Study of the Migration of Additives from Plasticized PVC

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Summary: The aim of this paper is to study the interactions between packaging and food. For that purpose, additives were first characterized. Kinetic studies of their specific migrations have been carried out by using different analytical methods such as gas chromatography, Fourier transform infrared spectroscopy, atomic absorption spectrometry and differential scanning calorimetric analysis. The influence of various parameters such as temperature, agitation, nature of food simulant and initial concentration of plasticizer was considered.

Introduction

Plastics are being used increasingly for packaging foodstuffs, but not all are suitable for this purpose. It is well known that, apart from high polymers, plastics materials also contain low molecular compounds, particularly additives such as stabilizers, lubricants and plasticizers. The addition of such substances is essential for processing and for achieving the desired chemical and mechanical properties[1].

The possible migration of minor constituents from polymeric packaging materials has become increasingly important. The migration from flexible packaging materials in contact with food would not normally include major components of the package itself but may contain minor constituents. Some of the migrants, can and do effect quality of the contained product as exhibited by sensorily determinable changes (odor and / or taste) or by toxicological symptoms from ingestion. The first case is of economic importance, while the second relates directly to health hazards with carcinogens as the worst case[2, 3].

Polyvinyl chloride (PVC) films have found wide applications in the packaging of large variety of foodstuffs, such as fresh meat, fruits and vegetables, and cheeses[4]. These commercial films, in addition to the polymeric component, contain a number of additives.The one used in the highest - proportion is the plasticizer[1].

Plasticizers are low- melting solids or high- boiling organic liquids added to plastic polymers in order to aid flow and processing, to extend and modify the natural properties of the resin and to develop new, technologically important properties not present in the resin itself[5].

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Among the most commonly used plasticizers are di-2 ethyl hexyl phtalate (DEHP) and di-2-ethyl hexyl adipate (DEHA)[6].

The amount of package components that may be leached by food or food simulating solvants depends on the original concentration of the particular component or migrant in the polymer, its solubility in the solvent and / or the partition coefficient between the polymer and solvent as well as temperature and time[7].

The aim of this paper is to study the migration of additives from plasticized PVC. Kinetic studies of their specific migrations have been carried out by using different analytical methods such as gas chromatography , Fourier transform infrared spectroscopy (FTIR), atomic absorption spectrometry (AAS) and differential scanning calorimetric analysis (DSC). The influence of various parameters such as temperature, agitation, nature of food simulant and initial concentration of plasticizer was considered.

Experimental

- **Materials**

Commercial grades of resin and additives listed in Table 1 were used without purification.

Table 1. compounds used in this study.

Compound	Commercial name	Source
Polyvinyl chloride	SHEINTECH	ITOCHU (FRANCE)
di-2-ethyl hexyl phtalate (plasticizer)	Palatinol AH-L	BASF (GERMANY)
Tin-based thermostabilizer	IRGASTAB 17 MOK	CIBA-GEIGY (SWITZERLAND)
Aid -process	FAIR PLAST PA 205	PROMOPACK(ITALY)
Esters of fatty acids (internal lubricant)	Loxiol GH4	HENKEL (GERMANY)
Metal soaps (external lubricant)	Loxiol G78	HENKEL (GERMANY)

Several formulations containing 3% of the processing aid, 4,5 % of the stabilizer, 3,6 % of the internal lubricant, 0,9 % of the external lubricant and, respectively, 30, 40, 50 and 60 % of plasticizer (DEHP) were realized. PVC and additives were mixed in a two-roll mill at 180°C. The specimens for migration tests were melt compressed at 150°C under a pressure of 12 bars during 15 minutes. Then, circular samples of 2 mm in thickness and 19 mm in diameter were cut.

- **Migration Testing**

Migration tests were conducted using four food simulants (sunflower oil, distilled water, 3% (w/v) aqueous acetic acid, 15% (v/v) aqueous ethanol). These food simulants represent all fatty, liquid and moist foods and beverages, except for beverages with a high alcoholic strength. The test conditions used were 10 days at 25 and 45°C with and without agitation. Ten (10) circular samples were immersed in 100 ml of each food simulant. A circular sample and 10 ml of food simulant were taken off every day to be analyzed. Each sample was wiped and weighed. The rate of variation of the mass (τ) was determined as a function of time following the relation:

$$\tau\,(\%) = \frac{m_t - m_0}{m_0} \times 100$$

where: m_0 = initial mass before immersion , m_t = mass of the sample at the time t.

- **Gas Chromatography (GC)**

A Philips PYE Unicam 304 GC with a flame ionization detector was used. Chromatographic conditions were as follows : column OVI of dimensions 1.8 m×4mm o.d ; column temperature : 280°C ; injection temperature: 300°C; detector temperature: 300°C; nitrogen flow: 20.5 ml /min

- **FTIR Analysis**

A Philips type PU 9800 FTIR spectrophotometer was used. The food simulants were placed between two KBr pellets and analyzed directly. On the other hand, the PVC circular samples were dissolved in tetrahydrofuran. After evaporation of the solvent, a polymeric film was recuperated and analyzed.

- **DSC Analysis**

Glass transition temperatures were measured with a Perkin Elmer DSC- 7 apparatus. Each sample was heated from 5 to 110°C under nitrogen with a heating rate of 10°C/ min.

- **Atomic Absorption Spectrometry**

A Philips PYE UNICAM SP 6 spectrometer was used.

Results and Discussion

- **Preliminary Study of the Rate of Mass Variation**

The rates of mass variation (τ) as a function of time gives informations about the phenomenon which occurred between the samples and the food simulants used. An increase means that the food simulant penetrated the sample while a decrease means that some

additives migrated in the food simulant. Hence τ gives informations about the overall migration that occurred. Figures 1 and 2 illustrate the variation of τ as a function of time for the four food simulants used at 45 °C with and without agitation, respectively. It can be noted that the highest rates of mass variations were obtained in sunflower oil indicating that migration of additives occurred. For aqueous simulants the rates of mass variations are practically the same and a very weak increase of τ was observed indicating penetration of the food simulant in the PVC discs. On the other hand, the highest values of τ were obtained during the migration tests with agitation and for the formulations containing the highest amounts of plasticizer. This is expected, since the solubility of DEHP is better in sunflower oil than in aqueous simulants. Furthermore, the migration of DEHP can involve the migration of the other additives which are present in the formulation like stabilizer and lubricant.

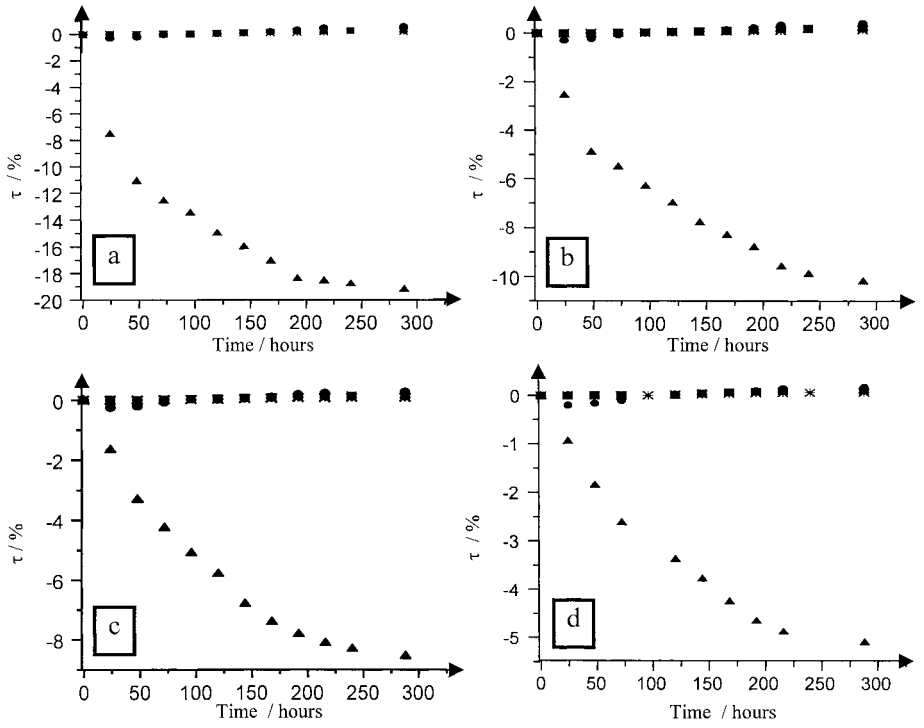

Figure 1. Effect of the nature of the food simulant on the rate of mass variation τ at 45°C with agitation : a) 60 % DEHP ; b) 50 %DEHP ; c) 40 % DEHP ; d) 30 % DEHP :
▲ Sunflower, ● 15 % v/ v aqueous ethanol, ■ 3 % w/v aqueous acetic acid ,
✱ Distilled water

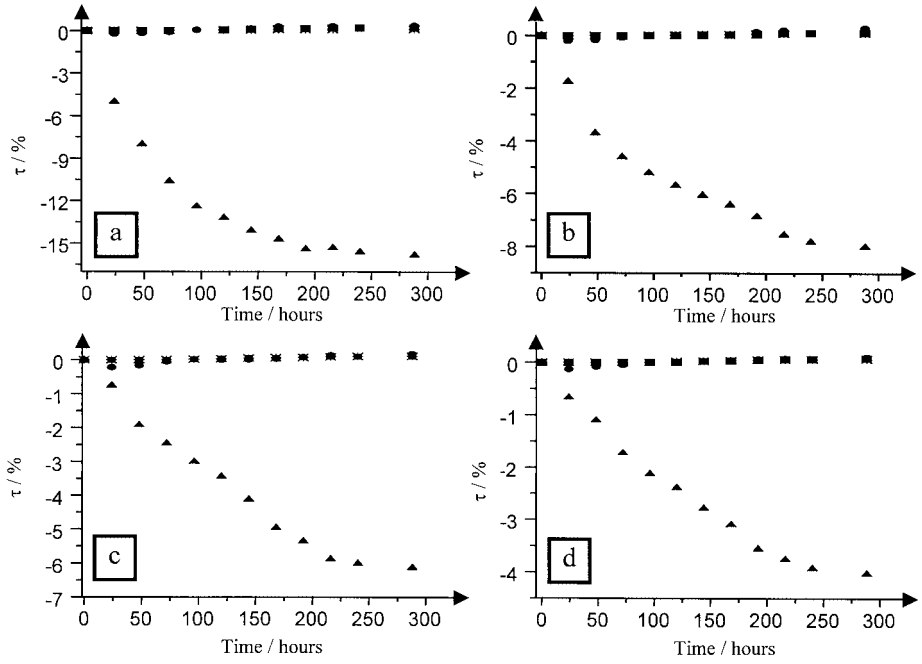

Figure 2. Effect of the nature of the food simulant on the rate of mass variation τ at 45°C without agitation : a) 60 % DEHP ; b) 50 % DEHP ; c) 40 % DEHP ; d) 30 % DEHP : ▲ Sunflower, ● ethanol , ■ acetic acid , ✳ water.

- **GC Determination of DEHP Migration**

The effect of the initial concentration of DEHP on its specific migration in sunflower oil is illustrated by Figure 3. It is observed that the amount of migrating DEHP is related to its initial concentration in the PVC discs, to the temperature of migration testing and to the presence or absence of agitation. It is obvious that the mobility of the plasticizer molecules increased with increasing temperature and that the migration is favoured by agitation.

Figures 4 and 5 illustrate the effect of the nature of food simulant on the migration of DEHP at 45°C and 25°C with agitation, respectively. In all the cases, it is observed that the amounts of migrating DEHP are more pronounced in sunflower oil than in aqueous ethanol. This is due to the better solubility of DEHP in sunflower oil. Furthermore, for a same initial concentration of plasticizer, the amounts of migrating DEHP are higher at 45°C in the two food simulants. This is due to the fact that the mobility of the plasticizer molecules increased with increasing temperature.

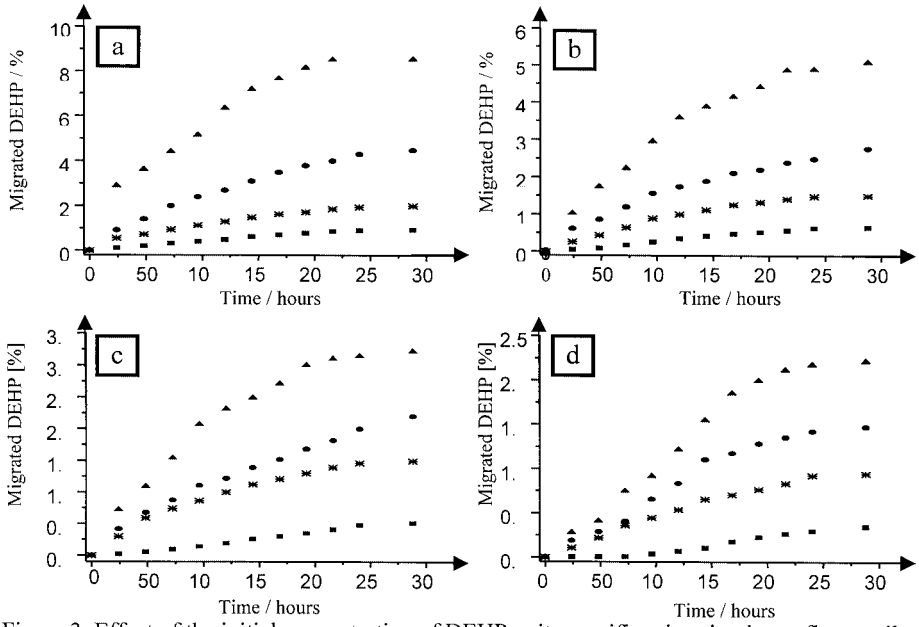

Figure 3. Effect of the initial concentration of DEHPon its specific migration in sunflower oil: a) 45 °C with agitation; b) 45 °C without agitation; c) 25 °C with agitation; d) 25 °C without agitation: ▲ 60% DEHP, ● 50% DEHP, ✱ 40% DEHP, ■ 30% DEHP.

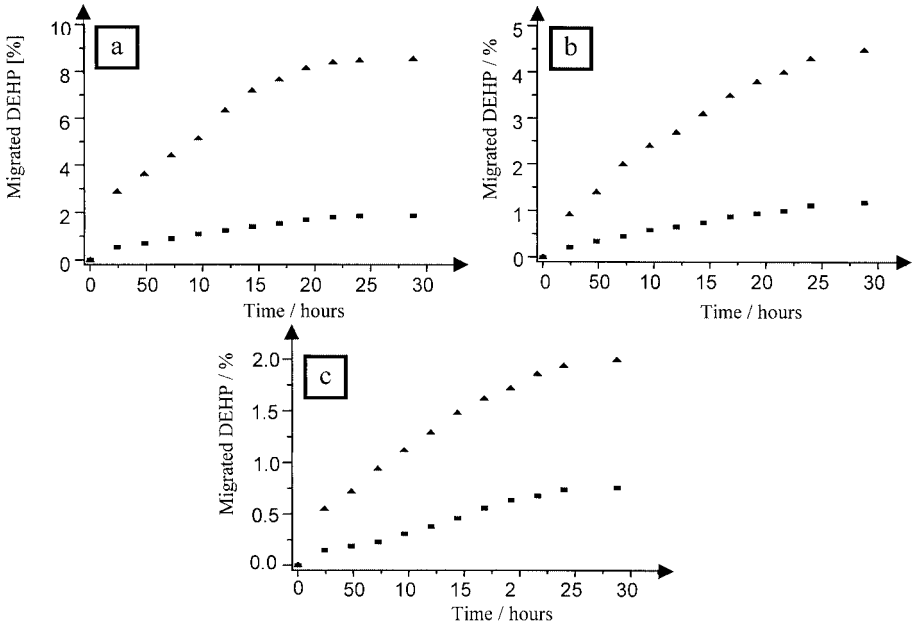

Figure 4. Effect of the nature of food simulant on the migration of DEHP at 45 °C with agitation : a) 60 % DEHP ; b) 50 % DEHP ; c) 40 % DEHP : ▲ sunflower oil, ■ ethanol.

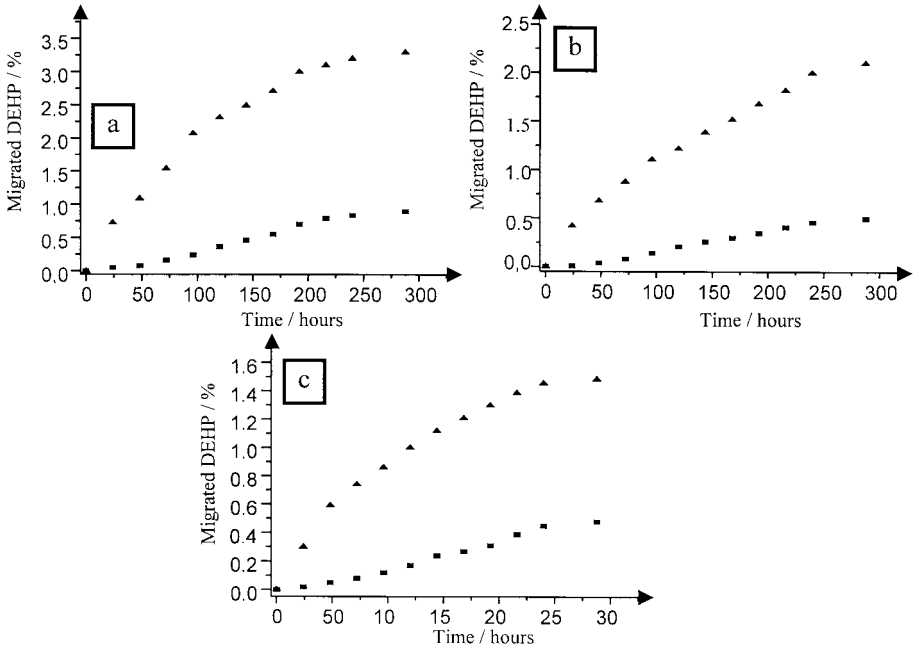

Figure 5. Effect of the nature of food simulant on the migration of DEHP at 25 °C with agitation : a) 60 % DEHP ; b) 50 % DEHP ; c) 40 % DEHP : ▲ sunflower oil, ■ ethanol.

- **FTIR Investigation**

The direct analysis of the spectra of food simulants hasn't permit to show the migration of additives because the overlapping of characteristic bands and the very low amounts of migrated additives. On the other hand, the investigation of the PVC films spectra evidenced the DEHP migration as shown by Figure 6.

A progressive decrease until disparition of the plasticizer bands located at 1585 cm^{-1}, 1128 cm^{-1} and 742 cm^{-1}. was observed; Figure 7 illustrates the variation of their respective absorbances as a function of time.

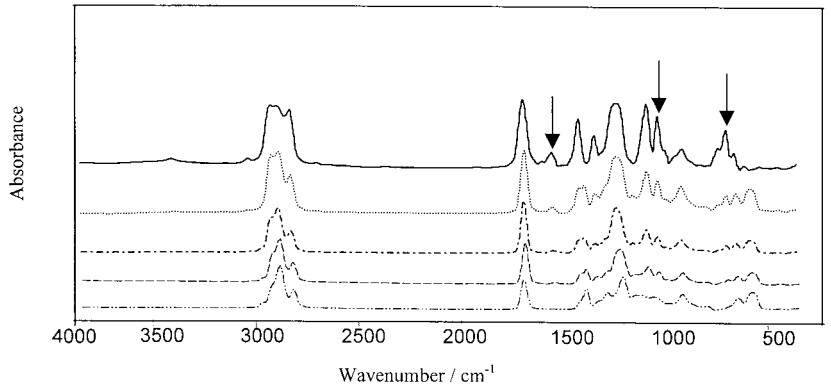

Figure 6. FTIR spectra of DEHP and PVC films obtained from the discs which were submitted to the migrating test with sunflower oil at 45°C with agitation. The initial content of DEHP in the PVC discs was 60 % : ——— DEHP, ... 0 day, - - - - - 1 day, — — — 5 days, — . . — . . 9 days.

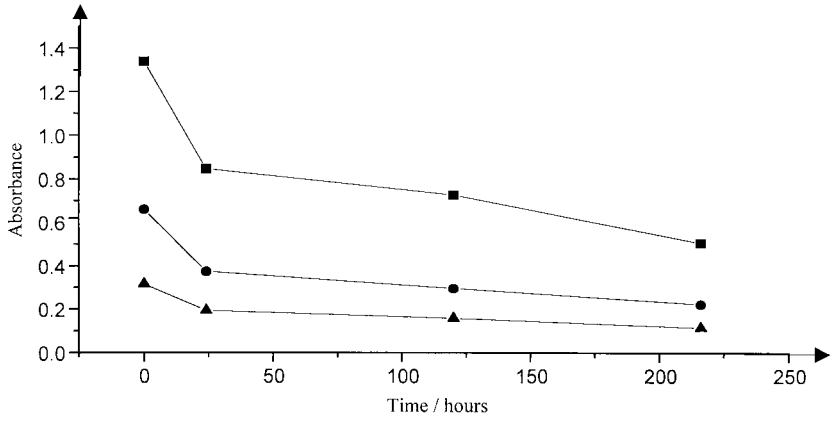

Figure 7. Variation of the absorbances of characteristic bands of DEHP as a function of time : —▲— 1585 cm^{-1}, —■— 1128 cm^{-1}, —●— 742 cm^{-1}.

- **DSC Analysis**

It is known that the presence of a plasticizer decreases the glass transition temperature (Tg) of PVC. For that purpose, the Tg's of virgin PVC and of four formulations containing 0, 10, 20 and 30 % of DEHP in addition to the other additives mentioned in Table 1 were determined. The results are given in Table 2 . It can be noted that the values of Tg decreased with increasing the amount of the plasticizer.

Table 2. Glass transition temperatures (Tg) for various formulations of PVC.

Sample	Tg
	°C
Virgin PVC	81.00
0 % DEHP	69.40
10 % DEHP	53.50
20 % DEHP	33.30
30 % DEHP	15.40

An eventual migration of DEHP will result in an increase of Tg. Hence, the Tg's of PVC discs, whose initial content of DEHP was 30 % and which were submitted to migrating test in sunflower oil at 45 °C with agitation, were determined. The results are given in Table 3. The Tg varied from an initial value of 15.40 °C to 48.50 °C after 10 days of contact with sunflower oil. This last value is close to the one obtained for a PVC containing 10 % DEHP and evidenced clearly the migration of the plasticizer.

Table 3. Tg's values after different times of contact with sunflower oil.

Sample	Tg
	°C
0 day	15.40
4 days	26.20
10 days	48.50

- **Atomic Absorption Spectrometry Investigation**

The amounts of metals contained in all the additives used as well as in the virgin sunflower oil were first determined. The results are given in Table 4.

Table 4. Amounts of metals in additives and sunflower oil.

Content (mg/l)	[Cu]	[Ca]	[Fe]	[Zn]	[Pb]	[Sn]	[Cd]	[Ni]
DEHP	*	8.5	*	*	*	*	2.6	*
Stabilizer	*	4.3	*	*	*	788.6	*	4.7
Loxiol G78	31.1	46.0	*	28.2	44.8	21.3	*	*
Loxiol GH4	18.0	21.6	3.0	6.2	21.1	*	4.1	*
Sunflower oil	6.0	*	4.2	2.1	*	*	3.5	1.1

*: undetected

The same metals were searched for in various samples of sunflower oil which were in contact with the PVC discs during the migrating test realized at 45 °C with agitation. The results are

given in Table 5. It is observed that the concentrations of Cu, Ca, Zn, Pb and Sn increased with the time of contact. The presence of the last metal in relatively high amounts can be related to the migration of the stabilizer while the presence of the others can be related to the migration of the lubricants (Loxiol G78 and Loxiol GH4).

Table 5. Amounts of metals detected in sunflower oil as a function of time in the case of the migrating test carried out with the formulation whose initial content of plasticizer was 50 %.

Time	[Cu]	[Ca]	[Fe]	[Zn]	[Pb]	[Sn]	[Cd]	[Ni]
3 days	32.0	50.0	*	9.2	10.5	395.0	*	*
8 days	34.5	60.	*	12.6	15.5	465.0	*	*
10 days	39.0	90.3	4.6	16.0	22.5	485.0	*	*
12 days	44.5	97.5	5.4	18.1	32.0	650.5	3.8	*

*: undetected

Conclusion

In the preliminary study of the mass variation, the results showed that the rates of mass variations decreased highly in sunflower oil indicating that migration of additives occurred while for aqueous simulants (15 % v/v aqueous ethanol, 3 % w/v aqueous acetic acid and distilled water) the rates of mass variations increased very weakly and were practically the same indicating that penetration of aqueous simulant in the PVC discs occurred. Furthermore, the highest values of the rates of mass variations were obtained for the migration tests with agitation and for the formulations containing the highest amounts of plasticizer.

The GC analysis of DEHP migration showed that the migration of this plasticizer is related to its initial concentration, to the temperature of migration testing and to the agitation. The highest migration of DEHP occurred in sunflower oil where its solubility is the best. FTIR and DSC investigations confirmed the migration of DEHP in sunflower oil.

The atomic absorption spectrometry showed an increase of the concentrations of Cu, Ca, Zn, Pb and Sn in various samples of sunflower oil which were in contact with the PVC discs. The presence of the last metal can be related to the migration of the stabilizer while the presence of the others can be related to the migration of the lubricants.

All the results obtained with the various analytical methods used (GC, FTIR, DSC and AAS) showed that the migration of the additives present in the PVC formulations such as stabilizer, plasticizer and lubricants occurred. The phenomenon is influenced by the nature of food simulant, the temperature, the agitation and the initial concentration of the plasticizer.

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