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Using different films in packaging virgin olive oil and its effects on the quality of oil

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Abstract

The purpose of this study was to find the best film for packaging single olive oil. Four films were used for packaging: 1. Stained glass as the control treatment (C) 2. A film containing transparent polyamide layer (L_1) 3. A film containing 65-75µ diameter aluminum layer (L_2) 4. A film containing 80-85 µ diameter aluminum (L_3).The treatments were preserved under the same conditions and were subjected to random sampling in the first, the third, and the sixth month. The sample underwent different experiments in order to find the best packaging films, including an experiment determining the oxidative decay by measuring the peroxide value (P.V), the index of acidity and determining the extinction index in the ultraviolet area within K_{270}. The experiments showed that, considering the oxidative decay, the treatments were ranked L_3>C>L_2>L_1. Considering the index of acidity, the best treatments were C and L_3, while in this index; none of the treatments exceeded the standards of virgin olive oil. With regard to the acidity and the absorption coefficient index in the ultraviolet area, the treatments were ranked C>L_1>L_2>L_3. Based on the results L_3 was the best film for packaging single olive oil.

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Introduction

Olea Europia is a member of *Oleaceac* family and belongs to the Olea material. Soybean, sunflower, corn, rape, palm, and olive are the most important oils produced and consumed worldwide. Among these oils, olive oil is highly remarkable since it contains favorable nutritive benefits and has large quantities of unsaturated fat acids, specially the oleic acid and also anti oxidants like vitamin E and natural pigments. This is the only oil that can be consumed immediately after being produced, without applying any additional processes (Mendez and Falque 2007). Olive oil should be processed like many other crops that are produced in a limited time but consumed all over the year. Meanwhile, this is the preservation and packaging conditions that determine the economic life and the quality of pure olive oil. In addition to the physical protection of the crop against strokes and other physical factors, and also the protection of the crop during the storing period and transportation, packaging also factors like should protect the crop against chemical decay-transmitting factors like steam and oxygen. Gasparoli (1991) compared the effect of light on the speed of the decay of virgin olive samples preserved in metal cans, colorless glass bottles, and PVC bottles. The results of his experiment showed that the oxidation progress in all of the samples was slow in darkness, fast in indirect light, and much faster in direct light, and the amount of oxidation decay in the samples that were preserved in glass bottles and metal cans was less than the other samples. He attributed the cause of that to the permeability of polymers to oxygen (Gasparoli *et al.* 1991). The packaging of the oil should be designed in a way that increases the endurance of the oil against oxidation. Three factors should be considered when choosing the packaging materials: permeability toward the fat, permeability toward darkness and protection against the light (Boskou 1996). Nowadays, because of the weak consumption features of glass and metal containers, using plastics is more useful and preferred for packaging food. On the other hand, polymeric packaging can hinder or delay the harmful changes in the food caused by numerous external effects such as those of oxygen, light, and micro organisms. They can also decrease combinations such as water or flavor from the food. Eventually, as a result of these protections, polymeric packaging enables consumers to preserve food for long periods of time in complete sanitary conditions without decreasing food quality. The only problem with polymers is their minor permeability to steam and oxygen; they are not completely insulating to such materials. Transition of gas through the film is due to the film construction. Other factors involved in the transitivity of the films are the thickness, surface, density and pressure difference of the two sides of the film, and the temperature (Johanson and Levfven 1995). Based on different researches, the amount of decay in olive oils that are preserved in darkness is much less than that of those preserved in light. They all agree that this phenomenon is caused by the anti-oxide operation of the natural pigment of olive oil (such as polyphenol combinations existing in olive oil) against free radicals (Pristouri *et al.* 2010). It has also been reported that among antioxidants, phenol combinations, α-tochopherol and β-carotene play a role in the protection of oil against oxidation, and that there is a significant correlation between their presence and the endurance of olive oil during preservation (Baldioli *et al.* 1996). They came to this conclusion that if such oils are preserved in darkness and are protected against light, the presence of pigments, with their preventive effect against radicals, will hinder the persistence of the oxidation circle. But at the presence of sunlight, because of the addition of photo-oxidation to the auto-oxidation these pigments will no longer be able to hinder the production of free radicals and their progress. They also function as a factor that expedites oxidation. So far, about single packaging of olive oil in different types of films has not been any research thus the aim of this study is to investigate the effects of different types of packaging on the qualitative indexes of olive oil, including peroxide value, acidity and k_{270} index during a period of 6 months.

Materials and methods

The olive oil used in the study was first-grade natural 100% pure olive oil (virgin and scented from Gilvan

Olive Company) which was purchased from Refah Chain Stores in Esfahan and was chosen from the bottles having the most recent production date. The virgin olive oil ought to have especial feature such as having the maximum acidity proportionate to oleic acid (2g in 100g oil). First, all the purchased oils were mixed together in a 4 liter container so that the result would be generalize to the whole population. The mixing process was carried out in the least amount of time possible in order that the oil would undergo the least chemical and physical changes and the amount of dissolved oxygen in the oil would not increase. Immediately a sample of 500ml oil was prepared in a stained glass to be used as the control sample for testing the parameters of acidity, Peroxide value and the absorption coefficient in the ultraviolet area. These three experiments were conducted 24 hours after preparing the sample.

The treatment investigated in this study

A three-layer transparent packaging film, consisting of polyester layers as the most external layer, polyamide layer as the middle layer, and polythene layer as the most internal layer. It should be mentioned that the internal layer should have the least amount of additive materials due to its direct exposure to the food (L_1) 2. A three-layer film, in which polyester layer was the most external layer, aluminum layer as the protective layer (the insulator) in the middle of the film, and the polyethylene layer in the most internal layer. The thick of this film was about 65-70 micrometer (L_2) 3.A three-layer film, similar to the previous one, consisting of three layer of polyester, aluminum layer, and polyethylene which differed from the previous film in the thickness of its aluminum layer, this layer had a thickness of about 80-85 micrometer (L_3) 4. A glass bottle with two volumes of 20 and 100ml for preparing the control samples(C). All of the films mentioned above were cut in similar dimensions, folded on one side and underwent a thermal sealing on the other 2sides, in similar time and thermal conditions, in Daroo Gostar Company situated in Isfahan. These conditions are totally in line with the conditions used in the industry for sealing such wrappers. Then, every sample was carefully and quickly filled with 20ml of oil, and the fourth side also underwent a thermal sealing. All of the samples were preserved in the same conditions, in indirect sunlight and open to air, for six months starting from the packaging date, so that the preservation conditions of oil in such packaging in stores and houses would be investigated. In the present study, chemical experiments were done on the samples in three stages, stage 1, 3 and 6 months in the laboratory of Techno Azma Company.

Determining Peroxide value (P.V)

Amount of Peroxide index in olive oil was determined using the standard ISO method, number 36902 of the year 2007.

Determining the amount of Acidity

Amount of acidity in olive oil was determined using the standard ISO method, number 5727 of the year 2000.

Determining the absorption coefficient of the oil in the ultraviolet area

Absorption coefficient of the olive oil in ultraviolet area was determined using the standard AOAC, method, number 5-91.

Results and discussion

The result of the primary analysis of the oil sample before packaging

According to table1, the olive oil used in the study was placed in the category of natural virgin olive oil (VOO), and had appropriate quantities for qualitative parameters such as peroxide value (P.V), acidity, but amount of K_{270} index was so high that it hindered the placement of olive oil or virgin olive oil (the Commission of European Communities).

The result of the oil oxidative decay test (P.V) in the investigation months.

The results of the test measuring the oxidative decay index of the olive oil in the first month (P.V1)

According to table2, L_1 had the highest and L_3 had the lowest mean. L_3 had the lowest amount of oxidation among all of the treatments. In addition, L_3 and L_2 both have an aluminum layer which prevents the light from passing through the packaging. As a result, in these two types of packaging, photo oxidation had practically no role in the production of hydroperoxides, which are the main factors examined by peroxide index. This type of oxidation, which originates accidentally and by creating free radicals, will persist until the packaging runs out of oxygen, and in the first stage, the oxidation will cause hydroperoxides. The reason why treatment L_2 stands in the last rate is the presence of photo oxidation along with auto oxidation as the tow factors of decay and creating hydroperoxides. As Gunstone (2008) suggests, photo oxidation acts 30,000 times faster that auto oxidation in oleic oils, and this can be a reason for the conspicuous discrepancy between L_1 and the other treatments (Gunstone 2008). The control treatment has a significant difference from L_3, there has been no major change in its hydroperoxide content since the olive oil has been packaged. This treatment has an opaque glass packaging, which prevents not only from the penetration of glasses, but also to a large extent from the transition of light. This type of packaging has been acknowledged as the source packaging by the natural standard organization for the packaging of olive oil, whose advantage is indeed in its stained nature. Perhaps if the glass had been transparent and the light had freely passed through it, the control would not have been any better that L_1. In the absence of light, when the photo oxidation does not occur, the natural pigments existing in the oil (chlorophylls) act as antioxidants and synergically with phenol antioxidants. It is worth mentioning that such preventive factors that act as antioxidants in the absence of light, completely change their role in the presence of light, and act as oxidation facilitators by transferring oxygen (Mendez and Falque 2007).

Table 1. The analysis of the oil samples before packaging.

K_{270}	Acidity	P.V
0.45	1.22	1.088

Table 2. The comparison of the mean of the oxidative decay index in the month of doing experiment.

		Month	
Treatment	One	Three	Six
C	11.50^{c}	11.92^{c}	12.02^{c}
L_1	27.25^{a}	49.65^{a}	78.84^{a}
L_2	12.05^{b}	12.27^{b}	12.42^{b}
L_3	11.08^{d}	9.79^{d}	9.330^{d}

In each column, means with the same letter are not significantly different ($P<0.05$).

The results of the test of measuring the oxidative decay of the olive oil in the third month (P.V2)

Based on table2, L_3 and L_1 had the least and the most amounts of peroxide index, respectively. According to table2, the increase in the P.V index in the treatments is because of the same reasons mentioned for the first month after doing experiment. In polymeric packaging, the role of photo oxidation is more than the speed of oxygen transition rate (OTR), and the oils gases packaged and preserved in transparent glass or polymer container, photo oxidation occur quickly in these containers and will be an important decaying factor in them (Min 1998). For L_2, the auto oxidation reaction still continues and its peroxide value has increased from 12.05 in the first month to 12.27 in the third month, although this increase is very insignificant (0.22 meq/kg). It still stands the third as a result of its significant content difference from the treatments. In this type of packaging, the existence of the aluminum layer to a large extent has hindered the decay; photo oxidation has been completely omitted from the decaying factors, and because of the existence of oxygen in head space and also the permeability in its multi-layer packaging film, the auto-oxidation still continues. On the other hand, L_3 is still the first and has a significant difference with the other treatments, because in this treatment a type of packaging is used which has an aluminum layer with a thickness of about 80-85 micrometers, the amount of OTR has reached the lowest level among the other treatments of L_1 and L_2. In L_3, the peroxide index has decreased from 11.08 meq/kg in the first month to 9.79 meq/kg in the third month. This rare phenomenon happened when the oxygen content in the packaging is finished, free radicals formed by oxidation reactions are completely inactivated, and photo oxidation has completely been omitted. After the first stage of oxidation is finished and free radicals are totally consumed, the hydroperoxides which have been formed start to be decomposed; they are transformed to combinations that are no longer measurable with peroxide value (P.V). Among these products, which are known as secondary oxidation products, we can refer to aldehids such as octanal, 2-disenla, 2- andisenal, and totanal, which are formed in most oleic acid oxidations.

Table 3. The comparison of the mean of the oxidative decay index in the months of doing experiments.

	Month		
Treatment	One	Three	Six
C	1.230 [c]	1.270 [c]	1.280 [c]
L_1	1.357 [b]	1.390 [b]	1.460 [b]
L_2	1.480 [a]	1.490 [a]	1.500 [a]
L_3	1.340 [c]	1.360 [c]	1.390 [c]

In each column, means with the same letter are not significantly different (P<0.05).

The results of the test of measuring the oxidation decay of the olive oil in the sixth month

According to table 2, L_1 with a P.V of 76.84 meq/kg and L_3 with a P.V of 9.33 meq/kg have the highest and lowest scores, respectively. In this period, L_1 with a P.V of 78.84 meq/kg is significantly different from other treatments. This significant difference can be traced back to the occurrence of auto-oxidation as a result of the existence of oxygen in head space, the existence of permeability in the packaging, the occurrence of photo oxidation and also to the exposure of oil to light. The control and L_2 keep the decay in progress, but since the amount of oxygen content of the packaging has dramatically fallen after the period of sixth month, the speed of oxidation reactions has also decreased in the package. Despite the significant mean difference of the treatments at $\alpha=5\%$ with an increase in the P.V of the control and L_2, which are 0.1meq/kg and 0.015meq/kg during six months, respectively. Two treatments have a very slow speed in the decaying path; but they still keep the decay in progress with a slight slope. The descending movement of hydroperoxides is decreased, and the amount of aldehids and cetones resulting from the second stage of oxidation is increased. Therefore, the P.V will become less and less.

The results of the acidity test in the first month

According to table 3, the control treatment with a mean of 1.230 and L_2 with a mean of 1.480 have the lowest and the highest means, respectively. Acidity index determines the amount of free fatty acids, which is represented on the basis of oleic acid. Since olive oil is oleic acid oil, this index seems to be an appropriate index for examining the amount of decay in olive oil. The reason is that the acidity index is a parameter which is strongly affected by the temperature of the storing place and also by the amount of headspace. The plastic packages showed more tendency to the hydrolysis of triglycerides, which can be explained by the fact that there is more permeability in plastics compared to glass. The high density of oxygen causes an increase in the speed of the formation of hydroperoxides, which eventually leads to the formation of carbocsilic acids which are responsible for increased acidity (Velasco and Dobarganes 2002). The control treatment and L_3 have a lower acidity. For the control treatment, it is because of having a low OTR, which results from using glass in packaging, and for L_3, it is because of having a thicker package which reduces the OTR.

The results of the acidity test in the third month

According to table 3, the control treatment and L_2 had the lowest and the highest mean, respectively. In all of the treatments, there is still some stability, because in the package of all these treatments, there is still some oxygen, which can lead to the oil decay and formation of fatty acids. On the other hand, because of the plastic nature of the packaging of the treatments, except the control treatment, and owing to the fact that no plastic polymer is 100% barrier against the penetration of gasses and water vapor, in almost all of the treatments there is a constant penetration of oxygen into the package, which makes the primary element of decay constantly available. But in L_1, because of its transparent package, the increase of acidity has a more intensity. In addition to being affected by the permeability of the package and the confined oxygen therein, this treatment is exposed to another decaying factor called light. Because this film is transparent and allows the light to pass trough, in fact it provides the required energy for the transformation of triple oxygen to the pigments available in olive oil, which leads to an increase in decay, an increase in free fatty acids, and consequently, an increase in the acidity index.

Table 4. The comparison of the means of the oxidative decay index in the month of doing experiment.

		Month	
Treatment	One	Third	Six
C	0.520^{a}	0.570^{a}	0.590^{c}
L_1	0.460^{b}	0.460^{b}	0.500^{d}
L_2	0.450^{b}	0.450^{b}	0.720^{b}
L_3	0.450^{b}	0.470^{b}	0.670^{c}

In each column, means with the same letter are not significantly different ($P<0.05$).

The results of the acidity test in sixth month

Based on table 3, the control treatment with a mean of 1.28 and L_2 with a mean of 1.50 have the lowest and the highest means, respectively. Accordingly, the reason of this increase in acidity index in all of the treatments is the existence of the headspace oxygen in the packaging of the treatments, and also the transition of oxygen through the polymeric packaging films. L_1 has an increase in its acidity index that, apart from the above mentioned reasons for all of the treatments, is caused by the existence of transparent packaging film in this treatment which acts synergic ally with other factors. A point to be considered about the acidity index in all of the treatments is the slight increase of this index during the 6 months of storage, which can be traced back to the important point that the acidity index, which increase as a result of the formation of free fatty acids, is sensitive to the light more than any other factor such as headspace, the OTR of the packaging, and permeability of the package toward the light. And since the factor of heating has been absent during the storage time of these treatments, the increase in this index has been within the normal limit in all of the treatments and even after this six months period of storage time, the amount of this index in all of the treatments has still been within the stated standard for virgin olive oil.

The results of the test of calculating the absorption coefficient in the ultraviolet area in K_{270}.

The results of the test of calculating the absorption coefficient K_{270} in the first month

According to table 4, L_3 has the lowest mean (0. 450), while the control treatment has the highest mean (0.52). Furthermore, the difference between the control treatment and other treatments is very significant at $\alpha=5\%$, while the difference between other three treatments (L_1, L_2, and L_3) are not statistically significant. The results obtained from the primary analysis of the olive oil before packaging showed that the primary amount of K_{270} index was 0.45; this figure was a little more than the normal limit at the beginning, which as it was mentioned before, hindered the placement of this type of oil in higher ranks of quality. Table 4 shows that L_2 and L_3 have no change in their K_{270} index. According to the results, the reason is that the two treatments of L_2 and L_3 are engaged in first stage of oxidation and have not entered the second stage of oxidation yet, during every time, the hydroperoxides formed in the first stage of oxidation are decomposed to conjugated denies and trines. These conjugated denies and trines are responsible for the absorption of the ultraviolet ray in the wavelength of 230nm and 270nm, which increase the index of K_{270} and K_{230}. Another reason can be the antioxidation role of chlorophyll in the darkness which hinders the formation of hydroperoxides. These pigments have a synergic role with the phenolic compound available in the oil for the prevention of decay. The same situation holds true for L_1, this treatment have undergone a change of 0.01 point and reached 0.46, which is excusable, and it can be due to the same reason mentioned for the two previous treatments. In general, in researchers view, the increase in the K_{270} index in olive oil is the result of the decomposition of the hydroperoxides that are formed by the decay of the linoleic acid available in the oil which caused by oxidation. As we know, linoleic acid is the most sensitive fatty acid available in virgin olive oil (Cosgrove *et al.* 1987).But, the considerable point is the noticeable increase of this index in the control treatment that has a glassy packaging; this treatment had an index of 0.45 before packaging, which has gone up to 0.52, that means an increase of 0.07 points. According to the results, the result of this increase is the oxygen dissolved in the primary oil, and also the oxygen available in the headspace, which causes an oxidative decay in the oil.

The results of the test of calculating the absorption coefficient K_{270} in the third month

According to the table 4, L_2 has the lowest mean (0.45), while the control treatment has the highest mean (0.57). In addition, the difference between the control treatment and other treatments is very significant at α=5%, while the difference between the other three treatments are not statistically significant. Actually, no significant change in the K_{270} index of the treatments is found in this period. The only significant difference belonges to the control treatment which can be due to the high amount of this index in this treatment in the first month. In general, the K_{270} index is affected by four factors: the transition of oxygen through the films of packaging; the passage of light through the packaging; heat; and headspace (Kanavouras and Coutelievis 2006). Among which, the effect of heat of the storage environment is more than other parameters. Hence, since in this study the heating treatment was not used, there must not be any noticeable change in the treatments.

The results of the test of calculating the absorption coefficient K_{270} in the sixth month

Based on table 4, L_1 has the lowest mean (0.5), while L_2 has the highest mean (0.72). Additionally, the difference between the treatments are very significant (α=5%). In this period, there were considerable changes in the results obtained from the study. L_2 and L_3 which had the lowest mean of K_{270} index in the previous periods, turned to treatments with the highest amounts of this index. Transforming the primary products of oxidation, i.e., the hydroperoxides, to the secondary products of oxidation, i.e., the conjugated dines and trines can be regarded as the cause of this increase in the said indexes. On the other hand, L_2 and L_3 which have an aluminum layer encountered a decrease in the P.V. It can be caused by the progress of the oxidation process from the first stage to the second and producing the secondary compound of oxidation. As the time passes from the third to sixth month, the density of oxygen in the headspace decreased. Because of the existence of the aluminum layer, the permeability of the packaging film to oxygen has highly reduced, and also the light has been prevented from penetrating through the packaging. Therefore, the oxidation process was ceased in the first stage, and entered the second stage during which for the decomposition of the hydroperoxides, the secondary products of oxidation, were responsible to increasing the K_{270} index. L_1 has the lowest amount of K_{270} index; the reason is contrary to the reason exist about L_3 and L_2. According to the results obtained, it can be clearly seen that treatment L_1 is severely engaged in an oxidation that is progressive and continues in any period. This packaging is transparent and is permeable to oxygen. As a result, the same pigments that had a protective and anti oxidation role in the darkness, have completely changed their role, and act as pro oxidant agent and cause more decay. On the other hand, because of the existence of permeability in packaging, oxygen will always be available as the primary element for decay.

Conclusions

Based on the result, considering of peroxide value index, acidity and absorption coefficient showed that the film containing 80-85µ diameter aluminium layer was the best treatment for packaging single olive oil.

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