



## Effects of different antioxidants on the properties of pectin-chitosan composite films

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**Abstract:** The objective of this study is to prepare a pectin chitosan composite film with antioxidant activity by using citrus pectin and chitosan as raw materials, microcrystalline cellulose and glycerol as plasticizers, and adding four natural extracts in phenols: Catechin powder (CatePD), blueberry powder (BluePD), grape seed proanthocyanidins powder (GrapePD), and citrus flavonoids powder (Citrus flavonoids powder). The results showed that there was no significant difference in the thickness of the composite film with added antioxidants within the range of 0.6%, while the tensile strength and elongation at break showed an increasing trend. The optimal amount of catechin was 0.9%, with a maximum tensile strength of 0.57 MPa and a fracture elongation of 29.15%. For BluePD, GrapePD, and CitrusPD, tensile strength and elongation rate reached their maximum values (0.664 MPa and 39.848%, 0.94 MPa and 29.97%, 1.36 MPa and 44.05%, respectively) at concentrations of 1.2%. Compared with the control film, the pectin chitosan composite film with added antioxidant substances showed a lower water vapor transmission rate, and the barrier properties of composite films with CatePD and BluePD against water vapor were superior to those of the CitrusPD and GrapePD. Additionally, the pectin-chitosan composite films with added antioxidants were superior to the control group in terms of radical-scavenging capability, and the most effective radical-scavenging capability was optimized at a mass fraction of 0.6%. In summary, the addition of antioxidant substances could improve the performance of the pectin-chitosan composite films, providing a reference for environmentally friendly and green packaging production in the food industry.

**Keywords:** citrus pectin, chitosan, composite film, antioxidation, package

### 1. Introduction:

An ideal alternative to reducing the environmental impact of plastic food packages involves the use of biomass polymers to produce degradable food packaging materials (Shi, J. H. 2023). The physicochemical and functional properties of food packaging materials can vary depending on the materials from which they were polymerized. Common biomass polymers include chitosan, alginate, starch, gelatin, cellulose, pectin, soya protein, glucomannan, and gum. Among biomass polymers, polysaccharides offer the advantages of abundance, cost-effectiveness, and high stability. Polysaccharide-based coatings and films can help protect food during storage by serving as barriers inhibiting microbial growth, limiting oxidative rancidity, minimizing moisture loss, delaying gas diffusion, blocking light, and resisting mechanical shock. Due to their non-toxic, biocompatible, and biodegradable properties, pectin and chitosan are commonly used natural polymers for preparing edible films.

Food and Agriculture Organization (FAO) World Citrus Production Report, 2016, revealed that the inedible components of food processing, such as citrus peel waste (CPW), account for 50% of the weight of fresh fruits, generating at least 10 million tons of peel waste annually worldwide (Jeong et al., 2021). This waste is an excellent raw material source for extracting pectin and other valuable compounds. By doing so, waste can be transformed into a valuable resource, minimizing the loss of materials. Pectin exhibits excellent gel-formation

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ability, biodegradability, and biocompatibility, making it an effective biomass polymer for producing edible films (Mellinas et al., 2020). Moreover, pectin films demonstrate good light transmission, heat resistance, and flexibility (Roy & Rhim, 2021). However, they have low mechanical performance, poor water barrier properties, and limited functionality (Nesic et al., 2022). One solution to the limitations of a single polymer is to mix two or more biomass polymers to form a composite film or to add other filler materials, such as nano-fillers, cross-linking agents, and natural compounds, to biomass polymers to enhance their physical and functional properties (Rukmanikrishnan et al., 2020). Consequently, pectin is often blended with biomass polymers such as starch, sodium alginate, chitosan, and gelatin to improve various properties of pectin films.

Chitosan, a derivative of chitin, has wide applications as it exhibits excellent film-forming, biocompatibility, biodegradability, and bacteriostatic properties (Liu et al., 2020; Salehi et al., 2016; Wang et al., 2021). However, chitosan films provide insufficient protection against oxidative deterioration, limiting their use in various food applications (Siripatrawan et al., 2016; Ubonrat et al., 2016). Meanwhile, the physical properties and bioactivity of chitosan-based composite films are reported to be enhanced by adding natural components such as polysaccharides, polyphenols, or essential oils (Dinika et al., 2020). This was demonstrated by Rambabu (Rambabu et al., 2019), who found that uniformly distributing mango leaf extracts on the pores of the chitosan substrate can reduce its porosity and oxygen permeability. Glycerol has good biocompatibility and contains many hydroxyl groups, which reportedly enhance the intermolecular compatibility between glycerol and chitosan (Bharti et al., 2023). These interactions reduce the crystallinity and brittleness of chitosan membranes, improving their toughness. Consequently, glycerol can be used as a plasticizer to improve the properties of chitosan films (Ghasemlou et al., 2011; Cao et al., 2018; Go & Song, 2020).

With the advancement of technology, the food industry increasingly expects food packaging materials to deliver enhanced performance. Antioxidation-active packaging materials hold broad applications as they prevent food oxidation and spoilage during storage by enabling low migration and sustained release of antioxidative components in packaging materials. In the past, synthetic antioxidants, such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), were added to packaging materials to inhibit oxidation. However, their use has become limited due to concerns over the potential toxicity of synthetic antioxidants to humans (Carocho et al., 2013). Therefore, natural plant extracts (e.g., anthocyanidin (CUR), polyphenols, essential oils, flavonoids, and catechin) have attracted significant attention in active food packaging due to their excellent biodegradability, edibility, and biosafety. Furthermore, films developed from pectin, sodium carboxymethyl cellulose, and thyme essential oil demonstrate excellent mechanical performance and bacteriostatic activity (Lin et al., 2020). Natural antioxidants, such as tea polyphenols, polyphenol extracts from plants, and vitamin E, have been added to chitosan films to form edible antioxidative films (Liu, 2017; Muhammad et al., 2021; Priyadarshi et al., 2022; Sabaghi et al., 2015; Suppakul et al., 2016). These films are used in the packaging of foods with high oil content, such as fats, walnuts, cashews, peanuts, and almonds. The addition of natural antioxidants in edible films significantly slowed down the oxidation rate of fats and oils, reduced the rancidity of fats and oils, minimized the loss of unsaturated fatty acids, phenolics, and other nutrients in the food products, and extended the shelf life of the products. Quercetin is a flavonol compound with multiple biological activities and is the most effective antioxidant among flavonoids. The double bonds and hydroxyl groups in it can effectively scavenge DPPH and ABTS free radicals and reduce Fe<sup>3+</sup> to Fe<sup>2+</sup> (MASEK et al., 2018). Quercetin was added by Giteru et al. (2017) to sorghum soluble protein edible films for chicken preservation. The results suggested that the introduction of quercetin inhibited microbial proliferation and lipid oxidation in the chicken during storage while slowing the rate of color change in meat.

The incorporation of antioxidant substances into pectin chitosan films is a method to expand the films' antioxidant functional properties. Grape seeds, blueberry pomace, and citrus pomace are the by-products of food processing. Grape seeds and blueberry pomace are rich in anthocyanins, and citrus pomace is rich in flavonoids. Catechins, possessing good antioxidant activity, are derived from tea leaves and belong to the tea polyphenol family. These substances have been used in various fiber membranes and edible films because of their good antibacterial and antioxidant effects (Zou et al., 2016; Shen et al., 2011; Zhang, 2022; Ruan, 2020). Meanwhile, the extraction and utilization of functional active substances from these agricultural by-products can promote the efficient use of resources. The addition of antioxidants can lead to a rearrangement of the original molecular structure of composite films, creating a different network structure that may impact the mechanical and barrier performance of edible films. It is, therefore, essential to carefully select the type and



concentration of natural antioxidants to be used in the films. This study prepared biomass-based films using chitosan and pectin, with the addition of microcrystalline cellulose and glycerol acting as a cross-linking agent and plasticizer to enhance the mechanical performance of the films, including their elasticity, brittleness, and fragility. The antioxidative edible films were created by combining catechin powder (CatePD), blueberry powder (BluePD), grape seed proanthocyanidins powder (GrapePD), and citrus flavonoids powder (CitrusPD) in varying ratios within the composite film solution. By evaluating the effects of antioxidant incorporation on the mechanical properties, water vapor transmission, and antioxidant properties of pectin chitosan films, the aim is to develop biodegradable films with antioxidant function using citrus pectin and chitosan.

## 2. Materials and Methods

### 2.1 Materials and Reagents

Pectin, chitosan (medium viscosity), microcrystalline cellulose, 1,1-diphenyl-2-picrylhydrazyl (DPPH), 1,1-diphenyl-2-picrylhydrazyl (ABTS), and phenanthroline solution were obtained from Shanghai Macklin Biochemical Co., Ltd. Hubei Yucheng E-commerce Co., Ltd supplied corn starch. Acetic acid was procured from Tianjin Fuyu Fine Chemical Co., Ltd. Glycerol was obtained from Tianjin Bodi Chemical Co., Ltd. CatePD, BluePD, GrapePD, and CitrusPD were procured from Xi'an Shouhe Biotechnology Co., Ltd.

### 2.2 Preparation of Pectin-Chitosan Composite Films

The composite films were prepared following the method of Wu et al. (2017) with minor modifications. At 25°C, 40 mL (10 g/L) of chitosan solution (The chitosan is dissolved in 2% acetic acid solution) was added dropwise with stirring to 100 mL (8 g/L) of pectin solution in a beaker to obtain a mixed pectin-chitosan solution. Next, 20 mL (10 g/L) of microcrystalline cellulose solution was slowly added, followed by heating the solution to 50°C with magnetic stirring for 30 min. Gelatinized starch solution (50 mL (20 g/L)) and glycerol solution (10 mL of (20%)) were added to the above system and stirred at 80°C for 24 h in a frequency-controlled double-layer glass reactor. The above composite was poured into petri dishes ( $\varnothing$  9.5 cm), approximately 20 mL/dish, incubated for 24 h, and finally placed in an electric blast drying oven at 40°C to dry. The pectin-chitosan composite film was obtained once the surface of the composite was dry and free of moisture, and was used as the control group.

### 2.3 Effects of Antioxidants on Pectin-Chitosan Composite Film

The prepared composite film solutions were mixed with CatePD, BluePD, GrapePD, and CitrusPD in different proportions (0.3%, 0.6%, 0.9% and 1.2%) per the above method of preparing pectin-chitosan mixtures. The obtained antioxidants and pectin-chitosan mixed solutions with different ratios were placed in a digital thermostatic water bath and stirred for 3 h using an electric mixer. Next, the mixture (20 mL) was measured and poured into a petri dish, spread out, and incubated for 24 h. The antioxidative pectin-chitosan composite films were obtained after drying in the electric blast drying oven at 40°C for 2 h.

### 2.4. Basic Properties of Films

#### 2.4.1 Determination of Mechanical Performance

The mechanical performance of the composite film was evaluated using the method of Wu et al. (2017). A texture analyzer was used to determine the tensile strength and elongation rate of the pectin-chitosan composite film. A piece of flat, dry, homogeneous, and flawless composite film was cut into 5 cm  $\times$  1.5 cm strips. Each sample was measured thrice, and the average value was recorded.

Membrane thickness: the membrane thickness of each membrane was determined by averaging three random measurements using a digital outside micrometer.

#### 2.4.2 Measurement of Water Vapor Transmittance of the Composite Films

The WVT is a critical index of the films and was determined via the GB/T 1037-2021 cup method (Liu, 2010) with minor modifications. Anhydrous CaCl<sub>2</sub> was dried and cooled in an oven at 200°C. Three reagent bottles with identical size, shape, and mass were selected, and one-third of the thickness of the anhydrous CaCl<sub>2</sub> was placed in each reagent bottle. After applying Vaseline evenly to the reagent bottles, the composite film was

tightly affixed to the bottle surface and sealed. Next, the total mass of the reagent bottles was weighed. The films were kept at 25°C and 70% relative humidity, and the mass change of the films was recorded until the mass increment was relatively stable.

The WVT [g/m<sup>2</sup> × 24 h] was calculated using the following Equation (1):

$$(1) \text{ WVT} = \frac{24 \times \Delta m}{t \times A}$$

Where t is time during which Δm occurred [h]; Δm is the weight change in time t, g; A is the testing cup area [m<sup>2</sup>]

### 2.4.3 Characterization by FT-IR

Fourier transform infrared spectroscopy spectra in attenuated total reflectance mode (FTIR-ATR) were collected in transmission mode in the range of 4000–400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. Then scanned and detected by FT-IR with a scanning range of 4000 ~ 400 cm<sup>-1</sup> and a resolution of 4 cm<sup>-1</sup> and 64 scans per composite film sample. (Li et al., 2019)

## 2.5 Determination of Antioxidation Performance of Composite Film

### 2.5.1 DPPH · Clearance Capability

DPPH clearance capability was determined following the method of Guo et al. (2020) with minor modifications. First, PBS buffer (pH = 7.3) was prepared. After weighing DPPH, 100 mL of anhydrous ethanol was added to make an anhydrous ethanol solution of DPPH (0.1 mmol/L). Next, PBS (pH = 7.3, 4 mL) and 0.1 mmol/L DPPH anhydrous ethanol (4 mL) were added to a 10 mL centrifuge tube, along with the composite film strips (2 cm × 20 cm), and shaken at 25°C for 30 min. The absorption of the solution was measured at 517 nm. Each sample was tested in triplicate, and the average value was recorded.

The clearance rate of DPPH (K1, %) was calculated as follows:

$$(2) \text{ K1} = \frac{A_0 - A_1}{A_0} \times 100\%$$

Where A<sub>0</sub> represented the absorbance of the DPPH solution, and A<sub>1</sub> represented the absorbance after clearance by the composite film.

### 2.5.2 ·OH Clearance Capability

Crystal violet solution (1 mL of 0.4 mmol/L) was added to a 10 mL conical flask, followed by the sequential addition of PBS solution (pH = 7.3, 5 mL), FeSO<sub>4</sub> solution (1 mL of 1 mmol/L), 6% H<sub>2</sub>O<sub>2</sub> solution (1 mL), and composite film strips (20 mm × 20 mm) into the conical flask. After shaking the conical flask at 25°C for 30 min till it fully reacted, the absorbance was measured at the maximum absorption wavelength in the UV-Vis range. Each sample was tested in triplicate, and the results were averaged. The blank samples were prepared using distilled water as the control group.

The clearance rate of ·OH (K2, %) was calculated as follows:

$$(3) \text{ K2} = \left(1 - \frac{A - A_1}{A_2}\right) \times 100\%$$

Where A represented the absorbance of the ·OH solution after clearance by the composite film, A<sub>1</sub> represented the absorbance of the composite film, and A<sub>2</sub> represented the absorbance of distilled water.

## 3. Results and Analysis

### 3.1 Effects of antioxidants on the mechanical performance of composite films

Thickness is a crucial parameter for calculating the mechanical, optical, and water barrier properties of films (Chaichi et al., 2019). As shown in Table 1, the thickness of composite films with antioxidants was greater than that of the control group. However, this difference was only significant when the antioxidant content was greater than 0.6%. This data also suggested that antioxidant levels below 0.6% have minimal effect on pectin-chitosan composite films, indicating that the antioxidants are evenly distributed within the pectin substrate. Film thickness has also been reported to be highly correlated with the antioxidant powder content in the film-forming solution (Mendes et al., 2019). The increase in film thickness, despite adding the same amount of powder to the film substrate, might be attributed to variations in phenolic content. Thus, the increase in film



thickness is largely due to the added antioxidants, which raise the mass fraction of solids within the film substrate (Wu et al., 2019).

Both the tensile strength as well as the elongation rate of composite films were enhanced after the addition of CatePD, BluePD, GrapePD, and CitrusPD. When the mass fraction of catechin was 0.9%, the composite film achieved the maximum tensile strength (0.57 MPa) and an elongation rate of 29.15%. This result was consistent with previous studies (Lei et al., 2021), wherein the strong adhesion of catechol groups can effectively improve the interfacial bonding force, disperse the force under the action of external force, prevent stress concentration, prolong the duration of external force, and ultimately improve the overall mechanical properties of the chitosan (C-CS)/polyvinyl alcohol (PVA) (C-CS/PVA) composite films. As the concentration of CatePD increased further, both the fracture strength and elongation rate decreased. This may be attributed to an increased number of voids due to repulsion between catechin molecules and the composite film when the catechin concentration is excessive. Meanwhile, the tensile strength and elongation rate reached maximum values of 0.66 MPa and 39.85% for BluePD, 0.94 MPa and 29.97% for GrapePD, and 1.36 MPa and 44.05% for CitrusPD, all at a content of 1.2%. This suggested that these antioxidants formed a composite network structure with pectin through electrostatic interaction, enhancing the mechanical properties of films. However, this finding differed slightly from the results reported by Otoni C.G. (Otoni et al., 2014) and Eça K.S. (Eça et al., 2015), who concluded that the addition of fruit extracts to pectin films increased the film's stretching capacity while decreasing its rigidity.

**Table 1:** Effects of antioxidant content on the mechanical properties of pectin chitosan film.

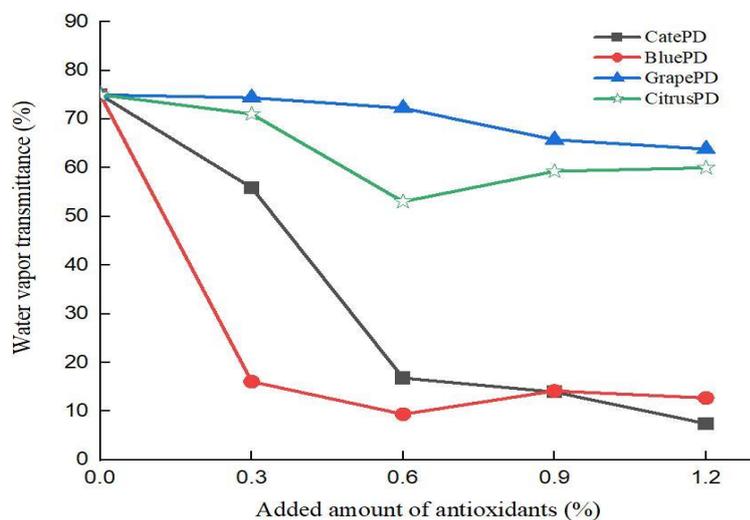
	Antioxidant Content/%	Thickness /mm	Tensile Strength /MPa	Elongation Rate /%
<b>CatePD</b>	0	0.16±0.00 <sup>b</sup>	0.18±0.01 <sup>e</sup>	10.25±0.13 <sup>e</sup>
	0.3	0.16±0.01 <sup>b</sup>	0.28±0.00 <sup>d</sup>	15.39±0.01 <sup>d</sup>
	0.6	0.16±0.00 <sup>b</sup>	0.42±0.00 <sup>c</sup>	27.04±0.00 <sup>c</sup>
	0.9	0.19±0.01 <sup>a</sup>	0.57±0.00 <sup>a</sup>	29.15±0.00 <sup>a</sup>
	1.2	0.19±0.01 <sup>a</sup>	0.55±0.01 <sup>b</sup>	27.48±0.01 <sup>b</sup>
<b>BluePD</b>	0	0.16±0.00 <sup>b</sup>	0.15±0.01 <sup>e</sup>	7.28±0.00 <sup>e</sup>
	0.3	0.17±0.00 <sup>b</sup>	0.21±0.01 <sup>d</sup>	8.82±0.01 <sup>d</sup>
	0.6	0.17±0.00 <sup>b</sup>	0.27±0.00 <sup>c</sup>	14.27±0.00 <sup>c</sup>
	0.9	0.17±0.01 <sup>b</sup>	0.56±0.01 <sup>b</sup>	28.94±0.00 <sup>b</sup>
	1.2	0.18±0.00 <sup>a</sup>	0.66±0.01 <sup>a</sup>	39.85±0.00 <sup>a</sup>
<b>GrapePD</b>	0	0.15±0.00 <sup>c</sup>	0.65±0.01 <sup>e</sup>	27.98±0.01 <sup>e</sup>
	0.3	0.15±0.01 <sup>bc</sup>	0.84±0.00 <sup>d</sup>	28.76±0.01 <sup>c</sup>
	0.6	0.16±0.00 <sup>bc</sup>	0.88±0.00 <sup>c</sup>	28.63±0.00 <sup>d</sup>
	0.9	0.16±0.00 <sup>ab</sup>	0.92±0.01 <sup>b</sup>	29.21±0.01 <sup>b</sup>
	1.2	0.16±0.01 <sup>a</sup>	0.94±0.00 <sup>a</sup>	29.97±0.01 <sup>a</sup>
<b>CitrusPD</b>	0	0.15±0.00 <sup>c</sup>	0.49±0.00 <sup>e</sup>	25.46±0.16 <sup>e</sup>
	0.3	0.15±0.01 <sup>c</sup>	0.55±0.00 <sup>d</sup>	29.31±0.57 <sup>d</sup>
	0.6	0.16±0.00 <sup>c</sup>	0.65±0.02 <sup>c</sup>	37.15±0.00 <sup>c</sup>
	0.9	0.18±0.01 <sup>b</sup>	1.22±0.00 <sup>b</sup>	40.13±0.07 <sup>b</sup>
	1.2	0.19±0.01 <sup>a</sup>	1.36±0.01 <sup>a</sup>	44.05±0.01 <sup>a</sup>

**Note:** Data in the table are expressed as mean ± standard deviation. Different letters in the same column indicate statistically significant differences ( $p < 0.05$ ), same below.

### 3.2 WVT of composite films with different antioxidants

The WVT is a crucial indicator for evaluating the overall performance of food packaging films. It significantly affects the shelf life of the packaged products, with a lower WVT in films being more favorable for food packaging (Yang et al., 2021). As shown in Figure 1, the WVT decreased with increasing antioxidant content, with the largest decrease in water vapor observed for films containing CatePD and BluePD, which decreased from 75.0% to 7.44% and 9.36%, respectively. This data suggested that films with CatePD and BluePD exhibited excellent barrier performance to water vapor. In contrast, the WVT of composite films with CitrusPD and

GrapePD showed no significant change with an increase in antioxidant content. As the contents of CitrusPD and BluePD increased from 0.3% to 1.2%, the WVT of composite films initially decreased and then increased slightly. This trend may be attributed to the disruption of the dense structure of the composite film, accompanied by a weakening of the intermolecular forces as the antioxidant concentration increased, leading to a weakened barrier effect against water vapor. These findings were consistent with a previous study (Han & Song, 2020) showing that the addition of sage leaf extracts led to reduced bonding strength between film components and increased the free volume of the polymer, resulting in increased WVT.



*Figure 1: Effect of antioxidant contents on the water vapor transmittance of the composite films.*

Typically, the addition of several antioxidants leads to a reduction in the WVT. This decrease is likely because the interactions between pectin and chitosan and the antioxidants decrease the content of free hydrophilic hydroxyl groups in pectin. Consequently, there are fewer interactions between the hydrophilic hydroxyl groups and water molecules, leading to an enhanced barrier performance of the pectin-chitosan composite films against water vapor. These results were consistent with those of Nisar et al. (2019). Lei et al. (2019) and Melo et al. (2019), also reported that the WVT of films decreased upon the addition of phenol extracts. The decrease in the WVT can be attributed to the increase in hydrophobicity of the formulations, which reduced the water solubility. Additionally, interactions, such as hydrogen bonding between phenolics and pectin substrate and the blocking of water transport channels and pathways, limited water permeation through the films (decreasing diffusivity) and contributed to a reduction in the WVT.

### 3.3 Characterization by FT-IR

The peak at 2062 nm<sup>-1</sup> could be attributed to the stretching of the C=O bonds, while the peaks at 1854 and 3852 nm<sup>-1</sup> corresponded to the -O-H stretching vibration. The decrease in intensity or the disappearance of the absorption peaks may result from the interactions between pectin and chitosan through their charged groups (Fu, X. C., 2023). These interactions not only partially consumed the charged groups but also altered their original vibrations. Although the wave number of the films did not change much after the addition of antioxidants, there was a marked increase in the intensity of the bands (Figure 2). The increase in band intensity could be primarily attributed to the increase in hydrogen bonds between pectin films and polyphenols (Nisar et al., 2018). Conversely, the reduced number of absorption peaks may result from the high water content of the films, affecting the appearance of the absorption peaks.

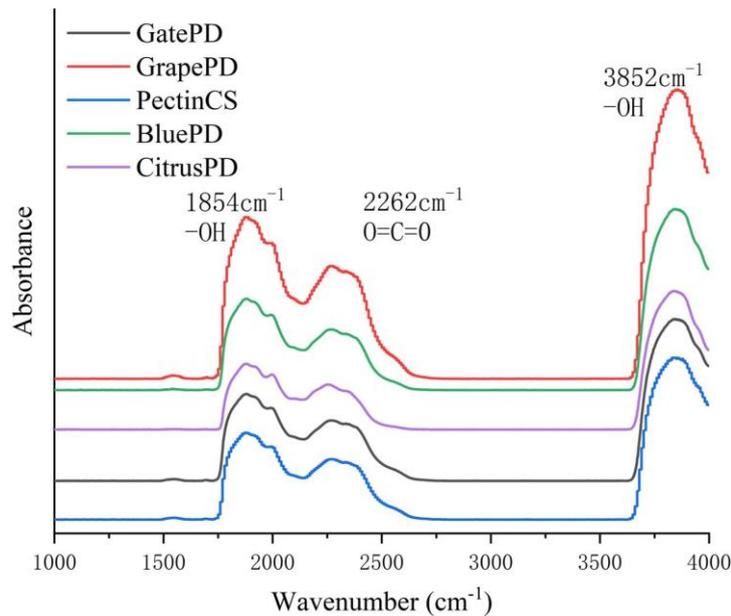


Figure 2: Infrared spectra of composite films with different antioxidants.

### 3.4 Antioxidation performances of composite films with different antioxidants

Free radicals are formed from the oxidation of fats and oils. While small quantities of free radicals have minimal impact on food quality, excessive levels can lead to significant deterioration, resulting in off-flavors, which are unacceptable to the human body.

#### 3.4.1 DPPH· clearance capability

DPPH· is a paramagnetic compound with a single unpaired electron. It can accept an electron from antioxidants to form stable DPPH-H compounds, which is accompanied by a change in the solution color from purple to yellow. Consequently, the change in absorption at 517 nm can be used to determine the DPPH· clearance capability (Pyrzynska et al., 2013).

As shown in Figure 3, the addition of CatePD, BluePD, and GrapePD significantly enhanced the DPPH· clearance capability of the pectin-chitosan composite films. Furthermore, the DPPH· clearance capability of the films was proportional to the contents of CatePD, BluePD, and GrapePD. The clearance rate reached 80% when the concentrations of the antioxidants were in the range of 0.9~1.2%. The DPPH· clearance rates of the pectin-chitosan composite films with BluePD and GrapePD continued to increase as their concentrations increased. In contrast, the addition of CitrusPD showed limited effects on the clearance rate of DPPH· by the as-prepared composite films; the optimized clearance rate was 51.8% (at the mass fraction of 0.6%), and the clearance rate of DPPH· by the films decreased with further increases in the CitrusPD concentration. Lei et al. reported a pectin and konjac glucomannan-composite edible film, observing a DPPH· clearance of only 10.05% (Lei et al., 2019). Compared to the control group, the films with increasing antioxidant content exhibited significantly higher DPPH clearance activity. This enhancement could be attributed to the presence of many phenolic ring hydroxyl groups in CatePD, BluePD, and GrapePD, which promote the rearrangement of unpaired electrons within the components of the composite films and enable the phenolic hydrogens to trap free radicals effectively (Dorta, Lobo, & Gonzalez, 2012; Dey, Chakraborty, Jain, Sharma, & Kuhad, 2016; Zhang et al., 2020). These observations were consistent with a previous study (Rodsamran & Sothornvit, 2019), wherein both total polyphenol content and antioxidant activity of pectin films increased with the addition of pineapple peel extracts. Overall, the antioxidant content and activity of pectin-based films are highly correlated, making these films suitable for use in food packaging and as coatings for oxidizable foods, such as edible nuts.

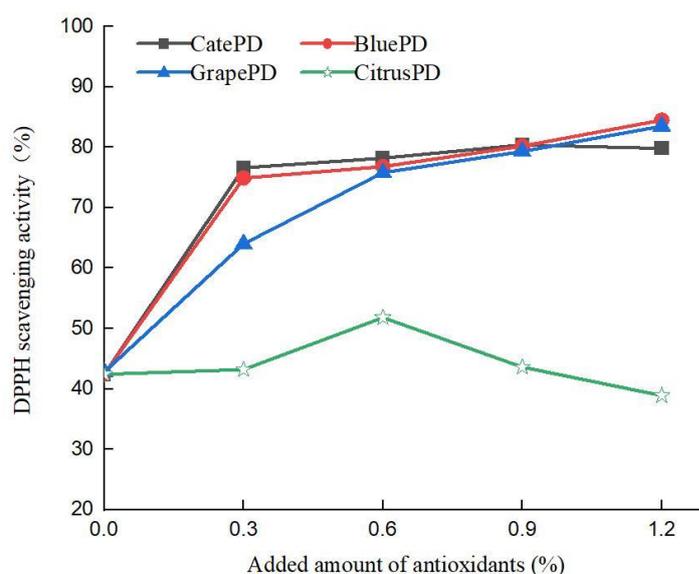


Figure 3: DPPH· clearance by composite films with different antioxidants.

### 3.4.2 ·OH clearance capability

With extremely strong oxidizing properties, ·OH is the strongest known active oxygen-free radical. Through electron transfer, addition, and dehydrogenation reactions, ·OH can interact with proteins, amino acids, fats, carbohydrates, vitamins, and minerals in foods. These interactions alter the functional properties of the foods, thereby reducing the organoleptic quality, nutritional value, and stability. Figure 4 shows that the ·OH clearance capability of composite films increased initially and then decreased with an increase in the concentrations of CatePD, BluePD, GrapePD, and CitrusPD. The maximum ·OH clearance rates of composite films with CatePD, BluePD, and CitrusPD were observed at antioxidative components of 0.6%, achieving values of 80.0%, 70%, and 88.3%, respectively. Meanwhile, the composite film containing GrapePD achieved its ·OH maximum clearance rate of 58.7% at a GrapePD concentration of 0.9%. Overall, the ·OH clearance capability of these antioxidants was not proportional to their doses. Typically, antioxidants trap and neutralize ·OH or react with it to form stable compounds.

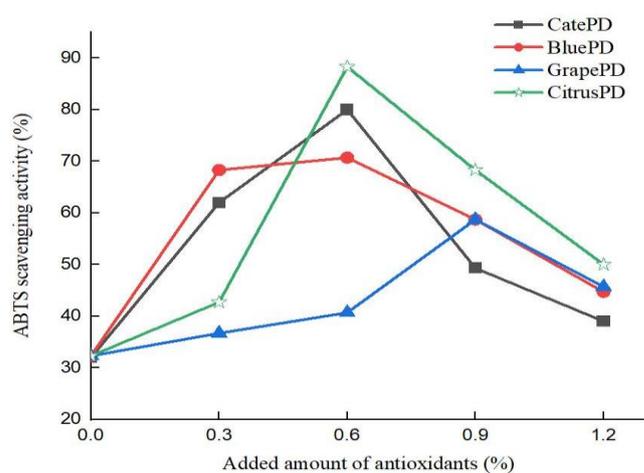


Figure 4: Clearance rates of ·OH by composite films with different antioxidant contents.



The antioxidants in CatePD, BluePD, GrapePD, and CitrusPD contain a high proportion of phenolic hydroxyl structures, making them susceptible to oxidation and potentially reducing their antioxidation performance. Therefore, when preparing antioxidative edible composite films, it is crucial to carefully consider the types of antioxidants used and strictly control their dosage. Han & Song demonstrated that mandarin peel pectin (MPP) films prepared using sage leaf extract (SLE) could serve as antioxidative packaging materials, delaying food deterioration caused by lipid oxidation.

#### 4. Conclusions

This study found that pectin-chitosan composite films with antioxidants demonstrated a strong tensile strength, elongation, and water vapor barrier properties. The pectin-chitosan composite films with 0.6% catechins and blueberry powder demonstrated a strong antioxidant activity at break. It could be used to make food packaging bag coatings or preservation films to protect oxidation-sensitive foods, delay lipid oxidation in food, retard lipid oxidation in food to maintain its quality and reduce the impact of synthetic materials on the environment. At the same time, it can also provide valuable academic references for the application of agricultural and sideline waste in the development of organic or green agricultural products in the future.

#### Author's contribution

Xumin Yin, Experiment and analyze data, Writing-original draft ; Sang Shang, Data analysis, Writing-original draft ; SHunde Zeng, Writing and editing ; Haixiang Wei, Writing-original draft, Give an opinion ; Xiaofeng Zeng, analyze data, Writing-original draft ; Xiaoying Li : Writing-original draft, proofread

#### Conflicts of Interest

The authors declare no conflict of interest.

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