

## The Effect of Tragacanth Edible Coating Containing $\alpha$ -Tocopherol on the Chemical and Sensory Properties of Roasted Pistachio Nuts During Storage

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Information	Abstract
<p><b>Article Type:</b> Original Article</p> <p><b>Article History:</b> Received: 12.02.2020 Accepted: 05.05.2020 DOI:10.22123/phj.2021.261235.1065</p> <p><b>Keywords:</b> Edible Coating Pistachio Nuts <math>\alpha</math>-Tocopherol Nanocapsule Spontaneous Emulsification Storage</p> <p><b>Corresponding Author:</b> Ali Dini Email: a.dini@rums.ac.ir Tel: +98-3434282703-5</p>	<p><b>Introduction:</b> Pistachio nuts are considered a functional foodstuff containing various antioxidants consumed mostly in a roasted form. Mild to severe roasting conditions can cause oil oxidation. Therefore, different methods, such as coating, are used to increase the shelf life of nuts.</p> <p><b>Materials and Methods:</b> Tragacanth-based edible coatings were prepared using propylene glycol as a plasticizer both individually and in combination with free <math>\alpha</math> tocopherol (FT), or its Nanocapsules (NC) and Nanoesphers (NS). Chemical and sensory properties of coated pistachio nuts were measured during 6-month storage at 40, 50, and 60°C.</p> <p><b>Results:</b> At storage temperatures of 40, 50, and 60°C, PV and Pa.V were evaluated 3.92, 3.85, 7.1 and 6.89, 13.3, 21.1 meq/kg, respectively. Unlike acidic value, coating with tragacanth caused a significant reduction in PV and Pa.V indices as they did not exceed 4 and 6, respectively. Sensory evaluation showed the overall acceptance of uncoated roasted pistachios to be lower than average after 120 and 60 days of storage at 50 and 60°C, respectively. Thus, the anisidine value was measured in the range of 2.9-5.6. No significant difference was observed in oxidation indices and sensory properties of coated samples with different forms of <math>\alpha</math>-tocopherol.</p> <p><b>Conclusion:</b> Using nanoparticle forms of <math>\alpha</math>-tocopherol in coating reduced the oxidation rate and improved overall acceptance during storage. There was a correlation between the chemical markers of oxidation and sensory properties of roasted pistachio nuts, and p-anisidine value was appropriate to monitor pistachio nuts' oxidative during shelf-life.</p>

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## 1. Introduction

Pistachio nuts are produced in different regions across the world, especially in Iran, the USA, and Turkey, at 600 to 800 thousand tons per year [1, 2]. It is used in many food products and plays a key role in the human diet due to phytochemicals [3]. Also, pistachio nuts contain 45- 65% oil, a large amount of which is made of unsaturated fatty acids (USFAs) [4]. This makes pistachios and heated pistachio products, such as roasted pistachios, so sensitive to lipid oxidation. However, the roasting process improves the sensory and textural properties of nuts due to physicochemical reactions, increasing the product marketability and possibility for consumption [5]. Mild to severe roasting can cause partial or extensive destruction of cell structure in the nuts, leading to the destruction of oleosomes and the release of oil in the oilseed tissues [6]. As a result, the oil resistance to oxidation and storage decreases [7].

Oxygen concentration is an instrumental factor among many others, including light, water activity ( $a_w$ ), fat content and composition, temperature, and relative humidity (RH) in the oxidation of oilseeds [8]. It could be reduced using different methods, such as vacuum packaging, modified atmosphere packaging [9, 10], active packaging containing oxygen adsorbent nanoparticles

[11], anti-oxidation active packaging [12], and an edible coating[13], leading to the extended shelf life of raw and processed oilseeds. Among these methods, the edible coating creates a protective barrier and a semi-permeable membrane against oxygen and carbon dioxide, as well as formatting a glossy surface with a favorable appearance, preventing the passage of moisture to the surface of the food and vice versa and preserving tissue properties during storage [14, 15]. Lipid oxidation in pistachio nuts may be prevented using effective barriers such as active edible coatings, isolating the nuts from atmospheric oxygen. Active edible coatings can contain the internal atmosphere of the foods if they have low gas permeability, as well as gradually releasing the active component such as antioxidants and antimicrobial agents on the food surface [16, 17]. Several factors, including coating composition, integrity, storage temperature, and relative humidity, may contribute to these coatings' capability to act as gas barriers and prevent oxidation [17, 18].

Active packaging is one of the initiatives over the last decade in the food packaging industry, increasing the food shelf life and improving its quality due to the packaging-food interaction. Antioxidants, as a food additive, have been used to prevent the oxidation of fats and the return of flavor, increasing storage in

combination with films and coatings [17]. Jongjareonrak et al. (2008) added 200 ppm of  $\alpha$ -tocopherol and BHT to the gelatin film extracted from fish skin; they could reduce oxidation over time [19]. In 2013, Abdolhaq et al. studied the effect of edible coating containing CMC and Cordia gum in increasing storage and reducing the rate of Chilgoza nut oxidation. Their research showed that using  $\alpha$ -tocopherol as a normal emulsion in glycerol as a plasticizer had a significant effect on reducing the oxidation rate, with the highest oxidation rate in the coated sample containing  $\alpha$ -tocopherol. Uncoated samples had a slower oxidation rate than the coated ones containing  $\alpha$ -tocopherol. The researchers attributed this to the prooxidating effects of  $\alpha$ -tocopherol due to its uncontrolled release on chilgoza's surface [13]. Therefore, ensuring proper and adequate release is essential to maximize antioxidant effects in active packaging [20]. For this purpose, Neurons et al. (2014) converted  $\alpha$ -tocopherol to nanocapsules for controlled release and used it in methylcellulose film [21].

Nanotechnology has opened a new chapter in food preservation, significantly impacting the food process, production, storage, and preservation. Studies on nanotechnology in the food industry have focused on developing new packaging materials, dietary supplements, and

antibacterial agents; thus, little is known about the technology's impact on food preservation and storage [22, 23]. Nanoparticles are defined as colloidal particles (100- 600 nm) produced using high- and low-energy methods. Mechanical devices, such as high-shear stirrers, high-pressure homogenizers, and ultrasound generators, have been applied in the high-energy method as cost-inefficient since a small amount of energy (0.1%) is consumed for emulsification, and the rest is used to excite the basis medium so that force is conveyed to droplets.

The low-energy approach relies on the spontaneous formation of oil droplets within mixed oil-water emulsifier systems when the solution or environmental conditions are changed as in phase inversion and solvent demixing methods. Despite greater oil to surfactant ratio in high-energy method, in that of low-energy, generally, membrane thickness control and smaller droplet size are produced. Furthermore, it is more energy-efficient compared to the high-energy approach. This study aims to add various forms of  $\alpha$ -tocopherol (FT, NC, and NS) to tragacanth-based edible coatings and investigate the effect of coating with/without antioxidants on the chemical and sensory properties of roasted pistachio nuts during 6-month storage at 40, 50, and 60°C temperature.

## 2. Materials and Methods

Polycaprolactone (PCL), pluronF68, ferrous sulfate, and ferric chloride were purchased from Tetrakam, Iran. Solvents of acetone, glacial acetic acid, methanol, hydrochloric acid, ethanol, chloroform, isooctane and chemical materials of ammonium thiocyanate, barium chloride dehydrated, p-anisidine, and phenolphthalein were prepared from Merck, Germany. Tragacanth gum was purchased from Sigma, the USA.

### Preparation of NC and NS

First,  $\alpha$ -tocopherol nanoparticles were prepared according to the method of Zambrano et al. [24] as follows, which is schematically shown in Figure 1.

The technique for creating self-emulsification has three stages:

a- Preparation of homogeneous organic solution composed of  $\alpha$ -tocopherol (400 mg) and lipophilic surfactant (PCL, 150 mg for NC or 300 mg for NS) in water-miscible solvent (40 ml acetone); The homogeneous aqueous phase was formed by deionized water (80 ml) and hydrophilic surfactant (136 mg pluronF68).

b- The organic phase was added gently to the aqueous phase under magnetic stirring (SMHS, Witeg, Germany). The NS

or NC was spontaneously formed by diffusion of organic solvent in the external aqueous phase, resulting in the formation of nanodroplets. The magnetic stirring was continued for about half an hour to obtain equilibrium in the system.

c- The totality of water-miscible solvent was removed by evaporation (Buchi Rotavapor, Type-R-114A29 B-480, Switzerland) at 45 °C over 40 min under reduced pressure. Microdroplets of  $\alpha$  tocopherol were dispersed in an aqueous solution of water and hydrophilic surfactant.

### Preparation of tragacanth-based edible coating with/without $\alpha$ -tocopherol

1 g of polypropylene glycol (with or without 200 mg of alpha-tocopherol) was weighed to a 1-liter volumetric vessel, bringing to volume using distilled water. Then, 5 g of tragacanth gum was slowly added to the solution under stirring for 20 minutes until being fully hydrated. The pistachios, roasted using hot air method at 135 °C, 0.6 m/s for 20 minutes, were immersed in the coating solution for 5 minutes. Then, excess coatings were removed by rinsing for 5 minutes and the coated samples were dried by hot air flow at 40 °C for 2 hours.

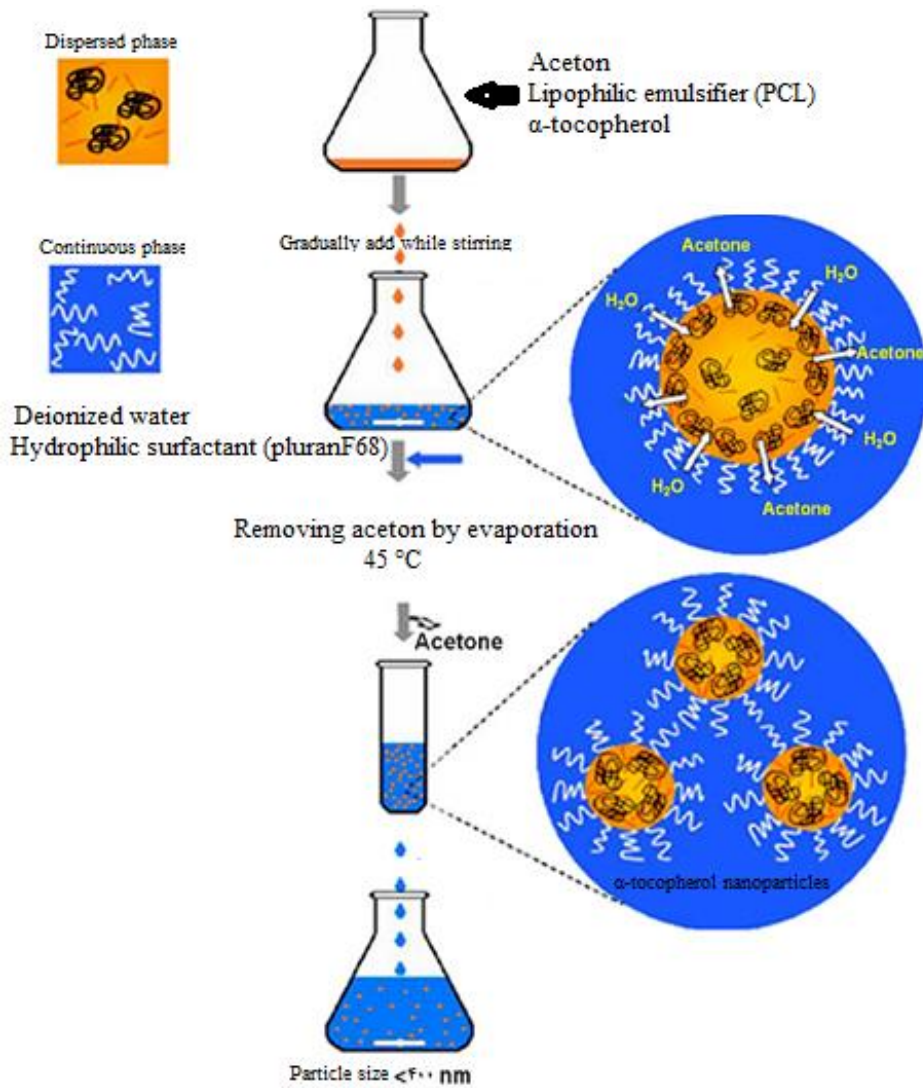


Fig.1- Schematic representation of the  $\alpha$ -tocopherol nanoparticles preparation process

### Analysis of PV

The peroxide value was determined using the spectrophotometry method described by Shantha et al. [25]. The oil samples (0.01- 0.3 g) were added to a disposable glass containing 9.8 ml of methanol and chloroform (3:7 v/v). 50 µl of a saturated solution of ammonium thiocyanate (30%) and iron II solution (0.5g FeSO<sub>4</sub>.7H<sub>2</sub>O and 0.4g barium chloride dihydrate were dissolved in 50 ml deionized water, individually. After mixing them, 2 ml 10 M HCl was added,

then barium sulfate precipitate was separated using filter paper) were added and them was mixed on a vortex mixer for 2-4 s. The absorbance was read at 500 nm after 5 min incubation in a dark room. The standard curve was prepared using the titrazole solution of stock iron chloride III in 3.7% hydrogen chloride solution. Working solutions were prepared using a stock solution (1040 µg/ml) in dilutions of 0-25 micrograms per ml; the curve slope was 40.39. The peroxide value was calculated by Equation 1 below.

$$PV \left( \frac{\text{meg}}{\text{kg}} \right) = \frac{\text{Slope of the calibration curve} \times \text{Sample absorption}}{55.85 \times \text{sample Weight} \times 2}$$

(1)

### Acid value (AV)

Acidic value is defined as the amount of potassium hydroxide (in mg) required for neutralizing 1 g of oil sample, measured according to the AOCS Cd 3d-63 standard. 50 ml of neutralized ethanol-chloroform (1:1 v/v) was poured on 10 g of oil sample and mixed, then titration was carried out with an ethanolic solution of 0.1 N potassium hydroxide in the presence of phenolphthalein as an indicator. Free fatty acid content (expressed as grams of oleic acid per 100 g of oil) was measured by multiplying the acid value by 0.503.

### The p-anisidine value measurement

First, 0.6-2.6 g of the sample oil was weighed in a 10 ml volumetric container with an accuracy of 0.001 g and made up to volume with isooctane solution. The solution absorbance was read at 350 nm against the blank (isooctane solution)(Ab).

After zeroing the spectrophotometer (5 ml of isooctane solution and 1 ml of p-anisidine indicator), 5 ml of the sample diluted with isooctane was placed in a 10 ml glass tube with a lid, and 1 ml of p-anisidine indicator (2.5 g/l indicator in

glacial acetic acid) was added. As the final stage, the reaction mixture was incubated in the dark at room temperature for 10 min, and the absorbance was read at 350 nm ( $A_s$ ). The anisidine value was calculated by Equation 2.

$$p - A.V = \frac{10 \times (1.2A_s - A_b)}{m} \quad (2)$$

### Alpha-tocopherol release from tragacanth film

To evaluate the alpha-tocopherol release, 10 samples were prepared, each with a piece of film containing 6.5% by weight of alpha-tocopherol or alpha-tocopherol nanoparticles (relative to tragacanth) as 0.6 g. The film was cut into pieces with sides 2\*3 cm and placed in a petri dish [20]. Then, 80 ml of ethanol (to simulate fatty foods according to the instructions of EC/19/2007 and EEC/8/93) was added, and the lid was sealed; it was stirred on a shaker at 100 rpm for 12 days [21]. Next, 0.5 ml of solution was monitored daily to test antioxidant capacity using the DPPH method. Once a standard diagram of solutions was prepared, containing a certain amount of alpha-tocopherol, the radical absorption activity curve was plotted to the level of alpha-tocopherol. Alpha-tocopherol in ethanol solution was measured in each container for 12 days using a curve. The  $M_t / M_\infty$  graph was plotted over time [26].

The release of alpha-tocopherol from the film containing free alpha-tocopherol, nanocapsules and nanospheres was performed using Zontao and Obinata methods [27, 28]. The diffusion coefficient was evaluated using Fick's 2nd law and the following hypotheses:

$$F = -D \frac{dC}{dx} \quad (3)$$

**A:** Surface resistance to the release of alpha-tocopherol from the film surface into the high-fat oil simulator was considered negligible (95% ethanol stirring at 100 rpm).

**B:** The initial concentration of alpha-tocopherol in ethanol was assumed to be zero.

**C:** There was no concentration gradient in ethanol (food simulator) due to agitation.

**D:** The interaction between ethanol and film was not significant.

The second equation for diffusion in one direction (film thickness) was defined as follows:

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta^2 x} \quad (4)$$

Solving the Fick equation by considering the film's flat shape and diffusing in the direction of the film thickness led to equation 5.

$$\frac{M_t}{M_\infty} = \left(\frac{2}{x}\right) * \left(\frac{D_t}{\pi}\right)^{0.5} \quad (5)$$

Where  $M_t$  is the level of alpha-tocopherol in ethanol at time  $t$ ,  $M_\infty$  represents the level of alpha-tocopherol in the equilibrium state in ethanol,  $x$  is film thickness,  $D$  represents diffusion coefficient,  $t$  is time,  $C$  indicates the concentration of tocopherol in film at time  $t$  and distance  $x$  from the surface; relative release chart of alpha-tocopherol ( $M_t/M_\infty$ ) was plotted on the second root of time ( $t^{0.5}$ ).

### **Sensory properties and preferences**

First, a series of preliminary tests to assess sensitivity to the main flavors, such as salinity, sweetness, sourness, bitterness, and umami, was performed, according to National Standard No. 18544. Among the panelists of two different companies (Salted Pistachio Processing Factory in Rafsanjan, Loura, and Rafsanjan Pistachio Producers Cooperative Company, RPPC), 12 were selected, of whom 8 were female, and 4 were male between the ages of 26 and 34 years.

Sensory evaluations were performed based on a quantitative descriptive method. Despite the experience of panelists in evaluating the roasted pistachio product, the necessary training on the sharp and bitter taste was provided by presenting an undesirable and fresh product. Moreover, concepts such as

brittleness (failure in anterior teeth), stiffness (failure in mill teeth), and their differences were taught (ISO: 1-8586, 1993). The test was performed in 6 stages during storage; the control sample was prepared for each test without /with coating from each treatment and was vacuum sealed and stored at  $-18\text{ }^\circ\text{C}$ . These samples, along with those stored at  $60\text{ }^\circ\text{C}$ , were given to the evaluators.

A descriptive quantitative method was used, and each sensory index was scored on a 15cm linear scale. Each trained panelist was given a bowl of roasted pistachios, a glass of water, and a scoring form. They evaluated all the samples randomly and individually; the participants rinsed their mouth with fresh tap water between each stage. The score of each test was extracted by measuring the line with a ruler [29].

### **Statistical analysis**

Experiments were performed in three replicates. The difference between the samples in terms of organoleptic characteristics was evaluated, and the data were analyzed using Minitab statistical software version 18. One-way analysis of variance (ANOVA) with Duncan's test with  $\alpha < 0.05$  was used to detect any significant differences between coatings. All graphs were drawn using Microsoft Excel 2013 software.



## 4. Results and Discussion

Roasted pistachio samples were stored at 40, 50, and 60°C for 6 months. Uncoated samples (NCo), coated with tragacanth (TC), tragacanth containing free alpha-tocopherol (TFC), and tragacanth containing alpha-tocopherol nanoparticles (4% tragacanth) in the form of nanocapsules (TNC) and nanospheres (TNS) were prepared and kept for 6 months. During storage, chemical properties, including AV, PV, Pa.V, sensory properties (taste and overall acceptance), were examined over time (every 18 days).

### Changes in chemical factors during storage

The changes in the PV are shown in Figure. 2. Peroxide value increased slowly during storage. No significant difference in PV was observed in samples stored at 40 and 50 °C. Changes in peroxide at a storage temperature of 60 °C for up to 150 days did not differ significantly from other storage temperatures. By the end of 6-month storage, in uncoated samples, the peroxide value at storage temperatures of 40, 50, and 60 °C was evaluated as 3.92, 3.85, and 7.1, respectively.

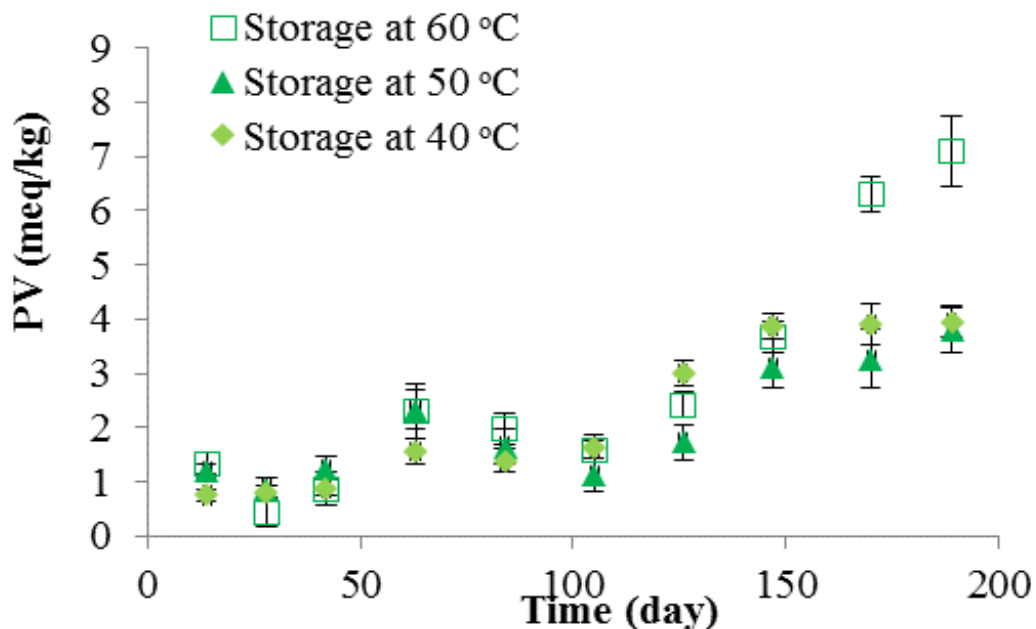
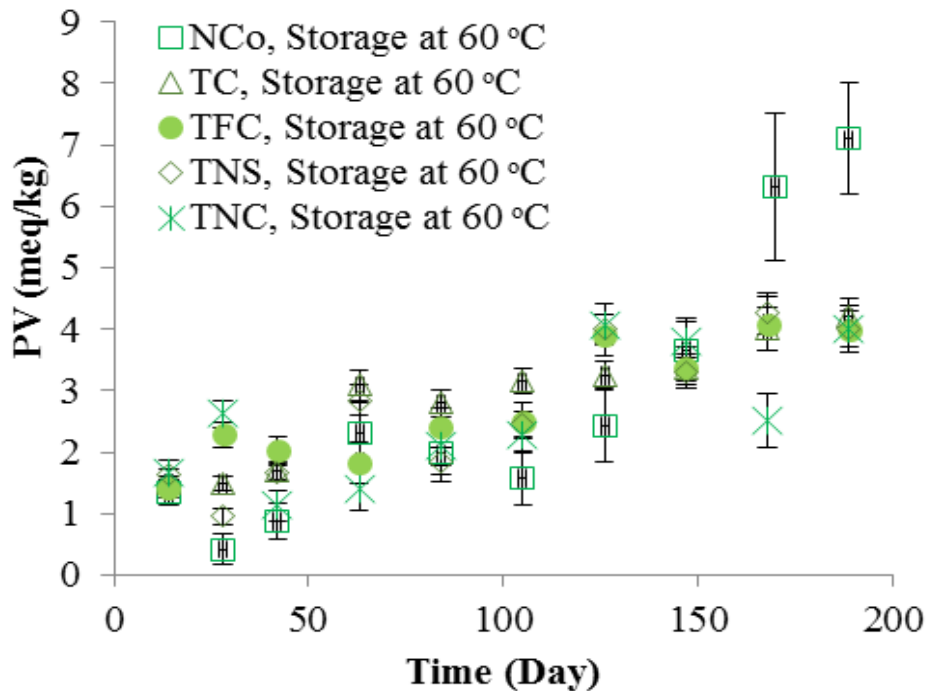


Fig.2- Peroxide value changes during 180 days of uncoated pistachio storage

Figure.3 shows the PV changes in the uncoated and coated samples in storage at 60 °C. A significant difference in peroxide value was observed in uncoated and coated samples after 150 days of storage (at 5% level). The peroxide value in the

latter did not exceed 4 in 180 days of storage at 60 °C. Also, no significant difference was observed in the peroxide value of coated samples with/without antioxidants.



**Fig. 3-** Peroxide value changes during 180 days of pistachios storage without/with tragacanth coating at 60 °C

According to the data related to pistachio oil oxidation at a temperature of 60°C, the PV at the induction period was considered 5 meq/kg. However, the results revealed that the peroxide value did not increase beyond 7 meq/kg even in samples with significant secondary compositions. A similar result has been reported by Mexis and Contominas (2009) for pistachios [30]. They found that the irradiated pistachio PV did not exceed 4

meq/kg, while it was rejected by the panelists and consumers in terms of taste. Ora et al. did not record PV greater than 4 meq/kg in the storage of walnut oil at ambient temperature for 120 days, while within 90 days, it was rejected by sensory evaluators [31]. Yakoub et al. (2008) estimated the PV in raw pistachios, almonds, and peanuts to be less than 0.25 meq/kg, while the Pa.V in these raw edible nuts ranged from 4.3 to 5.4, being higher

than the limits reported in the research, which is explained by the long-term storage of raw materials. They also suggested that peroxide value is not always a good indicator to reflect the storage history and process of edible nuts. Thus, this value cannot show the true oil oxidation state in edible nuts [32].

The acid value changes in the uncoated and coated samples are shown in Figure. 4. In the former stored at 40, 50, and 60 °C, acid value changes ranged from 0.14 to 0.25% and increased during storage; however, they were not significant. Although oxidation occurs during storage,

forming primary and secondary compounds, it seems that due to the insignificance of free fatty acids in uncoated samples, they are oxidized (peroxide) in the oxidation reaction [33]. The range of acid value changes in the latter at the storage time was 0.14-0.38. It increased with time, and a significant difference was not observed in terms of this factor among the coated treatments at a specific time. However, in one sample, a marked difference was observed in its acid value over time. The AV at storage time in coated samples was higher than uncovered samples.

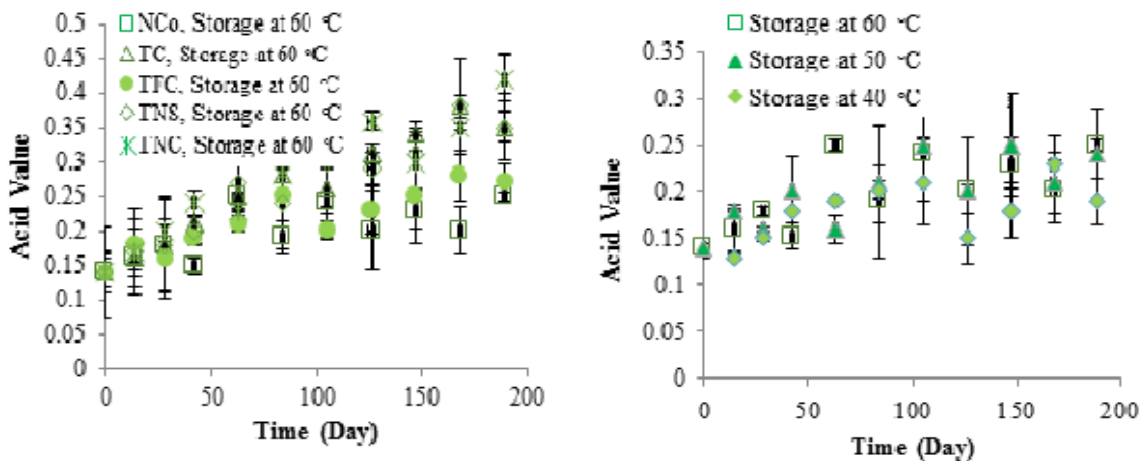
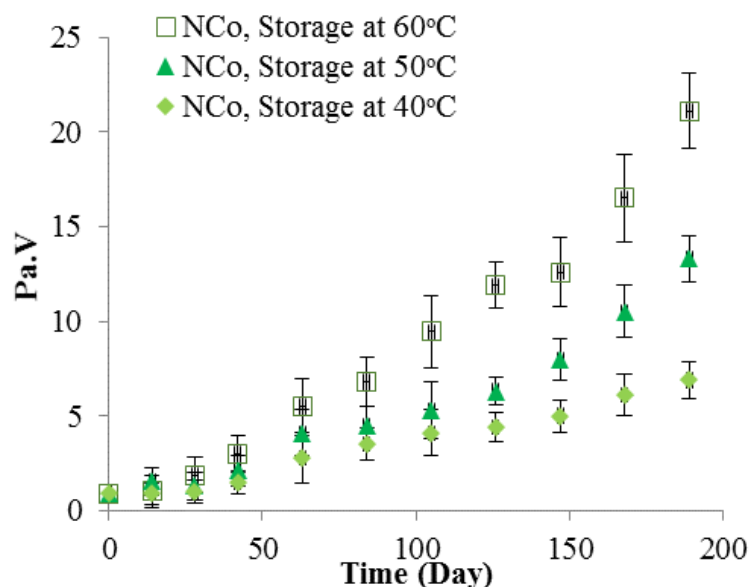


Fig. 4- AV changes in samples with/without coating during 6 months of stor

Figure.5 illustrates the changes of secondary oxidation compounds based on Pa.V in roasted pistachio without coating in a 6-month storage period at three temperatures of 40, 50, and 60 °C. No significant difference was observed in the value of Pa.V in the first 60 days of storage at different storage temperatures. Further, after storing for 60 days at 60 °C,

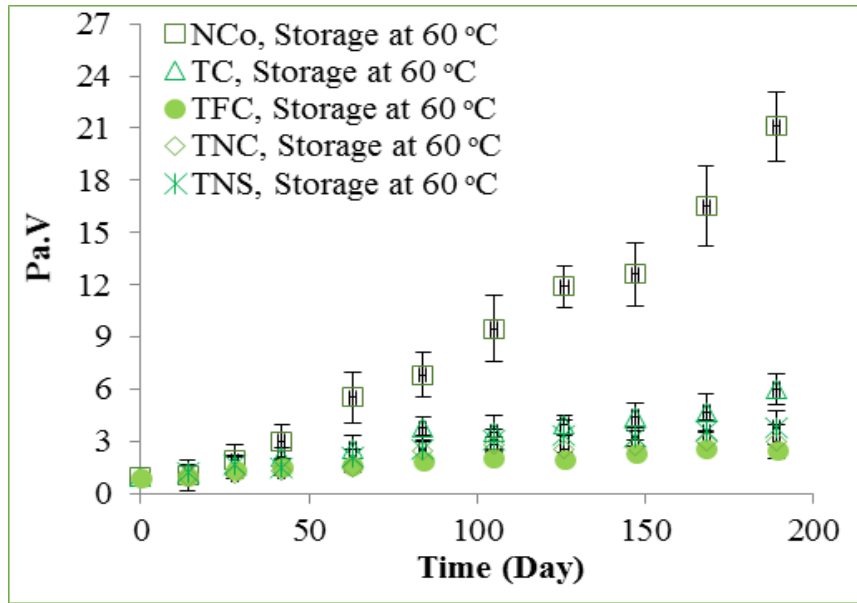
the anisidine value was significantly higher than the samples stored at 40 and 50 °C. Significant differences in Pa.V were observed in samples stored at 40 and 50 °C after 120 days of storage. At the end of 6 months of storage, Pa.V of uncoated samples at storage temperatures of 40, 50, and 60°C was evaluated as 6.89, 13.3, and 21.1, respectively.



**Fig. 5-** Investigation of changes in Pa.V of roasted pistachio during 6-month storage at different temperature

Figure. 6 shows the changes in the Pa.V in coated samples during storage at 60°C compared to uncoated samples. The samples containing antioxidants had a lower anisidine value than those coated without antioxidants, and the lowest anisidine value was related to the coated sample with free alpha-tocopherol (TFC). However, no significant difference was observed between the samples with nanocapsules (TNC) and alpha-tocopherol nanospheres (TNS) and the coated sample with alpha-tocopherol (TFC). The anisidine value in TNC and TNS samples was significantly different from those coated without antioxidants (TFC) after 180 days of storage. However, the coated samples containing free alpha-tocopherol

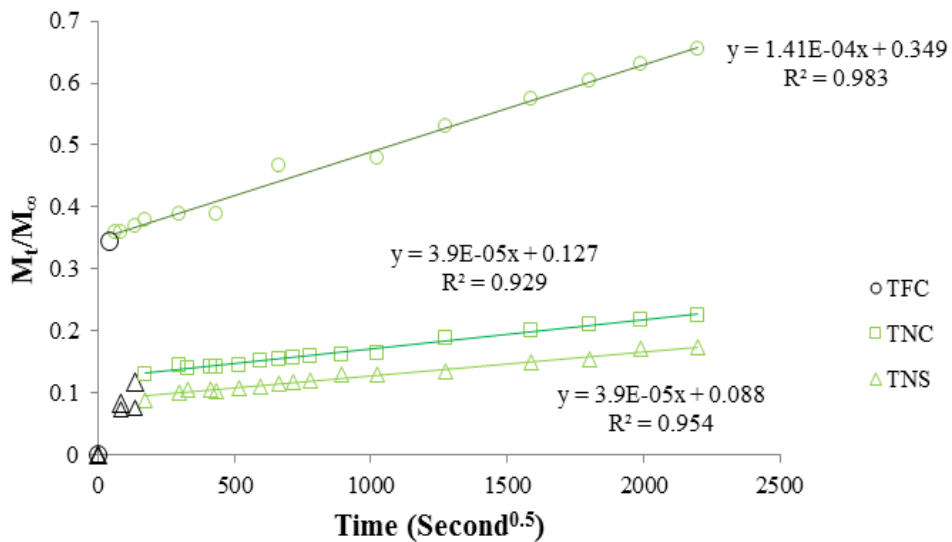
after 120 days showed a significant difference with those coated without antioxidants. The antioxidant properties of edible films and coatings are related to their low oxygen permeability. Carbohydrate and protein films are difficult to compress due to hydrogen bonds within the network and have low permeability to oxygen, and thus antioxidant effects [34, 35]. Tragacanth gum is a suitable barrier to oxygen permeability due to its high hydrogen bonds and structural compactness, such as carboxymethylcellulose, formatting secondary oxidation compounds in coated pistachio, which are significantly less than uncoated pistachios.



**Fig. 6-** Investigation of changes in Pa.V of roasted pistachio nuts with/without coating during 6-month storage

Alpha-tocopherol release rate in different coatings (Figure. 7) showed that the coating containing free alpha-tocopherol (about 30- 40% on the coating surface) caused a slower oxidation rate at

the pistachio kernel surface due to the faster release of antioxidants from the film; thus, a lower amount of Pa.V was estimated.

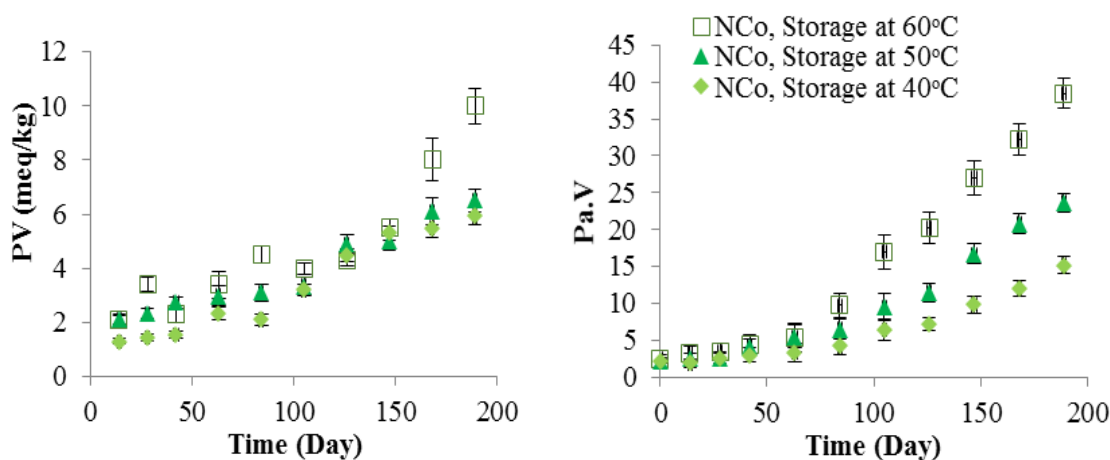


**Fig. 7-** Release of alpha-tocopherol from the film containing free alpha-tocopherol (TFC), nanocapsules (TNC), and nanosphere (TNS)

The oil in the edible nuts is inside the oleosome vesicles. It seems oleosomes that are close to the nut surface are always in contact with the heat at higher temperatures and suffer from the wall destruction, releasing oil from their inside. They are also exposed to more oxygen and oxidation than the oil in nearby oleosomes located in the kernel center. As a result, oxidation in the edible kernels takes place in a non-integrated manner, and the oil in different parts of the nut is not in an oxidation stage. The central parts affected by the protective effect of oleosome walls and pistachio protein go through the induction period. To confirm this hypothesis, pistachio samples were first peeled, and then approximately 20% of the pistachio kernel surface was separated by a fine grater, and the oil was extracted separately using a solvent. Subsequently, PV and Pa.V were carried out. Figure. 8 shows the changes in the value of peroxide and p.anisidine in the oil of the superficial part of the pistachio. There is a significant difference in the anisidine value in the oil extracted from the surface and central parts; so that this difference reaches 3.5-5.5 times in 6 months of storage at

60 °C. It caused the Pa.V to be almost twice that of the oil extracted from whole pistachio kernels. The reason is the ratio of oil extracted from the surface parts, which is 25-35% of total kernel oil. The difference in total Pa.V in the sample and oil from the surface is that oil from different parts tends to mix and dilute; therefore, the value is measured less than its real amount. There is a difference in the value of peroxides in the surface oil compared to whole kernel oil; however, the difference ratio is not as obvious as Pa.V since the peroxide is a primary and intermediate compound always decomposes into secondary compounds.

Since secondary compounds, such as aldehydes, have a very low taste recognition limit (e.g., 2,4- decadienals have a detection limit of less than one ppb, and 2,6-trans cis nonadienal has a detection limit of 0.0015 µg/L [36]), it seems that sensory changes can be affected by oil oxidation on the surface of the edible nuts. Pa.V can be used as a suitable chemical index for pistachios due to the cumulative amount of secondary compounds, such as aldehydes, as well as the ease of measurement.



**Fig. 8-** Investigation of PV and Pa.v changes in the surface of uncoated samples during 6 months of storage

### The evaluation of sensory properties during storage

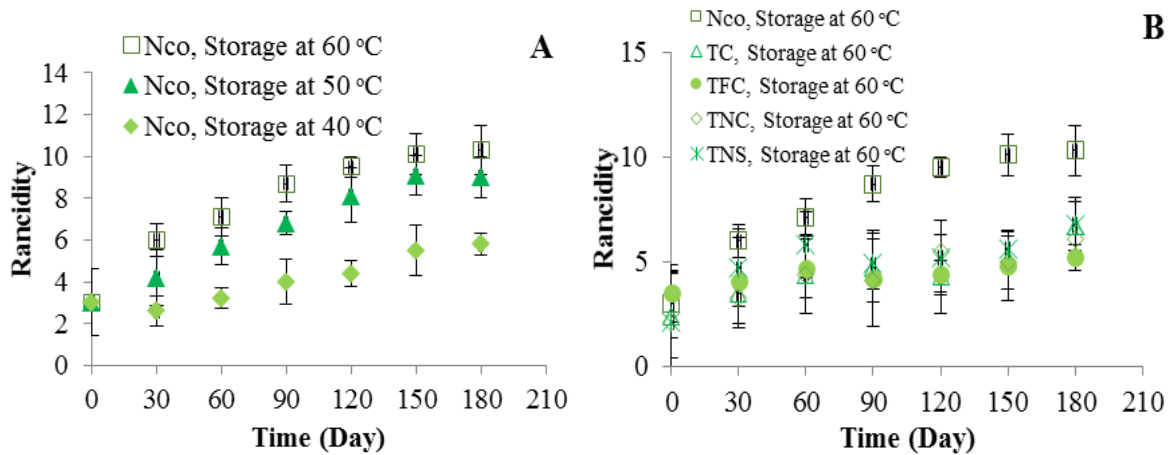
Oxidant flavor changes (rancidity) in uncoated samples are shown in Figure. 9. There was no significant difference in the control samples evaluated on the first day and in different evaluation stages, indicating the desired quality by trained panelists ( $P= 0.201$ ). There was a significant difference regarding the evaluation of rancidity in uncoated samples stored at 60°C compared to storage temperatures of 50 and 40 °C. Samples stored at 60 and 50 °C after 60 and 90 days were found to have a remarkable difference in taste with the control samples. The accumulation of oxidation secondary compounds represented by anisidine value in the range of 5.6- 6 made it possible for the panelists to detect differences in taste retention.

As presented in Table 1, the Pearson correlation coefficient was calculated between chemical and sensory properties (rancidity and overall acceptance). Concerning uncoated samples, the best chemical index was Pa.V; however, AV was reported as another factor with an acceptable correlation for coated samples. In uncoated samples, peroxide value and free fatty acids were converted to secondary compounds, despite being formed in the oxidation process due to the intermediate and reaction rate in the presence of oxygen. Moreover, the secondary compounds were accumulative and showed more correlation with sensory properties.

However, in coated samples, since tragacanth was a desirable barrier against oxygen, the production of oxidation by-products was slow, and enzymatic activity led to hydrolytic degradation and increased

concentration of free fatty acids. The conversion rate of fatty acids to hydroperoxide and decomposition of this primary compound decreased in the presence of limited access to oxygen. Due

to the reduced production of secondary compounds, a higher correlation between AV and sensory properties was observed in coated samples.



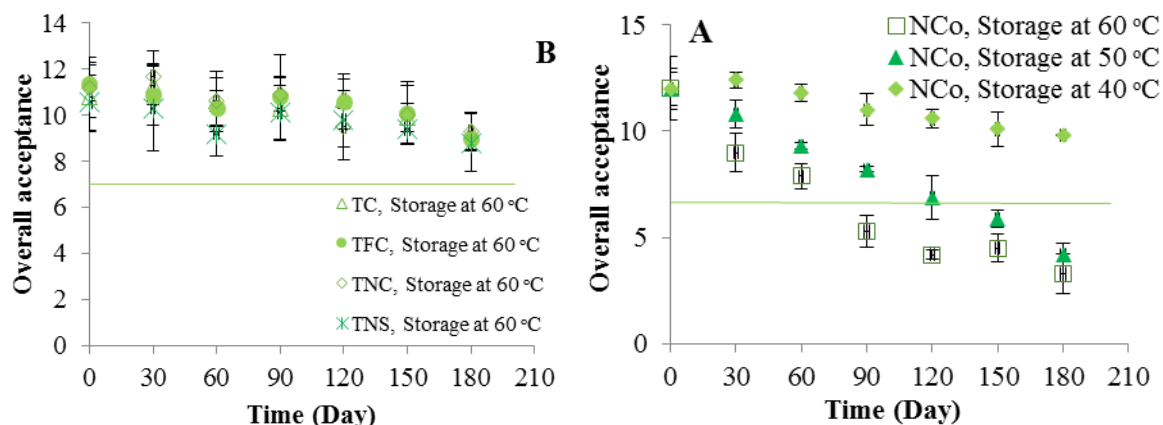
**Fig. 9-** Evaluation of rancidity of roasted pistachios (uncovered) at different storage temperatures: (A) Comparison with samples coated during 6 months of storage at 60 °C by panelists (B)

An inverse correlation was observed concerning overall acceptance and chemical factors. The Pa.V had the highest correlation coefficient with sensory properties in uncoated samples, being evaluated as a suitable chemical factor for predicting such properties. Zajdenweg et al. also observed a good correlation between Pa.V and sensory attributes of rancid taste and overall acceptance in Brazilian nuts during storage [37]. Uncoated samples stored at 60 and 50 °C were evaluated after 60 and 120 days with Pa.V of 6.2 and 7, respectively, with an overall acceptance below average (7) (Figure. 10b). The sample stored at 40 °C and the coated samples during 180 days of storage had above average overall

acceptance value, with their Pa.V measured in the range of 2.9-5.6. It was concluded that coating has improved sensory properties due to its significant reduction effect on oxidation rate.

Decomposition of hydroperoxides into carbonyl compounds affects sensory properties and overall acceptance degradation [38]. Pistachio nut has a high content of linoleic acid (28%), and volatile carbonyl compounds produced during the oxidation of linoleic acids in nuts have a specific taste and aroma, such as spicy flavors (related to pentanal), tallow, and raw vegetable flavors (related to hexane), bitter and almond flavors (2-heptanal), and soap flavors (2-nonanal) [38, 39].





**Fig. 10-** Effect of storage time and temperature on the overall acceptance of uncoated roasted pistachio: (A) Roasted pistachio with tragacanth coating (B) On sensory evaluations

The taste and aroma of oxidized nuts can be easily identified by trained panelists [40]. However, their taste and aroma return in some edible nuts did not correlate with chemical parameters, such as peroxide value. For example, Baker et al. did not observe any correlation between PV and sensory properties in peanut storage with high oleic acid content during four storage weeks. The reason was the absence of high peroxide (4-9 meq/kg) in the samples. However, Zajdenweg et al. highlighted a significant correlation between peroxide value and sensory properties in Brazilian nuts and reported the peroxide production during storage in the range of 5- 31 meq/kg [37, 39]. In the present work, in pistachios, high levels of peroxide were not observed in the stored samples; this could be the reason for the lack of proper correlation between

peroxide value and sensory properties, in addition to the fact that peroxides are tasteless compounds.

Oxidation secondary compounds are the main cause of negative changes in the taste and aroma of edible nuts, and they can cause adverse changes in tissue combining with proteins and amino acids [33]. Secondary compounds have also been identified as a suitable index for the study of oxidation in edible nuts due to their cumulative and increased concentration during storage in previous studies [32]. In pistachio, the accumulation of secondary oxidation compounds can increase the anisidine value by 5.5- 6. It is possible to detect changes in taste and aroma of aging by trained and experienced evaluators and use Pa.V as a suitable chemical indicator introduced to evaluate oxidation in roasted pistachios.

**Table 1-** The correlation coefficient between sensory scores given to samples and chemical factors measured in pistachios during storage

Chemical Parameters	Rancidity				Overall Acceptance			
	Sample without coating		Sample with coating		Sample without coating		Sample with coating	
	P-value	Correlation coefficient	P-value	Correlation coefficient	P-value	Correlation coefficient	P-value	Correlation coefficient
<b>AV</b>	<0.001	0.71	<0.001	0.854	<0.001	-0.745	<0.001	-0.746
<b>PV</b>	<0.01	0.60	<0.001	0.726	<0.001	-0.588	<0.001	-0.64
<b>Pa.V</b>	<0.001	0.867	<0.001	0.767	<0.001	-0.9	<0.001	-0.62

## 4. Conclusion

This study showed that the chemical indices of AV, PV, and Pa.V increased during storage and as storage temperature raised. Tragacanth coating with/without antioxidants could reduce the rate of oxidation, as well as enhancing the shelf life and the sensory properties during storage. Further, the addition of antioxidants to the coating reduced the oxidation rate, and no significant difference was observed in the evaluation of chemical oxidation indices and sensory properties in coated samples containing different forms of  $\alpha$ -tocopherol. The trained panel detected off-flavor defects in the treatment 5.5-6 Pa.V. Finally, there

was a correlation between chemical indicators of oxidation and sensory properties, and the value of p-anisidine was identified as a suitable chemical index in pistachio for oxidation

## Conflict of Interest

The authors of present researches declare that there is no conflict of interest.

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