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# 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.



## 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 foodstuffs, 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 being 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/cm$^3$, supplied by Elekeiroz S/A;
- Epoxidized soybean oil – ESBO, Soyflex 6250™, density 0.987–0.993 g/cm$^3$, molar mass 944 g/mol, supplied by BBC Indústria e Comércio Ltda.;
- Acetylated tributyl citrate – ATBC, Scandinol SP-22™, density 1.048 g/cm$^3$, supplied by Scandiflex do Brasil S/A.;
- Mixture of glycerin acetates (named as MGA) – Unimoll™ AGF, density 0.974 g/cm$^3$, 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/cm$^3$, 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/cm$^3$, 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,