

EFFECTS OF ALGINATE EDIBLE COATING ENRICHED WITH SALICYLIC AND OXALIC ACID ON PRESERVING PLUM FRUIT (*Prunus salicina* L. cv. 'BLACK AMBER') QUALITY DURING POSTHARVEST STORAGE

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ABSTRACT

The effect of alginate treatments with or without salicylic and oxalic acid as post-harvest coating in extending the postharvest life of plums (*Prunus salicina* L. cv. 'Black amber') and maintaining their quality were investigated. Plums were treated with 2% alginate coating with or without salicylic (1.0 mM) and oxalic acid (1.0 mM), and then stored at 0–1°C and 90 ±5% relative humidity for 40 days. The quality of plums was assessed at 10-day intervals by evaluating the following quality parameters: weight loss, soluble solids content, titratable acidity, firmness, respiration rate, ascorbic acid content, total anthocyanin content, total phenolic content and antioxidant activity. The respiration rate, weight loss and changes in quality parameters were much lower in coated plums as compared with the control. Alginate coating resulted in a significant reduction in weight loss of fruits. Alginate treatments with or without salicylic and oxalic acid were effective on delaying the evolution of parameters related to postharvest ripening, such as soluble solids content, softening and reducing respiration rate. At the end of the storage period, the edible coatings showed a positive effect on maintaining higher concentration of total phenolics, total anthocyanin content and antioxidant activity, which decreased in control plums as a result of over-ripening and senescence processes. The results suggested that the use of alginate enriched with salicylic acid could maintain considerably higher quality of fruits and level of bioactive compounds than other coating treatments during 40 days of storage at 0–1°C.

Key words: plum, edible coating, alginate, quality assurance, cold storage

INTRODUCTION

Plums are one of the most significant commercially produced stone fruit and are among the favorite fruits of the consumer in Turkey [Ozturk et al. 2012]. In order to reach the market with high quality fruit, it would be necessary to identify factors affecting the biochemical changes occurring during plum storage and ripening, such as the production of characteristic volatiles and aroma compounds, accumulation of anthocyanins leading to color development, reduction in fruit acidity and changes in the cell walls contributing to softening, and then to implement technologies to control these modifications [Manganaris et al. 2008].

Low-temperature storage is recommended to delay ripening and maintain plum quality. Depending on the cultivar, plums may only have a commercial life of 2–6 weeks even when stored at 0°C [Crisosto et al. 2004]. However, when the fruit is held for a long period at low temperatures, it may lead to the development of chilling injury symptoms manifested by flesh translucency and internal breakdown, which leads to loss of quality and reduction in consumer acceptability [Manganaris et al. 2008].

Various technologies have been developed for plum preservation, such as low temperature storage, modified

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atmosphere packaging, edible coatings and treatment with chemical agents such as 1-methylcyclopropene, salicylic acid and oxalic acid have been attempted [Wu et al. 2011, Bal 2013, Valero et al. 2013].

Edible coatings can be applied to the exterior of horticultural products to improve the safety and quality of fruits. Coatings protect them from deterioration by slowing a gas exchange, moisture, reducing or even suppressing physiological disorders, reducing respiration and oxidative reaction rates [Rojas-Grau et al. 2009], retaining volatile compounds, improving texture, and preserving nutritional value though limiting gas and water vapor exchanges between fruit and the surrounding atmosphere [Vargas et al. 2008].

Alginate can be considered a food material with good potential to be used as a coating, due to its peculiarity to form strong gels with metal cations, creating thick aqueous solutions [Roopa and Bhattacharya 2008]. Alginate-based edible coatings have been used effectively for extending the postharvest storage of fruit and vegetables such as tomato [Zapata et al. 2008], longan [Jiang et al. 2001], peach [Maftoonazad et al. 2008], strawberry [Fan et al. 2009], sweet cherry [Diaz-Mula et al. 2012, Koçak and Bal 2017], raspberry [Guerreiro et al. 2015] and table grapes [Takma and Korel 2017].

Moreover, incorporation of bioactive compounds such as antimicrobial agents, antioxidants, aroma compounds, nutraceuticals, and probiotics into the edible coatings represents an innovative concept [Huber and Embuscado 2009].

Salicylic acid (SA) and oxalic acid (OA) are metabolic products in plants and potentially effective agents to induce resistance in fruits. They might play important roles in induction of plant defense against a variety of biotic and abiotic stresses through morphological, physiological and biochemical mechanisms [Kim et al. 2008]. Moreover, postharvest application of exogenous SA and OA at non-toxic concentration to fruits has been shown to be effective in retarding the ripening and increasing the shelf-life of fruits like peach [Khademi and Ershadi 2013], plum [Wu et al. 2011], kiwifruit [Zhang et al. 2003, Bal and Celik 2010], cherry [Dokhanieh et al. 2013], nectarine [Bal 2016] and loquat [Öz et al. 2016].

This study evaluated the effects of alginate-based edible coatings enriched with SA and OA on biochem-

ical properties and postharvest quality of 'Black amber' plum during cold storage.

MATERIALS AND METHODS

Materials. Plums (*Prunus salicina* Lindley, cv. 'Black amber') were harvested at a pre-climacteric stage (ready-to-ripe, flesh firmness of ~40 N) from a commercial orchard in Kırklareli (Turkey) and transported immediately to the laboratory, where they were selected for the uniformity of shape, color and size. Any blemished or diseased plums were discarded.

Preparation and application coatings. The experiments were conducted to evaluate the effects of emulsions of alginate alone and alginate emulsion loaded with SA or OA on quality of the plums kept at cold storage.

Alginate solution (alginic acid sodium salt from brown algae purchased from Sigma, Madrid, Spain) was prepared at 2% concentration (w/v) dissolved in hot water (45°C) with continuous shaking until the solution became clear. After cooling to 20°C, glycerol at 2% v/v was added as plasticizer [Zapata et al. 2008].

To prepare the alginate emulsion (2%) loaded with SA (1.0 mM) or OA (1.0 mM), first SA or OA solution was prepared using a magnetic stirrer hot plate at 50°C for two hours followed by addition of alginate solution and Tween-20 (0.25%) as a surfactant. All treatments were performed by dipping the fruits twice in fresh coating solution for 1 min to assure the uniformity of the coating of the whole surface. Control fruits were dipped in distilled water (20°C). After dipping, fruits were dried for 30 min under air-flow heater at 25°C.

Coating treated fruits together with controls were placed in polypropylene baskets (2 kg) and stored at 0–1°C and 90 ±5% relative humidity for 40 days. Plums were evaluated by analyzing the physicochemical and biochemical traits using the following parameters at 0 day and at a regular interval of 10 days until the end of storage period of 40 days.

Analysis of quality attributes. Weight loss during storage was determined by measuring the fruit weight before and after the storage period and was expressed as the percentage of weight loss with respect to the initial weight. Flesh firmness was determined using a hand-held penetrometer with an 8-mm-long measuring plunger on the pared equatorial surface on 3 sides

of the fruit and was expressed as Newton (N). Soluble solids content (SSC) was determined with a hand refractometer (%). Titratable acidity (TA) was determined by titrating method and calculating the result as grams of malic acid per 100 g fresh weight (%). During each analysis period, 15 fruits from each replication for each treatment (45 fruits) were sampled for firmness, SSC and TA determinations.

Ascorbic acid content was measured using 2,6-dichloroindophenol method described by AOAC [1990] and expressed as mg 100 g⁻¹.

The anthocyanin content was determined by using pH differential method and expressed as milligrams of cyanidin-3-glucoside equivalent per kilogram of fresh weight (mg kg⁻¹) [Wrolstad et al. 2005]. Folin-Ciocalteu reagent method was used to determine the total phenol content of plums as mg gallic acid equivalent 100 g⁻¹ [Slinkard and Singleton 1977].

The antioxidant activity was evaluated by 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical-scavenging method as described by Brand-Williams et al. [1995] and was expressed as μmol Trolox equivalent (TE) g⁻¹ f.w.

Respiration rate in plums was recorded in the headspace of the container using an auto gas analyzer (Systech Gaspac advance GS3L). The individual fruit was enclosed in a hermetic container for 30 min (stored at 1°C and 90% RH) and from the headspace gas, concentration of CO₂ was measured by piercing the probe of auto gas analyzer in the container through the septa fixed on the lid of container and direct reading was noted from instrument screen. The CO₂ evolution was calculated in ml of CO₂ kg⁻¹ h⁻¹ using formula [Demirdoven and Batu 2004].

The experiment was of a completely randomized factorial design of three replications with two kilogram of fruit per plot (totally 120 kg). Analysis of variance (ANOVA) was the means for analyzing the difference between means, while LSD test being applied for mean separation at $p < 0.05$. All analyses were carried out through SPSS as statistical software. Results are reflected as the mean ± SE.

RESULTS AND DISCUSSION

The water content of fruits and vegetables is a major factor in maintaining the quality of horticultural

product. During storage period, fresh fruits and vegetables lose weight normally due to respiratory process and transpiration [Maftoonazad et al. 2008]. Figure 1 shows the percentage of weight loss as a function of storage time in coated and uncoated plums. The alginate significantly reduced the weight loss of the plum during storage compared to the control. Edible coatings act as an extra layer, which also coats the stomata leading to a decrease in transpiration and in turn, to a reduction in weight loss of fruits [Guerreiro et al. 2015]. Moreover, differences in the ability to reduce weight loss are attributed to different water vapor permeability of the edible coatings [Vargas et al. 2008]. The control treatment presented higher losses over the time reaching 9.2% after 40 days of storage. Alginate alone (3.8%), alginate coating with SA (3.5%) and with OA (5.2%) treatments could significantly restrict the weight loss up to 40th day of storage period. Nunes and Emond [2007] reported that weight loss up to 4–5% does not significantly affect the fruit freshness and consequently consumer acceptance. In our experiment, weight loss was within this range for up to 40 days, except for control. Alginate coatings reduced the respiration rate by forming a semipermeable barrier against water vapors and consequently retarded dehydration. In previous studies, reduction in weight loss by alginate coating was also demonstrated in fruit and vegetables including plum [Valero et al. 2013], tomato [Zapata et al. 2008], grape [Takma and Korel 2017], longan [Jiang et al. 2001], sweet cherry [Koçak and Bal 2017] and strawberry [Fan et al. 2009].

SSC content is directly related to taste and aroma of plums and should be acceptable for consumers. The data indicated that SSC increased significantly during storage for all treatments (Fig. 2). The increase in SSC observed in all samples is probably due to continuation of fruit maturation. However, all coating treatments significantly delayed the increase in SSC as compared to non-coated fruits (15.1%) at 40th day. The lower accumulation of SSC in the coated fruit may be due to the barrier of coating, which reduces the rate of respiration by preventing the gaseous exchange. As suggested by Ali et al. [2011] and Rao et al. [2016], slower respiration can lead to the delayed synthesis and use of metabolites resulting in lower SSC. Moreover, greater changes in SSC occurred in uncoated plums that suffered from greatest water loss.

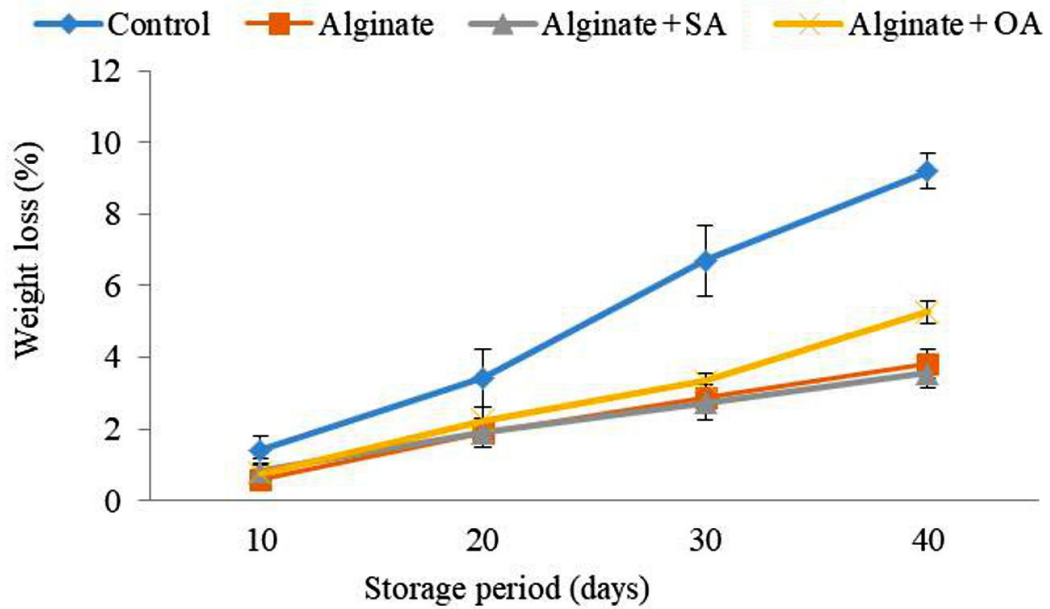


Fig. 1. Effect of alginate coatings on weight loss of plums during storage period

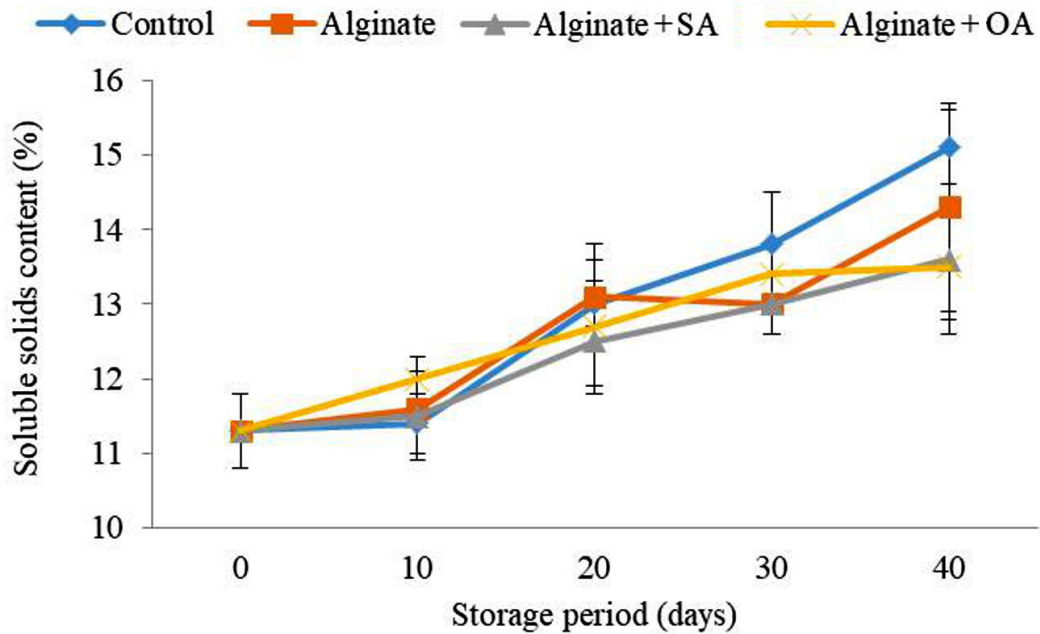


Fig. 2. Effect of alginate coatings on SSC of plums during storage period

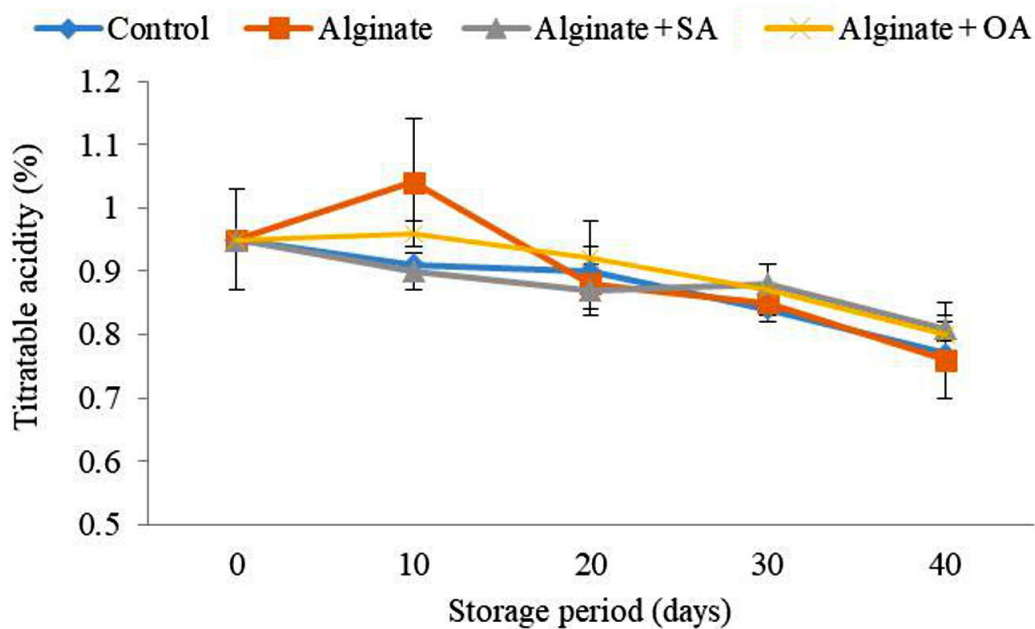


Fig. 3. Effect of alginate coatings on TA content of plums during storage period

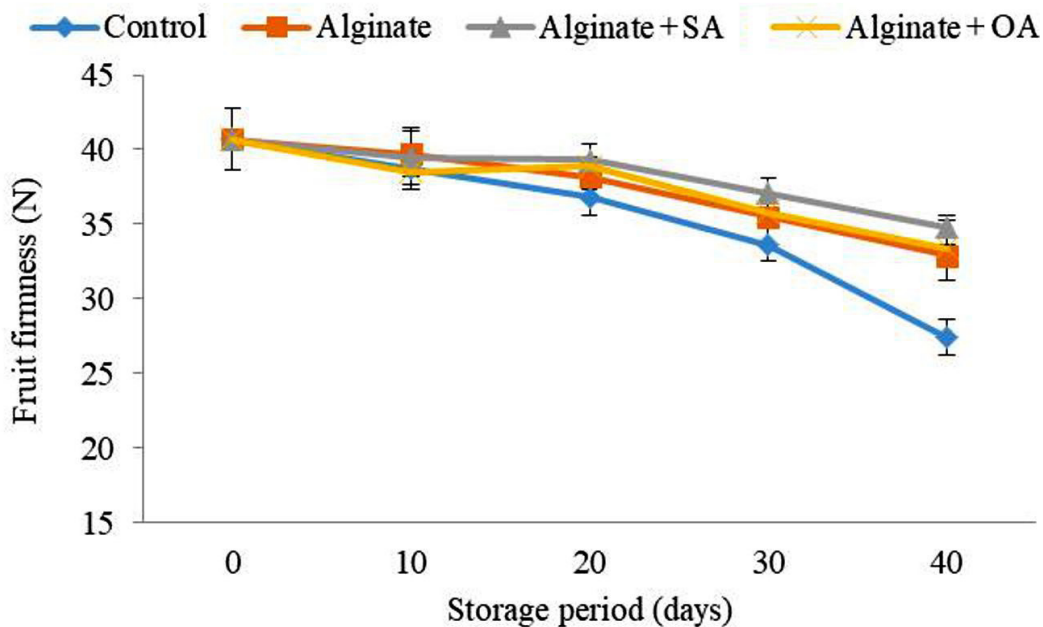


Fig. 4. Effect of alginate coatings on fruit firmness of plums during storage period

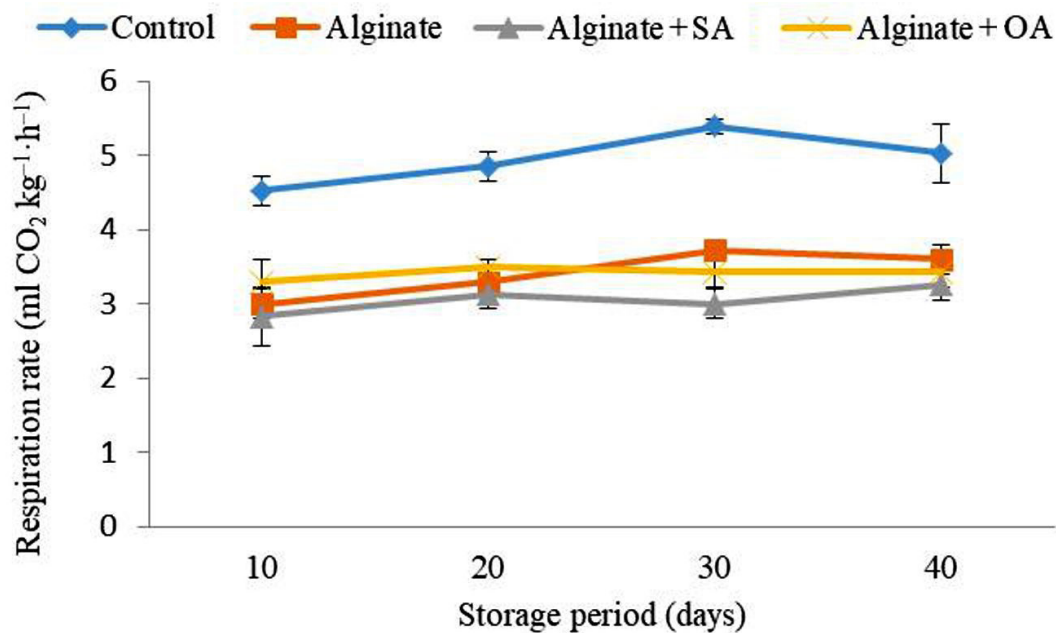


Fig. 5. Effect of alginate coatings on respiration rate of plums during storage period

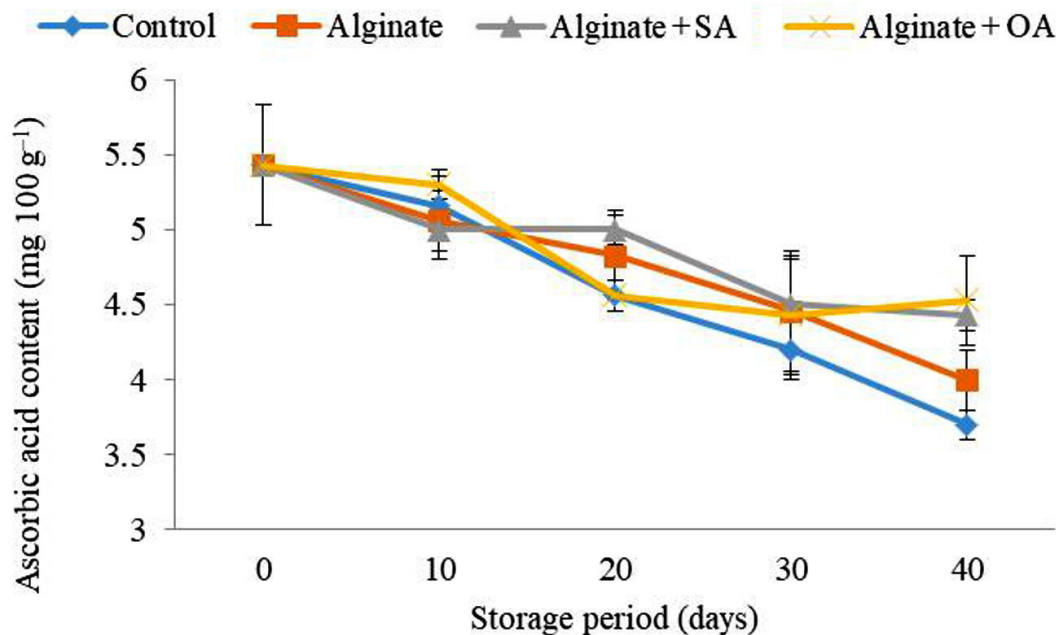


Fig. 6. Effect of alginate coatings on ascorbic acid content of plums during storage period

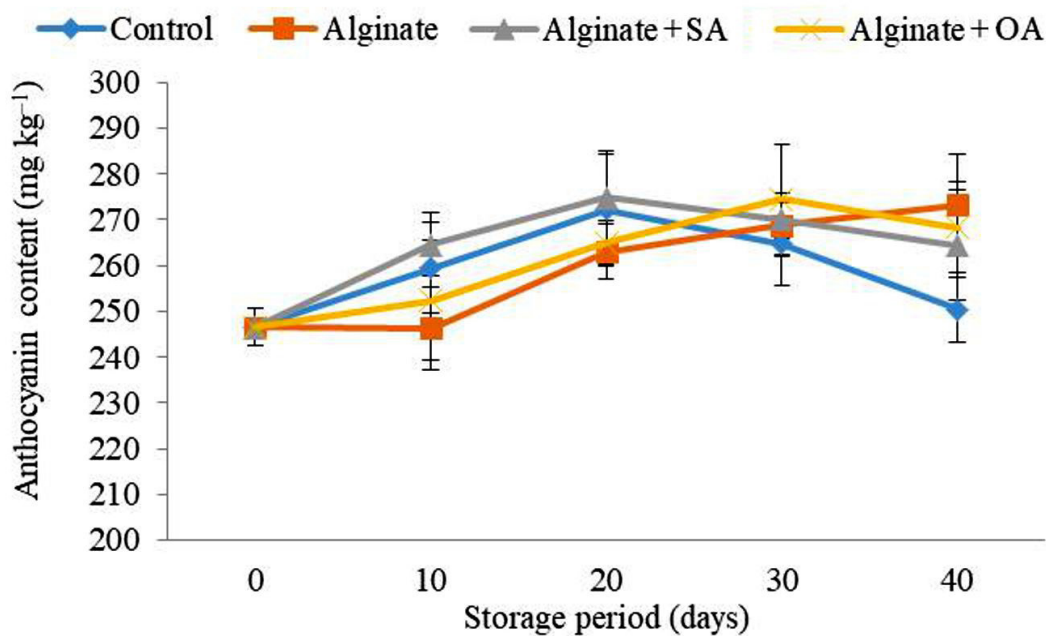


Fig. 7. Effect of alginate coatings on anthocyanin content of plums during storage period

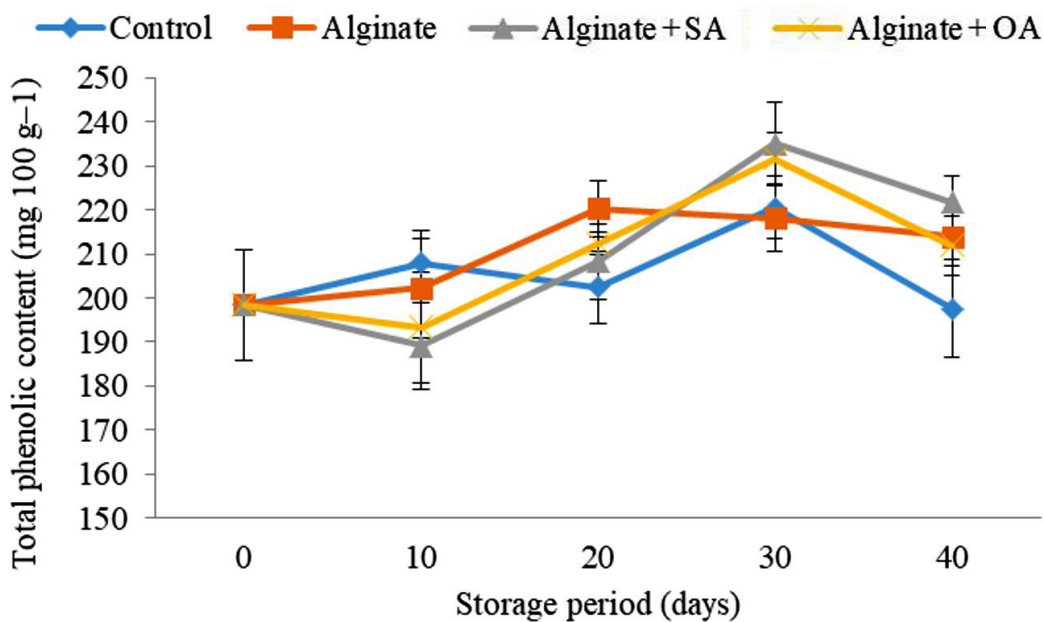


Fig. 8. Effect of alginate coatings on total phenolic content of plums during storage period

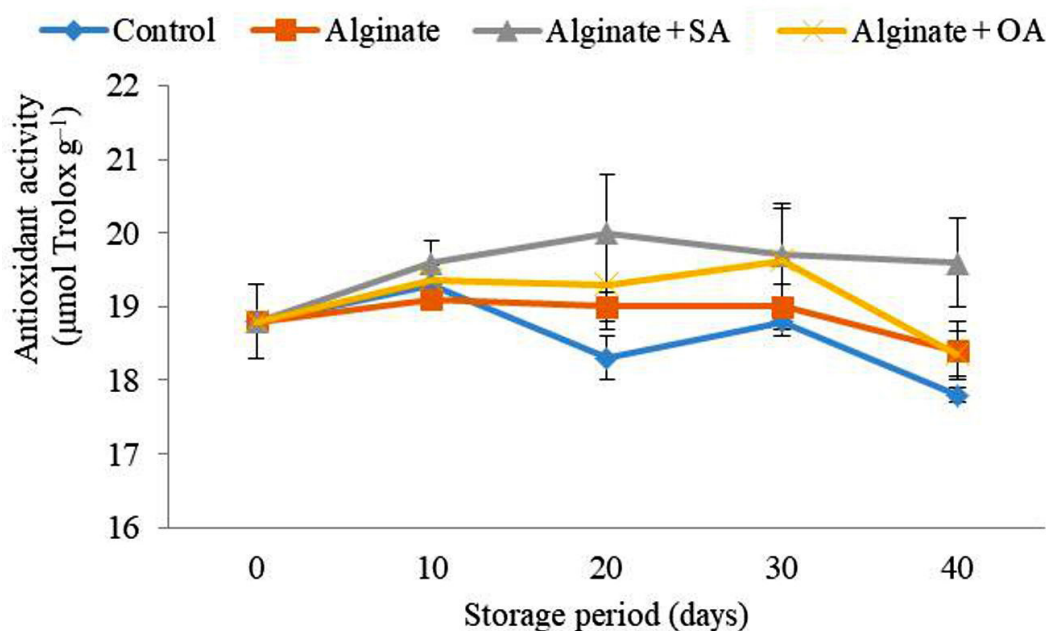


Fig. 9. Effect of alginate coatings on antioxidant activity of plums during storage period

Alginate + SA and alginate + OA treated samples exhibited similar SSC values and fruit coated with SA (13.6%) and OA (13.5%) resulted in lowest mean SSC at the end of the storage. The slower rates of increase in SSC values indicated that SA and OA delayed the ripening process of plums. These results are also in agreement with previous reports on kiwifruit [Zhang et al. 2003, Bal and Celik 2010], peach [Khademi and Ershadi 2013], pomegranate [Sayyari et al. 2009] and loquat [Öz et al. 2016].

In the study, it was found that there were no statistically significant differences among the treatments and TA decreased slightly with extended storage in all treatments (Fig. 3). It is known that similar TA losses in plum occurred in many postharvest studies [Bal 2013, Valero et al. 2013, Kumar et al. 2017]. This could be due to utilization of acid for the respiratory process or by its conversion into sugars and salts. At the beginning of storage, TA of plums amounted to 0.95%. After 40 days of storage, TA content was 0.76%, 0.77%, 0.81% and 0.8% in the control, alginate, alginate + SA and alginate + OA treatments, respectively.

Firmness is an external quality parameter for plums; however, it is associated with internal quali-

ty properties, such as eating quality, flesh color, and sugar content [Usenik et al. 2014]. A significant reducing trend was found regarding flesh firmness during storage time, as analysis of data indicated in Figure 4. Softening is generally with the dissolution of pectin, involving many enzyme actions including pectin-esterase, polygalacturonase and pectate lyases [White 2002]. The results indicated that alginate coatings exerted a beneficial effect on fruit firmness such that by the end of the storage period, all treatments gave rise to fruit with higher fruit firmness values than untreated fruit. The initial firmness of fruit was about 40.7 N. At the end of storage, alginate coatings alone (32.9 N), alginate coatings loaded with SA (34.8 N) and OA (33.4 N) treated fruits had similar fruit firmness values, while a significant decrease in control fruit firmness (27.4 N) was noted after 40 days of storage. The retention of firmness with alginate coating is in agreement with the results of Valero et al. [2013], where four plum cultivars treated with 1% or 3% alginate coating were firmer than the control during 40 days storage. Fruit softening is due to deterioration in the cell structure, the cell wall composition and the intracellular materials [Seymour et al. 1993]. Reduc-

tion in firmness loss by alginate coating could be explained by minimizing respiration and weight losses through coating application that has been reported in apples [Olivas et al. 2007], mango [Liu et al. 2014] and strawberry [Petriccione et al. 2015] by different edible coatings.

Respiration rate is a main indicator of metabolic activity and gives a signal of the possible shelf-life of the horticultural product. In the study, compared to the non-coated samples, the alginate-coated plums showed significantly reduced respiration rate during storage period (Fig. 5), which might be due to barrier properties of the alginate coating. These results match those observed in earlier studies that respiration rate suppressed by alginate coating in tomato [Zapata et al. 2008], peach [Maftoonazad et al. 2008], fresh-cut apple [Chiabrande and Giacalone 2014], raspberry [Guerreiro et al. 2015] and sweet cherry [Koçak and Bal 2017]. The results indicated that it was significantly higher over storage time in control fruits. At the end of 40 days cold storage, the highest respiration rate was recorded in control ($5.0 \text{ ml CO}_2 \text{ kg}^{-1} \text{ h}^{-1}$), while lowest respiration rate was recorded respectively in alginate + SA ($3.2 \text{ ml CO}_2 \text{ kg}^{-1} \text{ h}^{-1}$), alginate + OA ($3.4 \text{ ml CO}_2 \text{ kg}^{-1} \text{ h}^{-1}$) and alginate ($3.6 \text{ ml CO}_2 \text{ kg}^{-1} \text{ h}^{-1}$) treatments. These results indicate that coating treatment generates a semi-permeable barrier that modifies the levels of endogenous respiratory gases, which delays the senescence and increase the storage life of plums. Moreover, the tendency of higher water loss of uncoated plum was accompanied with the increase of respiration rate during cold storage. The similar results had been reported by Meighani et al. [2015].

Data obtained for ascorbic acid revealed that ascorbic acid content of plum was the highest at zero days of storage ($5.4 \text{ mg } 100 \text{ g}^{-1}$) and it decreased with the advancement of storage period (Fig. 6). This could be due to occurrence of ripening process in the fruits followed by senescence. Jiang et al. [2001] stated that, the ascorbic acid decreased during storage period, which was consistent with decline in eating quality. Until the 40th day, there was no significant difference between the treatments. However, at 40th day, alginate + OA ($4.5 \text{ mg } 100 \text{ g}^{-1}$) treatment and alginate + SA treatment ($4.4 \text{ mg } 100 \text{ g}^{-1}$) had the highest level of ascorbic acid while control ($3.7 \text{ mg } 100 \text{ g}^{-1}$) had the lowest level. These results showed that loading with OA

and SA treatments had a significant effect on retaining ascorbic acid content in plum. The influence of oxalic acid and salicylic acid might be due to decreased or delayed ascorbate oxidase activity. Ascorbic acid is lost due to the activities of phenoloxidase and ascorbic acid oxidase enzymes during storage [Salunkhe et al. 1991]. Findings of Sayyari et al. [2009] and Kazemi et al. [2011] support these results, where an increased ascorbic acid in pomegranate and apple fruits were reported by the application of OA and SA during storage.

Black amber has a black skin color mainly due to anthocyanins. Changes of anthocyanins in fruit skin was recorded in coated and control fruits over cold storage time (Fig. 7). Total anthocyanins content of plums was 413 mg kg^{-1} at the time of initial storage. In general, anthocyanin content of plums tended to increase during storage even though there were fluctuations in anthocyanins content. Postharvest increases in anthocyanin have been previously reported for plums and other small red fruits like cherries and strawberries [Serrano et al. 2009, Diaz-Mula et al. 2012, Valero et al. 2013]. The highest total anthocyanins content (274.9 mg kg^{-1}) was recorded in alginate + SA treatment after 20 days storage, but the lowest value (250.4 mg kg^{-1}) was found in control fruits after 40-day storage. Towards the end of the storage period, loss of anthocyanin in control fruits was accelerated due to increased weight loss and skin shriveling. On 40th day, the highest anthocyanins content was recorded in alginate treatment (273.2 mg kg^{-1}), followed by alginate + OA treatment (268.4 mg kg^{-1}) and alginate + SA treatment (264.5 mg kg^{-1}). Fruit coating treatments significantly maintained higher total anthocyanins content than control at the end of storage time. The inhibition of anthocyanin accumulation by coating treatments is consistent with the retard of fruit reddening. These results are in agreement with Martinez-Romero et al. [2017] and Kumar et al. [2017], who reported that aloe vera and chitosan coating in plums could delay the postharvest ripening process and slow down the anthocyanin synthesis.

Phenolic compounds are secondary metabolites contributing for the color and sensory characteristics of fruits and vegetables. In the study, the changes in total phenol content over the postharvest period were also similar in trend to those for anthocyanin content. The phenolic compounds of plums during the cold

storage period are presented in Figure 8. Total phenolic content in plums was $198.4 \text{ mg } 100 \text{ g}^{-1}$ at harvest. In all treatments, there was an increase in total phenols initially, followed by a gradual decline being more pronounced in control fruits during storage period. This could be due to the occurrence of ripening process in the fruits followed by senescence. During storage period, the highest total phenol content ($235.1 \text{ mg } 100 \text{ g}^{-1}$) was recorded in alginate + SA treatment on 30th day. The use of alginate loaded with SA showed as a positive effect in maintaining higher concentration of total phenolics. Davarynejad et al. [2015] also reported that SA postharvest treatment on plum plum led to maintenance of higher total phenolic content during storage with respect to control fruits. Similar results with previous work on various fruits such as pomegranate [Sayyari et al. 2009], cherry [Dokhanieh et al. 2013], grape [Champa et al. 2015] and peach [Razavi et al. 2014] have been reported, where SA treatment increased phenol content during storage period. After 40 days of storage, plum coated with alginate alone ($214 \text{ mg } 100 \text{ g}^{-1}$) and alginate loaded with SA ($221.8 \text{ mg } 100 \text{ g}^{-1}$) and OA ($212 \text{ mg } 100 \text{ g}^{-1}$) exhibited the highest levels of total phenols content as compared to control ($197.6 \text{ mg } 100 \text{ g}^{-1}$). The more rapid decline in the TP content in control may be attributed to its higher respiration rate resulting in the breakdown of total phenols [Ali et al. 2011, Naira et al. 2018].

Antioxidant activity is an important quality factor promoting health in food and plum is also a source of flavonoids and phenolic acids with a strong antioxidant capacity [Vinson et al. 2001]. At the beginning of the experiment, antioxidant activity was $18.8 \text{ } \mu\text{mol g}^{-1}$ (Fig. 9). In general, antioxidant activity increased initially followed by a progressive decline with the increase in storage duration. However, this decline was more pronounced in non-coated fruit. Aloui et al. [2014] reported restriction in the loss of AOA in case of table grapes coated with 2% alginate enriched with grape seed extract as compared to the control. Similarly, Wang and Gao [2013] and Kumar et al. [2017] reported that the fruits coated with chitosan maintained higher levels of antioxidant activity than non-coated fruits. The highest antioxidant activity ($20 \text{ } \mu\text{mol g}^{-1}$) was recorded in alginate + SA treatment after 20 days storage, but the lowest value ($17.8 \text{ } \mu\text{mol g}^{-1}$) was found in control fruits after 40 days cold storage. Results also

showed that antioxidant activity changes are parallel to phenolics, during postharvest storage. In previous researches, the positive correlation between antioxidant activity and total phenolics has been reported [Ghasemnezhad et al. 2010, Diaz-Mula et al. 2012]. On the 40th day, the highest antioxidant activity was observed in alginate + SA treatment ($19.6 \text{ } \mu\text{mol g}^{-1}$), followed by alginate ($18.4 \text{ } \mu\text{mol g}^{-1}$) and alginate + OA ($18.3 \text{ } \mu\text{mol g}^{-1}$) treatments. Among the treatments, coating with alginate + SA was the most effective in maintaining antioxidant activity. This benefit can be attributed to SA added to the coating. Davarynejad et al. [2015] and Bal [2016] also found that SA has the capacity of increasing antioxidant – the result that confirms the present study. It has also been reported in different studies that the application of alginate combined with the synergic effect of some preservatives has contributed to preserving the level of antioxidants [Guerreiro et al. 2015, Rao et al. 2016].

CONCLUSIONS

Results of the present study indicate that alginate coating alone and alginate coating with SA or OA treatments have significant beneficial impact on reducing the weight loss and delaying the changes of respiration rate. In uncoated fruits, weight loss at high levels was determined. Alginate edible coating enriched with SA treatment is a more effective way to retard postharvest plum ripening process demonstrated by reducing many physiological changes, for example: firmness, SSC and TA, as well as maintaining higher phytochemicals, including ascorbic acid, total phenolics and antioxidant activity. In conclusion, alginate coating treatment combined with SA showed promising results for maintaining 'Black amber' plums quality and extending storage life at $0-1^{\circ}\text{C}$ for 40 days.

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