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Jujube preservation using chitosan film with nano-silicon dioxide

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ABSTRACT

The effect of 1% chitosan film with 0.04% nano-silicon dioxide on the qualitative properties of harvested jujube under ambient temperature was investigated. After 32 d, the red index, decay incidence, weight loss, and respiration rate of the coated jujubes were lower compared with those of the control. The lower phenylalnine ammonialyase activity and higher activities of scavenger antioxidant enzymes (i.e., superoxide dismutase, peroxidase, and catalase) of the coated jujubes can be attributed to the compound coating. Increased malonaldehyde in the coated jujubes was restrained. Composite coating had shown to be superior in preserving total flavonoid than chitosan coating alone. But no differences were observed in terms of vitamin C loss and total polyphenol content between composite coating and control. Coating jujubes with chitosan + nano-silicon dioxide will be a promising alternative if nano-silicon dioxide is allowed for food use.

1. Introduction

Jujube is one of the famous fruits in the world, and its production has steadily increased in China in the last ten years. The current share of Chinese jujube is about 90%. People are fond of jujube because of its particular flavours and abundant nutrients, such as proteins, dietary fibres, minerals, and vitamins (Li et al., 2007). However, fresh jujube is subject to rot and water loss during transportation and storage because of respiration and other physiological actions (Wang et al., 2011). From bright green, the colour of the jujube surface gradually becomes red and even black because of anthocyanin oxidization and quinone polymerization under poor storage condition (Holton and Cornish, 1995). Thus, people tend to reject purchasing such deteriorated jujube. Generally, an ambient temperature condition is necessary to maintain the freshness of jujube during transportation and retailing. Properly prolonging the shelf life of fresh jujube is beneficial to the preservation of the commodity property and reduction of economic loss. For this purpose, fresh jujube is fumigated with nitric oxide, dipped with 1-methylcyclopropene, or wrapped with different improving materials (Zhu et al., 2009; Zhong and Xia 2007; Li et al., 2009).

Extending the shelf life of post-harvested fruits and vegetables by applying an edible coating is a promising method. Many materials, such as polysaccharides, proteins, essential oils, or their combinations, may serve as edible coatings (Maria et al., 2008; Lima et al., 2010; Bosquez-Molina et al., 2010). Chitosan is a safe, biocompatible, and biodegradable natural alkaline polysaccharide derived from the deacetylation of chitin (Aider, 2010). It can form a film on fruit and vegetable surfaces and reduces respiration rate by adjusting the permeability of carbon dioxide and oxygen. The $-NH_3^+$ group of chitosan may also restrain the propagation of harmful germs, thus effectively controlling fruit decay (Devlieghere et al., 2004). Considering these superior properties of chitosan, it has been successfully used in many post-harvested fruits and vegetables, such as grape, berry, jujube and fresh-cut lotus root through single coating or comprehensive treatments (Sánchez-González et al., 2011; Vu et al., 2011; Zhong and Xia, 2007; Xing et al., 2010).

Nanotechnology, which has emerged at the end of the 1980s, is currently rapidly developing and being widely used in the material, chemical, and physical fields. Different from normal-sized substances, nano-sized substances show quanta size, small size, surface, and macroscopic quanta size effects. If the particle size was equivalent or much smaller compared to physical characteristic size of de Broglie wave, the character including electricity, magnetism, light, sound and heat of usual substance will vary. This effect was defined small size effect. The surface effect is defined as followed. The ratio of surface atom amount and total atom amount sharply augmented once the particle size is small, which lead the substance character to variation. Quanta size effect is a phenomenon that electronic energy level in the vicinity of fermi level on metal become discrete level from continuous level and bandgap of nano-semiconductor particle becomes wide if the particle size decrease to a certain value. Macroscopic quanta size effect means

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that the particle can penetrate certain barrier even if the total energy of microcosmic particles is less than barrier height. Above the four effects, the usual substances have not the character (Hu et al., 2007). Nanotechnology is currently applied in the food industry, including food packaging, processing, and measurement (Johnston et al., 2008; Jafari et al., 2008; Taira and Sahashi, 2009). Silicon dioxide possesses a relatively high food safety, is quite stable, and cannot be digested by the digestive tract. This compound has been approved as a food additive (USFDA, 2011). At present, nano-silicon dioxide was strict in application of food field in some area. For example, if nanomaterial was used in food processing or preservation, related information must be marked in label according to novel food regulations of EU.

Consequently, the present work investigated the effect of chitosan film with nano-silicon dioxide on the preservation of jujube under ambient temperature. Relative physiological indices, biochemical parameters, and nutritional indicators were also measured. The current study aims to provide a novel method that could extend the shelf life of jujube, and to enlarge the application of nanotechnology in the food industry.

2. Materials and methods

2.1. Materials

Jujubes (*Ziziphus jujuba* Mill. cv. Dongzao) were purchased from an orchard in the vicinity of the Shanxi Normal University, and picked at a preclimacteric but physiologically mature stage in the moon. Jujubes with uniform shape, size, colour, and no defects were selected and quickly transported in open cartons to the laboratory.

Water-soluble chitosan with a molecular weight of approximately 200 kDa and 85% deacetyl degree was purchased from AK Biotech Ltd., (Shandong, China). Hydrophilic nano-silicon dioxide (JY100) was purchased from Jingyen Nanotechnical Co., Ltd., (Anhui, China). The sucrose ester of fatty acid (SL-SE-11) was purchased from Qizhida Addicative Stock Ltd., (Lizhou, China). Thiobarbituric acid, methionine, and nitroblue tetrazolium (biochemical reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd., (Shanghai China). Alfa Aesar Company (Tianjin, China) supplied other reagents, which were all analytical grade.

2.2. Preparation of the coating solution and fruit treatment

Solutions of 200 mL 5% chitosan, 200 mL 0.2% nano-silicon dioxide, 200 mL 5% chitosan + 200 mL 0.2% nano-silicon dioxide, and 200 mL deionized water (control) were diluted to 800 mL with deionized water. These four solutions were dispersed for 15 min via ultrasonication (KQ-250B, Kunshan Ultrasonic Instrument Co., Ltd., Kunshan, China) under 300 W at 60 °C. Afterwards, 100 mL 0.5% sucrose ester of fatty acid was added to each solution and dispersed for 5 min. Each solution was added with 1 mL glycerine, diluted to 1000 mL, and dispersed for 5 min. Thus, different coating solutions, namely, 1% chitosan solution, 0.04% nano-silicon dioxide suspension, compound solution (1% chitosan + 0.04% nano-silicon dioxide), and control solution, were acquired.

Whole jujubes were washed clean with tap water and then dipped into each prepared solution for 3 min. In each treatment, about 300 fruits were coated and each treatment was repeated three times. A fan generating low speed air was used to hasten the drying. The samples were then placed in plastic bags and stored under ambient temperature with 85% of relative humidity. The related parameters of the jujubes were determined periodically.

2.3. Determination of red indices and decay incidence

Red indices and decay incidence were assayed as Sun et al. (2007) had shown. In each treatment, 60 fruits were randomly selected from 300 fruits and classified in five ranks of red as follows: 1, no red; 2, red surface less than 1/4; 3, red surface between 1/4 and 1/2; 4, red surface between 1/2 and 3/4; and 5, red surface more than 3/4. The red surface was directly observed. The red indices for the treatment unit were calculated as follows: red index = $[(\Sigma \text{rank} \times \text{quantity})/(5 \times 60)] \times 100\%$.

Similarly, 60 fruits were randomly selected and classified in five ranks of rot as follows: 1, no rot; 2, rotten surface less than 1/4; 3, rotten surface between 1/4 and 1/2; 4, rotten surface between 1/2 and 3/4; and 5, rotten surface more than 3/4. The decay incidence for the treatment unit was calculated as follows: decay incidence = $[(\Sigma \text{ rank} \times \text{quantity})/(5 \times 60)] \times 100\%$.

2.4. Determination of respiration rate and weight loss

The respiration rate was assayed according to method described by Zhu and Zhou (2007) with slight modifications. Approximately 600 g of jujubes were sealed in a 10 L glass container under ambient temperature for 1 h. The carbon dioxide concentration was measured using an infrared carbon dioxide analyzer (GXH-3010F, Beijing Huayun Analysis Instrument Co., Ltd., Beijing, China). The respiration rate was calculated as mg CO_2 kg^{-1} h^{-1}.

Subsequently, in each treatment, 60 fruits were randomly selected. The weight loss was calculated as follows: weight loss (%) = $[(m_0 - m_1)/m_0] \times 100$, where m_0 is the initial weight and m_1 is the weight measured during storage.

2.5. Determination of enzyme activities

SOD (superoxide dismutase) activity was determined using a modified method (Zhao et al., 2009). About 2 g of fruit tissue from ten fruits was homogenized with 15 mL of 50 mmol/L sodium phosphate buffer (pH 7.8), and centrifuged at 8000*g* for 15 min at 4 °C with an Eppendorf 5417R centrifuge (Germany). The supernatant was collected as a crude enzyme of SOD. The reaction mixture (3 mL) containing 0.1 mL of enzyme extracts, 50 mmol/L sodium phosphate buffer (pH 7.8), 13 mmol/L methionine, 75 μmol/L nitrobluetetrazolium (NBT), 10 ηM EDTA, and 20 ηM riboflavin was illuminated using a fluorescent lamp (60 mol m^{-2} s^{-1}) for 20 min. The absorbance at 560 nm was recorded using a UV spectrophotometer (UV-1100, Shanghai Meipuda Instrument Co., Ltd., Shanghai, China). An aliquot of an identical solution was kept in the dark and served as the blank control. One unit of SOD activity was defined as the amount of enzyme that catalyzed a 50% decrease in the SOD-inhibitable NBT reduction.

POD (peroxidase) activity was analyzed using a modified method (Yang et al., 2009). The crude enzyme of POD was prepared as the crude SOD enzyme was extracted. The assay mixture contained 1.5 mL of enzyme extract, 2 mL of 50 mmol/L sodium phosphate buffer (pH 7.8), 0.6 mL of 0.04 M guaiacol, and 0.1 mL of 15% H_2O_2. POD activity was measured by an increase in absorbance at 470 nm. One unit of POD activity was defined as a 0.01 increase in absorbance at 470 nm per min.

CAT (catalase) activity was assayed according to the method described by García et al. (2007). Tissue (2 g) was homogenized with 15 mL of sodium phosphate buffer (pH 7.0) containing 1% polyvinyl-polypyrrolidone (PVPP), and centrifuged at 8000 *g* for 15 min at 4 °C. The supernatant was collected as the crude enzyme of CAT. CAT activity was measured by adding 0.6 mL of enzyme extract to 2 mL of sodium phosphate buffer (pH 7.0) containing

1 mL of 0.03% H_2O_2 as substrate. H_2O_2 decomposition was measured by the reduction in absorbance at 240 nm. One unit was defined as the change 0.1 absorbance per min.

PAL (phenylalnine ammonialyase) activity was assayed according to the method described by Assis et al. (2001). About 2 g of fruit tissue from 10 jujubes was homogenized with 10 mL of 200 μmol/L sodium borate buffer (pH 8.8) containing 1% PVPP, and centrifuged at 8000 *g* for 15 min at 4 °C. The supernatant was collected as the crude enzyme of PAL. About 1.0 mL of enzyme extract was incubated with an assay medium containing 2 mL of 200 mmol/L sodium borate buffer (pH 8.8), 1 mL of distilled water, and 1 mL of 50 mmol/L 1-phenylalanine as substrate at 35 °C for 1 h. The reaction was terminated by adding 0.2 mL of 6 mol L^{-1} HCl. PAL activity was measured by the change in absorbance at 290 nm. One unit was defined as the change 0.01 absorbance at 290 nm per h.

2.6. Determination of malonaldehyde (MDA) content

MDA was measured as previously described by Xing et al. (2008). Flesh tissue (2.0 g) from 10 fruits was homogenized with 10 mL of 10% trichloroacetic acid containing 0.5% (w/v) thiobarbituric acid. The mixture was then heated at 100 °C for 10 min. After the rapid cooling of the sample to room temperature and centrifugation at 4000*g* for 15 min at 25 °C, the absorbance of the supernatant was measured at both 532 and 600 nm. MDA concentration (μmol g^{-1} fresh weight) was calculated by an extinction coefficient of 155 Mm^{-1} cm^{-1} through the formula $(OD_{532} - OD_{600}) \times 40/(0.155 \times \text{formula weight})$.

2.7. Determination of vitamin C, total polyphenol, and total flavonoid

The vitamin C content was measured by 2, 6-dichloriondophenol titration (Bessey and King, 1933). Briefly, tissue (2 g) from 10 fruits was immediately homogenized in 10 mL of 2% oxalic acid solution, and then centrifuged at 8000*g* for 15 min at 4 °C. Afterwards, 2 mL of supernatant was titrated to a permanent pink colour using 0.1% of 2,6-dichlorpphenolindophenol titration. The vitamin C concentration was calculated according to the titration volume of 2, 6-dichloriondophenol, and expressed as mg 100 g^{-1} fresh weight.

Total polyphenol content was determined using Folin–Ciocalteu's phenol reagent (Xiao et al., 2010) via spectrophotometric analysis. Tissue (5 g) of 10 fruits was homogenized in 20 mL of 50% aqueous methanol, and centrifuged at 3000 *g* for 20 min. The clear supernatant was collected. An aliquot (1 mL) of a standard solution of gallic acid of concentration including 0, 10, 20, 30, 40, and 50 mg L^{-1} aqueous methanol, or supernatant was added to a 25 mL volumetric flask containing 9 mL of water. About 1 mL of Folin–Ciocalteu's phenol reagent was added to the mixture and shaken. After 8 min, 2 mL of 7.5% aqueous Na_2CO_3 solution was added. The solution was then immediately diluted to a final volume of 25 mL with water and thoroughly mixed. After incubation for 30 min at 25 °C, the absorbance versus the prepared blanks was read at 765 nm. Total polyphenol content was expressed as mg gallic acid equivalents per 100 g fresh weight.

Total flavonoid content was measured according to a colorimetric assay (Jia et al., 1999). Tissues (5 g) of 10 fruits was homogenized in 20 mL of 80% ethanol, and centrifuged at 3000*g* for 20 min. The clear supernatant was collected. An aliquot (1 mL) of a standard solution of rutin with different concentrations (0, 10, 20, 30, 40, and 50 mg L^{-1}), or supernatant was added to 10 mL volumetric flasks containing 4 mL of water. At the onset of each experiment, 0.4 mL of 5% $NaNO_2$ was added to the flask. After 5 min, 0.4 mL of 10% $AlCl_3$ was added. After 6 min, 2 mL of 4% NaOH was added. Immediately, the solution was diluted to a final volume of 10 mL with water and thoroughly stirred. The absorbance of the mixture was determined at 510 nm versus the prepared blanks. The total flavonoid content in jujube was expressed as mg rutin equivalents per 100 g fresh weight.

2.8. Statistical analysis

Experimental data were analyzed through ANOVA using the DPS7.05 statistical software (Refine Information Tech. Co., Ltd, Hangzhou, China). Experimental data were the means ± SE of three replicates of determinations for each sample. Mean separations were performed via the Tukey's test; $p < 0.05$ was considered to indicate statistical significance.

3. Results

3.1. Red index and decay incidence

As shown in Fig. 1a, the red index of jujubes increased over time during storage. The jujube coated with chitosan + nano-silicon dioxide showed the lowest red index, whereas that with nano-silicon dioxide showed a higher red index. Before the 16th day, the red index of jujube coated with nano-silicon dioxide alone was higher than that of the control. It was lower than that of the control after 20–32 d. After 32 d, the red index of jujube coated with chitosan + nano-silicon dioxide was 67.6%, which was 5.0%, 8.8%, and 13.0% lower than that of jujube coated with chitosan, nano-silicon dioxide, and the control, respectively.

The decay incidence of jujube increased with the storage time (Fig. 1b). The jujube coated with chitosan + nano-silicon dioxide began to rot after 16 d, and its decay incidence was the lowest

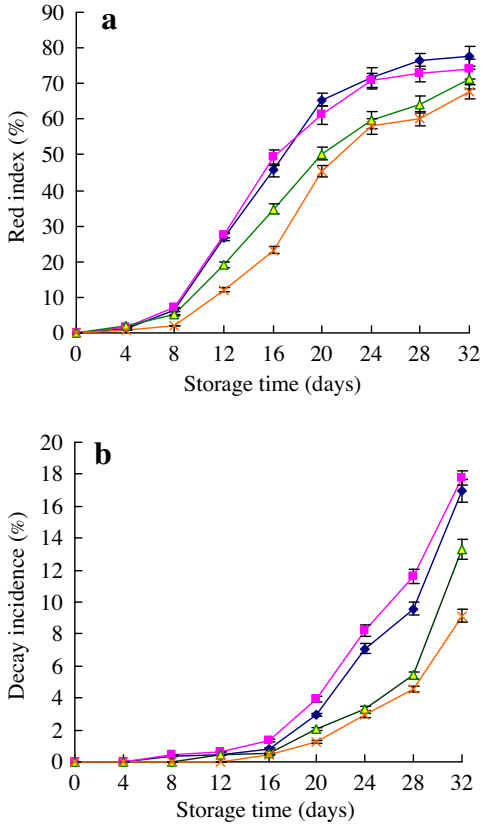

Fig. 1. Effects of (◆) control, (■) nano-SiO_2, (▲) chitosan, and (×) chitosan + nano-SiO_2 on the red index (a) and decay incidence (b) of jujube. Each point represents the mean value ± SE.

among the treated and control samples. The jujube coated with chitosan alone began to rot after 12 d, and its decay incidence was moderate. The jujube coated with nano-silicon dioxide alone or the control began to rot after 8 d, and the decay incidence of the jujube coated with nano-silicon dioxide alone was the highest. After 32 d, the decay incidence of the jujube coated with chitosan + nano-silicon dioxide was 9.15%, which decreased by 46.2% compared with the control ($p < 0.05$).

3.2. Respiration rate and weight loss

The respiration rates of the treated samples decreased during the first four days, and then increased after 4–16 d (Fig. 2a). Afterwards, they began to decrease after 16 d and reached the lowest point after 20 d. The treated samples increased after 20–28 d and then decreased after 28 d. The respiration rate of the control initially increased before 8 d, decreased after 8–20 d, increased, and again decreased after 28 d. Jujube, a non-climacteric fruit, exhibited a characteristic pattern during storage under ambient temperature. Throughout the storage period, the respiration rate of the jujube coated with chitosan + nano-silicon dioxide was the lowest. After 32 d, it was 5.95 mg CO_2 kg^{-1} h^{-1}, which was 29.0% lower than that of the control ($p < 0.05$).

The weight loss of jujube in the treated and control samples linearly increased (slope ≈0.3387) with the storage time (Fig. 2b). The weight loss of the jujube coated with chitosan + nano-silicon was the lowest. During the first 20 d, no difference was found in the weight loss between the samples coated with single chitosan and chitosan + nano-silicon dioxide ($p > 0.05$). After 24 and 28 d, notable differences were observed between them. After 32 d, the weight loss of the jujube coated with chitosan + nano-silicon dioxide was only 10.2%, which is 36.4% lower than that of the control ($p < 0.05$).

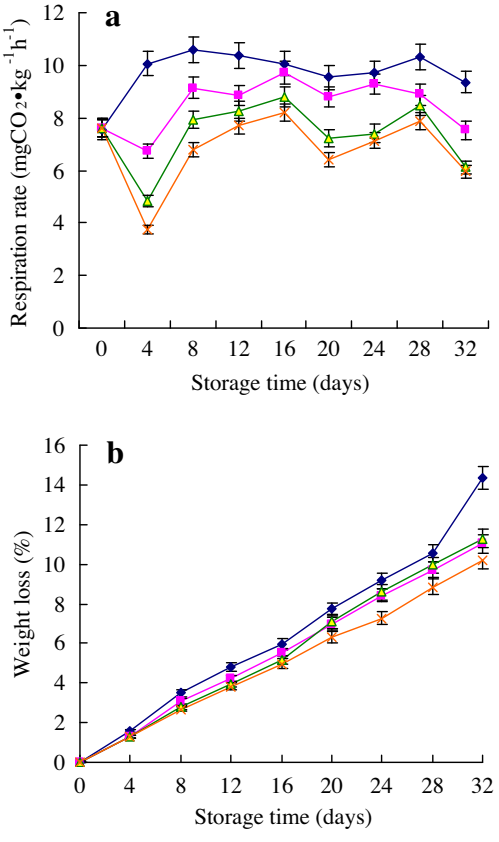

Fig. 2. Effects of (◆) control, (■) nano-SiO_2, (▲) chitosan, and (×) chitosan + nano-SiO_2 on the respiration rate (a) and weight loss (b) of jujube. Each point represents the mean value ± SE.

3.3. SOD, POD, CAT, and PAL activities

The effect of coating on the SOD activity of jujubes is summarized in Fig. 3a. The SOD activity of the jujube coated with chitosan alone or chitosan + nano-silicon dioxide demonstrated a similar pattern. That is, it increased to the peak after 8 d, and then decreased. It reached the bottom on after 24 d, and then remarkably increased. After 0–16 d, the SOD activity of the jujube coated with chitosan + nano-silicon dioxide was higher than that coated with chitosan alone. The SOD activity of the jujube coated with nano-silicon dioxide alone exhibited a similar fluctuation, but increased to the peak after 24 d, and then decreased. The SOD activity of the control was higher than that of the jujube coated with nano-silicon dioxide alone during storage. However, the SOD activity of the jujube coated with chitosan + nano-silicon dioxide was 1.88 times that of the control after 32 d.

As shown in Fig. 3b, the POD activity of jujube, except that coated with chitosan, increased during the first 16 d of storage, and then decreased after 16–32 d. The activity of the jujube coated with chitosan peaked after 8 d. After 16–32 d, the POD activity of the jujube coated with chitosan + nano-silicon dioxide maintained the highest levels compared with that of the control and the jujube coated with the chitosan alone and nano-silicon dioxide alone.

The CAT activity in both control and treated samples increased during the first 8 d and then decreased after 8–32 d (Fig. 3c). Compared with the control or other treated fruits, the CAT activity of the jujube coated with chitosan + nano-silicon dioxide was the highest (27.44 U g^{-1}) during the entire storage period. This value is approximately 28% higher than that of the control samples after 32 d ($p < 0.05$).

Similarly, the PAL activity of the treated jujubes increased after the first 16 d, and then decreased (Fig. 3d). The PAL activity of the control during the storage period sharply peaked after 8 d, decreased after 8–24 d, and then slightly increased after 32 d. The PAL activity of the jujube coated with chitosan + nano-silicon dioxide maintained the lowest level during the storage period compared with the control and the jujubes coated with chitosan alone or nano-silicon dioxide alone.

3.4. MDA content

As shown in Fig. 4, the MDA contents of all the samples continuously increased during the entire storage period. No significant difference was observed in the MDA content between the jujubes coated with chitosan + nano-silicon dioxide and chitosan alone ($p > 0.05$). The application of chitosan + nano-silicon dioxide coating also delayed the MDA increase in jujube. After 32 d, the MDA content of the jujube coated with chitosan + nano-silicon dioxide was 0.38 μmol g^{-1}, which was 15.6% lower than that of the jujube coated with chitosan alone.

3.5. Changes in functional nutrients

As shown in Table 1, the vitamin C content of the control or treated samples after 32 d decreased compared with that after 0 d. The vitamin C content of the jujube coated with chitosan + nano-silicon dioxide was statistically equal to that of control, and no difference between them was found ($p > 0.05$). Total polyphenol content variation was similar to vitamin C content after 32 d. The total flavonoid content of the treated or control sample was quiet different to that of vitamin C or total polyphenol content. The total flavonoid content of the control was the

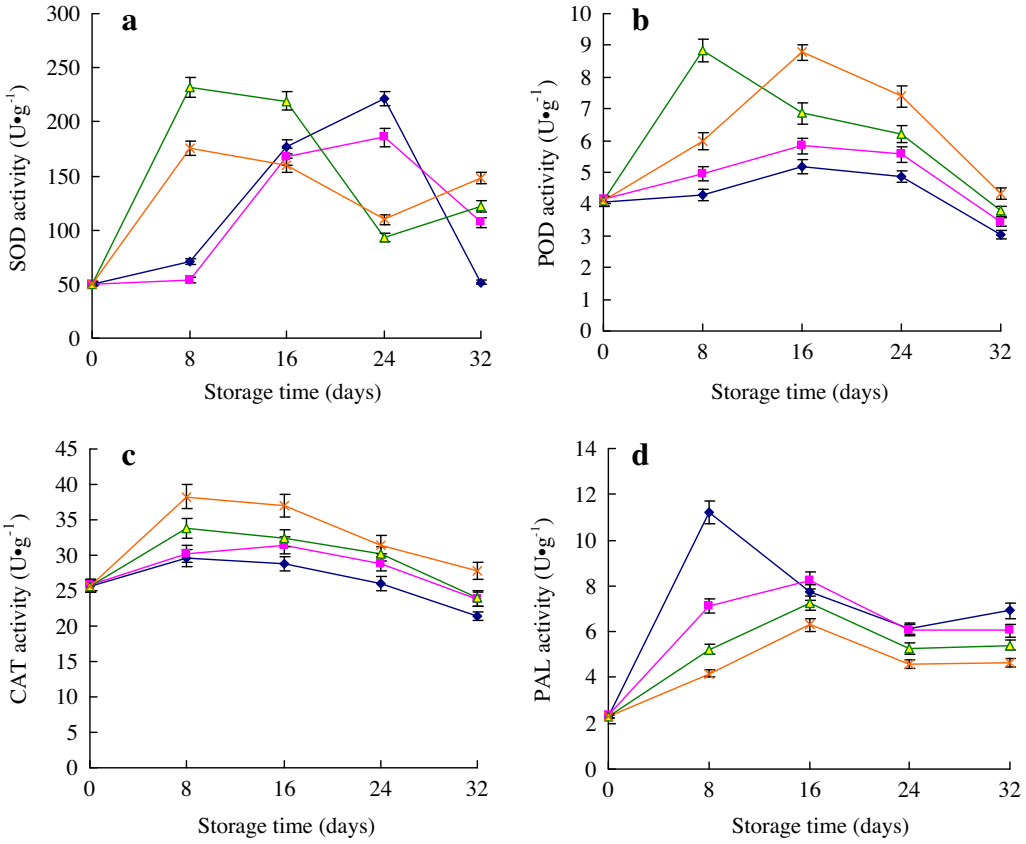

Fig. 3. Effects of (◆) control, (■) nano-SiO_2, (▲) chitosan, and (×) chitosan + nano-SiO_2 on the SOD (a), POD (b), CAT (c), and PAL (d) activities of jujube. Each point represents the mean value ± SE.

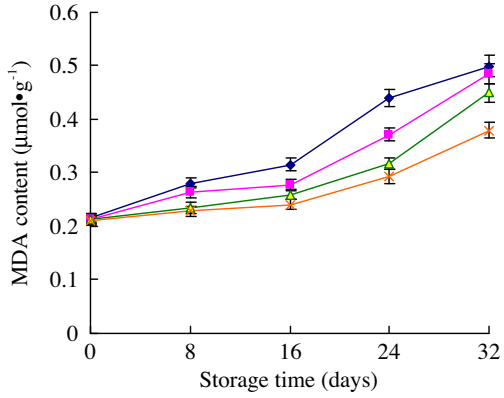

Fig. 4. Effects of (◆) control, (■) nano-SiO_2, (▲) chitosan, and (×) chitosan + nano-SiO_2 on the MDA content of jujube. Each point represents the mean value ± SE.

highest, and was 82.8% higher than that of the jujube coated with chitosan + nano-silicon dioxide. The total flavonoid content of the jujube coated with chitosan was the lowest (38.16 mg 100 g^{-1}). The data indicated that no significant differences were observed in terms of vitamin C loss and total polyphenol content between control samples and those coated with chitosan + nano-silicon oxide; this coating has shown to be superior in preserving total flavonoid than chitosan coating alone.

4. Discussion

The respiration rate and weight loss of the jujube coated with chitosan + nano-silicon dioxide were restrained compared with those of the control. This result indicates that compound coating can adjust the permeability of CO_2/O_2 and may prolong the shelf life of jujube (Lin et al., 2011). Red index, a mark of maturity degree in most fruits, is restrained to extend the shelf life of fresh jujube (Saranwong et al., 2004). The red index increase of the jujube coated with the compound film became slower, and thus the shelf life of jujube was correspondingly prolonged.

Harvested fruits and vegetables generate free radicals, such as O^{2-} and H_2O_2, because of biochemical reactions. Free radicals can oxidize and destroy the cytoplasmic membrane, thereby accelerating senescence. The harm induced by free radicals is resisted by defence enzyme systems (Pirker et al., 2002). SOD can change O^{2-} into H_2O_2, and POD or CAT can eliminate H_2O_2. The united action of these three enzymes can reduce the harm to the cytoplasmic membrane (Isamah et al., 2000; Doğan et al., 2007). The SOD,

Table 1
Effect of the different coatings on the functional nutrition content of jujube after 32 d of storage. Each point represents the mean value ± SE. All values are in mg 100 g^{-1}.

Treatment	Control (day 0)	Control (day 32)	Nano-SiO_2 (day 32)	Chitosan (day 32)	Chitosan + nano-SiO_2 (day 32)
Vitamin C	387.81 ± 15.35^{a}	294.85 ± 10.85^{b}	310.94 ± 11.83^{b}	325.31 ± 14.18^{b}	327.65 ± 11.18^{b}
Total polyphenol	629.08 ± 48.36^{a}	603.86 ± 35.82^{a}	615.46 ± 42.80^{a}	624.31 ± 51.46^{a}	634.64 ± 49.8^{a}
Total flavonoid	90.50 ± 4.35^{a}	64.19 ± 2.85^{b}	55.99 ± 2.58^{bc}	38.16 ± 1.57^{d}	49.60 ± 2.03^{c}

POD, and CAT activities of the jujube coated with the compound film exhibited higher activities (Fig.3), which could efficiently eliminate O^{2-} and H_2O_2. The reason was probably related with the composite coating. Through PAL catalysis, phenylalanine could transform cinnamic acid through deamination. In better circumstance, PAL activity of fresh fruits usually was lower; but in the worse condition, it increased (López-Galvez et al., 1996). Physiological state of uncoated jujube became worse owing to rot and weight loss, so the PAL activity increased. Whereas physiological state of jujube coated with composite film was in better condition, its PAL activity was lower. The result was similar with dipped plums using 1-methylcyclopropene-generating solution by Manganaris et al. (2007).

MDA is originated of cytoplasmic membrane oxidation, and it may indicate the degree of cell consenescence (Long et al., 2006). The MDA content of the jujube coated with the compound film was the lowest (Fig.4), and the reason was probably that higher activities of SOD, POD and CAT could quickly eliminate the free radical. Thus, the harm to the cytoplasmic membrane by the free radical was minimized to the least degree.

Decay incidence of the jujube coated with nano-silicon dioxide alone was higher than that of control during storage time (Fig. 1b). The reason was probably owing to surface effect of nanomaterial. There are many surface atoms in nanomaterial. The electrons of outermost layer were unsaturated in surface atoms, and they were apt to interact with other substance (Hu et al., 2007).There is a natural waxy protective layer in jujube surface. We speculated as followed. The coating composed of single nano-silicon dioxide might interact with the waxy layer, which destroyed the natural protective layer, and thus decay incidence increased. However in composite coating, nano-silicon dioxide might interact with chitosan, and the property of preservation was improved, so the decay incidence was lower than that of control. In addition, higher SOD activity was beneficial to fresh fruit preservation. Coating jujube with nano-silicon dioxide alone probably gave rise to destroy to the natural waxy protective surface, so the SOD activity is lower than that of control at the beginning of storage. But with increase of weight loss of control at the end of storage, the SOD activity of control probably become lower than that of jujube coated with single nano-silicon dioxide(Fig. 2b). The above statement is only a hypothesis, which needs to be verified in the future.

The characteristics of the jujubes coated with chitosan + nano-silicon dioxide were superior to those coated with nano-silicon dioxide or chitosan alone. Such characteristics include the red index, respiration rate, decay incidence, and weight loss. Similar results were observed by Luo and Zhang (2010), who coated freshly cut-asparagus with a compound film of chitosan and SiO_x.

5. Conclusion

After 32 d of storage under ambient temperature, the sample jujube coated with 1% chitosan + 0.04% nano-silicon dioxide showed lower red indices, decay incidence, respiration rate, and weight loss. The related defence enzymes including SOD, POD and CAT in fruits were induced by the compound coating and exhibited the higher activities, while the PAL exhibited the lowest level activity. The MDA increase of coated jujube was restrained and more total flavonoid was preserved. Coating jujubes with chitosan + nano-silicon dioxide will be a promising alternative if nano-silicon dioxide was allowed for food use.

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References

Aider, M., 2010. Chitosan application for active bio-based films production and potential in the food industry: review. LWT-Food Science and Technology 43, 837–842.

Assis, J.S., Maldonado, R., Mun~ oz, T., Escribano, M.I., Merodio, C., 2001. Effect of high carbon dioxide concentration on PAL activity and phenolic contents in ripening cherimoya fruit. Postharvest Biology and Technology 23, 33–39.

Bessey, O.A., King, C.G., 1933. The distribution of vitamin C in plant and animal tissues, and its determination. Journal of Biological Chemistry 103, 687–698.

Bosquez-Molina, E., Ronquillo-de, J.E., Bautista-Ba~nos, S., Verde-Calvo, J.R., Morales-López, J., 2010. Inhibitory effect of essential oils against *Colletotrichum gloeosporioides* and *Rhizopus stolonifer* in stored papaya fruit and their possible application in coatings. Postharvest Biology and Technology 57, 132–137.

Devlieghere, F., Vermeulen, A., Debevere, J., 2004. Chitosan: antimicrobial activity, interactions with food components and applicability as a coating on fruit and vegetables. Food Microbiology 21, 703–714.

Doğan, S., Turan, P., Doğan, M., Arslan, O., Alkan, M., 2007. Variations of peroxidase activity among Salvia species. Journal of Food Engineering 79, 375–382.

García, N.A.T., Iribarne, C., Palma, F., Lluch, C., 2007. Inhibition of the catalase activity from Phaseolus vulgaris and Medicago sativa by sodium chloride. Plant Physiology and Biochemistry 45, 535–541.

Holton, T.A., Cornish, E.C., 1995. Genetics and biochemistry of anthocyanin biosynthesis. Plant Cell 7 (7), 1071–1083.

Hu, G.H., Hoppe, S., Feng, L.F., Fonteix, C., 2007. Nano-scale phenomena and applications in polymer processing. Chemical Engineering Science 62, 3528–3537.

Isamah, G.K., Asagba, S.O., Thomas, A.E., 2000. Lipid peroxidation, o-diphenolase, superoxide dismutase and catalase profile along the three physiological regions of *Dioscorea rotundata* Poir cv Omi. Food Chemistry 69, 1–4.

Jafari, S.M., Assadpoor, E., Bhandari, B., He, Y.H., 2008. Nano-particle encapsulation of fish oil by spray drying. Food Research International 41, 172–183.

Jia, Z.S., Tang, M.C., Wu, J.M., 1999. The determination of flavonoid contents in mulberry and their scavenging effects on superoxide radicals. Food Chemistry 64, 555–559.

Johnston, J.H., Grindrod, J.E., Dodds, M., Schimitschek, K., 2008. Composite nano-structured calcium silicate phase change materials for thermal buffering in food packaging. Current Applied Physics 8, 508–511.

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., 2009. Effect of nano-packing on preservation quality of Chinese jujube (*Ziziphus jujuba* Mill. var. inermis (Bunge) Rehd. Food Chemistry 114, 547–552.

Li, J.W., Fan, L.P., Ding, S.D., Ding, X.L., 2007. Nutritional composition of five cultivars of Chinese jujube. Food Chemistry 103, 454–460.

Lima, Á.M., Cerqueira, M.A., Souza, B.W.S., Santos, E.C.M., Teixeira, J.A., Moreira, R.A., Vicente, A.A., 2010. New edible coatings composed of galactomannans and collagen blends to improve the postharvest quality of fruits -Influence on fruits gas transfer rate. Journal of Food Engineering 97, 101–109.

Lin, B.F., Du, Y.M., Liang, X.Q., Wang, X.Y., Wang, X.H., Yang, J.H., 2011. Effect of chitosan coating on respiratory behavior and quality of stored litchi under ambient temperature. Journal of Food Engineering 102, 94–99.

López-Galvez, G., Saltveit, M., Cantwell, M., 1996. Wound induced phenylalanine ammonia-lyase activity: factors affecting its induction and correlation with the quality of minimally processed lettuces. Postharvest Biology and Technology 9, 223–233.

Long, J.G., Wang, X.M., Gao, H.X., Liu, Z., Liu, C.S., Miao, M.Y., Liu, J.K., 2006. Malonaldehyde acts as a mitochondrial toxin: inhibitory effects on respiratory function and enzyme activities in isolated rat liver mitochondria. Life Sciences 79, 1466–1472.

Luo, Z.S., Zhang, L., 2010. Effect of chitosan/nano-SiOx complex on quality and physiology of fresh-Cut bamboo shoot. Scientia Agricultura Sinica 22, 4694–4700 (in Chinese).

Manganaris, G.A., Vicente, A.R., Crisosto, C.H., Labavitch, J.M., 2007. Effect of dips in a 1-methylcyclopropene-generating solution on 'harrow sun' plums stored under different temperature regimes. Journal of Agricultural Food Chemistry 55, 7015–7020.

Maria, A.R., Maria, S.T., Olga, M., 2008. Using polysaccharide-based edible coatings to maintain quality of fresh-cut Fuji apples. LWT - Food Science and Technology 41, 139–147.

Pirker, K.F., Goodman, B.A., Pascual, E.C., Kiefer, S., Soja, G., Reichenauer, T.G., 2002. Free radicals in the fruit of three strawberry cultivars exposed to drought stress in the field. Plant Physiology and Biochemistry 40, 709–717.

Sánchez-González, L., Pastor, C., Vargas, M., Chiralt, A., González-Martínez, C., Cháfer, M., 2011. Effect of hydroxypropylmethylcellulose and chitosan coatings with and without bergamot essential oil on quality and safety of cold-stored grapes. Postharvest Biology and Technology 60, 57–63.

Saranwong, S., Sornsrivichai, J., Kawano, S., 2004. Prediction of ripe-stage eating quality of mango fruit from its harvest quality measured nondestructively by near infrared spectroscopy. Postharvest Biology and Technology 31, 137–145.

Sun, L.N., Liu, M.C., Zhu, S.H., Zhou, J., Wang, M.L., 2007. Effect of nitric oxide on alcoholic fermentation and qualities of Chinese winter jujube during storage. Agricultural Sciences in China 6 (7), 849–856.

Taira, S., Sahashi, Y., 2009. Nanoparticle-assisted laser desorption/ionization (nano-PALDI) mass spectrometry for food analysis. Journal of Bioscience and Bioengineering 108, S147–S164.

U.S. Food and Drug Adminastration. (2011). Food additive status list. http://www.fda.gov/Food/FoodIngredientsPackaging/FoodAdditives/ucm191033.htm#ftnS.12.

Vu, K.D., Hollingswort, R.G., Leroux, E., Salmieri, S., Lacroix, M., 2011. Development of edible bioactive coating based on modified chitosan for increasing the shelf life of strawberries. Food Research International 44, 198–203.

Wang, Y.F., Tang, F., Xia, J.D., Yu, T., Wang, J., Azhati, R., Zheng, X.D., 2011. A combination of marine yeast and food additive enhances preventive effects on postharvest decay of jujubes (*Zizyphus jujuba*). Food Chemistry 125, 835–840.

Xiao, C.L., Zhu, L.W., Luo, W., Song, X.Y., Deng, Y., 2010. Combined action of pure oxygen pretreatment and chitosan coating incorporated with rosemary extracts on the quality of fresh-cut pears. Food Chemistry 121, 1003–1009.

Xing, Y., Li, X.H., Xu, Q.L., Jiang, Y.H., Yun, J., Li, W.L., 2010. Effects of chitosan-based coating and modified atmosphere packaging (MAP) on browning and shelf life of fresh-cut lotus root (*Nelumbo nucifera* Gaerth). Innovative Food Science and Emerging Technologies 11, 684–689.

Xing, Z.T., Wang, Y.S., Feng, Z.Y., Tan, Q., 2008. Effect of different packaging films on postharvest quality and selected enzyme activities of *Hypsizygus marmoreus* mushrooms. Journal of Agricultural Food Chemistry 56, 11838–11844.

Yang, Z.F., Zheng, Y.H., Cao, S.F., 2009. Effect of high oxygen atmosphere storage on quality, antioxidant enzymes, and DPPH-radical scavenging activity of Chinese bayberry fruit. Journal of Agricultural Food Chemistry 57, 176–181.

Zhao, Y., Tu, K., Su, J., Tu, S.C., Hou, Y.P., Liu, F.J., Zou, X.R., 2009. Heat treatment in combination with antagonistic yeast reduces diseases and elicits the active defense responses in harvested cherry tomato fruit. Journal of Agricultural Food Chemistry 57, 7565–7570.

Zhong, Q.P., Xia, W.S., 2007. Effect of 1-methylcyclopropene and/or chitosan coating treatments on storage life and quality maintenance of Indian jujube fruit. LWT - Food Science and Technology 40, 404–411.

Zhu, S.H., Sun, L., Zhou, J., 2009. Effects of nitric oxide fumigation on phenolic metabolism of postharvest Chinese winter jujube (*Zizyphus jujuba* Mill. cv. Dongzao) in relation to fruit quality. LWT - Food Science and Technology 42, 1009–1014.

Zhu, S.H., Zhou, J., 2007. Effect of nitric oxide on ethylene production in strawberry fruit during storage. Food Chemistry 100, 1517–1522.