

# Progress on biodegradable films for antibacterial food packaging

Guocheng Han<sup>1,a</sup>, Rui Guo<sup>1</sup>, Zhaohui Yu<sup>1</sup> and Guangxue Chen<sup>1,2</sup>

<sup>1</sup>Shenzhen YUTO Packaging Technology Co., Ltd., Shenzhen 518108, China

<sup>2</sup>State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China

**Abstract.** The applications of common-used antibacterial agents and biodegradable polymer materials in food packaging were reviewed. The research progress on biobased antibacterial agents (such as chitosan, plant essential oils, plant extracts, bacteriocins) in food packaging films synthesized from biodegradable polymer materials (such as starch and its derivatives, chitosan, cellulose, protein) was summarized. Most of the biodegradable antibacterial films are applied in the packaging of postharvest transportation and storage of fruits and vegetables. This work provides guidance to develop new intelligent food packaging materials featured by degradability, bacteriostasis and environmental protection.

## 1 Introduction

With the development of society and economy and the continuous increase of population, the problems of environmental pollution and food waste are getting severer. In order to improve the storage time of food and reduce food waste, food packaging has become an essential demand. At present, the most widely used raw material in the food packaging industry is plastic. Although plastic packaging has brought a lot of convenience to people, the white pollution caused by non-degradable waste plastics has also become serious [1]. Most of food packaging in China is discarded, which is likely to cause white pollution, and has seriously damaged the living environment of residents, as well as causes widespread concern around the world. Various countries have legislated corresponding laws and regulations to prohibit or restrict the use of non-degradable plastic products and packaging materials [2]. In addition, the raw materials for the preparation of traditional plastics are inadequate, such as petroleum, which is a non-renewable resource and will eventually meet depletion. The traditional plastic manufacturing industry using petroleum as its raw material will inevitably be hit hard. In summary, it is imminent to carry out related research on green and environmental-friendly degradable packaging. Sustainability is the basic concept of China's current social and economic development, and it is also the main trend in the development of the food packaging industry.

For the storage and preservation of food, the use of antibacterial packaging can effectively inhibit the growth of microorganisms in food. Life activities such as the growth and reproduction of microorganisms are the root causes of food corruption and quality degradation [3]. At present, the common methods for controlling the growth of microorganisms in food are to use processing techniques such as heat sterilization (pasteurization) and

cold sterilization during processing and to add preservatives to food to extend the shelf life of food. Among them, pasteurization will cause excessive energy waste, and due to the quality characteristics of some foods, thermal sterilization will cause the loss of nutritional content of the food itself. Although preservatives can effectively inhibit the growth and reproduction of microorganisms, most preservatives have toxic effects which bring hidden dangers in food safety. Antibacterial packaging is to add antibacterial agents to the food packaging materials, thereby protecting the quality and safety of food and reducing the loss of food nutrition [4]. Antibacterial packaging prepared by using natural biomass as the main material of packaging film and adding various antibacterial agents to the film can meet the requirements of low or no preservative content in the packaging material, and reduce environmental pollution due to degradability. In summary, the use of degradable polymer materials and antibacterial agents to synthesize degradable packaging can not only save resources and protect the environment, but also effectively increase the storage time of food and reduce food waste, which is the future direction of food packaging development.

## 2 Common antibacterial agents

### 2.1 Chitosan

The antibacterial activity of chitosan is mainly based on the following three aspects: (1) It is related to the positive charge of the amino group in its chemical structure, and it can interact with the negative charge of the microbial cell membrane, which can cause cell death by increasing the fluidity and permeability of the microbial membrane. (2) It can interfere the transcription

<sup>a</sup> Corresponding author: [yutulunwen@163.com](mailto:yutulunwen@163.com)

and replication of microbial DNA. (3) It can block the metabolism of pathogenic microorganisms.

In summary, chitosan can inhibit the growth of many microorganisms including yeast, fungi or pathogenic bacteria. In order to increase the bacteriostatic ability of chitosan, other bacteriostatic agents such as limonene and plant essential oils are added. Researchers found in the fresh-keeping study of the Ginkgo biloba seed nucleus that the combination of chitosan film and sodium alginate film has better preservation effect [5]. Jia prepared edible coating preservatives using chitosan as coating agent. It was found that the treatment with 1.5 w/v% chitosan could better inhibit the decrease of fruit hardness, soluble solids content, acid content, and chlorophyll decomposition [6]. Zhang successfully used chitosan and lauric acid to make an edible drug capsule film with 0.2~0.3 mm, which can be used to preserve the freshness of peeled fruits, as well as excellent transparency [7].

## 2.2 Plant essential oils and extracts

The antibacterial properties of essential oils mainly depend on volatile substances such as phenols, aldehydes and terpenes in essential oils. Therefore, the packaging film made of plant essential oil or its extract can not only inhibit and kill the microorganisms contacted to the film, but also inhibit the growth of microorganisms around the film. The essential oils that are widely used in the market and have good antibacterial effects include forsythia, cinnamon, oregano, anise, cumin, sage, pepper, etc. Chitosan film prepared with rosemary essential oil (REO) has shown high antibacterial activity and total phenol content, and has the potential to be used as food fresh-keeping active film [8]. When using chitosan and honeysuckle extract as raw materials to develop an active food packaging film, the addition of honeysuckle extract not only improves the antioxidant and antibacterial activity of the chitosan film, but also greatly improves the moisturizing performance of the chitosan film [9].

## 2.3 Bacteriocin

Bacteriocins are a class of proteins or peptides with bactericidal effects. Its main mechanism is to inhibit the Gram-positive bacteria (G+) whose characteristics are close to the producing bacteria. For example, Nisin is one of the most common bacteriocins. It is a small antibacterial peptide produced by lactic acid bacteria, which can inhibit the growth of Gram-positive bacteria (G+) and Gram-negative bacteria (G-) such as *Salmonella*. It has good application potential in antibacterial packaging. Nisin is now permitted in food in more than 50 countries.

## 2.4 Lysozyme

Lysozyme, also known as cell wall enzyme, is an alkaline enzyme that can hydrolyses mucopolysaccharides of microorganisms. The mainly

mechanism is to break the  $\beta$ -1,4 glycosidic bonds in the cell wall, decomposing the insoluble polysaccharides, and cause the cells to die. Lysozyme has a weaker effect on fungi and Gram-negative bacteria (G-), but has a stronger hydrolysis effect on Gram-positive bacteria (G+). Yu used a lysozyme/chitosan blended film to inhibit the growth of microorganisms on the surface of cheese [10]. Studies have found that in an acidic environment, the antibacterial effect of the film is stronger than other pH conditions, and the lysozyme/chitosan film has excellent effect on inhibiting fungi, yeast and bacteria.

## 2.5 Inorganic antibacterial agent

Inorganic antibacterial agents are made by utilizing the antibacterial properties of many metal elements. They can be divided into silver series, copper series, zinc series, titanium series, and other composite systems. It is believed that the mechanism of antibacterial metal ions (e.g. nano-silver materials) is that the interaction between silver cations and the anions of microbial cell membranes, which destroys the life activities of microorganisms and leads to their death. The oxidation reaction under light conditions plays a role on bactericidal and antibacterial. Although the inorganic antibacterial agent has good heat resistance, safety, and durability, it is expensive and has slow acting property.

## 2.6 Organic antibacterial agent

Organic antibacterial agents generally refer to antibacterial agents made of organic materials as antibacterial substrates. They can be divided into four categories: natural organic antibacterial agents, low molecular organic antibacterial agents, high molecular organic antibacterial agents, and organic-inorganic composite antibacterial agents. Organic antibacterial agents have the advantages of wide sources, convenient processing, low cost, stable colour, specificity and relatively high sterilization rate compared with other antibacterial agents, and it can obtain improved safety through organic-inorganic combination. Organic antibacterial agents are believed to have great potential development and application.

## 3 Progress on biodegradable films for antibacterial food packaging

### 3.1. Starch and derivatives

Starch is widely found in the root and stem tissues of plants. It is easy to obtain, has a short growth cycle, and is inexpensive. It is one of the most popular natural polymer materials. Compared with other degradable materials, although the starch film has the advantages of colorless, odorless, low oxygen permeability, high transparency, etc., its shortcomings of low mechanical properties and strong hydrophilicity are also obvious. Therefore, many researchers are committed to

developing packaging films by mixing starch with other substances to make up for the low mechanical properties of starch films as much as possible [11].

### 3.2 Chitosan

Chitosan is a basic amino polysaccharide obtained from deacetylating chitin. Chitosan film has excellent transparency and oxygen barrier properties and is widely used in food packaging. Chitosan is commonly used with other antibacterial agents to obtain composite films. In chitosan solution, silver nanoparticles can be synthesized by reducing silver nitrate with  $\gamma$ -ray irradiation. The incorporation of silver nanoparticles slightly improved stretch and oxygen barrier properties of chitosan film, and reduced the water vapor/moisture barrier properties. In addition, silver nanoparticle-supported chitosan films have strong antibacterial activity against *E. coli* and *S. aureus* [12]. Riza et al combined apple peel polyphenol with chitosan to develop a new functional film, namely CS-APP film with 0.50 w/v% of APP, which significantly increased the thickness, density, solubility, opacity and swelling rate of the film, and reduced the moisture content and water vapor transmission rate, and has excellent mechanical properties and antibacterial properties, it can be used as a bio-composite food packaging material in food industry [13]. Using yam starch and chitosan as raw materials, an edible antibacterial film was prepared, and the resultant film had bactericidal effect on *Salmonella enteritidis* with good flexibility [14]. Li et al [15] treated the red grape with chitosan/starch antibacterial composite film, and the mass loss rate of red grape was only 18% after 60 days of treatment, and the good fruit rate reached more than 60%.

### 3.3 Cellulose and derivatives

Cellulose is the main component of plant cell walls. It is a macromolecular polysaccharide composed of D-glucopyranose through  $\beta$ -1,4 glycosidic bonds. Cellulose is the most abundant biopolymer with good degradability, stability, and safety. They are very popular and are one of the raw materials for preparing degradable packaging. Methyl cellulose, hydroxypropyl methyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, etc. are the main derivatives. The transparent cellulose film prepared by using chitosan solution and coating method has good barrier properties and antibacterial properties; Compared with the blended film, the mechanical properties of pure cellulose film are relatively better, and the hydrophobic and oxygen barrier properties of the blended film are greatly improved [16]. In addition, its oxygen permeability coefficient is lower than oxygen barrier materials such as ethylene-vinyl alcohol copolymer. Antibacterial test carried out on *S. aureus* on cellulose film showed that the chitosan coating method can significantly improve the antibacterial performance of cellulose film [17]. Nanocellulose and microcellulose can improve the mechanical properties of cellulose/sodium alginate bio-composite film from

unmodified birch pulp, microfibrillated cellulose, nanocellulose and birch pulp derivatives. Dekina developed mucoadhesive films with entrapped lysozyme based on gelatin/sodium carboxymethyl cellulose. Lysozyme in mucoadhesive films retains more than 95 % of its initial activity for 3 years of storage, the mucoadhesive films with lysozyme have 100% bactericidal effect on the antibacterial test of *S. aureus* and thus could be considered as a perspective antimicrobial food packaging film [18].

### 3.4 Protein

The functional characteristics of proteins are very extensive since the unique spatial structure. Compared with other synthetic films, protein films have better mechanical properties and gas barrier properties, but their applications are inhibited because of their poor water barrier properties. Therefore, protein films are usually mixed with hydrophobic materials and high molecular polymers to obtain better barrier properties. Casein, zein, whey protein, and gelatin are proteins commonly used in degradable films. Wang prepared a whey protein isolate (WPI)-based bio-nanocomposite film embedded with zein nanoparticles by solution casting. Zein particles are coated with sodium casein, which makes them more evenly distributed in the film. Its addition can significantly improve the water vapor barrier and mechanical properties of whey protein isolate, and reduce the hydrophilic properties of the film [19]. A milk protein-based edible film containing 1.0% oregano, 1.0% pepper or 1.0% oregano-pepper powder (mass ratio of 1: 1) is coated on beef muscle slices in order to control the growth of pathogenic bacteria and improve the shelf life at 4 °C [20]. The whey protein film can slow down the corruption, weightlessness and softening of the virgin fruit to a certain extent. The whey protein added with potassium sorbate has better preservation on the virgin fruit than whey protein without potassium sorbate [21].

### 3.5 Poly-lactic acid (PLA)

PLA is a completely biodegradable and environmental-friendly aliphatic polyester material. It is polymerized from lactic acid produced by the fermentation of grains. It can be completely decomposed under the reaction of microorganisms, acids and alkalis, and the decomposition products are water and carbon dioxide. PLA can also be recovered, degraded into lactic acid under the reaction of enzymes, and can be recycled. PLA film has various advantages such as high transparency, good mechanical properties, and easy to process, so it is considered as the most promising degradable packaging material. PLA has been widely used and has developed a variety of green packaging materials using PLA as raw material.

Zhang [22] used biodegradable polylactic acid (PLLA), polyvinyl alcohol (PVA), and polycaprolactone (PCL) to prepare PLLA/PVA/PCL composite films, and combined with the natural preservative Nisin. After

using PLLA/PVA/PCL-Nisin composite antibacterial film packaging, the shelf life of cold fresh meat can be extended to 22 days, and the shelf life of cold fresh meat packaging using PLLA/PVA/PCL composite film is 17~19 days, while the shelf life of the cold fresh meat packaged with PE film was only 11 days. Martins used PLA as the substrate and immobilized green tea extract (GTE) by extrusion to develop a new type of packaging film with antioxidant activity. GTE in PLA film can better protect smoked salmon lipids from oxidizing [23]. Tawakkal uses PLA, kenaf fiber, and thymol as raw materials to prepare bio-based composite films; by adding 20% to 30% thymol, the film can maintain the number of *E. coli* in trypsinogen soybean soup at 37 °C for 2 days; the addition of natural fibres can reduce production costs and improve the mechanical properties of PLA; The addition of antibacterial agents such as essential oil extracts can further enhance packaging functions for better preservation of food. This research proposes a packaging system with enormous potential that uses bio-derived polymers (PLA) and natural fibres (kenaf) and essential oil extracts (thymol) as the basis for new materials that extend shelf life of meat products [24].

### 3.6 Polyvinyl alcohol (PVA)

PVA is a vinyl polymer with many excellent properties, which is resistant to water, oil, and solvents, and is therefore widely used in the food industry for filmmaking and food packaging. However, the hydroxyl content in the molecules of the PVA structure is too high, which causes its higher melting temperature than the decomposition temperature, making it difficult to perform thermoplastic molding. Therefore, PVA is usually modified by blending with other substances in manufacturing, such as glycerol and maltose composite additive, to improve the flexibility of PVA film. Gailwad added apple pomace (AP) with a mass fraction of 1%, 5%, 10%, and 30% to the PVA matrix to prepare an active antioxidant food packaging film. The results showed that the addition of AP increased the total phenol content and antioxidant properties of the PVA film; in terms of physical properties, the higher the AP content added to the PVA film, the significantly lower the tensile strength, elongation at break, and thickness of film. Compared with the control film, the PVA-AP film has a lower transparency, and the thermal stability of the PVA-AP film is improved with the increase of the AP concentration [25]. For mango packaging, compared with commercially available PE preservative film, bentonite/chitosan/PVA preservative film can more effectively reduce the mass loss rate and corruption index of mango, and inhibit the respiration of fruits, thereby extend the shelf life [26].

## 4 Conclusions

Attention to the development of biodegradable plastics in the field of food packaging is in line with China's "sustainable development" strategy. Biodegradable antibacterial packaging is an eco-friendly packaging

material, which has multiple advantages such as inhibiting food corruption and bacterial growth, and extending shelf life, etc. It has attracted widespread attention in the food industry and is one of the hot topics in food packaging research. In addition, the biodegradable antibacterial packaging has fair mechanical strength, high efficiency in antibacterial, and is non-toxic and harmless, so it will not have harmful effects on the human body. In the end of usage, the material will eventually enter the environment in the form of inorganic substances. Secondary pollution caused by microorganisms and ultraviolet rays in the natural environment can be avoided. Currently, biodegradable antibacterial film is often used for packaging of fruits and vegetables during post-harvest transportation and storage. The utilization of protecting fruits from pests and diseases in the field before picking is not common. If the biodegradable antibacterial film can be applied in the field, the fruit can be protected under precaution.

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