Study and Optimization of a Soaking Treatment to Reduce Migration from Plasticized Polyvinyl Chloride

M. O. Boussoum, N. Belhaneche-Bensemra

Laboratoire des Sciences et Techniques de l'Environnement, Ecole Nationale Polytechnique, BP 182 El-Harrach, Alger, Algeria

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ABSTRACT: Commercial sunflower oil was epoxidized, and epoxidized sunflower oil (ESO) was used as a thermal stabilizer for polyvinyl chloride (PVC). This work describes a process capable to reduce the additives migration between plasticized PVC stabilized with ESO and food simulants. For that purpose, samples were first soaked in *n*-heptane and then dried. Soaking temperature and drying temperature with time were optimized by using the methodology of experiment plans. The optimal conditions found were applied to study the migration of additives in a fatty simulant (olive oil) at 40°C. The test conditions were 12 days. Twelve circular samples of plasticized PVC were immersed in 120 mL of olive oil. A circular sample and 10 mL of food simulant were taken off every day to be analyzed. The rate of mass variation was followed. The specific migrations of the present additives were investigated by using Fourier transform infrared spectroscopy, atomic absorption spectrometry and gas chromatography- mass spectrometry. The results showed that the studied process reduced considerably the additives migration. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1241–1248, 2012

Key words: plasticized PVC; migration; soaking; drying; experiment plans

INTRODUCTION

PVC is currently one of the most produced and used plastic materials.[1] Plasticizers and phthalates in particular have been used in the production of flexible PVC for over 50 years for applications ranging from cable and wire covers, children toys to medical device and consumers products. However, for the past 20 years, phthalates have come under considerable attention from media, legislative and environmental concerns.[2–7] Although direct evidence has been found on 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.[8] In addition phthalates were suspected to increase asthma and bronchial obstruction in children.[9]

PVC materials also contain other low molecular compounds particularly additives such as heat and light stabilizers, antioxidants, lubricants... The addition of such substances is essential for processing and achieving the desired chemical and mechanical properties.[10]

Correspondence to: N. Belhaneche (n_belhaneche@yahoo.fr) and M. O. Boussoum (idir_boussoum@yahoo.fr).

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However, all these additives frequently possess a high mobility and are capable of migrating from the packaging material into the packed food.[11–18] According to current legislation (directive 90/128/EEC and its amendments; EEC1990), the overall migration to a food stuff from food contact plastics must be less than 10 mg of plastics compounds per dm^2 of surface area.

Several approaches have been developed to reduce the leaching of plasticizers into liquid foods or simulants.[5,19–21] These techniques vary in level of complexity and also cost. They consist to modify the surface, to use polymeric plasticizers and oligomers, to use alternative plasticizers of polymers.[5] The removal of plasticizer from the polymer surface by surface extraction was used by Fugit et al.[21] The material is briefly exposed to a solvent for the plasticizers and then dried. This leaves the polymer with a nonuniform distribution of plasticizer and a rigid surface which blocks interfacial mass transfer of the plasticizers. In fact, the effectiveness of the treatment depends on a number of factors that requires optimization such as time and temperature of soaking as well as time and temperature of drying. However, as the parameters are numerous and not necessarily independent of each other, the methodology of experiment plans is used in this work.[22–24] The optimized conditions of treatment were applied to study the interactions between plasticized PVC and olive oil as fatty simulant. The additives migration was investigated by using various analytical methods

TABLE I
Effect of Soaking Time

Soaking time (min)	1	2.5	4	5
Δm (%)	0.1208	0.1297	0.1302	0.1338

TABLE III
Effect of Drying Time

Drying time (min)	2	3	4	6
Δm (%)	0.1227	0.1430	0.2838	0.4030

such as Fourier transform infrared (FTIR) spectroscopy, atomic absorption spectrometry (AAS) and gas chromatography-mass spectrometry (CG-MS). The results are compared with those obtained without soaking treatment.

EXPERIMENTAL

Materials

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.[25] The level of oxirane oxygen was 5.2%. Heptane, tetrahydrofuran (THF), methanol and chloroform of high purity grade from Prolabo were used as received. The internal standards for GC-MS analysis of ESO and DOP were respectively, méthylnonadecanoate and dibutyl phthalate from Aldrich. Olive oil used as food simulant has the following characteristics:

Relative density = 0.906; acidity index = 1.38; iodine index = 83.07; saponification index = 182.9; peroxide index = 7.5.

Preparation of PVC films

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 and additives were mixed in a two-roll mill at 140°C and melt compressed at 170°C under a pressure of 300 kN/m^2. Then circular samples having a thickness of (2 ± 0.1) mm and a diameter of (22 ± 0.1) mm were cut.

Samples treatment

PVC discs were immersed in n-heptane. At determined intervals of times and temperature, a disc was taken off. It was weighed before and after immersing, then dried during a given time and weighed.

Migration testing

Migration tests were conducted in a thermo stated bath using olive oil as fatty simulant. The test conditions were 12 days at 40°C (directive 82/711EEC). They correspond to the worst case migration conditions. Twelve circular samples of plasticized PVC were immersed in 120 mL of olive oil. A circular sample and 10 mL of food simulant were taken off every day. Thus, the weight ratio between the discs and the liquid simulant remained constant. Glass pipettes and flasks were used to take off the olive oil samples and to store them. The rate of mass variation was calculated according to the following relation:

$$\tau(\%) = [(m_t\text{-}m_0)/m_0].100 \quad (1)$$

Where: m_0 = 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. It is to be noted that migration testing was carried out using samples with and without soaking in heptane.

FTIR spectroscopy analysis

The PVC samples were dissolved in tetrahydrofuran. After evaporation of the solvent, a polymeric film was recovered and analyzed with a Jasco FTIR- 430 spectrophotometer. The resolution was 2 cm^{-1}.

Atomic absorption spectrometry analysis

PVC samples were first mineralized. The concentrations of Zn, Pb, Cu, and Cd were determined using a Perkin–Elmer AAnalyst 3000 spetrometer.

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

TABLE II
Effect of Soaking Temperature

Soaking temperature (°C)	22	30	40	50
Δm (%)	0.0121	0.0231	0.0331	0.0921

TABLE IV
Effect of Drying Temperature

Drying temperature (°C)	77	87	90	100
Δm (%)	0.1149	0.1302	0.1793	0.2119

TABLE V
Results of the Factorial Plan Experiments

Experiment	t_s (min)	T_d (°C)	t_d (min)	Δm (%)
1	5.00	45.00	4.00	0.36
2	5.00	45.00	8.00	0.42
3	5.00	45.00	4.00	0.48
4	15.00	45.00	8.00	0.53
5	5.00	65.00	4.00	0.43
6	5.00	65.00	8.00	0.49
7	15.00	65.00	4.00	0.45
8	15.00	65.00	8.00	0.47

polysiloxane), i.d = 0.25mm; 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.

Extraction of additives from PVC samples

DOP analysis

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.

ESO analysis

The separation of ESO from PVC was done by dissolution/precipitation according to the method developed by Wang and Storm.[14] The filtrate was separated from PVC and the solvent evaporated. The filtrate was dried at 80°C for 30 min. The dried extract was dissolved in 1 mL of chloroform and analyzed. The analysis was carried out under the following conditions: 90°C held for 1min, raised up to 300°C at a rate of 10°C/min and held for 20 min. Molecular mass in the range 50–450 amu was scanned. The quantification of ESO was performed using m/Z 281. Calibration curve was prepared in chloroform at concentrations that covered the concentration range found in the polymer extracts. The resulting line was linear with correlation coefficients of 0.9930. Three analytical replicates were analyzed for each concentration.

RESULTS AND DISCUSSION

Choice of optimization conditions

To study the influence of each parameter on the migration phenomenon, we have chosen to modelize and optimize the relative variation of the mass (Δm%) as a function of the following factors:

1. Time of soaking (t_s)
2. Time of drying (t_d)
3. Temperature of soaking (T_s)
4. Temperature of drying (T_d)

$$\Delta m(\%) = [(m_t\text{-}m_0)/m_0].100 \quad (2)$$

m_0 is the initial mass of the sample before immersion in *n*-heptane and m_t is the mass of the sample at the time *t* after soaking in *n*-heptane and drying.

The following experimental conditions were chosen according to Fugit et al.[21]

Optimization of soaking time

The experimental conditions were:
Temperature of soaking: $T_s = 22$°C
Temperature of drying: $T_d = 90$°C
Time of drying $t_d = 1$ min

TABLE VI
Estimated Effects from the Complete Factorial Plan

Var : ($y = \Delta m$ (%));$R^2 = 0.994$; R^2_{Aj} =:0.960; MC Residues = 0.0001125

	Effet	Err-type	*P*	−95% lim. cof	+95% lim.cof
Moy/Ord.Orig	0.454	0.003	0.005	0.406	0.501
(1) T_d (°C)	0.013	0.007	0.344	−0.083	0.108
(2) t_s (min)	0.058	0.007	0.082	−0.038	0.153
(3) t_d (min)	0.048	0.007	0.099	−0.049	0.144
1 * 2	−0.058	0.007	0.082	−0.153	0.038
1 * 3	−0.008	0.007	0.500	−0.103	0.088
2 * 3	−0.013	0.0 07	0.344	−0.108	0.083

R^2, Correlation coefficient; R^2_{Aj}, adjusted correlation coefficient; Err-type, Standard error; *P*, *P*-value; Lim.cof, limit coefficient; MC residues, average square residues.

TABLE VII
Results of the Focused Composite Plan

Experiment	T_s (°C)	t_p (min)	t_s (min)	Δm (%)
1	45.00	5.00	4.00	0.36
2	45.00	5.00	8.00	0.42
3	45.00	15.00	4.00	0.48
4	45.00	15.00	8.00	0.53
5	65.00	5.00	4.00	0.43
6	65.00	5.00	8.00	0.49
7	65.00	15.00	4.00	0.45
8	65.00	15.00	8.00	0.47
9	38.20	10.00	6.00	0.43
10	71.80	10.00	6.00	0.56
11	55.00	1.60	6.00	0.32
12	55.00	18.40	6.00	0.44
13	55.00	10.00	2.64	0.36
14	55.00	10.00	9.36	0.43
15 (C)	55.00	10.00	6.00	0.39
16 (C)	55.00	10.00	6.00	0.38
17 (C)	55.00	10.00	6.00	0.34
18 (C)	55.00	10.00	6.00	0.36
19 (C)	55.00	10.00	6.00	0.41
20 (C)	55.00	10.00	6.00	0.39

Table I shows the variation of (Δm) as a function of soaking time. The absence of an optimum can be noted.

Optimization of soaking temperature

The experimental conditions were:
Time of soaking: $t_s = 1$ min
Temperature of drying: $T_{d=}$ 90°C
Time of drying: $t_d = 1$ min
Table II shows the variation of Δm as a function of soaking temperature. The absence of an optimum can be noted.

Optimization of drying time

The experimental conditions were:
Temperature of soaking: $T_s = 22$°C
Time of soaking: $t_s = 4$ min
Temperature of drying: $T_d = 90$°C
The absence of an optimum can be noted (Table III).

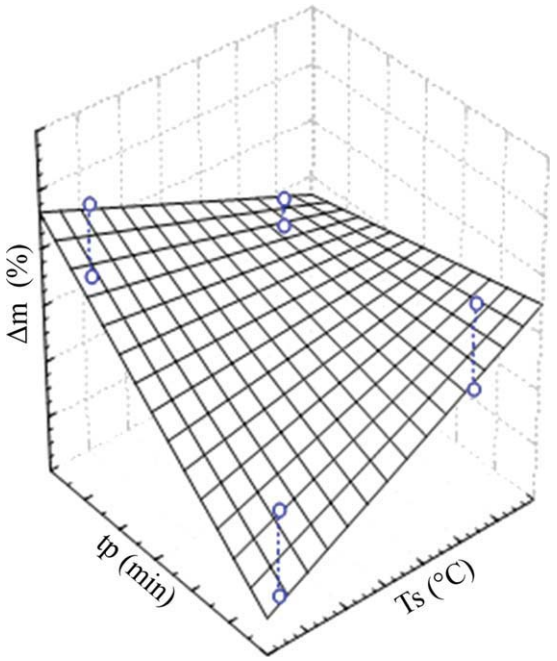

Figure 1 Response surface associated to the quadratic model.

Optimization of drying temperature

The experimental conditions were:
Temperature of soaking: $T_s = 22$°C
Time of soaking: $t_s = 4$ min
Time of drying $t_d = 1$ min
Table IV shows the absence of an optimum.
The experimental results allow to notice that each parameter selected does not result to an optimum. It needs other experiments. It also leads us to set apart a nonsignificant parameter which is the temperature of soaking because of the weak variation of the mass. Further selection of influent factors was realized with two levels factorial plan.

Factorial plan

The preliminary experiences lead to the selection of the three following factors:

TABLE VIII
Estimated Effects from the Focused Composite Plan

Var : (Δm (%)); $R^2 = 0.870$; $R_{Aj.} = 0.800$; MC Residues = 0.0001125

	Effect	Err-type	P	−95% lim. cof	+95% lim.cof
Moy/Ord.Orig	0.383	0.009	0.000	0.361	0.403
(1) T_d (°C) (L)	0.039	0.015	0.022	0.006	0.072
T_d (°C) (Q)	0.093	0.014	0.000	0.061	0.125
(2) t_s (min)	0.063	0.015	0.001	0.030	0.096
(3) t_s (min) (L)	0.045	0.015	0.011	0.012	0.078
t_s (min) (Q)	0.022	0.014	0.156	-0.009	0.054
1L * 2L	-0.058	0.019	0.012	-0.101	-0.014

L, linear; Q, quadratic.

TABLE IX
Results of Model Validation

Experimental Δm (%)	Calculated Δm (%)	Residues (%)
0.56	0.54	3.57
0.56	0.51	8.93
0.56	0.53	5.36

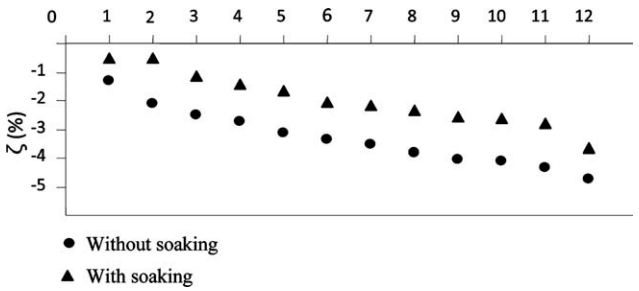

Figure 2 Effect of heptane treatment on the rate of mass variation in olive oil at 40°C.

Time of soaking whose extreme levels are[5,15] (min),

Time of drying whose extreme levels are[4,8] (min),

Temperature of drying whose extreme levels are[45,65] (°C).

The choice of these limit values of parameters was based on the following facts:

Thermal degradation of PVC starts at 80°C,[25]

Time of drying preconised for economy of operation is about 10 min,

for economic reasons the duration of soaking is inferior to 30 min.

The experimental plan selected is a complete one $2.^3$ The corresponding results are given in Table V.

The estimated effects obtained with Statistica software are shown in Table VI.

The examination of the obtained experimental results shows that the values of the adjusted correlation coefficient (R^2_A) and the correlation coefficient (R^2) are close to 1. These two parameters are important to observe as they indicate the quality of the adjustment of the model which is the first demand of experimenter.[22–24] However, this is not sufficient to judge if the model is adequate or not. The software Statistica allowed to calculate the following equation:

$$Y = \Delta m(\%) = 0.454 + 0.013\ T_d + 0.058\ t_s + 0.048\ t_d - 0.058\ T_d t_s - 0.008\ T_d t_d - 0.013\ t_s t_d \quad (3)$$

TABLE X
Overall Migration in Olive Oil at 40°C

Overall migration (mg/dm^2)	
Without heptane treatment	With heptane treatment
1.164	0.887

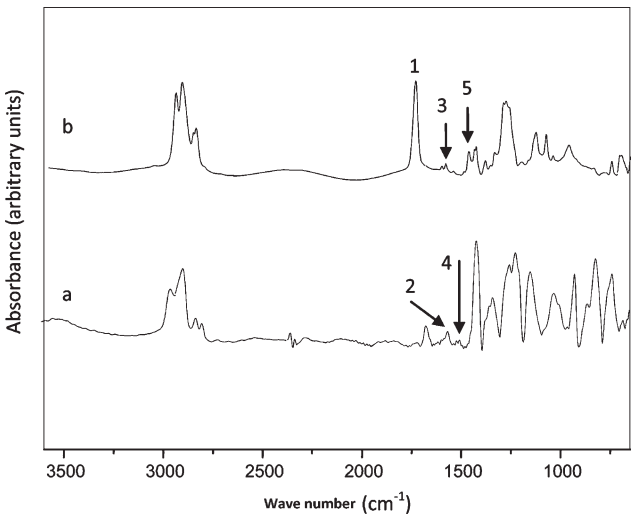

Figure 3 FTIR spectra of PVC film alone (a) and PVC film with additives (b).

On the other hand, Table V shows that the P values are superior than 0.05 which means that the effects of each factor are non significant.[24] Then, the factorial plan is not adapted to the study of the migration phenomenon. The choice of another plan is necessary.

Focused composite plan

The optimization consists to determine the optimum values of each factor. The rate of mass variation of PVC samples doesn't vary linearly as a function of these three factors. It is to determine the optimum of the curves by researching the correspondent quadratic model. We have carried out a focused composite plan composed with 20 essays (Table VII): six in center of the domain (experiments 15–20), 8 corresponding to the factorial plan 2^3 (experiments 1–8) and six in star form (experiments 9–14). By keeping the experimental conditions as described previously (Table V), the curves of response surface associated to the quadratic model represented in Figure 1 were determined.

TABLE XI
Characteristic Bands of the Used Additives Present in PVC film[27]

N°	Wave number (cm^{-1})	Functional group	Additve
1	1738	C = O (ester)	DOP, HTE
2	1579	CO_2^- (carboxylic acid salt)	Zn and Ca complex
3	1541	CO_2^- (carboxylic acid salt)	Zn and Ca complex
4	1463	CH_2 (methyl, methylene)	HTE, Zn and Ca complex, stearine

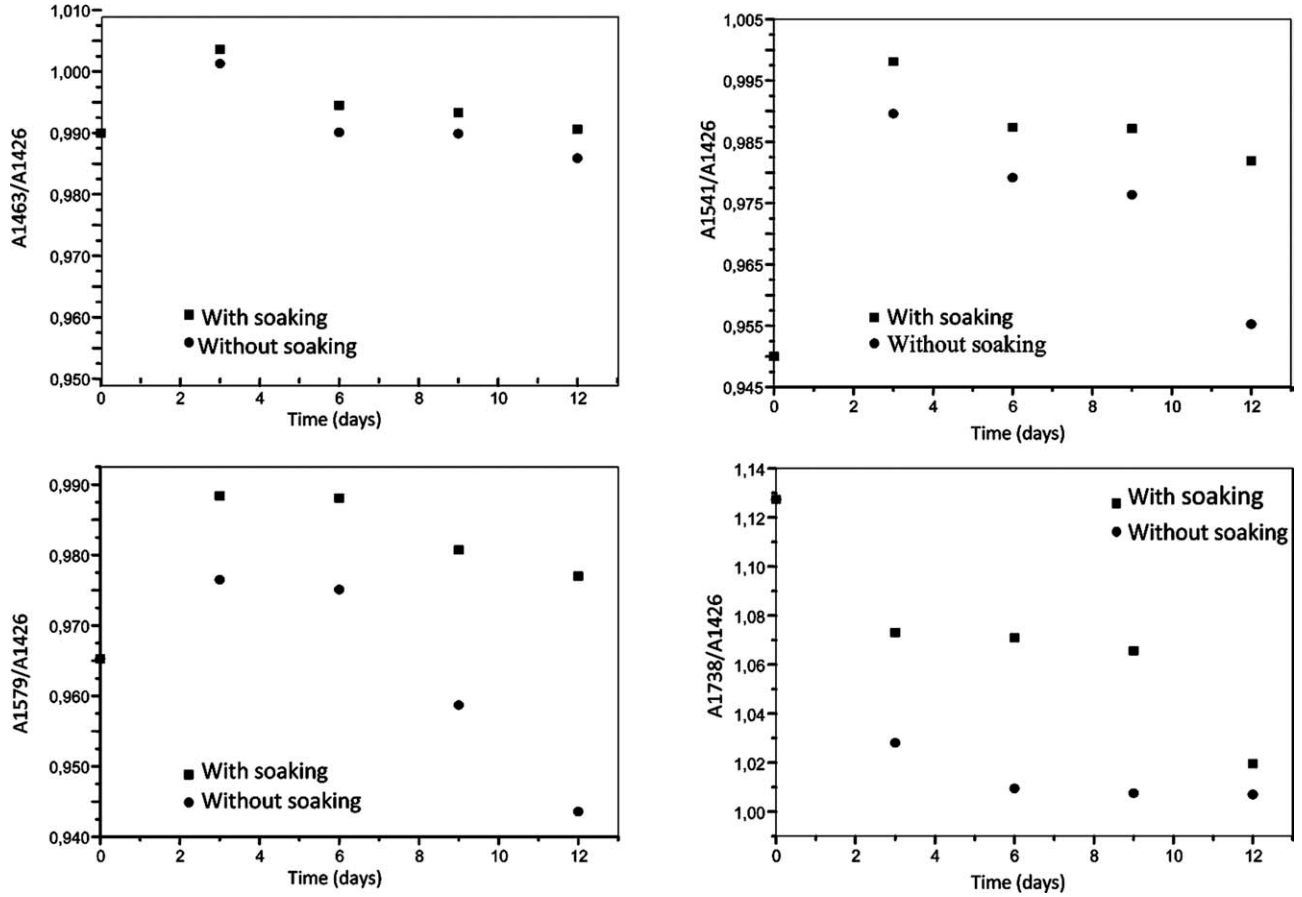

Figure 4 Variation of absorbance's ratios as a function of time of contact with olive oil.

Results based on the analysis with Statistica software giving the different coefficients are shown in Table VIII.

It can be noted that the coefficient of correlation R^2 is practically of the same order as R^2_{Aj} which allow to say that the R^2 value is satisfactory as the threshold of the value is inferior to 5%. The only value of the *P*-value exceeding 0.05 was determined on the drying time factor. This result can be explained by the noncomplete elimination of the liquid phase from the PVC sample.

For the 20 experiments, the coefficients of the postulated model lead to:

$$Y = \Delta m(\%) = 0.383 + 0.039\ T_d + 0.093\ T_d^2 + 0.063\ t_s + 0.045\ t_d + 0.022\ t_d^2 - 0.058\ T_d t_s \quad (4)$$

The model expression allows to evaluate the effects of the studied factors. The increase of the drying temperature and the soaking time favors the rate of mass variation. Furthermore, the effect of drying time is not significant because the value of the *P*-value is greater than 0.05. However, the interaction effect of drying temperature/soaking time is significant.

The resolution of this model boils down to find the extremum of a three variables function defined and differentiable in the field of study. If the function admits at one point in the field a relative extremum, the differential Δm cancelled at this point. This comes to calculate the point corresponding to:

$$\partial \Delta m/\partial\ T_d = \partial \Delta m/\partial\ t_s = \partial \Delta m/\partial t_d = 0 \quad (5)$$

The resolution of the obtained system of equations is delicate. That is why we opted for assessing the optimum from the experimental results shown in Figure 1. This allowed to deduce the optimum

TABLE XII
Concentrations (mg/L) of Metals in Additives and Olive Oil

Concentration	[Zn]	[Pb]	[Cu]	[Cd]
Olive oil	1.736	0.005	0.202	0.005
PVC alone	0.766	0.017	0.183	0.017
ESO	0.122	0.004	0.170	0.004
Zn and Ca complex	15.460	0.120	0.260	0.120
DOP	0.186	0.004	0.231	0.120
Stearine	0.978	0.015	1.958	0.015

TABLE XIII
Residual Concentrations (mg/L) of Metals in PVC Samples After Contact with Olive Oil

Concentration	With soaking				Without soaking			
Time (days)	[Zn]	[Pb] $.10^3$	[Cu]	[Cd].10^3	[Zn]	[Pb] $.10^3$	[Cu]	[Cd] $.10^3$
0	12.89	77.125	0.559	2.535	12.89	77.125	0.559	2.535
2	12.30	24.415	0.335	2.246	4.522	18.770	0.298	1.271
4	10.92	14.273	0.234	1.281	2.325	7.500	0.173	0.476
8	6.596	13.153	0.176	1.192	1.558	6.950	0.172	0.425
10	3.107	11.300	0.171	0.500	1.084	3.220	0.170	0.268
11	0.238	7.868	0.165	0.335	0.476	3.183	0.163	0.252

coordinates corresponding to the maximum value of (Δm) inside the studied area. These optimum conditions are:

Drying temperature is about 72°C;
Drying time is 6 min;
Soaking time is 10 min;
Rate of mass variation is 0.56%.

Method validation

For the evaluated optimum conditions, the experimental rate of mass variation Δm (%) was compared to the calculated one using the model of the focused composite plan. The results given in Table IX correspond to the average of three values for each PVC sample. The differences are called residues; they do not exceed 9% of the order of magnitude of the variability of experimental results due to the process. Therefore the model can be considered as valid.

To improve the correlation coefficient R^2, it is necessary to take into account other factors such as viscosity, superficial tension of liquids and the solubility parameters of PVC and DOP, if one wants to model the phenomenon of migration while getting as close as possible to the reality.

Migration testing

The rates of mass variation (τ) as a function of time give information about the phenomenon which occurred between the samples and the food simulants. An increase means that the food simulants penetrated the sample while a decrease means that some additives migrated in the food simulants. Hence (τ) gives informations about the overall migration that occurred.

The mass variation data for plasticized PVC with and without heptane treatment are given in Figure 2. It can be noted that (τ) decreases in both cases. This means that migration of some additives occurred in the fatty simulant but it is more important in the case of the samples which were not submitted to the optimized heptane treatment.

The values of the overall migration in olive oil are given in Table X. They are lower than the maximum allowable overall migration 10 mg/dm^2 in both cases. On the other hand, the overall migration was considerably reduced by the optimized heptane treatment. The reduction is about 24%.

FTIR spectrometry analysis

Figure 3 represents the spectra of PVC alone and with all the used additives. The comparison of the two spectra allowed the identification of some characteristic bands which are related to the additives present in the formulation as shown in Table XI. A semi quantitative estimation of the migration of additives was done. For that purpose, the following absorbance's ratios were calculated:

A1738/A1426: ESO and DOP migration
A1579/A1426: Ca and Zn stearates complex migration
A1541/A1426: Ca and Zn stearates complex migration
A1463/A1426: ESO, Ca and Zn stearates complex, stearine migration

The band at 1426 cm^{-1} is due to the vibration of CH_2 of PVC[26] and was taken as a reference band. The variations of these four ratios of absorbances as a function of time of contact with olive oil are given in Figure 4. An initial increase is first observed indicating the penetration of olive oil in the PVC discs. It is followed by a decrease of all the curves with time. This can be directly related to a phenomenon of migration of ESO, DOP, Zn, and Ca stearates complex and stearine in olive oil. It seems that the penetration of olive oil in the PVC discs favored the mobility of the additives and their migration. On the other hand, the highest absorbance's ratios were obtained for PVC samples soaked in heptane. This feature indicates that residual concentration of all these additives is higher in comparison to samples without soaking. Then, it is obvious that the highest

TABLE XIV
Specific Migration of DOP in Olive Oil

Migrated DOP	ppm	%
11 days without soaking	0.8300	12.6900
11 days with soaking	0.0300	0.4600

TABLE XV
Specific Migration of ESO in Olive Oil

Migrated ESO	ppm	%
12 days without soaking	0.3550	21.6463
12 days with soaking	0.1500	9.1643

migration occurred in the case of the samples without soaking.

Atomic absorption spectrometry analysis

The amounts of some metals (Zn, Pb, Cu, and Cd) contained in all the additives used as well as in the virgin olive oil used as food stimulant were first evaluated (Table XII). The same metals were searched for in the PVC samples which were in contact with olive oil (Table XIII). It can be noted that the residual concentrations in the PVC samples decreased with time. This decrease is related to the migration of ESO, DOP, Zn, and Ca stearates complex and stearine. On the other hand, the lowest residual concentrations were measured in the case of the samples without soaking in heptane. This feature is an indication of a highest migration and is in accordance with the results obtained by FTIR analysis.

CG-SM analysis

The determination of the migrated DOP and ESO in olive oil was achieved by GC-MS. The corresponding values are given in Tables XIV and XV, respectively. According to these tables, it appears clearly that the soaking treatment decreased considerably migrations of DOP and ESO.

CONCLUSIONS

This work showed that the methodology of experiment plans can be successfully used for the optimization of a treatment process to decrease the interactions between PVC samples and food/simulants. The optimal conditions found are soaking time average of 10 min; drying temperature of 72°C and drying time of the order of 6 min.

These optimized conditions allowed a notable decrease of the overall migration in olive oil at 40°C. This result was confirmed by all the analytical methods used (FTIR spectroscopy, atomic absorption spectrometry, and GC-SM).

Overall, this study has evidenced that migration took place and that the optimized soaking treatment reduced the migration of all the additives present in PVC samples.

References

1. Mulder, K.; Knot, M. Technol Soc 2001, 23, 265.
2. Cadogan, D. Plastics additives compounding 2002, June, 28.
3. Mersiowsky, J. Prog Polym Sci 2002, 27, 2227.
4. Earls, A.; Axford, I. P.; Braybrook, J. H. J Chromatogr 2003, 983, 237.
5. Rahman, M.; Brazel, C. S. Prog Polym Sci 2004, 29, 1223.
6. Marcilla, A.; Garcia, S.; Garcia-Quesada, J. C. J Anal Appl Pyrolysis 2004, 71, 457.
7. Fankhauser-Noti, A.; Grob, G. Trends Food Sci Technol 2006, 17, 105.
8. Wilkinson, C. F.; Lamb, J. C. Regul Toxical Pharm 1990, 30, 140.
9. Allsopp, M.; Santillo, D.; Johnston, P. Technical Note 14/00; Greenpeace Research Laboratories: Exeter, 2000.
10. Murphy, J. Additives for Plastics Handbook, 2nd ed; Elsevier Advanced Technology; Oxford, 2003.
11. Figge, K. Fd Cosmet Toxical 1972, 10, 815.
12. Lan, O. W.; Wong, S. K. Chromatography 1996, A737, 338.
13. Steiner, J.; Scharf, L.; Fiala, F.; Washuttl, J. Food Additives Contaminants 1998, 15, 812.
14. Wang, Q.; Storm, B. K. Polym Test 2005, 24, 290.
15. Atek, D.; Belhaneche-Bensemra, N. Eur Polym Mater 2005, 41, 707.
16. Boussoum, M. O.,Atek, D.; Belhaneche-Bensemra, N. Polym Degrad Stab 2006, 91, 579.
17. Zeddam, C.; Belhaneche-Bensemra, N. Int J Polym Mater 2010, 59, 318.
18. Atek, D.; Belhaneche-Bensemra, N.; Turki, M. Int J Polym Mater 2010, 59, 342.
19. Castle, L.; Mercer, A. J.; Gilbert, J. Food Additives Contaminants 1988, 5, 277.
20. Andic, J. L.; Reyx, D.; Brosse, J. C.; Poncin-Paillard, F. Ann Fal Exp Chim 2000, 93, 201.
21. Fugit, J. L.; Taverdet, J. L.; Mazellier, P. Ann Fal Exp Chim 2000, 93, 301.
22. Perrin, R.; Scharff, J. P. The Optimization of Reactors; Masson: Paris, 1993.
23. Goupy, J. Design of experiments, Techniques de l'ingénieur 2002, P230, 1.
24. Benoist, D.; Tourbier, Y. Plans Experiences, Construction and Analysis, Tec & Doc, Paris; 1994.
25. Benaniba, M. T.; Belhaneche-Bensemra, N.; Gelbard, G. Polym Degrad Stab 2001, 74, 501.
26. Krimm, S.; Folt, V. L.; Shipman, J. J.; Berens, A. R. J Polym Sci 1963, A1, 2621.
27. Socrates, G. Infrared Characteristic Group Frequencies; Wiley: New York, 2001.