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Progress in Application of Chitosan-based Food Packaging Materials

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Abstract

At present, most of the food packaging materials are mainly petroleum-based plastics, whose disadvantages are non-degradable regeneration and the possibility of migration of harmful substances, which are related to the safety of food quality and human health. Chitosan (CTS) is a natural biodegradable material extracted from crustacean shells and has non-toxic, antibacterial and antioxidant properties that make it a promising functional food packaging material, but its poor water solubility makes its application limited. Therefore, it is one of the current research hotspots to improve the water solubility and optimize the comprehensive performance of chitosan through modification. This paper discusses the structure and functional properties of chitosan; summarizes the preparation methods of chitosan films such as flow casting and coating and the film performance research; finally elaborates the progress of chitosan films in meat, fruits and vegetables and other food applications, in order to provide a theoretical basis for the preparation of green functional food packaging materials in the future and promote the development and application of functional food packaging materials. Finally, the progress of the application of chitosan films in meat, fruit and vegetable foodstuffs is presented, with a view to providing a theoretical basis for the preparation of green functional food packaging materials and promoting the development and application of functional food packaging materials.

Keywords: *Chitosan; Antibacterial mechanism; Coating; Food preservation.*

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I. INTRODUCTION

Food packaging materials are inseparable from food circulation and storage, so they can directly or indirectly affect food quality and human health and safety. Its impact on human health is generally due to the harmful substances contained in its material, which gradually migrate to the food with which it comes into contact with over time and eventually damage human health.

Current methods to improve food safety include heating, pasteurization, freezing, and direct addition of preservatives. In addition to the methods of food quality and safety by treating the food itself, the use of functional packaging materials with certain antibacterial properties and freshness preservation is also favored to protect food, such as chitosan, polyethylene, and nano-silver.Among them, Chitosan (CTS)is a natural degradable material that can be extracted from the shells of crustaceans (such as crabs and shrimps) in large quantities and obtained through processing.CTS, a deacetylated derivative of chitin, is a degradable biopolymer in nature second only to cellulose in terms of resource abundance. The structural difference between chitin and chitosan lies mainly in the attachment of N-acetamide group to C-2 in the former and amino group in the latter. Because of the presence of the amino group, chitosan is the only positively charged basic biobased linear polysaccharide present in large quantities [1]. In addition to the amino group, the hydroxyl groups located at C-3 and C-6 are also nucleophilic groups on the chitosan chain, which can be chemically modified to produce derivatives containing cationic, hydrophilic or hydrophobic groups. According to the molecular chain arrangement, chitosan can be divided into three types, namely α-chitosan, β-chitosan and γ-chitosan. Among them, α-chitosan is two parallel and inversely arranged polysaccharide chains, which are widely used due to their ordered structure and high crystallinity that increases their strength.

II. FUNCTIONAL FEATURES

2.1Degradability.

Chitosan molecules contain more free amino groups, which are easy to combine with hydrogen ions in solution under the action of strong inorganic acids (hydrochloric acid, nitric acid), so that their inter- and intra-molecular hydrogen bonds are broken and the structure is stretched; and because the glycosidic bonds in the long chain part are easy to break to form molecular fragments with different degrees of polymerization, chitosan has better biodegradability [2].

2.2Solubility.

Chitosan is readily soluble in organic acids (e.g., acetic acid, formic acid), but the hydrophobic nature of the acetyl group in the molecule makes it less soluble in water and some organic solvents. Its solubility is mainly related to the amino group, which is completely protonated when the solution pH is <6, when the solubility is higher [3]; when the pH is >6, the amino group loses its positive charge due to deprotonation, and the solubility decreases gradually. In addition, the solubility of chitosan is also related to the degree of deacetylation and molecular weight. Generally, the degree of deacetylation is positively correlated with the amount of protonated amino acids, which in turn is positively correlated with the solubility of chitosan. However, the higher the molecular weight of chitosan, the higher the density of the hydrogen bond within and between molecular chains, the less solubility [4].

2.3Anti-oxidation.

Chitosan is considered as a food packaging material with research value due to the functional amino and hydroxyl groups in the structure that can scavenge excess free radicals [5]. The antioxidant and radical scavenging activities of chitosan are molecular weight dependent [6], and the DPPH radical scavenging activity of low molecular weight chitosan is stronger than that of high molecular weight chitosan, which deactivates peroxyl radicals. In acidic solutions, the amino group of chitosan is easily protonated and attracts other anions by electrostatic interaction. However, chitosan is a semi-crystalline polymer and the hydrogen bonds between the molecular chains tend to dissociate under acidic conditions, and the accessibility of active reactive sites (amino and hydroxyl groups) is still challenging for biomolecules [7].

2.3Antimicrobial Properties.

The amino-poly cationic structure of chitosan gives it antimicrobial properties, but the antimicrobial mechanism has not yet been determined. Among the hypotheses proposed so far the following three have the highest acceptance [8]. Firstly, under acidic conditions, the amino group at the C-2 position of chitosan is easily protonated to -NH3+, which subsequently binds to the bacterial cell wall and attaches to the outside, thereby destroying the cell structure and causing the leakage of intracellular material to cause death [9]. 20 min after the treatment of Staphylococcus aureus contraction zone split cell membrane was incomplete and intracellular material was lost. This may be the result of the interaction between -NH3+ and phosphorylated groups in the phospholipids of the cell membrane.

Further, the mechanism of protein synthesis inhibition. Low concentrations of chitosan penetrate into the cell nucleus and interact with DNA, affecting the transcription of RNA polymerase and protein synthesis as a means of inhibition. Imelda et al [10], when investigating whether β-galactosidase induction activity is reduced by fusion-containing yeast constructs, fusion-constructed yeast cells were transferred to medium containing galactose for 8 h. When yeast cells were exposed to 0.35 mg/ml of chitosan, the galactosidase activity decreased to 32 % of that without chitosan; and the higher the chitosan concentration, the lower the galactosidase activity. This experiment confirmed that chitosan affects protein synthesis.

In addition, the mechanism of chelation is generally accepted. The amino and hydroxyl groups in chitosan molecules can selectively adsorb metal ions and chelate with metal ions, such as Fe3+ and Mg2+, which are essential for ATPase on the surface of bacteria. The enzymes are essential for bacterial survival, and if inactivated will cause blockage of cellular metabolism and affect microbial growth and reproduction. Metal ions act as electron acceptors, forming bridges with hydroxyl groups through amino groups, connecting one or more chitosan chains and attaching to the bacterial surface, blocking the flow of some nutrients and causing cell death [11].KHAN et al [12], in their study of chitosan and its derivatives for the preparation of psychiatric drugs, found that chitosan disrupts cell membranes and fungal cell walls, chelates with trace metals and thus inhibits mRNA synthesis.

During the study of antimicrobial properties of chitosan it is also important to consider its own factors, such as molecular weight. High molecular weight chitosan cannot pass through the bacterial outer membrane and can only adhere to the cell surface and form an impermeable layer around it, blocking the transport of nutrients to the cell [13]. Low molecular weight chitosan can penetrate into the nucleus of microorganisms, bind to DNA and inhibit mRNA synthesis [14].

The degradability, solubility, antioxidant, and antimicrobial properties of chitosan are interdependent due to the presence of amino groups. The degree of protonation of the amino group determines the charge density on the chitosan chain and thus the solubility. As the same charge groups repel each other on the chain to make the chain extend, i.e., the charge density affects the chitosan chain conformation which in turn affects the mechanical and barrier properties. In addition to the above functional properties, chitosan also has good film-forming properties and biocompatibility, making it highly suitable for the preparation of food packaging films.

III. CHITOSAN PACKAGING FILM PREPARATION METHOD

Food packaging films can be prepared by cast film formation, coating, and layer-by-layer assembly to give them better mechanical, barrier, antibacterial, and antioxidant properties to extend food shelf life while maintaining food quality and taste.

3.1 Cast Film Forming Method.

The cast film formation method is widely used because of its simplicity of preparation. The preparation process is shown in Figure 1: co-mixing and stirring → filtration and centrifugation → casting and drying → peeling to form a film.PRIYADARI et al [15] prepared ZnO/chitosan nanocomposite films using the cast film formation method. Three different mass concentrations of ZnO containing 0 %, 1 % and 2 % were added to the chitosan solution, and then the mixture was stirred at 70 °C for 12 h and poured onto a glass plate and dried in a hot air oven at 50 °C for 24 h. The films were subsequently uncovered for characterization. It was observed by electron micrographs that the particles of single chitosan film were not uniformly distributed with aggregation phenomenon; while the particles of the composite film with the addition of ZnO nanoparticles were uniformly dispersed with little aggregation phenomenon, indicating that the addition of ZnO nanoparticles could prevent the aggregation of chitosan.

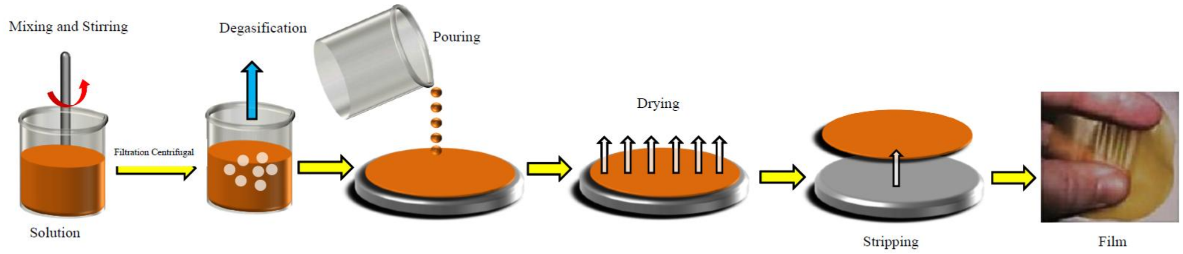


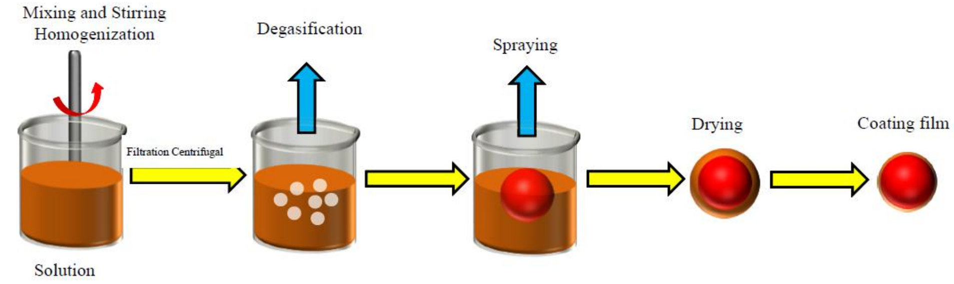
Figure 1: Process of Cast Film Preparation

3.2Coating Method.

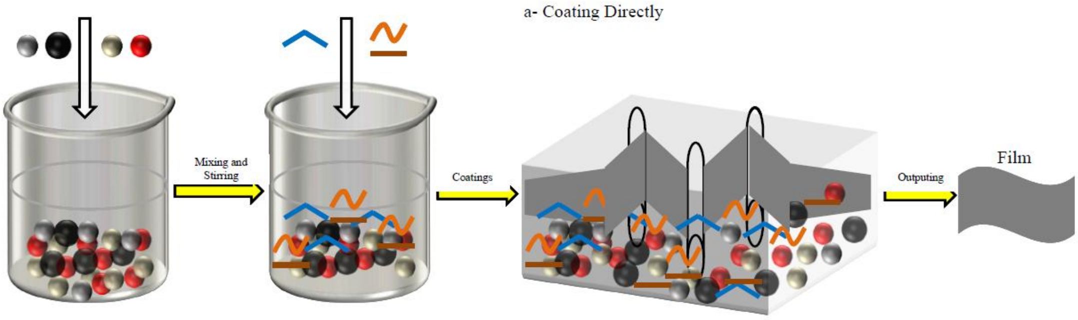
The coating method refers to the application of chitosan-based solutions directly on the surface of food materials (fruits and vegetables, meat products) or indirectly on the surface of packaging materials.

Direct coating is an important method to inhibit the growth of microorganisms on the food surface. It is generally carried out by dip coating, electrostatic spraying and brushing. Among them, dip coating is widely used to study the preservative preservation of fruits because of its convenience and ease of operation. The method involves dipping the food material into chitosan solution to form a uniform film on its surface, as shown in Figure 2-a: Configuring the solution → stirring well → degassing → dipping or spraying → drying into a film. Directly coated food samples have better resistance to freezing damage and lower color change and spoilage rates, resulting in longer shelf life.

Indirect coating is aimed at manufacturing multilayer functional packaging materials, and the preparation process is shown in Figure 2-b: configuring the solution → mixing well → coating into a film. The multilayer functional package has better performance compared to single-layer packaging.TANPICHAI et al [16] coated chitosan on cellulose-based paper using a coating machine. The clear chitosan solution was obtained by dipping 2 g of chitosan powder into 200 mL of 1 % v/v acetic acid solution and stirring the mixture at room temperature for 24 h. The chitosan solution was then coated on the paper by a coater at a speed of 2 m/min and dried in an oven at 100 °C for 5 min to obtain the final coated paper. The uncoated paper was characterized to have a cellulose fiber porous structure with a large number of cavities, while the pores of the cellulose fibers of the chitosan-coated paper decreased with the increase of the number of coated layers due to the electrostatic interaction between chitosan and cellulose.



a- Coating Directly



b- Indirectly Coated

Figure 2:Preparation of Coating Film

The layer-by-layer assembly method uses the principle of alternating layer-by-layer deposition to alternately deposit charged substrates in oppositely charged polyelectrolyte solutions to produce multilayer films with structural integrity, stable properties, and specific functions. As shown in Figure 3: Configuration of electrolyte solution → primary impregnation → static rinsing and drying → secondary impregnation → static rinsing and drying. If a cationic substrate is obtained after primary impregnation, an anionic substrate is obtained by secondary treatment, and so on and so forth. LIU [17] prepared edible composite films based on chitosan and carboxymethyl chitosan using electrostatic deposition. The membrane was characterized and found to have a flat surface, a dense structure and no obvious pores, and a three-layer lamellar structure with similar thickness between layers in the cross-sectional view. This is due to the combination of chitosan and carboxymethyl chitosan through hydrogen bonding and ionic bonding during the assembly process, forming a laminar membrane structure by stacking layers on top of the original structure of the membrane.

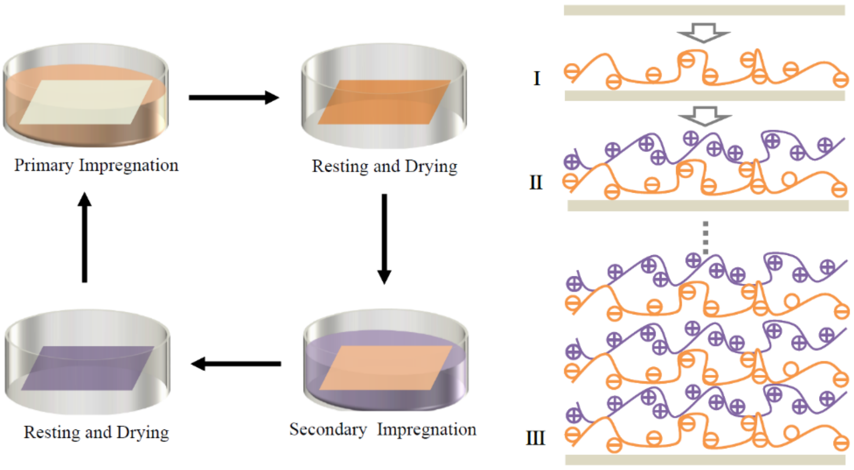


Figure 3: The preparation Process of Layer-by-layer Self-assembly Edible Film

IV. PERFORMANCE OF CHITOSAN-BASED PACKAGING FILMS

4.1Mechanical Properties.

Mechanical properties are the basis for maintaining the structural integrity of packaging and preventing leakage during transportation and storage.BAJI´C et al [18] studied the effect of hop extract on the mechanical properties of chitosan-based films. It was found that as the concentration of hop extract increased, the tensile strength and elastic modulus of the films showed a decreasing trend from 14.4 MPa to 6.4 MPa and from 218.8 MPa to 26.9 MPa, respectively, while the elongation at break increased from 10.7 % to 35.1 %. This indicates that the interfacial adhesion between hydrophilic chitosan and hydrophobic extract chains reduces the intra- and intermolecular linkages of chitosan, enhances the overall chain migration and improves the flexibility and ductility of the films.

4.2Barrier Properties.

The barrier properties of films are related to the length of shelf life and food safety.LAN et al [19] prepared chitosan-based films using titanium dioxide nanoparticles/red apple pomace extract/chitosan and tested their water content and water vapor transmission rate. The tests revealed that the highest water content was found in the CTS/TiO2-NPs composite film, while the water content of the film after the addition of the extract was significantly lower compared to the CTS film. This is due to the porous structure of TiO2-NPs which facilitates the accumulation of water in CTS films, while the addition of extracts reduces the binding between CTS and water. The nano-TiO2 and red apple pomace extracts synergistically interacted with the hydrophilic groups of chitosan to form a continuous dense network, which in turn improved the barrier properties of the films.

4.3Antimicrobial Properties.

The transportability of hazardous substances in food packaging materials is directly related to food quality and safety, so antimicrobial packaging materials should be used to ensure food safety.CHENG et al [20] prepared starch/chitosan/nanotitanium dioxide composite films and investigated their antimicrobial ability against Escherichia coli. It was found that the antimicrobial activity of the starch/chitosan films increased with the increase of chitosan, but the enhanced interaction between the two reduced the antimicrobial property of chitosan by decreasing the binding of -NH3+ to the cell membrane. Therefore, the antimicrobial activity of starch to chitosan mass ratio up to 2:1 suddenly decreased but still much higher than that of starch film. And the antimicrobial property increased with the addition of TiO2-NPs with the increase of its amount. When 0.04 g TiO2 was added to the film with a starch to chitosan mass ratio of 3:1, the inhibition rate of E. coli reached 94±2 %. This is the result of the synergistic antibacterial activity of chitosan and TiO2. The hydroxyl radicals produced by TiO2 under light conditions attack the cell membrane oxidatively and destroy it causing cell death.

4.4Anti-oxidationProperties.

One of the main causes of food spoilage is lipid oxidation. Antioxidation is the key to maintain stable food quality and extend shelf life. Some researchers have introduced silver oxide nanoparticles and purple corn extract into chitosan films to enhance the antioxidant properties of the films. It was found that the chitosan film had the weakest DPPH radical scavenging activity, while the silver oxide nanoparticles/purple corn extract/chitosan composite film was the strongest. This is because when the membrane contains only chitosan, there are a large number of active hydroxyl and amino groups in its backbone, which can scavenge excessive reactive oxygen species and thus inhibit the occurrence of related chain reactions [21]. And the presence groups on the surface of silver oxide nanoparticles in the latter membrane and the presence of anthocyanins in purple rice extract, both synergistically antioxidant reduce the production of reactive oxygen species.

V. CHITOSAN-BASED PACKAGING FILMS IN FOOD APPLICATIONS

5.1 Fresh.

Since raw fish are susceptible to bacterial invasion after being removed from their original living environment, and their water content, fragile tissues, and easy oxidation of unsaturated fatty acids make them highly susceptible to spoilage, LAN et al [19] prepared a salmon packaging film using titanium dioxide/chitosan/apple pomace extract. Since the apple pomace extract in this film contains anthocyanins, its structure changes at different pH levels and shows different colors, so the pH value can be used to reflect the degree of salmon spoilage, where pH 7 is the threshold value for fresh and safe fish. The test results are shown in Table 1, where the pH of the film increased from 6.08 to 6.62 at 24 h and reached 7.14 after 48 h. The brightness (L value) and reddening (a value) of the film decreased significantly, and the total color difference (ΔE) of this composite film exceeded 3 at 24 h and reached 7.25 at 48 h, which was better than the chitosan-alizarin film. The composite film can be used for smart packaging of food products to detect the freshness of meat by color change.

Table 1: PH Value and Color Difference Value of Composite Film[19].

Time (h)	Salmon'pH	L	a	b	Δ E
0	**6.08 ± 0.02a**	**48.11 ± 0.16b**	**36.42 ± 0.13c**	**33.88 ± 0.11c**	**–**
24	6.62 ± 0.04b	50.21 ± 0.22a	21.83 ± 0.12b	29.39 ± 0.13a	3.14 ± 0.05
48	**7.14 ± 0.04c**	**55.76 ± 0.15c**	**16.71 ± 0.09a**	**25.23 ± 0.15b**	**7.25 ± 0.09**

5.2 Fruit and Vegetables.

The nutrients of fruits and vegetables are continuously consumed by respiration, while heat is generated to break down water to accelerate spoilage.PAN et al [22] prepared fruit packaging films using quaternary ammonium and quaternary phosphate double-modified chitosan (HA-CS-NP) and polyvinyl alcohol (PVA) and tested the effect of their ratios on the freshness of papaya and mango. The mangoes treated with both control CK and experimental HACC/PVA (5/5) films showed obvious black spots after 12 d of storage, while the fruits treated with HA-CS-NP/PVA films had less wrinkling and smooth surfaces. The mango and papaya in the CK group reached 7-9 % in the first 3 d, while the HA-CS-NP/PVA film wrapped fruits had no decay. With the increase of storage time, the decay rate in the CK group increased from 9 % to 33 %, while the latter composite film was only 10 %. The main reason was the strong antibacterial properties of the quaternary ammonium group in this composite film, which significantly retarded fruit decay.

5.3 Livestock and Poultry Meat.

All foods deteriorate under certain conditions (temperature, humidity, pH, etc.), but meat is more prone to deterioration due to its composition and nature.MEHDIZADEH et al [23] prepared food preservation films using chitosan/propolis extract/essential oil, which successfully extended the shelf life of chicken breast by inhibiting the growth of microorganisms.DENG et al [24] investigated the effect of cellulose nanofibers (Celluouse Nanofibers, CNF) with low and high concentrations of chitosan composite films on the fresh beef patties freshness preservation, respectively. The beef patties were stored in the refrigerator for 7 d while the water absorption capacity of the films was tested. CNF film turned red while the composite film did not change significantly due to the absorption of more water and blood in the beef patties. It shows that the composite film is durable to high humidity conditions and can be applied to high humidity surfaces as a food separator sheet to prevent water transfer between layered products and reduce water loss.

VI. CONCLUSION

Most of the current food packaging materials are still based on petroleum-based plastics, whose disadvantage is that they are not degradable and renewable. With the increasing awareness of human health and safety and environmental safety, new packaging materials with functionalities such as antibacterial, degradable and regenerative have become a hot research topic. Chitosan is a biodegradable biopolymer second only to cellulose in terms of natural resource abundance and has non-toxic, antibacterial and antioxidant properties making it a preferred material for the food industry, medical industry and even the textile industry. However, due to poor water solubility, chitosan has some limitations in film production and application, and its antimicrobial properties are also affected to some extent. Modification by quaternization can improve water solubility and optimize the overall performance, making it more convenient to be used in the film making process. Chitosan-based films prepared by cast and coated methods can extend shelf life while maintaining stable quality of meat, fruits and vegetables. As a green and natural packaging material, chitosan is a much better alternative to petroleum-based plastics in terms of practical processing and stability and has great potential for development.

REFERENCES

[1]. SUI ZHENQUAN,MAO JINCHAO,XU GUIYUN,FAN JINSHI. Preparation, properties and applications of natural biomass materials (I) - the only alkaline polysaccharide in nature: chitin/chitosan[J]. Daily use chemical industry,2022,52(01):7-14.

[2]. LAI, N. J., JIANG, X., CHEN, M. Z., LI, P., XU, H. W., AND GAO, H. Evaluation of chitosan-modified polymer application and biodegradability investigation[J]. Petrochemicals,2022,51(06):647-652.

[3]. MORAN, HANNAH B T et al. Immunomodulatory properties of chitosan polymers[J]. Biomaterials,2018,184: 1-9.

[4]. WANG, CHENJIE et al. Biopolymer films based on chitosan/potato protein/linseed oil/ZnO NPs to maintain the storage quality of raw meat[J]. Food chemistry,2020,332: 127375.

[5]. WEI, LIJIE et al. The antioxidant and antifungal activity of chitosan derivatives bearing Schiff bases and quaternary ammonium salts[J]. Carbohydrate polymers,2019,226: 115256.

[6]. TOMIDA, HISAO et al. Antioxidant properties of some different molecular weight chitosans[J]. Carbohydrate research,2009,344(13): 1690-6.

[7]. JUNG, JOOYEOUN, YANYUN ZHAO. Comparison in antioxidant action between α-chitosan and β-chitosan at a wide range of molecular weight and chitosan concentration[J]. Bioorganic & medicinal chemistry,2012,20(9): 2905-11.

[8]. Liu Zhuoran,Li Yumei,Liu Junyan,Yin Tong,Jiang Ming,Li Yourui. The role of chitosan and its derivatives in oral antimicrobial field[J/OL]. China Tissue Engineering Research:1-7.

[9]. Hou Jingjing. Construction and properties of nano-lignin/chitosan functional materials[D]. Qingdao:Qingdao University of Science and Technology,2021.

[10]. LIU, HUI et al. Chitosan kills bacteria through cell membrane damage[J]. International journal of food microbiology,2004,95(2): 147-55.

[11]. GALVÁN MÁRQUEZ, IMELDA et al. Disruption of protein synthesis as antifungal mode of action by chitosan[J]. International journal of food microbiology,2013,164(1): 108-12.

[12]. KHAN, MOHAMMED S. et al. Preparation and evaluation of spray dried microparticles using chitosan and novel chitosan derivative for controlled release of an antipsychotic drug[J]. Int. J. Biol. Pharm. Res,2012,3: 113–121.

[13]. CAZÓN, PATRICIA, MANUEL VÁZQUEZ. Applications of Chitosan as Food Packaging Materials[J]. Sustainable Agriculture Reviews,2019,36: n. pag.

[14]. HOSSEINNEJAD, M., SEID MAHDI JAFARI. Evaluation of different factors affecting antimicrobial properties of chitosan[J]. International journal of biological macromolecules,2016,85: 467-75.

[15]. PRIYADARSHI, RUCHIR, YUVRAJ SINGH NEGI. Effect of Varying Filler Concentration on Zinc Oxide Nanoparticle Embedded Chitosan Films as Potential Food Packaging Material[J]. Journal of Polymers and the Environment,2016,25: 1087-1098.

[16]. TANPICHAI, SUPACHOK et al. Chitosan coating for the preparation of multilayer coated paper for food-contact packaging: Wettability, mechanical properties, and overall migration[J]. International journal of biological macromolecules,2022: n. pag.

[17]. LIU XUEFAN,GE YUQI,DONG SHIXIANG et al. Performance investigation of layer-wise self-assembled edible cling film[J]. Packaging Engineering, 2017. 38(9): 23-28.

[18]. BAJIĆ, MARIJAN et al. Chitosan-based films with incorporated supercritical CO2 hop extract: Structural, physicochemical, and antibacterial properties[J]. Carbohydrate polymers,2019: 261-268.

[19]. LAN, WEIJIE et al. Development of red apple pomace extract/chitosan-based films reinforced by TiO2 nanoparticles as a multifunctional packaging material[J]. International journal of biological macromolecules,2020: n. pag.

[20]. CHENG, LONG et al. Effects of Chitosan and Nano Titanium Dioxide on the Mechanical, Physicochemical and Antibacterial Properties of Corn Starch Films[J]. Journal of Macromolecular Science, Part B,2021,60: 616 – 630.

[21]. M.R. NUNES, et al. Antioxidant and antimicrobial methylcellulose films containing Lippia alba extract and silver nanoparticles[J]. Carbohydrate Polymers, 2018, 192: 37-43.

[22]. PAN, Q et al. Preparation and characterization of chitosan derivatives modified with quaternary ammonium salt and quaternary phosphate salt and its effect on tropical fruit preservation[J]. Food chemistry, 2022,387: 132878.

[23]. MEHDIZADEH, T et al. Chitosan coatings incorporated with propolis extract and Zataria multiflora Boiss oil for active packaging of chicken breast meat[J]. International Journal of Biological Macromolecules, 2019,141: 401–409.

[24]. DENG, Z et al. Development, characterization, and validation of chitosan adsorbed cellulose nanofiber (CNF) films as water resistant and antibacterial food contact packaging[J]. Lwt - Food Science and Technology, 2017,83: 132-140.