



Effect of thymol on physical properties, antimicrobial properties and fresh-keeping application of cherry tomato of starch/PBAT extrusion blowing films

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Abstract

In order to explore the effects of thymol on the antimicrobial activity, structure, physical properties and fresh-keeping application of starch/PBAT composite films, different contents of thymol (0, 1%, 3% and 5%) were used to prepare antimicrobial composite films by extrusion blow molding. The results indicated that Fourier transform infrared spectroscopy showed there was intermolecular hydrogen bonding force among starch/PBAT and thymol. The inhibition effect on *Botrytis cinerea* and the preservation effect of cherry tomato of the composite film were significantly improved, the hardness and nutritional characteristics of cherry tomato were maintained, and the fruit decay rate was reduced. The addition of thymol increased the water vapor permeability of the starch based composite films, but reduced the interaction between the composite film and water. Although thymol reduced the mechanical properties of the composite film, high concentration of thymol further improved the mechanical properties. In conclusion, the high concentration of thymol improved the comprehensive properties of starch composite film, and proved the application prospect of the film as active food packaging material.

Keywords: starch/PBAT composite film; thymol; antibacterial activity; cherry tomato preservation.

Practical Application: Provide a reference for the application of antimicrobial starch based degradable film in cherry tomato preservation.

1 Introduction

Traditional petroleum based plastic packaging causes problems such as lack of resources, environmental pollution and food safety (Cano et al., 2015; Piñeros-Hernandez et al., 2017; Tian et al., 2017). Starch is one of the most promising biopolymers to replace petroleum based plastics. Because it has the advantages of low price, good film-forming, good biodegradability and good regeneration. And starch based fully degradable composite film is also the frontier hotspot of international research (Gao et al., 2021; Cui et al., 2021; Santoso et al., 2022). However, the water vapor barrier and tensile properties of the film are poor, which seriously limits its application as packaging materials (Dilkes-Hoffman et al., 2018; Gómez-Aldapa et al., 2020; Song & Wang, 2021). In order to make the processing properties of starch based materials better, starch is usually blended with hydrophobic biodegradable polymers such as polyhydroxyalkanoates (PHA) (Sun et al., 2018), polylactic acid (PLA) (Pizzoli et al., 2016; Shirai et al., 2013), pol (ε-caprolactone) (PCL) (Mahieu et al., 2013) and poly (butylene succinate-co-butylene adipate) (PBSA) (Mahieu et al., 2017) to prepare composite films, which is an effective method to produce more suitable thin film materials. Compared with other materials, poly (butylene adipate-co-terephthalate) (PBAT) is similar to low-density polyethylene (LDPE) due to its processing conditions and mechanical properties, so starch/PBAT composite films has attracted much attention due to its high performance and low cost (Seligra et al., 2016;

Olivato et al., 2017). Until now, the blend film of starch and PBAT had been studied, and the composite film with excellent properties had been successfully prepared (Nunes et al., 2018; Zhai et al., 2020).

Active packaging is a new packaging method that added antibacterial agent, antioxidant, deoxidizer and ethylene absorbent to the film matrix. Its purpose is to prolong the shelf life of food and maintain or improve the characteristics of packaged food (Azadbakht et al., 2018; Lian et al., 2022). Plant antibacterial agents are used to improve the antibacterial activity of films because of their safety and strong antibacterial activity. However, the preparation of antibacterial starch/PBAT composite blown film and its application in postharvest storage of fruits and vegetables have not been reported. And extrusion blow molding is more conducive to the practical application of antibacterial film. In this study, thymol was used as antibacterial agent to solve the problems of loss of antibacterial agent and poor antibacterial effect in the process of preparing starch based composite film by extrusion blow molding. Because thymol is solid at room temperature, it is suitable to be used as the active agent in the film blowing process (Petchwattana & Naknaen, 2015). Thymol is the main component extracted from oregano, thyme and other herbs, which is rich in phenolic compounds (Jafri et al., 2019). It was usually regarded as an important antibacterial agent and showed strong and broad antibacterial activity against microorganisms

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in vitro and food system in previous studies (Boonruang et al., 2017; Qin et al., 2016; Suwanamornlert et al., 2018).

Cherry tomato is popular because of its rich nutrition and juicy taste. However, the postharvest life of this fruit is relatively short, which is limited by postharvest water loss, disease, ripening and aging (Ruiz-Cisneros et al., 2022; Panjai et al., 2017), reducing the acceptance and quality of fruit after storage. *Botrytis cinerea* is the most common microbial infectious disease of cherry tomato (Wang et al., 2010). At present, the main method to control the disease was still the use of chemical synthetic fungicides, but the continuous use of a large number of chemicals not only made the fruit resistant, but also posed a potential threat to environmental safety and human health (Jiao et al., 2018). Therefore, it is particularly important to take safe and effective biological preservation measures. Biodegradable films and edible coatings based on biomacromolecules were designed to reduce water loss, oxygen and other gas migration by promoting semi permeable barriers, which helped to extend the shelf life of fruits (Fakhouri et al., 2007; Rodsamran & Sothornvit, 2018). In addition, the presence of antimicrobial components in the polymer matrix was conducive to inhibiting the growth of pathogens, and played an active role in fruit preservation (Sganzerla et al., 2020). Therefore, proper functional packaging is beneficial to extend the shelf life of perishable fruits. Thymol could effectively inhibit the growth of *Botrytis cinerea* during tomato storage (Kong et al., 2019; Robledo et al., 2018), but it was worth exploring whether the effect of adding thymol to film material was better.

In this study, starch and PBAT were used as film-forming substrate, and different concentrations of thymol were added to prepare antibacterial packaging films. The effects of thymol on the physical properties and structure of the film were studied, the antibacterial activity of packaging materials and the preservation effect of cherry tomato during storage was mainly investigated.

2 Materials and methods

2.1 Materials

The substrate hydroxypropyl distarch phosphate (HPDSP) used for composite film was provided by Puluoxing Starch Co., Ltd. (Hangzhou, China). The PBAT (BASF-C1200) was obtained from Daman International Co., Ltd. (Shanghai, China). Thymol was purchased from Kabuda Chemical Co., Ltd. (Wuhan, China). Cherry tomato (Variety: Qianxi) were purchased from local supermarket in Jinan city of Shandong province. Glycerol, citric acid, NaCl, $Mg(NO_3)_2$ and methanol were obtained from Kaitong Chemical Reagent Co., Ltd. (Tianjin, China).

2.2 Preparation of antimicrobial film by extrusion blow molding

Starch and PBAT were compounded in the ratio of 1:1 and the total mass was 5 kg. Firstly, the starch, PBAT, nano-clay (2%, w/w total starch and PBAT) and thymol (0, 1%, 3% and 5%, w/w) were poured into the SHR10L high-speed mixer (Lianjiang Machinery Co., Ltd., Zhangjiagang, China), then citric acid (2%, w/w) and 30% (w/w starch) glycerol were added, and mixed at 800 rpm for 5 min until the mixture was

uniform. Using laboratory twin screw extruder (Lianjiang Machinery Co., Ltd., Zhangjiagang, China) for granulation, the temperature of each section was 110/120/125/125/125 °C, the head temperature was 120 °C, the screw speed was 100-200 rpm, and the cutter speed was 230-280 r/min. The extruded strands were air-cooled and cut into particles. Finally, the composite film was prepared by SCM-25 film machine (Lianjiang Machinery Co., Ltd., Zhangjiagang, China). From the inlet to the outlet, the temperature of each section was 135/150/150/145/130 °C, the screw speed of the main engine was 30-300 rpm, and the traction speed was 300 rpm. The prepared composite films was placed at 25 °C and 53% RH for at least 48 h before measuring the indexes of the films.

Four formulations were studied: pure starch and PBAT films (SP), starch and PBAT composite films with different thymol concentrations (1%, 3% and 5%, w/w) were named as SP-T1, SP-T3 and SP-T5, respectively.

2.3 Physical properties of antimicrobial composite films

Physical properties of composite films including thickness, opacity, color, indicators of interaction with water and water vapor permeability (WVP) were determined according to the following method.

Several points were randomly selected with digital vernier caliper (Shanghai Meinaite Hardware Tools Co., Ltd., Shanghai, China) to measure the film thickness.

The color of the composite film was measured with HP-200 precision colorimeter (Shenzhen Hanpu Testing Instrument Co., Ltd., Shenzhen, China), and recorded L^* , a^* and b^* .

The opacity was measured according to Park & Zhao's method (Park & Zhao, 2004) and expressed by the absorbance measured by UV-1800 spectrophotometer (Shanghai MAPADA Instrument Co., Ltd., Shanghai, China) at 600 nm wavelength. The calculation formula was as follows (Equation 1):

$$O = \frac{Abs_{600}}{L} \quad (1)$$

Where O and L were the opacity and thickness (mm) of the film sample, respectively.

According to the method used by Homez-Jara et al. (2018), the indicators of the interaction between the composite film and water include water content (WC), swelling degree (SD) and water solubility (WS) were measured. The specific experimental steps were as follows: weighed the composite film (2 cm × 2 cm) to obtain M_1 , and dried in an oven at 105 °C for 24 h to obtain M_2 . Then placed the dry film in a beaker, added 30 mL distilled water and placed it at 25 °C for 24 h. Took out the film, dried the water with filter paper and weighed to obtain M_3 . Finally, put the film back into the oven for 24 h and weighed it to get the weight M_4 . The WC, SD, and WS were calculated according to the following formula (Equation 2):

$$WC(\%) = \left(\frac{M1 - M2}{M1} \right) \times 100$$

$$SD(\%) = \left(\frac{M3 - M2}{M2} \right) \times 100 \quad (2)$$

$$WS(\%) = \left(\frac{M2 - M4}{M2} \right) \times 100$$

Water vapor permeability (WVP) of composite film was determined according to the method of Peng et al. (2013). The film was covered on a weighing dish containing anhydrous calcium chloride, and placed the weighing dish in a constant temperature and humidity box with a relative humidity of 75% at 25 °C and weighed it every 24 h until the weight change was close to 0.001 g, so as to obtain the weight of water passing through the composite film within a certain period of time. The WVP of the film was calculated as follows (Equation 3):

$$WVP = \frac{(m_1 - m_0)L}{At\Delta P} \quad (3)$$

Where ($m_1 - m_0$) was the weight difference of the dish, g; L was the thickness of the film, m; A was the exposed area of the film, m²; t was the time, s; ΔP was the water vapor pressure on both sides of the film, Pa.

2.4 Mechanical properties of composite films

The mechanical properties of the film, including tensile strength (TS) and elongation at break (EAB), were measured based on the method described in ASTM D882-12 (American Society for Testing and Materials, 2012). Before the test, the film samples were balanced at 53% relative humidity and 25 °C for at least 24 h. After the samples (15 mm × 150 mm) were taken out, used immediately the XLW automatic tensile testing machine (Jinan Labthink Electromechanical Technology Co., Ltd., Jinan, Shandong) for determination. Set the initial distance to 100 mm, pulled the film apart at the test speed of 10 mm/min until it broke, and repeated each group at least 6 times.

2.5 Inhibitory effect of film on the plaque diameter of *Botrytis cinerea* in vitro

The inhibitory effect of composite film on *Botrytis cinerea* was determined by inhibition zone method. Firstly, used an Oxford cup with a diameter of 8mm to take the bacterial cake on the activated gray mold culture medium, then placed the

bacterial cake in the center of the new PDA culture medium, and pasted the film with a diameter of 6 mm on the top of the culture dish. After 48 h of incubation at 28 °C and 80% relative humidity, the plaque diameter was measured and repeated it three times.

2.6 Scanning Electron Microscope (SEM)

The surface morphology and cross section of the films were observed by scanning electron microscope (SEM). The film samples were dried in a desiccator containing silica gel for at least 2 weeks. Before observation, the film was frozen cracked with liquid nitrogen and cut into 1 mm × 6 mm rectangle, adhered to the metal plate with double-sided adhesive tape. Then, the surface and cross section of the film were observed by a SUPRATM55 scanning electron microscope (Zeiss AG, Germany) at an accelerating voltage of 3 KV and 1000 times magnification.

2.7 Attenuated total reflection-Fourier transformed infrared spectroscopy (ATR-FTIR)

Before the test, the film was dried in a dryer for 2 weeks and cut into 20 mm × 20 mm square. The total reflection mode of Nicolet 710 FTIR instrument (Brimrose, America) was used for infrared scanning to observe the changes of heavy chemical structure and groups of the composite films. The spectral resolution was set to 4 cm⁻¹ and the infrared spectrum curve of the composite film was obtained by scanning 32 times in the range of 4000-550 cm⁻¹.

2.8 Preservation application effect of composite film on cherry tomato

Cherry tomatoes treatment

The composite film had good heat sealing property and could be prepared into packaging bag. The changes of physiological indexes of tomato fruits were evaluated to verify the application performance of the composite film. Cherry tomatoes with the same maturity, uniform size, no mechanical damage and diseases and insect pests were washed with distilled water and then dried. The composite film was made into a 20 cm × 25 cm bag, and 300 g cherry tomato was put into the bag (Figure 1). Each treatment included 3 replicates. All samples were kept in cold

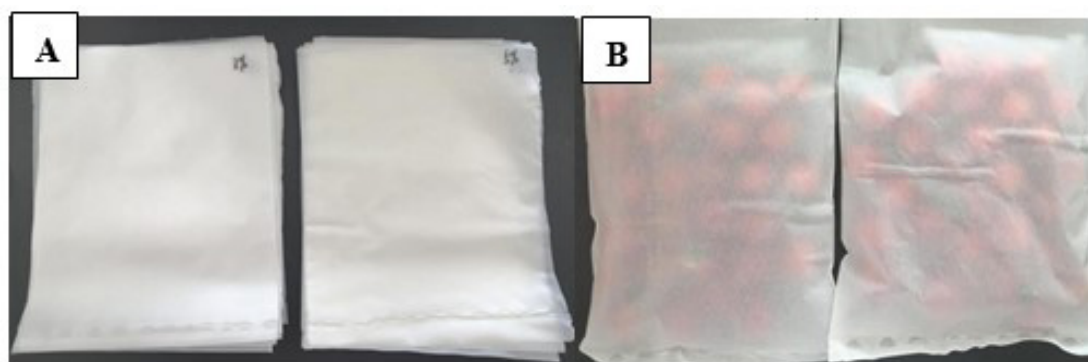


Figure 1. Fresh keeping bag made of starch/PBAT composite films (A); Tomatoes packed in bags (B).

storage (0 °C), and all packaged and unpackaged (Blank control) samples were evaluated after 0, 7, 14, 21 and 28 days of storage.

Weight loss rate

The weight loss of tomato was measured by weighing method and calculated by the following formula (Equation 4):

$$\text{Weight loss rate (\%)} = \frac{m_0 - m_1}{m_0} \times 100\% \quad (4)$$

Where m_0 was the initial sample weight, and m_1 was the sample weight after the time interval.

Firmness of fruit

The hardness of tomato peel was measured by texture analyzer (Beijing wechat Chaoji Instrument Technology Co., Ltd., Beijing, China). The probe with diameter of 2 mm was selected. The initial test speed, test speed and return speed were 1 mm/s, the insertion depth was 1 cm and the trigger force was 5.0 g. Six fruits were randomly selected for each test.

Decay rate

The number of rotten fruits was recorded every 7 d, and the rotten rate was calculated during storage (Equation 5).

$$\text{Decay rate (\%)} = \frac{NIF}{INF} \times 100\% \quad (5)$$

Among them, NIF was the number of infected tomatoes, INF was the number of initial tomatoes.

Soluble solids content

The soluble solids of cherry tomato were determined by digital refractometer.

2.9 Statistical analysis

Excel was used to process and analyze the data, and ANOVA by means of the SPSS software was used for variance analysis.

3 Result and discussion

3.1 Physical properties of composite films

Table 1 showed the thickness, color and opacity of the composite film. The thickness of SP film was 0.063 mm, and the addition of thymol significantly increased the thickness of the film, this was consistent with Reddy & Rhim (2014). Among them, the thickness of film with 1% and 3% thymol were the largest, which were 0.092 mm and 0.093 mm, respectively, while the thickness of SP-T5 film decreased. The increase of film thickness is mainly related to the correlation between starch, PBAT and thymol (Nordin et al., 2020).

The L^* , a^* and b^* values of the SP film were 98.36, -0.49 and -0.18, respectively shown in Table 1. Thymol had no significant effect on L^* and a^* of the film, but increased the b^* value (yellow value) to make the film yellow deeper. The different yellowness of the composite film might be related to the color of thymol itself (Lian et al., 2020). The opacity of SP film was 19.29, the addition of thymol increased the transparency of the composite film.

Table 2 contained the change of Water content (WC), Swelling degree (SD), Water solubility (WS) and Water Vapour Permeability (WVP) of composite films. The water content of SP film was 95.08%, the addition of thymol reduced the moisture content of the composite films, indicating that thymol reduced the hydrophilicity of the composite films. Among them, the moisture content of SP-T1 composite film was the lowest, decreased by 19.05% compared with SP film, and increased with the increase of thymol concentration. The interaction between thymol and the film matrix destroyed the hydrogen bond interaction between the initial PBAT and the starch, resulting in the decrease of the water content of the composite film (Aydin & Ilberg, 2016).

The swelling degree and water solubility of SP composite films were the highest, while thymol reduced the swelling degree and water solubility of the composite film, and SP-T1 film was the lowest. And the change trend of these three indicators is consistent. The swelling degree and water solubility of the film were related to the hydrophilicity of the film components. Thymol itself is a hydrophobic substance, which lead to the decrease of

Table 1. Thickness, color and opacity of starch/PBAT antimicrobial composite film.

Films	Thickness/mm	L^*	a^*	b^*	Opacity (Abs600/mm)
SP	0.063 ± 0.003 ^a	98.36 ± 0.44 ^a	-0.49 ± 0.11 ^a	-0.18 ± 0.14 ^c	19.29 ± 1.67 ^a
SP-T1	0.092 ± 0.002 ^c	98.06 ± 0.00 ^a	-0.46 ± 0.03 ^a	0.45 ± 0.03 ^a	13.55 ± 0.10 ^{cd}
SP-T3	0.093 ± 0.001 ^c	98.10 ± 0.10 ^a	-0.49 ± 0.02 ^a	0.33 ± 0.18 ^{ab}	13.37 ± 0.50 ^d
SP-T5	0.082 ± 0.003 ^b	98.23 ± 0.28 ^a	-0.52 ± 0.05 ^a	0.47 ± 0.08 ^a	15.99 ± 0.79 ^b

Note: The lowercase letters in each column represent significant differences at 0.05 level.

Table 2. The water content, swelling degree, water solubility, and water vapor permeability of starch and PBAT composite film.

Films	Water content /%	Swelling degree /%	Water solubility /%	Water Vapour Permeability/10 ⁻¹¹ g/(m·s·pa)
SP	95.08 ± 1.71 ^a	96.03 ± 1.12 ^a	93.12 ± 93.12 ^a	7.72 ± 0.59 ^b
SP-T1	76.97 ± 0.85 ^c	79.60 ± 1.31 ^c	65.58 ± 6.04 ^c	19.81 ± 2.84 ^a
SP-T3	85.27 ± 3.51 ^b	86.47 ± 3.19 ^b	75.55 ± 4.58 ^b	19.80 ± 1.09 ^a
SP-T5	87.45 ± 4.61 ^b	89.92 ± 2.69 ^b	79.33 ± 7.18 ^b	10.94 ± 2.24 ^b

the SD and WS of composite films (Nordin et al., 2020). Thymol is added to the composite film matrix to form a network structure through strong interaction through hydrogen bond, which reduce the affinity of the composite film to water, so as to reduce the solubility and expansibility. Kavooosi et al. (2013) also obtained the same results that hydrophilic compounds increased the solubility of the film, while hydrophobic compounds decreased the solubility.

For water vapor permeability, the WVP of SP film was 7.72×10^{-11} g/(m·s·pa). The composite films containing 1% and 3% thymol had the highest moisture permeability, and there was no significant difference between the two groups, which were 19.81×10^{-11} g/(m·s·pa) and 19.80×10^{-11} g/(m·s·pa), respectively. On the contrary, the WVP of SP-T5 films decreased, and there was no significant difference with the control film. The addition of thymol reduce the interaction between starch and PBAT, resulting in a loose film structure, which improve the WVP of the film (Nordin et al., 2020). The osmotic diffusion coefficient depend on the fluidity of polymer segments and the free volume of matrix, and the fluidity of polymer segments is affected by the crystallinity of polymer (George & Thomas, 2001).

3.2 Tensile properties

It could be seen from Figure 2 that thymol had a certain effect on the tensile strength (TS) and elongation at break (EAB) of starch/PBAT antibacterial film. The TS and EAB of SP composite films were 3.87 MPa and 55.1%, respectively. And the mechanical

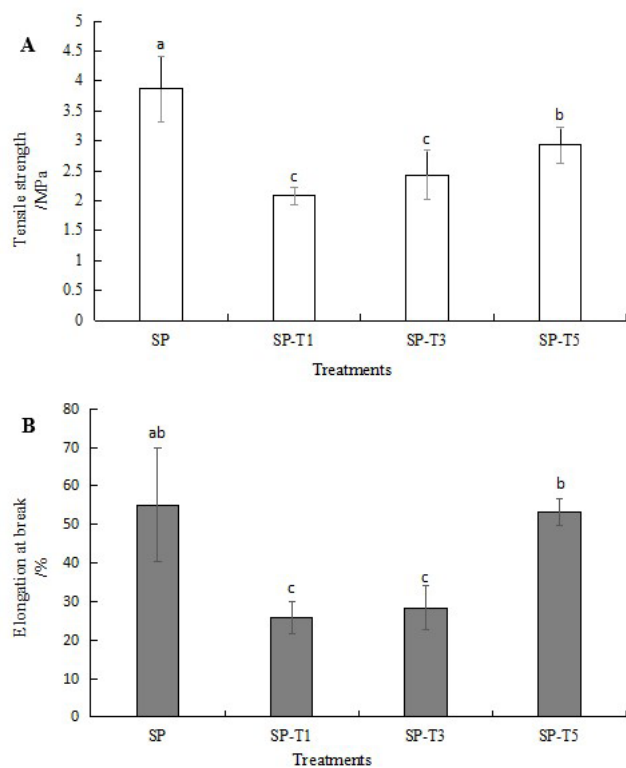


Figure 2. Tensile properties of starch and PBAT composite film including tensile strength (A) and elongation at break (B). Note: The lowercase letters in each column represent significant differences at 0.05 level.

properties were reduced by adding thymol, the SP-T5 films were better than SP-T1 and SP-T3 films, and the TS and EAB were 2.93 MPa and 53.2%, respectively. Starch, PBAT and thymol were mixed to form the composite films. However, the hydrophilicity and hydrophobicity of the composite film are different, which result in obvious separation between components and voids in the matrix, which reduce the mechanical properties of the composite film (Wei et al., 2015; Pouyamanesh et al., 2022). Nordin et al. (2020) explained that the incorporation of thymol as a lipid agent led to the heterogeneity of the film matrix, which might hinder the interaction between polymer chains. The cross section structure of the films was observed by scanning electron microscope, the results showed that the higher the concentration of thymol was, the denser the film structure was and the better the mechanical properties were.

The significant decrease of elongation at break indicated that thymol reduced the flexibility of the composite film, the fluidity of the molecular chain and the intermolecular force. The change of mechanical properties of the film is closely related to the structure and intermolecular force of the film, the addition of thymol may form an immiscible phase at a certain point in the starch matrix, leading to the separation of starch chains, thus reducing the elasticity of the film (Othman et al., 2021). However, Davoodi et al. (2017) found that adding thymol to potato starch film with polysorbate as emulsifier could reduce TS and increase EAB. They attributed this phenomenon to the new bond or the interaction between starch and polysorbate thymol micelles replacing the interaction between the original polymer chains, increasing the fluidity and sliding effect of starch chain segments, thus increasing the flexibility of the film. High concentration of thymol also increased the elongation at break of starch/PBAT composite film, which might be due to the plasticization of glycerol and thymol changing the strong intramolecular bonding of starch chain.

3.3 Inhibitory effect of composite film on the plaque diameter of *Botrytis cinerea* in vitro

As shown in Figure 3 and Table 3, starch/PBAT composite film had obvious inhibitory effect on the growth of *Botrytis cinerea*. The bacterial colony edge pigmentation, mycelium atrophy and aging, and the plaque diameter of each treatment was significantly smaller than that of the blank control and SP film. The presence of thymol in the starch/PBAT composite film significantly improved its inhibitory effect on *Botrytis cinerea*. Among them, the plaque diameter of the composite film added with 1% and 3% thymol were 12.16 mm and 14.30 mm, and the antibacterial difference was not significant. The antibacterial activity of SP-T5 film was the best, and the antibacterial rate reached 83.49%. Many studies have shown that thymol had strong and extensive antibacterial activity against bacteria and fungi in vitro and food system (Zhou et al., 2019; Suwanamornlert et al., 2018). High concentration of thymol enhance the interaction between starch and PBAT, delay the release of active components, and improve the antifungal activity of the composite film.

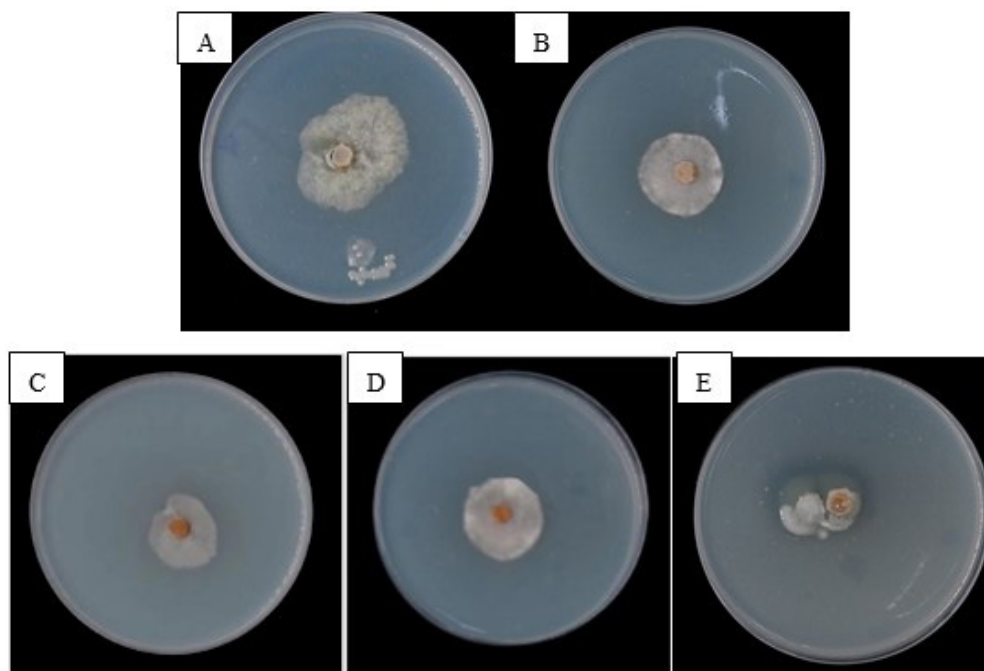


Figure 3. Inhibitory effect of starch/PBAT films on the plaque diameter of *Botrytis cinerea*. Blank control (A), SP film (B), SP-T1 film (C), SP-T3 film (D) and SP-T5 film (E).

Table 3. The plaque diameter of gray mold growing for 48 h.

Films	48 h Plaque Diameter/mm
Blank control	23.20 ± 2.40 ^a
SP	20.59 ± 1.15 ^a
SP-T1	12.16 ± 2.36 ^b
SP-T3	14.30 ± 1.45 ^b
SP-T5	3.83 ± 1.75 ^c

3.4 Microstructure of composite films

In order to explore the effect of different contents of thymol on the microstructure of starch/PBAT composite films, the surface and cross-section images of the four composite films were shown in Figure 4. The structure of starch/PBAT composite film without thymol was compact (Figure 4A-a), the addition of thymol led to the rough surface and obvious texture of the film (Figure 4B-b to 4D-d).

The surface and cross section images of thymol and starch/PBAT showed good compatibility in different treatments. The surface roughness of SP-T1 and SP-T3 films increased with the increase of thymol content. However, 5% thymol significantly improved the surface structure of the films, showing a smooth, dense and uniform appearance. The addition of thymol resulted in the appearance of particles and pores in the cross section of SP-T5 film, and the small particles disappeared in SP-T5 film, resulting in a more compact structure. These results were of great significance for the mechanical properties and barrier properties of starch/PBAT composite films. As mentioned earlier, the difference of hydrophilicity between thymol and starch lead to the obvious phase separation between the components, the formation of immiscible phase at a certain point in the starch

matrix, and the appearance of pores in the film matrix (Wei et al., 2015). Therefore, the change of the structure of the composite film is attributed to the interaction between the matrix and thymol.

3.5 Chemical structure of composite films

FTIR analysis could effectively study the interaction between molecules in reactive extrusion process. It could be seen from Figure 5 that the control group and the starch/PBAT composite film treatment group with different thymol content had similar spectral characteristics in the range of 550 to 4000 cm^{-1} , which might be due to the high content of starch on the surface of the film masking the effect of glycerol and/or thymol on the composite film (Nordin et al., 2020).

The obvious peaks at 1017 cm^{-1} , 1713 cm^{-1} and 2946 cm^{-1} were attributed to the C-O tensile vibration in the C-O-C bond, the ester carbonyl extension of ester group (C=O) and the stretching vibration of C-H methyl, Edhirej et al. (2017) obtained similar results. The C-O tensile vibration in C-O-C bond mainly appears in glycosidic bond (Olivato et al., 2012; Garcia et al., 2014), and the ester carbonyl extension of ester group (C = O) initially appears in PBAT structure (Wei et al., 2015). In addition, the wide peak at 3300 cm^{-1} is due to the presence of a large number of hydroxyl groups (-OH) in the starch chain. PBAT destroy the intermolecular and intramolecular hydrogen bonds between starch particles and exposes more hydroxyl groups, which is conducive to the movement of starch molecular chain and provided the possibility for the formation of new hydrogen bonds and esterification between starch and PBAT molecules (Aydn & Ilberg, 2016).

With the addition of thymol, the peak strength of the composite film decreased (Garcia et al., 2011). Compared with

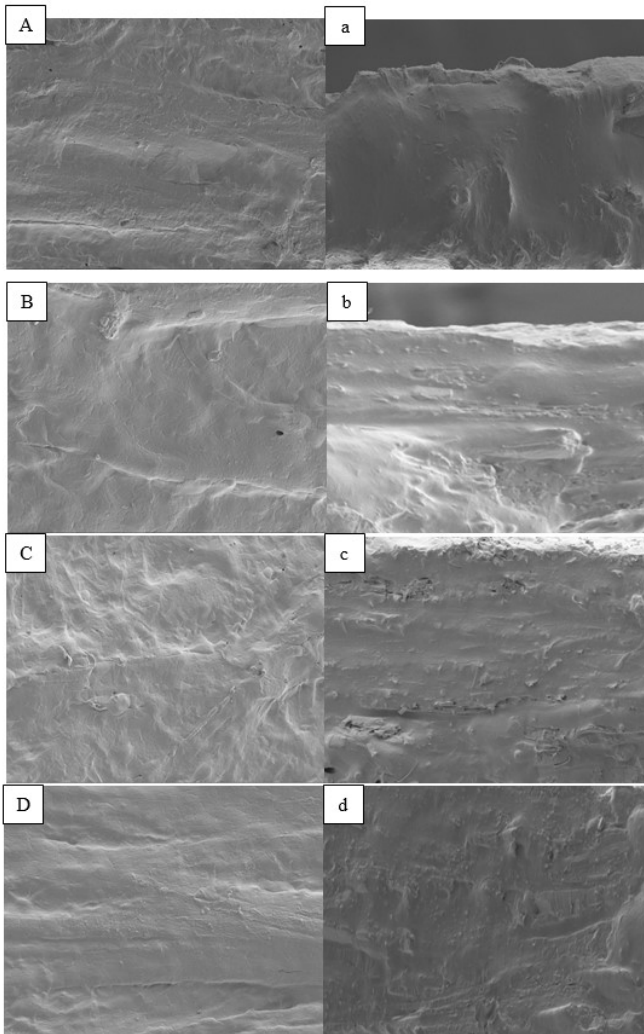


Figure 4. SEM images of starch and PBAT composite films. SP film surface (A) and cross section (a), SP-T1 film surface (B) and cross section (b), SP-T3 film surface (C) and cross section (c), and SP-T5 film surface (D) and cross section (d).

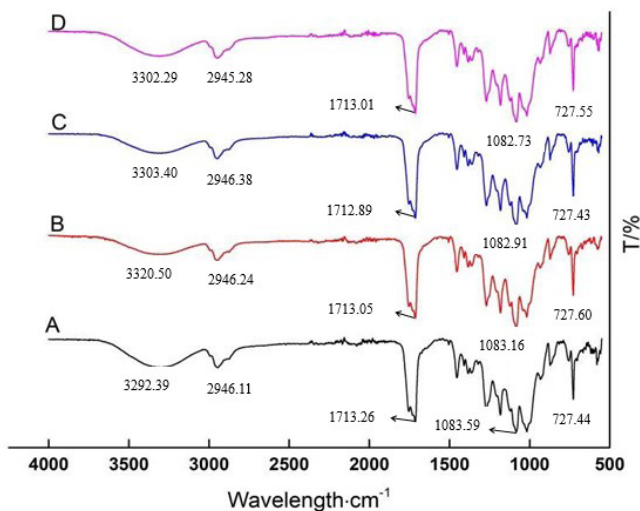


Figure 5. FTIR spectra image of starch/PBAT antimicrobial composite films. SP(A), SP-T1(B), SP-T3(C) and SP-T5(D).

the SP film, the tensile vibration of O-H group was reduced due to the hydrophobic effect of thymol and the interaction between thymol functional groups and starch and glycerol molecules, resulting in the lower peak strength of thymol composite film at 1713 cm^{-1} . Another point was that the band intensity at 1083 cm^{-1} was lower than that of the control sample (SP). According to the research of Shi et al. (2007), this reduction showed that citric acid had high acid hydrolysis in the glycosidic bond of starch, thymol formed hydrogen bond with hydroxyl, and inhibited the reaction between citric acid and starch molecules (Wu et al., 2009). The change of peak amplitude caused by the addition of thymol to the film might be caused by the rearrangement and conformational change of film structure caused by the interaction between thymol and other film components (Campos et al., 2019), which was consistent with the study of Nordin et al. (2020).

3.6 Preservation application effect of composite film on cherry tomato

The changes of firmness, weight loss rate, decay rate and soluble solid content of cherry tomato during storage for 28 d were shown in Figure 6. With the extension of storage time, the hardness and soluble solid content of cherry tomato decreased, while the weight loss rate and decay rate increased. This result was consistent with the research results of Sun et al. (2021) and others on the preservation effect of lavender essential oil gelatin film on cherry tomato.

As shown in Figure 6A, the hardness gradually decreased during postharvest storage due to the degradation of cell structure, cell wall components and intracellular substances in the fruit (Rao et al., 2011). The peel hardness of Tomato in the blank control group decreased from 462.60 g to 418.02 g, which decreased the fastest, and the fruit wrapped with composite film decreased slowly. Compared with other treatments, the hardness of tomato packaged with 5% thymol composite film had no significant change after 28 d of storage.

Figure 6B showed the weight loss of cherry tomato packed in antimicrobial composite film during storage. The weight loss rate of fruit treated with SP-T1 film and SP-T5 film was the lowest, but the difference was not significant. Ethylene gas promoted the respiration of cherry tomato, increased the evaporation of water, and led to weight loss, wilting and degradation (Dhital et al., 2018).

Figure 6C showed the change of decay rate of cherry tomato during storage. At 28 d of storage, the decay rate of fruits packed with SP-T5 film decreased by 16.07% compared with the blank control. The decay rate was mainly related to the content of antibacterial agent in the composite film. The higher the content was, the stronger the antibacterial activity was, resulting in the lower decay rate of fruit.

The change of soluble solid content of cherry tomato during storage was shown in Figure 6D. The soluble solid content of fruit was 7.10% before storage. During the whole storage period, the soluble solid content of fruit first decreased slowly and decreased sharply. This might be because tomato metabolizes solid matter for respiration, which led to the gradual decrease of soluble

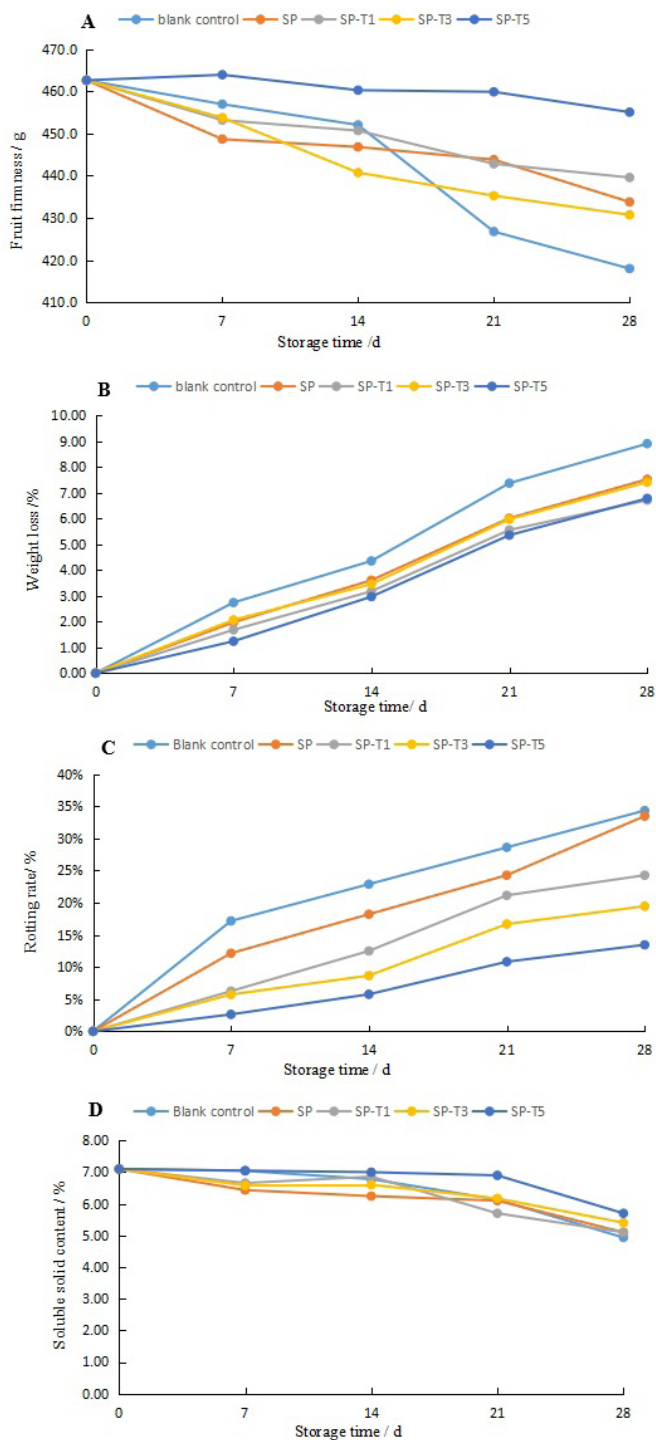


Figure 6. Effect of composite films on the firmness (A), weight loss rate (B), rotting rate (C) and soluble solid content (D) of cherry tomato during storage.

solid content during storage, the respiration of tomato packed with compound film was inhibited (Boonsiriwit et al., 2020).

In general, the use of starch/PBAT antimicrobial film was conducive to maintaining the firmness and nutrients of the fruit, reducing the decay of the fruit, so as to maintain the freshness of cherry tomato. Among them, SP-T5 film had the best preservation effect on cherry tomato.

4 Conclusion

The soft and thermoplastic starch/PBAT based antibacterial composite film was prepared by extrusion blow molding. Thymol improved the water resistance of starch based composite film, and had good antimicrobial activity and fresh-keeping effect on cherry tomato, but it had a certain adverse effect on the tensile properties of the composite film. The composite film with 5% thymol was the best choice for the preparation of active starch based degradable composite film because of its lower moisture permeability (compared with other treatments), higher mechanical properties and antibacterial activity and better fresh-keeping effect. This study provided a reference to develop active packaging and the application of starch based degradable film in food preservation, and further explored the potential of packaging material.

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Reference

- American Society for Testing and Materials – ASTM (2012). *D882-12: standard test method for tensile properties of thin plastic sheeting* (Annual Book of ASTM Standards). Philadelphia: ASTM.
- Aydın, A. A., & Ilberg, V. (2016). Effect of different polyol-based plasticizers on thermal properties of polyvinyl alcohol: starch blends films. *Carbohydrate Polymers*, 136, 441-448. <http://dx.doi.org/10.1016/j.carbpol.2015.08.093>. PMID:26572374.
- Azadbakht, E., Maghsoudlou, Y., Khomiri, M., & Kashiri, M. (2018). Development and structural characterization of chitosan films containing Eucalyptus globulus essential oil: potential as an antimicrobial carrier for packaging of sliced sausage. *Food Packaging and Shelf Life*, 17, 65-72. <http://dx.doi.org/10.1016/j.fpsl.2018.03.007>.
- Boonruang, K., Kerddonfag, N., Chinsirikul, W., Mitcham, E. J., & Chonhenchob, V. (2017). Antifungal effect of poly(lactic acid) films containing thymol and R(-)-carvone against anthracnose pathogens isolated from avocado and citrus. *Food Control*, 78, 85-93. <http://dx.doi.org/10.1016/j.foodcont.2017.02.032>.
- Boonsiriwit, A., Xiao, Y., Joung, J., Kim, M., Singh, S., & Lee, Y. S. (2020). Alkaline halloysite nanotubes/low density polyethylene nanocomposite films with increased ethylene absorption capacity: applications in cherry tomato packaging. *Food Packaging and Shelf Life*, 25, 100533. <http://dx.doi.org/10.1016/j.fpsl.2020.100533>.
- Campos, S. S., Oliveira, A., Moreira, T. F. M., Silva, T. B. V., Silva, M. V., Pinto, J. A., Bilck, A. P., Gonçalves, O. H., Fernandes, I. P., Barreiro, M.-F., Yamashita, F., Valderrama, P., Shirai, M. A., & Leimann, F. V. (2019). Tpcs/pbat blown extruded films added with curcumin as a technological approach for active packaging materials. *Food Packaging and Shelf Life*, 22, 100424. <http://dx.doi.org/10.1016/j.fpsl.2019.100424>.
- Cano, A., Fortunati, E., Cháfer, M., Kenny, J. M., Chiralt, A., & González-Martínez, C. (2015). Properties and ageing behaviour of pea starch

- films as affected by blend with poly(vinyl alcohol). *Food Hydrocolloids*, 48, 84-93. <http://dx.doi.org/10.1016/j.foodhyd.2015.01.008>.
- Cui, Y., Cheng, M., Han, M., Zhang, R., & Wang, X. (2021). Characterization and release kinetics study of potato starch nanocomposite films containing mesoporous nano-silica incorporated with Thyme essential oil. *International Journal of Biological Macromolecules*, 184, 566-573. <http://dx.doi.org/10.1016/j.ijbiomac.2021.06.134>. PMID:34174300.
- Davoodi, M., Kavooosi, G., & Shakeri, R. (2017). Preparation and characterization of potato starch-thymol dispersion and film as potential antioxidant and antibacterial materials. *International Journal of Biological Macromolecules*, 104(Pt A), 173-179. <http://dx.doi.org/10.1016/j.ijbiomac.2017.05.145>. PMID:28579465.
- Dhital, R., Mora, N. B., Watson, D. G., Kohli, P., & Choudhary, R. (2018). Efficacy of limonene nano coatings on post-harvest shelf life of strawberries. *LWT*, 97, 124-134. <http://dx.doi.org/10.1016/j.lwt.2018.06.038>.
- Dilkies-Hoffman, L. S., Pratt, S., Lant, P. A., Levett, I., & Laycock, B. (2018). Polyhydroxyalkanoate coatings restrict moisture uptake and associated loss of barrier properties of thermoplastic starch films. *Journal of Applied Polymer Science*, 135(25), 46379. <http://dx.doi.org/10.1002/app.46379>.
- Ehdirej, A., Sapuan, S. M., Jawaid, M., & Zahari, N. I. (2017). Cassava/sugar palm fiber reinforced cassava starch hybrid composites: physical, thermal and structural properties. *International Journal of Biological Macromolecules*, 101, 75-83. <http://dx.doi.org/10.1016/j.ijbiomac.2017.03.045>. PMID:28288881.
- Fakhouri, F. M., Fontes, L. C. B., Gonçalves, P. V. M., Milanez, C. R., Steel, C. J., & Collares-Queiroz, F. P. (2007). Filmes e coberturas comestíveis compostas à base de amidos nativos e gelatina na conservação e aceitação sensorial de uvas Crimson. *Food Science and Technology*, 27(2), 369-375. <http://dx.doi.org/10.1590/S0101-20612007000200027>.
- Gao, W., Zhu, J., Kang, X., Wang, B., Liu, P., Cui, B., & El-Aty, A. M. A. (2021). Development and characterization of starch films prepared by extrusion blowing: the synergistic plasticizing effect of water and glycerol. *LWT*, 148, 111820. <http://dx.doi.org/10.1016/j.lwt.2021.111820>.
- Garcia, P. S., Grossmann, M. V. E., Shirai, M. A., Lazaretti, M. M., Yamashita, F., Muller, C. M. O., & Mali, S. (2014). Improving action of citric acid as compatibiliser in starch/polyester blown films. *Industrial Crops and Products*, 52, 305-312. <http://dx.doi.org/10.1016/j.indcrop.2013.11.001>.
- Garcia, P. S., Grossmann, M. V. E., Yamashita, F., Mali, S., Dall'Antonia, L. H., & Barreto, W. J. (2011). Citric acid as multifunctional agent in blowing films of starch/PBAT. *Química Nova*, 34(9), 1507-1510. <http://dx.doi.org/10.1590/S0100-40422011000900005>.
- George, S. C., & Thomas, S. (2001). Transport phenomena through polymeric systems. *Progress in Polymer Science*, 26(6), 985-1017. [http://dx.doi.org/10.1016/S0079-6700\(00\)00036-8](http://dx.doi.org/10.1016/S0079-6700(00)00036-8).
- Gómez-Aldapa, C. A., Velazquez, G., Gutierrez, M. C., Rangel-Vargas, E., Castro-Rosas, J., & Aguirre-Loredo, R. Y. (2020). Effect of polyvinyl alcohol on the physicochemical properties of biodegradable starch films. *Materials Chemistry and Physics*, 239, 122027. <http://dx.doi.org/10.1016/j.matchemphys.2019.122027>.
- Homez-Jara, A., Daza, L. D., Aguirre, D. M., Munoz, J. A., Solanilla, J. F., & Vaquiro, H. A. (2018). Characterization of chitosan edible films obtained with various polymer concentrations and drying temperatures. *International Journal of Biological Macromolecules*, 113, 1233-1240. <http://dx.doi.org/10.1016/j.ijbiomac.2018.03.057>. PMID:29548921.
- Jafri, H., Ansari, F. A., & Ahmad, I. (2019). Prospects of essential oils in controlling pathogenic biofilm. In M. S. A. Khan, I. Ahmad & D. Chattopadhyay (Eds.), *New look to phytomedicine advancements in herbal products as novel drug leads* (pp. 203-236). London: Elsevier. <http://dx.doi.org/10.1016/B978-0-12-814619-4.00009-4>.
- Jiao, W., Li, X., Wang, X., Cao, J., & Jiang, W. (2018). Chlorogenic acid induces resistance against penicillium expansum in peach fruit by activating the salicylic acid signaling pathway. *Food Chemistry*, 260(15), 274-282. <http://dx.doi.org/10.1016/j.foodchem.2018.04.010>. PMID:29699670.
- Kavooosi, G., Dadfar, S. M. M., & Purfard, A. M. (2013). Mechanical, physical, antioxidant, and antimicrobial properties of gelatin films incorporated with thymol for potential use as nano wound dressing. *Journal of Food Science*, 78(2), E244-E250. <http://dx.doi.org/10.1111/1750-3841.12015>. PMID:23317304.
- Kong, J., Zhang, Y., Ju, J., Xie, Y., Guo, Y., Cheng, Y., Qian, H., Quek, S. Y., & Yao, W. (2019). Antifungal effects of thymol and salicylic acid on cell membrane and mitochondria of rhizopus stolonifer and their application in postharvest preservation of tomatoes. *Food Chemistry*, 285, 380-388. <http://dx.doi.org/10.1016/j.foodchem.2019.01.099>. PMID:30797360.
- Lian, H., Shi, J., Zhang, X., & Peng, Y. (2020). Effect of the added polysaccharide on the release of thyme essential oil and structure properties of chitosan based film. *Food Packaging and Shelf Life*, 23, 100467. <http://dx.doi.org/10.1016/j.fpsl.2020.100467>.
- Lian, H., Shi, J., Zhang, X., Peng, Y., Meng, W., & Pei, L. (2022). Effects of different kinds of polysaccharides on the properties and inhibition of *Monilinia fructicola* of the thyme essential oil-chitosan based composite films. *Food Science and Technology*, 42, e57420. <http://dx.doi.org/10.1590/fst.57420>.
- Mahieu, A., Terrie, C., & Leblanc, N. (2017). Role of ascorbic acid and iron in mechanical and oxygen absorption properties of starch and polycaprolactone multilayer film. *Packaging Research*, 2(1), 1-11. <http://dx.doi.org/10.1515/pacres-2017-0001>.
- Mahieu, A., Terrié, C., Agoulon, A., Leblanc, N., & Youssef, B. (2013). Thermoplastic starch and poly(ϵ -caprolactone) blends: morphology and mechanical properties as a function of relative humidity. *Journal of Polymer Research*, 20(9), 229. <http://dx.doi.org/10.1007/s10965-013-0229-y>.
- Nordin, N., Othman, S. H., Rashid, S. A., & Basha, R. K. (2020). Effects of glycerol and thymol on physical, mechanical, and thermal properties of corn starch films. *Food Hydrocolloids*, 106, 105884. <http://dx.doi.org/10.1016/j.foodhyd.2020.105884>.
- Nunes, M. A. B. S., Marinho, V. A. D., Falcão, G. A. M., Canedo, E. L., Bardi, M. A. G., & Carvalho, L. H. (2018). Rheological, mechanical and morphological properties of poly(butylene adipate-co-terephthalate)/thermoplastic starch blends and its biocomposite with babassu mesocarp. *Polymer Testing*, 70, 281-288. <http://dx.doi.org/10.1016/j.polymertesting.2018.07.009>.
- Olivato, J. B., Grossmann, M. V. E., Bilck, A. P., & Yamashita, F. (2012). Effect of organic acids as additives on the performance of thermoplastic starch/polyester blown films. *Carbohydrate Polymers*, 90(1), 159-164. <http://dx.doi.org/10.1016/j.carbpol.2012.05.009>. PMID:24751025.
- Olivato, J. B., Marini, J., Yamashita, F., Pollet, E., Grossmann, M. V. E., & Avérous, L. (2017). Sepiolite as a promising nanoclay for nano-biocomposites based on starch and biodegradable polyester. *Materials Science and Engineering C*, 70(Pt 1), 296-302. <http://dx.doi.org/10.1016/j.msec.2016.08.077>. PMID:27770894.
- Othman, S. H., Nordin, N., Azman, N., Tawakkal, I., & Basha, R. K. (2021). Effects of nanocellulose fiber and thymol on mechanical, thermal, and barrier properties of corn starch films. *International*

- Journal of Biological Macromolecules*, 183(3), 1352-1361. <http://dx.doi.org/10.1016/j.ijbiomac.2021.05.082>. PMID:34000310.
- Panjai, L., Noga, G., Fiebig, A., & Hunsche, M. (2017). Effects of continuous red light and short daily UV exposure during postharvest on carotenoid concentration and antioxidant capacity in stored tomatoes. *Scientia Horticulturae*, 226, 97-103. <http://dx.doi.org/10.1016/j.scienta.2017.08.035>.
- Park, S. I., & Zhao, Y. (2004). Incorporation of a high concentration of mineral or vitamin into chitosan-based films. *Journal of Agricultural and Food Chemistry*, 52(7), 1933-1939. <http://dx.doi.org/10.1021/jf034612p>. PMID:15053532.
- Peng, Y., Wu, Y., & Li, Y. (2013). Development of tea extracts and chitosan composite films for active packaging materials. *International Journal of Biological Macromolecules*, 59, 282-289. <http://dx.doi.org/10.1016/j.ijbiomac.2013.04.019>. PMID:23603075.
- Petchwattana, N., & Naknaen, P. (2015). Utilization of thymol as an antimicrobial agent for biodegradable poly(butylene succinate). *Materials Chemistry and Physics*, 163, 369-375. <http://dx.doi.org/10.1016/j.matchemphys.2015.07.052>.
- Piñeros-Hernandez, D., Medina-Jaramillo, C., López-Córdoba, A., & Goyanes, S. (2017). Edible cassava starch films carrying rosemary antioxidant extracts for potential use as active food packaging. *Food Hydrocolloids*, 63, 488-495. <http://dx.doi.org/10.1016/j.foodhyd.2016.09.034>.
- Pizzoli, A. P. O., Marchiore, N. G., Souza, S. J., Santos, P. D. F., Gonçalves, O. H., Yamashita, F., Bracht, L., Shirai, M. A., & Leimann, F. V. (2016). Antimicrobial PLA/TPS/gelatin sheets with enzymatically crosslinked surface containing silver nanoparticles. *Journal of Applied Polymer Science*, 133(8), 43039-43047.
- Pouyamanesh, M., Ahari, H., Anvar, A. A., & Karim, G. (2022). Packaging based on ag-low density polyethylene for shelf-life extension of pasteurized and traditional butters at refrigerated temperature. *Food Science and Technology*, 42, e67020. <http://dx.doi.org/10.1590/fst.67020>.
- Qin, Y., Zhuang, Y., Wu, Y., & Li, L. (2016). Quality evaluation of hot peppers stored in biodegradable poly(lactic acid)-based active packaging. *Scientia Horticulturae*, 202, 1-8. <http://dx.doi.org/10.1016/j.scienta.2016.02.003>.
- Rao, T. R., Gol, N. B., & Shah, K. K. (2011). Effect of postharvest treatments and storage temperatures on the quality and shelf life of sweet pepper (*Capsicum annum* L.). *Scientia Horticulturae*, 132, 18-26. <http://dx.doi.org/10.1016/j.scienta.2011.09.032>.
- Reddy, J. P., & Rhim, J. W. (2014). Characterization of bionanocomposite films prepared with agar and paper-mulberry pulp nanocellulose. *Carbohydrate Polymers*, 110, 480-488. <http://dx.doi.org/10.1016/j.carbpol.2014.04.056>. PMID:24906782.
- Robledo, N., Vera, P., Lopez, L., Yazdani-Pedram, M., Tapia, C., & Abugoch, L. (2018). Thymol nanoemulsions incorporated in quinoa protein/chitosan edible films; antifungal effect in cherry tomatoes. *Food Chemistry*, 246(25), 211-219. <http://dx.doi.org/10.1016/j.foodchem.2017.11.032>. PMID:29291841.
- Rodsamran, P., & Sothornvit, R. (2018). Carboxymethyl cellulose from renewable rice stubble incorporated with Thai rice grass extract as a bioactive packaging film for green tea. *Journal of Food Processing and Preservation*, 42(9), e13762. <http://dx.doi.org/10.1111/jfpp.13762>.
- Ruiz-Cisneros, M. F., Ornelas-Paz, J. J., Olivas-Orozco, G. I., Acosta-Muñiz, C. H., Salas-Marina, M. Á., Molina-Corral, F. J., Berlanga-Reyes, D. I., Fernández-Pavía, S. P., Cambero-Campos, O. J., & Rios-Velasco, C. (2022). Effect of rhizosphere inoculation with bacillus strains and phytopathogens on the contents of volatiles and human health-related compounds in tomato fruits. *Food Science and Technology*, 42, e51120. <http://dx.doi.org/10.1590/fst.51120>.
- Santoso, B., Sinaga, T., Priyanto, G., & Hermanto (2022). Effect of natural active compound addition on mechanical and functional properties of canna starch based edible film. *Food Science and Technology*, 42, e51020. <http://dx.doi.org/10.1590/fst.51020>.
- Selgra, P. G., Moura, L. E., Famá, L., Druzian, J. I., & Goyanes, S. (2016). Influence of incorporation of starch nanoparticles in PBAT/TPS composite films. *Polymer International*, 65(8), 938-945. <http://dx.doi.org/10.1002/pi.5127>.
- Sganzerla, W. G., Rosa, G. B., Ferreira, A. L. A., Rosa, C. G., Beling, P. C., Xavier, L. O., Hansen, C. M., Ferrareze, J. P., Nunes, M. R., Barreto, P. L. M., & Veeck, A. P. L. (2020). Bioactive food packaging based on starch, citric pectin and functionalized with *Acca sellowiana* waste by-product: characterization and application in the postharvest conservation of apple. *International Journal of Biological Macromolecules*, 147, 295-303. <http://dx.doi.org/10.1016/j.ijbiomac.2020.01.074>. PMID:31926234.
- Shi, R., Zhang, Z., Liu, Q., Han, Y., Zhang, L., Chen, D., & Tian, W. (2007). Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending. *Carbohydrate Polymers*, 69(4), 748-755. <http://dx.doi.org/10.1016/j.carbpol.2007.02.010>.
- Shirai, M. A., Grossmann, M. V. E., Mali, S., Yamashita, F., Garcia, P. S., & Müller, C. M. (2013). Development of biodegradable flexible films of starch and poly (lactic acid) plasticized with adipate or citrate esters. *Carbohydrate Polymers*, 92(1), 19-22. <http://dx.doi.org/10.1016/j.carbpol.2012.09.038>. PMID:23218260.
- Song, X. Y., & Wang, Y. Q. (2021). Development and characterization of edible bilayer films based on iron yam-pea starch blend and corn zein. *Food Science and Technology*, 41(Suppl. 2), 684-694. <http://dx.doi.org/10.1590/fst.29820>.
- Sun, S. L., Liu, P. F., Ji, N., Hou, H. X., & Dong, H. Z. (2018). Effects of various crosslinking agents on the physicochemical properties of starch/PHA composite films produced by extrusion blowing. *Food Hydrocolloids*, 77, 964-975. <http://dx.doi.org/10.1016/j.foodhyd.2017.11.046>.
- Sun, X., Wang, J., Zhang, H., Dong, M., Li, L., Jia, P., Bu, T., Wang, X., & Wang, L. (2021). Development of functional gelatin-based composite films incorporating oil-in-water lavender essential oil nano-emulsions: effects on physicochemical properties and cherry tomatoes preservation. *LWT*, 142, 110987. <http://dx.doi.org/10.1016/j.lwt.2021.110987>.
- Suwanamornlert, P., Sangchote, S., Chinsirikul, W., Sane, A., & Chonhenchob, V. (2018). Antifungal activity of plant-derived compounds and their synergism against major postharvest pathogens of longan fruit in vitro. *International Journal of Food Microbiology*, 271, 8-14. <http://dx.doi.org/10.1016/j.ijfoodmicro.2018.02.009>. PMID:29459244.
- Tian, H., Wang, K., Liu, D., Yan, J., Xiang, A., & Rajulu, A. V. (2017). Enhanced mechanical and thermal properties of poly (vinyl alcohol)/corn starch blends by nanoclay intercalation. *International Journal of Biological Macromolecules*, 101, 314-320. <http://dx.doi.org/10.1016/j.ijbiomac.2017.03.111>. PMID:28341175.
- Wang, Y., Yu, T., Xia, J., Yu, D., Wang, J., & Zheng, X. (2010). Biocontrol of postharvest gray mold of cherry tomatoes with the marine yeast *Rhodospiridium paludigenum*. *Biological Control*, 53(2), 178-182. <http://dx.doi.org/10.1016/j.biocontrol.2010.01.002>.
- Wei, D., Wang, H., Xiao, H., Zheng, A., & Yang, Y. (2015). Morphology and mechanical properties of poly(butylene adipate-co-terephthalate)/potato starch blends in the presence of synthesized reactive compatibilizer or modified poly(butylene adipate-co-terephthalate).

- Carbohydrate Polymers*, 123, 275-282. <http://dx.doi.org/10.1016/j.carbpol.2015.01.058>. PMID:25843859.
- Wu, Y., Chen, Z., Li, X., & Li, M. (2009). Effect of tea polyphenols on the retrogradation of rice starch. *Food Research International*, 42(2), 221-225. <http://dx.doi.org/10.1016/j.foodres.2008.11.001>.
- Zhai, X., Wang, W., Zhang, H., Dai, Y., Dong, H., & Hou, H. (2020). Effects of high starch content on the physicochemical properties of starch/pbat nanocomposite films prepared by extrusion blowing. *Carbohydrate Polymers*, 239, 116231. <http://dx.doi.org/10.1016/j.carbpol.2020.116231>. PMID:32414453.
- Zhou, W., Wang, Z., Mo, H., Zhao, Y., Li, H., Zhang, H., Hu, L., & Zhou, X. (2019). Thymol mediates bactericidal activity against *Staphylococcus aureus* by targeting an aldo-keto reductase and consequent depletion of NADPH. *Journal of Agricultural and Food Chemistry*, 67(30), 8382-8392. <http://dx.doi.org/10.1021/acs.jafc.9b03517>. PMID:31271032.