Algerian Journal of Environmental Science and Technology
April edition. Vol.2. N°1. (2016)
ISSN : 2437-1114
www.aljest.webs.com

Environmental impact of the presence of phthalates (dop) in food packaging

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ARTICLE INFO

Article History:

Received ***: 00/00/2016***
Accepted ***:00/00/2016***

***Key Words*:**

PVC ;
Migration ;
DOP ;
CG/SM.

ABSTRACT/RESUME

Abstract: *This work is therefore in order to study the partial replacement of the plasticizer ordinarily used di-octyl phtalate (DOP) by the permanent plasticizers EVA and ABS in order to reduce migration of additives initially contents in polyvinyl chloride (PVC) stabilized with expoxidized sunflower oil (ESO). Migration tests with agitation to 40° C in sunflower oil and ethanol at 15 % were made. Migration phenomenon is studied on the basis of mass and peroxyd indication of sunflower oil variation, and the technical analysis: Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM).*

I. Introduction

Poly (vinyl chloride) (PVC) is used in many countries as a food packaging material. It is a versatile material that can be formulated for many different packaging applications. It is well known that PVC suffers from poor thermal stability.
It undergoes severe degradation via zip elimination of HCl at relatively low temperatures. Degraded PVC is characterised by the development of intense discoloration resulting from the formation of conjugated polyene structures [1]. The poor thermal stability of PVC requires the use of heat stabilisers in the processing of the polymer. The most important stabilisers of PVC are different metal soaps like Pb, Cd, Ca and Zn carboxylates and some di- and mono-alkyltin compounds.
Epoxidised sunflower oil (ESO) was obtained by epoxidation of commercial sunflower oil and used as thermal heat stabiliser for PVC [2, 3]. ESO is of considerable interest for ogano-chlorine polymer products. It comes from renewable resources and it combines the properties of a stabiliser and a plasticiser.
The migration tests were carried out with stirring at 40 °C in two food simulants, namely, olive oil and 15% aqueous ethanol.
Plasticisers and phthalates in particular have been used in the production of flexible PVC for more than 50 years for applications ranging from cable and wire covers and children's toys to medical devices and consumers products. During the past 20 years, phthalates have come under considerable attention from media, legislative and environmental concerns [4–6]. Although no direct evidence has been found of the toxic effect of phthalates to human beings, it has been proved that high dosage and long-term exposure of phthalates to rodents resulted in liver cancer and adverse effect on the reproductive development for young male rats [7]. In addition, phthalates were suspected of increasing asthma and bronchial obstruction in children [8]. The phenomenon of migration taking place from the pellets of plasticized PVC is mainly due to the presence of DOP plasticizer of low molecular weight. To deduce this, we placed pellets plasticized PVC in four environments simulators considered in testing and migration based on:

- The mass variation of samples by determining the rate of change of mass and moisture content in the four environments simulators.
- Morphological analysis of PVC samples by scanning electron microscope.
- Various physicochemical methods of analysis (GC/ MS).

II. Materials and Methods

II.1. Materials

Samples were prepared using the following recipe:
100 g of PVC stabilized by 2 g of Zn and Ca stearates and 10 g of ESO, 40 g of DOP and 1 g of stearine. PVC resin with K-Wert value of 70 produced by CIRES (Portugal), dioctyl phthalate (DOP) from SGP (Tunisia), Zn and Ca stearates complex (Reapak BCV/3037) from IACN (Italy), and stearine produced by SO.G.I.S. spa (Italy) were commercial products used without preliminary purification. The epoxidised sunflower oil (ESO) was especially prepared as described previously [9]. The level of oxirane oxygen was 5.2%. The olive oil used as food simulant was first characterised. Its acidity index, iodine index, saponification index and peroxide index were measured, respectively, according to the ISO 660, ISO 3961, ISO 3957 and ISO 3960. The following characteristics were measured: Acidity index = 1.38; iodine index = 83.07; saponification index = 182.9; peroxide index = 7.5 and relative density = 0.906. Ethanol and tetrahydrofuran (THF) of high purity grade from Prolabo were used as received.

II.2. Preparation of PVC films

PVC and additives were mixed in a two-roll mill at 140 ^{o}C and melt compressed at 170 ^{o}C under a pressure of 300 kN/m^2.

II.3. Migration testing

Circular samples having a thickness of 2 ± 0.1 mm and a diameter of 22 ± 0.1 mm were cut from the selected PVC films. Migration tests were conducted using olive oil as fatty stimulant and aqueous ethanol. The test conditions were 12 days at 40 ^{o}C (directive 82/711EEC). Twelve circular samples of plasticised PVC were immersed in 120 ml of food simulant. A circular sample and 10 ml of food simulant were taken off every day. The rate of mass variation was calculated according to the following equation:

$$\tau\ (\%) = [(m_t - m_0)].100 \qquad (1)$$

Where: m_o = initial mass before immersion and m_t = mass of the sample at the time t.
The weights were measured to an accuracy of 10^{-4}g.

II.4. SEM characterisation

The PVC samples were analysed after metallisation by a scanning electron microscope PHILIPS type ESEM XL.

II.5. GC-MS analysis

GC-MS analysis was performed on a Perkin–Elmer GC connected with a MS detector. A 30 m capillary column PE-5MS (5% diphenyl, 95% dimethyl polysiloxane), i.d = 0.25 mm; d_f = 0.25 µm, Perkin–Elmer) was used. The analysis was carried out using electron impact mode and an ionizaton potential of 70 eV. The carrier gas was helium with a flow of 2 ml/min.

DOP analysis

The separation of DOP from PVC was done by Soxhlet extraction with chloroform according to the method developed by Wang and Storm [10]. The analysis was conducted under the following conditions: 90 ^{o}C held for 3min, heated up to 250^{o}C at a rate of 6 ^{o}C /min and held for 13min. Molecular mass in the range 50–450 amu was scanned. The identification of different peaks was deduced by searching in the MS library (NIST) and further confirmed by running the known chemical for DOP. The quantification was performed using m/Z 149. Calibration curve for DOP was prepared in chloroform at concentrations that covered the concentration range found in the polymer extracts. The resulting line was linear with correlation coefficient of 0.9977. Three analytical replicates were analyzed for each concentration.

III. Results and discussion

III.1. Study of changes in the rate of mass change

Figure 1 illustrates the change in the rate of mass change versus time of contact in the case of the formulation considered.
Note that in the case of aqueous ethanol and acetic acid in the formulation in question, that the curves is increasing, indicating the penetration of the latter in the free volume due to the presence of plasticizer DOP . This phenomenon is facilitated by the polarity, low mass and low viscosity of ethanol and acetic acid.
Thus, given the characteristics of the environment simulator aqueous penetration of liquid into the test tube is favored and prevails over the migration of additives in the mid simulator.
Moreover, in the case of crude olive oil and isooctane, the curves are decreasing indicating a decreased rate of mass change with time and therefore a migration of some additives took place and in the case of the three formulations considered. The presence of plasticizer DOP decreases the interactions between PVC chains and promotes diffusion phenomena additives from the material. Thus, the concentration of DOP decreases within the material, resulting in increased rigidity of PVC [11].

Figure 2 illustrates the influence of the nature of the environment simulator (HOB, ethanol) on the rate of mass change, and this over a period of 12 days under the influence of agitation and a temperature of 40 °C, in the case of the three formulations considered.
The shape of the curves is decreasing in the case of HOB, indicating a migration of additives.

Moreover, in the case of aqueous environment simulator (ethanol), the curves are increasing which proves that there was penetration of the latter in the pellets.
However, we note that the rate of change of mass is higher in the case of isooctane and the crude olive oil, indicating that the phenomenon of migration is more important. Due to the good solubility of the plasticizer in isooctane and olive oil crude, and its low solubility in aqueous media, the interaction of pellets with fatty media are more pronounced. It is known that triglycerides are likely to interact with lipophilic polymers are good solvents and additives, they are weakly polar or apolar [12, 13].

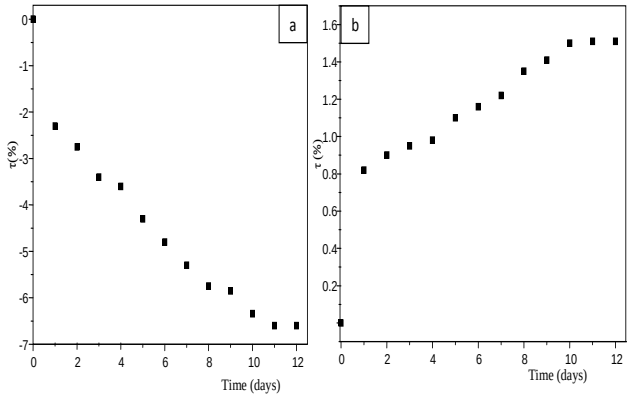

Figure 1: Evolution of the rate of mass change versus time of contact in the case:
- a: Olive oil crude
- b: Ethanol aqueous

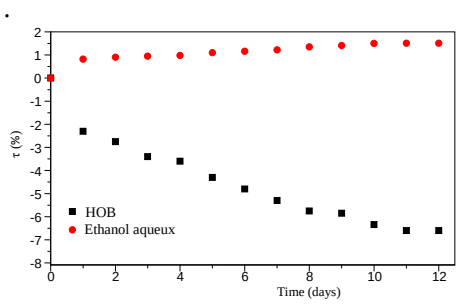

Figure 2: Influence of the nature of the environment simulator on the rate of change of mass in the case of the formulation F40DOP.

III.2. Morphological analysis by SEM

Figure 3 shows the images of the PVC samples analyzed by scanning electron microscopy. Analyses were performed on samples that had contact with the crude olive oil. By comparing the images of control samples (0j) and those having undergone migration tests for 10 days in the three media simulators, we observe:
• The appearance of dark areas (holes) indicating that there was migration of additives in the mid simulator.
• The surfaces of the pellets have undergone migration tests are rough compared with the witnesses who have surfaces much smoother indicating that there was migration of the plasticizer DOP.
The incorporation of permanent plasticizers in formulations provides a profile of DOP concentration low enough to the surface, thereby reducing the amount of DOP may migrate to the middle simulator.

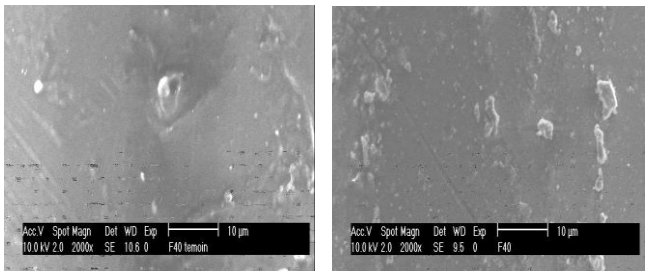

Figure 4: Analysis by scanning electron microscope specimens have been in contact with the crude olive oil

III.3. Application of GC / MS to study the specific migration of DOP

The gas chromatography coupled with mass spectrometry is applied in order to study the specific migration of DOP from PVC pellets that have been in contact with the media simulators. We first looked for the optimal operating conditions for the analysis of the additive in question (DOP) here based on the measurement of retention time to increase the sensitivity and specificity of the chromatographic system chosen. To assess the amount of plasticizer (DOP) in specimens of PVC witnesses and those who underwent migration tests at 40 ° C for 12 days, an internal calibration technique was used.
Figure 5 shows the chromatogram and fragmentation of the standard peak (m / z = 149) of the internal standard DOP is dibutyl phthalate (DBP), whose initial concentration is 2.4 ppm. Figure 6 shows the chromatograms of different samples analyzed.

The determination of DOP in the crude olive oil of the formulation studied is made by GC / MS by measuring each of chromatograms the peak area of standard DOP. A calibration curve was established, on the Y axis the surfaces of the DOP standard peak (m / z = 149 and t_r = 28.77 min) and the X axis on the various concentrations of DOP.
The values of DOP concentrations are given in Table 1.

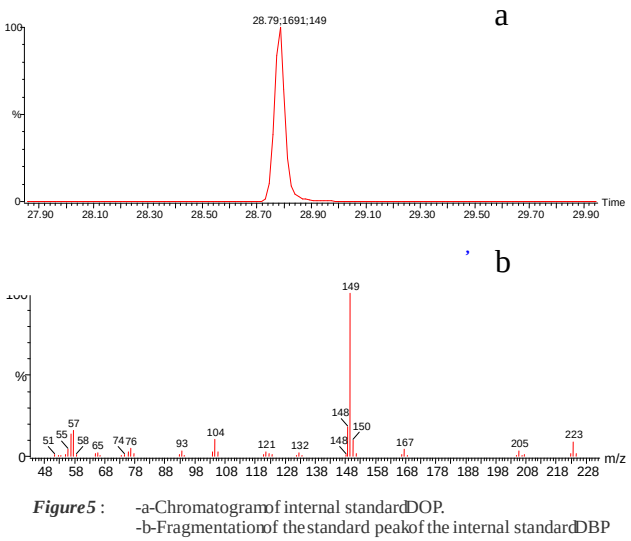

Figure5 : -a-Chromatogram of internal standard DOP.
-b-Fragmentation of the standard peak of the internal standard DBP

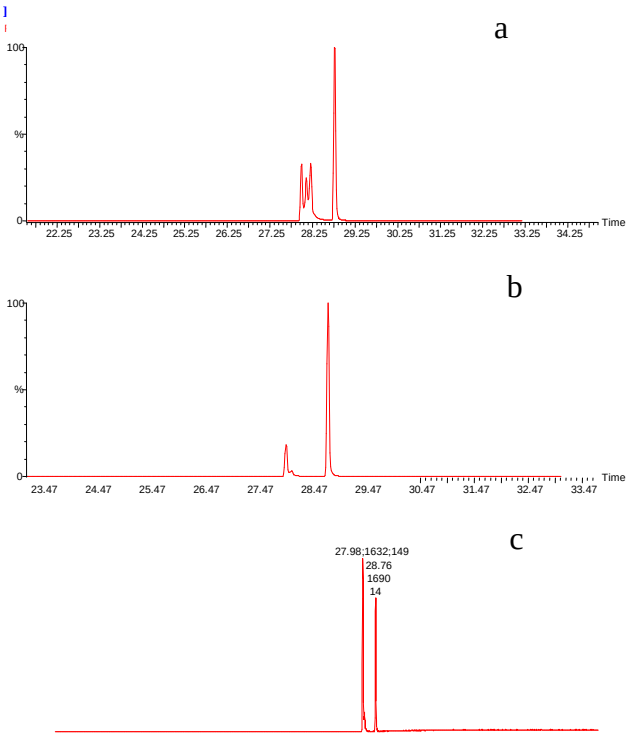

Figure6: Chromatogram of the sample of F40DOP.
-a-witness.
-b-brought into contact with aqueous ethanol for 12 days.
-c-contacted with the crude olive oil for 12 days.

From this table it appears that:

- The amount of DOP migrated in the case of specimens which have been tested for migration into olive oil is greater than that determined in aqueous ethanol, which means that the nature of the simulator environment plays a very important regarding the transfer of DOP, since each simulator has a different behavior by its physicochemical properties (degree of affinity presented vis-à-vis the DOP).

- The use of permanent plasticizers decreased the migration of DOP.

Table 1. *Quantity of DOP migrated.*

Formulation	**F40DOP**	
[DOP] migrate	**ppm**	***%***
0 days	2,230	34,100
Aqueous ethanol	1,240	18,960
HOB	*0,830*	*12,690*

IV Conclusions

The study of the changing rate of mass change shows that the phenomenon of migration of additives has occurred, and that in the four environments simulators, and for the three formulations studied. The rate of change of mass in the case of HOB are more important than other simulator (aqueous ethanol).
This phenomenon depends on the nature of the environment simulator. Indeed, in the case of the crude olive oil and isooctane, there is migration additives in the mid simulator, while, in the case of ethanol and acetic acid is the penetration of the liquid in the pellets of PVC wins. Interactions between PVC pellets and environments are more important in the case of crude olive oil for the three formulations considered.
The morphological study of specimens of PVC confirmed the diffusion of additives to the media simulators. Disseminating the most important took place in the case of DOP in plasticized specimens.

Analysis by GC / MS, allowed:
- To select the operating conditions to be applied to the analysis of DOP.
- Obtain the chromatograms of the DOP, the HTE, witness and test-tested migration in the four environments used simulators.
- The amount of DOP migrated in the case of specimens F40DOP-tested for migration into olive oil is greater than that determined in aqueous ethanol.

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Please cite this Article as:
Boussoum M.O., Belhaneche-Bensemra N., *Environmental impact of the presence of phthalates (dop) in food packaging*, ***Algerian J. Env. Sc. Technology***, ***2*:1 (2016) 17-21**