

Effect of the Complex of Zinc(II) and Cerium(IV) with Chitosan on the Preservation Quality and Degradation of Organophosphorus Pesticides in Chinese Jujube (*Zizyphus jujuba* Mill. cv. Dongzao)

Hao Wu,^{†,‡} Dongfeng Wang,^{*,†} John Shi,^{*,‡} Sophia Xue,[‡] and Meiling Gao^{\dagger}

[†]Laboratory of Food Chemistry and Nutrition, College of Food Science and Technology, Ocean University of China, Number 5 Yushan Road, Qingdao, Shandong 266003, People's Republic of China, and [‡]Guelph Food Research Center, Agriculture and Agri-Food Canada, Guelph, Ontario N1G 5C9, Canada

The effects of a novel complex of zinc(II) and cerium(IV) with chitosan film-forming material on the preservation quality of Chinese jujube fruits (*Zizyphus jujuba* Mill. cv. Dongzao) and degradation of organophosphorus pesticides in the fruits during the room temperature storage were investigated. The results showed that after 18 days of storage, the weight loss, respiratory intensity, and polyphenol oxidase (PPO) activity of fruits treated with the complex were 11.72, 31.51, and 7.07% lower than the control. Furthermore, total soluble solids, ascorbic acid, and polyphenol contents were 15.45, 14.55, and 13.93% higher than the control. The degradation rates of chlorpyrifos and parathion were increased to 97.31 and 92.70% for the complex treatment, which were 30.18 and 17.02% higher than the control, respectively. Therefore, the complex can be applied for preserving Chinese jujube fruits to expand their shelf life and decrease residues of organophosphorus pesticides on the fruits.

KEYWORDS: Chinese jujube; chitosan; preservation; oganophosphorus pesticides

1. INTRODUCTION

The Chinese jujube fruit is a native fruit of China and has a long history of more than 2500 years (1). Chinese jujube fruit is a favored and profitable fruit because of its high nutritional value. It has been commonly used in traditional Chinese medicine as an analeptic and a palliative. Jujube fruits have also been commonly used as food, food additives, and flavourants for thousands of years. The Chinese share of the world jujube production is about 90%, and its production for food and pharmaceutical applications has increased in the last 10 years (2). The respiration rate and ethylene production of Chinese winter jujube increase but show no peak during storage, indicating that the fruit is non-climacteric (3).

The ripening and senescence of jujube fruits will result in a short storage life. The use of organophosphorus pesticides on the jujube fruits has resulted in a potential risk to consumers. Now much attention had been paid to improve the shelf life and degrade the residues of organophosphorus pesticides in jujube fruits. Parathion and chlorpyrifos are highly efficient, broadspectrum organophosphorus pesticides used in great quantities worldwide. However, the presence of pesticide residues is regarded as a potential chemical hazard in both the final products and raw materials of ready-to-eat foods, such as fruits and vegetables, and they are always a major potential risk to food safety. However, most of these strategies are expensive and timeconsuming. Thus, there is an urgent need to have alternative technologies to inhibit undesirable physicochemical and physiological changes of fresh fruits and degrade organophosphorus pesticides during storage.

There has been a growing interest recently in developing materials with film-forming capacity, which can contribute to improvements in food safety and shelf life. Chitosan (abbreviated as CTS) might be considered as an ideal preservative coating material for fresh fruits because of its excellent film-forming and biochemical properties. The coating is also safe and shows antifungal activity against several fungi (4). The coating could improve external luster and adjust respiration and metabolism. CTS is a polysaccharide derived from chitin and is mainly composed of repeating 2-amino-2-deoxy- β -D-glucopyranose units. The structure has many amino groups, allowing for excellent complexing capacity with metal ions, particularly for the transition and post-transition metals.

Cerium ion has good antibiotic capability (5) and cleavage of the phosphodiester (6). Wang et al. (7) used alginic acid, fucoidan, and laminaran to bind cerium ion to synthesize liquid complexes and studied their hydrolysis activities. The results showed that they all had the ability to hydrolyze organophorous pesticides. Zinc ion also attracted the interest of several researchers, because of its physiological functions. Zinc is one of the most important essential micro-metallic elements in the human body. It is an essential component of a number of important proteins and is

^{*}To whom correspondence should be addressed. Telephone: +86-532-82031575. Fax: +86-532-82032468. E-mail: wangdf@ouc.edu.cn (D.W.); Telephone: 5197808035. Fax: 5198292602. E-mail: john.shi@ agr.gc.ca (J.S.).

indispensable for its stability and catalytic functions (8). Some zinc(II) complex also has hydrolysis activity. Liu et al. (9) reported that the zinc(II) complex of 1,1,1-tris(aminomethyl)-propane effectively catalyzed the *p*-nitrophenol acetate hydrolysis under neutral or slightly basic conditions. Two metal ions with synergic effects in the active sites of many enzymes that were related to hydrolysis were attributed to the degradation of organophosphorus pesticides.

The safety of zinc(II) and cerium(IV) coated on fruits might be of concern by consumers. Controversies exist about any biological effects of cerium. Toxicity studies have shown that cerium can cause liver damage in rodents (10). However, some experts (11, 12) think that the low concentrations of cerium in their study could not have been responsible for any toxicity; further, they suggest cerium may have significant antioxidative potential. Although the knowledge of zinc toxicity is scarce, the most important evidence is its interference with copper metabolism (13). Nevertheless, it is well-known that the amounts of zinc that provoke toxic effects are much higher than those contained in regular diets (14).

The concentration of cerium(IV) in organs or tissues and the dietary daily intake of zinc(II) for Chinese adult men are 2.06 mg burden per kilogram of fresh weight of the organ and 13 mg daily intake per kilogram of body weight, respectively (*15*, *16*).

The addition of cerium(IV) and zinc(II) in this research was less than 6.0 and 5.0 mg per kilogram of jujube fruits. Therefore, cerium(IV) and zinc(II) should not produce undesirable residuals to pollute the environment and harm human health because of their trace content.

Little scientific literature covers the use of a complex of zinc(II) and cerium(IV) with CTS coating to maintain the quality and degrade the organophosphorus pesticides of fresh jujube fruits. The objective of this study was to prepare a novel coating material and investigate its effects on the preservation of Chinese jujube fruits and degradation of organophosphorus pesticides in the surface of Chinese jujube fruits during room-temperature storage.

2. MATERIALS AND METHODS

2.1. Materials. The Chinese jujube fruits harvested at mature yellow-green stage were purchased from the Qidong Road farm market in Qingdao. After transporting them to our laboratory, the jujube fruits were immediately screened by their shape, size, and color and for freedom of physical damage or disease.

Commercial CTS prepared from crab shells (molecular weight of 500 kDa and 85% deacetylation degree) was provided by the Aquatic Product Chemical Laboratory of The Ocean University of China. Ammonium ceric nitrate and zinc acetate were purchased from Sigma-Aldrich (Shanghai, People's Republic of China). Organophosphorus pesticides and standard (mix) were obtained from the Shandong Agriculture Academy of Science. All other chemicals were obtained from Fisher Chemicals (Shanghai, People's Republic of China) and were of analytical grade.

2.2. Preparation of Complex of Zinc(II) and Cerium(IV) with CTS (CTS-M). Ammonium ceric nitrate and zinc acetate were first dissolved in a 0.5% acetic acid solution, and then CTS (1%, w/v) was added and stirred for 12 h after CTS had swelled. The complex was precipitated after adjusting the pH to 5–6. The mixed solution was filtered under reduced pressure, and the residue was washed with acetone and alcohol solvent, then washed with distilled water, and dried under vacuum, and CTS-M was obtained.

2.3. Film Preparation. CTS-M (1%, w/v) solution was prepared by dissolving solids in acetic acid (0.5%, v/v) with constant stirring, and the viscous solution was filtered (0.8 μ m) under vacuum to remove any undissolved impurities. The solution was then degassed using a vacuum pump to remove the entrapped air. The film-forming solutions, with the same dry matter content to guarantee a constant thickness, were poured onto rectangular acrylic plates (10 × 20 cm). The solutions were dried at 40 °C in an oven during 24 h. The films were stored at 20 °C and a relative

humidity (RH) of 65% for mechanical property determinations. Besides, CTS films were also prepared at the same way as the CTS-M film and analyzed to compare their performance to CTS-M films.

About 15 kg of the selected jujube fruits were randomly coated with the complex of zinc(II) and cerium(IV) with CTS (thereby called CTS-M) and CTS, which were then stored at temperatures ranging from 5 to 15 °C for 18 days preparatory to subsequent analysis. The uncoated fresh jujube fruits were used as a control to compare to the coated samples. Each treatment was conducted in triplicate.

2.4. Physical Property Analysis and Characterization of Coating Film. The physical properties of CTS-M and CTS films, including thickness, tensile strength, elongation at break, water vapor permeability, and oxygen transmission rate, were measured.

2.4.1. Thickness Measurements. The film thickness was measured with a constant load micrometer (Testing Machines, Minneapolis, MN). Five thickness values were taken on each CTS and CTS-M sample, one at the center and four around the perimeter, and the mean values were used for calculation purposes.

2.4.2. Mechanical Properties. A LLOYDS Universal Testing (LLOYDS-50K, London, U.K.) instrument was used to measure tensile strength (TS) and elongation at break (% ε). The tests were carried out according to the American Society for Testing and Materials (ASTM) D-882 standard test (17), with initial grip separation of 50 mm and crosshead speed of 50 mm/min.

2.4.3. Barrier Properties. Water vapor permeability (WVP) of films was determined using aluminum dishes according to the ASTM E-96-97 method (18). Films with an exposed area of 50 cm² were tested at 90% RH in a humidity cabinet. The oxygen transmission rate (OTR) was determined using a volumetric permeability cell (Customs Scientific Instruments, Newark, NJ) according to the ASTM D-1434 procedure (19).

2.5. Quality Evaluation of Jujube Fruits. *2.5.1. Weight Loss Rate.* A total of 30 fruits were checked regularly for weight loss. All experiments were replicated 3 times. The weight loss rate was measured according to the following formula:

weight loss rate
$$(\%) = (W_1 - W_2) \times 100/W_1$$

where W_1 is the original weight (g) and W_2 is the weight after storage (g).

2.5.2. Respiration Rate. The respiration rate was assayed according to the method by Zhou (20), with slight modifications. About 1 kg of fruits were sealed in a 2.5 L glass container for 2 h, and 1 mL of gas sample was withdrawn from the headspace with a gastight hypodermic syringe and analyzed with a Hewlett-Packard 5890A gas chromatograph (GC) equipped with a thermal conductivity detector and a Poropak N column (2.4 m × 3.2 mm outer diameter) (Shimadzu GC-9A, Japan). The carrier gas (He) flow rate was 30 mL min⁻¹, and the column was 100 °C. The injector and detector port temperature was 140 °C. The respiration rate was expressed as mg kg⁻¹ h⁻¹ of CO₂ evolved. The gas sample withdrawn from the same volume of container without fruit was taken as the control.

2.5.3. Measurement of Total Soluble Solids (TSS) and Ascorbic Acid (AA). The TSS content was determined at room temperature (15-20 °C) by refractometry using a digital refractometer (PR1, Atago, Japan) on the juice obtained from the jujube fruits.

The AA content was measured by 2,6-dichlorophenolindophenol titration (21). Briefly, tissue (50 g) from 30 fruits was immediately homogenized in 50 mL of a 0.02 g/mL oxalic acid solution and then centrifuged at 5000g and 4 °C for 15 min. Afterward, 10 mL of supernatant was titrated to a permanent pink color by titration with 0.1% of 2,6-dichlorophenolindophenol titration. The AA concentration was calculated according to the titration volume of 2, 6-dichlorophenolindophenol and expressed as mg/100 g of fresh weight.

2.5.4. Polyphenol Content. Ground lyophilized sample (1 g) was weighed into a centrifuge tube; 10 mL of solvent (70% aqueous acetone) were added; and the sample was homogenized (Ultra-Turrax) for 1 min. Tubes were centrifuged (3000g for 15 min), and the clear supernatant was collected. The extraction was repeated with another 10 mL of solvent. Supernatants were combined and evaporated to dryness. The solid residue was then dissolved in methanol. Their polyphenol contents were determined according to the Folin–Ciocalteu method (22) by reading the absorbances at 760 nm. Results were expressed as milligrams of gallic acid equivalents (GAE) per gram of jujube sample.

2.5.5. Polyphenol Oxidase (PPO) Activity. PPO activity was determined according to the method by Siriphanich and Kader (23). A total of 1 mL of reaction mixture contained 0.1 mL of enzyme extract and 0.9 mL of 10 mmol/L phosphate buffer (pH 7.0). Catechol, as the substrate, was added at a final concentration of 20 mmol/L, and the mixture was aerated for 2 min in a small test tube. PPO activity was determined from the initial rate of quinone formation, as indicated by an increase in absorbance at 420 nm with a UV-2450 spectrophotometer (Shimadzu, Japan). PPO activity was expressed as an increase of 0.001 per minute in absorbance per gram of fresh weight.

2.6. Degradation of Organophosphorus Pesticides. A GC (Agilent Technology 6890) equipped with a flame photometric detector (FPD) (Agilent, Wilmington, DE) and a hot splitless injector was used. The separation of analytical sample components was performed with a Rtx-5 ms, 30 m \times 0.32 mm inner diameter \times 0.25 μ m film thickness (Restek, Bellefonte, PA) capillary column. The oven temperature was programmed as follows: initial temperature of 120 °C for 2 min and raised at 25 °C/min to 200 °C for 5 min. The carrier gas flow rate was in constant flow mode at 1.0 mL/min. Splitless injection of a 1 μ L volume was carried out at 220 °C. An organophosphorus pesticide Standard (mixture) was used to identify the organophosphorus pesticides.

2.7. Statistical Analysis. All analyses were carried out in triplicate, and data were expressed as means \pm standard deviation. A one-way analysis of variance (ANOVA) was performed to calculate significant differences in treatment means, and multiple comparisons of means were performed by the least significant difference (LSD) test. A probability value of < 0.05 was considered significant, and only significant differences were considered unless stated otherwise.

3. RESULTS AND DISCUSSION

3.1. Physical Properties. The physical properties of CTS-M and CTS films are shown in Table 1. The results indicated that the addition of metal ions influenced the mechanical properties of the film, giving more thickness, tensile strength, and elongation at break but less water vapor permeability and oxygen transmission rate to the film, as compared to CTS. The thickness and elongation at break of the CTS-M film were 0.015 ± 0.003 mm and $3.69 \pm 0.33\%$, respectively, which were increased by 29.31 and 2.79% compared to those of the CTS film. However, elongation at break values of CTS and CTS-M films did not differ significantly (p > 0.05). The result of thickness was in good agreement with previously reported values for CTS films upon metal binding (24). With respect to the elongation at break of the CTS-M and CTS films, it was possible to observe that these values were relatively low in comparison to those of CTS-based clay film obtained by Casariego et al. (25), probably because of the different source of CTS. In addition, the tensile strength of CTS-M film was 2.39-fold higher than that of CTS. This may be partly because the introduction of metal ions could enhance the structural bonds in the polymer network, leading to an increase in the tensile strength and elongation at break of CTS-M films.

The water barrier efficiency of film is desirable to retard the surface dehydration of fresh products. In most cases, the gas permeability of food packaging materials is of great importance for food preservation (26). The WVP and OTR of the CTS-M film were both lower than those of the CTS film. Incorporation of metal ions affected the WVP of the CTS film to a considerable extent. WVP of the CTS-M film decreased, with the value found to be 1.240 ± 0.059 g mm m⁻² h⁻¹ Pa⁻¹. This decrease could be due to the formation of coordinate bonds between the metal ions and CTS, thereby influencing water retardation. In our research, WVP of the CTS-M film decreased by 30.73% compared to that of the CTS film. The value obtained in our work was comparable to the results of Souza et al. (27), who pointed out that WVP of CTS films decreased (up to 17.3%) with the increase of the field strengths for values of 100 V cm⁻¹ or higher. The OTR values suggested that the CTS-M film had a superior oxygen

Table 1. Properties of CTS and CTS-M Films

	CTS	CTS-M
thickness (mm)	0.0116 ± 0.0015	0.0150±0.0028
tensile strength (K N m ^{-1})	29.180 ± 1.439	69.850 ± 2.150
elongation at break (%)	3.590 ± 0.120	3.690 ± 0.330
water vapor permeability (g mm m ^{-2} h ^{-1} Pa ^{-1})	1.790 ± 0.031	1.240 ± 0.059
oxygen transmission rate (mL m ⁻² day ⁻¹ atm ⁻¹)	50.576 ± 0.157	49.764 ± 0.298

transmission barrier, but the differences were not significant (p > 0.05). This property of CTS-M film is versatile for use in modified atmosphere packaging of fruits and vegetables. It has been reported that the decrease in oxygen permeability is due to molecular orientation of the polymeric chains (28). Maybe the addition of metal ions influenced the molecular orientation of CTS chains. Furthermore, the decreased WVP and OTR of the CTS-M film may be associated with the increased film thickness. Because of all of the results mentioned above, the CTS-M film possessed better barrier and mechanical properties.

3.2. Quality Changes of Jujube Fruits during Storage. 3.2.1. Weight Loss. The rate of weight loss is one of the most direct indices used to evaluate the preservative effect of vegetables and fruits. Weight loss is caused by respiratory weight loss and evaporation of water from the fruit (29). The main mechanism contributing to weight loss is the evaporation of water, activated by a gradient of water vapor pressure at different locations in the fruits (30).

Figure 1a indicated that the weights of jujube fruits decreased during storage. With prolonged storage, the rates of weight loss increased. In comparison to the control (CK) and CTS, jujube fruits stored with CTS-M coating exhibited a significantly lower weight loss. On day 18, the weight losses of the control and CTS fruit reached 26.36 and 23.81% reduction, respectively. However, the weight loss of jujube fruits that were coated by CTS-M was only 23.27% (p > 0.05). The result indicated that the CTS-M film had a greater effect in preventing weight loss of fruits, which could be attributed to its better barrier properties against water evaporation. Water loss can cause flesh softening, fruit ripening, and senescence by metabolic reactions (31). Clearly, a relatively lower weight loss in the jujube fruits that were coated by CTS-M film contributed to maintaining better fruit quality during roomtemperature storage. However, the weight loss of jujube fruits coated by CTS-M, CTS, and control were all really higher than other literature reported (32). This might be attributed to the different types of respiration, resulting from different kinds of jujube.

3.2.2. Respiratory Intensity. The respiration intensity is a good index of the quality of fruits during storage. Edible coatings lead to high carbon dioxide and low oxygen internal gas concentrations in coated fruits by lowering their respiration rates, which contribute to a longer shelf life of fruit (33). The rate of CO₂ production exhibited a characteristic non-respiration climacteric pattern during room-temperature storage (Figure 1b). According to these results, throughout the storage period, the respiration rates of jujube fruits coated with CTS-M film were significantly reduced (p < 0.05) compared to the control and the CTS-coated samples. These values were only 68.53-87.37% of those of the control and CTS-treated samples at the end of the room-temperature storage period. By day 18, the respiration intensities of the control and CTS-treated samples were 1.46 and 1.20 times higher than that of fruits treated with CTS-M film, respectively. Zhong et al. (32) reported that the respiratory rate of 1-MCP + CTS-coated fruit represented about 82% of the control

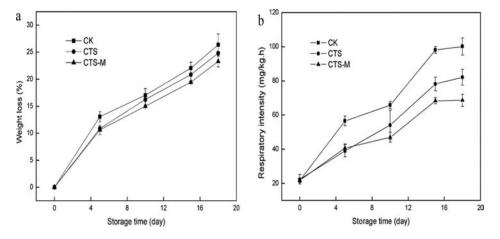


Figure 1. Effects of CTS-M and CTS films on physicochemical indices of jujube during room-temperature storage: (a) weight loss and (b) respiratory intensity.

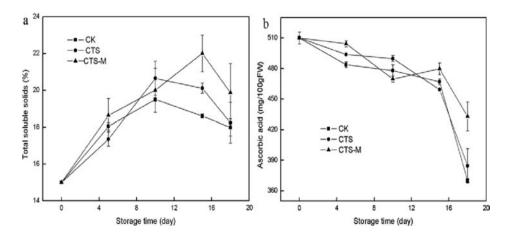


Figure 2. Effects of CTS-M and CTS films on physicochemical indices of jujube during room-temperature storage: (a) TSS and (b) AA.

maximum. CTS-M film showed lower respiratory intensity than it. The CTS-M film coating is more effective in reducing the respiration intensity of fruits compared to CTS, maybe because the CTS-M film coating is more efficient in restricting the gas exchange between fruits and the atmosphere during storage.

3.2.3. TSS. The TSS of jujube fruits increased initially and then declined during 18 days of storage at room temperature (Figure 2a). The TSS of the control uncoated samples and the jujube fruits coated by CTS reached their maximum peak value at day 10, while the peak was postponed to day 15 for CTS-Mcoated jujube fruits. On day 15, the TSS of the control and CTS fruits reached 18.60 and 20.11% but CTS-M was 22.10% (p <0.05). The CTS-M film was better for maintaining the content of TSS compared to the control and CTS film. TSS of fruit were substrates that are consumed by respiration during storage (30, 33). In the present study, the CTS-M film coating was more effective in the retention of TSS levels because of the lower gas permeability of CTS-M film coating that inhibited the respiratory rates and retarded the overall metabolic activities of jujube fruits during storage. The change in TSS contrasted with the report by Li et al. (34), who found that the TSS of jujube fruits increased with time during room-temperature storage. This might be attributed to the different physicochemical changes of jujube fruits, resulting from different treatments.

3.2.4. AA. AA has an important physiological function for humans; thus, it could be considered as a critical index to evaluate the quality of vegetables and fruits. Fresh jujube fruits present higher total AA content (250–600 mg/100 g) than most commonly consumed vegetables (peas, 31–26 mg/100 g; green beans,

25-10 mg/100 g; carrots, 4 mg/100 g; spinach, 31-22 mg/100 g; tomatoes, 14 mg/100 g; and broccoli, 97-77 mg/100 g) (35, 36). This result demonstrates that jujube fruits are a good AA source and an important fruit for the human diet.

The initial AA content of jujube fruits was recorded as 510.10 mg/100 g (fresh weight). The AA content of jujube fruits decreased greatly after 18 days of storage (Figure 2b), especially toward the end of the 18 day period. In the present study, the jujube fruits treated with the CTS-M film showed a significantly (p < 0.05) higher retention of AA (84.87%), as compared to control samples (72.52%) and the samples treated with the CTS film (75.39%) after the 18 day storage period. The change of TSS and AA were consistent with the reports by Zhong and Xia (32), who reported that TSS and TA in Indian jujube fruit increased initially and then declined during 16 days of storage when the fruits were coated with 1-methylcyclopropene and/or CTS. Lower respiratory activity could contribute to a higher retention of AA content and a restriction in enzymatic oxidation of AA into dehydroascorbic acid. This phenomenon was largely influenced by the restriction in respiratory output and low O2 atmosphere generated by the CTS-M film.

3.2.5. Polyphenol Content. Usually the degree of reduction during minimal processing is accredited with the accumulation of polyphenol in many fruits and vegetables, where cells rapidly synthesize a larger amount of phenolic acids as a defense for wound healing and to provide disease resistance. In the present study, it was observed that the polyphenol content significantly decreased during storage of jujube fruits in CTS or CTS-M film as well as in the control samples compared to the initial polyphenol

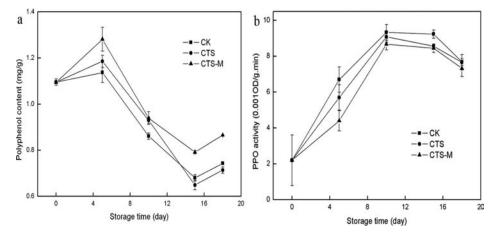


Figure 3. Effects of CTS-M and CTS films on physicochemical indices of jujube fruits during room-temperature storage: (a) polyphenol content and (b) PPO activity.

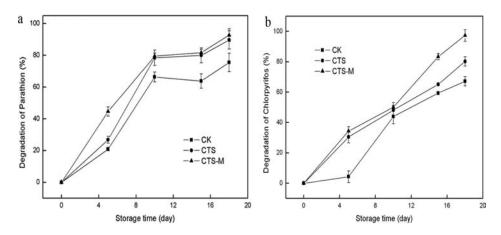


Figure 4. Effects of CTS-M and CTS films on the degradation of organophosphorus pesticides of jujube fruits during room-temperature storage: (a) degradation of parathion and (b) degradation of chlorpyrifos.

content. From the polyphenol content results (Figure 3a), it was possible to see that treated jujube fruits with CTS-M film underwent a lower decrease in these compounds during storage. It was important to highlight that the polyphenol degradation for all jujube fruits occurred during the 5-15 days of storage. The maximum polyphenol content in all treatments was found at day 5. The polyphenol content in CTS-M-treated fruits was about 1.16 and 1.21 times as great as the control and CTS-treated fruits at day 5 (p < 0.05). For jujube fruits stored with control and CTS film, the polyphenol levels decreased by more than 32 and 34%, respectively, whereas only a 21% loss occurred in the CTS-Mtreated fruits (p < 0.05) after 18 days of storage. The CTS-M film treatment caused a higher retention of polyphenol, because of the decrease in the biological activity mediated by anti-respiratory functions of the specific additives as well as a low O₂ and high CO₂ atmosphere provided by the CTS-M film.

3.2.6. PPO Activity. PPO participates in browning by oxidizing the phenolic compounds into quinines, which subsequently form brown color pigments (37). Oxidation of phenolic substrates by PPO is believed to be a major cause of browning of many fruits and vegetables, including jujube fruits. The level of PPO activity may be considered as an index for the prediction of susceptibility to browning.

Figure 3b showed that the activities of PPO all increased first and then decreased during storage of the jujube fruits. In contrast with the CTS-M-treated samples, the PPO activities in the control and CTS groups reached the highest levels at day 10 [9.33 and 9.28 (0.0010D) g^{-1} min⁻¹], respectively. The CTS-M film treatment dramatically inhibited the increase of PPO activity, and the maximal value was 8.67 (0.001OD) g^{-1} min⁻¹, which was 7.07 and 6.57% lower than the control and CTS film treatment, respectively. The results suggested that the treatments with CTS-M reduced the PPO activity of jujube fruits, demonstrating that the CTS-M film could induce jujube fruits to produce a recovery reaction, thereby enhancing its immunocompetence, postponing senescence, controlling browning speed, and improving the preservative effect and the edible quality of jujube fruits during storage.

3.3. Degradation of Organophosphorus Pesticides. The degradation of parathion and chlorpyrifos on the fruits during storage was shown in Figure 4. The results indicated that parathion and chlorpyrifos were degraded by themselves at room temperature. However, in comparison to the self-degradation, CTS-M can obviously promote the degradation effectively. After 18 days of storage, the degradation rates of parathion and chlorpyrifos on the fruits treated by CTS-M film coating were 92.70 and 97.31%, which were 17.02 and 30.18% higher than the control, respectively. In recent years, it was reported that cerium ion showed hydrolysis activities on phosphodiester (6). CTS-M contained Ce^{IV}, maybe acting as a kind of hydrolase simulation, which can hydrolyze the phosphate ester bonds of parathion and chlorpyrifos. The exact mechanism for the degradation of organophosphorus pesticides by CTS-M needs further research.

In this study, a novel complex film-forming material with better mechanical properties was successfully synthesized and then applied to the preservation of Chinese jujube fruits and the degradation of organophosphorus pesticides during roomtemperature storage. The coating formed a good film on the surface of the jujube fruit, giving the fruit a bright, translucent, fresh-like appearance. The results showed that the CTS-M film had quite beneficial effects on the physiological quality and degradation of organophosphorus pesticides compared to the CTS film and control. It could prolong the shelf life and decrease the potential risk of jujube safety. Furthermore, the CTS-M film has the advantages of simple processing and industrial feasibility in contrast with other storage enhancers, some of which are timeconsuming, costly, or alter color and flavor. Therefore, the CTS-M film may provide an attractive alternative to improve the preservation qualities and degrade organophosphorus pesticides of Chinese jujube fruits during extended storage. The effect of the degradation of organophosphorus pesticides by CTS-M during storage would facilitate the application of the CTS-M film over a broader range in the future.

LITERATURE CITED

- Li, J. W.; Fan, L. P.; Ding, S. D.; Ding, X. L. Nutritional composition of five cultivars of Chinese jujube. *Food Chem.* 2007, 103, 454–460.
- (2) Yan, Y. H.; Gao, Z. P. Industrialization of Chinese jujube. J. Northwest Sci. Technol. 2002, 30, 95–98.
- (3) Sheng, J.; Luo, Y.; Lin, S. Storage of Chinese winter jujube fruit. Acta Hortic. 2003, 620, 203–208.
- (4) Jiao, Z. G.; Liu, J. C.; Zheng, H. The mechanism of preservation of chitosan. *Food Res. Dev.* 2003, 24, 114–116.
- (5) Huang, L. F. The biological function of rare earth element. Acta Med. Sin. 2002, 15, 693–695.
- (6) Zhang, H. J.; Zhang, Y. S.; Hao, X. Study on decreasing nitrate content in vegetables by applying RE-composite-microfertilizer. *J. Chin. Rare Earth* 2002, 20, 283–285.
- (7) Wang, D. F.; Sumaoka, J.; Wang, C. H.; Liang, X. G.; Komiyama, M. Effect of complexes coordinating alginic polysaccharides with cerium on cleavage of plasmid DNA and bovine serum albumin. *J. Chin. Rare Earth* **2002**, *20*, 283–285.
- (8) Wagnera, C. C.; Baran, E. J. Vibrational spectra of Zn(II) complexes of the amino acids with hydrophobic residues. *Spectrochim. Acta, Part A* 2009, 72, 936–940.
- (9) Liu, X. L.; Chen, W. D.; Zhu, S. R. Hydrolytic metalloenzyme activity of zinc(II) complex of 1,1,1-tris(aminomethyl) propane. *Chin. J. Inorg. Chem.* **2001**, *17*, 234–238 (in Chinese).
- (10) Huang, S. F.; Li, Z. Y.; Wang, X. Q.; Wang, Q. X.; Hu, F. F. Cerium caused life span shortening and oxidative stress resistance in *Drosophila melanogaster. Ecotoxicol. Environ. Saf.* 2010, 73, 89–93.
- (11) Schubert, D.; Dargusch, R.; Raitano, J.; Chan, S. W. Cerium and yttrium oxide nanoparticles are neuroprotective. *Biochem. Biophys. Res. Commun.* 2006, 342, 86–91.
- (12) Chen, Y.; Cao, X. D.; Lu, Y.; Wang, X. R. Effects of rare earth metal ions and their EDTA complexes on antioxidant enzymes of fish liver. *Bull. Environ. Contam. Toxicol.* 2000, 65, 357–365.
- (13) Cousins, R. J.; Hempe, J. M. Conocimientos Actuales Sobre Nutricion, 6th ed.; International Life Sciences Institute (ILSI) Press: Washington, D.C., 1991; pp 289–300.
- (14) Salgueiro, M. J.; Zubillaga, M.; Lysionek, A.; Sarabia, M. I.; Caro, R.; De Paoli, T.; Hager, A.; Weill, R.; Boccio, J. Zinc as an essential micronutrient: A review. *Nutr. Res.* 2000, 20, 737–755.
- (15) Zhu, H. D.; Wang, J. X.; Chen, R. S. Food concentrations and dietary intakes of elements for a Chinese man. *Chin. J. Radiol. Med. Prot.* 2000, 20, 378–384 (in Chinese).
- (16) Zhu, H. D.; Ou, Y. G.; Zhang, Y. B. Dietary intake and burden of lanthanide in main organs and tissues for a Chinese man. *Chin. J. Radiol. Med. Prot.* 2004, 24, 1–5 (in Chinese).
- (17) American Society for Testing and Materials (ASTM). Standard test methods for tensile properties of thin plastic sheeting. *Annual Book* of ASTM Standards; ASTM: West Conshohocken, PA, 1995; pp 159–167.
- (18) American Society for Testing and Materials (ASTM). Standard test methods for water vapor transmission of materials. *Annual Book*

of ASTM Standards; ASTM: West Conshohocken, PA, 1980; pp 760-767.

- (19) American Society for Testing and Materials (ASTM). Standard test methods for gas transmission of materials. *Annual Book of ASTM Standards*; ASTM: West Conshohocken, PA, 1983; pp 632–647.
- (20) Zhou, T. Application of heat treatment and modified atmosphere package to preservation of peaches and water bamboo shoot. Ph.D. Thesis, Southern Yangtze University, Wuxi, China, 2002.
- (21) Chen, F.; Li, Y. B.; Chen, M. D. The production of ethylene of litchi fruit during storage and its control. *Acta Hortic. Sin.* 1986, *13*, 152– 156 (in Chinese).
- (22) Ainsworth, E. A.; Gillespie, K. M. Estimation of total phenolic content and other oxidation substrates in plant tissues using Folin– Ciocalteu reagent. *Nat. Protoc.* 2007, *2*, 875–877.
- (23) Siriphanich, J.; Kader, A. A. Effects of CO₂ on total phenolics, phenylalanine ammonia lyase and polyphenol oxidase in lettuce tissue. J. Am. Soc. Hortic. Sci. 1985, 110, 249–253.
- (24) Caroline, L. S.; Chen, M. S.; Mandy, C. Color changes in chitosan and poly(allyl amine) films upon metal binding. *Thin Solid Films* 2003, 434, 250–257.
- (25) Casariego, A.; Souza, B. W. S.; Cerqueira, M. A.; Teixeira, J. A.; Cruz, L.; Díaz, R.; Vicente, A. A. Chitosan/clay films' properties as affected by biopolymer and clay micro/nanoparticles' concentrations. *Food Hydrocolloids* **2009**, *23*, 1895–1902.
- (26) Arvanitoyannis, I.; Nakayama, A.; Aiba, S. Chitosan and gelatin based edible films: State diagrams, mechanical and permeation properties. *Carbohydr. Polym.* **1998**, *37*, 371–382.
- (27) Souza, B. W. S.; Cerqueira, M. A.; Casariego, A.; Lima, A. M.; Teixeira, J. A.; Vicente, A. A. Effect of moderate electric fields in the permeation properties of chitosan coatings. *Food Hydrocolloids* 2009, 23, 2110–2115.
- (28) Salame, M.; Steingiser, S. Barrier polymers. Polym.-Plast. Technol. Eng. 1977, 8, 155–175.
- (29) Amarante, C.; Banks, N. H.; Ganesh, S. Relationship between character of skin cover of coated pears and permeance to water vapour and gases. *Postharvest Biol. Technol.* 2001, 21, 291–301.
- (30) Yaman, O.; Bayoundurlu, L. Effects of an edible coating and cold storage on shelf-life and quality of cherries. *LWT-Food Sci. Technol.* 2002, 35, 146–150.
- (31) Bai, J.; Baldwin, E. A.; Hagenmaier, R. H. Alternatives to shellac coatings provide comparable gloss, internal gas modification, and quality for delicious apple fruit. *HortScience* 2002, *37*, 559–563.
- (32) Zhong, Q. P.; Xia, W. S. Effect of 1-methylcyclopropene and/or chitosan coating treatments on storage life and quality maintenance of Indian jujube fruit. *LWT-Food Sci. Technol.* 2007, 40, 404–411.
- (33) Özden, Ç.; Bayindirli, L. Effects of combinational use of controlled atmosphere, cold storage and edible coating applications on shelf life and quality attributes of green peppers. *Eur. Food Res. Technol.* 2002, 214, 320–326.
- (34) Li, H. M.; Li, F.; Wang, L.; Sheng, J. C.; Xin, Z. H.; Zhao, L. Y.; Xiao, H. M.; Zheng, Y. H.; Hu, Q. H. Effect of nano-packing on preservation quality of Chinese jujube (*Ziziphus jujuba* Mill. var. *inermis* (Bunge) Rehd. *Food Chem.* **2009**, *114*, 547–552.
- (35) Giannakourou, M. C.; Taoukis, P. S. Kinetics modelling of vitamin C loss in frozen green vegetables under variable storage conditions. *Food Chem.* 2003, 83, 33–41.
- (36) Lee, S. K.; Kader, A. A. Preharvest and postharvest factors influencing vitamin C content of horticultural crops. *Postharvest Biol. Technol.* 2000, 20, 207–220.
- (37) Tomas-Barberan, F. A.; Espin, J. C. Phenolic compounds and related enzymes as determinants of quality in fruits and vegetables. *J. Sci. Food Agric.* 2001, *81*, 853–876.

Received for review February 8, 2010. Revised manuscript received March 23, 2010. Accepted March 31, 2010. The authors gratefully acknowledge the contribution of the MOE/AAFC Program and the Guelph Food Research Center, Agriculture and Agri-Food Canada (AAFC Journal Series S5890). The authors also greatly appreciate the financial support provided by the Key Program of Shandong Province (2007GG10009005), People's Republic of China.