Journal of Food Science and Technology (Iran)

Homepage: www.fsct.modares.ir

Scientific Research

The effect of nanocomposite films based on polylactic acid/polycaprolactone reinforced with TiO_2 nanoparticles and basil essential oil nanocapsules on physicochemical and sensory properties of UF cheese

Sahar Khanahmadloo[a], Leila Najafian[a*], Ismail Ghasemi[b], Navid Naeimian[c]

[a]Department of Food Science and Technology, Sari Branch, Islamic Azad University, Sari, Iran

[b]Faculty of Polymer Processing, Iran Polymer and Petrochemical Institute, Tehran, Iran

[c] Department of Wood and Paper Science and Technology, Sari Branch, Islamic Azad University, Sari, Iran

ARTICLE INFO

Article History:

Received:

Accepted:

Keywords:

Basil,
Encapsulation,
Polycaprolactone,
Polylactic acid,
Titanium dioxide,
UF cheese.

DOI: **10.22034/FSCT.22.161.297.**

*Corresponding Author E-

najafian_5828@yahoo.com

ABSTRACT

In this research, the effect of nanocomposite films based on PLA-PCL containing TiO_2 nanoparticles (3% by weight) and different levels of BEN (0, 1, 3 and 7% by weight based on polymer) on physicochemical and sensory properties of UF cheese during the 60-day storage at 4°C were determined. The weight loss percentage, pH, acidity, hardness and peroxide value as well as sensory properties of the cheeses were examined. The results showed that during the storage period, the values of weight loss, acidity, hardness, peroxide value and microbial load of the cheese samples increased, and their pH decreased significantly ($p<0.05$), and the use of nanocomposite films based on PLA-PCL reinforced with TiO_2 and different levels of BEN could reduce the rate of changes in physicochemical parameters of UF cheese during the storage period compared to the control. A positive and direct relationship was observed between the BEN level and the antioxidant of the films in vitro conditions and in the food model. In terms of sensory properties, cheeses packed in films containing TiO_2 and different levels of BEN were acceptable until the last day of storage. According to the results obtained in this research, it can be concluded that it is possible to maintain the quality and safety and extend the shelf life of UF cheese by using nanocomposite films based on PLA-PCL reinforced with TiO_2 nanoparticles and BEN, and the best results are related to films containing 7% BEN.

1-Introduction

Cheese is one of the most important and widely consumed dairy products worldwide and has a high nutritional value. Like milk, cheese contains vitamins and minerals (calcium, phosphorus, sodium, zinc, iron and potassium) [1]. However, during the ripening and storage period, this product is subject to microbial spoilage and oxidative changes [2]. UF cheese is a cheese obtained by the ultrafiltration process and is classified as a soft cheese with high moisture content, so the possibility of spoilage and microbial growth is high, so usage of an optimal and appropriate storage method seems essential to extend the shelf life of this food product [3]. During the storage period, if packaging is not used, due to the growth of bacteria, molds and yeasts, bad taste and odor are created in the cheese and its quality decreases. On the other hand, a high drop in humidity can also cause a firmer texture of the cheese, which may reduce the organoleptic acceptability of this product. Various packaging systems have been used to solve this problem [4]. Active films with antioxidant and antimicrobial properties are an effective solution for this purpose.

In recent years, plastics have been widely used in food packaging. Plastics are neutral and non-biodegradable and account for 30% of municipal solid waste [5]. Several biopolymers including starch, cellulose, chitosan, polylactic acid (PLA), polycaprolactone (PCL) and polyhydroxybutyrate (PHB) have been widely used in food packaging [6]. PLA is a linear, aliphatic thermoplastic polyester found in sugar beet and corn starch and obtained by bacterial fermentation [7]. PLA is considered as one of the most promising bio-based and biodegradable polymers for food packaging due to its mechanical properties similar to petroleum polymers such as polyethylene and polypropylene. Furthermore, PLA is safe for food applications as it has been proven to be safe [8]. However, pure PLA film lacks antimicrobial and antioxidant activities, which limits its application in packaging [9]. On the other hand, PLA is a semi-crystalline polymer whose crystallization kinetics are very slow due to its low nucleation capacity. Therefore, this limits its applications, since the mechanical properties of PLA depend on the degree of crystallinity. In general, PLA has a crystallization rate in the range of 10-20°C/min at temperatures below 100°C and has a crystallinity of less than 10% due to its poor crystallinity. This is why some materials are needed to reinforce and thus improve its crystallinity in order to maintain or even improve its properties [10].

Currently, the mechanical properties and permeability of PLA films can be improved by adding plasticizers, polymer blends, conjugates, copolymers, and nano-technology. Polymers with high elongation, such as polycaprolactone (PCL) are also suitable for overcoming the brittleness of PLA [9]. PCL is a linear, semi-crystalline thermoplastic polyester with hydrophobic, biocompatible, and biodegradable properties. It has a 700% elongation and a relatively low melting temperature (60°C) and has an easy process-ability [11]. According to research, by combining PLA and PCL can greatly overcome the shortcomings of both, reducing the brittleness of PLA films and improving the flexibility of these films [12, 13].

Nano-metals are considered as one of the most direct and effective strategies to improving the antimicrobial and UV-blocking properties of PLA and other biodegradable films [14]. Among metal oxide nanoparticles, titanium dioxide (TiO_2) has recently been widely used in the preparation of various composites, because these nanoparticles are neutral, non-toxic, environmentally friendly, inexpensive and have excellent biocompatibility [15]. The incorporation of TiO_2 nanoparticles can improve the physical, mechanical, UV-blocking, thermal, optical, and antimicrobial properties of composite films [16]. TiO_2

nanoparticles are widely used in various fields such as environmental pollution treatment, food preservatives, wound healing, and biosensors [17].

Active packaging systems have emerged as an innovative approach to extend the shelf life and improve the safety of food products while maintaining their quality. These packaging systems contain components that can be released or absorbed into the packaged food or its environment. The addition of active ingredients with antimicrobial or antioxidant properties (usually active agents derived from natural compounds) into the packaging material, rather than directly adding them to the food, reduces the required amount of these ingredients [12]. Basil, scientifically known as *Ocimum basilicum,* is an annual herbaceous plant of the *Lamiaceae* family that is used in traditional medicine to treat seizures, cancer, heart diseases, enlarged spleen, toothache, sore throat, and bronchitis [18]. This plant contains approximately 0.5% to 1.5% essential oil, and its essential oil contains various phytochemical compounds, including estragole, eugenol, linalool, bergamotene, and eucalyptol [19]. The antibacterial and antioxidant activities of basil essential oil have been reported in previous studies [20]. In a study by Bakhshi et al. [21], significant antimicrobial activity of basil essential oil against aerobic mesophilic bacteria, coliforms, and *Staphylococcus aureus* in traditional Iranian white cheese was also reported.

With increasing attention towards the use of plant essential oils as natural plant preservatives in food, the use of these active compounds has faced problems, some of these problems include their low solubility, as well as their sensitivity to heat, light, and oxygen. The encapsulation process has been proposed to overcome these problems [22]. During the encapsulation process, bioactive and antimicrobial agents are covered by wall materials, thus protecting them from the destructive conditions of the human body and harsh environmental conditions and improving their solubility [23]. Various biopolymers have been used singly or in combination as wall materials or coating agents [24]. The aim of the study was to investigate the effect of using nanocomposite films based on PLA-PCL reinforced with TiO_2 nanoparticles and basil essential oil nanocapsules in order to maintain the quality and improvement the shelf life of ultra-filtered cheese.

2- Materials and methods

Basil plant was purchased from Shiraz market in Iran. Maltodextrin, gum arabic, Tween 80, PLA, PCL, TiO_2 nanoparticles, methanol, acetic acid, sodium carbonate, DPPH powder, chloroform, ethanol, phenolphthalein, sodium hydroxide, potassium iodide, sodium thiosulfate were purchased from Merck Company (Germany). Commercial cheese starter was obtained from Danisco and raw milk with 3.5% fat prepared from Pegah Company (Karaj).

2.1. Preparation of PLA-PCL-based films containing TiO_2 nanoparticles and basil essential oil nanocapsules (BEN)

To preparation PLA-PCL films, first 9.5 g of PLA was dissolved in chloroform (142.5 mL) and in another glass 0.5 g of PCL was dissolved in chloroform (7.5 mL). The PLA and PCL solutions were first kept at room temperature for 24 h and then mixed together using a magnetic stirrer at room temperature for 8 h (700 rpm). Then the resulting mixture was poured into a Petri dish (30 × 24 cm) and dried in the air for one week [12]. To prepare basil essential oil nanocapsules (BEN), 6% w/w basil essential oil and Tween 80 (2% w/w) were added to the gum arabic-maltodextrin solution and after stirring for 30 min (500 rpm). The solution was sonicated for 120 s (24 kHz) to obtain a basil essential oil nanoemulsion [23], which was finally dried using a spray dryer. The inlet temperature of the dryer was set at 150°C and its outlet temperature was set at 100°C. To prepare films containing nanoparticles and

BEN, TiO_2 nanoparticles at 3% and BEN at 0, 1, 3, and 7% by weight (based on polymer) were added to PLA-PCL solutions and thoroughly homogenized by magnetic stirring for 24 h [24]. The morphology of the produced films was examined by scanning electron microscopy (SEM) at an accelerated voltage of 15 kV.

2.2. Ultra-filtered cheese production

Cheese samples were produced in Pegah Company of Karaj (Iran) according to the UF cheese production process proposed by the company. For this purpose, raw milk with 3.5% fat was pasteurized using the HTST method and then concentrated at 50°C in an ultrafiltration system with tubular membrane filters until a dry matter content of 34% was reached. After homogenization pressure (5 MPa) and pasteurization (75°C for 15 s), inoculation of commercial cheese starter (containing equal proportions of thermophiles and mesophiles) was carried out at 32-35°C. After adding rent to the retentates and coagulation, 4% salt was added and sealed. After reaching a pH of 4.7 (in an incubator at 28°C for approximately 24 h), it was transferred to a cold room and stored in the cold room at 6°C until the time of testing.

2.3. Packaging of UF cheese with nanocomposite film

After preparation of ultra-filtered cheese, the cheese was cut into 10 g pieces and the cheese samples were packaged in nanocomposite films and stored at refrigerator temperature for 60 days. Tests were performed on the cheese samples every 15 days. A sample packaged in plastic (polypropylene) was also considered as control sample.

2.4. Tests of the packaged UF cheese

2.4.1. Measuring the percentage of weight loss

To determine the percentage of weight loss of cheese, the weight of the cheeses was recorded during different days of storage and the percentage of weight loss of the cheeses was obtained through the following equation. W1 is the initial weight and W2 is the final weight [25]:

$$\text{Weight loss (\%)} = \frac{W1-W2}{W1} \times 100 \quad (1)$$

2.4.2. Measuring the pH

The pH of cheese samples was measured using a pH meter at 20°C [26].

2.4.3. Measuring the acidity

To determine the acidity, in a 250 mL volumetric flask, cheese sample (10 g) was mixed with distilled water (10 mL) and stirred, then made up to volume. After filtering, 0.5 mL of phenolphthalein reagent was added to 25 mL of the filtered solution in a beaker and titration was performed with 0.1 N sodium hydroxide solution until a pink color appeared. Finally, the acidity of the cheeses was obtained in terms of lactic acid percentage using the following equation [26]:

$$\text{Acidity (\%)} = \text{sodium hydroxide volume} \times 0.45 \times 100 \quad (2)$$

2.4.4. Measuring hardness

To examine the hardness of cheese, a texture analyzer equipped with a cylindrical probe (height 38.1 mm and diameter 5 mm) was used, and the Penetration distance and speed probe of the device were set at 15 mm and 2 mm/s, respectively [27].

2.4.5. Measuring the peroxide index

To determine the peroxide index of cheeses, first each cheese sample (5 g) was mixed with methanol (20 mL) and chloroform (10 mL) for 120 s and after filtering with Whatman paper NO.1, its solvent was removed by rotary evaporator. Then, each fat sample (1 g) was mixed with 25 mL of chloroform-glacial acetic acid mixture (10 to 15 v/v) and potassium iodide (1 mL) was added to it and kept in the dark room for 10 min. Then 20 mL of distilled water and 1.5%

starch reagent were added to it and titrated with 0.02 N sodium thiosulfate [28].

2.4.6. Sensory evaluation

To evaluate the sensory characteristics of cheeses, including color, texture, flavor, odor, and overall acceptability, a five-point hedonic method (5 very good, 4 good, 3 average, 2 bad and 1 very bad) and 10 trained evaluators were used. Cheese samples were placed in white plastic containers, randomly coded, and provided to the evaluators along with a sensory evaluation form [29].

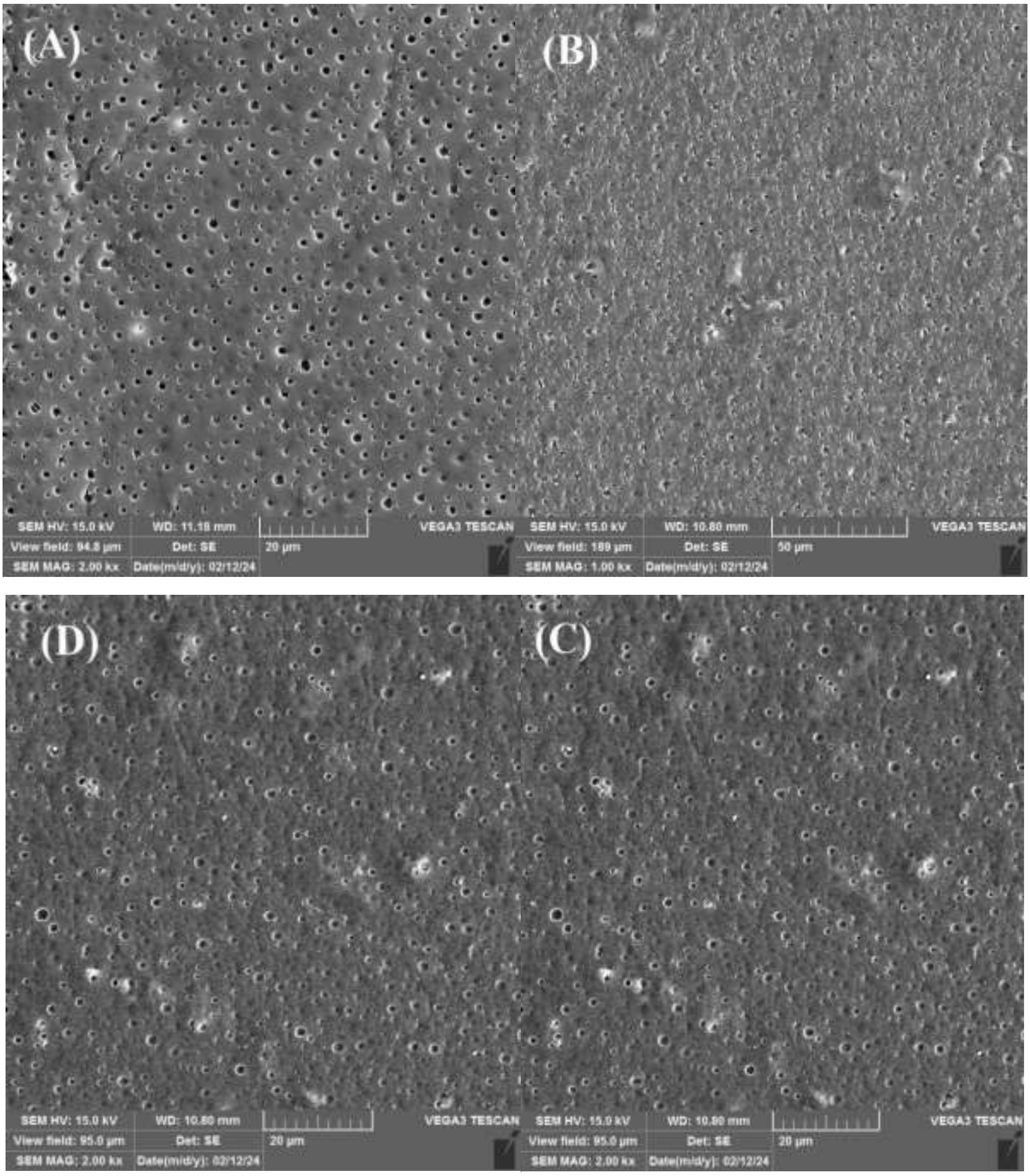
2.5. Statistical analysis of data

In this research, a completely randomized experiment design was used. All experiments were repeated 3 times and SPSS 22.0 software and ANOVA analysis of variance were used to statistical analyze the data obtained from the experiments. Statistically significant differences between cheese treatments were expressed at the 95% probability level ($p<0.05$) using Duncan's multiple range test. Finally, the results were reported as mean ± standard deviation and graphs were drawn using Excel.

3-Results and discussion

3.1. Morphology of films

The results of the morphology examination of the produced films by SEM microscope (Fig. 1) showed that there are pores in the PLA-PCL film, which is related to the partial mixing of PCL with PLA during the solvent casting process [30]. The presence of pores on the surface of PLA-PCL films has also been reported in studies conducted by Lukic et al., (2020) and Milovanovic et al (2018) [12, 31]. As a result of the addition of TiO_2 nanoparticles, the structure of the films became denser, which could be a reason for the increase in the mechanical strength of the films containing these nanoparticles. The addition of different levels of BEN resulted in a more uniform structure of the films, and no breakage was observed in these films, and the pores in these films were significantly reduced compared to the control sample, which indicates the uniform dispersion of the essential oil nanocapsules in the PLA-PCL film matrix and the filling the pores of the film structure by the nanocapsules. In line with these results, Milovanovic et al, (2018) also observed in their study a reduction in pores and a more uniform structure of PLA-PCL films after the incorporation of thymol extract [31]. In the study of Sadeghi et al. (2022), PLA-PCL films had a porous and cracked structure, but the addition of green tea extract and its increase in the surface area in the films caused the film structure to become denser and the pores to decrease, but the film structure became more uneven [32].


(A)
(B)
(D)
(C)
SEM HV: 15.0 kV
WD: 11.19 mm
View field: 94.8 µm
Det: SE
SEM MAG: 2.00 kx
Date(m/d/y): 02/12/24
20 µm
VEGA3 TESCAN
SEM HV: 15.0 kV
WD: 10.80 mm
View field: 189 µm
Det: SE
SEM MAG: 1.00 kx
Date(m/d/y): 02/12/24
50 µm
VEGA3 TESCAN
SEM HV: 15.0 kV
WD: 10.80 mm
View field: 95.0 µm
Det: SE
SEM MAG: 2.00 kx
Date(m/d/y): 02/12/24
20 µm
VEGA3 TESCAN
SEM HV: 15.0 kV
WD: 10.80 mm
View field: 95.0 µm
Det: SE
SEM MAG: 2.00 kx
Date(m/d/y): 02/12/24
20 µm
VEGA3 TESCAN

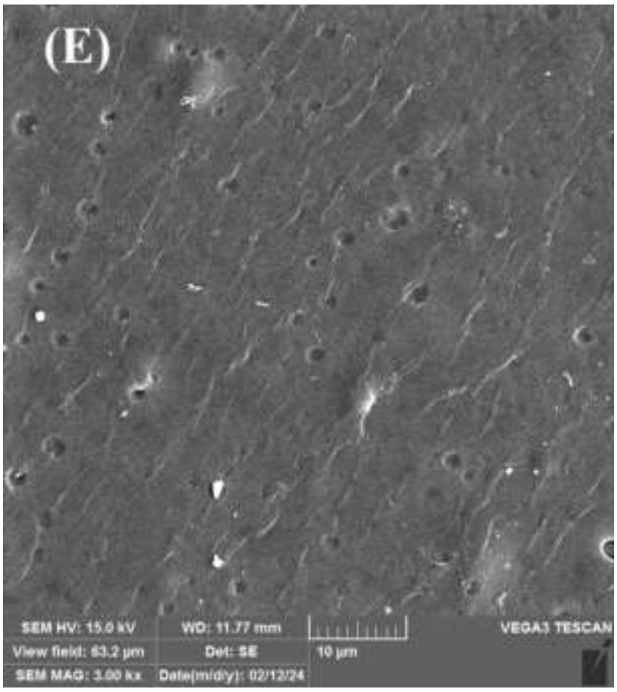


Fig 1. SEM images of A: PLA-PCL control film; B: PLA-PCL film containing TiO_2+BEN0%; C: PLA-PCL film containing TiO_2+BEN1%; D: PLA-PCL film containing TiO_2+BEN3%; E: PLA-PCL film containing TiO_2+BEN7%.

3.2. Weight loss of cheeses

The results of the study of the effect of nanocomposite films based on PLA-PCL reinforced with TiO_2 nanoparticles and different levels of BEN on the weight loss of UF cheeses (Fig. 2) showed that during the storage period at refrigerator temperature, the percentage of weight loss of cheese samples increased significantly ($p<0.05$), but the use of active nanocomposite films containing nanoparticles and essential oil nanocapsules was able to significantly reduce the rate of weight loss of cheese samples during the storage period compared to the control sample. The increase in weight loss of cheese samples during the storage period is related to the loss of moisture of cheeses during the storage period, in such a way that over time, moisture gradually moves from the center to the surface of the cheese and then evaporates from the surface of the cheese, caused weight loss of the cheeses. The use of films can reduce the moisture loss in cheeses during storage and therefore significantly reduce the percentage of weight loss of cheeses during storage. In agreement with these results, Li et al. [33] also reported a reduction in the weight loss of cottage cheese samples packaged in PLA films containing TiO_2 nanoparticles during storage compared to the control sample. In another study, a reduction in weight loss and moisture loss of Ras cheese was observed as a result of the use of chitosan/whey protein concentrate bionanocomposites containing different levels of Moringa essential oil nanoemulsion [34]. Khazaei et al. [35] also stated that the use of cinnamon, ginger and garlic essential oils and increasing their levels in packaging films could reduce the percentage of weight loss of cheeses during a 60-day storage period at refrigerator temperature. Sharma et al. [24] also found that packaging cheese in PLA-PBAT-TiO_2 films containing cinnamon essential oil reduced the weight loss of cheeses during storage at refrigerator temperature, which was consistent with the results of the present study. The decrease in moisture content of UF cheeses during storage and the increase in weight loss of cheeses were also shown in the study of Gohargani et al. [36].

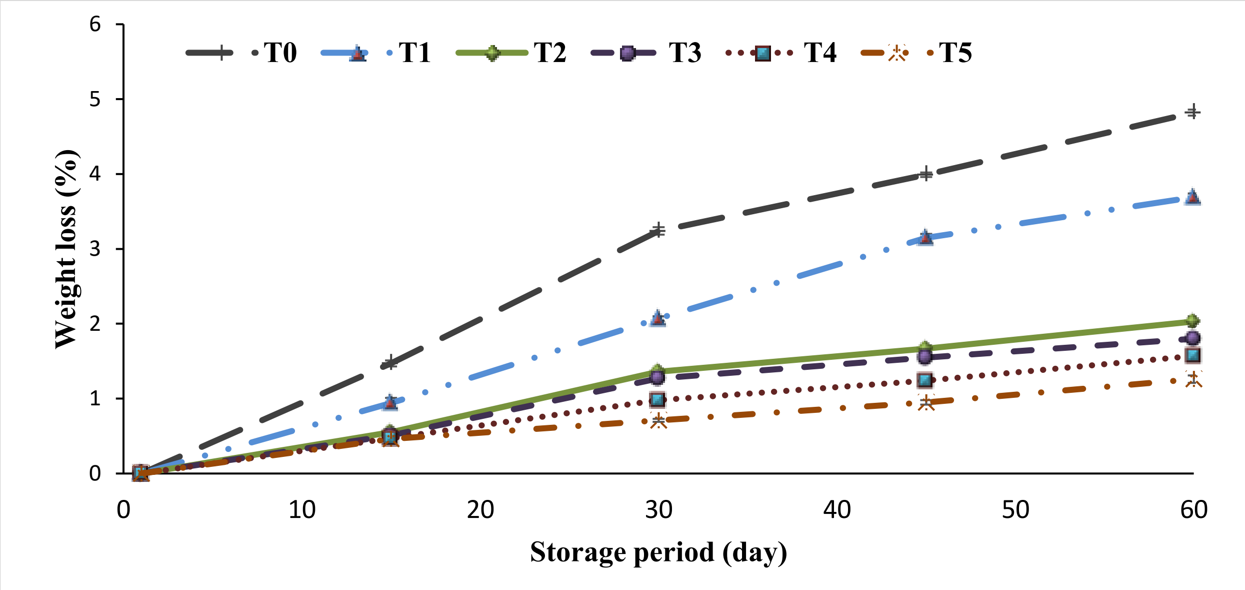


Fig 2. Changes in weight loss (%) of UF cheese samples during the storage time at 4°C.

T0: Control sample; T1: sample covered with PLA-PCL control film; T2: sample covered with PLA-PCL film containing TiO_2+BEN0%; T3: sample covered with PLA-PCL film containing TiO_2+BEN1%; T4: sample covered with PLA-PCL film containing TiO_2+BEN3%; T5: sample covered with PLA-PCL film containing TiO_2+BEN7%.

3.3. pH values of cheeses

The changes in the pH values of cheese samples during 60 days of storage at refrigerator temperature are also shown in Fig. 3. As can be seen in this figure, at the beginning of the storage period, the pH of UF cheese was 5.23, and over the time, the pH of the cheese samples decreased significantly and reached the lowest level on the last day of storage. However, the use of PLA-PCL-based nanocomposite films reinforced with TiO_2 nanoparticles and different levels of BEN caused a decrease in the rate of pH loss of the cheeses during the storage period compared to the control sample ($p<0.05$). On the last day of storage, the lowest pH value was obtained in the control sample (4.59) and the highest pH value on this day was related to the cheese packaged in the film containing TiO_2 nanoparticles and 7% level of BEN (5.04). In the study of Abbas et al. [37], the pH values of cheese samples decreased during the storage period due to bacterial activity. The decrease in pH values of UF cheese samples during storage at refrigerator temperature was also observed in the study of Karimi Sani et al. [26]. In agreement with the results of the present study, Li et al. [33] found that PLA films containing TiO_2 nanoparticles were able to reduce the pH changes of cottage cheese during storage period.

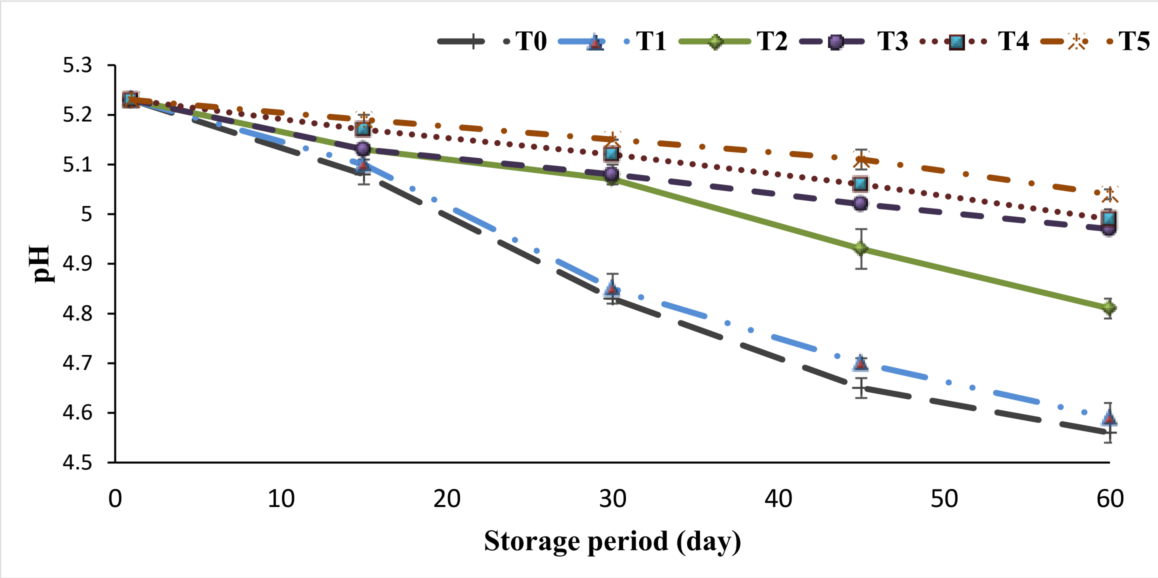


Fig 3. Changes in pH of UF cheese samples during the storage time at 4°C.

T0: Control sample; T1: sample covered with PLA-PCL control film; T2: sample covered with PLA-PCL film containing TiO_2+BEN0%; T3: sample covered with PLA-PCL film containing TiO_2+BEN1%; T4: sample covered with PLA-PCL film containing TiO_2+BEN3%; T5: sample covered with PLA-PCL film containing TiO_2+BEN7%.

3.4. Acidity values of cheeses

The changes in the acidity values of cheese samples during 60 days of storage at refrigerator temperature are also shown in Fig. 4. As can be seen in this figure, at the beginning of the storage period, the acidity of UF cheese was 0.84% (in terms of lactic acid), and over the time, the acidity of cheese samples increased significantly and reached the highest level on the last day of storage. The decrease in pH and increase in acidity of cheese samples during the storage period are related to the fermentation of lactose sugar by microorganisms (especially lactic acid bacteria) and its conversion into organic acids [38]. On the other hand, during the storage period of cheese, amino acids and free fatty acids are released by lipolysis, proteolysis and lipolysis reactions, which are another reason for the increase in acidity and decrease in pH of cheese during the storage or ripening period [39]. In the study of Gohargani et al. [36], during the storage period at refrigerator temperature, the pH values of UF cheese samples gradually decreased and the acidity values of the cheeses increased. However, the use of PLA-PCL-based nanocomposite films reinforced with TiO_2 nanoparticles and different levels of BEN caused a decrease in the rate of increase in the acidity of the cheeses during the storage period compared to the control sample ($p<0.05$), which is related to the significant effect of the films in reducing the growth and proliferation of microorganisms in the cheese samples during the storage period. On the last day of storage period, the highest acidity was obtained in the control sample (1.91%) and the lowest acidity on this day was related to the cheese packaged in the film containing TiO_2 nanoparticles and 7% level of BEN (1.06%).

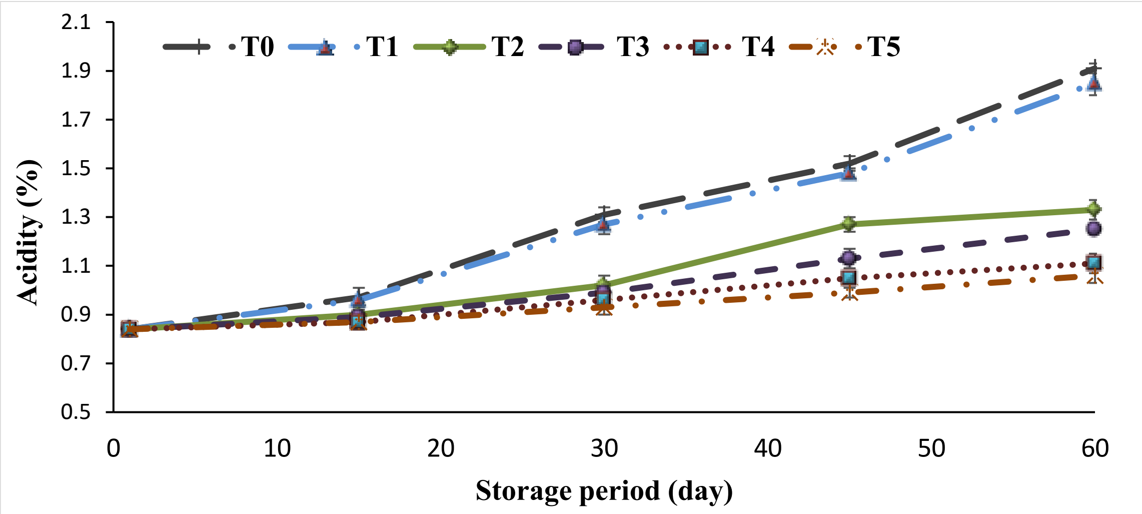


Fig 4. Changes in acidity of UF cheese samples during the storage time at 4°C.

T0: Control sample; T1: sample covered with PLA-PCL control film; T2: sample covered with PLA-PCL film containing TiO_2+BEN0%; T3: sample covered with PLA-PCL film containing TiO_2+BEN1%; T4: sample covered with PLA-PCL film containing TiO_2+BEN3%; T5: sample covered with PLA-PCL film containing TiO_2+BEN7%.

3.5. Hardness of cheese

The hardness of cheese is directly related to fat content, moisture, pH, emulsifying salt, type of cheese and characteristics of the product [40]. The changes in the hardness values of cheese samples during 60 days of storage at refrigerator temperature are also shown in Fig. 5. At the beginning of the storage period, the hardness of UF cheese was 317.44 g and over the time, the hardness of cheese samples increased significantly and reached the highest level on the last day of storage period. However, the use of PLA-PCL-based nanocomposite films reinforced with TiO_2 nanoparticles and different levels of BEN caused a decrease in the rate of hardening of cheeses during the storage period compared to the control sample ($p<0.05$). On the last day of storage, the highest hardness was obtained in the control sample (549.32 g) and the lowest hardness on this day was for the cheese packaged in a film containing TiO_2 nanoparticles and 7% BEN (380.11 g). Better moisture retention and reduced pH changes in cheeses due to the usage of nanocomposite films could be the reason for the slower hardening of cheese samples packaged in these active films compared to the control. Gohargani et al. [36] also reported an increase in the hardness of cheese samples during storage at refrigerator temperature, in agreement with the results of the present study. These researchers also showed a decrease in the rate of firmness of UF white cheeses due to the use of chitosan-whey protein nanocomposites containing TiO_2 nanoparticles and *Zataria multiflora* essential oil. In the study of Adel et al. [34], it was observed that chitosan/whey protein concentrate bionanocomposites containing different levels of moringa essential oil nanoemulsion had a negligible effect on the texture of Ras cheese.

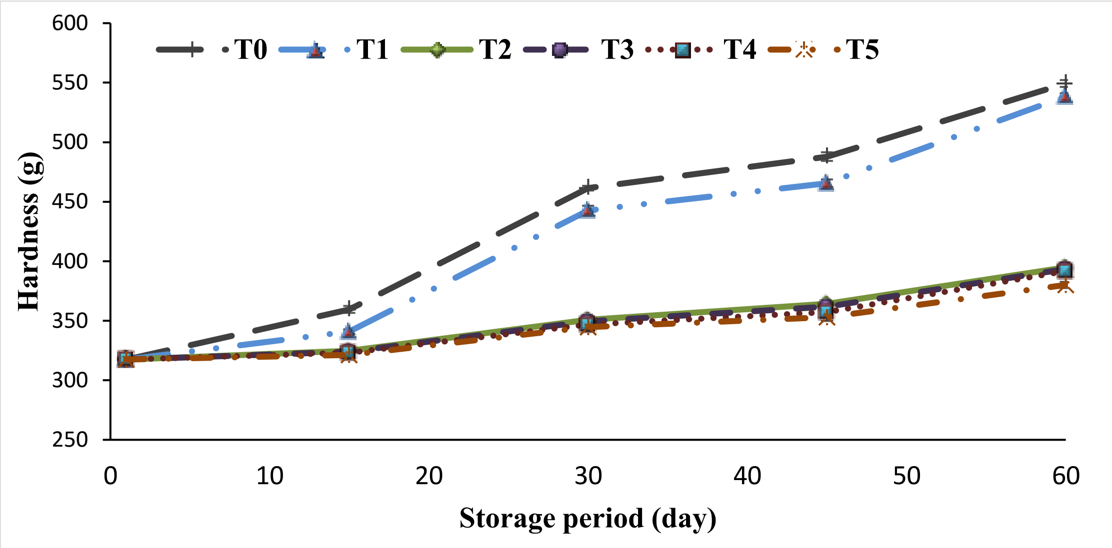


Fig 5. Changes in peroxide value (meq/kg) of UF cheese samples during the storage time at 4°C.

T0: Control sample; T1: sample covered with PLA-PCL control film; T2: sample covered with PLA-PCL film containing TiO_2+BEN0%; T3: sample covered with PLA-PCL film containing TiO_2+BEN1%; T4: sample covered with PLA-PCL film containing TiO_2+BEN3%; T5: sample covered with PLA-PCL film containing TiO_2+BEN7%.

3.6. Peroxide index of cheeses

Lipid oxidation is a destructive chemical reaction that, in addition to reducing the quality and shelf life of food products, has an adverse effect on the organoleptic properties of food products. During lipid oxidation, various primary and secondary products are produced. Hydroperoxides are the primary products of lipid oxidation and their levels in food products are examined using the peroxide index test [41]. The changes in the peroxide index values of cheese samples during 60 days of storage at refrigerator temperature are also shown in Fig. 6. As can be seen in this figure, at the beginning of the storage period, the peroxide index of UF cheese was 0.478 meq/kg, and over the time, the level of this oxidation index in cheese samples increased significantly and reached the highest level on the last day of storage. However, the use of PLA-PCL-based nanocomposite films reinforced with TiO_2 nanoparticles and different levels of BEN caused a decrease in the rate of hydroperoxide production in cheeses during the storage period compared to the control ($p<0.05$). On the last day of storage, the highest peroxide index was obtained in the control sample (2.517 meq/kg) and the lowest on this day was for cheese packaged in a film containing TiO_2 nanoparticle and 7% BEN (1.583 meq/kg). In their study, Hojatoleslami et al. [42] showed a decrease in the rate of lipid oxidation in fish fillets packaged with a composite film based on PLA combined with nanoemulsions of lemon and bay leaf essential oils compared to the control. The increase in antioxidant activity of ricotta cheese due to the combination of basil, rosemary, and thyme was also reported in the study of Hamdi and Hafez [43]. The effect of natural preservatives obtained from plant sources such as potato peel extracts and peanut peel on the reduction of the peroxide index of soft cheese during storage was also shown in another study [44].

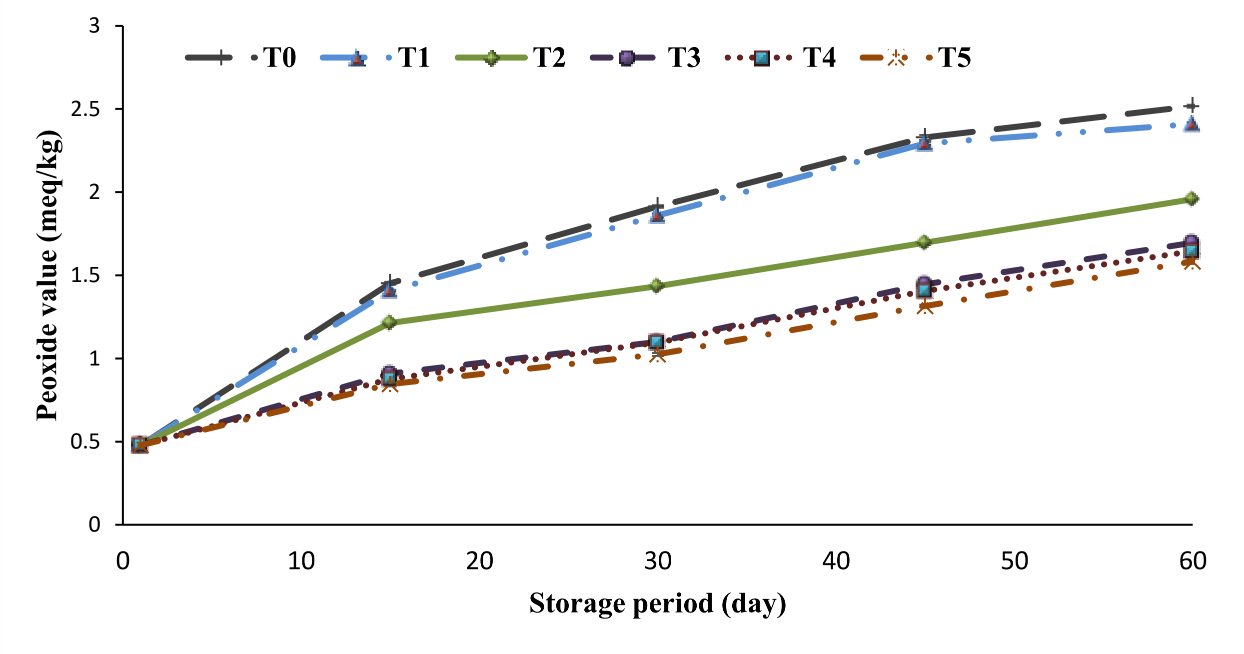


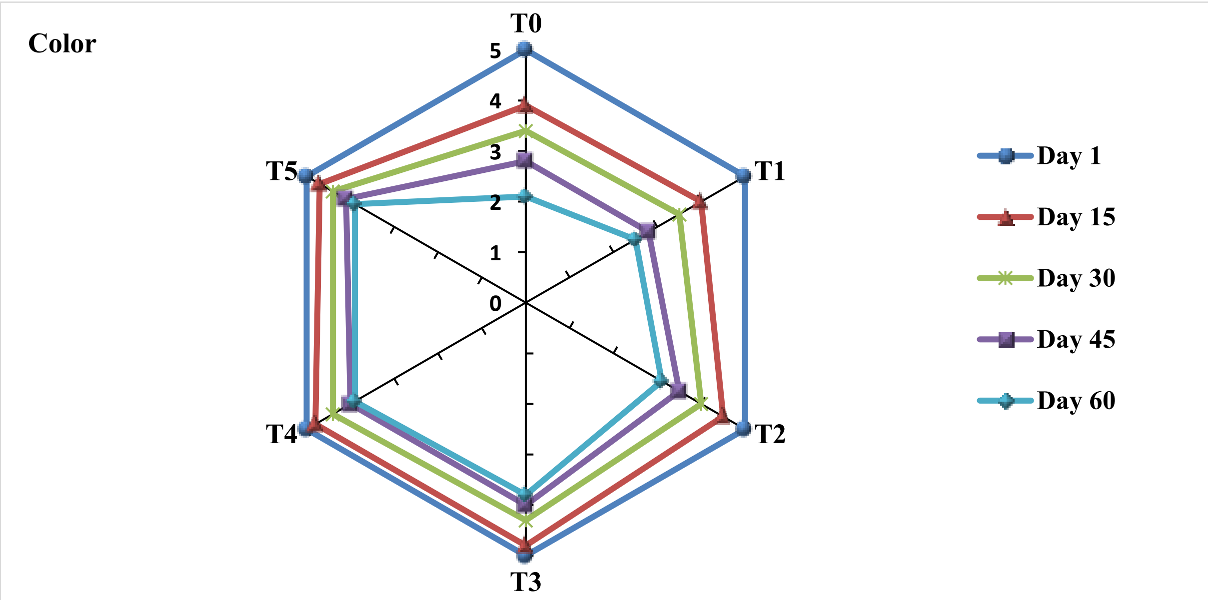
Fig 6. Changes in peroxide value (meq/kg) of UF cheese samples during the storage time at 4°C.

T0: Control sample; T1: sample covered with PLA-PCL control film; T2: sample covered with PLA-PCL film containing TiO_2+BEN0%; T3: sample covered with PLA-PCL film containing TiO_2+BEN1%; T4: sample covered with PLA-PCL film containing TiO_2+BEN3%; T5: sample covered with PLA-PCL film containing TiO_2+BEN7%.

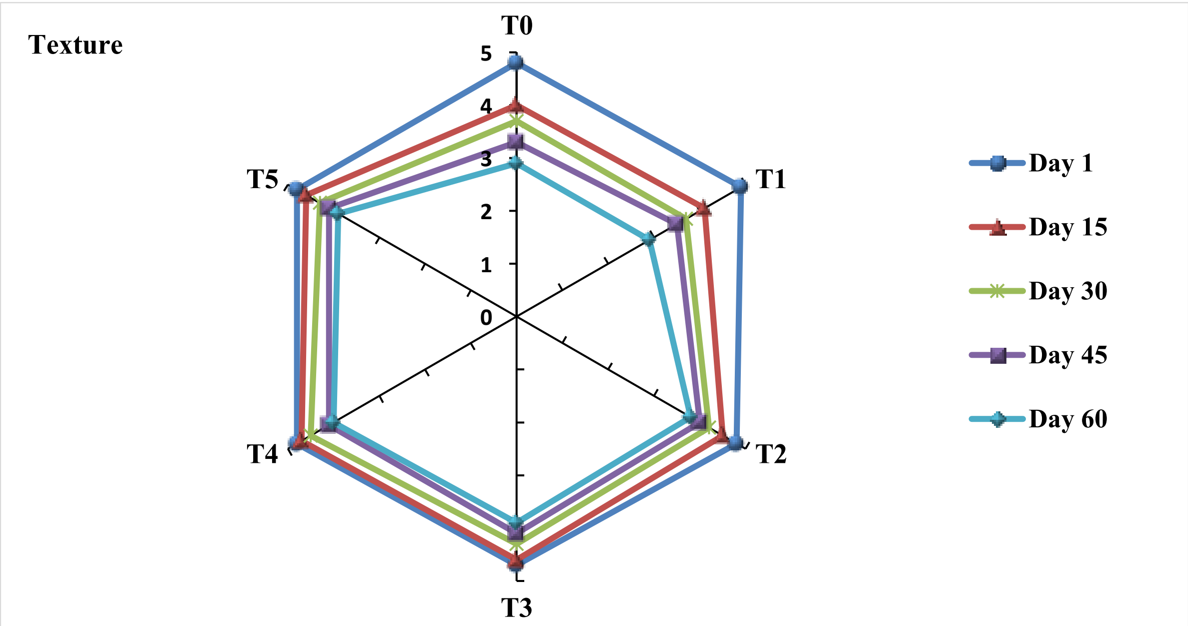
3.7. Sensory evaluation of cheeses

In this study, the sensory properties of UF cheese samples, including color, texture, flavor, odor, and overall acceptability were examined by a five-point hedonic test during storage at refrigerator temperature. As shown in Fig. 7. At the beginning of the storage period, all cheese samples obtained high sensory scores and there was no statistically significant difference between the different samples. Over the time, the color, texture, flavor, odor, and overall acceptability scores of the cheese samples gradually decreased, but the fastest rate of decrease in sensory scores was for the control cheese and the cheese packaged in PLA-PCL film without additives. The decrease in the texture score of the cheeses over time is related to the decrease in moisture and the hardening of the cheeses. The reduction of color score is related to the chemical reactions (oxidation) and microbial activity that cause cheese spoilage on the one hand, and is related to moisture loss on the other. This is because the higher the moisture content of the cheeses, the higher the amount of light reflection and makes the cheeses appear whiter. The decrease in the flavor and odor scores of cheeses over time is also related to lipid oxidation and the production of secondary oxidation products, as well as the growth of microorganisms and secondary metabolites produced by them. The decrease in these sensory properties can ultimately lead to a decrease in the overall acceptability of cheeses over time. As the results of physicochemical tests performed on cheese samples during storage at refrigerator temperature showed, the use of PLA-PCL-based nanocomposite films reinforced with TiO_2 nanoparticles and different levels of BEN was able to delay the oxidation of fats in cheese samples compared to the control. Therefore, these films by delaying the spoilage of UF cheese resulted in better preservation of the sensory properties of cheeses during storage. In line with these results, in the study of Abbas et al. [37]. the incorporation of basil essential oil was able to improve the organoleptic properties of soft cheese samples compared to the control. In the study of Li et al. [33], PLA films containing TiO_2 nanoparticles were able to maintain the sensory quality of cottage cheese during storage compared to the control. El-Sayed et al. [45] found that soft white cheeses containing 0.50% and 0.75% cumin essential oil nanoemulsion had the highest sensory properties. A gradual decrease in the overall acceptability scores of UF cheese samples during storage at refrigerator temperature was also reported in the study of Karimi Sani et al. [29]. In the study of Bakhshi et al. [21], different levels of basil essential oil did not have an adverse or bad effect on the organoleptic properties of Iranian white cheese.

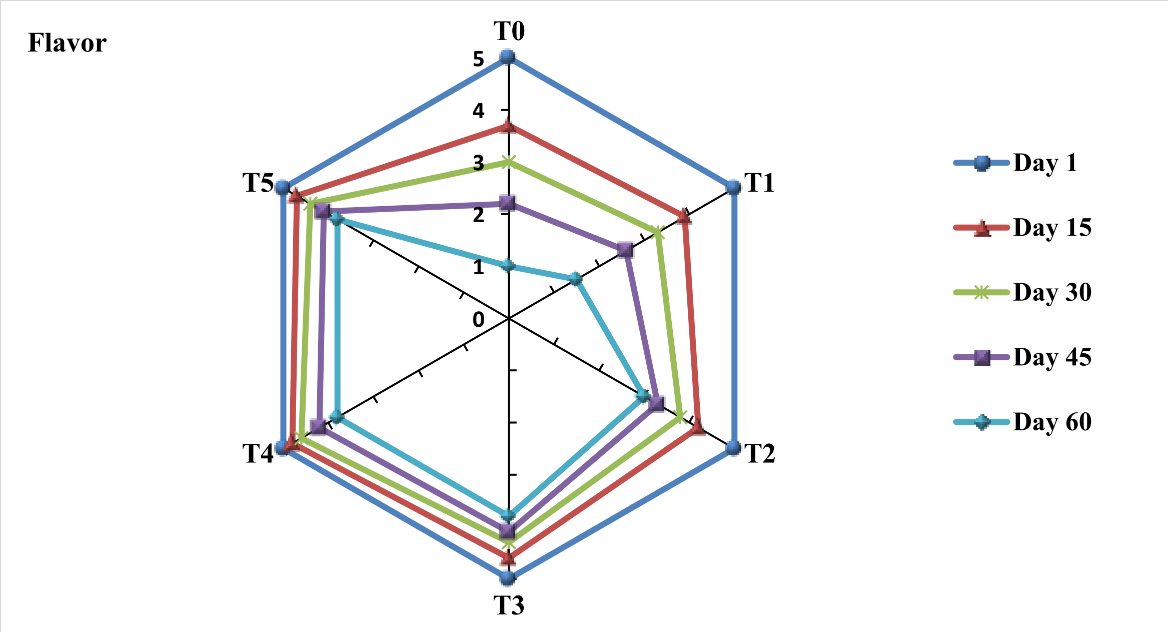
(A)



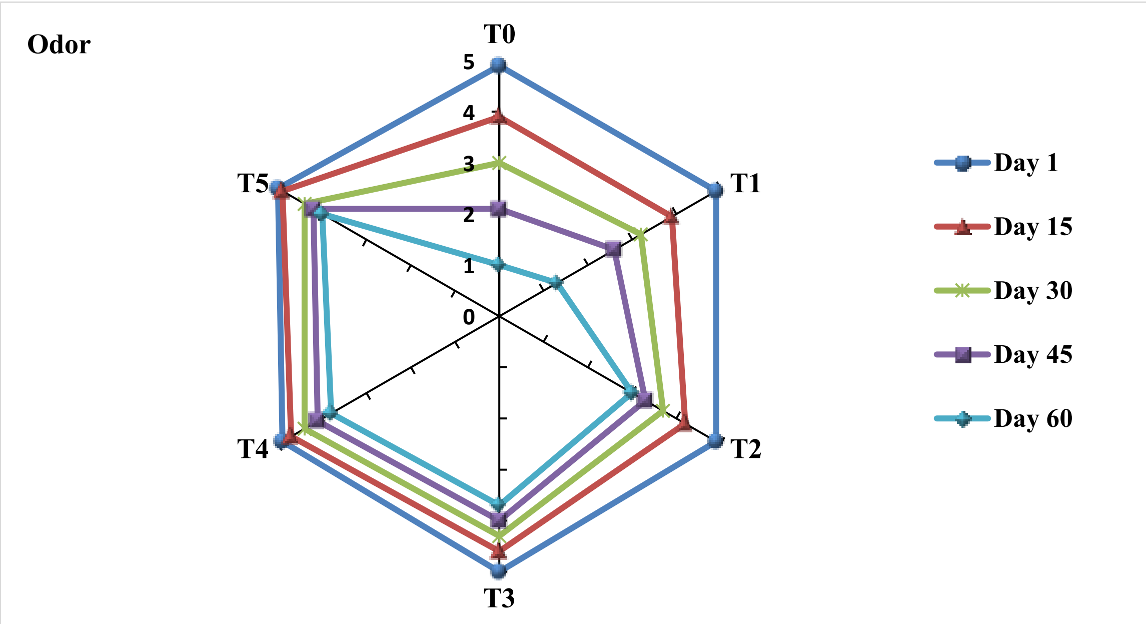
(B)



(C)


Flavor
T0
5
4
3
2
1
0
T1
T2
T3
T4
T5
Day 1
Day 15
Day 30
Day 45
Day 60

(D)


Odor
T0
5
4
3
2
1
0
T1
T2
T3
T4
T5
Day 1
Day 15
Day 30
Day 45
Day 60

(E)

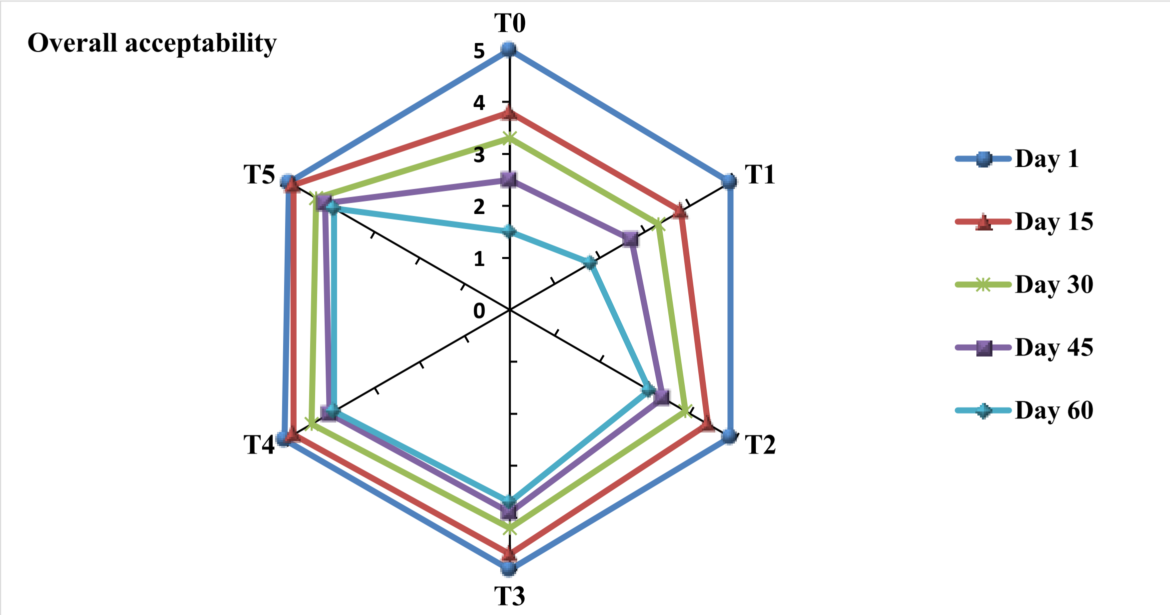


Fig 7 Comparison of color (A), texture (B), flavor (C), odor (D) and overall acceptability (E) scores of UF cheese samples during the storage time at 4°C.

T0: Control sample; T1: sample covered with PLA-PCL control film; T2: sample covered with PLA-PCL film containing TiO_2+BEN0%; T3: sample covered with PLA-PCL film containing TiO_2+BEN1%; T4: sample covered with PLA-PCL film containing TiO_2+BEN3%; T5: sample covered with PLA-PCL film containing TiO_2+BEN7%.

4- Conclusion

In this research, the effect of nanocomposite films based on PLA-PCL reinforced with TiO_2 nanoparticles and different levels of BEN on the quality and sensory properties of UF cheese was investigated. The results showed that over the time, the percentage of weight loss, acidity, peroxide index and hardness of the cheeses increased and their pH decreased significantly. The PLA-PCL film without additives didn't have a significant effect on the rate of these changes in the cheese samples, and its changes were almost similar to the control. However, the use of PLA-PCL-based nanocomposite films reinforced with TiO_2 nanoparticles and different levels of BEN was able to significantly reduce the rate of changes in the physicochemical properties of the cheeses compared to the control and delay the oxidation of lipids in the cheese samples. The results of the evaluation of the sensory properties of the cheeses showed that during the storage period, the scores of color, texture, flavor, odor, and overall acceptability of the cheese samples gradually decreased, and the fastest rate of decrease was observed in the control sample and cheese packaged in PLA-PCL film without additives, and these samples obtained unacceptable sensory scores from the 30th day onwards. In cheeses packaged in PLA-PCL-based nanocomposite films reinforced with TiO_2 nanoparticles and different levels of BEN, the sensory properties of the cheeses were significantly maintained during the storage period, and these samples were acceptable in terms of sensory properties until the last day of storage. The results of this study generally indicated the desirable inhibitory and antioxidant activity of PLA-PCL-based films reinforced with TiO_2 nanoparticles and different levels of BEN. These films were able to significantly reduce the rate of lipid oxidation of UF cheeses during storage and maintain the sensory properties of cheeses until the last day of storage. Therefore, they are recommended for improving the quality and safety and extending the shelf life of cheeses. Based on the results obtained in this study, PLA-PCL film containing TiO_2 nanoparticles and 7%

level of BEN can be introduced as the best treatment.

5-References

[1] Kamath, R., Basak, S., & Gokhale, J. (2022). Recent trends in the development of healthy and functional cheese analogues-a review. *LWT*, 155: 112991.

[2] Bulat, T., & Topcu, A. (2019). The effect of oxidation-reduction potential on the characteristics of UF white cheese produced using single strains of *Lactococcus lactis*. *LWT*, 109: 296-304.

[3] Mahmoodi, Z., Zendeboodi, F., Mortazavian, A.M., Farhoodi, M., Mofid, V., Mohammadi Moghaddam, T., & Mehraban Sang Atash, M. (2022). Effect of adding salty-taste enhancers on physicochemical and microstructural characteristics of reduced-NaCl UF cheese using mixture design methodology. *International Journal of Dairy Technology*, 75(1): 214-238.

[4] Iqbal, M.W., Riaz, T., Yasmin, I., Leghari, A.A., Amin, S., Bilal, M., & Qi, X. (2021). Chitosan-based materials as edible coating of cheese: A review. *Starch‐Stärke*, 73(11-12): 2100088.

[5] Dai, L., Li, R., Liang, Y., Liu, Y., Zhang, W., & Shi, S. (2022). Development of pomegranate peel extract and nano ZnO co-reinforced polylactic acid film for active food packaging. *Membranes*, 12(11): 1108.

[6] Ncube, L.K., Ude, A.U., Ogunmuyiwa, E.N., Zulkifli, R., & Beas, I.N. (2020). Environmental impact of food packaging materials: A review of contemporary development from conventional plastics to polylactic acid based materials. *Materials*, 13(21): 4994.

[7] Kim, I., Viswanathan, K., Kasi, G., Sadeghi, K., Thanakkasaranee, S., & Seo, J. (2019). Poly (lactic acid)/ZnO bionanocomposite films with positively charged ZnO as potential antimicrobial food packaging materials. *Polymers*, 11(9): 1427.

[8] Kian, L.K., Saba, N., Jawaid, M., & Sultan, M.T.H. (2019). A review on processing techniques of bast fibers nanocellulose and its polylactic acid (PLA) nanocomposites. *International Journal of Biological Macromolecules*, 121: 1314-1328.

[9] Swaroop, C., & Shukla, M. (2018). Nano-magnesium oxide reinforced polylactic acid biofilms for food packaging applications. *International Journal of Biological Macromolecules*, 113: 729-736.

[10] Martínez-Aguilar, V., Peña-Juárez, M.G., Carrillo-Sanchez, P.C., López-Zamora, L., Delgado-Alvarado, E., Gutierrez-Castañeda, E.J., & Gonzalez-Calderon, J.A. (2023). Evaluation of the Antioxidant and Antimicrobial Potential of SiO2 Modified with Cinnamon Essential Oil (*Cinnamomum Verum*) for Its Use as a Nanofiller in Active Packaging PLA Films. *Antioxidants*, 12(5): 1090.

[11] Golshan Ebrahimi, N. (2020). Optimization of ternary blends based on poly (lactic acid) according to physical and biological properties. *Journal of Applied Research of Chemical-Polymer Engineering*, 4(1): 66-53.

[12] Lukic, I., Vulic, J., & Ivanovic, J. (2020). Antioxidant activity of PLA/PCL films loaded with thymol and/or carvacrol using scCO2 for active food packaging. *Food Packaging and Shelf Life*, 26: 100578.

[13] Tuancharoensri, N., Ross, G.M., Kongprayoon, A., Mahasaranon, S., Pratumshat, S., Viyoch, J., & Ross, S. (2023). In situ compatibilized blends of PLA/PCL/CAB Melt-Blown Films with High Elongation: investigation of miscibility, morphology, crystallinity and modelling. *Polymers*, 15(2): 303.

[14] Li, W., Zhang, C., Chi, H., Li, L., Lan, T., Han, P., & Qin, Y. (2017). Development of antimicrobial packaging film made from poly (lactic acid) incorporating titanium dioxide and silver nanoparticles. *Molecules*, 22(7): 1170.

[15] Yousefi, A.R., Savadkoohi, B., Zahedi, Y., Hatami, M., & Ako, K. (2019). Fabrication and characterization of hybrid sodium montmorillonite/TiO2 reinforced cross-linked wheat starch-based nanocomposites. *International Journal of Biological Macromolecules*, 131: 253-263.

[16] Roy, S., Zhai, L., Kim, H.C., Pham, D.H., Alrobei, H., & Kim, J. (2021). Tannic-acid-cross-linked and TiO_2-nanoparticle-reinforced chitosan-based nanocomposite film. *Polymers*, 13(2): 228.

[17] Joy, J., Mathew, J., & George, S.C. (2018). Nano-materials for photo-electrochemical water splitting–review. *International Journal of Hydrogen Energy*, 43: 4804-4817.

[18] Ahmed, A.F., Attia, F.A., Liu, Z., Li, C., Wei, J., & Kang, W. (2019). Antioxidant activity and total phenolic content of essential oils and extracts of sweet basil (*Ocimum basilicum* L.) plants. *Food Science and Human Wellness*, 8(3): 299-305.

[19] da Silva, W.M.F., Kringel, D.H., de Souza, E.J.D., da Rosa Zavareze, E., & Dias, A.R.G. (2022). Basil essential oil: Methods of extraction, chemical composition, biological activities, and food applications. *Food and Bioprocess Technology*, 15(1): 1-27.

[20] He, R., Chen, W., Chen, H., Zhong, Q., Zhang, H., Zhang, M., & Chen, W. (2022). Antibacterial mechanism of linalool against L. monocytogenes, a metabolomic study. *Food Control*, 132: 108533.

[21] Bakhshi, F., Mirzaei, H. & Asefi, N. (2019). Effect of Basil Essential Oil on the Microbial and Sensory Characteristics of Iranian Traditional White Cheese During Ripening, *Journal of Veterinary Research,* 75(1), 47-56.

[22] Mahdi, A.A., Al-Maqtari, Q.A., Mohammed, J.K., Al-Ansi, W., Aqeel, S.M., Cui, H., & Lin, L. (2021). Nanoencapsulation of Mandarin essential oil: Fabrication, characterization, and storage stability. *Foods*, 11(1): 54.

[23] Vahidmoghadam, F., Pourahmad, R., Mortazavi, A., Davoodi, D., & Azizinezhad, R. (2019). Characteristics of freeze-dried nanoencapsulated fish oil with whey protein concentrate and gum arabic as wall materials. *Food Science and Technology*, 39: 475-481.

[24] Sharma, S., Byrne, M., Perera, K.Y., Duffy, B., Jaiswal, A.K., & Jaiswal, S. (2023). Active film packaging based on bio-nanocomposite TiO2 and cinnamon essential oil for enhanced preservation of cheese quality. *Food Chemistry*, 405: 134798.

[25] Costa, M.J., Maciel, L.C., Teixeira, J.A., Vicente, A.A., & Cerqueira, M.A. (2018). Use of edible films and coatings in cheese preservation: Opportunities and challenges. *Food Research International,* 107: 84-92.

[26] Karimi Sani, I., Alizadeh Khaledabad, M., Pirsa, S., & Moghaddas Kia, E. (2020). Physico-chemical, organoleptic, antioxidative and release characteristics of flavoured yoghurt enriched with microencapsulated *Melissa officinalis* essential oil. *International Journal of Dairy Technology*, 73(3): 542-551.

[27] Mahcene, Z., Khelil, A., Hasni, S., Bozkurt, F., Goudjil, M.B., & Tornuk, F. (2021). Home-made cheese preservation using sodium alginate based on edible film incorporating essential oils. *Journal of Food Science and Technology*, 58: 2406-2419.

[28] Saravani, M., Ehsani, A., Aliakbarlu, J., & Ghasempour, Z. (2019). Gouda cheese spoilage prevention: Biodegradable coating induced by *Bunium persicum* essential oil and lactoperoxidase system. *Food Science & Nutrition*, 7(3): 959-968.

[29] Karimi Sani I, Alizadeh M. (2022). Packaging of UF cheese with edible film of nanocomposite isolated mung bean protein-apple pectin containing microencapsulation of cardamom extract and serum oxide nanoparticles and quantum carbon Graphite dots: Investigation of its physicochemical properties. *FSCT*, 19 (128) :235-247.

[30] Wu, Y., Qin, Y., Yuan, M., Li, L., Chen, H., Cao, J., & Yang, J. (2014). Characterization of an antimicrobial poly(lactic acid) film prepared with poly(ε-caprolactone) and thymol for active packaging. *Polymers for Advanced Technologies, 25*(9), 948-954.

[31] Milovanovic, S., Hollermann, G., Errenst, C., Pajnik, J., Frerich, S., Kroll, S., . . . Ivanovic, J. (2018). Supercritical CO2 impregnation of PLA/PCL films with natural substances for bacterial growth control in food packaging. *Food Research International, 107*, 486-495.

[32] Sadeghi, A., Razavi, S. M. A., & Shahrampour, D. (2022). Fabrication and characterization of biodegradable active films with modified morphology based on polycaprolactone-polylactic acid-green tea extract. *International Journal of Biological Macromolecules, 205*, 341-356.

[33] Li, W., Li, L., Zhang, H., Yuan, M., & Qin, Y. (2018). Evaluation of PLA nanocomposite films on physicochemical and microbiological properties of refrigerated cottage cheese. *Journal of Food Processing and Preservation*, 42(1): e13362.

[34] Adel, M.K., Youssef, A.M., Awad, R.A., & El Deen, A.M.G. (2023). Development of CS/WPC/MO-NE bionanocomposites for coating Ras cheese based on Moringa essential oil nanoemulsion. *Al-Azhar Journal of Agricultural Research*, 48(1): 41-53.

[35] Nateghi L, Khazaei A, Zand N, orumiyeh ei A R. (2021). Evaluation of physicochemical and sensory properties of Jug cheese packed in biodegradable film based on polyvinyl alcohol and pinto bean starch containing essential oils of garlic, ginger and cinnamon. *FSCT*, 18 (119) :95-112

[36] Gohargani, M., Lashkari, H. & Shirazinejad, A. R. (2021) The effect of chitosan-whey protein based edible coating containing bionanocomposite material and Zataria

multiflora essential oil on UF-Feta type cheese shelf life *Iranian Food Science and Technology Research Journal.* 17, 5, 729-745.

[37] Abbas, H.M., Kassem, J.M., Mohamed, S.H.S., & Zaky, W.M. (2018). Quality appraisal of ultra-filtered soft buffalo cheese using basil essential oil. *Acta Scientiarum Polonorum Technologia Alimentaria*, 17(4): 305-312.

[38] Jalilzadeh, A., Hesari, J., Peighambardoust, S. H., & Javidipour, I. (2018). The effect of ultrasound treatment on microbial and physicochemical properties of Iranian ultrafiltered feta-type cheese. *Journal of Dairy Science*, 101: 5809-5820.

[39] Rashtchi, P., Bazmi, A., Noshirvani, N., & Moosavy, M.H. (2021). Comparison of the microbial, physicochemical, and sensorial properties of raw and pasteurized Lighvan cheeses during ripening time. *Food Science and Nutrition*, 9(10): 5527-5535.

[40] Shamsia, S., & El-Ghannam, M. (2017). Production and evaluation of processed cheese analogue using ricotta cheese prepared from sweet whey. *Alexandria Journal of Food Science and Technology*, 14: 1-11.

[41] El-Hadary, A.E., & Taha, M. (2020). Pomegranate peel methanolic-extract improves the shelf-life of edible-oils under accelerated oxidation conditions. *Food Science & Nutrition*, 8(4): 1798-1811.

[42] Hojatoleslami, M., Ahari, H., Larijani, K., & Sharifan, A. (2022). Preservation effect of *Lippia citriodora* and *Laurus nobilis* nanoemulsions incorporated with polylactic acid composite film for rainbow trout fillet packaging. *Food Science and Technology*, 42: e83921.

[43] Hamdy, S.M., & Hafaz, Y.M. (2018). The Combined Effect of Dried Rosemary, Thyme and Basil with Fresh Garlic on Quality Characteristics of Ricotta Cheese during Storage. *Egypt Journal of Food Science*, 46: 125-132.

[44] El-Galeel, A., Ali, A.A., & El-Zahar, K.M. (2018). Production of white soft cheese fortified with natural antioxidants as a functional dairy food. *Zagazig Journal of Agricultural Research*, 45(2): 637-656.

[45] El-Sayed, H.S., & El-Sayed, S.M. (2021). A modern trend to preserve white soft cheese using nano-emulsified solutions containing cumin essential oil. *Environmental Nanotechnology, Monitoring and Management*, 16: 100499.

مجله علوم و صنایع غذایی ایران

سایت مجله: www.fsct.modares.ac.ir

مقاله علمی_پژوهشی

تاثیر فیلم نانوکامپوزیتی بر پایه پلی‌لاکتیک اسید/پلی‌کاپرولاکتون تقویت شده با نانوذرات TiO_2 و نانوکپسول اسانس ریحان بر ویژگی های فیزیکوشیمیایی و حسی پنیر فراپالایش

سحر خان احمدلو[1]، لیلا نجفیان*[2]، اسماعیل قاسمی[3]، نوید نعیمیان[4]

۱- دانشجوی دکتری علوم و مهندسی مواد غذایی، دانشکده علوم و صنایع غذایی، واحد ساری، دانشگاه آزاد اسلامی، ساری، ایران
۲- استادیار گروه علوم و صنایع غذایی، دانشکده علوم و صنایع غذایی، واحد ساری، دانشگاه آزاد اسلامی، ساری، ایران
۳- استاد گروه فرآیند، پژوهشگاه پلیمر و پتروشیمی ایران، پژوهشگاه فرآیند، تهران، ایران
۴- استادیار گروه صنایع چوب و کاغذ، دانشکده صنایع چوب و کاغذ، واحد ساری، دانشگاه آزاد اسلامی، ساری، ایران

اطلاعات مقاله

تاریخ های مقاله :

تاریخ دریافت:

تاریخ پذیرش:

کلمات کلیدی:

پلی‌کاپرولاکتون،
پلی‌لاکتیک اسید،
دی‌اکسید تیتانیوم،
ریحان،
ریزپوشانی،
پنیر فراپالایش

DOI: 10.22034/FSCT.22.161.297.

* مسئول مکاتبات:

najafian_5828@yahoo.com

چکیده

در این تحقیق تاثیر فیلم‌های نانوکامپوزیتی بر پایه PLA-PCL حاوی نانوذرات TiO_2 (۳ درصد وزنی) و سطوح مختلف نانوکپسول اسانس ریحان (۰، ۱، ۳ و ۷ درصد وزنی بر اساس پلیمر) بر ویژگی های فیزیکوشیمیایی و حسی پنیر فراپالایش (UF) طی دوره انبارمانی ۶۰ روزه در دمای ٤ درجه سانتی‌گراد بررسی گردید. درصد اُفت وزن، مقادیر pH، اسیدیته، سفتی بافت، عدد پراکسید و همچنین ویژگی‌های حسی پنیرها مورد آزمون قرار گرفت. نتایج آزمون‌ها نشان داد که طی دوره انبارمانی مقادیر اُفت وزن، اسیدیته، سفتی بافت و اندیس پراکسید نمونه‌های پنیر افزایش و میزان pH آن‌ها به طور معنی‌داری کاهش یافت ($p<0.05$) و استفاده از فیلم‌های نانوکامپوزیتی بر پایه PLA-PCL تقویت شده با نانوذرات TiO_2 و سطوح مختلف نانوکپسول‌های اسانس ریحان توانستند موجب کاهش سرعت تغییرات در پارامترهای فیزیکوشیمیایی پنیر فراپالایش طی دوره انبارمانی در مقایسه با شاهد گردند. از لحاظ ویژگی‌های حسی، پنیرهای بسته‌بندی شده در فیلم‌های حاوی نانوذرات TiO_2 و سطوح مختلف نانوکپسول‌های اسانس ریحان تا روز آخر انبارمانی قابل پذیرش بودند. بر طبق نتایج حاصله در این تحقیق می‌توان نتیجه گرفت که امکان حفظ کیفیت و ایمنی و توسعه عمر ماندگاری پنیر فراپالایش با استفاده از فیلم‌های نانوکامپوزیتی بر پایه PLA-PCL تقویت شده با نانوذرات TiO_2 و نانوکپسول‌های اسانس ریحان وجود دارد و بهترین نتایج مربوط به فیلم‌های حاوی سطح ۷ درصد نانوکپسول‌های اسانس ریحان می‌باشد.