [86]. Due to the high-cost limitation, freeze-drying technique is more used for heat-sensitive food with high value.

4.4. Coacervation Technique. The core material is emulsified or suspended in the solution of wall material, and then another substance or solvent is added to reduce the solubility of the wall material, which is evenly aggregated and surrounded by the core material to form microcapsules. The coacervation technique includes the complex condensation and the single condensation. In the complex coacervation, two materials with opposite charges are used as wall materials, and the core materials are emulsified and dispersed in the wall materials solution. By regulating the pH, temperature, or concentration of aqueous solution of the system, the two wall materials are aggregated with the core material through the interaction between the opposite charges to form microcapsules [87]. Complex coacervation is a commonly used technique for embedding fat-soluble food ingredients with advantages of no need of special equipment, mild process conditions, less damage to core material quality, and higher product encapsulation efficiency, as well as the better antioxidation and release controlling properties. Gelatin and gum Arabic wall materials are more applied in the microcapsule preparation by coacervation method [88, 89]. The main disadvantages of coacervation technique are high cost, a lot of coagulants consumed, difficult to control the conditions of coacervation reaction, fewer coagulants available for wall materials, and easily produced chemical residue during processing [3]. Due to these shortcomings, this technique is still at the experimental stage and has not been widely applied in food industry. However, it is still a potential technique due to the great release control ability.

4.5. Layer-by-Layer (LBL) Assembly Technique. Layer-by-layer (LBL) self-assembly is a process in which layers are spontaneously attached with each other to form the stable molecular aggregates or supramolecular structures which possess specific functions or performances by noncovalent interactions, like electrostatic attraction, hydrogen bond, and coordination bond. LBL assembly technology does well in controlling the size, shape, composition, thickness, and structure of the capsule on the nanometer scale accurately [90, 91]. Therefore, LBL assembly technology is a promising method for the preparation of multilayer microcapsules matching variable environment [90]. However, the preparation process of LBL self-assembly, where multiple wall materials with different charges are needed, takes a long time; therefore, this technique is not suitable in mass rapid production yet. Moreover, the insufficient stability of LBL assembly that resulted from the weak interactions may impact the product quality.

4.6. Extrusion Technique. Extrusion is a physical embedding method for forming microcapsules by squeezing core material and colloid mixture into the hardening bath in the form of the liquid drops through the needle tube under pressure.

The cost is more than twice as much as the spray-drying, but this technique could effectively protect oil from volatilization and oxygen to significantly extend the shelf life of products due to its small surface area of micropores [3]. However, the low production rate could not meet the demand of large-scale production in industrial application, and the large particle size affects its taste [47]. And carbohydrates that could form glassy structures are commonly used as wall materials [92]. Extrusion technique is commonly used for embedding all kinds of volatile, vitamin, and pigment compounds or other heat-sensitive materials.

4.7. Supercritical Technique. The nonvolatile substance is dissolved in the supercritical fluid, which could rapidly expand in a very short time when decompressed through the pore capillary, so that the solute oversaturates and a large number of fine particles are formed. By controlling the experimental conditions, the hollow microcapsules with a certain particle size could be precipitated and separated [93]. Then, the generated hollow microcapsules and the core material collide with each other frequently and evenly wrapped together. Afterwards, the microcapsule product could be obtained after removing the unembedded core material [93]. Among the supercritical fluid, the supercritical CO_2 is most widely applied because of the low critical temperature, low viscosity, high solvent, high dispersion, high mass transfer, and nontoxicity. Usually, the supercritical CO_2 to prepare microcapsules requires almost no organic solvents, green and environmentally friendly, and the resulting product has a small particle size and is suitable for heat-sensitive substances [93]. In addition, hydrophobic or hydrophilic materials that can be dissolved in CO_2 can be used as microcapsule wall materials [94]. However, the solubility of CO_2 to different solutes varies greatly, and materials with low boiling point, low polarity, or low molecular weight are generally more suitable [94].

4.8. Electrospray Technique. Electrospray is to decompose the polymer fluid transported by the conductive capillary pump into the fine droplets through a high-voltage electric field [95]. After the solvent evaporates, the polymer particles are generated and collected on the metal collector to obtain microcapsules [95]. This electrospray technique does not require additional reaction solvent and could be realized in one-step and eco-friendly [96]. Microcapsules prepared by electrostatic spray are homogeneous and nanometer in size, which has attracted more and more attention [5]. The electrospray technology has widely been applied in the pharmaceutical industry and has great potential in the encapsulation of bioactive substances, volatile compounds, sustained-release preservatives, and functional foods in food industry [5].

4.9. Nanocapsulation Technique. With the development of microcapsule technology, the particle size of microcapsule can reach the nanoscale, that is, the nanocapsule. Nanocapsule is characterized by a small particle size, large specific surface area, and easy formation of uniform and stable colloidal solution. Besides inheriting the advantages of ordinary microcapsules, nanocapsules are smaller in size, which can increase the adhesion of active substances to tissues, so they effectively improve the bioavailability of nutrients in functional foods [97]. Nanocapsules can also penetrate through capillaries, penetrate into tissues, and be absorbed by cells, thus enabling more precise targeting of the core materials [98]. Therefore, nanocapsule has become an emerging direction in the microcapsule research field.

Compared with ordinary microcapsules with particle size in microns, nanocapsules have higher requirements on particle size; thus, nanocapsules need additional special treatments, usually high energy, based on the preparation of ordinary capsules, such as ultrasound, high pressure, or intense mechanical agitation [5, 93].

5. Conclusions

This paper offers an overview on the recent development of microencapsulation in food industry, especially the advances in polymer wall materials, food applications, and embedding technologies. Microencapsulation technology is mainly applied in the delivery of functional ingredients, which contributed to the extension of shelf life, the enhancement of thermal stability, the inhibition of pathogenic microorganism development, the enrichment of nutrition, the controlled release, etc. A variety of materials were used to prepare microcapsules, including polysaccharides, proteins, and other rich natural sources. And the composite materials were increasingly attractive to meet the needs of different delivery systems in response to various environmental stress stimuli. A database can be built based on the characteristics of different wall materials and various microencapsulation techniques to help/guide researchers to design and produce suitable microcapsules. Moreover, microencapsulation was widely used in animal-derived food, including dairy and meat, and plant-derived food, especially the preservation of fresh fruits and vegetables or color-protection in baking. Besides, additives with microencapsulation got further progressed and wider application. Among the microencapsulation technologies, the spray-drying technique was ranked first for the low cost and suitability for large-scale production. However, other novel techniques free from environmental pollution, such as the LBL self-assembly and electrospray, are potential and likely to be new directions in the future.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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Research Article

Chitosan-Based Layer-by-Layer Assembly: Towards Application on Quality Maintenance of Lemon Fruits

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We fabricated a novel chitosan-carboxymethyl cellulose (CMC) layer-by-layer assembly system to facilitate the postharvest quality of the fresh produce. Fourier transform infrared spectroscopy (FTIR), TA-XT2 texture analyzer, water vapor permeability (WVP) analyzer, and scanning electron microscopy (SEM) were applied to compare the properties of chitosan and layer-by-layer assembly. The strategy involved the optimization of water vapor permeability, puncture strength, and elasticity properties of multiplayer polymer coating. Results showed that the lemon (*Citrus limon* (L.) Burm. f.), coated by chitosan-CMC layer-by-layer assembly, displayed significantly higher lemon firmness and vitamin C content with excellent morphology, as well as inhibited weight loss and flesh browning. This study could provide support for quality maintenance in the fruit and vegetable industry and make a significant contribution to the utilization of the natural polysaccharide as a viable resource.

1. Introduction

Recently, due to the increasing awareness of human health and environment pollution issues, the development of natural biodegradable polymers for the quality maintenance of fresh produce has been increasingly attractive [1]. Natural polysaccharides have been proved to be promising natural products and widely used as the edible coating of fresh fruits and vegetables [2]. Polysaccharide edible coatings are based on edible and biodegradable materials since they are sustainable, plentiful, environmental friendly, and biocompatible and have low toxicity, which meets the demand for human health free of chemical residues and environmental concerns [3].

Recently, the research on green and sustainable polymers has been increasingly attractive, such as alginate [4], polarclean [5], bamboo [6], cellulose [7], Tamisolve [8], and biocoatings [9]. Chitosan, the biodegradable polymer made from the deacetylation of natural polysaccharide chitin [10], exhibits the intrinsic antimicrobial activity and has been widely utilized in fresh produce [11]. Chitosan-based edible coating, due to its selective permeability to O_2 and CO_2 and excellent film-forming capacity [12], was demonstrated to be effective in inhibiting the decay development and in maintaining the quality of fresh produce [13]. Additionally, carboxymethyl cellulose (CMC) is the anticipated material due to its nontoxicity, biodegradability, and good film-processing properties [14].

Layer-by-layer (LBL) is a novel nanoscale approach, which mainly leverages the electrostatic deposition of charged materials (such as the nanoparticles, polymers, and polyelectrolytes) onto the assembly surface [15, 16].

Additionally, other charged materials, such as DNA, proteins, polysaccharides, and nanoparticles, could be used in the LBL deposition approach, which could be used in combination with one another to provide various LBL assemblies [17]. In recent years, the LBL electrostatic deposition approach was applied to prepare biogradable edible coatings which resulted in the notable quality improvement of the fresh produce [18]. Multilayered LBL edible coating, based on pectin and chitosan, was proved to prolong the shelf life of fresh-cut papaya [19]. LBL edible coating, made of alginate and chitosan, was reported to notably improve the microbial and physiological attributes of fresh-cut melon [20]. Lemon (*Citrus limon* (L.) Burm. f.) is the third most top species among all citrus worldwide after orange and mandarin and is cultivated in several countries all over the world [21]. The mature season of the lemon fruit is averagely from August to December in every year. Lemon fruit is abundant in carotenoids, flavonoids, minerals, vitamins, essential oils, and dietary fibres. The valuable biological properties, antioxidant, and free radical scavenging potentials, as well as the health beneficial effects of lemon have been abundantly been evident in several studies; And, also it was proved that the antimicrobial and antiinflammatory properties of lemon contributed to lowering the risk of cardiovascular disorders and certain types of cancer [22–25]. Therefore, it is used worldwide not only as a fresh ready-to-eat fruit, but also as ingredients in beverages, desserts, salads, and many meat and vegetable dishes and even herbs. Nevertheless, the major postharvest loss of fresh lemons resulted from the physiological disorders, weight loss, and fungal infection, which eventually lead to the commercial revenue losses, including nutrients loss, water loss, and decay development during storage and transportation [25]. The limited application of chemical residues and urgent demand of natural biodegradable materials motivated the new breakthrough in the industry of fresh produce such as lemon.

The efficacy of a chitosan-CMC LBL assembly, formed by CMC and chitosan, on postharvest quality maintenance of the lemon fruit was evaluated in the present study. The characteristic properties, including thickness, water vapor permeability (WVP), puncture strength (PS), and elasticity of LBL assembly, were investigated, and the representative quality attributes of the lemon fruit, including weight loss, total soluble solid (TSS), and titratable acidity (TA), were studied. This study may promote the application of CMC-chitosan or other polysaccharides on the postharvest quality maintenance of the fresh produce.

2. Materials and Methods

2.1. Materials. Chitosan powder (molecular weight: 161.16 kDa; degree of deacetylation 95%) have been purchased from Zhejiang Golden Shell Pharmaceutical Co., Ltd. (Yuhuan city, Zhejiang province, China). Glacial acetic acid and oxalic acid dihydrate of analytical grade have been purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Ascorbic acid and 2,6-dichlorophenolindophenol sodium salt and CMC of analytical grade (molecular weight 242.16 kDa) have been purchased from Shanghai Runjie Chemical Reagent Co., Ltd. (Shanghai, China). Lemon fruits were hand-harvested from the commercial orchard (Quzhou city, Zhejiang province, China). After harvest, the fruits were transferred to the laboratory in 2 h, manually sorted into uniform fruit size, and without any pest, or mechanical damage. All experiments were repeated three times for the reproducibility of the materials and the performance.

2.2. Preparation of Chitosan-CMC Assembly. Chitosan was dissolved in the acetic acid solution (1.0%, v/v) to make the chitosan solution (1.5%, w/v). CMC solution (1.5%, w/v) was prepared by dissolving CMC-sodium salt in sterilized water. The chitosan and CMC solutions were heated at 40°C and stirred for 20 min until absolutely dissolved. The chitosan-CMC LBL assembly was prepared by 1.5% chitosan and 1.5% CMC solution, and the pH was adjusted to pH 6.3. The resulting LBL assembly was air-dried and homogenously distributed in a flat plate.

2.3. Properties of Chitosan-CMC Assembly. Fourier transform infrared spectroscopy (FTIR), coating mechanical properties, and water vapor permeability were measured according to the methodology proposed by Poverenov et al. [26].

2.3.1. Mechanical Properties. The thickness of the assembly was determined using the quartz crystal microbalance (QCM). The mechanical properties of the LBL assembly were determined by the TA-XT2 Texture Analyzer (Shanghai, China) with the stainless cylinder probe TA-52 (2 mm in diameter) at a speed of 1.0 mm s^{-1}. The puncture strength (PS) was measured by dividing the maximum force needed to break the assembly by the thickness, and the elasticity was defined as a distance that the assembly stretched before being broken.

2.3.2. Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra of the LBL assembly were obtained by recording the spectra from 400 cm^{-1} to 4,000 cm^{-1}, with the resolution of 4 cm^{-1} and 100 scans in average.

2.3.3. Water Vapor Permeability (WVP). The WVP was determined according to the ASTM E-96 method (2005). The beaker full with 10 mL of distilled water was sealed with the assembly placed in desiccators containing dry silica gel (50% RH; 23°C). The beaker was allowed for 2 h to reach the equilibrium state and weighed every 8 h. The water vapor transmission rate (WVTR, $g\,h^{-1}\,m^{-2}$) was calculated by plotting the weight loss versus time in a linear regression ($r \geq 0.99$) and dividing the slope by the exposed area of assembly (m^2):

$$\mathrm{WVP} = \frac{\mathrm{WVTR} \times L}{\Delta P}, \tag{1}$$

where L is the mean of assembly thickness (mm) and ΔP is the partial water vapor pressure difference (kPa) across the two sides of the assembly.

2.3.4. Scanning Electron Microscopy (SEM). The morphology of the LBL assembly was examined using a field emission SEM operated at 10 kV. The samples were mounted on metal stubs and coated with gold using a Polaron sputter coater.

2.4. LBL Assembly Coating Study. Lemon (*Citrus limon* (L.) Burm. f.) fruits were randomly divided into three groups. Then, the lemons were immersed in distilled water (control, CT), 1.5% chitosan, and chitosan-CMC LBL assembly (LBL) for 5 min. After completely air-dried, the lemons were stored in polyethylene terephthalate clamshell containers at 0°C for 20 days. Lemon samples were frozen in liquid nitrogen for later investigation of quality attributes. Three biological replications were carried out in the whole experiment.

2.5. Lemon Quality Attributes

2.5.1. Weight Loss. The results of weight loss were determined from 30 randomly selected lemons:

$$W(\%) = \frac{m_0 - m_1}{m_0} \times 100\%, \quad (2)$$

where W is the mean weight loss, m_0 is the initial fruit weight before storage (g), and m_1 is the weight of the fruit after storage (g).

2.5.2. Lemon Firmness. Textural properties of the lemon fruit were assessed using the puncture test with a TA-XT2i Texture Analyzer. The maximum force required to puncture the lemon was recorded, and the ATA-52 5-mm diameter stainless cylinder probe at a speed of 0.5 mm s^{-1} was used for penetration to a depth of 10 mm [20].

2.5.3. Lemon Vitamin C. Determination of vitamin C content in lemon was determined by the 2,6-dichloroindophenol titrimetric method. The lemon extract was prepared by maceration using 1.0% oxalic acid ($C_2H_2O_4$), filtered, and titrated with 2,6-dichloroindophenol until the pink color persisted for 15–20 s [27]. The vitamin C content was presented as mg per 100 g of fresh weight.

2.5.4. Lemon Color. The lemon peel color of five fruits for each treatment was evaluated with a Chroma Meter (CR-400).

2.5.5. Lemon Morphology and Microstructure. Five fruits were randomly selected from each group, and both the whole fruit and cross-sectional lemons were taken. 1 cm^2 of size and a thickness of 1 mm of the lemon epidermis was cut into four small pieces, soaked in 2.5% formaldehyde solution at 4°C for 12 h, and rinsed three times with 0.2 M phosphate buffer (PBS) and was then fixed in 2% osmium acid for 1 h, following by rinsing three times with PBS. After rinsing, the samples were successively soaked in 30%, 50%, 70%, 80%, 90%, and 95% ethanol for each 15 min to dehydrate and were then dehydrated twice with absolute ethanol for 20 min. The microstructure images were obtained after the samples were mounted on metal stubs and coated with gold.

2.5.6. Total Soluble Solid (TSS) and Titratable Acidity (TA). Five lemons were randomly selected in each treatment and squeezed with four layers of gauze. TSS and TA contents of lemon juice were determined by PAL-BX/ACID F5.

2.6. Statistical Analysis. All data were expressed as means ± standard deviations (SD) from three technical and biological replications. Microsoft Office Excel was used to calculate means and SD values. One-way analysis of variance (ANOVA) with a 95% confidence interval of the data was accomplished using SPSS 23.0 (SPSS Inc., Chicago, IL, USA). A Tukey–Kramer test was utilized when significant differences ($p < 0.05$) were detected. The data were analyzed and graphically plotted using Origin 8 software (OriginLab Software Inc. Hampton, Massachusetts, USA).

3. Results and Discussion

3.1. Assembly Properties. The physical properties of the chitosan and chitosan-CMC LBL assembly are presented in Table 1. It is noted that, in spite of the greater thickness, the water vapor permeability of the LBL assembly was significantly (1.74 times) greater than that of chitosan ($p < 0.05$), in agreement with their higher hydration level. The phenomenon was presumably related to the swelling behavior of the chitosan coating in the humid atmosphere, or related to the crosslinking between CMC and chitosan which results in a formation of a more loosely packed poriferous matrix rather than of a denser one and enlarges the intermolecular space and promotes the transport of water molecules in the assembly structure. It was consistently reported that the stratified structure and linear increase in the absorbance verified a linear increase in coating thickness [28]. In addition, the mechanical properties of the LBL assembly were significantly improved, in terms of both strength and elasticity ($p < 0.05$, Table 1). The physical properties of the LBL assembly are vitally important to the further application in the fresh produce. It has been demonstrated that from the SEM images in Figure 1, the chitosan showed a smooth and uniform surface and the LBL deposition resulted in the drastic alteration in the coating morphology and the cross-sectional structure. Microstructure indicated the tight connection between chitosan and CMC.

The crosslinking structure and FTIR spectra of chitosan and chitosan-CMC LBL assembly are shown in Figure 2. It was proved that 1,570 cm^{-1} and 3,000~3,500 cm^{-1} contributed to the characteristic bands of chitosan. Results revealed that the process of chitosan ethylation did not break the representative structure of the indigenous chitosan molecule. The absorption band at 1603 cm^{-1} was attributed to COO^- stretching vibration; additionally, the 1086 cm^{-1}

Table 1: Thickness, water vapor permeability (WVP), puncture strength (PS), and elasticity of chitosan and chitosan-CMC LBL assembly.

	Thickness (μm)	WVP (g mm/kPa^{-1} hm^{-2})	PS (N/mm)	Elasticity (mm)
Chitosan	26.3 ± 7.2^{b}	47.36 ± 0.00^{b}	252 ± 35^{a}	3.17 ± 0.52^{a}
LBL assembly	43.5 ± 5.1^{a}	82.55 ± 4.64^{a}	314 ± 48^{a}	3.09 ± 0.25^{a}

Different letters indicated significant difference at $p < 0.05$.

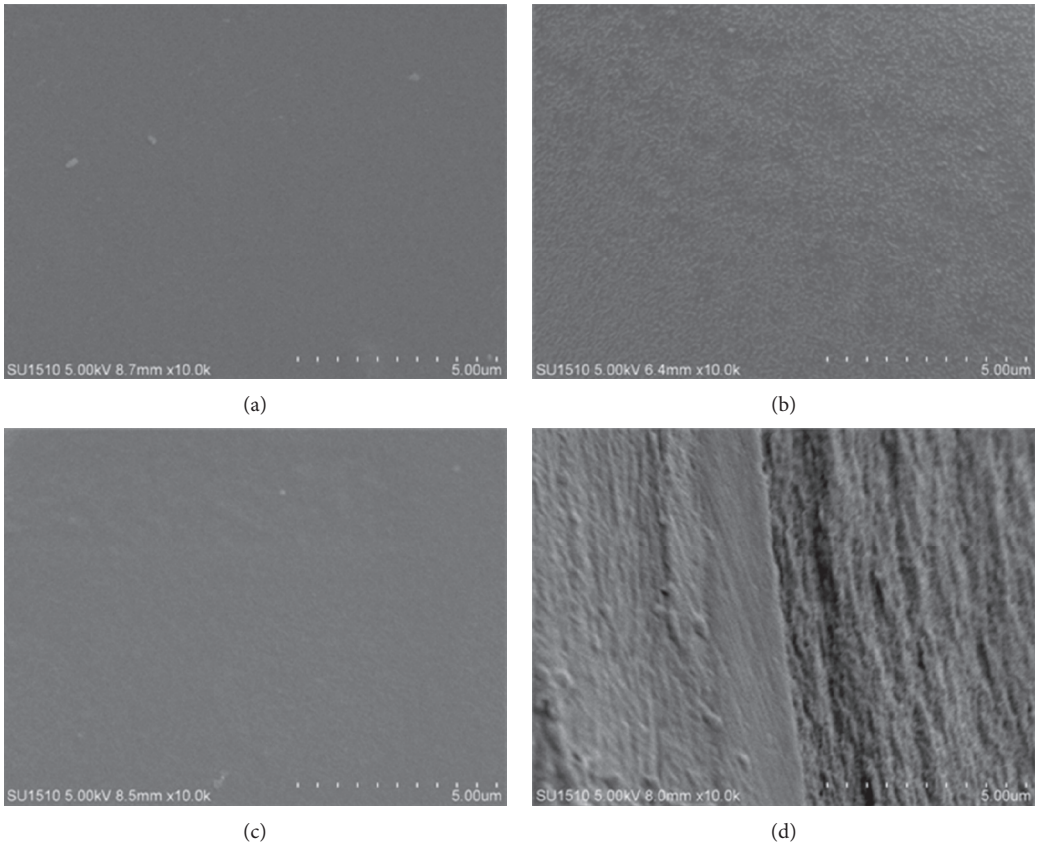


Figure 1: SEM images of cross section and vertical section of chitosan ((a) and (b), respectively) and chitosan-CMC LBL assembly ((c) and (d), respectively).

contributed to the C–O stretching vibration. Results demonstrated that the characteristic position of the absorption peaks of the assembled LBL was basically consistent with the chitosan and CMC, indicating that the characteristic functional groups of the two polysaccharides were consistent with the crosslinking structure.

3.2. Lemon Quality Attributes. With regard to the weight loss, it was observed that the chitosan-CMC LBL assembly has effectively been beneficial to the quality maintenance of the lemon fruit (Figure 3(a)). Results showed that the weight loss of lemon was significantly inhibited by the LBL assembly, in comparison to the monolayer chitosan and control ($p < 0.05$). The benefit of the LBL assembly on fruit weight loss probably resulted from the increased WVP value than chitosan. The layer-by-layer coating helped pores sealing and alleviated the water loss of the lemon peel, thus improving the postharvest quality and shelf life of the fresh lemon fruit. Firmness is an important basic attribute for evaluation of fruit quality, which is widely used for quality supervision of the fresh produce during storage and transportation. It can be shown from Figure 3(b) that the lemon firmness was significantly increased by the LBL assembly after storage for 20 days ($p < 0.05$), followed by chitosan and control.

The regulation of TSS and TA content reflects the taste of the lemon fruit in response to the LBL assembly and chitosan coating. It can be seen from Figure 3(c) that, after 20 days of storage, the average content of lemon TSS in the control group was significantly higher than that in the other two groups, and the overall value was above 7.5% ($p < 0.05$). It might be from the significant inhibition of the respiration rate of the lemon fruit, and from the reduction of the nutrient decomposition, especially starch and other polysaccharides, by the exogenous application of both LBL assembly and monolayer chitosan ($p < 0.05$). There was no significant difference in the content of lemon TSS between monolayer and layer-by-layer treatments ($p > 0.05$). It was consistently found that the chitosan coating had no significant effect on

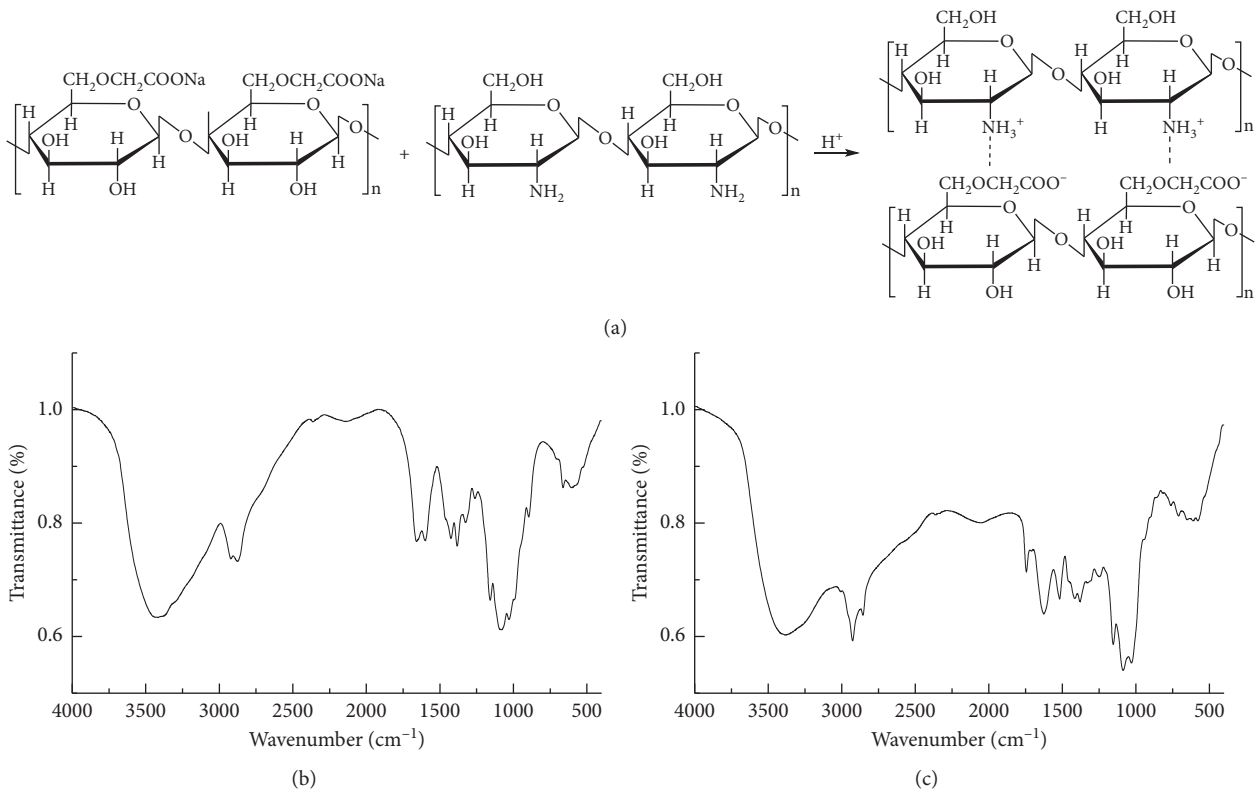


Figure 2: Crosslinking structure (a) and FTIR spectra of chitosan (b) and chitosan-CMC LBL assembly (c).

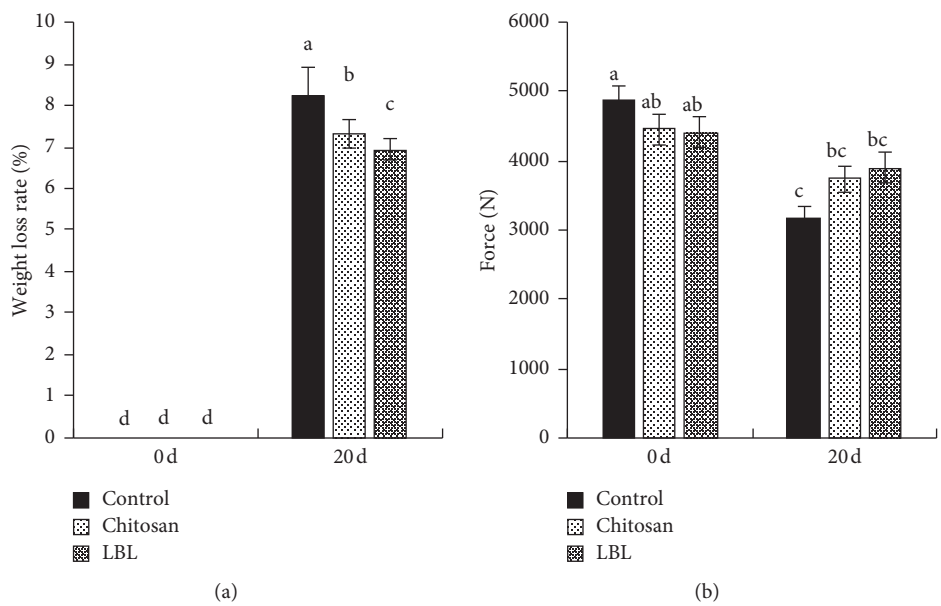


Figure 3: Continued.

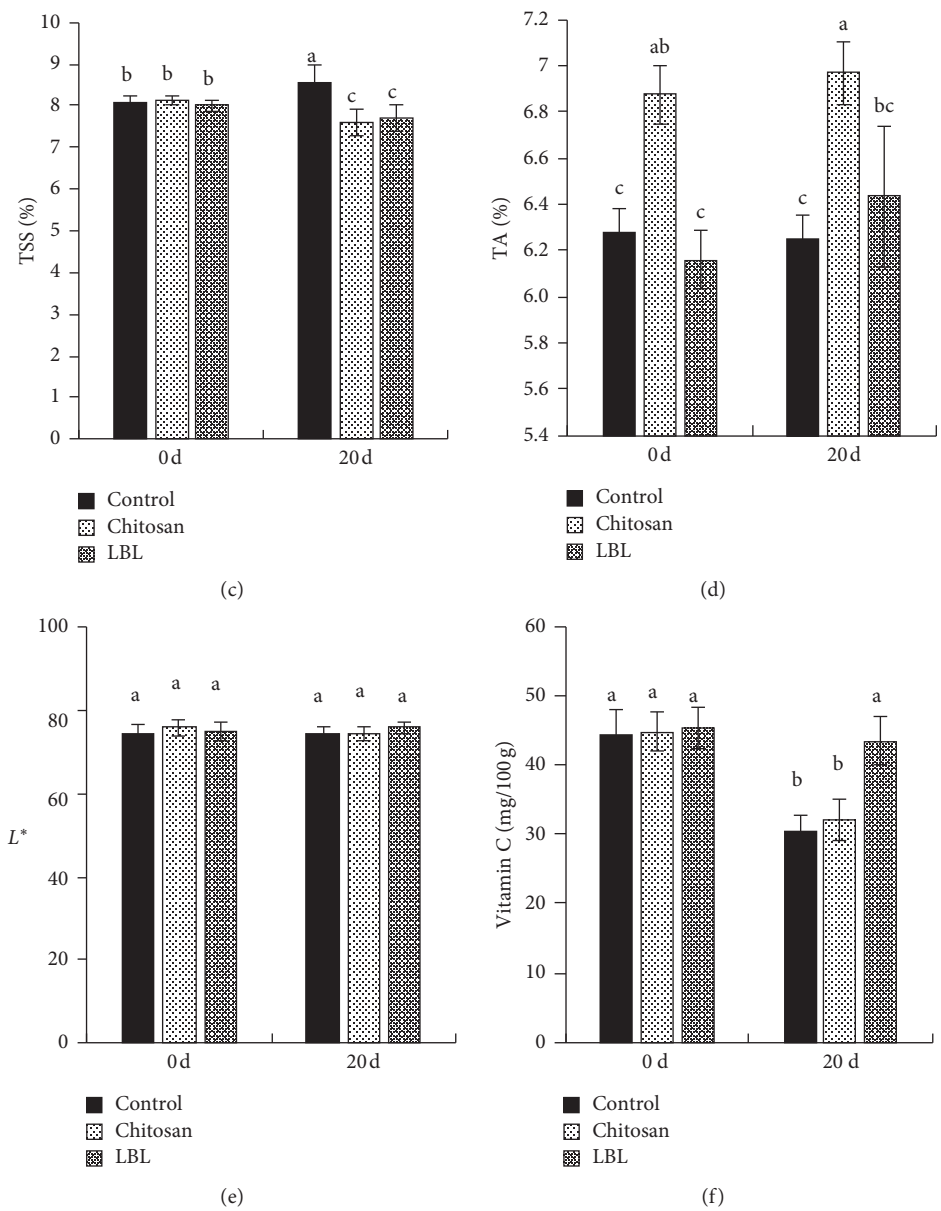


Figure 3: Weight loss (a), firmness (b), TSS (c), TA (d), L^* value (e), and vitamin C content (f) of lemon fruits before and after storage.

the TSS content of strawberry and citrus fruit by Arnon et al. [27]. Additionally, TA mainly refers to the organic acid in the lemon fruit and TA content could affect the acidity and taste related to fruit ripening and senescence. It could be proved from Figure 3(d) that the content of lemon TA in the chitosan group was significantly higher than that in the other two groups, both before and after storage, indicating that the difference was caused by the significant inhibition of the organic acid decomposition of the lemon fruit ($p < 0.05$). It was also previously reported that the chitosan coating had significant effect on the TA content of papaya [29], grape, and strawberry by delaying the rate of TA decline [30]. Results indicated that the chitosan-CMC significantly increased the TA content, in comparison to chitosan and control groups, which provided further evidence that the LBL assembly beneficially maintained lemon taste quality after storage.

The color of the lemon peel can be used as a criterion for the evaluation of fruit ripeness and senescence during commercial storage and transportation. The L^* value indicated the brightness and freshness of the lemon peel. In the present study, there was no significant difference in the brightness of the lemon between the coating treatment and the control group, according to the Figure 3(e), while the chitosan-CMC LBL assembly did not significantly injure the fruit gloss and overall visual appearance ($p > 0.05$).

Another quality attribute, the vitamin C content, has strong reducing ability and belongs to the important non-enzymatic active oxygen scavenging system in the fresh produce. It functions in free radical scavenging and

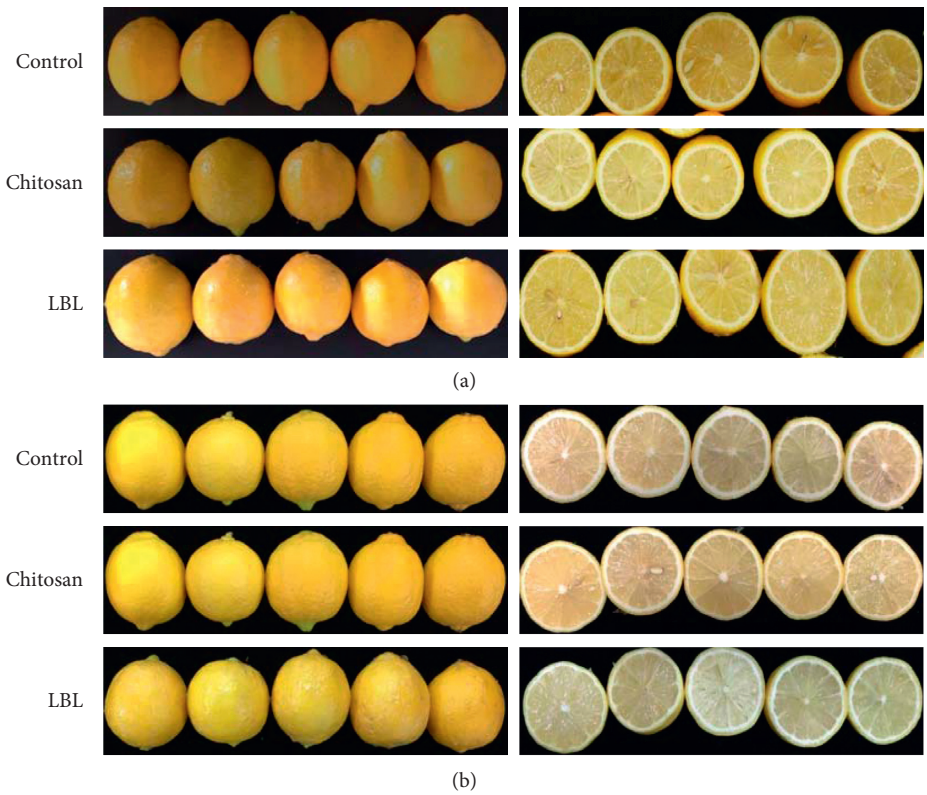
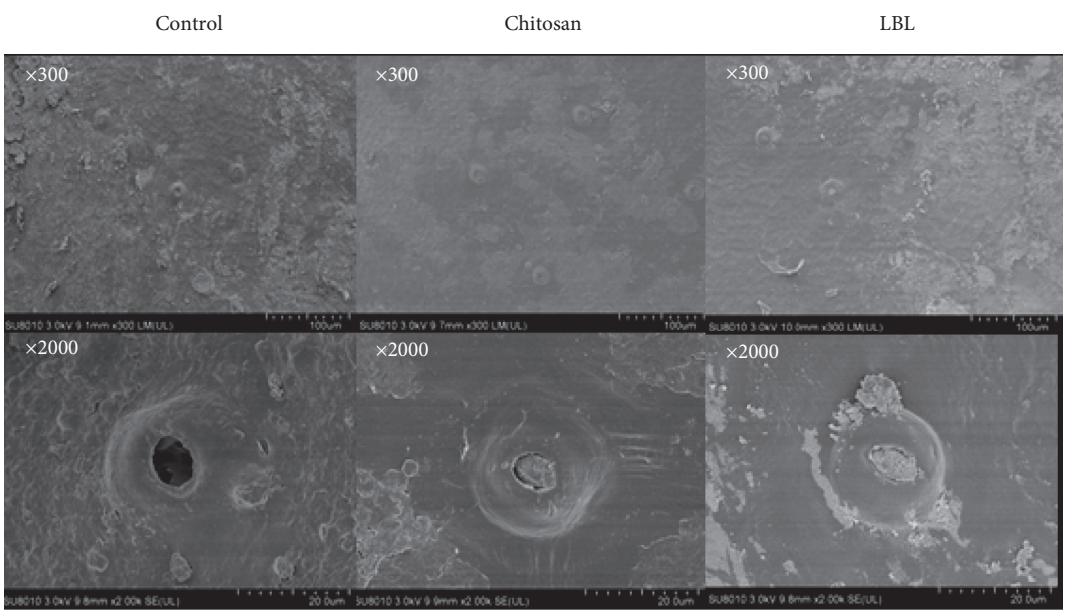
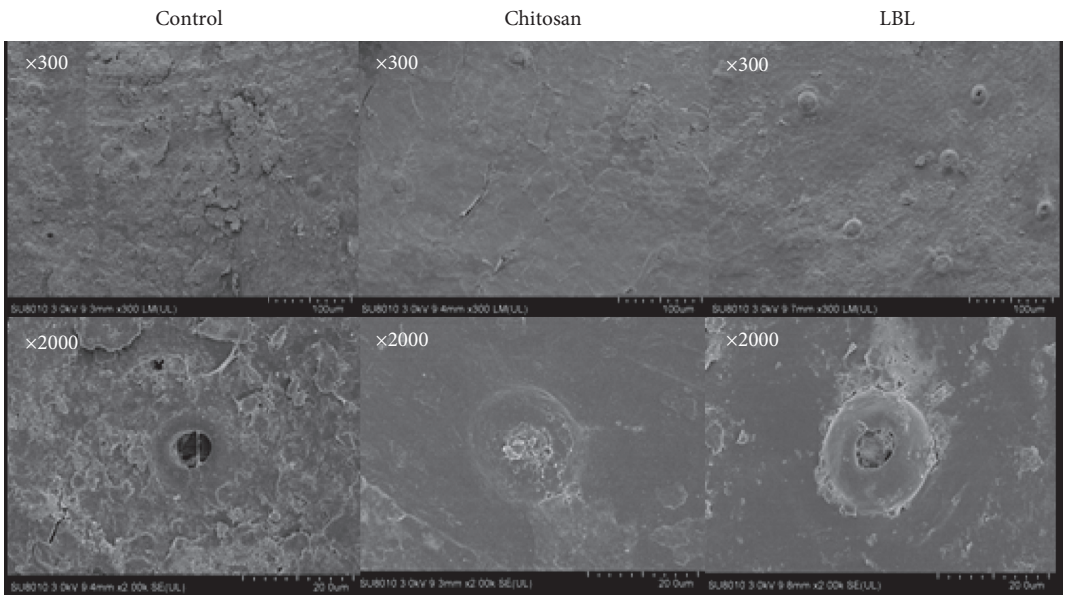


Figure 4: Morphology of lemon fruits before (a) and after storage (b).



(a)

Figure 5: Continued.



(b)

Figure 5: SEM images of lemon fruits before (a) and after storage (b).

antioxidation, involving in the delay of lemon senescence. In the present study, there was no significant difference in the original vitamin C content of the three groups in the initial storage period ($p > 0.05$). After storage, the vitamin C content was significantly elevated by the LBL assembly, followed by chitosan monolayer coating ($p < 0.05$, Figure 3(f)), which improved the antioxidation capacity during lemon senescence process. This is consistent with the results of the longan fruit coated by the chitosan composite [31].

3.3. Lemon Morphology and Microstructure. Results of the lemon morphology clearly demonstrated that the edible coating, especially the chitosan-CMC layer-by-layer assembly significantly inhibited the flesh browning, while maintaining the surface glossiness and visual appearance of the lemon fruit after storage ($p < 0.05$, Figure 4). The SEM images of the lemon microstructure indicated that the exogenous coating affected the size and number of stomata in the lemon epidermis (Figure 5). The stomata is the channel of the air and water vapor exchange from the fresh lemon and is the invasion site of the pathogen; the opening and closing action of the stomata in the guarding cell is involved in the regulations of carbon assimilation, respiration, and transpiration. It was clearly shown that both chitosan monolayer and chitosan-CMC LBL assembly reduced the number and the opening of stomata, thus contributing to the transpiration inhibition and senescence delay of the lemon fruit. Results in the present study revealed that the LBL assembly tremendously enhanced the fruit barrier and protection against abiotic and biotic stress stimuli.

4. Conclusions

This study developed a novel chitosan-CMC layer-by-layer deposition assembly, which exhibited excellent water vapor permeability, puncture strength, and elasticity properties (1.25–1.74 times greater than that of chitosan). The research provides substantial evidence to support the hypothesis that the LBL assembly maintained the lemon quality, such as fruit firmness and vitamin C content, during storage at 0°C for 20 days. These findings provide an alternative route to maintain quality and postponing senescence of the postharvest fresh produce. The methodology and procedure proposed in the present study need to be further confirmed in dependence of the polymer concentrations and fruit cultivars.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Authors' Contributions

Fangyuan Chen and Jinglin Zhang contributed equally to this work.

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