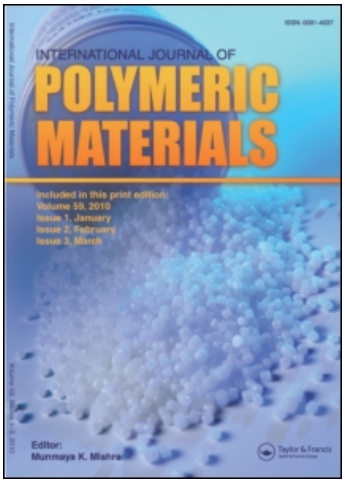

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Migration of Epoxidized Sunflower Oil and Dioctyl Phthalate from Rigid and Plasticized Poly(vinyl chloride)

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Migration of Epoxidized Sunflower Oil and Dioctyl Phthalate from Rigid and Plasticized Poly(vinyl chloride)

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The aim of this paper is the determination of the specific migration of epoxidized sunflower oil (ESO) from rigid and plasticized poly(vinyl chloride) (PVC) into food simulants. ESO was obtained by epoxidation of commercial sunflower oil and used as a thermal organic co-stabilizer for PVC. For that purpose, rigid and plasticized (0, 15, 30, and 45 wt% of dioctyl phthalate or DOP) PVC films stabilized with ESO in the presence of Zn and Ca stearates were used to perform migration testing in olive oil. The test conditions were 12 d at 20 and 40°C and 2 h at 70°C with and without agitation.

The determination of ESO migration was carried out by gas chromatography-mass spectrometry (GC-MS). ESO was quantified by an external standard addition method, using linoleic acid ($C_{18:2}$) as the external standard. The influence of various parameters, such as the agitation and time of contact, the temperature, the presence or the absence of the plasticizer, and the plasticizer concentration, was considered.

Keywords DOP, epoxidized sunflower oil, GC-MS, migration, PVC

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INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most widely used polymeric materials in the plastics industry, which is used in food packaging material. It is difficult to process, so plasticizers are used in many applications. It suffers from poor thermal stability, so heat stabilizers are required in the processing of the polymer [1]. However, these low molecular weight additives (plasticizers, heat stabilizers and others) frequently possess a high mobility in plastic materials and, in contrast to the polymeric chains, are capable of migrating from the packaging material into the packed product [2–5]. Some of the migrants may affect the quality of the packed product as exhibited by sensorily determinable changes (odor and/or taste) or by toxicological symptoms from ingestion [6]. Therefore, the detection and quantification of contaminants migrating from the polymers are essential for the safety assessment of food contact plastic packaging materials.

In previous studies [7,8], commercial sunflower oil was epoxidized. Epoxidation is the formation of oxirane groups by the reaction of peroxyacids (peracids) with olefinic double bonds. The products of epoxidation are termed epoxides. The epoxidation of sunflower oil was carried out at 50°C using peracetic acid prepared in situ by reacting hydrogen peroxide with excess glacial acetic acid in the presence of Amberlite IR 120, a crosslinked ion exchange resin. The effects of epoxidized sunflower oil (ESO) on the thermal degradation and stabilization of PVC were investigated. ESO comes from renewable resources and it combines the properties of a stabilizer and a plasticizer. For applications in the packaging of food stuffs, migration testing must be performed [9]. Natural migration is simulated in model tests to determine the migrated or extracted additives in food simulants which can more easily be analyzed. On the other hand, the use of a new substance must be preceded by a toxicological study. The fullness of the toxicological dossier depends on the level of migration of the substance. If the specific migration is lower than 0.05 mg/kg of food or simulant, the use of the substance would be authorized if the substance is not a mutagen [6]. The toxicological dossier is much more important for substances whose migration attains 5 mg/kg [6,10]. As the majority of monomers and additives are lipophiles, generally the most important migrations occur in fatty foods or simulants. So, the migrations in these media are determinant concerning the fullness of the toxicological dossier. Among recommended fat simulants are sunflower oil, olive oil and heptane [6]. As a volatile substance, isooctane was also recommended to perform rapid tests, accompanied by simple analytical procedures, to determine specific migration [11]. In previous works [12,13], the specific migration of ESO in food simulants was evidenced by FTIR spectroscopy. The direct analysis of the food simulants was difficult because of overlapping of the bands of additives, but the analysis of PVC films obtained by dissolution in tetrahydrofuran (THF) and evaporation of the solvent was more conclusive.

The aim of this paper is the quantitative determination of the specific migration of ESO by using GC-SM. The migration is investigated by measuring the residual ESO in PVC where ESO is extracted from the PVC matrix before analysis. The extraction of analytes from the polymeric matrix prior to identification and quantification is necessary. The separation methods include the traditional soxhlet solvent extraction (method 1) or the dissolution of the whole polymer first followed by separation of the additive from PVC by precipitation of the polymer (method 2) [14]. In the present work, the second method is chosen considering its great output of extraction. Linoleic acid is used as the external standard.

EXPERIMENTAL

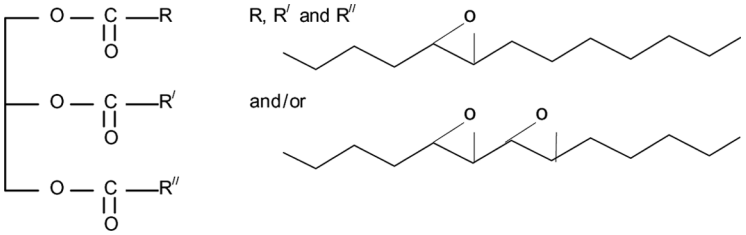
Materials

Algerian PVC from ENIP-Skikda with K wert-value 65–67, which is a measure of relative viscosity according to the standard DIN 53-726, Zn stearate from Aldrich, Ca stearate from Prolabo, di-octyl phthalate (DOP) from SGP (Tunisia) and stearic acid from SO.G.I. SPAS (Italy) were used as received. ESO (Scheme 1) was especially prepared as described previously [7]. The level of oxyrane oxygen was 6.4%. Tetrahydrofuran (THF), methanol and chloroform of high purity HPLC grade from Prolabo were used as received. The external standards for GC-SM analysis of ESO and DOP were linoleic acid ($C_{18:2}$) of 99% purity from Merck and DOP from SGP. Olive oil used as a food simulant has the following characteristics:

Relative density = 0.89; acidity index = 2.69; iodine index = 83.07; saponification index = 187.5; peroxide index = 8.

The composition of fatty acids of ESO is:

- 7.77% of palmitic acid ($C_{16:0}$)
- 5.75% of oleic acid ($C_{18:1}$).
- 1.98% of linoleic acid ($C_{18:2}$).



Scheme 1: Chemical structure of epoxidized sunflower oil (15).

Preparation of PVC Films

Four formulations containing 1 wt% of zinc stearate, 1 wt% of calcium stearate, 1 wt% of stearic acid, 5 wt% of ESO, 0 wt% (rigid PVC) and 15, 30, and 45 wt% of DOP (plasticized PVC) were prepared. The various concentrations of plasticizer were used to study the influence of plasticizer concentration on ESO migration from PVC into a food simulant. The resin and the additives were mixed in a two – roll mile at 140°C and melt-compressed at 170°C under a pressure of 300 kN/m^2. The obtained films have a thickness of 1.75 mm. Then. circular samples having a diameter of (18 ± 0.1) mm were cut by using a template.

Migration Testing

Migration tests were conducted in a thermostated bath using olive oil as a food simulant. The test conditions were 12 d at 40 and 20°C and 2 h at 70°C. They were chosen according to the standard NF EN 1186-1 [16]. They correspond to the worst case migration conditions. For the first test, twelve circular samples of rigid and plasticized PVC were immersed in 120 ml of each food simulant with and without magnetic agitation. The agitation was carried out in a transient state with a $Re \approx 3000$. A circular sample and 10 ml of food simulant were taken off every day to be analyzed. Thus, the weight ratio between the discs and the liquid simulant remained constant. Glass pipettes and flasks were used to take off the food simulants and to store them.

Separation of Additives From PVC Discs

The separation of ESO and DOP from PVC was done by dissolution/precipitation. The discs were cut into small pieces with length of 7 mm, weighed and dissolved in THF at a ratio of 1 g plastics in 40 ml THF. PVC was precipitated by the addition of methanol (MeOH) (THF/MeOH = 1/2.5 v/v). The filtrate was separated from PVC and the solvent evaporated. This filtrate was dried at 80°C for 30 min. The dried extract was dissolved in 2 ml of chloroform and analyzed by GC-MS.

GC-MS Analysis

GC-MS analysis was performed on a Perkin Elmer GC connected with a MS detector. ESO was directly analyzed. The injector temperature was 250°C with splitless mode. The detector temperatures were 180°C for the carrier liquid and 150°C for the source. Carrier gas was helium with a flow 1.1 ml/min. A 60 m capillary column PE-5MS (5% phenyl methyl polysiloxane), i.d = 0.25 mm, $d_f = 0.25$ μm, Perkin Elmer) was used under the following

conditions: 90°C held for 3 min, heated up to 250°C at a rate of 6°C/min and held for 14 min. Molecular mass in the range 40–650 amu was scanned.

The identification of different peaks was deduced by searching in the MS libraries (NIST) and further confirmed by running the known chemicals for DOP, ESO and linoleic acid.

The quantification of ESO in food simulants was performed using m/Z 280 for ESO and m/Z 280 for the external standard, whereas the quantification of DOP was performed using m/Z 279 for DOP and m/Z 279 for the external standard.

Calibration curves for DOP and ESO were prepared in chloroform at concentrations that covered the concentration range found in the polymer extracts. Peak areas were plotted against concentration (mg/ml). The resulting lines were linear with correlation coefficients of 0.99 and 0.968 for ESO and DOP, respectively. Three analytical replicates were analyzed for each concentration.

RESULTS AND DISCUSSION

GC-MS was chosen for the analysis of the migration of ESO and DOP in olive oil. The amounts of additives migrating from the PVC samples were calculated according to Eq. (1).

$$C_m = C_i - C_r \tag{1}$$

where

C_m = concentration of migrated ESO (DOP) in olive oil (g/ml),

C_i = initial concentration of ESO (DOP) in PVC sample evaluated by GC-MS after extraction (g/ml), and

C_r = residual concentration of ESO (DOP) in PVC sample after contact with olive oil evaluated by GC-MS after extraction (g/ml).

The quantification of ESO was based on the molecular ion peak which appears at M/Z280 (Figure 1) while the quantification of DOP was based on the qualifier ion M/Z 279 (Figure 2).

It can be noted (Figure 1) that the spectrum of linoleic acid is dominated by ions of low mass produced by rupture (Mac Lafferty rearrangement) starting from the ester grouping [17] and the molecular ion peak appears at M/Z 280. The double links are located by intervals of 26 mass units (C_2H_2) which correspond to the fractionation of the link C–C of each with dimensions of the double link [17,18].

Thus the interval of 26 mass units from M/Z 150 to 123 is associated with the presence of a double link in position C_{11} on the aliphatic chain, whereas the fragments of mass M/Z 110 and 84 make it possible to locate the second double link at position C_8 of the chain as shown by the characteristic model of defragmentation of $C_{18:2}$ (Scheme 2).

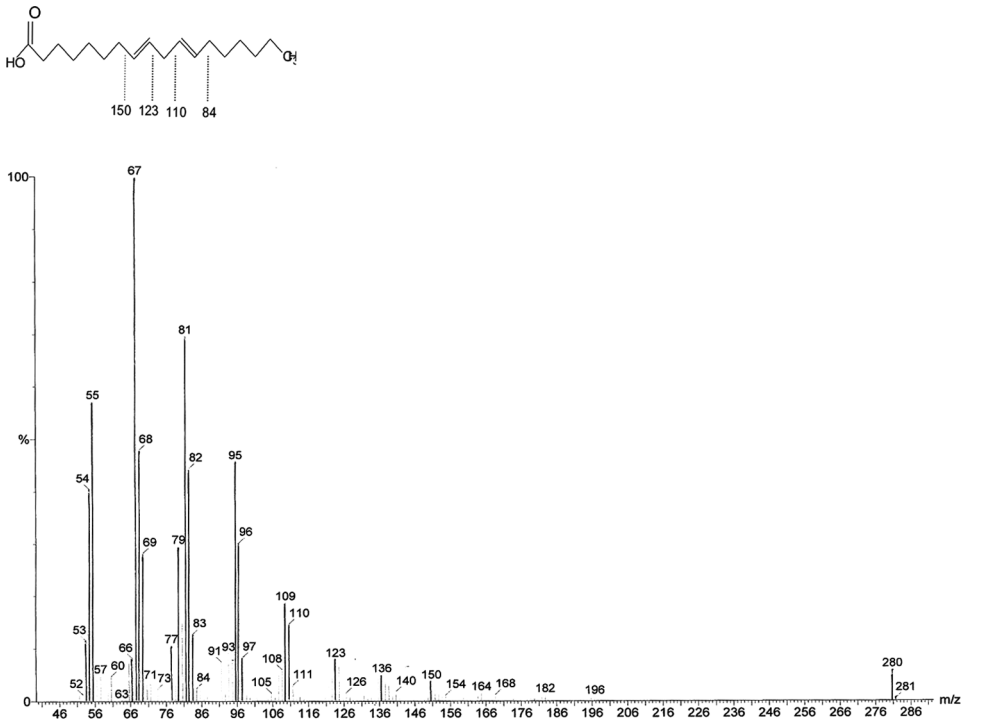


Figure 1: Mass spectrum of linoleic acid ($C_{18:2}$) of epoxidized sunflower oil (ESO).

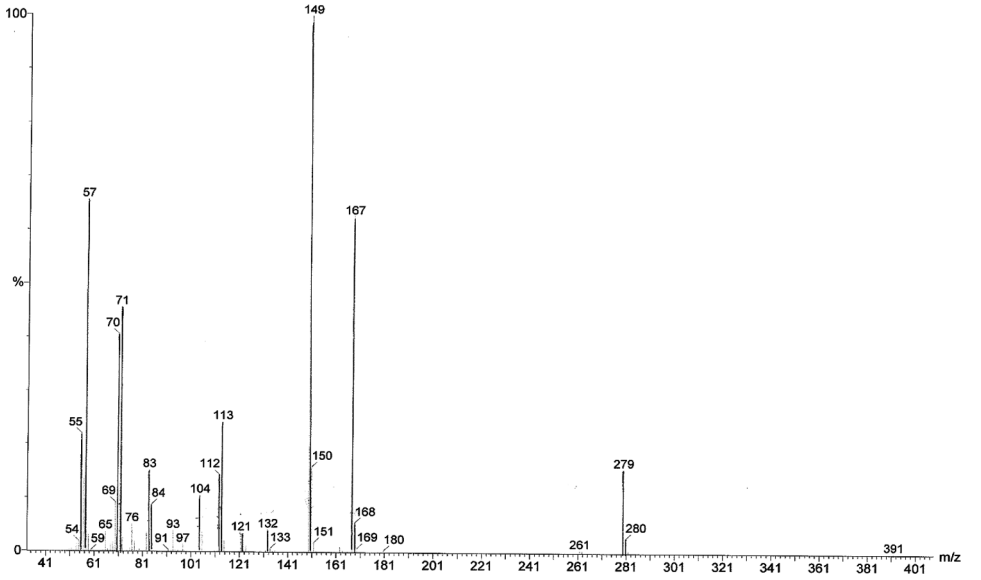
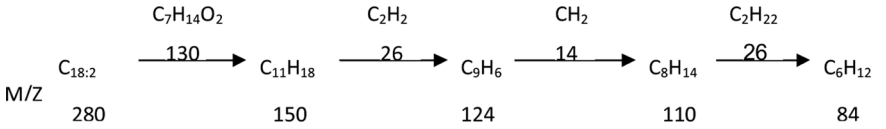


Figure 2: Mass spectrum of di-octyl phthalate (DOP) showing the base peak at m/z 149 and the qualifier ions at their intensities at m/z 279 and 167.



Scheme 2: Defragmentation model of $C_{18:2}$.

The amount per cent of migrated ESO (DOP) was calculated according to Eq. (2).

$$\text{Migrated ESO (DOP)}\ (\%) = \frac{C_m}{C_i} \times 100 \qquad (2)$$

The migration data of ESO from the plasticized formulation (45 wt% DOP) with and without agitation in olive oil are given in Figure 3. The highest migrated values were obtained during the migration test with agitation. This factor allows us to renew the gradient of concentration at the surface of the PVC samples and favors additive migration. The latter is also favored by temperature as shown in Figure 4. The mobility of additives and then their migration is enhanced with increasing temperature. It is to be noted that the migration testing at 70°C was carried out during 2 h while the ones at 20 and 40°C were carried out during 12 days. The ESO percentage migration was about 80% at 70 and 40°C and 55% at 20°C.

From these preliminary results, the kinetics of leaching of ESO and DOP from PVC films containing various amounts of DOP in olive oil at 40°C with agitation for 12 days were investigated. The data are given in Figures 5 and 6, respectively. In both figures, migrated ESO and DOP increased with time in the initial stage, but tend to level off after 120 h practically in all the curves.

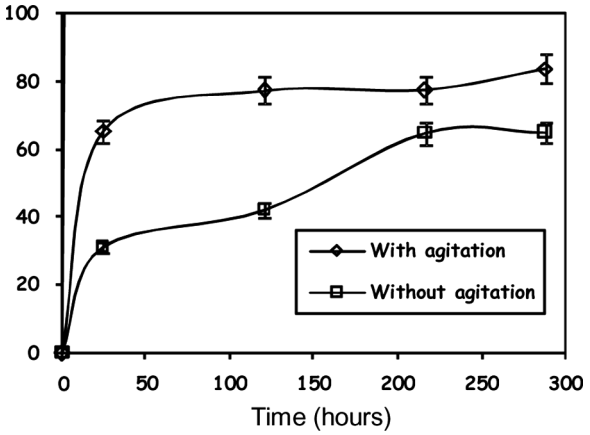


Figure 3: Influence of agitation on the migration of ESO in olive oil at 40°C from rigid PVC plasticized with 45% DOP.

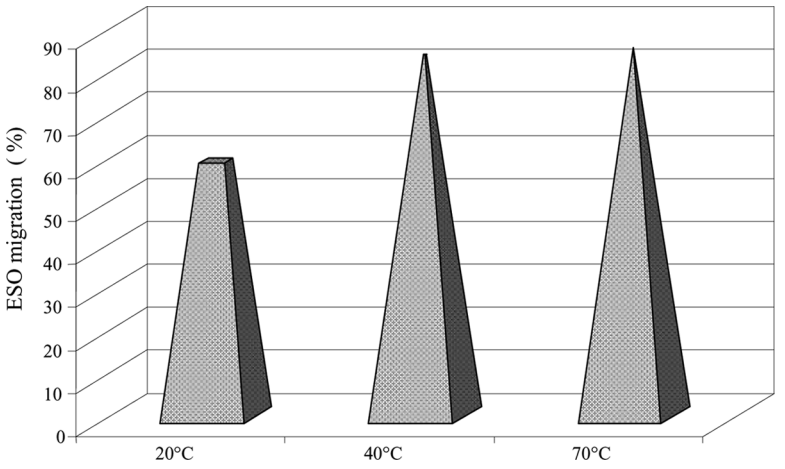


Figure 4: Comparison of the rates of migration of the ESO from rigid PVC in olive oil at various temperatures with agitation.

Furthermore, it can be noted that ESO migration decreased with increasing the level of DOP in the PVC films (Figure 5) while DOP migration increased with the same factor (Figure 6). The larger the amount of DOP, the more intensively DOP migration takes place. This phenomenon can be explained by the fact that intramolecular interaction between the polymer chains decreases to release more DOP from PVC matrix.

Figure 7 shows a comparison of the rates of migration of ESO and DOP from plasticized PVC containing 45 wt% of DOP in olive oil at 40°C with agitation. Although the two rates decrease with time, it is clear that rates of DOP migration are relatively higher than those of ESO. This can be directly

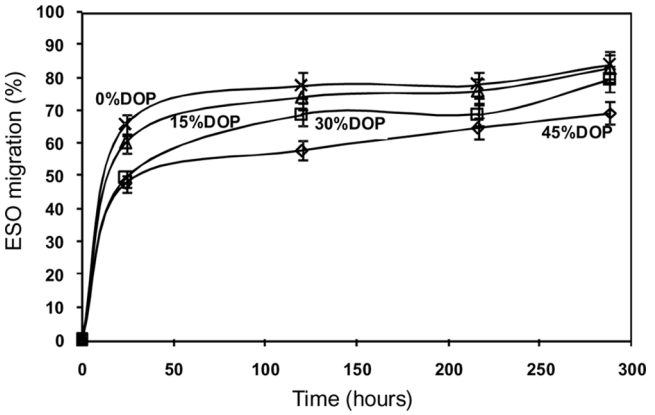


Figure 5: Kinetics of leaching of ESO from PVC films containing various amounts of DOP in olive oil at 40°C with agitation.

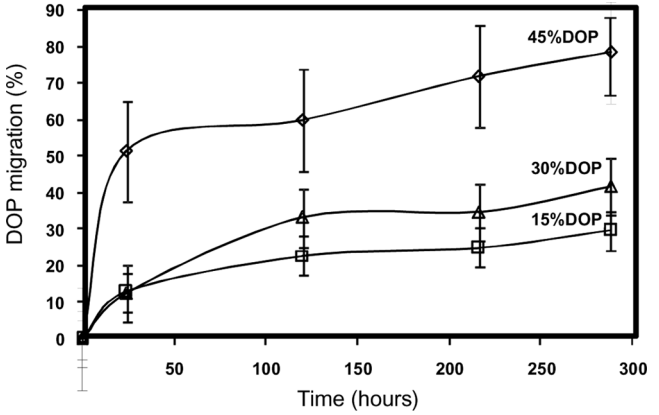


Figure 6: Kinetics of leaching of DOP from plasticized PVC films in olive oil at 40°C with agitation.

related to the lower molecular weight and steric hindrance of DOP in comparison with ESO.

In order to investigate the effect of DOP concentration on the migration of ESO, the rates of migration of ESO were calculated. The results are presented in Figure 8. The lower the amount of DOP, the higher the rate of migration of ESO. For the three formulations considered, the ESO rates of migration steeply decrease at the initial period and then level off, suggesting that migration of ESO mostly takes place at the initial stage regardless of the amount of added DOP.

The levels of specific migration of ESO in olive oil at 40°C were calculated for the rigid (0% DOP) and the most plasticized (45% DOP) formulations.

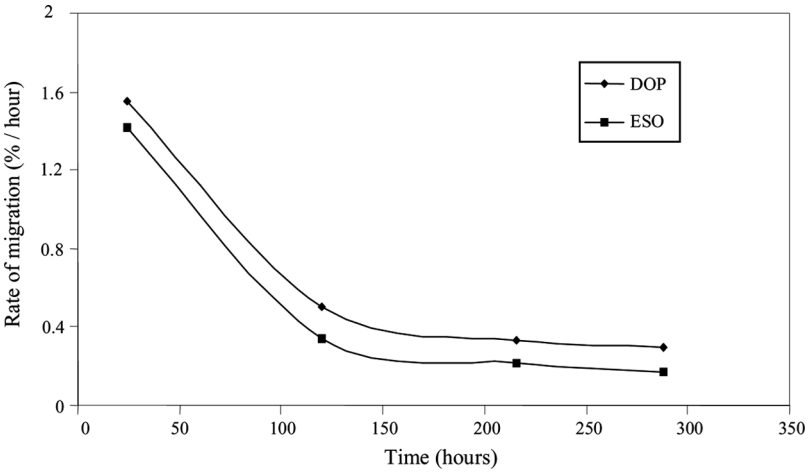


Figure 7: Comparison of the rates of migration of ESO and DOP from plasticized PVC containing 45 wt% of DOP in olive oil at 40°C with agitation.

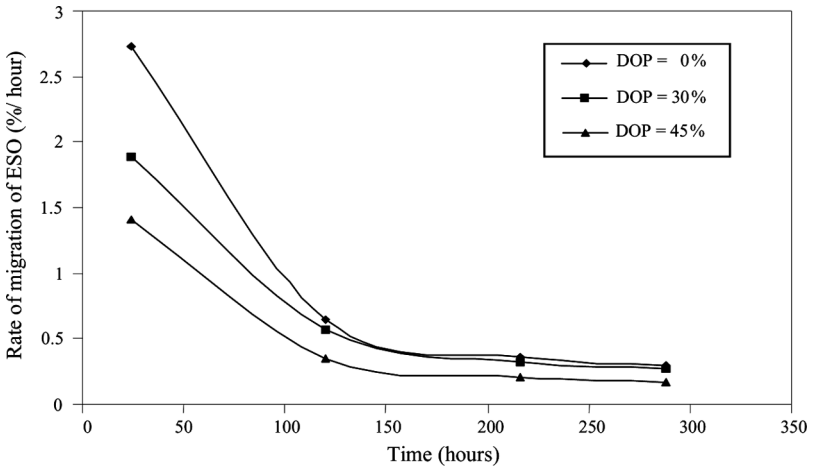


Figure 8: Effect of the plasticizer content on the rate of migration of ESO in olive oil at 40°C with agitation.

Table 1: Specific Migration of ESO in Olive Oil at 40°C with Agitation

Formulation	0 wt% DOP	45 wt% DOP
Specific migration (mg/kg olive oil)	9.00	1.08

The results are given in Table 1. As expected, the highest specific migration was obtained with the rigid formulation: 9 times that of the plasticized one. As the most important migrations occur in fatty foods or simulants, so the specific migrations evaluated in olive oil determine the fullness of the toxicological dossier. Although similar stabilizers, like epoxidized soya bean oil, are accepted as additives for food contact plastics, complete toxicological tests are required to assess the safety of this new stabilizer as the specific migration is higher than 5 mg/kg of food simulant.

The recommended toxicological studies according to the Council Directive 85/772/EEC of European communities are: mutagenesis, bioaccumulation, oral toxicity during 90 days, absorption, distribution, metabolism, reproduction, teratogen properties, long term toxicity and carcinogenicity.

CONCLUSIONS

From the experimental results the following conclusions can be drawn:

1. ESO migration from rigid PVC and ESO and DOP migrations from plasticized PVC occurred in olive oil.

2. ESO migration is influenced by the agitation, the temperature, the time of contact, the presence or the absence of DOP and the concentration of the plasticizer.
3. Specific migration of ESO in olive oil was found to equal 9 mg/kg from rigid PVC and 1.08 mg/kg from plasticized PVC (45 wt% DOP).
4. Complete toxicological tests are required to assess the safety of this new stabilizer.

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