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Application of Zein Compound System in Food Packaging

Haoyu Liu[1, *]

[1]College of Food Science and Engineering, Northwest A&F University, XianYang,712100, China
*Corresponding author: a31415903@outlook.com

Abstract:

In recent years, with the exposure of the problem that traditional plastic packaging is difficult to degrade, the serious problem of white pollution urgently needs to be solved. Zein has attracted much attention in the field of food packaging due to its superior film-forming property and degradability. However, pure Zein membranes have functional defects such as high brittleness and poor hydrophilicity. Therefore, research on the compounding system of Zein membranes became particularly important. The physical and chemical properties and film-forming properties of zein were reviewed, and the synergistic mechanism of zein with polysaccharides, proteins and polyphenols was introduced in detail. Taking the most popular and best compound substances among the three kinds of substances as examples, the improvement points of the composite membrane in mechanical properties, antibacterial properties, antioxidant capacity, thermal stability and other aspects compared with zein single membrane were discussed, and the application effects of the current technology were analyzed. Finally, the future research directions and challenges of zein composite film were put forward, and the broad prospects of zein composite film in the field of food packaging were prospected.

Keywords: Zein; Protein membrane; Food film materials; Composite membrane; Degradability.

1. Introduction

Food packaging plays a vital role in the modern food industry. It has many advantages, such as protecting food quality, preventing physical damage, facilitating circulation and storage, ensuring food safety and health, promoting sales and enhancing product value, and facilitating consumer use. Up to now, the most common food packaging films on the market are made of petroleum-based plastics. Petroleum-based plastics are high-molecular materials derived from fossil fuels such as petroleum, coal or natural gas. Therefore, they have poor hydrophobicity and are difficult to be degraded by microorganisms. Long-term accumulation causes pollution to the soil, water bodies and air, leading to serious “white pollution”.

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Therefore, it is imperative to develop green and degradable alternative packaging materials.

In this context, the development of green and biodegradable alternative packaging materials has become a major research focus in the field of food. Among many bio-based materials, zein is regarded as a potential packaging material because of its good film-forming properties and excellent gas barrier properties, which are beneficial to food packaging processing. Moreover, as the most abundant type of corn protein, zeololytic protein has abundant raw materials and high biocompatibility, which is more conducive to being used as the basis of food packaging materials. However, the single Zein membrane has multiple constraints such as high brittleness and insufficient hydrophilicity. Therefore, the research on the compounding and synergistic mechanism of Zein becomes particularly important. The existing research results have not systematically summarized the compounding mechanism of zein. Therefore, this paper will focus on the compounding system of zein with polysaccharides, proteins and polyphenols, and discuss the improvement of the composite membrane in terms of mechanical properties, antibacterial activity, antioxidant capacity and thermal stability compared with zein single membrane by taking the most popular and best compounding substances among the three kinds of substances as examples. The research findings in recent years and the future development of zein composite membrane are systematically reviewed.

2. Overview of Zein

Corn, commonly known as bract rice, Baogu and Bangzi, is one of the three major food crops in the world. It is one of the important food, feed and industrial crops in China, and its planting area and yield are in the forefront. The starch content in corn grain is as high as 70%. Therefore, in addition to direct consumption, the most widely used use of corn is to extract corn starch for industrial production. Some by-products - corn protein will be generated in the extraction process, but it is usually only sold at a low price or directly discarded as ordinary animal feed protein, which will not only cause waste, but also aggravate environmental pollution. Therefore, if the diversified application of corn protein can be realized, it can not only improve the utilization rate of corn raw materials but also improve the application value of corn protein itself.

2.1 Composition and Physicochemical Properties of Zein

Zein is an important plant storage protein, accounting for about 70% of the total protein in corn. It is a type of glycoprotein and is widely present in plants. It has the characteristics of being renewable, non-toxic and highly biocompatible, and thus is widely used in the fields of food, medicine, textile and papermaking. Zein can be roughly divided into α - zein and β - zein according to the solubility. However, because β - zein is unstable and prone to condensation or sedimentation, α - zein is mostly used in the market and industrial production. The amino acid composition of zein is mostly hydrophobic amino acids, and there are more sulfur-containing amino acids, which leads to that zein itself is neither soluble in water nor in anhydrous ethanol, but only soluble in 60% -95% alcohol aqueous solution or some organic solvents. Zein molecules are rod-shaped or oblate-ellipsoid and these rod-shaped structures can form a delicate network structure by intertwining, which is one of the important reasons for zein's film-forming property [1].

2.2 Study on Zein Membrane

Corn alcohol-soluble protein also has unique film-forming properties. Corn alcohol-soluble protein is rich in sulfur-containing amino acids, and the protein molecules are connected by strong disulfide bonds and hydrophobic bonds. This is the basis for the easy formation of films by corn alcohol-soluble protein. After being coated as a film solution, as the solvent evaporates, the film dehydrates and dries, increasing the protein concentration in the film formation solution. When the concentration exceeds a certain value, the protein agglomerates, forming hydrogen bonds, disulfide bonds and hydrophobic bonds between molecules to maintain the network structure of the film, forming a transparent and shiny zein film. However, due to the brittleness and poor ductility of pure zein film, it cannot be more widely used. The existing research is also gradually deepening the property changes of zein film after adding other substances, in order to obtain green degradable materials that can replace petroleum-based plastics in the field of food packaging.

3. Compound System of Zein and Polysaccharide

Protein and polysaccharide can form covalent bonds through Maillard reaction and can also be combined through non-covalent interactions such as electrostatic interaction and hydrogen bonds. Therefore, protein and polysaccharide show good compounding potential in food science and medical materials, and the obtained amino acid derivatives have better emulsification and stability, so they can be used as functional materials for food packaging. The combination of zein and polysaccharide can effectively improve the thermal stability and physical

strength of the composite membrane, and the combination effect with zein is better. The three polysaccharides that are widely studied are chitosan, cellulose and starch.

3.1 Compound of Zein and Chitosan

Chitosan is a natural biopolymer that is non-toxic and harmless to the human body and does not cause environmental pollution. Like zeolinolytic protein, it is a safe industrial biopolymer in the 21st century. The chitosan-zeolinolytic protein nanocomposite (NC) prepared from the two is a very promising food packaging material, which has better antioxidant, antibacterial and mechanical properties. Kasaai discovered that the composite film with a chitosan-zeolin-soluble protein mixture ratio (1:1) exhibited the best elasticity and the greatest tensile strength. Meanwhile, this ratio is also regarded as the optimal ratio-or mushroom packaging and storage [2].

3.2 Compound of Zein and Cellulose

Cellulose is the main component of plant cell wall, presenting a slender strip shape, so when it is combined with polysaccharide to form a packaging film, it will form a breathable grid structure, and cellulose based materials can also be naturally decomposed into water, carbon dioxide and other harmless substances, which are environmentally friendly, and because of the wide source of cellulose, low cost, renewable, and high mechanical strength of the zein cellulose composite film made of mixed cellulose, it has a very broad prospect in the field of food packaging. Zhang Ying found that the composite film can reduce the changes of water content and sugar content of aloe, prolong the storage time of strawberry and reduce the weight loss of eggs, which proved the effective application of zein cellulose film in the field of food packaging [1].

3.3 Compound of Zein and Starch

Starch is a polysaccharide polymerized by glucose molecules. Because of its edible and good film-forming properties, starch-based materials can be made into edible capsule shells, convenient food packages and various food packaging, which can effectively protect food and extend the shelf life. Protein starch complex is also widely used in many fields, such as edible food packaging, bionic materials, textile materials and so on. The hydrophobicity of waxy corn starch (WCS) - zein composite film and phosphate bisstarch (DP) - zein composite film made by gaopingping based on Maillard reaction principle increased by 44.2% and 46.6% respectively, and the tensile strength increased by 60% and 20% respectively [3].

After being compounded with three types of polysaccharides, zeolin has various properties enhanced and improved. The most significant advantage of the composite membrane after compounding with the polysaccharides is the greatly enhanced physical strength and mechanical properties of the membrane. The comparison of other properties with Zein single membranes is detailed in Table 1.

Table 1 Summary of properties of zein mixed with three polysaccharides

Zein complex	Chitosan	Cellulose	Starch
Mechanical properties	***	***	***
Bacteriostasis	**	*	*
Antioxidant apacity	**	**	**
Thermal stability	*	*	*
Other			Increased hydrophobicity

Note: assume that the performance of zein single film is*

4. Compound system of Zein and protein

Proteins may combine with each other through non-covalent interactions such as hydrogen bonds and hydrophobic interactions. The high biocompatibility of Zein enables it to bind with various proteins, thus forming packaging films composed of multiple proteins. The outstanding stability of gelatin and the powerful antioxidant capacity of casein make it possible for these two proteins to combine with Zein Compared with a single Zein film, it is more conducive to food packaging.

4.1 Composite Films of Zein and Gelatin

Gelatin is a peptide molecular polymer and a natural high protein food thickener. In recent years, Japan and other countries have used gelatin for food coating to inhibit browning reaction and prevent food moisture absorption. Nanofiber films made of gelatin and corn gluten have potential application prospects in biological activity transfer and controlled release in food [4]. The zein gelatin antibacterial film prepared by cuichengjun shows strong

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hydrophobicity, and it only takes one month for the soil to degrade naturally [5]. It has good environmental friendliness and can extend the shelf life of three days after being applied to pork preservation, which is enough to prove that this composite film has a good application prospect in the field of food packaging.

4.2 Composite Membrane of Zein and Casein

Casein is the main protein in mammalian milk, including cow, sheep and human milk. It is also an important nutritional component in dairy products. It has good biocompatibility and biodegradability. In recent years, casein has been widely used in the field of food packaging, such as edible packaging film close to food, antibacterial and fresh-keeping packaging. It can be effectively assembled into a composite film with zein through intermolecular bonds and covalent coupling. This film has shown excellent long-term stability and antioxidant capacity, but its mechanical properties still need to be further improved [6]. In conclusion, the compound membranes formed by Zein and various proteins have multiple advantages over single Zein membranes. Moreover, due to the relatively easy binding between proteins, the application of compound systems with proteins is also more extensive. The comparison of properties after compounding is detailed in Table 2.

Table 2 Summary of properties of zein mixed with two proteins

Zein complex	Gelatin	Casein
Mechanical properties	**	*
Bacteriostasis	**	*
Antioxidant capacity	*	***
Thermal stability	*	***
Other	Increased hydrophobicity	

Note: assume that the performance of zein single film is*

5. Compound System of Zein and Polyphenols

Zein is mainly linked to polyphenols through non-covalent interactions (such as hydrophobic interactions between hydrophobic amino acid residues in zein and non-polar aromatic rings of polyphenols) and covalent interactions (covalent bonds between zein and polyphenols) [7]. And most of the polyphenols have antibacterial and antioxidant functions, so it is a hot research topic to compound polyphenols and zein into food packaging [8]. Compared with the single zein film, adding polyphenols can prolong the shelf life of food and improve the packaging function.

5.1 Compound of Zein and Magnolol

Magnolol is an effective antibacterial component in the bark of the traditional Chinese medicine Magnolia officinalis, and it has a powerful inhibitory effect on many pathogens [9]. After complexing with plant proteins, it can enhance the chemical stability of substances. For instance, Wei Fangyuan et al. developed CMC films using the zeolinolytic protein-magnolol (ZMC) complex, which were highly effective in preventing ultraviolet rays, antioxidation, and antibacterial properties. Moreover, after experiments with jackfruit, the shelf life was extended from 5 days to 8 days [10].

5.2 The Blend of Zein and Tea Polyphenols

Tea polyphenols are the general name of polyphenols in tea. Most of them contain more than two o-hydroxy polyphenols. It is an ideal antioxidant and has inhibitory effect on nearly 100 kinds of bacteria in nature. It is a good food preservative. Chi Haibo found that after adding tea polyphenols, the thermal stability of zein film was enhanced, the elongation at break was significantly improved, but the tensile strength was decreased [11].

5.3 Compound of Zein and Chlorogenic Acid

Chlorogenic acid is a common polyphenol. It is one of the main antibacterial and antiviral active pharmacological components of Lonicera japonica Thunb. It is also an effective phenolic antioxidant. Wangdexiong et al. found that the combination of zein and chlorogenic acid can enhance thermal stability, antioxidant effect and improve antibacterial performance [7]. Compared with zein film, the mechanical properties of zein chlorogenic acid film made by Wang Xinya and others are significantly improved, the antioxidant capacity is increased by 26%, and the antibacterial property and thermal stability are also improved [8]. It can be seen from this that when zeololytic protein is compounded with polyphenols, due to the excellent antibacterial and antioxidant capabilities of polyphenols, these two properties of the composite film have also been qualitatively improved. However, there is still much room for improvement in other aspects. For a detailed compari-

son of the properties, please refer to Table 3.

Table 3 Summary of properties of zein mixed with three polyphenols

Zein complex	Magnolol	Tea polyphenols	Chlorogenic acid
Mechanical properties	*	*	***
Bacteriostasis	***	***	**
Antioxidant capacity	***	***	**
Thermal stability	*	***	**

Note: assume that the performance of zein single film is*

6. Future Challenges

Although the research on the compounding system of Zein has become a major core hotspot in recent years, due to various factors such as high production costs and low technical popularity, the future development of Zein compounding films still faces many challenges.

6.1 Challenges of Performance Balance

It is a major difficulty to achieve the "perfect balance" of the properties of the composite membrane. For example, in the compound with purple onion extract, although it can significantly improve the antioxidant property of the film, excessive addition will lead to a significant decrease in tensile strength and elongation at break. And the performance requirements of different application scenarios are different, so future research should focus on the collaborative optimization of membrane performance through the accurate formulation design of a variety of substances.

6.2 The Control of Production Cost and the Challenge of Large-scale Production

For laboratory achievements to enter the market, it is inevitable to control production costs and repeatedly optimize the process. In the research on the compounding of Zein, the first and foremost issue is the cost of materials. The purchase cost of Zein and most compounding substances is relatively high. Secondly, the cost of the technology or equipment required in the production process is also relatively high. Future research should focus on the control of production costs in order to bring this process to the market to replace petroleum-based plastics and achieve green development.

6.3 Development of Safety and Standardization

Food is the foundation of people's livelihood. As the first line of defense in direct contact with food, food packaging, while striving for green development, should also pay attention to the safety of food packaging. Every additive added to the packaging film must comply with the national standards, and it is also necessary to consider whether the new substances that may be produced after their combination meet the safety standards.

7. Conclusion

In this paper, the synergistic mechanism of zein with polysaccharides, proteins and polyphenols was systematically reviewed. Research showed that zein has become a core hotspot in the field of food in recent years. The composite film is superior to the single zein film in bacteriostasis, physical strength, antioxidant capacity, thermal stability and other aspects, and has been used in meat, fruit and other food packaging and some edible packaging. Experiments have proved that this kind of composite film can extend the quality assurance period of food, so that buyers can buy more fresh food. However, due to the fact that the composite film of a single Zein and another single substance still has certain deficiencies in some aspects, in the coming years, research on Zein composite films should be further deepened to prepare high-quality films that can meet the packaging requirements of various foods through the synergistic action of multiple substances, and they should be vigorously promoted. At the same time, the development cost should be reduced to enable large-scale application in the market. This will further achieve the replacement of traditional petroleum-based plastics and realize green and low-carbon development.

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