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Interaction study of PVC / Saliva-based toys and application of the ultrasound method to reduce migration

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ABSTRACT/RESUME

Abstract: *This work is therefore in order to study a process of treatment by ultrasound, used for reducing the migration of additives contained initially in toys plasticized by DOP based on polyvinyl chloride stabilized with expoxidised sunflower oil (ESO).*
Two formulations were carried out at different rates plasticizers (15% and 45%), migration tests in synthetic saliva in absence and in presence of α-amylase with and without agitation to 37 ° C were made out over a period of 1, 3 and 6 hours.
The phenomenon of migration is studied on the basis of preliminary studies based on the change in mass, and only with the technical analysis: infrared Fourier Transform (IRTF) and gas chromatography coupled with mass spectrometry (GC/ MS).

I. Introduction

Polyvinyl chloride (PVC) is one of the most successful modern plastics. It is used in our daily life for various applications. It is made from two natural raw materials: oil and salt [1].
PVC alone is a very unstable plastic and it breaks easily. Additives such as plasticizers, lubricants and thermal stabilizers are added to give certain characteristics to plastics such as flexibility; heat resistance and durability .The most used are phthalates and other organic compounds such as bisphenol A and organotin [2].
But the question of the toxicity of phthalates has been raised for several years, leading then to the gradual introduction of precautionary measures or even prohibition on the use of phthalates as a plasticizer in certain fields of application. Dioctyl phthalate (DOP) is the most widely used plasticizer for PVC. Inside the PVC, the DOP remains within the matrix as a semi-solid element having no covalent bond with it, which gives the PVC a flexible structure. It can therefore easily migrate out of the PVC structure [3].
In recent years, special attention has been paid to toys made from plasticized PVC. Research carried out in this way has made it possible to highlight that [4, 5].
- Soft PVC toys contain significant amounts of phthalates;
– Babies and young children suck and chew their toys so that phthalates dissolve and escape and end up in the child's saliva, exposing them to their potential risks;
– Some phthalates can cause kidney and liver damage and cancer in laboratory animals; these are effects related to exposure, however none of these effects were observed in children.
By cons, what is ignored:
– The precise duration of exposure of children to plasticizers;
– The precise nature of the damage to children exposed to soft PVC.

In the context of present work, we sought to reduce this migratory phenomenon by modifying the surface of the polymer by crosslinking using an ultrasound treatment. This method aims to bring the molecular chains closer to the polymer thus increasing its cohesion thus decreasing the free volume and create a three-dimensional network that will act as a barrier thus preventing the additives contained in the toy from migrating to saliva and vice versa, that saliva does not penetrate the polymer interior.

In the present work, two formulations at different plasticizer levels (15% and 45% DOP) were carried out. Migration assays in synthetic saliva in the presence and absence of an α-amylase enzyme at 37 ° C were performed with and without agitation.

The samples used are specimens of dimensions (5 × 2) cm immersed in saliva. The kinetics of migration was monitored for specific durations (1, 3 and 6) hours.

The migration phenomenon is analyzed based on a preliminary study based on the mass variation of the PVC specimens in contact with the simulating media as well as using physico-chemical analysis techniques, namely: infrared Fourier transform (FTIR) and gas chromatography-mass spectrometry (GC/MS).

II. Materials and methods

II.1. Products

PVC resin with K-Wert value of 70 produced by CIRES (Portugal), dioctyl phthalate (DOP) produced by SGP (Tunisia), Zn and Ca stearates complex produced by IACN (Italy) and stearine produced by SO.G.I.S.SPA (Italy) were commercial products used without preliminary purification. The epoxidized sunflower oil (ESO) was especially prepared as described previously [6]. The level of oxirane oxygen was 6.4%. Heptane, tetrahydrofuran (THF), methanol and chloroform of high purity grade from Prolabo were used as received.

II.2. Preparation of PVC Films

Formulations containing 1 wt % of Zn stearate and and 1 wt % of Ca stearate, 5 wt % of ESO, 1 wt % of stearic acid and 15 and 45 wt % of plasticizer were prepared. PVC and additives were mixed in a two- roll mill at 140°C for 20 min and melt compressed at 170 °C for 5 min under a pressure of 300 kN/m^2 in order to obtain the desired thickness (2±0.1 mm).

II.3. Saliva simulator Backgrounds

The products used for the preparation of synthetic saliva solution are composed of magnesium chloride (166.7 mg / L), calcium (147 mg / L), sodium (327.3 mg / L) potassium (745, 5 mg / L), potassium carbonate (525.2 mg / L), potassium hydrophosphate (753.1 mg / L) and the α-amylase enzyme (0: 3000g). The compounds are then dissolved in 1 liter of distilled water; the pH of the solution is adjusted to 6.8 with a 3M hydrochloric acid solution [7].

II.4. Migration tests

The surface area of the PVC test pieces intended for the migration tests is 10 cm^2, the migration tests were carried out over a period of (1, 3 and 6) hours. Each specimen was immersed in 100 ml of saliva simulant medium in the presence or absence of the α-amylase enzyme at 37 ° C with and without shaking [4, 5]

The tests without stirring are intended to mimic the action of sucking the objects, moreover the objective of the agitation is to be able to simulate the action of the chewing to be done, 20 glass balls of diameter 4 and 30 mm were introduced into the migration cell.

II.5. FTIR Analysis

The PVC circular samples were dissolved in titrahydofurane (THF). After evaporation of the solvent, a polymeric film was recovered and analyzed with a JASCO FTIR-430 spectrophotometer at a resolution of 2 cm^{-1}.

II.6. 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; df = 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.

The separation of DOP from PVC was done by Soxhlet extraction with chloroform according to the method developed by Wang and Storm.14 The analysis was conducted under the following conditions:

90°C held for 3min, heated up to 250°C at a rate of 6°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 & discussions

III.1. Migration study based on mass variation rate

The monitoring of the evolution of the mass variation rate of the test pieces (FIG. 1) made it possible to demonstrate the presence of interactions between the specimens and the simulating media; on the one hand, the migration of the additives in the simulating medium in the presence of the α-amylase enzyme and, on the other hand, the penetration of synthetic saliva without amylase into the material. In addition, the mass change rate of the F45 formulation test pieces is higher than that of F 15 due to the initial DOP content. Moreover, the results obtained show that the ultrasound treatment influences the mass variation in the two simulator media considered, and therefore on the migrating amount. This treatment has an effect on the phenomenon of migration.

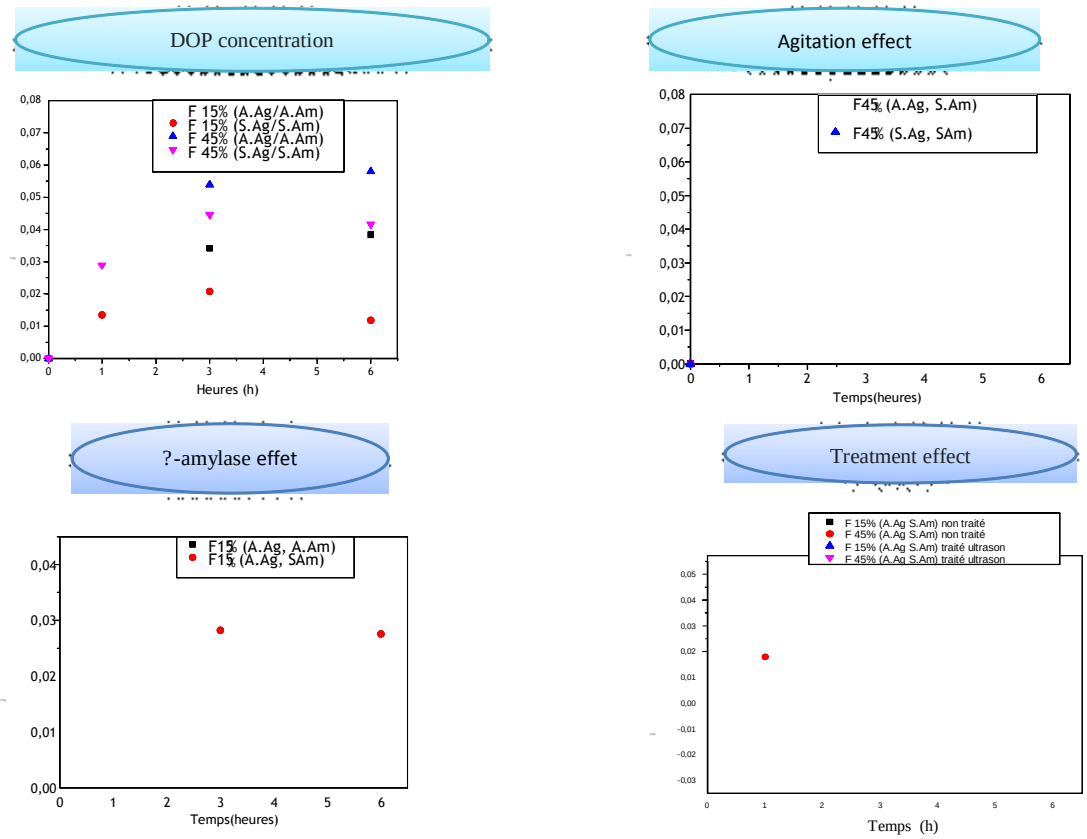

Figure 1. *Mass rate variation as a function of contact time*

III.2. Identification of additives from PVC films

FIG. 2 represents the superposition of infrared spectra of PVC alone and studied formulations (F45 and F15).

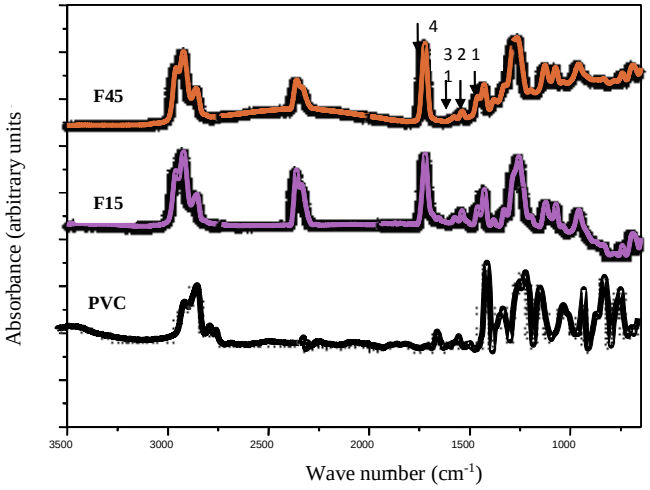

Figure 2. *Infrared spectra: PVC resin, F15, F 45*

Comparing the spectrum of PVC alone with those of the two semi-rigid formulations and plasticized, additional bands have been identified. Table 1 summarizes the bands due to the additives detected in the two spectra of the F15 formulations.

Table 1. *Strips of distinct additives present in the spectra of plasticized and semi-rigid formulations.F45 and absent in that of PVC alone by attributing them to each additive present.*

N°	Wave number (cm^{-1})	Characteristic grouping	Additive
1	1739,5	C = O (ester)	HTE
2	1578	C = O (ester)	Ca stearate
3	1723,4	C = O (ester)	DOP
4	1537,7	COO (ester)	Zn Stearate
5	1461,1	CH_2	HTE, Zn stearate

III.3. Study of the phenomenon of specific migration

Depending on the interaction phenomena taking place, there will be a change in the intensity of the characteristic bands. An increase in intensity would correspond to absorption of the liquid by the PVC specimens, and conversely, a decrease in intensity would correspond to a migration of one or more constituents. Knowing that the 1426 cm^{-1} band corresponds to the CH_2 bond in PVC **[8]**, we made a semi-quantitative estimation of the migration of the additives present by calculating the absorbance ratios A1731 / A1426, A1719 / 1426, A1557 / 1426, A1541 / A1426 which gives us information on the specific migration of HTE, DOP, Ca, Zn stearate. The A1457 / 1426 report allow us to study the global migration of all additives.

Fig. 3 illustrates the variations of the absorbance ratios as a function of the contact time (in hours) with the two simulating media (synthetic saliva in the presence and in the absence of the α-amylase enzyme) and the effect of the agitation in the migration tests carried out at 37 ° C for the two formulations studied.

According to the results obtained, we see increasing speeds in the time interval of less than 3 hours, which means penetration of the simulator medium to the PVC specimens, indeed in the time interval (3h-6h), we note the gaits are decreasing which indicates a migration of additives HTE, DOP, Zn Stearate, Ca Stearate, to the simulating medium.

This figure also clearly shows that the absorbance ratios for the test pieces that have undergone the treatment are lower than those that have not been treated, it is observed that the concentration of the additives is low, which indicates the decrease of the absorbance, which means the migration is weak, but against the specimens that have not treated, it is observed that the concentrations of the latter are higher which confirms the migration of the additives inside the test tube to the middle simulator.

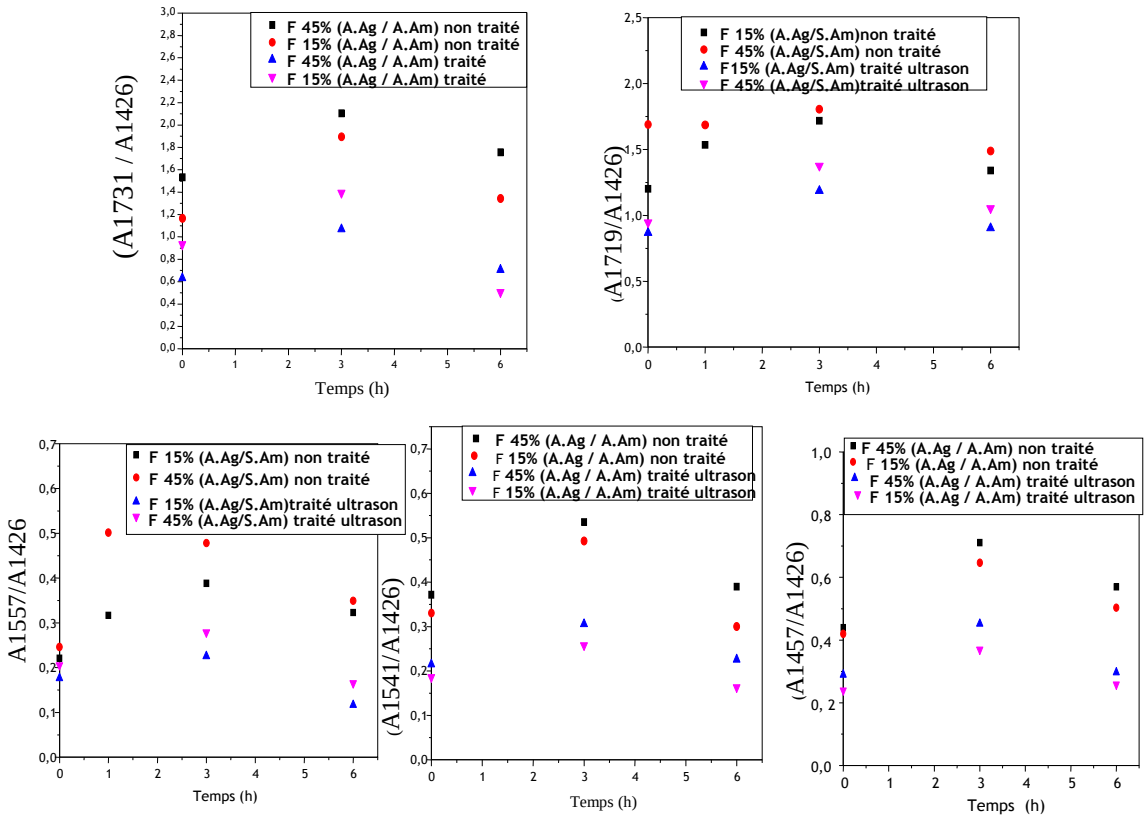

Figure 3. *Variation of absorbance ratios as a function of time*

III.4. Application of GC / MS to the study of specific migration

Gas chromatography coupled with mass spectrometry is applied in purpose of studying the specific migration of DOP from PVC specimens having been in contact with simulator media. The dosage of the DOP in the two simulating media is performed by GC / MS by measuring on each of the chromatograms obtained the peak area standard of the DOP. A calibration curve has been established, bearing on the Y axis the areas of the standard peak of the DOP (m / z = 149 and tr = 23.77) and on the X axis the different DOP concentrations.

Fig.4 shows, respectively, the chromatogram of the internal standard of DOP and fragmentation of the standard peak (m / z = 149).

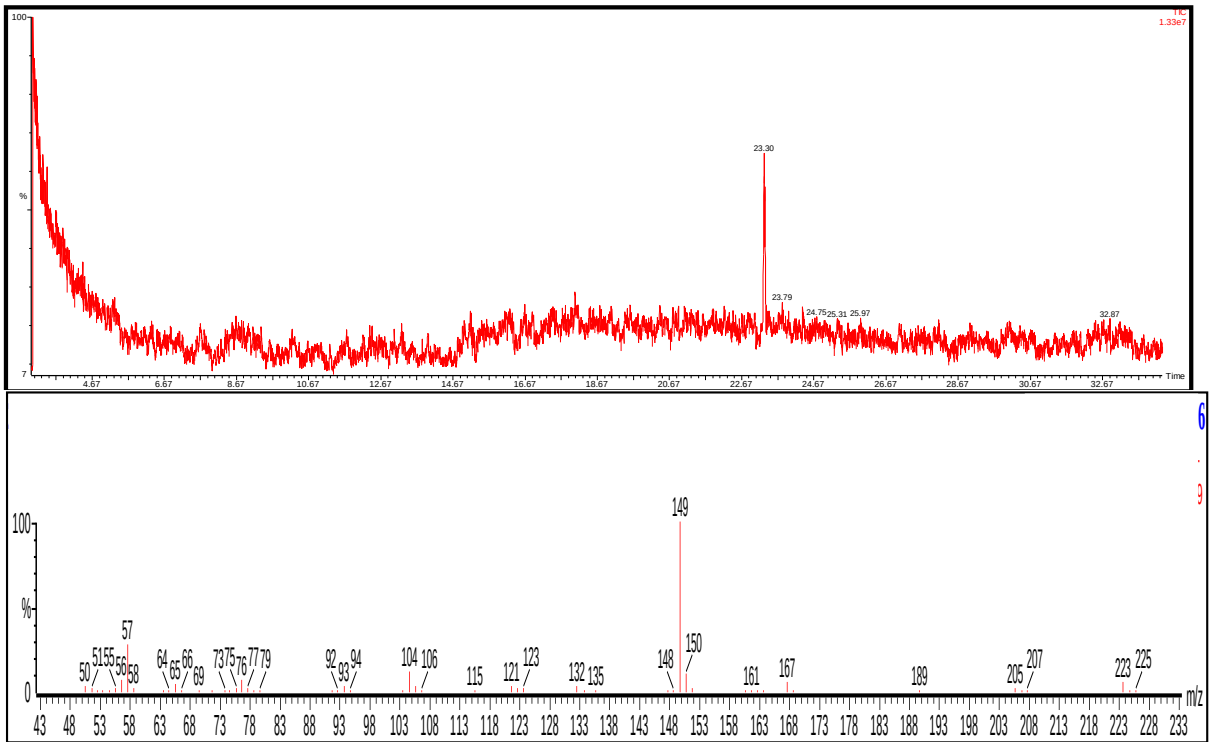

Figure 4. *Chromatogram and fragmentation (m / z = 149) of the DOP internal standard*

The results obtained reproduced in Figure 5 clearly establish the influence of the plasticizer on the migratory process, thus the mass of the plasticizer transferred to the solvent and the quantity of the incoming liquid are all the more important that the level of plasticization is high

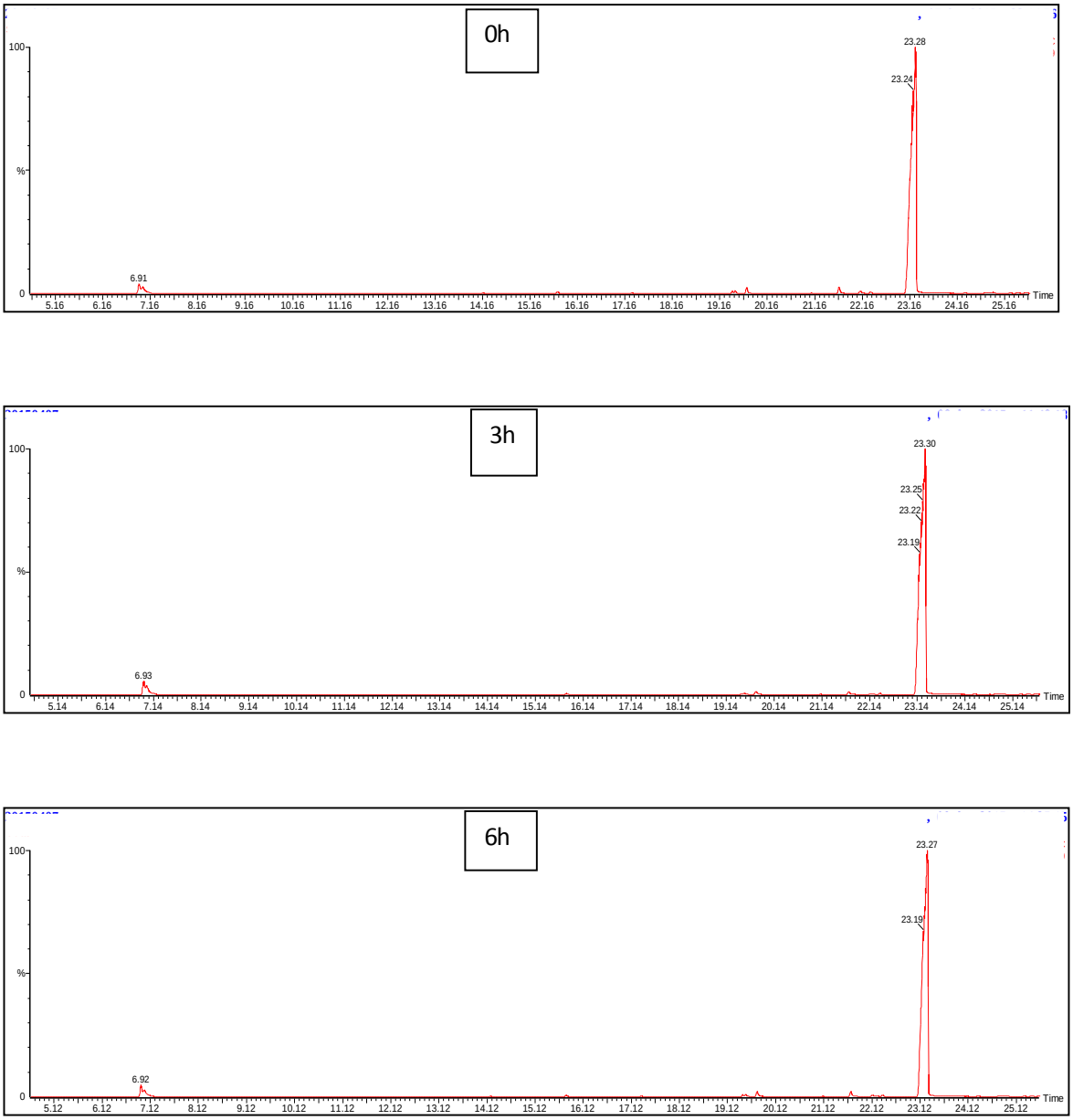

Figure 5. *Chromatogram of specimens of F45 treated with ultrasound brought into contact with saliva in the presence of agitation and α amylase.*

DOP concentration values are given in Table 2.
According to this table, it appears that:
- The quantity of migrated DOP in the case of specimens that have been tested for saliva migration in the presence of the enzyme is greater than that determined in saliva in the absence of the enzyme, which means that the nature of the medium simulator plays a very important role in the transfer of DOP, since each simulator behaves differently by its physicochemical properties (degree of affinity presented vis-à-vis the DOP).
- The quantity of migrated DOP in the case of the F45 formulation is greater than that of the F15 formulation, which shows the influence of the initial DOP content on the migratory phenomenon.
- The amount of DOP migrated in the case of the two formulations studied under the effect of agitation is greater than that in the absence of agitation which shows the influence of agitation on the migratory phenomenon.
- Ultrasound treatment decreased the migration of DOP.

Table 2. *Quantity of migrated DOP*

Formulations	F 15 DOP					F 45 DOP				
[DOP] (ppm)	Without treatment			With treatment		Without treatment			With treatment	
	S.Am		A.Am	S.Am	A.Am	S.Am		A.Am	S.Am	A.Am
	S.Ag	A.Ag	A.Ag	A.Ag	A.Ag	S.Ag	A.Ag	A.Ag	A.Ag	A.Ag
0h	0.022	0.022	0.022	0.022	0.020	0.046	0.046	0.046	0.046	0.046
1h	0.004	0.022	…..	……	…..	0.045	0.045	…..	…..	……
3h	0.003	0.022	0.018	0.020	0.004	0.041	0.043	…..	0.045	0.026
6h	0.002	0.021	0.016	0.015	0.001	0.035	0.040	0.010	0.039	0.019

IV. Conclusion

The present work has shown that the method of ultrasound treatment can be used to reduce the migratory phenomenon.

The highest rates of mass change were observed in saliva in the presence of the enzyme during ultrasound treatment trials. Moreover, it is the plasticized formulation which gave the highest rates of mass variation, which shows the influence of the nature of the simulating medium, the stirring and the treatment as well as the initial content of the plasticizer (DOP) on the phenomenon of migration.

The FTIR technique made it possible to characterize all the additives entering into the two formulations in a first step. It is the calculations based on the absorbance ratios which made it possible to confirm the migrations of the additives present, in particular the HTE and the plasticizer in the case of the plasticized formulation with stirring in the case of saliva in the presence of the enzyme. .

Finally, the GC / MS made it possible to obtain the chromatograms of the DOP of the control and the samples treated or not with ultrasound having undergone migration tests. Moreover, the amount of migrated DOP in the case of test specimens (F45DOP) having undergone migration tests is greater than that of F15. In addition, the ultrasound treatment decreased the amount of migrated DOP in the formulations studied as well in both saliva simulators.

Overall, this study has therefore confirmed that the migration phenomenon has taken place and that the ultrasound treatment makes it possible to reduce the migration of the additives contained in the PVC specimens.

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