International Food Research Journal 22(5): 1888-1893 (2015)
Journal homepage: *http://www.ifrj.upm.edu.my*

Study of the effect of fatty acids profile on overall migration from PET into different types of oil

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Article history

Received: 26 January 2015
Received in revised form: 2 April 2015
Accepted: 13 April 2015

Keywords

Fatty acid profile
PET
Oil
Overall migration

Abstract

Overall migration (OM) of polyethylene terephthalate (PET) pieces into three types of commercial oils, namely sunflower oil, canola oil and blended oil (which included sunflower oil, soybean oil, and cottonseed oil) has been investigated by the determination of the weight variation of plastic pieces before and after 20, 60 days contact with oil at 25, 45˚C and also determination the amount of absorbed oil. Also Fatty acid profiles of each type of oil were determined by using a Gas Chromatography (GC) system before and after experiments to find the correlation between the amount of overall migration and fatty acid profile. The result shows that the highest migration level was noticed with PET pieces contacted with blended oil. Also the effect of temperature, storage time, kind of oils and amount of unsaturated fatty acids and degree of unsaturation in amount of migration were observed. The amount of migration has correlation with fatty acid profile, especially the amount of unsaturated fatty acids and also, the degree of unsaturation. The reasons of these subjects can be investigated in future trends. Previous investigations have been performed on food stimulant such as olive oil and synthetic triglyceric mixture HB307, the present study has the advantage of working on real food samples so obtaining more accurate results were possible.

Introduction

Application of plastics in food packaging has been largely extended during the last decades. The major increase in the use of PET in direct contact with food came with bottles. PET bottles are now extensively used for carbonated soft drinks, mineral waters, beers, wines, spirits and edible oils (Ashby, 1988). One the important part of the human diet is edible oil (Tawfik, 2005). More than 90% of the world oil production of vegetable, animal and marine sources is used as food or as an ingredient in food products (Tawfik and Huyghebaret, 1999).

PET used in oil packaging is going to be one of the most popular plastics all around the world, because it has excellent protection, appearance, mechanical properties and lower price in comparation with glass (Brook and Giles, 2002; Kucuk and Caner, 2005; Cooper, 2007). However one of the most important limitation of plastic application in food contact is associated with mass transport phenomena such as migration and scalping (Hotchkiss, 1995). In another hand, one of the required properties of plastic materials which are being used in food packaging or containers is that they should be practically inert. This means that their potentially harmful constituents should not migrate into the foodstuffs in specific conditions of useage (Figge, 1972; Figge, 1996; Grob, 2002; Robertson, 2005; Tawfik, 2005). For this reason, migrants present in the foods at a concentration of potential toxicological concern should be known and documented to be of no risk to human health

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(Grob, 2002). As defined by some legislative rules, like the EU Framework 10/2011 on plastic materials, overall and specific migrations represent traditional ways to assess migration into foods. In particular, overall migration is a generic level of the inertness of a plastic material. It is defined as the maximum permitted amount of non-volatile substances released from a material or particle into food stimulants (Figge, 1996; Grob, 2002; Robertson, 2005). The EU limit of the overall migration is 10 milligrams per square decimeter of surface area of material or article (mg/dm2). In another term, According to EU legislation: Food contact materials, Migration of any constituent may not exceed 60 milligrams of the constituents released per kilogram of food or food simulant (mg/kg) (Sheftel, 2000; Cooper, 2007).

The methods for determination of the overall migration of plastic materials are various. The determination of an overall migration for plastics in fat releasing foods by using fatty food simulants such as olive oil, synthetic triglyceric mixture HB307 and sunflower oil have been described by previous investigations (Figge, 1973; Sheftel, 2000; Tawfik, 2005). The uses of simulating solvents have proved to be relatively unsatisfactory, whereas the determination of actual total migration in a suitable fat leads to more reliable results (Figge, 1973). However in such cases only migration into typical fatty food simulants can have a deciding meaning (Czerniawski and Pogorzelska, 1997).

To the best of our knowledge, relatively few migration studies have been published dealt with the overall migration from plastics packaging for oils and the effect of fatty acids profiles on overall migration from packaging. The migration of two different additives from high-density polyethylene (HD-PE), from polyvinyl chloride (PVC) and from polystyrene (PS) into edible oils and fat simulants has been investigated using the radiotracer technique and contact times of 60 days at 20°C and 5 h at 65°C as test conditions by Figge and his colleagues. The edible oils used were Biskin (partially hydrogenated groundnut oil), coconut oil, sunflower seed oil, olive oil and butter. They found that the characters of fatty acids (the length of chain and the degree of fatty acid saturation) have an effect on the fat adsorption and migration phenomena (Figge *et al*., 1972). The effects of temperature, time and different types of plastics: Polyethylene terephthalate (PET), Polyvinylchloride (PVC), Polypropylene (PP) and Polystyrene (PS) on the stability of olive, sunflower and palm oils were studied by Tawfik and Huyghebaert in 1999. They concluded that passing the time, temperature and packing materials have a significant effect on stability of mentioned oils (Tawfik and Huyghebaret, 1999). In 2005, Tawfik has investigated the overall migration and oil absorption of different types of plastics: PET, PVC, PP and PS into different types of vegetable oils (olive, sunflower and palm oil). His findings showed that, overall migration from plastic packaging material into a vegetable oil is affected by the type of plastic packaging and also the kind of oil. Tawfik concluded that absorption of oil by polymer is clearly influenced by the chain length of the fatty acids and the degree of saturation (Tawfik, 2005).

In present study, overall migration (OM) from polyethylene terephthalate (PET) into three types of commercial oils, namely sunflower oil, canola oil, and blended oil which included sunflower oil, soybean oil, and cottonseed oil were determined after 20 and 60 days of storage at 25 and 45 ˚C. In compare with previous investigations, for the first time profiles of fatty acid for each type of oil was determined by gas chromatography (GC) before and after experiments to find the correlation between the amount of overall migration and fatty acid profiles.

Materials and Methods

Oils and PET bottles: Three types of commercial oils, namely sunflower oil, canola oil, and blended oil which included sunflower oil, soybean oil, and cottonseed oil (amount of added BHT as antioxidant 100 mg/kg in all of the oils) and PET bottles were obtained from Savola Behshahr Co., Tehran. Iran. 1, 1, 2-Trichlorotriflouroethane (TCTFE) were purchased from Merck Co, Darmstadt, Germany.

Sample preparation

After measuring a specific surface (0.5 dm^2) of the bottles, they were cut into 3 pieces with the same sizes (0.5 dm^2). The test pieces were conditioned in desiccators, maintained at 50% relative humidity, for 1 day. The pieces were weighted and were put into 250 ml glass vessels that each glass vessel was poured with oil up to 150 ml, so the test pieces were immersed completely in each type of oil. The glass vessels that contain test pieces were stored in an oven thermostatically controlled at 25 and 45°C for 20 and 60 days. The temperature was controlled and the data were recorded by the data logger (LASCAR, England). Glass vessels containing only oils were put in the same condition and served as blank samples. During the experiment each of test pieces were remained well apart from another by the supports. At the end of the prescribed time, pieces were drip-dried and removed from their supports. Any adhering oil was removed by gently pressing between filter papers

Table 1. Overall migration of PET pieces in contact with different types of oils at 25 and 45°C for 20 and 60 days

Type of Oil	Temperature (°C)	Time (days)	Mean overall migration (mg/dm^2)	*Treatment*
Canola	25	20	0.175 ± 0.034^{a}	1
Canola	25	60	0.507 ± 0.096^{b}	2
Canola	45	20	0.967 ± 0.09^{d}	3
Canola	45	60	1.889 ± 0.162^{f}	4
Sunflower	25	20	0.178 ± 0.05^{a}	5
Sunflower	25	60	0.646 ± 0.054^{bc}	6
Sunflower	45	20	1.139 ± 0.159^{d}	7
Sunflower	45	60	2.671 ± 0.113^{g}	8
Blended	25	20	0.295 ± 0.057^{a}	9
Blended	25	60	0.732 ± 0.11^{c}	10
Blended	45	20	1.637 ± 0.131^{e}	11
Blended	45	60	3.484 ± 0.124^{h}	12

(lint-free filter paper: Whatman No1). This operation was repeated until the filter paper has shown no spot of oil (Gramiccioni *et al*., 1986; Tawfik, 2005).

Extraction of absorbed oil

The test specimens were placed in the Soxhlet type extractor. Sufficient extraction solvent (approximately 200 ml of trichlorotriflouroethane) was added to the flasks to allow cycling of Soxhelt type extractor with anti bumping beads to control boiling. The extraction was performed for 24 hours. Test pieces were immersed into the solvent during each Soxhelt cycle, and were remained separated from each other. The flasks were removed from Soxhelt type extractors and then the solvent was evaporated to dryness using a rotary evaporator (IKA Basic Rotary Evaporator, 115VAC, USA). The remaining solvent was transferred from each of the flasks to 50 ml separated flasks. The flasks which contained residue oils were evaporated to dryness by hot plate. By trans-methylation, the residual fatty acids were quantified by using a gas chromatography system (Tawfik, 2005).

For determination of the fatty acid profile, a trans-methylation technique followed by GC-FID determination (AOAC 969.22) was used as practical method. The gas chromatograph system (Agilent Technologies model 6890N, Germany) equipped with flame ionization detector (FID) and HP88 column with the specifications of $100m^{*}O.25\ mm^{*}0.2$ µm (AOAC, 2000a, b). Temperature of the column has been raised from 170 to 190°C in 5 minutes by 0.5°C per minute and remained at this temperature for 20 minutes; the detector temperature was 250°C; the speed of helium as carrier gas was 0.7ml/min; the pressure was 10 PSI and the volume of sample injection was 1 micro liter (AOCS, 1999; AOAC, 2000a).

Overall migration was calculated by this formula $M=[(m_b-m_c)-m_a)]/s$, where "M" is the overall migration of plastic packaging material into oil and was reported as mg/dm^2"m_a" is the initial mass of the test specimen, before contact with the oils in mg. "m_b" is the mass of the test specimen after contact with oil in mg. "m_c" is the mass of oil which is absorbed by plastic pieces in mg, "S" is the surface area of the test specimens which are in contact with oils (Gramiccioni *et al.*, 1986; Tawfik, 2005).

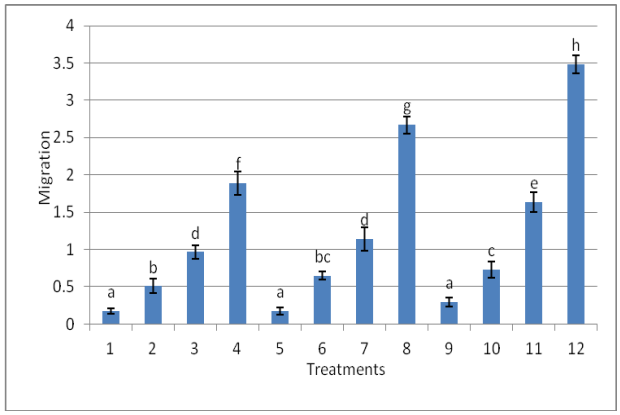

Figure 1. Comparison amounts of migration in different treatments (expressed by mg/kg)

Experimental plan and statistical analysis

Experiments on 5 selected PET bottles with each type of oil sample were performed with three replicates. Data were analyzed using multi-variables variance analysis (ANOVA) and Duncan test by SPSS 18.0 (Cox, 1992; Steel *et al*., 1996). Level of significance value (P) was 0.05.

Result and Discussion

In Table 1, the amounts overall migration of PET packaging pieces in contact with different types of oils at 25°C and 45°C for 20 and 60 days are shown. In this experiment we had 12 treatments (Oil kind with 3 types, temperature with 2 types, time with 2 types, in 3 replicates). We analyzed our results in three bases and four cross affects. The results show

Table 2. Profile of main fatty acids for sunflower oil at described conditions of storage (expressed by %)

Storage condition									
Types of fatty acid	Original* oil	20 days Without PET pieces**		20 days With PET pieces***		60 days Without PET pieces		60 days With PET pieces	
		25°C	45°C	25°C	45°C	25°C	45°C	25°C	45°C
C16:0	7.55±0.02	7.93±0.05	8.02±0.05	8.06±0.08	7.98±0.03	7.81±0.02	7.85±0.02	8.08±0.08	8.07±0.02
C18:0	2.97±0.07	4.03±0.09	4.10±0.09	4.03±0.03	3.93±0.06	3.63±0.09	3.63±0.09	3.94±0.04	4.01±0.08
C18:1	23.37±0.04	24.95±0.03	24.96±0.03	25.23±0.05	24.69±0.09	24.32±0.02	24.10±0.06	24.95±0.07	25.15±0.04
C18:2	61.76±0.03	57.94±0.03	57.94±0.05	57.87±0.06	58.20±0.08	59.33±0.01	59.42±0.08	58.25±0.07	57.83±0.05
C18:3	1.67±0.08	1.98±0.02	1.94±0.08	1.97±0.03	1.97±0.02	1.87±0.06	1.87±0.09	1.96±0.09	1.93±0.07

Original oil *: The oil which has any treatment
Without PET pieces**: The oil which has not been in contact with PET pieces
With PET pieces***: The oil which has been in contact with PET piece

Table 3. Profile of main fatty acids for blended oil at described conditions of storage (expressed by %)

Storage condition									
Types of fatty acid	Original oil	20 days Without PET pieces**		20 days With PET pieces***		60 days Without PET pieces		60 days With PET pieces	
		25°C	45°C	25°C	45°C	25°C	45°C	25°C	45°C
C16:0	9.43±0.05	9.65±0.06	9.62±0.11	9.65±0.02	9.77±0.08	9.4221±0.05	9.77±0.04	9.60±0.02	9.63±0.05
C18:0	3.33±0.02	4.00±0.04	4.03±0.07	4.05±0.05	3.96±0.04	3.41±0.07	3.28±0.03	4.04±0.03	4.026±0.04
C18:1	23.80±0.03	24.85±0.09	24.83±0.04	24.70±0.02	24.74±0.06	24.25±0.02	24.55±0.06	24.79±0.12	24.86±0.09
C18:2	58.00±0.08	55.56±0.03	55.54±0.03	55.53±0.03	55.55±0.03	57.50±0.06	57.93±0.07	55.54±0.09	55.56±0.06
C18:3	2.42±0.10	2.64±0.06	2.70±0.05	2.677±0.06	2.69±0.09	2.47±0.01	2.32±0.02	2.68±0.08	2.67±0.07

Original oil *: The oil which has any treatment
Without PET pieces**: The oil which has not been in contact with PET pieces
With PET pieces***: The oil which has been in contact with PET pieces

that at the same conditions the overall migration from plastic pieces in oils was as following order (blended>sunflower>canola) ($p \leq 0.01$). According to Table 1 and Figure 1, there is no significant difference between treatments 1, 5 and 9. Moreover, there is no significant difference between treatment 6 with treatments 2 and 10. ($p \leq 0.01$). So treatments 1, 5 and 9 have lower amount of migration than the other treatments and treatment 12 is the worse one. On the other hand the highest migration level was noticed for PET pieces in contact with blended oil. For example the amounts of the overall migration in blended, sunflower and canola oils at 45°C for 60 days (as severe condition) were 3.484±0.124mg/dm^2, 2.671±0.113mg/dm^2 and 1.889±0.162mg/dm^2, respectively.

At 25°C and 45°C, the level of migration has increased significantly ($p \leq 0.01$) after 20 and 60 days. Two mentioned periods of incubation (20 and 60 days) have significant difference ($p \leq 0.01$) on the amount of migration. These results were confirmed by previous investigations (Figge *et al*., 1972; Tawfik, 2005). Furthermore, when we analyzed interaction of oil and temperature we concluded that in canola oil at 25°C the amount of overall migration was at minimum level. Tables 2, 3 and 4 show the main fatty acid compositions of sunflower oil, blended oil (sunflower, soybean and cotton seed oil) and canola oil after 20 and 60 days storage at 25 and 45°C, respectively. As it is shown in the tables as composition of fatty acids, some small changes in the amount of saturated and unsaturated fatty acids in

Table 4. Profile of main fatty acids for canola oil at described conditions of storage (expressed by %)

Storage condition									
Types of fatty acid	Original oil	20 days Without PET pieces**		20 days With PET pieces***		60 days Without PET pieces		60 days With PET pieces	
		25°C	45°C	25°C	45°C	25°C	45°C	25°C	45°C
C16:0	5.07±0.08	5.02±0.09	4.95±0.11	5.10±0.05	5.09±0.09	4.92±0.08	4.85±0.04	5.06±0.04	5.00±0.02
C18:0	2.03±0.03	2.06±0.06	2.05±0.02	2.04±0.03	2.03±0.02	1.86±0.06	1.74±0.06	2.04±0.06	2.08±0.05
C18:1	56.01±0.07	55.85±0.03	55.91±0.07	55.61±0.06	55.59±0.05	55.59±0.03	56.07±0.09	56.08±0.03	55.85±0.07
C18:2	20.94±0.05	20.85±0.04	20.84±0.05	21.06±0.08	21.10±0.07	21.22±0.05	21.33±0.03	20.82±0.07	20.87±0.09
C18:3	9.15±0.02	9.16±0.06	9.17±0.03	9.17±0.04	9.23±0.03	9.05±0.10	9.06±0.02	9.07±0.06	9.16±0.08

Original oil *: The oil which has any treatment
Without PET pieces**: The oil which has not been in contact with PET pieces
With PET pieces***: The oil which has been in contact with PET pieces

above mentioned oils were observed.

The main fatty acids in the sunflower oil include palmitic acid 7.55 (%), oleic acid 23.37 (%) and linoleic acid 61.76 (%). As an example the profile of the sunflower oil was altered concerning thepalmitic acid 8.07 (%), oleic acid 25.15 (%), and linoleic acid 57.83 (%) after 60 days storage at 45°C. As a result the amount of polyunsaturated fatty acids like linoleic acid was decreased and the amount of mono unsaturated and saturated fatty acids like oleic acid, and palmitic acid were increased, respectively. Most notable fatty acids in the blended oil include palmitic acid 9.43 (%), oleic acid 23.80 (%) and linoleic acid 58.00 (%) that after storage some slight changes were observed, similar to sunflower oil. The composition of indicated fatty acids was changed to palmitic acid 9.63 (%), oleic acid 24.79 (%), and linoleic acid 55.56 (%) after 60 days storage for at 45°C. In canola oil with this initial fatty acid profile: palmitic acid 5.07 (%), oleic acid 56.01 (%) and linoleic acid 20.94 (%) small changes in fatty acid profile were observed after storage at the same conditions. Since all of the samples have been stored in a dark place and in a sealed container (in glass vessels 250 ml) the effects of light and oxygen parameters in all specimens were similar. Presence or absence of plastic pieces has no significant effect on the alteration of fatty acid profiles.

As it is shown in Table 1, highest level of migration was detected in blended oil at the worst condition (at 45°C for 60 days). According to Tables 3, 4 in blended oil, the amount of Linoleic acid is high (around 58%) also in canola oil the amount of Linoleic acid is low (around 20.9%), so this finding confirms the effect of the type of fatty acids and amount of unsaturated fatty acid on the amount of the overall migration from PET packaging into oil. The obtained results are in good agreement with previous investigation which explained that the chain length of fatty acids (shorter chain length of fatty acids could stimulate the migration more than long chain one) and the degree of saturation, clearly influence the migration into different types of oil, which resulted in distinctly higher migration into oils which contain unsaturated fatty acids (Czerniawski and Pogorzelska, 1997). In spite of the fact that canola oil contains linolenic acid (C18:3) and it has a relatively high degree of unsaturation, it contains lower amounts of migration in comparison with other fatty acids because of low amount of linolenic acid fatty acid (9.15%). So this fact was proved the amount of unsaturated fatty acids and the degree of unsaturation, both have a significant effect on the amount of overall migration.

Conclusion

Overall migration (OM) of polyethylene terephthalate (PET) pieces into three types of commercial oil, namely sunflower oil, canola oil, and blended oil which included sunflower oil, soybean oil, and cottonseed oil, have been investigated by determination of difference between weight of plastic pieces before and after 20, 60 days contact with oil at 25, 45˚C and the amount of absorbed oil. The results showed that the highest migration level was noticed for PET pieces contacted with blended oil. In comparison with previous investigations that have been performed on food stimulant such as olive oil and synthetic triglyceric mixture HB307, the present study has the advantage of working on real food samples so acquiring more accurate results are possible. The correlation with fatty acid profile with the amount of migration was conducted, especially

the amount of unsaturated fatty acids and also, the degree of unsaturation. The reasons of these subjects could be investigated in future trends. The condition of storage for oil products packed in PET bottles is very effective on the amount of migration, so it is essential to control and improve the distribution chains and the conditions of storage to guarantee the safety of products. The author suggested that the edible oils which are packaged in PET containers should be kept at a temperature lower than 25°C to control migration.

Acknowledgment

The authors are grateful to Dr. Bahmanei, Mr. Shoaei and Mrs. Kalantari from Savola, Co, Iran, for their supports during this research, also to the staffs of Packaging and Toxicology Labs, Food and Drug Control Labs, for their helpful cooperation during this project.

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