# Biomass-based Bilayer Film Derived from Corn Starch and Polylactic Acid for Banana Packaging

Zheng Cheng, a,b,c,d,\* Mei Ning, a,c,d Xinmei Nong, a,c,d Wenhua Gao, Naiyu Xiao, a,c,d Honglei Wang, a,c,d Xueqin Zhang, a,c,d Le Zhong, a,c,d Qianbin Mo, a,c,d and Yunyun Zhong a,c,d

Biomass-based materials have the potential to protect fruits and meet environmental requirements when applied to fruit packaging. However, their mechanical properties and barrier properties are insufficient compared with plastic packaging, which limits their application. In this study, a high-barrier bilayer film derived from corn starch (CS) and polylactic acid (PLA) was applied for banana pulp preservation. Results indicated that the bilayer film exhibited good barrier performance. The water vapor permeability and oxygen permeability of bilayer films were lower than that of pure CS or PLA film. In the 3 days preservation experiment, the weight loss of banana pulp packaged by CS/PLA bilayer film at ratio of 15:45 was the lowest (1.36%), while the pH and firmness of banana pulp packaged by this ratio bilayer film were the largest, reflecting that the bilayer film could effectively delay the oxidation and deterioration of banana pulp. Moreover, the CS/PLA bilayer film was analyzed by scanning electron microscopy and Fourier transform infrared spectrometry, which also evidenced that PLA could provide better mechanical strength and barrier properties, and CS had hydrophilic and biodegradable potential. In conclusion, it is feasible to combine CS and PLA to prepare the bilayer films. The study is beneficial to promote the development and application of eco-friendly bio-based packaging film.

DOI: 10.15376/biores.21.1.959-972

Keywords: Corn starch; Polylactic acid; Bilayer film; Packaging

Contact information: a: College of Light Industry and Food Technology, Zhongkai University of Agriculture and Engineering, Guangzhou CN 510225, China; b: State Key Laboratory of Advanced Papermaking and Paper-based Materials, South China University of Technology, Guangzhou, CN 510640, China; c: Guangdong Engineering Research Center of Food Green Packaging, Zhongkai University of Agriculture and Engineering, Guangzhou, Guangdong Province, CN 510225 China; d: Key Laboratory of Green Processing and Intelligent Manufacturing of Lingnan Specialty Food, Ministry of Agriculture and Rural Affairs, Zhongkai University of Agriculture and Engineering, Guangzhou 510225, China; \*Corresponding author: chengzheng@zhku.edu.cn

#### INTRODUCTION

Traditional petroleum-based plastic film has struggled to meet sustainability needs due to pollution and resource issues, making the development of sustainable bio-based film a current research hotspot (Tardy *et al.* 2023). Furthermore, due to the continuous advancement of global sustainable development policies, bio-based materials demonstrate huge potential market demand. Bio-based materials are normally processed *via* chemical, physical, or biological means to enhance the overall performance and gain new functions to meet various applications (Jariyasakoolroj and Chirachanchai 2014).

Starch and polylactic acid (PLA) are bio-based polymers that have received extensive attention in the field of food packaging (Goswami et al. 2022; Kumari et al.

2022). Starch as a plant polysaccharide, widely found in grains and tubers, which has good film-forming properties, low cost, and low oxygen permeability. Thus, it has a wide range of applications in food, medicine, and other fields (Muller *et al.* 2017; Li *et al.* 2018). However, starch is hydrophilic and has insufficient mechanical properties, limiting its application in the packaging field. Several studies have used plasticizers such as glycerol and sorbitol in combination with corn starch to reduce intermolecular forces and improve the mechanical properties of the films (Liu *et al.* 2013; Han *et al.* 2022). Some defects of starch films could be overcome by incorporating other biodegradable materials (Sanyang *et al.* 2016). The PLA is derived from renewable plant resources, with hydrophobicity and low water vapor permeability (Chen and Patel 2012). However, PLA is fragile, having poor oxygen and impact resistances (Chu 2017). Therefore, it is of interest to determine whether they can be used as blends or multilayer films to provide properties that are more suitable for packaging applications based on their complementary characteristics.

Up to this point, some methods have been adopted for preparing starch/PLA composites (Yang et al. 2021), such as solution blending, hot pressing, casting, multi-layer film structure, etc. For example, pea starch (PS), octenyl succinic anhydride modified PS, and PLA were used to fabricate biodegradable sandwich-structured double-layer films with high barrier properties in different proportions. The film effectively reduced the weight loss of strawberries and the loss of vitamin C, thereby slowing down the ripening of strawberries (Zhou et al. 2021). The preparation method of multilayer film has good controllability and expansibility, which allows starch and polylactic acid to be distributed in different layers to exert better packaging characteristics. Zhou et al. (2019) developed a double-layer film using PS and PLA, and applied it to the preservation packaging of cherry tomatoes. The results showed that the introduction of the double-layer structure improved the waterproof and thermal properties of the PS film, and the double-layer film had excellent oxygen barrier and water vapor barrier properties, which effectively prolonged the shelf life of cherry tomatoes. Although many research teams have made some progress in the preparation or application of starch/PLA bilayer films (Muller et al. 2017; Hernández-García et al. 2022; Chen et al. 2022), they are still in the laboratory-scale trial production stage at present. In general, biomass-based materials are universally utilized to prepare double-layer films, which serve as biodegradable and renewable materials in fruit packaging, and this approach has important potential.

There have been some studies on the preparation of single-layer films by using starch and PLA composite materials, but the research on starch/PLA bilayer films are still relatively few. Besides, corn starch made from corn grains has a high yield and a relatively low cost. In this study, a bilayer CS/PLA film was constructed by layer-by-layer casting of the corn starch layer and the polylactic acid layer through the solution casting method, which could effectively make up for the defect of the two materials forming films separately as packaging film materials. Furthermore, the mechanical properties, water vapor transmission, oxygen transmission, and preservative effect of bilayer CS/PLA film on banana pulp were thoroughly analyzed. The results indicated that when the ratio of CS/PLA was appropriate, the bilayer films exhibited enhanced barrier properties, which effectively extended the shelf life of banana pulp. Therefore, the CS/PLA bilayer films, when used as fruit packaging materials, not only offer novel insights and approaches for the research and development of biodegradable packaging film but also provide innovative ideas for the high-value utilization of bio-based polymers. Consequently, this study holds significant promise for advancing the field of green packaging.

#### **EXPERIMENTAL**

#### **Materials**

Corn starch was provided by Laishui County Golden Valley Grain and Oil Food Co., Ltd. (Baoding, China). Polylactic acid, D-sorbate, and dichloromethane were obtained from Shanghai Maclin Biochemical Technology Co., Ltd. (Shanghai, China). Calcium chloride was purchased from Shandong Haiyang Star Chemical Technology Co., Ltd. (Shouguang, China). The water utilized throughout the experimental procedures was distilled water at room temperature.

#### Methods

Preparation of CS/PLA bilayer films

First, the corn starch film solution was prepared: 16 g dry corn starch was mixed with 299.2 mL distilled water and stirred for 30 min in a magnetic stirring water bath at 90 °C and a rate of 500 rpm. Then, 30% (compared to the dry weight of starch) glycerol and sorbitol (2:1) were added with continued stirring for 30 min to obtain a corn starch solution with a mass fraction of 5.0 %. Secondly, the polylactic acid solution was prepared: 50 mL of dichloromethane was mixed with 2 g of dried polylactic acid under the magnetic stirring (Shi *et al.* 2017), and the polylactic acid was dissolved completely to obtain a polylactic acid solution with a mass fraction of 2.0 %, which was refrigerated. The CS/PLA bilayer films were prepared in five mass ratios of CS/PLA, namely 60:0, 45:15, 30:30, 15:45, and 0:60. Specifically, 40.0 g, 30.0 g, 20.0 g, 10.0 g, and 0 g corn starch solutions were respectively poured into circular petri dishes (diameter: 150 mm), and dried at 25 °C and 60% relative humidity for at least 24 h to obtain a starch layer (Zuo *et al.* 2013). Then 0 g, 25.0 g, 50.0 g, 75.0 g, and 100.0 g polylactic acid solution were added to the dry starch layer in petri dish. After drying at 25 °C, the dichloromethane was completely evaporated, and then the film was removed from the petri dishes to obtain the CS/PLA bilayer films.

## Barrier property testing of CS/PLA bilayer films

In the water absorption test, the method of Zhou et al. (2018) was slightly modified, and the film was cut into a strip of 2 cm × 1 cm. After recording the initial quality, it was placed in a beaker filled with distilled water and was taken out regularly and weighed after being drained of water. After repeating the above steps until the quality reached equilibrium, the water absorption was calculated. For the solubility test, the film was cut into 2 cm × 2 cm samples first and dried at 105 °C for 24 h to obtain the initial quality. Then, it was combined with distilled water in sealed container after 24 h. Subsequently, the film was dried at 105 °C for another 24 h and weighed. The solubility was calculated based on the rate of quality change. In the water vapor permeability (WVP) test, the CaCl<sub>2</sub> was first dried and then placed in a weighing bottle. The mouth of the weighing bottle was covered with the bilayer film; then the bilayer film and the bottle mouth were firmly tied with a rubber band. After weighing, it was placed in a dry chamber with high humidity and room temperature and weighed once every 24 h for 7 days. Finally, the water vapor permeability was calculated, and the result was expressed in g·m<sup>-1</sup>·s<sup>-1</sup> ·Pa<sup>-1</sup>. Oxvgen permeability (OP) was measured by a differential pressure gas permeameter (Yang 1994) (LabTRinkVAC-V1) at 25 °C and 50% relative humidity, and the sample was measured three times to obtain the value of oxygen permeability.

Water contact angle of CS/PLA bilayer films

The water contact angles of films were measured using a JC2000C1 contact angle goniometer (Shanghai Zhongchen Digital Technology Co., Ltd, China). Five points were tested for each film sample.

# Transparency test of CS/PLA bilayer films

Transparency of films were measured by using a Hach DR6000 UV-vis spectrophotometer (Hach, Colorado, USA) at 560 nm.

# Measurement of tensile properties of CS/PLA bilayer films

The CS/PLA bilayer films were cut into strips with a width of 10 mm and a length of 70 mm. Then the bilayer film strip was tested by using GBH-1 electronic universal testing machine, and it was tested 5 times in 25 °C, relative humidity of 50%, ranging of 30 mm, and the speed of 2 mm/min to obtain the average tensile data of the film.

# Scanning electron microscopy (SEM) observations of CS/PLA bilayer films

The film sample with a length of 30 mm and a width of 0.5 mm was frozen in liquid nitrogen until brittle, and then its cross section and surface were sprayed with gold for SEM observation (González and Igarzabal 2013). The accelerating voltage was 10.0 kV

# Fourier transform infrared spectrometry (FTIR) analysis of CS/PLA bilayer films

The film sample was analyzed with a FTIR spectrophotometer (Bruker Nicolet FTIR 5700). The sample was scanned in the range of 4000 to 500 cm<sup>-1</sup>, and the resolution was 4.0 cm<sup>-1</sup> at 25 °C.

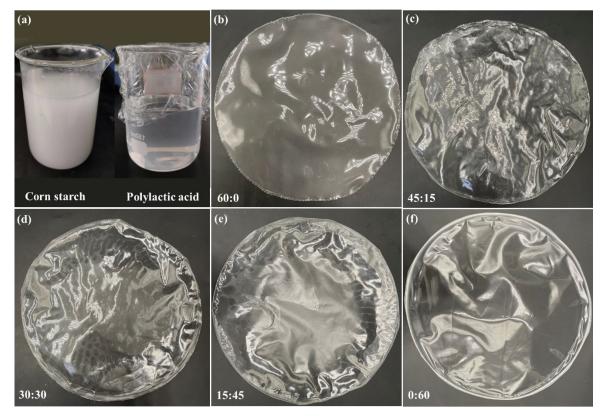
# CS/PLA bilayer films application for packaging preservation

The preservation application of the bilayer film packaging on banana pulp was divided into 7 groups. Two sections of banana pulps were placed in each plastic petri dish and then sealed with various types of films. The control group was directly exposed to the air. These 7 group samples were placed at room temperature for quality evaluation within three days. The weight loss rate of banana pulp was tested by the mass change in the beginning and end of the storage period. The firmness of banana pulp was characterized by employing the texture analyzer (TA-SR01, Jinan, China). Three points of every banana pulp were tested, and the average value was obtained as the data. The banana pulp was blended by high-speed mixer (HB60A, Zhejiang, China) to make a uniform puree. Next, pH value of the puree was measured by using a calibrated digital pH meter (PH838, Shenzhen, China), and the measurement results were recorded.

## **RESULTS AND DISCUSSION**

# Physical Properties of CS/PLA Bilayer Films with Different Ratios

As shown in Fig. 1, five different ratios of CS/PLA bilayer films were prepared *via* layer-by-layer casting of the corn starch layer and the polylactic acid layer through the solution casting method, and these films presented a relatively transparent (transparence: 86.4% to 92.3%) and smooth appearance, which was conducive to being used as packaging film material. The layer-by-layer casting strategy could elevate its water resistance of the composite bilayer films.



**Fig. 1.** Five different ratios of CS/PLA films: (a) corn starch solution and polylactic acid solution; (b) 60:0; (c) 45:15; (d) 30:30; (e) 15:45; (f) 0:60

Table 1 shows that the thickness, water absorption, and solubility of CS/PLA bilayer films displayed an obvious downward trend as the content of PLA increased. From the thickness analysis, the addition of PLA reduced the thickness of bilayer film from 0.116 mm to 0.075 mm. This is mainly attributed to the fact that the PLA molecular chain was regular and had high crystallinity (Khouri *et al.* 2024).

**Table 1.** Comprehensive Performance Analysis of CS/PLA Films in Different Ratios

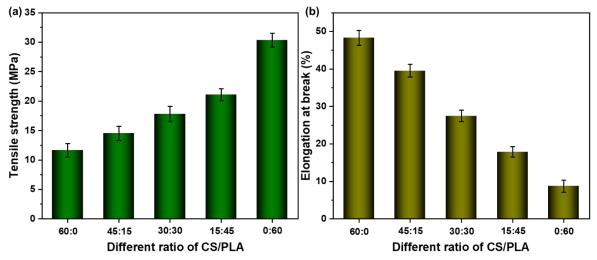
CS/PLA	Thickness	Water	Solubility	Transparency	Water contact angle (°)	
Ratio	(mm)	Absorption (%)	(%)	(%)	CS layer	PLA layer
60:0	0.116±0.06	128.20±0.51	20.47±0.12	86.41±0.12	43.58±0.13	-
45:15	0.108±0.03	65.39±0.17	19.31±0.07	88.05±0.14	46.27±0.11	88.72±0.19
30:30	0.097±0.05	54.84±0.24	15.29±0.16	89.58±0.08	47.93±0.07	89.54±0.13
15:45	0.089±0.04	31.72±0.36	9.18±0.20	90.26±0.17	49.02±0.15	91.03±0.11
0:60	0.075±0.01	1.52±0.15	2.47±0.14	92.34±0.23	-	92.86±0.26

When it was blended with corn starch, it can fill the molecular gaps, make the composite film structure closer, and inhibit the aggregation of corn starch, which ultimately led to a decrease in film thickness. With increased PLA content, the water absorption capacity of the bilayer film decreased from 128.2% to 1.52%. This was because there were a large number of hydroxyl groups on the starch molecular chain, and its molecules were easy to absorb water (Debnath *et al.* 2022). In addition, the pure PLA film had strong

hydrophobicity because of its less hydrophilic groups in the molecular chain (Yun et al. 2024). Studies have shown that increasing the content of PLA could effectively reduce the hydrophilicity of the bilayer film (Almgren et al. 2009). Therefore, increasing the proportion of PLA or reducing the proportion of CS could reduce the water absorption of the bilayer film. Corn starch also could be surface modified to yield cationic starch, which can further reduce water absorption. The change of solubility was similar to that of water absorption. When the proportion of PLA increased, the solubility of the bilayer film decreased from 20.5% to 2.5%, which was attributed to the fact that PLA was a hydrophobic polymer (Xu et al. 2023). When PLA was added to the CS film, the solubility of bilayer film could be effectively reduced. Although CS could be used as a packaging film, its high solubility in water has limited its application (Yuan et al. 2010). Besides, the surface wettability of bilayer films was confirmed by the water contact angle. The hydrophobic PLA layer had the highest water contact angle of 92.9°, while the PS layer exhibited hydrophilicity with the water, with a contact angle below 50°. As can be seen, the addition of PLA effectively improved the physical properties of CS/PLA bilayer film, which reduced the film's thickness, as well as its water absorption rate, dissolution

# Analysis of Mechanical Properties of CS/PLA Bilayer Films with Different Ratios

The effect of various CS/PLA ratios on the tensile strength (Fig. 2a) and elongation at break (Fig. 2b) of bilayer film were investigated. The tensile strength reflects the mechanical strength, and the elongation at break is an indicator of the flexibility of the bilayer film (Wu *et al.* 2013). The pure CS film (60:0) had the lowest tensile strength (11.6 MPa) and the highest elongation at break (48.3%). The pure PLA film (0:60) had the highest tensile strength (30.4 MPa) and the lowest elongation at break (8.7%). Especially, the tensile strength (21.1%) and elongation at break (17.9%) of the bilayer film (15:45) group were all higher than those previously reported for this kind of bilayer film (Hernández-García *et al.* 2022).



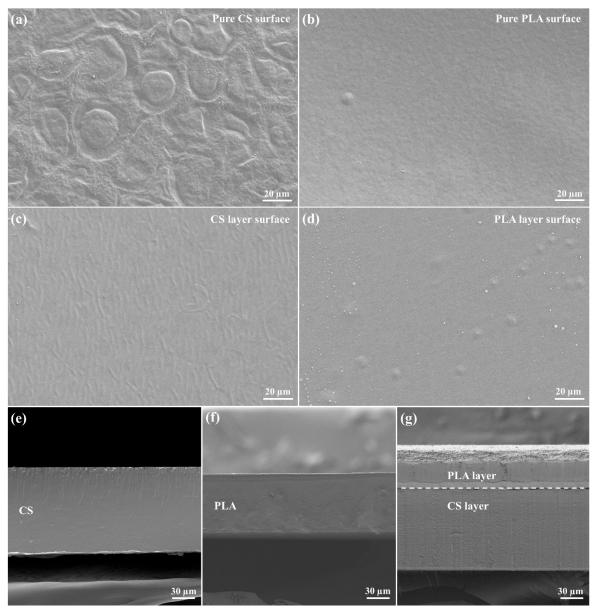
**Fig. 2.** The effects of different ratios of CS/PLA on the (a) tensile strength and (b) elongation at break of the bilayer films

The results indicated that with the addition of the PLA layer to the CS layer, the tensile strength of the bilayer film had greatly increased, but the elongation at break had

decreased significantly. This was because the PLA layer had rigidity, which can withstand strong pressure, and the CS layer had good plasticity. The mechanical properties of CS/PLA bilayer films combined the toughness of CS layer and the tensile strength of PLA layer. Its tensile strength was higher than that of pure CS films, and its elongation at break was greater than that of pure PLA films. Therefore, to achieve a balance between the mechanical strength and flexibility of packaging materials, the CS/PLA bilayer film with a appropriate ratio is the key based on the actual needs.

# Morphology and Structure Analysis of Bilayer Films Composed of CS/PLA

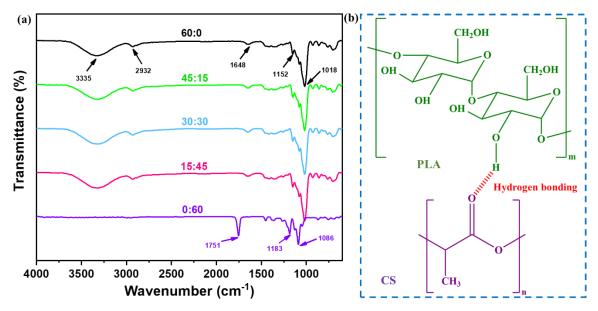
SEM images of pure CS film, pure PLA film, as well as a cross-section of the CS/PLA (30:30) bilayer film are shown in Fig. 3.



**Fig. 3.** SEM images of the surface (magnification: 600 x): (a) pure CS, (b) pure PLA, (c) CS layer of bilayer film (30:30), (d) PLA layer of bilayer film (30:30). SEM images of the cross section (magnification: 300 x): (e) pure CS film, (f) pure PLA film, (g) bilayer film (30:30)

The surface of pure CS film (Fig. 3a) was rough, with some CS particles, but no obvious holes or cracks. These findings indicated that the CS had been completely gelatinized during the thermoplastic process and had good film-forming performance. While the surface of pure PLA film (Fig. 3b) was smooth, without obvious holes or cracks, there were still a few small particles. As for bilayer film, the CS layer (Fig. 3c) exhibited a relatively rough surface, which was smoother than pure CS film. The PLA layer (Fig. 3d) displayed a dense, homogeneous surface, similar to pure PLA film. Both the cross section of CS film (Fig. 3e) and PLA (Fig. 3f) exhibited a dense structure without distinct cracks or holes. Besides, the cross section of the CS/PLA bilayer film (Fig. 3g) showed an obvious double-layer structure consisting of PLA layer and CS layer. The cross-section images showed a relatively compact and regular structure; no obvious separation was found at the boundary of CS/PLA layer. SEM observations of the cross-section of the CS/PLA bilayer film demonstrated that the PLA layer was tightly bonded to the CS layer, contributing to a dense structure and strong interfacial adhesion.

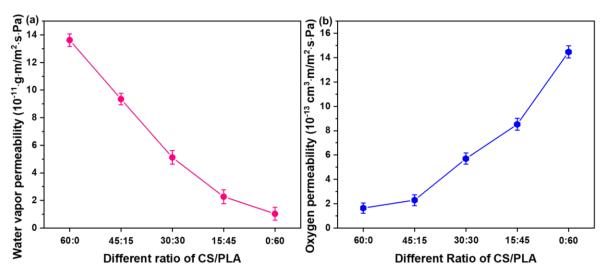
In addition, the FTIR spectra of CS/PLA bilayer films with different ratios are presented in Fig. 4. The absorbance peak at 3335 cm<sup>-1</sup> was due to the stretching vibration of O-H in adsorbed water and CS molecule. Another characteristic peak was observed at 2932 cm<sup>-1</sup> originated from the stretching vibration of C-H. The peak at 1648 cm<sup>-1</sup> was attributed to the O-H bending of the bound water molecules. Besides, the C-O bond stretching generated several discernible absorbance peaks at 1152 and 1018 cm<sup>-1</sup>. In the FTIR spectra of pure PLA film, the peak at 1751 cm<sup>-1</sup> was ascribed to the C=O stretching vibration of the generated carbonyl groups. The peaks at 1183 and 1086 cm<sup>-1</sup> were assigned to C-O-C stretching. It can be seen from the FTIR results that no new characteristic peaks different from those of the pure CS film or the pure PLA film appeared in the CS/PLA bilayer films. The interactions between PLA and CS is depicted in Fig. 4b. There was only hydrogen bond interaction between the interface of CS and PLA, and no chemical bond combination was apparent. Therefore, it could be concluded that the bilayer film was formed primarily by the physical action rather than chemical action of the two components.



**Fig. 4.** (a) FTIR spectra of CS/PLA bilayer film with different ratios, (b) scheme of interactions between PLA and CS

# Analysis of Barrier properties of CS/PLA Bilayer Films with Different Ratios

Barrier properties are an important characteristic of packaging materials. Barrier layers can impact the difference between the internal and external environments and thereby affect the products inside. As shown in Fig. 5a, pure CS film had the largest WVP, which was 13.63×10<sup>-11</sup> g·m/m<sup>2</sup>·s·Pa, while pure PLA film had the smallest WVP, which was  $1.02 \times 10^{-11}$  g·m/m<sup>2</sup>·s·Pa, indicating that PLA was a material with excellent water vapor barrier properties, while the water vapor barrier property of CS film was relatively poor. The WVP of CS film was nearly 13.4 times higher than that of PLA film. When the ratio of CS/PLA was changed from 0:60 to 15:45, the WVP of the bilayer film decreased to 2.27×10<sup>-11</sup> g·m/m<sup>2</sup>·s·Pa. This indicated that the higher the PLA content, the lower the WVP value of bilayer film, while the relatively better the water vapor barrier performance. When the CS/PLA ratio was 15:45, the WVP was close to that of the pure PLA film. As exhibited in Fig. 5b, the OP values (2.29~8.52×10<sup>-13</sup> cm<sup>3</sup>·m/m<sup>2</sup>·s·Pa) of CS/PLA bilayer films were little higher than that of pure CS film (1.64×10<sup>-13</sup> cm<sup>3</sup>·m/m<sup>2</sup>·s·Pa) and markedly lower than that of pure PLA film (14.47×10<sup>-13</sup> cm<sup>3</sup>·m/m<sup>2</sup>·s·Pa). The excellent oxygen barrier was attributed to the dense PS layer and the compact structure within the interfacial layer. Notably, the WVP and OP values of the CS/PLA bilayer film were similar to those reported in another study (Zhou et al. 2019). Thus, the combination of PLA layer with CS layer to construct bilayer films could obviously improve the barrier properties of bilayer film. This preparation process by adjusting the layer ratio enabled us to achieve expected barrier performances that meet the requirements for food packaging application.



**Fig. 5.** The effect of different CS/PLA ratio on the (a) water vapor permeability and (b) oxygen permeability of the bilayer film

## Application of CS/PLA Bilayer Films in Banana Pulp Preservation

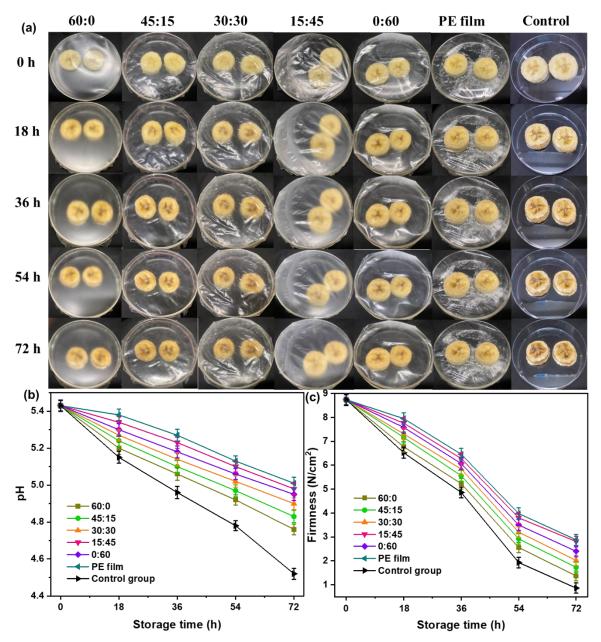
The weight loss rate for different ratios of CS/PLA bilayer films on the preservation of banana pulp were tracked over the course of three days. As summarized in Table 2, The results showed that the weight loss rate of banana pulp packaged by CS/PLA bilayer film gradually increased with the increase of PLA ratio over the study period. The weight loss of pure PLA film was 2.58%, which was better than that of the control group (3.56%), but not as good as that of CS/PLA bilayer film. Notably, the weight loss of CS/PLA bilayer film (15:45) was the lowest, only 1.36% on the third day, which was close to the PE film group, indicating that it had the best preservation effect on banana pulp. Compared with

the control group, the packaging films could prevent moisture in packaged banana pulp from escaping into the external environment. The CS/PLA bilayer films showed excellent moisture-proof barrier, which could inhibit the diffusion of water vapor during storage, thus weakening the transpiration of banana.

**Table 2.** The Three-day Weight Loss Rate (%) of Banana Pulp Fresh-keeping with Various Films

Film Type	0 h	18 h	36 h	54 h	72 h
Pure CS film (60:0)	0.62±0.03	1.15±0.05	1.63±0.07	2.02±0.06	2.58±0.04
CS/PLA film (45:15)	0.62±0.01	0.94±0.04	1.42±0.02	1.87±0.04	2.13±0.05
CS/PLA film (30:30)	0.64±0.03	0.85±0.03	1.03±0.03	1.34±0.05	1.77±0.03
CS/PLA film (15:45)	0.63±0.02	0.79±0.02	0.91±0.05	1.08±0.01	1.36±0.01
Pure PLA film (0:60)	0.65±0.01	0.82±0.01	0.95±0.03	1.11±0.03	1.38±0.02
PE film	0.62±0.02	0.77±0.05	0.89±0.04	1.05±0.02	1.34±0.01
Control group	0.63±0.03	1.22±0.03	1.95±0.05	2.78±0.05	3.56±0.06

Furthermore, the appearance change of banana pulp during 3 days of storage was investigated (Fig. 6a). The color of banana pulp in the control group changed most obviously within three days and browned rapidly. The color of banana pulp preserved by PE film changed slowly, the third day appeared little brown. The color change rate of pure CS film group was faster than that of CS/PLA bilayer film group. As the proportion of PLA increased, the preservation effect of bilayer for banana pulp became better, and the best preservation effect of the bilayer film ratio was 15:45. The phenomenon was attributed to the compact structure of the bilayer films derived from the CS layer and PLA layer. The layer of PLA can block moisture, and the layer of CS can absorb banana pulp moisture. Therefore, the CS/PLA bilayer film had an obvious effect on delaying the oxidation and deterioration of banana pulp. In addition, pH value is an important indicator for evaluating the quality of banana pulp during storage. Figure 6b shows the changes in pH of banana pulp during 3-day storage. It can be seen that the pH displayed a slight downward trend during the storage period. After 3 days of storage, the pH of banana pulp in the CS/PLA bilayer film group (15:45) gradually increased from 5.43 to 4.98, which was higher than 4.52 in the control group and close to 5.01 in the PE film group. The results indicated that the CS/PLA bilayer film could prevent the change of pH in preserving bananas pulp, which was related to the transformation of pectin in banana into pectic acid and the increase of soluble solid content. The phenomenon was consistent with the changing trend of firmness analysis next. The firmness of fruit is usually a vital factor reflecting its texture characteristics and quality. As can be seen from Fig. 6c, with the extension of storage time, the firmness of banana pulp in all groups decreased to varying degrees. The firmness of banana pulp in the control group decreased most significantly, which dropped from 8.74 to 0.86 N/cm<sup>2</sup> at the end of third day. It was obviously lower than (1.73~2.81 N/cm<sup>2</sup>) in the CS/PLA film and slightly lower than 1.37 N/cm<sup>2</sup> in the pure CS film group. The results showed that the CS/PLA bilayer film could effectively slow down the softening of banana pulp caused by ethylene accumulation. Thus it was able to maintain the original texture characteristics.



**Fig. 6.** (a) Three-day appearance changes of banana pulp with different packaging films; (b) firmness and (c) pH value of banana pulp in different groups during storage time

#### CONCLUSIONS

- 1. In this study, corn starch (CS) and polylactic acid (PLA) were used as film-forming materials to prepare a bilayer film and applied for the preservation of banana pulp. Through analyzing the physical properties, mechanical properties, morphology, structure, and water vapor permeability, oxygen permeability of CS/PLA bilayer film, it was found that the comprehensive performance of the bilayer film could be effectively improved by adjusting the CS/PLA ratio.
- 2. When the ratio of CS/PLA was 15:45, the preservation effects of banana pulp packaged by the bilayer film were optimal. The weight loss rate of banana pulp reached to the

- lowest (1.36%), while the pH and firmness of banana pulp possessed the largest value, 4.98 and 2.81 N/cm<sup>2</sup>, respectively. These confirmed that the CS/PLA bilayer film had a good effect on banana pulp packaging preservation.
- 3. Corn starch has a wide range of sources and low cost, while polylactic acid has excellent mechanical properties and water resistance. The combination of these two biomass-based materials to prepare a bilayer film comprehensively utilizes the advantages of these two components, thus yielding the functional bilayer packaging film. It provides a research path for the application of biodegradable packaging materials in the field of fruit packaging.

#### ACKNOWLEDGMENTS

The research is supported by the State Key Laboratory of Advanced Papermaking and Paper-based Materials (202501), Science and Technology Planning Project of Guangzhou (2024A04J2301 and 2024E04J1231), Fundamental Research Funds from the Zhongkai University of Agriculture and Engineering (KA25YY17011), and the Special Project of Graduate Science and Technology Backyard from Zhongkai University of Agriculture and Engineering (KA25YY16748). The authors are grateful for this financial support.

#### REFERENCES CITED

- Almgren, K. M., Gamstedt, E. K., Berthold, F., and Lindstrom, M. (2009). "Moisture uptake and hygroexpansion of wood fiber composite materials with polylactide and polypropylene matrix materials," *Polymer Composites* 30(12), 1809-1816. https://doi.org/10.1002/pc.20753
- Chen, G. Q., and Patel, M. K. (2012). "Plastics derived from biological sources: Present and future: A technical and environmental review," *Chemical Reviews* 112(4), 2082-2099. https://doi.org/10.1021/cr200162d
- Chen, M. L., Yan, X. R., Cheng, M., Zhao, P. X., Wang, Y. R., Zhang, R. F., Wang, X. Y., Wang, J., and Chen, M. M. (2022). "Preparation, characterization and application of poly(lactic acid)/corn starch/eucalyptus leaf essential oil microencapsulated active bilayer degradable film," *International Journal of Biological Macromolecules* 195, 264-273. https://doi.org/10.1016/j.ijbiomac.2021.12.023
- Chu, X. Y. (2017). "Study on modification of polylactic and its application performance," *Chinese & Foreign Entrepreneurs* 2017(15), 81. https://doi.org/10.3969/j.issn.1000-8772.2017.15.058
- Debnath, B., Duarah, P., Haldar, D., and Purkait, M. K. (2022). "Improving the properties of corn starch films for application as packaging material *via* reinforcement with microcrystalline cellulose synthesized from elephant grass," *Food Packaging and Shelf Life* 34, article 100937. https://doi.org/10.1016/j.fpsl.2022.100937
- GB/T 1040.3 (2006). "Standard test methods for tensile properties of plastics," Standardization Administration of China, Beijing, China.

- González, A., and Igarzabal, C. I. A. (2013). "Soy protein–poly (lactic acid) bilayer films as biodegradable material for active food packaging," *Food Hydrocolloids* 33(2), 289-296. https://doi.org/10.1016/j.foodhyd.2013.03.010
- Goswami, S. R., Nair, S. S., Wang, S., and Yan, N. (2022). "Recent progress on starch maleate/polylactic acid blends for compostable food packaging applications," *ACS Sustainable Chemistry & Engineering* 10(1), 3-15. https://doi.org/10.1021/acssuschemeng.1c04940
- Han, N., Fan, J. L., Chen, N., and Chen, H. Q. (2022). "Effect of ball milling treatment on the structural, physicochemical and digestive properties of wheat starch, A- and B-type starch granules," *Journal of Cereal Science* 104, article 103439. https://doi.org/10.1016/j.jcs.2022.103439
- Hernández-García, E., Vargas, M., and Chiralt, A. (2022). "Active starch-polyester bilayer films with surface-incorporated ferulic acid," *Membranes* 12, 976. https://doi.org/10.3390/membranes12100976
- Jariyasakoolroj, P., and Chirachanchai, S. (2014). "Silane modified starch for compatible reactive blend with polylactic acid," *Carbohydrate Polymers* 106, 255-263. https://doi.org/10.1016/j.carbpol.2014.02.018
- Khouri, N. G., Bahu, J. O., Llamero, C. B., Severino, P., Concha, V. O. C., and Souto, E. B. (2024). "Polylactic acid (PLA): Properties, synthesis, and biomedical applications-a review of the literature," *Journal of Molecular Structure* 1309, article 138243. https://doi.org/10.1016/j.molstruc.2024.138243
- Kumari, S. V. G., Pakshirajan, K., and Pugazhenthi, G. (2022). "Recent advances and future prospects of cellulose, starch, chitosan, polylactic acid and polyhydroxyalkanoates for sustainable food packaging applications," *International Journal of Biological Macromolecules* 211, 163-182. https://doi.org/10.1016/j.ijbiomac.2022.08.203
- Li, Q. W., and Du, C. (2018). "Preparation and properties of nano-SiO<sub>2</sub> modified PVA/starch composite membrane," *Food Science and Technology* 43(03), 74-79. https://doi.org/10.13684/j.cnki.spkj.2018.03.015
- Liu, H. H., Adhikari, R., Guo, Q. P., and Adhikari, B. (2013). "Preparation and characterization of glycerol plasticized (high-amylose) starch—chitosan films," *Journal of Food Engineering* 116(2), 588-597. DOI: 10.1016/j. jfoodeng.2012.12.037
- Muller, J., González-Martínez, C., and Chiralt, A. (2017). "Combination of poly (lactic) acid and starch for biodegradable food packaging," *Materials* 10(8), article 952. https://doi.org/10.3390/ma10080952
- Sanyang, M. L., Sapuan, S. M., Jawaid, M., Ishak, M. R., Sahari, J. (2016). "Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (*Arenga pinnata*) starch for food packaging," *Journal of Food Science and Technology* 53(1), 326-36. https://doi.org/10.1007/s13197-015-2009-7
- Shi, Y. J., Zhang, H. J., Zhang, Z. H., Chi, Y. J., Lv, X. P., and Yin, T. T. (2017). "The effect of components of soy protein-based gelatin composite films on the mechanical properties," *Journal of Chinese Institute of Food Science and Technology* 17(04), 123-131. https://doi.org/10.16429/j.1009-7848.2017.04.016
- Tardy, B. L., Richardson, J. J., Greca, L.G., Guo, J. L., Bras, J. L., and Rojas, O. J. (2023). "Advancing bio-based materials for sustainable solutions to food packaging," *Nature Sustainability* 6(4), 360-367. https://doi.org/10.1038/s41893-022-01012-5
- Wu, J., Zhong, F., Li, Y., Shoemaker, C. F., and Xia, W. (2013). "Preparation and characterization of pullulan–chitosan and pullulan–carboxymethyl chitosan blended

- films," *Food Hydrocolloids* 30(1), 82-91. https://doi.org/10.1016/j.foodhyd.2012.04.002
- Xu, X. B., Yu, J., Yang, F. F., Li, Y. L., Qu, R. X., Liu, Z. Z., Liu, T., and Wang, Q. W. (2023). "Preparation of degradable chemically cross-linked polylactic acid films and its application on disposable straws," *International Journal of Biological Macromolecules* 251, article 126394. https://doi.org/10.1016/j.ijbiomac.2023.126394
- Yang, K. X., Zhang, H., Ma, B. M., and Wang, X. L. (2021). "Progress in natural polymer/PLA composite," *Plastics* 50(02), 93-98.
- Yang, Q. X. (1994). "Research on the production formula and technology of wood/plastic composites," *Acta Materiae Compositae Sinica* 1994(04), 9-13.
- Yuan, P., Pan, Z., Zhou, L., and Yu, H. (2010). "Application of deep-processed products of corn starch," *Cereal & Food Industry* 17(04), 23-25. https://doi.org/10.3969/j.issn.1672-5026.2010.04.00
- Yun, X. Y., Liu, L. Z., Hu, J., Sun, T., Zhang, J. T., and Dong, T. (2024). "Mechanical and gas permeability properties of poly(L-lactic acid)-based films and their application in fresh produce preservation-Review," *Packaging Technology and Science* 37(4), 293-317. https://doi.org/10.1002/pts.2796
- Zhou, X. M., Cheng, R., Wang, B., Zeng, J. S., Li, J. P., Kang, L., Cheng, Z., Gao, W. H., and Chen, K. F. (2021). "Biodegradable sandwich-architectured films derived from pea starch and polylactic acid with enhanced shelf-life for fruit preservation," *Carbohydrate Polymers* 251, article 117117. https://doi.org/10.1016/j.carbpol.2020.117117
- Zhou, X. M., Sheng, J., Liu, X., and Yang, R. D. (2018). "Preparation and characterization of pea starch /polylactic acid double layer film," *Biomass Chemical Engineering* 52(02), 18-22. https://doi.org/10.3969/j.issn.1673-5
- Zhou, X. M., Yang, R. D., Wang, B., and Chen, K. F. (2019). "Development and characterization of bilayer films based on pea starch/polylactic acid and use in the cherry tomatoes packaging," *Carbohydrate Polymers* 222, 114912-1-114912-7. https://doi.org/10.1016/j.carbpol.2019.05.042
- Zuo, Y. F., Gu, J. Y., Tan, H. Y., and Zhang, Y. H. (2013). "Effect of composite plasticizer types on plasticization properties of corn starch," *Journal of Functional Materials* 44(09), 1365-1368. https://doi.org/10.3969/j.issn.1001-9731.2013.09.035

Article submitted: July 15, 2025; Peer review completed: August 23, 2025; Revised version received: November 20, 2025; Accepted: November 30, 2025; Published: December 11, 2025.

DOI: 10.15376/biores.21.1.959-972