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Migration of di-(2-ethylhexyl)adipate and acetyltributyl citrate plasticizers from food-grade PVC film into isooctane: Effect of gamma radiation

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Abstract

The effect of gamma radiation on the migration of both di-(2-ethylhexyl)adipate (DEHA) and acetyltributyl citrate (ATBC) plasticizers from PVC film into the food simulant isooctane was studied as a function of time (0–48 h) at 20 °C. Food-grade PVC cling-film used contained 5.3% (w/w) DEHA, 3.0% (w/w) ATBC and polyadipate polymeric plasticizer. Irradiation of the films was carried out at doses of 5, 10 and 25 kGy using a [^{60}Co] gamma-radiation source. Determination of both plasticizers was performed using a direct gas chromatographic method. No radiation-induced transformation of the two plasticizers was observed after absorbed doses of 5–25 kGy. DEHA migrated rapidly into isooctane in contrast with ATBC. ATBC migrating amounts at equilibrium were approximately three times lower than the corresponding amounts of DEHA. Irradiation at doses 10 and 25 kGy had a small but statistically significant ($P < 0.05$) effect on the migration of both DEHA and ATBC into isooctane. Migration amount increased with increasing irradiation dose and contact time. The irradiation-induced increase of ATBC migration was significantly higher than the corresponding increase of DEHA migration. Results are discussed in relation to EU proposed upper limit for DEHA specific migration (18 mg/L). Diffusion coefficients for both plasticizers calculated, showed differences between irradiated and control samples.

Keywords: PVC; Fatty food simulant; Gamma radiation; Diffusion coefficients

1. Introduction

Plasticizers are low molecular weight synthetic organic molecules added to the polymer resin to modify properties such as flexibility and processibility. Such additives normally possess a high mobility due to relatively low molecular weight and easily diffuse to the surrounding media (food, solvent etc.) particularly those with a high fat content (Cooper, Goodson, & O'Brien, 1998; Goulas & Kontominas, 1996; Goulas, Anifantaki, Kolioulis, & Kontominas, 2000; Lau & Wong, 2000; Tsumura, Ishimitsu, Kaihara, Yoshii, & Tonogai, 2002).

There are many studies published in the literature on the migration of plasticizers from poly(vinyl chloride) (PVC) (flexible films, children toys, gaskets, blood and serum storage bags etc.) into foods, food simulants and saliva simulants (Cooper et al., 1998; Fantoni & Simoneau, 2003; Goulas et al., 2000; Goulas, Kokkinos, & Kontominas, 1995; Goulas & Kontominas, 1996; Goulas, Riganakos, Ehlermann, Demertzis, & Kontominas, 1998; Hammarling, Gustavsson, Svensson, Karlsson, & Oskarsson, 1998; Hirayama, Tanaka, Kawana, Tani, & Nakazawa, 2001; Lakshmi & Jayakrishnan, 1998; Nerin, Gancedo, & Cacho, 1992; Petersen, Naamansen, & Nielsen, 1995;

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Steiner, Scharf, Fiala, & Washuttl, 1998; Till et al., 1982; Tsumura et al., 2002).

The more commonly used monomeric plasticizers for food packaging PVC cling-films include di-(2-ethylhexyl)adipate (DEHA) and acetyltributyl citrate (ATBC).

The diffusion of plasticizers from PVC films to solvents or foods can be visualized as a two step process: within the polymer (Fickian in nature) and at the interface between solvent and polymer (Lau & Wong, 2000; Till et al., 1982). A number of models have been proposed describing this process of diffusion (Chatwin & Katan, 1989; Lau & Wong, 2000; Lickly, Rainey, Burgert, Breder, & Borodinsky, 1997; Reynier, Dole, & Feigenbaum, 2002; Till et al., 1982).

The factors that may affect the diffusion *kinetics* of plasticizers include the nature and thickness of the polymer, the initial concentration of plasticizer in the polymer, the plasticization process, the surrounding medium, the nature and amount of plasticizer and the conditions of polymer/food contact (time, temperature) (Audic, Reyx, & Brosse, 2003; Cooper et al., 1998; Goulas et al., 2000; Goulas & Kontominas, 1996; Lakshmi & Jayakrishnan, 1998; Marcilla, Garcia, & Garcia-Quesada, 2004; Petersen et al., 1995; Till et al., 1982; Vergnaud, 1983).

Irradiation using ionizing radiation has been successfully used commercially over the past several years for the preservation of foods (poultry, meat, fruits and vegetables) at various dose levels mostly corresponding to "cold pasteurization" (1–10 kGy) and to a lesser degree to "cold sterilization" (10–20 kGy) (Ehlermann, 2002; Morehouse, 2002; WHO, 1988).

Foods to be preserved by irradiation are usually prepackaged to avoid subsequent microbial recontamination. Depending on the nature of the polymer being used and the specific irradiation conditions (absorbed dose, dose rate, temperature) changes in the packaging material have been documented in the literature such as: production of free radicals, hydroperoxides, carboxylic acids, carbonyl compounds, discoloration, chain scission, crosslinking, changes in the mechanical properties etc. (Buchalla, Schoettler, & Bogl, 1993a, 1993b; Chytiri, Goulas, Riganakos, Badeka, & Kontominas, 2005; Goulas et al., 1998; Goulas, Riganakos, & Kontominas, 2003, 2004; Komolprasert, McNeal, & Begley, 2003; Mendizabal, Cruz, Tasso, Burillo, & Dakin, 1996; Riganakos, Koller, Ehlermann, Bauer, & Kontominas, 1999; Saxena, Kalliyanakrishnan, & Pal, 1987).

Among these changes, migration from the plastic packaging material into the food is a phenomenon of prime importance given that certain additives e.g. plasticizers are known to produce adverse effects to humans (Bernal, Martinelli, & Mocchiutti, 2002; Dalgaard et al., 2003; EC, 1999). This concern becomes even greater in the case of irradiated packaged foodstuffs (Goulas et al., 1998).

According to EU Directive 97/48/EC (EC, 1997) both isooctane and 95% ethanol may be used as alternative fatty food simulants when olive oil or sunflower oil introduce technical problems related to the method of analysis. In cases where migrants such as plasticizers are being studied, isooctane is the preferred simulant due to its high affinity towards the specific migrants. De Kruijf and Rijk (1997) reported that isooctane is specified for polar polymers, such as PVC, as a non-polar solvent.

Although global migration has been examined extensively, there is limited information in the literature concerning the effect of ionizing radiation on the specific migration of plasticizers into foods or food simulants (Goulas et al., 1995; Goulas & Kontominas, 1996; Goulas et al., 1998).

There are several methods reported in the literature for the determination of migrating plasticizers, such as GC (both direct and indirect), GC/MS, pyrolysis–GC/MS, HPLC, FTIR, ^{1}H NMR and radioanalytical techniques (Castle, Jickells, Sharman, Gramshaw, & Gilbert, 1988; Cooper et al., 1998; Goulas & Kontominas, 1996; Hamdani & Feigenbaum, 1996; Hammarling et al., 1998; Nerin et al., 1992; Till et al., 1982; Tsumura et al., 2002; Wang, 2000).

Thus, the objectives of the present work were: (a) to study the effect of intermediate (5 and 10 kGy) and high doses (25 kGy) of γ-radiation on the migration of DEHA and ATBC plasticizers from food-grade PVC cling-film into isooctane as a function of time (b) to calculate diffusion coefficients of both plasticizers based on simple mathematical treatment of migration data and (c) to improve the existing direct GC method for the determination of plasticizers (Cooper et al., 1998).

2. Materials and methods

2.1. Materials

The PVC film used was food-grade commercial product, 10 μm in thickness, containing $5.3 \pm 0.1\%$ (w/w) DEHA and $3.0 \pm 0.1\%$ (w/w) ATBC. According to the supplier the film also contained a polyadipate polymeric plasticizer. The levels of both plasticizers were determined by chloroform extraction of the film followed by capillary GC analysis (Petersen et al., 1995). Analytical grade DEHA and the internal standard (IS) $C_{18}H_{38}$ (octadecane) were purchased from Fluka (Buchs, Switzerland). Analytical grade ATBC was purchased from Unitex Chemical, NC, USA. The solvents used were "pro analysis"-grade and purchased from Merck (Darmstadt, Germany).

2.2. Irradiation and migration experiments

Rectangular strips of PVC cling-film (total area 120 cm^2) were placed on a stainless-steel screen in order to avoid clumping and folding. The film/screen combination was placed into a wide-mouthed glass jar of 250 mL capacity. The jars were subsequently irradiated with a 240 kCi [^{60}Co] source at an appropriate distance from the source in order to achieve absorbed doses of 5, 10 and 25 kGy. Irradiation was carried out in the presence of air, at room temperature and in the absence of isooctane because in its presence the migration of both plasticizers is completed during the irradiation, thus making early