STORAGE STABILITY OF MICROENCAPSULATED EXTRA VIRGIN OLIVE OIL POWDER

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Abstract

Microencapsulation is the process that aims to increase the stability of food components (oil, pigments, aroma, etc.) during the processing and storage. Microencapsulation is used to convert extra virgin olive oil to powder form maintaining high oxidation stability, phenolic content and antioxidant capacity along the storage. In this study, the storage stability of microencapsulated extra virgin olive oil powder coated with maltodextrin and whey protein isolate as wall materials was investigated by evaluating microencapsulation efficiency, peroxide value, phenolic content and antioxidant activity during storage in aluminium polyethylene pouches at 25 °C and 50% relative humidity (RH) for 180 days. The results showed that microencapsulation efficiency (ME), phenolic content and antioxidant activity of microencapsulated extra virgin olive oil powder (MEVOP) during storage decreased 16%, 44.6% and 58.6%, respectively as compared to initial value, whereas the peroxide value of sample increased from 11.6 meq O_2 kg^{-1} oil to 35.6 meq O_2 kg^{-1} oil in the 180 days of storage. During storage, the degradation of phenolic content, antioxidant activity and the increase in the peroxide value of microencapsulated extra virgin olive oil were found to fit the first-order kinetic model. Although microencapsulation efficiency of samples changed slightly, phenolic content and antioxidant activity drastically reduced and peroxide value of samples increased sharply during the storage. This is possibly caused by small particle size and/or huge surface area of olive oil powder.

Keywords: microencapsulation, extra virgin olive oil, storage, oxidation.

Introduction

Extra virgin olive oil is obtained mechanically from ripe fruit of the olive tree without any chemical treatment. Extra virgin olive oil is an important vegetable oil with unique taste and odour which can be consumed naturally (Gögüş et al., 2009). Among the different categories of olive oil, the extra virgin olive oil is outstanding in gastronomic, nutritional, therapeutic and economic importance (Mendez, Falque, 2007). Studies conducted by other researchers attributed these benefits were due to its mono unsaturated fatty acid content (Fernández-Jarne et al., 2002; Martínez-González et al., 2002; Tripoli et al., 2005). However, recent research indicates that minor constituents appear to prevent several diseases. The phenolic fraction has importance regarding to antioxidant activities (Bendini et al., 2010) and the changes in the phenolic compounds over time could be an important quality control parameter of extra virgin olive oil.

The environmental conditions including oxygen, light, moisture and temperature make olive oil susceptible to oxidation due to high amount of monounsaturated fatty acid (oleic acid) content (Calvo et al., 2010; O'Brien, 2004). Oxidation is the main cause of olive oil quality deterioration and its reaction rate determines the shelf life of oil (Gomez-Alonso et al., 2007). Oxidation that occurs in edible oils relates to the loss of minor components and formation of new compounds, causing nutritional loss as well as the development of rancid and other off-flavours (Velasco et al., 2003; Sun-Waterhouse et al., 2011, Cicerale et al., 2013).

Storage conditions are considered as critical variables that affect the quality of olive oil and its shelf life which is attributed to lipid oxidation mechanism which leads to rancidity (Vacca et al., 2006). Because olive oil is produced in a limited period of time, but consumed throughout the year, it must be stored, and this storage period determines the commercial life of the olive oil (Hrncirik, Fritsche, 2005; Kiritsakis, Dugan, 1984; Zanoni et al., 2005). Many studies on oxidation of virgin olive oils were based on accelerated test measurements (Aparicio et al., 1999; Baldioli, 1996; Gutierrez et al., 2002; Krichene et al., 2010). In these studies, good correlations between changes in various components and stability were found.

Microencapsulation can be used to protect fragrances or other active agents of olive oil from oxidation caused by heat, light, moisture, from contact with other substances over a long shelf life, to prevent evaporation of volatile compounds (Ghosh, 2006; Soest, 2007). Microencapsulation is a process of coating individual particles or droplets with a continuous film to produce capsules in a micrometer to milimeter in size (Tyagi et al., 2011). Microencapsulation process provides protection of reactive substances from the environment, converting liquid active component into a dry solid system and separation incompatible components for functional reasons. The surface oil content or microencapsulation efficiency of microencapsulated oil powder determines the storage stability. While converting olive oil to powder form, the surface area of olive oil expands that makes it more sensitive to oxidation.

The aim of this study was to evaluate the storage stability of microencapsulated extra virgin olive oil powder by analysing microencapsulation efficiency, peroxide value, total phenol content and antioxidant activity during 180 days storage.

Materials and Methods

Material

Extra virgin olive oil (ρ=910 kg m^{-3}, μ=0.083 Pa·s at 20 ºC) was purchased from a local grocery store in

Turkey. The whey protein isolate (WPI) supplied by Ak Gıda San. Tic. A.Ş. and maltodextrin (MD, DE19) provided by Qinhuangdao Starch Co Ltd., were used as wall materials in this study. Tween 20 (Merck, Darmstadt, Germany) was used to stabilize the olive oil-water emulsion.

Preparation of olive oil in water emulsion

Maltodextrin (128.8 g) was dissolved in water (200 g) and kept in the dark for one night. Whey protein isolate (9.8 g) was mixed with water (100 g) using mechanical homogenizer (Ultra Turrax T25) at 0.167 kHz for 60 s. Tween 20 was added to olive oil in concentration 1% (w/w) as a stabilizer. Mixture of olive oil and Tween 20 was poured drop wise into the WPI solution using the mechanical homogenizer at 0.167 kHz for 60 s for pre-mixing. In order to obtain stable olive oil in water emulsions (o/w), WPI, olive oil and Tween 20 containing solution was mixed with MD solution and the whole mixture were homogenized using a mechanical homogenizer (Ultra Turrax T25) at 0.291 kHz for 300 s. Prepared emulsion contains 92% (db) maltodextrin and 7% (db) whey protein isolate as wall material. The total solids concentration of feeding emulsion is 40%. The olive oil concentration of the emulsion is 30% in dry basis.

Microencapsulation of olive oil by spray drying and storage of powder

The prepared emulsions were dried in a laboratory scale spray drier (Buchi, B-290, Switzerland) equipment with 0.7 mm diameter nozzle. The spray dryer conditions; the inlet air temperature 200°C, pump rate 22%, aspiration ratio 0.0067 $m^3 s^{-1}$ and air flow rate 0.00013 $m^3 s^{-1}$ were kept constant during the experiments The feeding emulsions at 25 °C were fed to spray dryer and the obtained powder was packed in hermetically sealed aluminium laminated polyethylene (ALPE) pouches.

Microencapsulated olive oil powders were stored at 25 °C and 50% RH for 180 days. In the first 90 days of storage period, the analyses were be carried out in 15 days periods and then 30 days period was followed.

Total oil content

Total oil content of samples was determined according to method of Folch et al. (1957) with some modification. The microencapsulated extra virgin olive oil powder (4 g) was put into an extraction thimble that contained chloroform/methanol (80 mL; 3 : 2 v/v). The obtained mixture was homogenized at 0.0026 kHz for 900 s. Then water (16 mL) was added, and the mixture was shaken vigorously to facilitate the transfer of oil into the chloroform and other products into the water-methanol layer. The chloroform layer was then separated via a separation funnel and collected. The extraction steps were repeated two times. The obtained chloroform layers were combined and evaporated using a rotary evaporator at 65 °C, for 20–30 min. Then the trace amount of chloroform was evaporated in drying oven (at 102 °C temperature for 4 hours). After oven drying remaining is the amount of total oil of MEVOP.

Surface oil content

To determine surface oil, 5 g encapsulated beads were weighed into flaks and 25 mL petroleum ether was added. The mixture was extracted for 5min at room temperature in the dark. The mixture was filtered and petroleum ether was evaporated. Then trace amount of petroleum ether was evaporated in drying oven (at 102 °C temperature for 4 hours) (Folch et al., 1957). After oven drying remaining is the amount of surface oil of MEVOP.

Microencapsulation efficiency (ME)

Microencapsulation efficiency of extra virgin olive oil powder was calculated using the following formula:

$$\mathrm{ME} = \frac{\text{Total oil content} - \text{Surface oil content}}{\text{Total oil content}} \times 100 \quad (1)$$

Peroxide value

The peroxide value of extracted olive oil was expressed as peroxide milliequivalent per kg oil. Extracted olive oil (0.5 g) was dissolved in acetic acid-chloroform solution (3 mL, 3 : 2 v/v). After saturated potassium iodide KI solution was added, the mixture was left to stand for 1 min with occasional shaking. An aliquot (3 mL) of Milli-Q water was added. The mixture was titrated with 0.01 N standardized sodium thiosulphate solution until the yellow iodine colour just disappeared. Starch indicator solution (0.2 mL, 10 kg m^{-3}) was added. The titration continued until the blue colour derived from the iodine just disappeared. A blank sample as reagent control was set up and carried through all the steps (AOCS, 1998).

Phenol Extraction from Olive Oil and Total Phenol Analysis

For phenolic components analysis, firstly the cartridge (Maxi-Clean™ SPE 300mg Hi-Cap C18 cartridge) was conditioned by using dietylether / n-hexane (98 : 2 ratio). Then, 5 g extracted olive oil from microencapsules was weighed and 5 mL hexane was added. This mixture was filtered through the cartridge and cartridge was washed by using 2 mL hexane. Finally the 1.5 mL methanol was filtered from cartridge and the phenolic components were extracted from olive oil (Pellegrini et al., 2001). From the last extract, 50 µL sample was taken and 250 µL Folin-Ciocalteau reactive was added. After 5 min of holdingin dark at room temperature, 750 µL 7% Na_2CO_3 solution was added and the mixture was completed to 5mL by using distilled water. After 2 hours waited at room temperature in dark, the absorbance of the extracts was determined at 765 nm by using spectrometer. All these steps were done for blank. The standard curve was plotted by using caffeic acid as a standard (Singleton, Rossi, 1965; Singleton et al., 1999).

Total Antioxidant Activity Measurement-ABTS Method

Firstly ABTS radical was prepared as, 7mM ABTS water solutions and 2.45 mM potassium persulphate (1 : 0.5 ratio, v : v) were mixed and diluted by ethanol till the absorbance (730 nm) was 0.70. Then, 1 mL

ABTS radical was added into 20μL sample (0.1 g oil 1 mL chloroform). The absorbance was read at 730 nm. Finally, standard curve was drawn by using Trolox (1 mM to 5 mM). The results are given as Trolox equivalent (Pellegrini et al., 2001).

Kinetic analysis of the given quality parameters during storage

The obtained data were subjected to the kinetic modelling in order to determine the degradation kinetics of some quality characteristics (peroxide value, phenolic content and antioxidant activity) during storage. Reaction rate and the relevant coefficients were determined with Eq. (2) using SPSS version 13.0 Windows program (SPSS Inc., Chicago, IL).

$$-\frac{dC}{dt} = k \times C \qquad (2)$$

where: C is the given quality parameter values, t is time and the k is the kinetic constant.

Results and Discussion

The amount of surface oil content of encapsulated product is important for ensuring the storage stability (Anandaraman, Reineccius, 1987). The microencapsulated products, which have high surface oil content, could be more sensitive to oxidation. The change in total oil content, surface oil content and microencapsulation efficiency of microencapsulated extra virgin olive oil powder during storage were given in Table 1. Along the storage of microencapsulated extra virgin olive oil powder, surface oil content increased without a change in total oil content. Therefore, microencapsulation efficiency decreased with increasing storage time. This indicates that, microcapsules were broken and oil in the capsules moves to the surface.

Peroxide value (PV) is an indicator of the oxidation level of oils and fats during processing and storage (Sun-Waterhouse et al., 2011). In general, the PVs of oils increased when the storage proceeded. Initial peroxide value (11.59 meq O_2 kg^{-1} oil) of microencapsulated extra virgin olive oil powder is coherent with the study of Sun-Waterhouse et al. (2011). Peroxide value of our samples increased approximately three times during the storage period of 180 days, comparing to the initial peroxide value (Table 2). This circumstance was possibly related with high oil content at the surface and large surface area of samples. Surface oil content increased during the storage, so that more oil was exposed to oxidation.

The changes in total phenolic content and antioxidant activity of microencapsulated extra virgin olive oil powder during the storage period were given in Table 2.

Olive oil matrix (Fakourelis et al., 1987; Gutfinger 1981; Tripoli et al., 2005), storage temperature and period, oil extraction method and encapsulation materials (Naczk, Shahidi, 2004; Perez-Jimenez, Saura-Calixto, 2006; Reichardt, 1988; Yang et al., 2007) are the factors affecting the total phenolic content. Total phenolic content of microencapsulated extra virgin olive oil powder decreased 44.6% during storage as compared to initial value. Sharp decrease in the total phenol content of extra virgin olive oil was observed in the study of Mendez and Falque (2007), during storage.

Table 1

Total and surface oil content and microencapsulation efficiency values of MEVOP during storage

Time, days	Total oil, %	Surface oil, %	ME,%
0	27.28±0.22	3.63±0.30	86.69±1.91
15	26.45±0.40	4.19±0.11	84.15±1.91
30	27.05±0.41	4.70±0.56	82.63±1.76
45	27.54±0.47	5.10±0.25	81.45±1.18
60	28.02±0.34	5.36±0.71	80.84±0.82
75	27.34±0.27	5.44±0.13	80.12±1.09
90	28.39±0.30	5.73±0.14	79.83±0.70
120	27.11±0.50	6.68±0.68	75.35±2.41
150	27.97±0.88	8.15±0.54	73.49±1.59
180	28.39±0.50	6.77±0.99	72.80±3.46

Table 2

Peroxide, total phenolic content and antioxidant activity values of MEVOP during storage

Time, days	Peroxide value, meq O_2 kg^{-1} oil	Antioxidant activity, ppm	Total phenolic content, ppm
0	11.59±0.75	681.54±5.44	106.69±0.47
15	13.09±0.22	599.07±1.70	97.26±1.40
30	21.27±1.56	583.56±3.94	95.56±0.43
45	21.89±0.47	547.64±5.71	93.85±0.57
60	24.01±0.31	502.65±1.24	90.81±0.08
75	27.42±0.32	393.26±6.81	87.59±0.60
90	28.58±0.31	357.32±4.40	82.27±1.46
120	30.37±0.53	302.82±2.01	77.95±1.16
150	31.05±0.76	293.54±1.77	59.32±2.79
180	35.56±1.73	282.50±1.35	59.13±3.15

Extra virgin olive oil is the only common food rich in a potent antioxidant called hydroxytyrosol. Antioxidants in the olive oil absorb free radicals and appear to have a positive impact on cardiovascular and cancer ailments, as attributed to the Mediterranean diet. For this reason, antioxidant capacity of olive oil must be protected during the conversion to the powder form and the storage period. Antioxidant activity decreased slightly in the early months of storage, but after the second months of storage decrease in the antioxidant activity has accelerated.

Table 3

Estimated reaction rate constants and R^2 values

	k day^{-1}	R^2
Peroxide value	0.004	0.818
Total phenolic content	-0.003	0.945
Antioxidant activity	-0.006	0.952

During storage, the degradation kinetics of phenolic compounds and antioxidant activity and the oxidation kinetics using peroxide value of microencapsulated extra virgin olive oil powder were determined using the first-order reaction kinetic model (Eq 2). Estimated reaction rate constants and R^2 values were given in Table 3.

Conclusions

The present work showed that microencapsulation efficiency of the extra virgin olive oil powder decreased with respect to storage time. Peroxide value of sample increased from 11.6 meq O_2 kg^{-1} oil to 35.6 meq O_2 kg^{-1} oil at the end of storage period. Natural or synthetic antioxidants could be used to prevent lipid oxidation. During 180 days of storage period at 25 °C, antioxidant activity and total phenolic content values of microencapsulated extra virgin olive oil powder decreased 58.6% and 44.6%, respectively. First order reaction kinetic model was found to be suitable to describe the degradation kinetics for total phenol content and antioxidant activity of samples and the increase in peroxide value of samples.

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