

Interaction of Packaging Materials and Vegetable Oils: Global Migration and Oil Absorption

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Abstract: Global migration of different types of plastic food packaging materials including (Polyethyleneterephthalate (PET), Polyvinylchloride (PVC), Polypropylene (PP) and Polystyrene (PS) into different type of vegetable oils (olive, sunflower and palm oils) has been determined after 20 and 60 days of storage at 24 and 37°C. The global migration was calculated by determination the weight of plastic strips before and after contact with oil and the amount of absorbed oil. The absorbed oil was determined by Gas Chromatographic (GC) analysis. The rate of migration and final yield were temperature dependent. The major fatty acids in each type of oil at the equilibrium were used to calculate this amount of absorbed oil. In general overall migration (global migration) from plastics was found to be lower in PET and PVC compared to PS and PP. When comparing the absorption of different oils into plastics, the ranking was PS> PP >PVC> PET. The type of oil was found not only influence the global migration but also the amount of the absorbed oil. Global migration was found to be slightly higher into oil contained high amount of short- chain and unsaturated fatty acids. The results are also discussed the effect of temperature and storage time on the migration level and oil absorption.

Key words: Migration, vegetable oils, oil absorption, plastics

INTRODUCTION

The rigid packs are used for oils and the other fatty foods. PVC, PET, PP and PS are widely used instead of glass bottles. Bottles for packaging salad oils are made of PVC, e.g. blow moulding. A more development is the so-called stretch-blow moulding for PVC and PET which gives the bottles an improved gloss and strength at reduced weight^[1].

One of the properties required of plastic materials used in foodstuff packaging or containers is that they should be practically inert, i.e. that their constituents should not migrate into the foodstuffs with which they come in contact. A global migration limit for plastic materials intended to come into contact with foodstuffs has been set by law in some countries (Belgium, France, Italy, The Netherlands, Switzerland, The United States) or exists in practice^[2].

Global migration is the total quantity of constituents which can migrate from plastic materials into foodstuffs in contact. The main value of this limit is that it prevents the contamination, albeit nontoxic, of foodstuffs and reduces the number of determination of specific migrations of potentially noxious constituents^[2].

The amounts of low molecular weight substances that may migrate from given plastic materials into foods, the fat or oil types of the foodstuff would seem to be a

major influence. It has previously been reported^[3,4] that in the case of LDPE there is a correlation between the fat release properties of a particular foodstuff and the migration of components from the plastics material into the foodstuff. It was of interest to know if and to what extend this correlation also exists for other plastics materials.

There are different methods to determine the global migration of plastic materials. The Rossi^[2] Or Van Battum method^[5], the Community method (1974) specified olive oil as the simulating liquid since it is thought to be more stable than sunflower oil and less expensive and more practical than HB 307 which solidified at ambient temperature and complicated the analysis. In contrast, the general validity of the community method (1974) had been contested by one of the laboratories^[6] following the observation that fatty acid composition of the olive oil was different before and after the extraction and this caused errors in the final results.

Limits on overall migration of specific substances using a scheme of testing with food simulating liquids (simulants). Directive 85/572/EEC specifies the simulants that should be employed in migration testing. Plastics intended to come into contact with fatty foods must comply with migration limits using the olive oil simulant (or approved alternatives). There are however, many foods that have a high fat content on a compositional basis but do not exhibit a high fat release

with a plastic. Conversely, some foods that contain little fat have that fat concentrated at the surface could give a higher migration rate. Since olive oil (and its alternatives) is technically the most difficult simulant to study and also tends to be the most aggressive simulant towards plastics, there is a need to be clear when it should and should not be employed^[7]. The global migration from plastics into aqueous acetic acid and fat HB 307 was found to decrease in the order Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE), Polypropylene (PP), high-impact Polystyrene (SB) and Acrylonitrile-butadiene-styrene (ABS)^[8].

To solve some of the problems in the determination of the total migration of additives from plastic materials into fats contained in food different simulants have been used. The use of simulating solvents has proved to be completely unsatisfactory, whereas the determination of the actual total migration in a suitable fat gives more reliable results. In Figgeet *et al.*^[9] Study they used groundnut oil, coconut oil, butter for 60 days at 20°C to determine the global migration. They concluded that the nature of the fatty foods is affected the migration of the components out of the plastic materials while the chain length and the degree of saturation of fatty acids are influenced the fat absorption by plastic materials. Hernandez-Munoz^[10] showed that the limits of sorption and migration must be measured in the presence of the specific food or an appropriate food simulant.

The aim of the present study is to determine the global migration and the oil absorption of different plastic materials including PET, PVC, PP, and PS during their contact with and stored with different vegetable oils (olive, sunflower and palm oils) for 60 days at 24 and 37°C.

MATERIALS AND METHODS

Materials

Oils: Commercially sunflower, olive and palm oils were obtained from a local retail store.

Plastic materials: Polyethyleneterephthalate (PET), polyvinylchloride (PVC), polypropylene (PP) and polystyrene (PS) bottles were obtained from local company in Egypt.

Chemicals: 1,1,2-Trichlorotrifluoroethane (TCTFE) were obtained from Aldrich chemical.

Methods

Samples preparation: For glass support, use 4 rectangular plastic pieces with slides 7x5 cm. The test pieces were kept a part and emerged completely in the oil.

The support glasses together with test pieces

constituting test sample were placed in glass vessel. Then, quantities of oils were poured into vessel to obtain a ratio of 2 between sample surface area (sq.dm) and oil volume (mL). The vessels were stored at 24 and 37°C for 20 and 60 days. During contact stage the test pieces were always remained well apart from one to another. At the end of prescribed time, test pieces were taken out let drip removed from support with the tweezers and dried between 2 sheets of Whatman No.1 filter paper, pressing gently with rubber roller. The operation was repeated until sheets of filter paper no longer showed any oil spots. Glass vessels containing oils only were placed in the same condition and served as a control^[11].

Extraction of absorbed oil: Using tweezers, test sample was placed and its support in soxhlet extractor. A 200 mL of trichlorotrifluoroethane and some quartz beads to control boiling were added. During extraction the test pieces were remained submerged in solvent and separate from one another.

Extraction of absorbed oil was performed for 18 h. Another 6 h of extraction using the same solvent was used to be sure that all the oil is completely extracted. After cooling, the sample was concentrated in the rotary evaporator. Extraction of blank samples was performed in soxhlet extractor under the same conditions used for test sample. After transmethylation, the residual fatty acids were determined using gas chromatography determination of each kind of oils as described by Rossi^[11].

Global migration Global migration was calculated using the following formula $M = (G_1 + F) - G_2$ ^[11]. When M is the total migration from plastic into oil, G₁ and G₂ are the weight of plastic before and after contact with oils respectively and F is the amount of absorbed oil, determined as a fatty acids by GC.

Statistical analysis: Every treatment was performed three times. Two analyses were taken from the test samples at each specific time interval. Mean values and standard deviations were calculated at each time interval and analysed by SPSS version 6 (SPSS Inc. 444 N. Michigan Avenue, Chicago, Illinois, 60611) for Analysis Of Variance (one way, two way and three way), F-ratio (at level 0.05) and Multiple Regression.

RESULTS AND DISCUSSION

The initial fatty acids composition of olive oil, sunflower oil and palm oil used in the present study is shown in Table1. The major fatty acids were oleic acid and linoleic acid in olive oil and sunflower oil, respectively,

Table 1: Fatty acids composition of the olive oil, sunflower oil and palm oil used throughout this study

Fatty acids	Olive oil (%)	Sunflower oil (%)	Palm oil (%)
12:00	-	-	0.02
14:00	-	0.05	0.82
16:00	8.82	6.22	40.65
16:01	0.71	0.05	0.08
17:00	-	-	0.08
18:00	2.19	4.96	5.33
18:01	75.92	20.8	42.95
18:02	11.31	67.36	9.34
18:03	0.78	0.44	0.46
20:00	0.27	0.11	0.27

Table 2: Amount of absorbed oil into different types of packaging material stored in different types of oil at 24 and 37°C for 20 and 60 days

Type of oil	Temp (°C)	Time (days)	Amount of oil absorbed (mg dm ⁻²)			
			PET*	PVC	PP	PS
Olive oil	24	20	w _{0.56} ^a	x _{0.64} ^a	y _{2.62} ^a	z _{15.94} ^a
		60	w _{0.69} ^b	x _{0.88} ^{bc}	y _{2.92} ^b	z _{17.73} ^b
	37	20	w _{0.72} ^b	x _{0.99} ^c	y _{3.09} ^{bc}	z _{6.18} ^b
		60	w _{1.01} ^c	x _{1.08} ^c	y _{3.46} ^c	z _{7.54} ^b
Sunflower oil	24	20	w _{0.39} ^d	x _{0.56} ^d	y _{2.53} ^a	z _{20.59} ^c
		60	w _{0.82} ^e	x _{1.75} ^e	y _{2.93} ^b	z _{23.79} ^d
	37	20	w _{0.85} ^f	x _{1.58} ^e	y _{2.72} ^b	z _{24.34} ^d
		60	w _{0.97} ^f	x _{2.05} ^f	y _{3.49} ^c	z _{29.89} ^e
Palm oil	24	20	w _{0.65} ^b	x _{0.72} ^e	y _{2.54} ^a	z _{16.12} ^b
		60	w _{0.89} ^e	x _{0.93} ^c	y _{2.95} ^b	z _{18.83} ^f
	37	20	w _{0.85} ^e	x _{1.02} ^c	y _{3.14} ^{bc}	z _{24.51} ^g
		60	w _{0.97} ^{ef}	x _{1.25} ^c	y _{3.56} ^c	z _{25.67} ^h

*PET= Polyethylene tere-phthalate

PVC= Polyvinylchloride

PP= Polypropylene

PS= Polystyrene

Mean values in the same column not sharing a superscript to the right are significantly different. Mean values in the same row not sharing a subscript to the left are significantly different

whereas in palm oil, palmitic and oleic acid were the main acid components. Hence, these fatty acids were used to calculate the amount of absorbed oil.

From the analysis of variance (4-way) it is established that the level of migration affected significantly (0.05) by all the tested parameters (type of plastics, type of oil, temperature and storage time). Generally, the global migration of plastic constituents from tested plastics into vegetable oils was found to be decreased in order PS, PP, PVC and PET (Table 2). It is noticed that palm oil stimulated the migration of plastic additives and constituents than sunflower and olive oil which gave the lowest level (Table 2).

The migration increased with increasing temperature and extending storage time during 60 days of incubation. Bieber *et al.*^[12] examined the migration of additives from different type of plastics into acetic acid and test fat HB after 10 days at 40°C. They observed that the transfer of antioxidant from plastics is ranked in the order Low Density Polyethylene (LDPE) > High Density Polyethylene (HDPE) > Polypropylene (PP) > high/ impact

Table 3: Global migration of different type of packaging materials contacted with different types of oils at 24 and 37°C for 20 and 60 days

Type of oil	Temp (°C)	Time (days)	Global migration (mg/dm ²)			
			PET	PVC	PP	PS
Olive oil	24	20	w _{0.12} ^a	x _{0.40} ^a	y _{1.42} ^a	z _{5.26} ^a
		60	w _{0.29} ^b	x _{0.90} ^b	y _{2.35} ^b	z _{6.53} ^b
	37	20	w _{0.20} ^b	x _{0.88} ^b	y _{2.33} ^b	z _{6.35} ^b
		60	w _{0.25} ^b	x _{0.94} ^b	y _{2.61} ^b	z _{7.08} ^c
Sunflower oil	24	20	w _{0.12} ^a	x _{0.62} ^c	y _{2.34} ^b	z _{7.26} ^d
		60	w _{0.31} ^b	x _{1.43} ^d	y _{2.14} ^c	z _{8.51} ^e
	37	20	w _{0.66} ^c	x _{1.46} ^d	y _{2.87} ^d	z _{8.13} ^e
		60	w _{0.68} ^c	x _{1.50} ^d	y _{2.87} ^d	z _{8.78} ^e
Palm oil	24	20	w _{0.60} ^d	x _{1.52} ^d	y _{2.11} ^c	z _{6.33} ^b
		60	w _{0.71} ^e	x _{1.60} ^e	y _{3.21} ^e	z _{7.20} ^f
	37	20	w _{0.75} ^e	x _{1.61} ^e	y _{3.71} ^e	z _{6.42} ^b
		60	w _{0.92} ^f	x _{1.70} ^f	y _{3.02} ^e	z _{9.51} ^f

*PET= Polyethylene tere-phthalate

PVC= Polyvinylchloride

PP= Polypropylene

PS= Polystyrene

Mean values in the same column not sharing a superscript to the right are significantly different. Mean values in the same row not sharing a subscript to the left are significantly different

Polystyrene (SB) and acrylonitrile/butadiene/styrene whereas the migration was higher into fat simulant (HB). In another study Rossi^[2,11] observed that the migration was always lower in olive oil compared to that obtained with fat simulant HB 307. At high temperature polypropylene film allows contaminant migration from recycled paperboard packaging into fatty and high-moisture food^[12].

The highest migration level was noticed with the plastics contacted with palm oil. This may be explained by the high amount of short chain length of fatty acids (palmitic acid 40.7 %) in the composition of palm oil. These acids could stimulate the migration more than long chain one^[8].

It is demonstrated that PS and PP absorbed more oil than PET and PVC (Table 3). This could be attributed to the fact that PS and PP have low crystallinity and large amorphous areas. Swelling of the polymers occurs in their amorphous areas. The polymers of high rigidity and high crystallinity would swell less than those which are mainly amorphous^[7]. Choi *et al.*^[13] reported that several variables such as coating thickness, temperature and suspected contaminants need to be considered to control the possible contamination risk from recycled or printed paper.

No correlation could be established between oil absorption and migration is recognized when comparing between different groups of polymers. In this case the migration from PS into vegetable oils is three times higher than that from PP whereas the fat absorption is distinctly higher. This is due to polystyrene having a higher capacity for fat than polyolefins^[14]; in other words, the same amount of fat is absorbed by a smaller volume of

polystyrene than polyolefines. Therefore, in the polyolefins the same amount of an additive is mobilized by a smaller amount of fat than in polystyrene. Bieber *et al.*^[8] discussed that the relation between migration value and amount of fat absorbed in LDPE is not as close as might be expected. This may be understood according to what was outlined previously. The transfer of additives from plastics materials into foodstuffs is independent with the amount of oil if there is enough oil available for migration can take place without being governed by this amount of oil.

The oil properties may depend on the nature of the plastics materials being in contact with it, e.g. the global migration from the different kind of plastic into palm and sunflower oil is higher than that into olive oil. In Bieber *et al.*^[8] study the transfer of antioxidant into the fat or fat emulsions is highest from LDPE, followed by HDPE and PP. It is low from SB and ABS. Furthermore, the migration of the antioxidant is normally highest into pure fat and, at least in the case of polyolefins.

A slight dependence of additive transfer upon the chain length of the fatty acids. Slightly higher amounts of additive are transferred into the oils of shorter chain length of fatty acids. The type of oil has very little or no influence on the amount of oil absorbed in contact with these polymers.

CONCLUSIONS

From these findings it is concluded that the transfer of low molecular, hydrophobic components from a plastics packaging material into a vegetable oils is governed by the type of plastics packaging and the kind of oils. The correlation between oil properties and migration rates is only recognized if the speed of oil absorption cause different amounts of oils being absorbed by the polymer. The chain length of the fatty acids and the degree of saturation clearly influences the oil absorption by polymers, resulting in distinctly higher absorption of the short-chain species, whereas the migration of components out of plastics is not influenced to the same extend.

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