



Migration of conventional and new plasticizers from PVC films into food simulants: A comparative study



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ABSTRACT

PVC is one of the resins with the higher quantity of additives and the possibility of migration is always a concern when its intended use is food packaging. In this study, the migration of several plasticizers was investigated with the aim of finding out a relationship between migration and conformance with legislation in force, and tensile properties as well. Therefore, six PVC cling films intended to come into contact with foodstuffs have been formulated in order to have same hardness and thickness. The reference film was produced with DEHA and ESBO, while the other films were produced with conventional plasticizers (ATBC and Polyadipate), new plasticizers from renewable resources (Mixture of glycerin acetates – MGA and Acetic acid esters of mono- and diglycerides of fatty acids – AGM) or a plasticizer employed in toy and childcare applications (DEHT). The films were evaluated as to the overall and specific migration to food simulants and the effect of the formulation was studied. The results have shown that the coefficient of apparent partition of DEHT is similar to that of DEHA, whereas MGA and AGM plasticizers displayed higher coefficients of apparent partition than the other plasticizers under study. This difference in migration has been attributed to the different molecular structures of plasticizers. In addition, commercial films have been evaluated as to plasticizers concentration and specific migration into food simulants. It was found that 25% of the samples comply with the specific migration limits for fatty foods contact while 50% might be used for contact with fatty foods with FRF 2–5. On the other hand, all commercial samples showed no restriction for aqueous acidic food contact. Thus, it has been demonstrated that a contact for prolonged time up to 40 °C did not promote the migration of plasticizers into acidic foodstuffs, but the migration of plasticizers to fatty foods can be high (75%–90% loss of plasticizers) and limit the use of PVC films as fatty food packaging.

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1. Introduction

Plasticizers usually have high mobility in the polymeric matrix due to the relatively low molecular weight of these additives and due to the high concentration used initially, so that diffusion takes place easily to the surrounding medium (food, simulant etc.). Diffusion happens particularly with food and simulants that have high fat contents due to the lipophilic nature of plasticizers

molecules (Goulas, Zygoura, Karatapanis, Georgantelis, & Kontominas, 2007).

The diffusion of the PVC film plasticizer to food or to food simulants occurs in two steps:

- 1) within the polymer – migration takes place via diffusion process, usually according to Fick's Second Law, and
- 2) in food or food simulant – the transport mechanism of the migrant depends on the physical properties of this phase.

The quantity of plasticizer that migrates to the packed food depends on several factors such as the fat contents of the food, type and initial concentration of the plasticizer in the packaging material, storage time and temperature and the contact area (Goulas, Salpea, & Kontominas, 2008).

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Some studies developed in the 90's showed that some plasticizers of the phthalate family caused genetic changes in mice. DEHP is recognized as endocrine disruptor which alters reproductive hormone regulation in rats, but that was not observed in humans. DEHP is not acutely toxic, but exposure over a reasonable period of time may cause harm. However, providing a direct correlation between DEHP exposure and the effect on human reproductive system still remains a controversial issue (Magdouli, Daghrir, Brar, Drogui, & Tyagi, 2013).

Anyway, the concept of precaution was placed on low molecular weight phthalates, such as benzyl-butyl phthalate (BBP), dibutyl phthalate (DBP), di-isobutyl phthalate (DIBP) and di-2-ethyl-hexyl phthalate (DEHP), limiting their use in some products. These phthalates are classified as very dangerous in REACH (Registration, Evaluation, Authorization and Restriction of Chemicals substances). On the other hand, high molecular weight phthalates such as di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP) are not toxic for human health and they do not have any restrictions to use (Ventrice, Ventrice, Russo, & Sarro, 2013).

Since PVC films are employed to pack a broad variety of food-stuffs, such as meat, cheese, fruits, vegetables etc. and due to the high amount of additives used in these films it is very important to evaluate the safety of eating the foods in contact with the packaging material. That is the reason why several studies have been undertaken on specific migration of plasticizers into foods, food simulants and saliva as well (Biedermann et al., 2008; Chen et al., 2014; Goulas, Zygoura, Karatapanis, Georgantelis, & Kontominas, 2007; Fankhauser-Noti & Grob, 2006; Fasano, Bono-Blay, Cirillo, Montuori, & Lacorte, 2012; Freire, Santana, & Reyes, 2006; Goulas et al., 2008; Grob et al., 2007; Zygoura, Goulas, Riganakos, & Kontominas, 2007).

Thus, some companies and sectors have looked for alternatives to certain phthalates, either voluntarily or compulsorily. There are many alternatives, but many others have appeared, such as plasticizers of vegetable origin. These plasticizers also have a strong environmental appeal, since they are made from renewable resources. Numerous are the examples of raw materials used, such as corn, soybean, sunflower, palm, castor bean and flaxseed, among others. Usually the processes of transesterification, alkylation and epoxidation are used to manufacture these potential PVC plasticizers. The results have been quite promising and some markets are already trying and using these plasticizers.

Therefore, the possibility of new PVC plasticizers is very important as well as evaluating performance and conformance of these packaging materials as to the legislation in force. DEHA (di(2-ethylhexyl) adipate), ESBO (epoxidized soybean oil), ATBC (acetylated tributyl citrate) and polymeric plasticizers are used in plastic packages for food (the last two plasticizers are used mainly in Europe due to their high cost) and are not hard to find them in packages available in the market. Beside these plasticizers, new plasticizers from renewable sources are being evaluated as plasticizers for PVC cling films intended to come into contact with foodstuffs (Deyo, 2008; Lau & Wong, 2000; Lundsgard, Kontogeorgis, Kristiansen, & Jensen, 2009; Madaleno, Rosa, Zawadzki, Pedrozo, & Ramos, 2009; Navarro, Perrino, Tardajos, & Reinecke, 2010; Rodolfo, Nunes, & Ormanji, 2006).

The aim of this study was to evaluate the migration performance of several plasticizers for PVC cling films intended to come into contact with foodstuffs in order to get information for technical specification and control of overall and specific migration to different types of foodstuffs according to the legislation in Brazil, Mercosur and Europe. Correlation of the migration results and tensile properties of the films were considered as well.

2. Materials and methods

2.1. Materials

The following PVC resin and plasticizers have been used in this study:

- PVC SP 1300 resin, *K* value 71 ± 1 , supplied by Braskem S/A;
- Di(2-ethylhexyl) adipate – DEHA, density 0.924–0.929 g/cm³, supplied by Elekeiroz S/A;
- Epoxidized soybean oil – ESBO, Soyflex 6250™, density 0.987–0.993 g/cm³, molar mass 944 g/mol, supplied by BBC Indústria e Comércio Ltda.;
- Acetylated tributyl citrate – ATBC, Scandinol SP-22™, density 1.048 g/cm³, supplied by Scandiflex do Brasil S/A.;
- Mixture of glycerin acetates (named as MGA) – Unimoll™ AGF, density 0.974 g/cm³, supplied by LANXESS Indústria de Produtos Químicos e Plásticos Ltda.;
- Di(2-ethylhexyl)-1,4-benzenedicarboxylate – DEHT, Eastman 168™, molar mass 390.57 g/mol, density 0.983–0.988 g/cm³, supplied by Eastman Chemical Company;
- Acetic acid esters of mono- and diglycerides of fatty acids (named as Acetylated glycerol monoester – AGM) – Grindsted™ Acetem 95 Co kosher (Acetic Acid Ester), molar mass 360 g/mole, density 0.98 g/cm³, supplied by Danisco Brasil Ltda.;
- Polyadipate – Plaxter P52™, molar mass approx. 2100 Da, supplied by Coim Brasil Ltda.

The plasticizers were not purified prior to analysis.

2.2. Samples

The following samples of bi-axially oriented PVC cling film, 30 cm width, intended to come into contact with foodstuffs have been produced for this study in a commercial blowing machine operating at 25 rpm for 2 min at 170 °C:

- 1 – DEHA + ESBO (reference)
- 2 – DEHA + ESBO + ATBC
- 3 – DEHA + ESBO + Mixture of glycerin acetates (MGA)
- 4 – DEHA + ESBO + DEHT
- 5 – DEHA + ESBO + Acetylated glycerol monoester (AGM)
- 6 – DEHA + ESBO + Polyadipate

The composition of the films is approx. 20% of main plasticizer, 5% of ESBO and 1.5% of DEHA. This composition was selected in order to get approx. 80 Shore A hardness, which corresponds to a medium hard and somewhat flexible material like shoe soles. All films were prepared of same nominal thickness of 15 µm. Detailed information of samples characterization was described previously (Coltro, Pitta, & Madaleno, 2013). Sample 1 was adopted as reference to rate conformance of the PVC cling films as to overall migration and specific migration, since this sample was produced with the most commonly used plasticizers in the Brazilian market – DEHA and ESBO.

Besides those formulated PVC samples four PVC cling films, from three different producers, were acquired in commercial shops in Campinas, Brazil, in order to check their conformance as to specific migration limits established by Brazilian legislation.

2.3. Migration tests

2.3.1. Overall migration to food simulants

The analysis was carried out in compliance with the requirements of Resolution RDC no. 51 of November 26th, 2010,

issued by the Brazilian National Health Surveillance Agency (ANVISA – Agência Nacional de Vigilância Sanitária) of the Brazilian Ministry of Health (ANVISA, 1999; ANVISA, 2010).

Resolution RDC no. 51/10 incorporates into the Brazilian National Legal Framework all specifications, limits and requirements laid down in GMC Mercosur Resolution no. 32/10 (GMC means Mercosur Common Market Group) and revokes Annexes I, V, VI, XIII and XIV of ANVISA Resolution no. 105/99 (GMC, 2010). The present resolution stipulates that the methods described in EN 1186 Standard Series must be applied to determine total migration.

In accordance with the proposed study, PVC films were designed to come into contact with acidic and fatty foodstuffs and should be used for long-term storage at temperatures up to 40 °C. According to their intended use, the samples were evaluated under the contact conditions of 40 °C, for 10 days established by ANVISA regulation.

As the samples analyzed are single-layer and less than 0.5 mm thick, the specimens were dipped in the food simulant and only one face of the film was taken into account in the calculations. Due to the reduced thickness of the samples, it is assumed conventionally there is no migration of the substance from the outside surface and only the surface area of the foodstuff contact side is used in the calculation of migration (CEN, 2004).

2.3.1.1. Acidic food simulant. The quantification of overall migration was based on the procedures set forth in EN 1186-1 and EN 1186-3 (CEN, 2003; CEN, 2002). The methodology to quantify overall migration in acidic simulant consists of contact of the sample with extraction solutions for certain times and temperatures that simulate their actual condition of use. The residues of overall migration were determined by the difference in weight after the contact and evaporation of the solutions on an analytical scale with 0.01 mg accuracy.

2.3.1.2. Fatty food simulant. Overall migration using olive oil as a fatty simulant was determined for the PVC film samples following EN 1186-2 Standard with some adjustments (SFS, 2003). In this analysis, a test specimen with known area and weight was immersed in olive oil under selected conditions of time and temperature. At the end of the contact time, the test specimen was dried between sheets of Whatman n. 1 filter paper and weighed. Before and after the contact with olive oil, the test specimens were conditioned at 23 °C ± 2 °C and 50% ± 5% relative humidity to get constant weight. Then, the oil absorbed by the test specimen was extracted with hexane in Soxhlet during 18 h and its weight was determined by gas chromatography after saponification and methylation of the fatty acids. The oil mass absorbed was used as a correction factor to calculate overall migration. The chromatographic analysis was carried out in a HP7890 gas chromatograph with flame ionization detector, operating with a capillary column DB1 (30 m length × 0.25 mm I.D. × 0.25 µm film thickness).

The quantification of the mass of oil absorbed was made by gas chromatography, using the peak of methyl ester of oleic acid C 18:1 (methyl oleate) as reference and external standardization. The overall migration was expressed in mg/dm² and compared with the migration limit established by Resolution no. 105/99 (ANVISA, 1999).

2.3.2. Specific migration to food simulants

The samples of PVC film were evaluated as to specific migration of plasticizers employing the methods developed in this study and using aqueous acidic and fatty food simulants. The samples were placed in contact with the food simulants (dipped), following the surface-to-volume ratio of 600 cm²/1000 mL of food simulant. This surface-to-volume ratio is conventionally adopted in the total

immersion test since the specific migration limits (SML) have been set with the assumption that 6 dm² of surface area of plastics comes into contact with 1 kg of food, and the specific gravity of all simulants is assumed to be 1 (European Commission, 2007). The contact condition used in the test was 40 °C for 10 days (for aqueous acidic food simulant) and 20 °C for 2 days (for isooctane), to simulate the condition of use for prolonged contact at temperatures up to 40 °C (ANVISA, 2010).

Except for ESBO, the method to determine migration of plasticizers to aqueous acidic foods (aqueous solution of 3% m/v acetic acid) was based on the liquid–liquid extraction made with 3 aliquots of 5 mL of n-heptane and 25 mL of simulant. For ESBO, the acidic simulant was completely evaporated prior to esterification of ESBO.

Isooctane was adopted as the fatty food simulant for ESBO, MGA and AGM, since these plasticizers are derived from oils, and the olive oil simulant interferes with the chromatographic analysis of these plasticizers. Migration of plasticizers into isooctane simulant was determined by means of direct injection in the GC-FID, except for ESBO, which was esterified according to the rapid method described in ISO 12966-2 Standard (ISO, 2011), after the simulant was concentrated from 20 mL down to 2 mL.

In the case of DEHA and DEHT, migration to the fatty food simulant was also determined with the use of olive oil as the simulant, since in these cases there was no interference of the olive oil in the chromatographic peaks of plasticizers.

The chromatographic analysis of the food simulants after the contact with the samples was carried out in a GC-FID Agilent Technologies 7890A equipped with an automatic injector Agilent Technologies 7683B, operating with DB1 capillary column (30 m length × 0.25 mm I.D. × 0.25 µm film thickness). Two chromatographic conditions were adopted:

- *New plasticizers analysis* – Helium carrier gas flow rate of 1.2 mL/min. Temperature for injector and detector was 270 °C and 300 °C, respectively. The column temperature was programmed at 60 °C (hold 1 min), from 60 °C to 100 °C at 7 °C/min heating rate, from 100 °C to 280 °C at 15 °C/min heating rate (hold 5 min). Injection volume was 0.2 µL. Split mode 35:1. Total run time is 23.7 min.
- *ESBO analysis* – Helium carrier gas flow rate of 1.8 mL/min. Temperature for injector and detector was 280 °C. The column temperature was programmed at 175 °C (hold 1 min), from 175 °C to 250 °C at 25 °C/min heating rate (hold 4 min). Injection volume was 0.5 µL. Split mode 60:1. Total run time is 8 min.

In the case of DEHA analysis, a method previously developed at CETEA based on O'Brien, Cooper, and Tice (1997) and Simoneau and Hannaert (1999) was adopted. The chromatographic analysis of the food simulants after the contact with the samples was carried out in a GC-FID Agilent Technologies 6890N equipped with an automatic injector Agilent Technologies 7683B. The HP-5 capillary column (30 m length × 0.32 mm I.D. × 0.25 µm film thickness) was operated at helium carrier gas flow rate of 1.4 mL/min. Temperature for injector and detector was 280 °C and 250 °C, respectively. The column temperature was programmed from 70 °C to 310 °C at 15 °C/min heating rate. Injection volume was 1.0 µL. Splitless mode.

Di-isobutyl phthalate (DIBP) was employed as internal standard to quantify the plasticizers in the food simulants since this plasticizer is not used in food packaging.

2.3.2.1. Method validation. The methods were validated according to parameters of selectivity, linearity range, detection limit, quantification limit, recovery, precision and accuracy (Ribani, Bottoli, Collins, Jardim, & Melo, 2004; Ribeiro & Ferreira, 2008).

2.3.2.1.1. Linearity range. The calibration curves were built in the 5–350 mg/kg range from the ratio of the areas (plasticizer area/internal standard area) and the respective concentration of plasticizer of the solutions. The coefficients of linear and angular correlation were calculated through the linear regression model.

2.3.2.1.2. Detection limit (LOD) and quantification limit (LOQ). The detection limit was calculated from 7 replicates of the solution of 5 or 10 mg/kg of plasticizer, using the following equation:

$$\text{LOD} = t_{(n-1, 1-\alpha)} \cdot S$$

where: t = Student's distribution, dependent on the size of the sample and on the degree of confidence. In the case of 7 aliquots and 99% degree of confidence, the value of t is 3.143; S = sample standard deviation of the concentrations.

The quantification limit was calculated using the following equation:

$$\text{LOQ} = X_{\text{mean}} + 5 \cdot S$$

where: X_{mean} = mean of concentrations; S = sample standard deviation of the concentrations.

2.3.2.1.3. Precision and accuracy. Two analytical curves were built with concentrations ranging from 5 to 90 mg/kg of plasticizer and 50 mg/kg of DIBP (internal standard). Each curve was obtained by a different analyst. The intraday repeatability was estimated from the Relative Standard Deviation (RSD) among the replicates of the points of one same curve. The intermediate precision was obtained by calculating the relative standard deviation, but considering both analytical curves. The accuracy was assessed via calculation of the relative error (RE), expressed in percentage.

2.3.2.1.4. Recovery. The recovery rate was obtained via the ratio between the concentrations obtained in the tests and the expected concentration, as represented by the standard solution.

2.3.3. Quantification of plasticizers in PVC films

The quantification of plasticizers in the samples of PVC film was performed in triplicate following ABNT NBR 15403 Standard (ABNT, 2010). Specimens weighing 2 g of PVC film cut in small pieces were placed in reflux with 50 mL of hexane for 5 h. DIBP was used as the internal standard.

After reaching room temperature, the homogenized extracts were injected in a GC-FID Agilent Technologies 7890A instrument equipped with an automatic injector (Agilent Technologies 7683B). The HP1 capillary column (50 m × 0.2 mm I.D. × 0.33 μm film thickness) was operated at helium carrier gas flow rate of 1 mL/min. Temperature for injector and detector was 280 °C. The column temperature was programmed from 160 °C to 280 °C at 20 °C/min heating rate (hold 19 min). Injection volume was 1.0 μL.

2.3.4. Statistical analysis

Analysis of variance was applied to the results and Fisher's least significant difference (LSD) test was used to determine statistically significant differences ($p < 0.05$) between averages using Software Statgraphics Plus 5.0 (swing).

3. Results and discussion

3.1. PVC-new plasticizers samples

3.1.1. Plasticizers quantification

The retention times of the chromatographic analyses are shown in Table 1. Injections in two chromatographic methods were made. Method A was suitable to detect ESBO (after esterification), and method B was suitable to detect the other plasticizers. However,

Table 1
Retention time of plasticizers in isooctane.^a

Plasticizer	Retention time (min)	
	Method A	Method B
DIBP ^b	2.98	14.6
ESBO	3.27/4.90/5.87/6.13	—
ATBC	4.02/4.07/4.58	16.35/16.92
MGA	4.68/4.72	16.81/16.85
AGM	4.7	16.81/16.84/17.88/17.91/18.88/18.92
DEHA	5.63	17.60
DEHP	6.94	18.49
DEHT	9.6	19.71

MGA = Mixture of glycerin acetates.

AGM = Acetylated glycerol monoester.

^a Results from 3 experimental determinations.

^b Internal standard.

some plasticizers were detected in both methods. The chromatographic conditions are quite good since the chromatograms have shown well-resolved peaks that makes possible to identify and measure in relatively short time all the plasticizers studied.

The selectivity of the methods is suitable for the plasticizers under study, since only the two first peaks of MGA and of AGM overlapped (method B). In this case, the identification of these plasticizers via GC-FID can be made from the presence of the other peaks of AGM. Moreover, these plasticizers are hardly ever used in one same formulation because they are both from vegetable origin, with very similar structure and performance.

Some of the plasticizers have several chromatographic peaks, like ATBC, MGA, AGM and ESBO. The highest peaks (first doublet) were adopted for measurement of these plasticizers, except for ESBO which quantification was based on the peak of methyl ester of diepoxy linoleic acid (18:2 2E1) at 5.8 min. The chromatograms of MGA and AGM were composed by doublets of peaks with areas ratio of 1:2.

The quantification of plasticizers present in the PVC films is shown in Table 2. The total amount of plasticizers added to the films ranged from 21% to 28%, with approx. constant concentrations of DEHA (1.3%–1.7%), ESBO (3.1%–5.5%) and the third plasticizer (16%–18%). In the case of sample 1 (reference), the concentration of DEHA was set as the third plasticizer (16%), since this sample was formulated with only DEHA and ESBO for the purpose of comparison to the performance of the other plasticizers.

DEHP was not added to sample 1 as a third plasticizer. Therefore the presence of this plasticizer in the film is due to contamination from the processing line (probably this was the first film to be

Table 2
Concentration of plasticizers in the PVC films evaluated (%).^a

Sample	Unit	DEHA	ESBO	3rd Plasticizer ^b	Total
1 (ref)	%	16.1 ± 0.3	3.1 ± 0.2	8.6 ± 0.1	27.8
	mg/dm ²	33.6 ± 0.6	6.5 ± 0.5	17.9 ± 0.2	58.1
2	%	1.4 ± 0.0	3.7 ± 0.0	15.8 ± 0.9	20.9
	mg/dm ²	2.9 ± 0.0	7.5 ± 0.1	32.1 ± 1.9	42.3
3	%	1.7 ± 0.0	3.8 ± 0.3	18.6 ± 0.0	24.1
	mg/dm ²	3.8 ± 0.0	8.2 ± 0.6	40.9 ± 0.0	52.9
4	%	1.6 ± 0.0	3.4 ± 0.1	17.5 ± 0.2	22.5
	mg/dm ²	3.7 ± 0.0	8.2 ± 0.2	41.7 ± 0.4	53.6
5	%	1.3 ± 0.0	4.6 ± 0.3	17.8 ± 0.1	23.7
	mg/dm ²	3.0 ± 0.0	10.8 ± 0.8	41.7 ± 0.3	55.4
6	%	1.3 ± 0.0	5.5 ± 0.1	18.2 ^c	25.0
	mg/dm ²	3.2 ± 0.0	13.9 ± 0.3	45.6 ^c	62.7

^a Average ± standard deviation of 2 experimental determinations.

^b Sample-3rd plasticizer: 1 – DEHP; 2 – ATBC; 3 – Mixture of glycerin acetates; 4 – DEHT, 5 – Acetylated glycerol monoester; 6 – Polyadipate.

^c Concentration used in the film formulation.

Table 3
Residues from the overall migration to acidic food simulant (mg/dm²).^a

Sample	Average \pm SD ^b	Range
1 (ref)	1.46 \pm 0.35	1.07–1.85
2	$\leq 1.27 \pm 0.78$	$\leq 0.50^c$ –2.10
3	1.51 \pm 0.66	0.80–2.23
4	0.82 \pm 0.19	0.70–1.10
5	$\leq 0.58 \pm 0.10$	$\leq 0.50^c$ –0.70
6	$\leq 0.50^c$	^d

^a Contact condition of 40 °C, for 10 days.

^b Average \pm standard deviation of 4 experimental determinations.

^c Quantification limit of the method.

^d Not applicable.

processed). The concentrations experimentally obtained differ from the concentrations used in the formulation of films (Coltro, Pitta & Madaleno, 2013). This is probably due to losses in the process or to contamination (in the case of DEHP in sample 1). The quantification of polyadipate was not made due to experimental difficulties.

3.1.2. Overall migration to acidic food simulant

The results of the overall migration to acidic food simulant are shown in Table 3. According to ANVISA Resolution no. 105/99, the overall migration limit is 8.0 mg of residue/dm² of polymeric material, with analytical tolerance of 10% (ANVISA, 1999). So, the maximum tolerable value is 8.8 mg of residue/dm². All PVC films evaluated in this study showed lower overall migration to acidic food simulant than the limit established in the legislation. Therefore, no restrictions exist as to the use of these films in contact with acidic foodstuffs. Nevertheless, these samples must also be evaluated in relation to specific migration limits when pertinent.

3.1.3. Overall migration to fatty food simulant

The results of overall migration to olive oil fatty food simulant are shown in Table 4. The analytical tolerance of olive oil food simulant was 3.0 mg of residue/dm² according to the specification of the EN 1186-1 Standard (CEN, 2003). The residues corrected by the analytical tolerance are also shown in Table 4. The results showed the following decreasing overall migration to olive oil: 1 = 5, 5 = 3 > 4 > 2 > 6.

Despite total plasticizers concentration of sample 5 is lower than sample 1 (Table 2), sample 5 – formulated with the vegetable-origin plasticizer AGM – displayed values for overall migration to the fatty food simulant that were not statistically different from the values of sample 1, with 95% confidence degree (Table 4). This is probably due to the greater diffusion coefficient of AGM (6.42–66.29 10^{−9} cm²/s at 40 °C, for a sample with 30% of plasticizer) in comparison to DEHA (0.45 \times 10^{−11} cm²/s) (Goulas et al., 2008; Lundsgaard et al., 2009).

Sample 3 – formulated with MGA – displayed overall migration lower than sample 1, with 95% confidence degree (Table 4), to indicate that the diffusion coefficient of MGA must be greater than that of DEHA, since the total plasticizers concentration of sample 3

is lower than sample 1 (Table 2). Probably MGA has a diffusion coefficient similar to that of AGM, since overall migration of samples 3 and 5 are not statistically different ($p < 0.05$), as well as the total plasticizers concentration of these samples.

Samples 2 and 4 were formulated with ATBC and DEHT monomeric plasticizers. They probably displayed lower overall migration into fatty food simulant than sample 1 (DEHA) due to the decreasing total plasticizers concentration in relation to the other samples, as well as the greater degree of interaction of their molecules with polymeric chains of PVC than DEHA. Their chemical structures have a greater number of polar groups (ATBC has twice the number of oxygen atoms of DEHA) or benzenic ring (DEHT), which intensifies van der Waals interactions with chlorine atoms of PVC. Moreover, ATBC has greater steric impediment than DEHT, which probably makes its migration difficult in the PVC structure and its extraction to the simulant. This produces lower values of overall migration of sample 2 (ATBC) than the values of sample 4 (DEHT), with 95% degree of confidence (Table 4).

Sample 6 was formulated with polyadipate, which is a polymeric plasticizer with less extraction power due to the large size of its molecules, which account for the smaller relative value of overall migration of this film (Table 4), despite the high total plasticizers concentration of this sample (Table 2).

Despite the relative difference of the residues from overall migration, all the samples showed visible alteration besides loss of their original flexibility after contact with olive oil as a result of the plasticizers migration to the food simulant.

According to ANVISA Resolution no. 105/99 and Resolution no. 51/10, fat consumption reduction factors (FRF) as a function of the extractive power of the simulant in relation to the food classification can be applied to the results of overall migration (ANVISA, 1999; ANVISA, 2010). The corrected results of the samples are shown below:

- Samples 1, 3 and 5 could not be used for packing fatty foods;
- Sample 2 could be applied to pack fatty foods with FRF 4 and 5;
- Sample 4 could be employed as package for fatty foods with FRF 5;
- Sample 6 could be used for packing fatty foods with FRF 3, 4 and 5.

Then, only sample 6 can be used to pack a broader variety of fatty foods (with FRF 3, 4 and 5) taking into account the lowest overall migration limit of 16.29 mg/dm².

On the other hand, even considering the lower limit of overall migration and the greatest FRF of 5, samples 1, 3 and 5 of PVC film could not be used for packing fatty foods, since the lowest result obtained exceeded the migration limit of 8.0 mg/dm².

Therefore, samples formulated with approximately 16% of DEHA (sample 1) and 18% of MGA and AGM – vegetable-origin plasticizers (samples 3 and 5) were the samples that produced the greatest values for overall migration, as can be seen in Fig. 1. This indicates that there is greater mobility of the PVC structure deriving from the plasticizing effect of these additives, which was confirmed by lower values of tensile strength of these samples, as shown in Fig. 1 and previously published (Coltro, Pitta, & Madaleno, 2013).

3.1.4. Validation of the specific migration analytical methods

Tables 5 and 6 show the validation parameters of the methods of specific migration into simulants of aqueous acidic food and fatty foods for the various plasticizers evaluated. At least five calibration standards with concentrations between 5 mg/kg and 100 mg/kg were prepared in order to evaluate linearity. The solutions were injected in triplicate. This range was selected since it was necessary to ensure linearity at a working range where the SML of the

Table 4
Residues from overall migration to olive oil fatty food simulant (mg/dm²).^a

Sample	Average \pm SD ^b	Range with analytical tolerance
1 (ref)	50.4 \pm 3.9a	47.4–53.4
2	31.3 \pm 2.0d	28.3–34.3
3	44.5 \pm 3.9b	41.5–47.5
4	39.4 \pm 4.6c	36.4–42.4
5	47.0 \pm 3.0ab	44.0–50.0
6	19.3 \pm 1.8e	16.3–22.3

Different letters in the same column indicate significant differences ($p < 0.05$).

^a Contact condition of 40 °C, for 10 days.

^b Average \pm standard deviation of 5 experimental determinations.

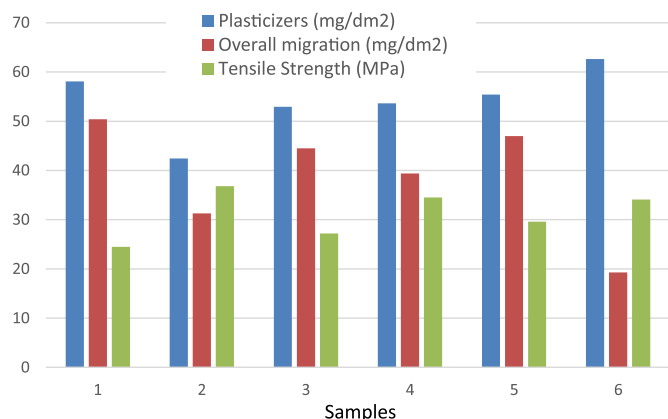


Fig. 1. Ratio between total plasticizers concentration, overall migration and tensile strength for the PVC films evaluated.

plasticizers was inserted approx. in the middle of the curve. All the calibration curves have shown acceptable determination coefficient (r^2) values (>0.9900). LOD and LOQ were lower than SML of the plasticizers studied and sensitive enough to evaluate the possible migration of these plasticizers from commercial samples. The results of precision, calculated in terms of intraday repeatability (one analyst) and intermediate precision (two analysts), were lower than 5% for all plasticizers indicating an acceptable repeatability of the methods. The recovery ranged from 90% to 110% and the accuracy ranged from -5% to 9% which are acceptable values and similar to those obtained by other authors (Bonini, Errani, Zerbinati, Ferri, & Girotti, 2008; Bueno-Ferrer, Jiménez, & Garrigós, 2010).

The detection limit of the method of specific migration of DEHA into aqueous acidic food simulant is 0.20 mg/kg, and the quantification limit is 0.70 mg/kg. For the fatty food simulant, the detection limit of the method is 0.50 mg/kg, and the quantification limit is 3.70 mg/kg. As can be seeing all the methods are suitable to determine the specific migration of the studied plasticizers since the specific migration limit (SML) of them are included in the linearity range and all the other parameters are adequate.

3.1.5. Specific migration into food simulants

Due to its relatively low molecular weight (370 g/mol), DEHA migrates to packed foods, particularly to fatty foods. From the toxicity data of DEHA, the European Union set the SML of 18 mg/kg of food via Directive 2002/72 (European Commission, 2007). The other plasticizers under study have the following SML set by the legislations in force: ESBO = 60 mg/kg, MGA = 60 mg/kg and DEHT = 60 mg/kg (ANVISA, 2008; EFSA, 2008; European Commission, 2007). For this reason, the samples of PVC cling film were submitted to the specific migration test in aqueous acidic and fatty food simulants to check if they meet the requirement of SML

Table 5
Validation parameters of the specific migration methods into aqueous acidic simulant.

Plasticizer	ESBO	MGA	DEHT
Detection limit – LOD (mg/kg)	0.46	0.29	0.22
Quantification limit – LOQ (mg/kg)	5.45	4.93	6.23
Working range (mg/kg)	5–90	5–90	5–90
Intraday repeatability (%)	1.7–2.8	0.8–3.0	0.1–2.3
Intermediate precision (%)	1.6–3.3	2.2–3.8	1.9–4.6
Recovery (%)	96.4–104.6	93.8–104.7	91.4–112.0
Accuracy (%)	–3.4 to 3.5	0.3–4.8	1.1–8.7

MGA = Mixture of glycerin acetates.

Table 6
Validation parameters of the specific migration methods into fatty food simulant.

Plasticizer	ESBO	MGA	DEHT
Detection limit – LOD (mg/kg)	0.35	0.16	2.00
Quantification limit – LOQ (mg/kg)	4.65	3.06	12.36
Working range (mg/kg)	5–100	5–90	10–90
Intraday repeatability (%)	0.0–2.4	0.3–3.0	1.6–2.4
Intermediate precision (%)	1.2–4.8	0.8–2.5	2.2–4.8
Recovery (%)	n.a.	n.a.	101.3–109.1
Accuracy (%)	–2.5 to 2.6	–0.5 to 0.0	–3.8 to 4.4

MGA = Mixture of glycerin acetates.

n.a. = not applicable.

set forth in the legislations in force. Fig. 2 shows examples of chromatograms of the specific migration tests of the samples of PVC film analyzed for the isooctane simulant. All samples displayed migration of ESBO and DEHA plasticizers. Fig. 2a shows the doublet of peaks of MGA and Fig. 2d shows the several peaks of AGM plasticizer. The quantification of AGM was based on the first doublet of peaks since they have the highest areas. All the peaks are well defined and there is no overlap between them.

Besides the plasticizers of interest, chromatographic peaks relating to DEHP (sample 1) were also observed. This plasticizer was not forecasted in the study and it is probably due to contamination of the equipment where the PVC films were processed. Besides other not identified peaks were observed in the chromatograms and which are probably due to migration of other additives included in the formulation of the films.

Table 7 shows the results obtained for specific migration of the plasticizers assessed in this study for aqueous acidic and fatty food simulants. As can be seen, the samples of PVC film displayed lower values of specific migration of plasticizers into aqueous acidic food simulant than the quantification limit (LOQ) of the respective methods, even with concentrations of 15% – 20% in the formulation of the film (Table 2). Therefore, considering the requirement of specific migration of these plasticizers, the PVC film analyzed could be used in contact with aqueous acidic foods. This is due to the low affinity of plasticizers for aqueous medium.

The results obtained are in accordance with study conducted with PVC samples formulated with 30% , 40% and 50% of ESBO in contact with aqueous foods simulant (water), in which migration of ESBO was not detected indicating that these formulations can be used to pack aqueous foods (Bueno-Ferrer et al., 2010).

However, considering contact with fatty foods and drinks (olive oil simulant) for a prolonged time at temperatures up to 40 °C, sample 1 did not comply with the specific migration limit of 18 mg/kg of simulant for DEHA plasticizer. Sample 4 met the requirement of specific migration of 60 mg/kg of fatty food simulant (olive oil) for DEHT plasticizer, under these same conditions. Both plasticizers displayed specific migration of the same order of magnitude (20 mg/kg). This indicates that the degree of interaction with the polymeric matrix is similar for DEHA and DEHT.

On the other hand, the specific migration of films 1 and 4 was much higher than the specific migration limit set for DEHA and DEHT when isooctane fatty food simulant was used (Table 7) due to the greater extractive power of this simulant in comparison to olive oil. However, also in this simulant, both plasticizers displayed similar values of specific migration, with 95% confidence degree, thus corroborating the values obtained for olive oil. Therefore, the results indicate that the diffusion coefficient of DEHT must be similar to the diffusion coefficient of DEHA.

Goulas et al. (2008) determined the diffusion coefficient of 0.45×10^{-11} cm²/s for migration of DEHA into isooctane fatty food

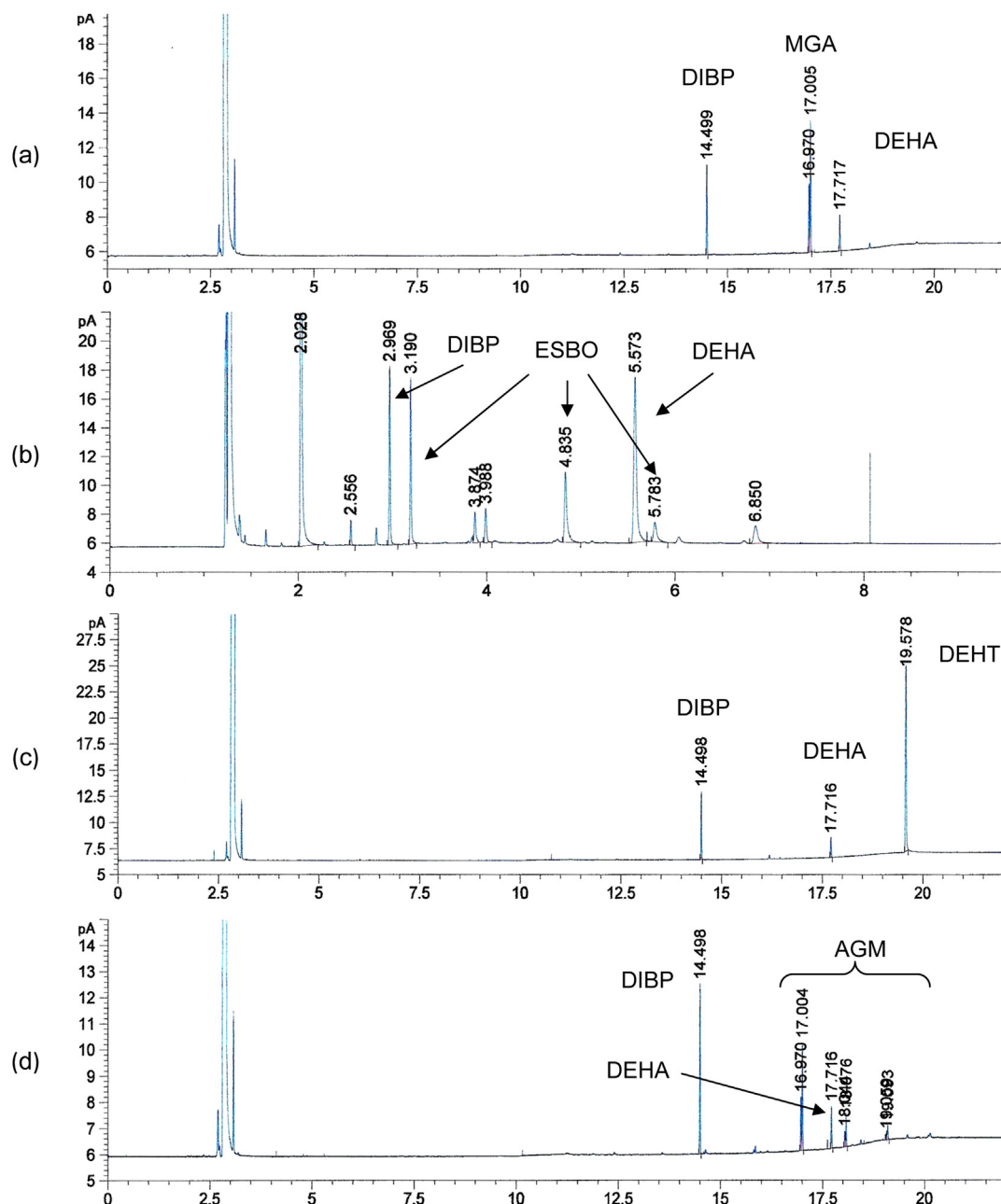


Fig. 2. Chromatograms of the migration of plasticizers into isooctane fatty food simulant: (a) film 3 – method B; (b) film 3 – method A; (c) film 4 and (d) film 5 (DIBP – internal standard; MGA = Mixture of glycerin acetates; AGM = Acetylated glycerol monoester).

simulant. Isooctane is more aggressive as a fatty food simulant than olive oil due to its high solubility in plastic. It is known that solvents with high affinity for a particular polymer lead to swelling of the polymer, thus facilitating diffusion of potential migrants from the polymeric matrix to the contact medium.

Sample 3 also did not meet the SML of 60 mg/kg of fatty food simulant (isooctane) for MGA plasticizer (Table 7), as set forth in Directive 2007/19/EC (European Commission, 2007). Moreover, MGA was the plasticizer with the greatest migration value.

ESBO was the plasticizer with the smallest migration in comparison to the other plasticizers under study (Table 7). Although ESBO was added to all films in the same rate, a significant difference was noticed in migration of ESBO in the films that were assessed, with a degree of confidence of 95%, as follows: $1 = 5 > 6 = 3, 3 = 4 > 2$.

Except for film 6, the pattern of ESBO migration was similar to the overall migration of the films evaluated. The migration of ESBO to the fatty food simulant was of the same order of magnitude (20 mg/kg) for films 1 and 5, and approximately 30%–50% lower for the other films. The smallest migration was found for film 2 (approx. 10 mg/kg) (Table 7).

This relative difference of migration of ESBO is probably due to the difference in efficiency of plasticization of the various formulations of the PVC films studied, which affects mobility of the plasticizer molecules in the PVC structure. The greatest migration of ESBO detected for samples 1 and 5 is probably due to the greater plasticization of the PVC structure due to the presence of DEHP in the film (sample 1) and greater plasticization efficiency of AGM (sample 5), associated to its affinity for the lipophilic medium of the simulant.

Table 7
Specific migration of the plasticizers from the PVC samples (mg/kg of simulant).^a

Simulant	Sample	Plasticizer	Average \pm SD ^d	Range	SML ^e
Acidic aqueous ^c	1 ^b –6	DEHA	<QL ^f = 0.70	n.a.	18
	1 ^b –6	ESBO	<QL = 5.45	n.a.	60
	2	ATBC	n.d.	n.a.	–
	3	MGA	<QL = 4.93	n.a.	60
	4	DEHT	<QL = 6.23	n.a.	60
	5	AGM	n.d.	n.a.	–
Fatty olive oil	6	Polyadipate	n.d.	n.a.	–
	1 ^b	DEHA	20.8 \pm 1.1	19.6–22.2	18
	2–6	DEHT	<QL = 3.68	n.a.	60
Fatty isooctane	4	DEHT	19.3 \pm 9.6	17.3–21.6	60
	1 ^b	ESBO	20.9 \pm 6.8 b	19.7–23.3	60
	2		10.5 \pm 8.8 e	9.8–11.2	–
	3		13.9 \pm 6.0 cd	12.7–14.6	–
	4		13.0 \pm 3.2 d	12.4–13.3	–
	5		21.3 \pm 9.2 a	19.4–23.7	–
	6		14.7 \pm 1.8 c	14.4–15.1	–
	1 ^b	DEHA	215.6 \pm 10.1 B	187.7–236.1	18
	2	ATBC	158.2 \pm 2.5 A	153.1–161.0	–
	3	MGA	253.5 \pm 10.2 C	244.0–267.0	60
	4	DEHT	208.7 \pm 5.6 B	195.2–231.9	60
	5	AGM	212.9 \pm 5.2 B	208.0–220.0	–
	6	Polyadipate	n.d.	n.a.	–

MGA = Mixture of glycerin acetates.

AGM = Acetylated glycerol monoester.

Different letters in the same column indicate significant differences ($p < 0.05$).

n.a./n.d. = not applicable and not detected, respectively.

^a Contact condition of 40 °C, for 10 days (acidic and olive oil simulants) and 20 °C, for 2 days (isooctane).

^b Reference sample.

^c Aqueous solution of acetic acid at 3% (w/v).

^d Average \pm standard deviation of 3 experimental determinations.

^e SML established by ANVISA (BRASIL, 2010) and/or EFSA (OPINION..., 2008).

^f QL = Quantification limit of the method.

Despite the difference of 4 times in the concentration of AGM and ESBO plasticizers in the formulation of sample 5 (Table 2), the migration of AGM detected was approximately 10 times higher than that of ESBO (Table 7). This result is in accordance with the results obtained by Lundsgaard et al. (2009), which estimated the diffusion coefficient of AGM into isooctane as $6.42 \times 10^{-9} \text{ cm}^2/\text{s}$, at 40 °C. The authors concluded that the diffusion coefficient of this plasticizer is 50 times greater than that of ESBO ($0.24\text{--}0.95 \times 10^{-9} \text{ cm}^2/\text{s}$ at 40 °C, for samples with 30–40% of plasticizers) and, therefore, its migration must be more accentuated.

The results showed that the migration of DEHA was at least 10 times greater than ESBO (Table 7). This is in conformance with the study conducted by Fankhauser-Noti & Grob (2006), who demonstrated that ESBO migrates much less to fatty foods than the other plasticizers (DEHA, DEHP, DIDP, DINP, ATBC and DEHS), and it may sometimes reach a factor of 10. The greater migration of these plasticizers in comparison to ESBO is because they are monomeric and therefore have greater mobility and greater diffusion coefficient in the molecular structure of PVC than ESBO.

The migration of ESBO in films evaluated in this study was much lower than the values obtained in a study conducted by Ezerskis, Morkunas, Suman, and Simoneau (2007), probably because these authors evaluated PVC sealants with much higher concentrations of ESBO than the one used in the films evaluated in this study (approximately 6%). The study conducted by Ezerskis et al. (2007) with 14 PVC sealants and 15 types of fatty foods showed that ESBO is the key plasticizer used in the 8 packages evaluated, and the concentration of ESBO varied from 15% to 42%. The migration of ESBO for the samples of food exceeded the limit of 60 mg/kg for three samples evaluated with the maximum value of 281.9 mg/kg and 61.3 mg/kg in average. In addition, DEHP was detected in the samples of food, and the migration varied from 2.5 to 8.7 mg/kg,

exceeding the SML in five samples. Eight samples of food displayed lower total concentration of polyadipate than SML (30 mg/kg). The migration rate of polyadipate for the foods ranged from 1% to 7%.

A study on migration of ESBO into olive oil fatty food simulant conducted with samples of PVC formulated with 30%, 40% and 50% of ESBO displayed high values of migration (2100 mg of ESBO/kg of olive oil for the sample with 30% of ESBO, and even higher values for the other samples). This high rate of migration was attributed to the high exchange of fatty acids between the PVC material and the olive oil fatty food simulant due to their high similarity in molecular composition (Bueno-Ferrer et al., 2010).

Therefore, considering the requirement of specific migration of the plasticizers ESBO, DEHA, MGA and DEHT, the PVC cling films analyzed in this study could be used in contact with some types of fatty foods with application of FRF, since only ESBO displayed migration values lower than SML (60 mg/kg). Therefore, the corrected values of specific migration for the PVC samples evaluated indicate that:

- Samples 1, 3 and 5 could not be used for fatty food packages;
- Samples 2 and 6 could be used for fatty food packages;
- Sample 4 could be used for contact with fatty foods with FRF 4 and 5.

So, the specific migration of the samples 1, 3 and 5 showed the same restriction observed for overall migration results, while for the other samples the overall migration was more restrictive.

Table 8 shows a worst case estimate, i.e., an estimate of the migration supposing that 100% of the mass of additives of the film migrate to the food simulant. For this estimate, the concentrations of plasticizers experimentally determined were considered (Table 2), added to the concentrations of the other additives (stabilizer, internal lubricant and antifogging agent) according to the concentrations used in the formulations of the films. Table 8 also shows the values of overall migration for purposes of comparison with the values of specific migration. Therefore, the values of specific migration, in mg/kg, were divided by 6 since one kilogram of simulant gets in contact with the equivalent to 6 dm² of film (CEN, 2003).

By comparing the values of overall migration to the worst case estimate, values were obtained ranging from 30% to 80%, indicating that 30%–80% of the additives added to the films migrated into food simulant (Table 8). Film 6 was the one that displayed the smallest quantity of migrated material. This can be attributed to the fact that this film was formulated with polyadipate, which is a plasticizer characterized by low migration because it is polymeric. On the other hand, the high migration value of film 1 (80%) can be

Table 8

Ratio between the specific migration of plasticizers into fatty food simulant (isooctane), overall migration (olive oil) and worst case of additives.^a

Sample	1 (ref)	2	3	4	5	6
Worst case (mg/dm ²) ^b	63.4	47.6	58.6	59.7	61.4	68.7
Overall migration (mg/dm ²)	50.4	31.3	44.5	39.4	47.0	19.3
Specific migration (mg/dm ²)	56.2	31.5	47.9	41.2	41.8	7.1
OM \times worst case (%)	79.5	65.7	76.0	66.0	76.5	28.1
SM \times worst case (%)	88.7	66.1	81.8	69.0	68.1	10.3
SM \times OM (%)	111.6	100.6	107.7	104.6	89.0	36.6
Loss of plasticizers (%)	96.8	74.2	90.5	76.9	75.4	11.3
Loss of ESBO (%)	53.3	23.4	28.1	26.3	33.0	17.7
Loss of the 3rd plasticizer (%)	n.a.	82.2	103.4	83.5	85.1	n.d.

OM/SM = Overall migration and specific migration, respectively.

n.a./n.d. = not applicable and not detected, respectively.

^a Contact condition of 40 °C, for 10 days (olive oil) and 20 °C, for 2 days (isooctane).

^b Estimation of the migration taking into account 100% of the mass of plasticizers of the film migrate into the food simulant.

attributed to the fact that the formulation of this film includes DEHP due to the contamination of the processing line, besides DEHA and ESBO plasticizers.

The rate of loss of plasticizers from the films was approx. 75–90%, except for film 6, with rate of loss approx. 10%, and of film 1, which was approx. 100% (Table 8). Since the loss of ESBO and of DEHA of film 1 was of the order of 50% and 100% respectively, this value is probably due the DEHP present in this film as a consequence of the contamination in the processing line.

The percentage of loss of plasticizer of the PVC film to the simulant corresponds to the coefficient of apparent partition (k) between the food simulant and the film, being defined as $[\text{plasticizer}]_{\text{simulant}}/[\text{plasticizer}]_{\text{film}}$. According to the data obtained, the loss of ESBO from the films to the isooctane simulant ranged from 20% to 50% (Table 8). In the case of the other plasticizers, which were added to the films at a concentration of the order of 20% (Table 2), the loss for isooctane simulant was approx. 75%–90%. The literature also shows values of migration of plasticizers of PVC film into food simulants and foods of this same order of magnitude (Bueno-Ferrer et al., 2010; Ezerskis et al., 2007; Goulas et al., 2008; Lundsgaard et al., 2009; VWA, 2005).

As the total concentration of plasticizers is similar for all films (Table 2), the combination of plasticizers influenced the migration of films (overall migration of 19.3 mg/dm², was determined for film 6, up to an overall migration of 50.4 mg/dm² for film 1). Therefore, it can be concluded that there are other components of the formulation of the films besides the plasticizers that are migrating in a sufficient amount to exceed the permitted limit of overall migration.

A comparison of the values of specific migration of plasticizers to the values of overall migration to the fatty food simulant (Table 8) produced the following contribution to the plasticizers analyzed for the overall migration value:

- Film 1: migration of plasticizers exceeded the residue of overall migration;
- Films 2–5: migration of plasticizers corresponded to the residue of overall migration (values close to 90%–100%);
- Film 6: migration of plasticizers corresponded to 37% of the residue of overall migration. However, it must be noted that, in this case, the specific migration of polyadipate was not determined due to analytical difficulties associated to this test.

The fact that the specific migration of plasticizers corresponds to the values of overall migration for most films evaluated may be due to the fact that the tests of specific migration were conducted with isooctane simulant, which has greater extractive power than olive oil (simulant used in the overall migration test).

Anyway, films 3 and 5 were the ones that displayed the greatest migration of plasticizers into fatty food simulant. Probably because these films were formulated with plasticizers derived from vegetable oils, which have provided greater migration of plasticizers into simulant due to the increased chemical affinity between the simulant and the plasticizers, besides the highest mobility in the PVC structure (plasticization effect).

Although film 6 was the one with the greatest concentration of additives in its formulation, (greatest worst case value), it displayed the smallest overall migration in comparison to the worst case (28.1%), which is characteristic of the type of plasticizer used in this film (polymeric).

On the other hand, film 1 (reference sample) was the one with the worst ratio between overall migration and the worst case (79.5%), probably due to the presence of DEHP in its formulation (Table 8). Despite DEHP was not used in the formulations evaluated in this study; its migration is high in film 1 (101 mg/kg), which was

probably the first film to be processed. The other films indicated the presence of small concentrations of DEHP. This plasticizer easily contaminates glassware, equipment etc. and it is difficult to be eliminated. Due to the excellent cost/performance ratio of DEHP, this plasticizer is very much used. However, the use of DEHP in packages of fatty foods is practically impossible due to the low SML (1.5 mg/kg) (ANVISA, 2008).

A comparison of the values of specific migration to the worst case shows that plasticizers are the key migrants into food simulant (in the case of samples 1–5). The smallest contribution of migration of sample 6 as to the worst case is due to the reduced migration that is characteristic of the polymeric plasticizer, besides the specific migration of polyadipate was not quantified.

Therefore, besides the better relative plasticizing efficiency of various plasticizers, it is important to seek a formulation that meets the requirements of overall and specific migration for contact with food, even if this means a mechanical performance somewhat lower than the values obtained in this study.

3.2. Assessment of commercial PVC films

The thickness of commercial samples ranged between 6 and 8 μm , which is much less than the thicknesses of the samples produced specially for this study (15–20 μm). The grammage of the samples ranged between 7.8 and 11.5 g/m². These differences must influence both the mechanical performance of the films and migration.

3.2.1. Analysis of the plasticizers used in commercial PVC films

According to the chromatograms obtained, the plasticizers identified and quantified in the commercial samples of PVC are shown in Table 9. Due to the small concentration of MGA in the formulation of sample 2C, it was probably caused by contamination of the processing line of the film and it is not formulation component, since plasticizers are usually added in large quantities to the formulations. Besides the plasticizers listed in Table 9, other peaks were also observed in the chromatograms of the samples of PVC films. These peaks are probably due to other additives used in the formulation of the films, but they were not identified.

Except for MGA, the specific migration limit of all plasticizers is set by Resolution RDC no. 17 (ANVISA, 2008). For this reason, these samples of PVC film were submitted to the specific migration test in aqueous acidic and fatty food simulants to check if they were in conformance with the legislation in force.

3.2.2. Specific migration into food simulants

The samples of commercial PVC film displayed lower values of specific migration of plasticizers into aqueous acidic foods simulant than the quantification limit (LOQ) of the respective methods, even with concentration of approx. 40% in the formulation of the film (Table 9). Therefore, considering the requirement of specific migration of these plasticizers, the PVC films analyzed could be used in contact with aqueous acidic foodstuffs. This is due to the low affinity of plasticizers for aqueous medium.

Table 9
Plasticizers found in commercial PVC cling films.^a

Sample	DEHA (%)	DEHP (%)	MGA (%)	ESBO (%)	Total (%)
1C	10.0 \pm 1.7	0.4 \pm 1.4	2.2 \pm 0.2	14.6 \pm 8.1	27.2
2C	1.4 \pm 0.1	n.d.	0.8 \pm 3.3	41.5 \pm 2.5	43.7
3C	2.1 \pm 0.1	n.d.	5.5 \pm 0.8	15.9 \pm 0.7	23.5
4C	n.d.	11.1 \pm 1.6	2.2 \pm 0.4	10.7 \pm 1.0	24.0

MGA = Mixture of glycerin acetates.

n.d. = not detected.

^a Average \pm standard deviation of 3 experimental determinations.

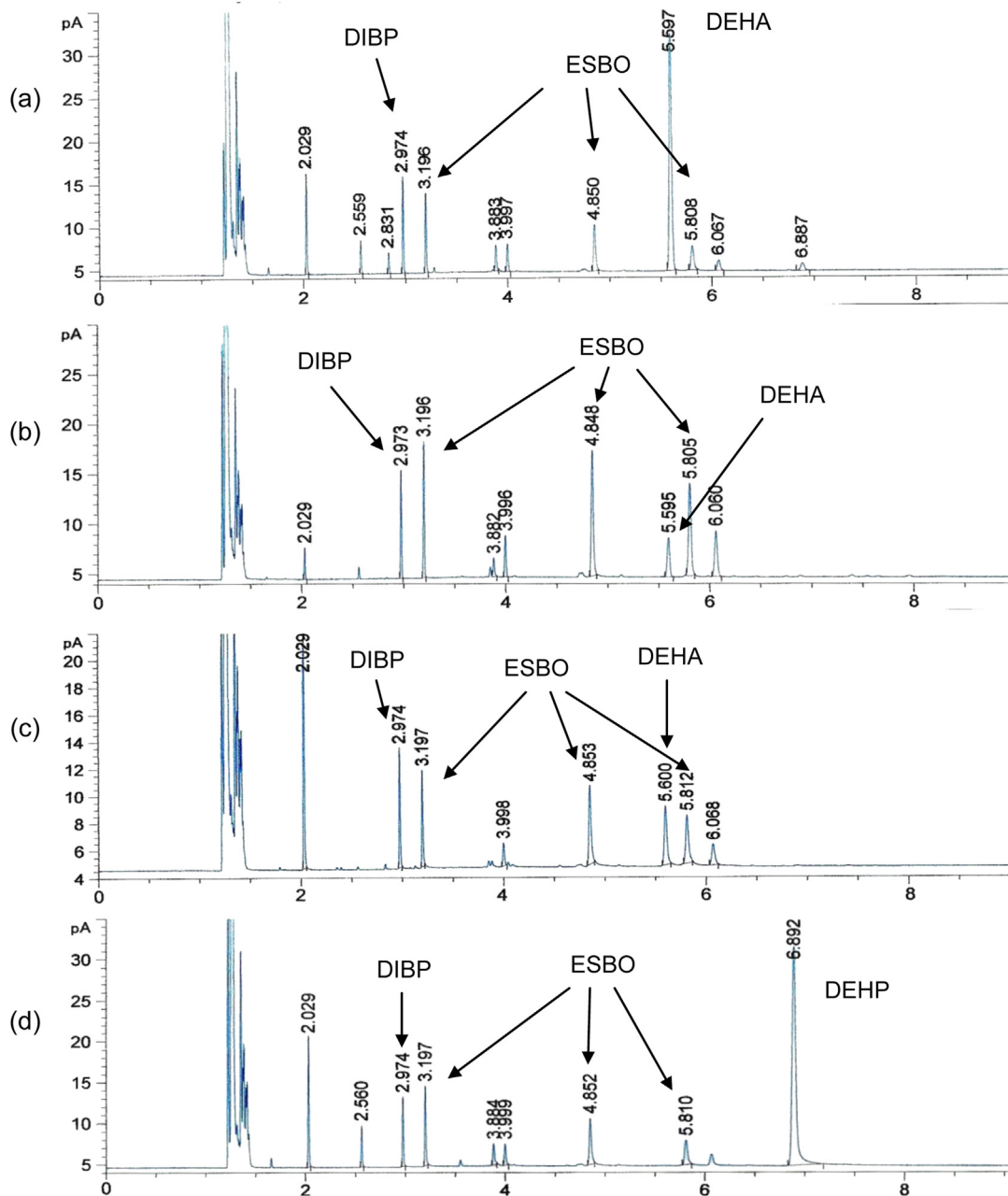


Fig. 3. Chromatograms of the migration of plasticizers of commercial PVC cling films into isooctane fatty food simulant: (a) film 1C; (b) film 2C; (c) film 3C; (d) film 4C (DIBP – internal standard).

On the other hand, the chromatograms indicate migration of ESBO, DEHA and DEHP of commercial PVC samples into isooctane simulant (Fig. 3). As Table 10 shows, samples 1C, 3C and 4C displayed migration of ESBO approx. 30 mg/kg, which is lower than the specific migration limit for this plasticizer (SML = 60 mg/kg) (ANVISA, 2008). On the other hand, sample 2C displayed migration of ESBO approx. 80 mg/kg, being therefore non-conformant with the set SML.

Taking into account the migration of DEHA, samples 2C and 3C met the SML of 18 mg/kg, whereas sample 1C exceeded this value (Table 10). Similar results were obtained by Bonini et al. (2008), which evaluated cling films for food packaging acquired in the local retail market (Bologna, Italy). According to the authors, the results showed a broad range of DEHA migration into fatty food simulants (from 2 to 8 mg/dm²) and only few of the analyzed films were

acceptable without restrictions for use in foodstuffs packaging since the SML for DEHA is 3 mg/dm². In order to ensure the safe use of these films it was pointed out the need of a clear labeling of plasticized films, stating the recommended and the inadvisable uses of the product, while another option should be the use of low-migration plasticizers as polymeric ones.

Besides sample 4C displayed approx. 50 mg/kg of DEHP migration, which has SML of 1.5 mg/kg (Table 10). The use of DEHP for fatty food packages is prohibitive due to the requirement of very low SML set forth by the legislation. This value is a consequence of the toxicity observed in tests conducted with this plasticizer. Studies performed with animals showed that DEHP is toxic to the male reproductive system. When DEHP is metabolized in the human body, it produces compounds that interfere with the reproductive system (Institute, Harriman, Civie, & Ellenbecker, 2013). For

Table 10

Specific migration of plasticizers of commercial PVC cling films into isooctane simulant.

Sample	Average \pm SD ^a	Range	SML (mg/kg)
ESBO (mg/kg)			60
1C	22.7 \pm 4.8	22.2–27.4	
2C	82.4 \pm 16.2	68.0–103.5	
3C	31.2 \pm 2.0	29.2–34.0	
4C	28.3 \pm 4.4	22.0–31.0	
DEHA (mg/kg)			18
1C	36.5 \pm 1.6	35.0–38.2	
2C	15.6 \pm 1.1	14.8–16.8	
3C	15.9 \pm 0.8	15.4–16.8	
DEHP (mg/kg)			1.5
4C	51.9 \pm 1.5	50.3–53.3	

SML = specific migration limit (ANVISA, 2010).

^a Average \pm standard deviation of 3 experimental determinations.

this reason, the market has replaced DEHP with other plasticizers. However, some manufacturers insist on using DEHP because it is less expensive, which was confirmed by sample 4C.

From the point of view of conformance with specific migration limits for use as food package, out of this sampling only sample 3C might be used as fatty food-contact package for prolonged time at temperatures up to 40 °C. Therefore, 25% of the samples evaluated are in conformance with the specific migration set forth by the legislation in force for food contact packages, while the other 50% might be used for contact with fatty food with FRF 2–5. Thus, the use of different colors for PVC films or labeling declaring the recommended and the inadvisable uses of these films (ABNT, 2010; Bonini et al., 2008) could advise the consumer for the proper use of them.

4. Conclusions

All PVC films evaluated in this study showed very low or non-detectable overall migration and specific migration into acidic food simulant. Therefore, there are no restrictions to use these PVC films in contact with acidic foodstuffs.

Regarding overall migration to olive oil food simulant, the reference samples and the samples formulated with vegetable-origin plasticizers could not be used to pack fatty foods while the others could be used to pack some types of fatty foods by applying FRF 3–5.

Taking into account the specific migration of plasticizers into fatty food simulant the results showed that:

- The migration of ESBO was higher for film 1 (reference) and film 5 (AGM) than the other films indicating highest efficiency of plasticization of these formulations of PVC films;
- The migration of MGA and AGM, vegetable-origin plasticizers, was more accentuated than the other plasticizers analyzed which indicates greater mobility of these plasticizers in the PVC structure and explains their higher plasticization efficiency verified by the tensile properties of the films;
- The coefficient of apparent partition of DEHT is similar to that of DEHA, whereas MGA and AGM plasticizers displayed higher coefficients of apparent partition and greater chemical affinity with the fatty food simulant than the other plasticizers under study. This difference in migration was attributed to the different molecular structures of plasticizers.

Out of the commercial PVC films evaluated, 25% of the samples met the requirements of SML for contact with fatty foods and there are no restrictions for use, while the other 50% might be used for contact with fatty foods with FRF 2–5. Regarding aqueous acidic

foods contact all the commercial films showed no restrictions for use. Then, the use of different colors or labels could advise the consumer for the proper use of these films.

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