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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

Panagiota D. Zygoura [a], Antonios E. Goulas [b], Kyriakos A. Riganakos [a], Michael G. Kontominas [a,*]

[a] *Laboratory of Food Chemistry and Technology, Department of Chemistry, University of Ioannina, Ioannina 45110, Greece*
[b] *Department of Materials Science and Technology, University of Ioannina, Ioannina 45110, Greece*

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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;

* Corresponding author. Tel.: +30 26510 98342; fax: +30 26510 98795.
E-mail address: mkontomi@cc.uoi.gr (M.G. Kontominas).

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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

stage sampling impossible. Irradiation doses were measured using Harwell Perspex Polymethylmethacrylate (PMMA) type Red 4034 FW dosimeters. The average dose rate was 0.7 kGy/h for all irradiated samples. After irradiation the jars were filled with 200 mL isooctane (two side contact), sealed and placed in an incubator at 20 ± 1 °C. Isooctane was thermostated at the same temperature prior to the experiments. Sampling was carried out at predetermined periods of time up to 48 h (EC, 1997) and isooctane was analysed for DEHA and ATBC using GC-FID. All experiments were carried out in triplicate. For purposes of comparison identical non-irradiated (control) PVC/isooctane samples were analysed for DEHA and ATBC content after storage at 20 ± 1 °C for a period up to 48 h.

2.3. Direct GC determination of DEHA and ATBC plasticizers

Amounts of migrating DEHA and ATBC plasticizers were determined using the method reported by Cooper et al. (1998) after appropriate modification: 9 mL of contaminated isooctane were transferred to a 10 mL volumetric flask and the volume was made up with the addition of 1 mL from a stock solution of octadecane in isooctane (1 mg/mL). All samples were analysed subsequently by gas chromatography (GC-FID) on a Hewlett Packard HP 5890 series II unit (Wilmington, USA). A non-polar capillary column (HP-5, J. & W. Scientific, Folsom, USA) of 30 m length, 0.32 mm internal diameter and 0.25 μm film thickness was used. The GC oven was programmed as follows: the temperature was initially held at 200 °C for 1 min, heated from 200 to 280 °C at 20 °C/min, then held at 280 °C for 3 min. The injector and detector temperatures were 250 °C and 300 °C respectively. Injection volume was 1 μL and carrier gas was helium at 75 kPa. Detection was performed at a split (1:20) mode. Analysis was carried out using an appropriate calibration curve.

2.4. Calibration curve and spiking

A calibration curve was constructed by preparing solutions of DEHA and ATBC in isooctane in the range of 5–186 mg/L and 10–210 mg/L respectively. In all above solutions 1 mL of octadecane (IS) solution in isooctane (1 mg/mL) was added.

Recovery experiments with spiked simulant were performed at four concentrations (6, 15, 25 and 50 μL of each plasticizer per 1 L isooctane) and mean recoveries were calculated. All analyses were carried out using Hamilton microsyringes and precision pipettes.

The detection limit for DEHA was 0.8 mg/L (0.13 mg/dm^2), defined as three times the signal:noise ratio. For ATBC the detection limit was 3.1 mg/L (0.52 mg/dm^2).

3. Results and discussion

3.1. Migration of DEHA and ATBC

A mean recovery factor of 100.2% for DEHA and 99.9% for ATBC was obtained. The amounts of DEHA and ATBC that migrated into isooctane from irradiated and non-irradiated samples at 20 °C as a function of time, are given in Tables 1 and 2.

The equilibrium migrating amounts of DEHA plasticizer into isooctane range from levels of 10.8–13.1 mg/L DEHA, corresponding to a migration from the film of 1.8–2.2 mg/dm^2. As the film contained 3.2 mg/dm^2 of DEHA, these migration levels represent losses ranging from 48.0% to 57.2% of the available plasticizer. The equilibrium migrating amounts of ATBC range from levels of 3.4–6.4 mg/L ATBC, corresponding to a migration from the film of 0.6–1.1 mg/dm^2. As the film contained 1.8 mg/dm^2 of ATBC, these migration levels represent losses ranging from 32.0% to 60.0% of the available plasticizer. Thus ATBC migrating amounts at equilibrium are approximately three times lower than the corresponding amounts of DEHA plasticizer from PVC non-irradiated films. The

Table 1
Migration of DEHA from non-irradiated and irradiated PVC film samples into isooctane at 20 ± 1 °C

Contact time (min)	Migrated amount[a] of DEHA							
	Non-irradiated		5 kGy		10 kGy		25 kGy	
	(mg/L)	(mg/dm^2)	(mg/L)	(mg/dm^2)	(mg/L)	(mg/dm^2)	(mg/L)	(mg/dm^2)
2	2.9 ± 0.1	0.48 ± 0.02	2.9 ± 0.1	0.49 ± 0.02	3.0 ± 0.1	0.50 ± 0.02	3.1 ± 0.1	0.52 ± 0.02
5	8.2 ± 0.3	1.37 ± 0.05	7.1 ± 0.3	1.18 ± 0.05	9.1 ± 0.4	1.51 ± 0.06	9.2 ± 0.4	1.53 ± 0.06
15	10.1 ± 0.4	1.68 ± 0.07	10.1 ± 0.4	1.69 ± 0.07	10.8 ± 0.4	1.80 ± 0.07	11.1 ± 0.4	1.85 ± 0.07
30	10.7 ± 0.4	1.79 ± 0.07	10.8 ± 0.4	1.79 ± 0.08	11.7 ± 0.5	1.94 ± 0.08	12.2 ± 0.5	2.03 ± 0.08
180 (3 h)	10.9 ± 0.5	1.82 ± 0.07	10.9 ± 0.5	1.82 ± 0.08	12.8 ± 0.5	2.13 ± 0.09	13.0 ± 0.5	2.17 ± 0.09
420 (7 h)	10.8 ± 0.5	1.81 ± 0.07	10.9 ± 0.5	1.82 ± 0.08	12.8 ± 0.5	2.13 ± 0.09	13.0 ± 0.5	2.17 ± 0.09
720 (12 h)	11.0 ± 0.5	1.84 ± 0.08	10.9 ± 0.5	1.82 ± 0.08	12.8 ± 0.5	2.13 ± 0.09	13.0 ± 0.5	2.17 ± 0.09
1440 (24 h)	11.0 ± 0.5	1.84 ± 0.08	10.9 ± 0.5	1.82 ± 0.08	12.8 ± 0.5	2.13 ± 0.09	13.0 ± 0.5	2.17 ± 0.09
2880 (48 h)	11.0 ± 0.5	1.84 ± 0.08	10.9 ± 0.5	1.82 ± 0.08	12.8 ± 0.5	2.13 ± 0.09	13.0 ± 0.5	2.17 ± 0.09

[a] Data are mean values of triplicate samples ± standard deviation.

Table 2
Migration of ATBC from non-irradiated and irradiated PVC film samples into isooctane at 20 ± 1 °C

Contact time (min)	Migrated amount[a] of ATBC							
	Non-irradiated		5 kGy		10 kGy		25 kGy	
	(mg/L)	(mg/dm^2)	(mg/L)	(mg/dm^2)	(mg/L)	(mg/dm^2)	(mg/L)	(mg/dm^2)
2	ND[b]	ND	ND	ND	ND	ND	ND	ND
5	ND	ND	ND	ND	ND	ND	3.9 ± 0.2	0.65 ± 0.03
15	ND	ND	ND	ND	3.9 ± 0.1	0.65 ± 0.02	4.3 ± 0.2	0.72 ± 0.03
30	ND	ND	ND	ND	4.1 ± 0.1	0.69 ± 0.02	4.7 ± 0.2	0.79 ± 0.03
180 (3 h)	3.3 ± 0.1	0.54 ± 0.02	3.9 ± 0.1	0.65 ± 0.03	4.9 ± 0.1	0.82 ± 0.03	5.5 ± 0.2	0.92 ± 0.04
420 (7 h)	3.4 ± 0.1	0.57 ± 0.02	4.1 ± 0.2	0.69 ± 0.03	5.5 ± 0.2	0.92 ± 0.04	6.0 ± 0.3	0.99 ± 0.04
720 (12 h)	3.4 ± 0.1	0.57 ± 0.02	4.1 ± 0.2	0.69 ± 0.03	5.5 ± 0.2	0.92 ± 0.04	6.4 ± 0.3	1.06 ± 0.04
1440 (24 h)	3.5 ± 0.2	0.58 ± 0.02	4.1 ± 0.2	0.69 ± 0.03	5.5 ± 0.2	0.92 ± 0.04	6.6 ± 0.3	1.09 ± 0.04
2880 (48 h)	3.5 ± 0.2	0.58 ± 0.02	4.1 ± 0.2	0.69 ± 0.03	5.5 ± 0.2	0.92 ± 0.04	6.6 ± 0.3	1.09 ± 0.04

[a] Data are mean values of triplicate samples ± standard deviation.
[b] ND, not detected.

lower level of migration of ATBC as compared to DEHA is almost entirely due to its lower initial concentration in the PVC film of 1.8 mg/dm^2 as compared with 3.2 mg/dm^2 for DEHA, as well as to different molecular weight and chemical nature of the two plasticizers.

As reported in the literature, in most cases a linear correlation has been established between the initial additive concentration in the polymer and the migration of the additive into the food simulant (Figge, 1996; O'Brien, Cooper, & Tice, 1997). Migration depends also on size and structure of the migrating plastic components (Figge, 1996).

Comparison of the chromatograms obtained prior to and after irradiation (Figs. 1 and 2), shows that no radiation-induced transformation of the two plasticizers occurs after absorbed doses of 5–25 kGy (absence of new peaks). As reported in the literature (Krylova et al., 1979) this effect is observed after significantly greater irradiation doses.

An interesting observation to be made is the rapid DEHA migration into isooctane at the initial PVC/simulant contact period. An average of 3.0 mg/L of DEHA (0.5 mg/dm^2) was found to be extracted from the PVC film within just the first 2 min of contact with the food simulant. This value corresponds to ≈13.0% loss of the initial amount of DEHA contained in the film. It is obvious from both irradiated and non-irradiated samples, as sampling progressed, that the migration rate decreases with time, while within 15 min of contact almost 90.0% of the extractable DEHA fraction has been transferred to isooctane. This observation can be attributed to the aggressiveness of isooctane towards plastic packaging materials and can be defined on the basis of its solubility in the plastic causing swelling of the latter. This effect facilitates diffusion of the potential migrants out of the plastic matrix (Baner, Bieber, Figge, Franz, & Piringer, 1992; Feigenbaum et al., 2002).

Petersen et al. (1995) reported that the migration obtained after only 2 h of PVC exposure to isooctane at 40 °C can be compared with the 10 days exposure period at 40 °C using olive oil as a food simulant.

Feigenbaum et al. (2002) reported that the aggressiveness of isooctane (non-polar solvent) expressed as mmole absorbed per gram of polymer was ≈64 times greater than the aggessiveness of olive oil after contact with PP (non-polar polymer). Of course aggressiveness of isooctane towards PVC (polar polymer) is lower (De Kruijf & Rijk, 1997).

No statistically significant differences ($P > 0.05$) were observed in DEHA migration after a dose of 5 kGy, while doses of 10 and 25 kGy produced slight but statistically

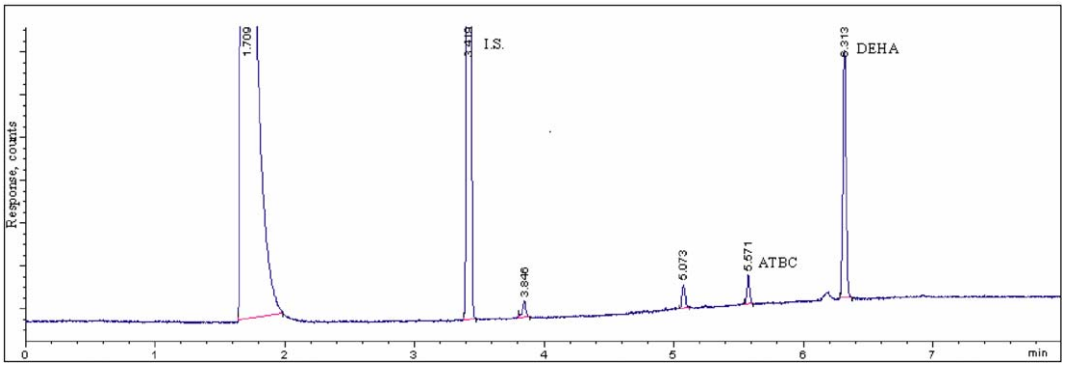

Fig. 1. Gas chromatogram of DEHA and ATBC in non-irradiated PVC film into isooctane at 20 °C.

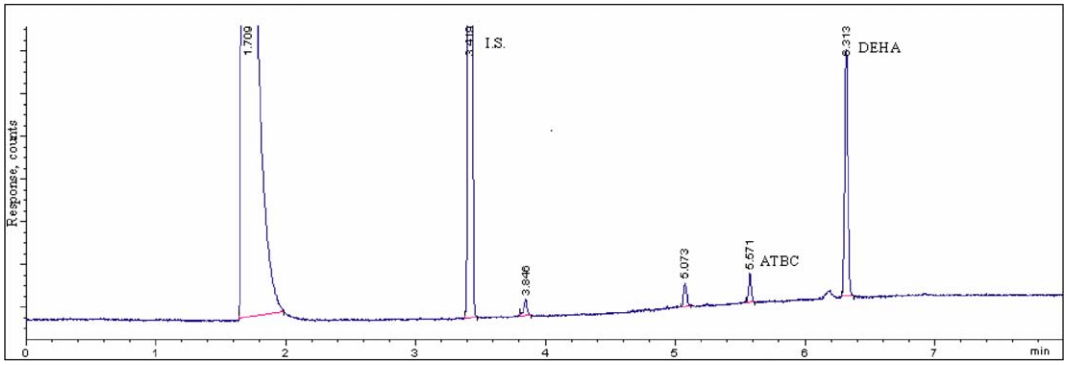

Fig. 2. Gas chromatogram of DEHA and ATBC in irradiated at 25 kGy PVC film into isooctane at 20 °C.

significant differences ($P < 0.05$) in terms of equilibrium time. For the non-irradiated samples and samples irradiated at a dose of 5 kGy equilibrium was reached after 0.5 h of contact, while for the rest the DEHA "bleed" continued for another 2.5 h, increasing the extractable amount of DEHA by ≈9%. The final concentration of DEHA (equilibrium state) in isooctane was approximately 10.8 mg/L (1.8 mg/dm^2), corresponding to a loss of 47.2% DEHA from PVC for non-irradiated and irradiated at a dose of 5 kGy samples. For irradiated samples at doses of 10 and 25 kGy the values at equilibrium state are ≈12.9 mg/L (2.2 mg/dm^2) corresponding to a loss of 56.7% of the plasticizer. Irradiation at doses of 10 and 25 kGy resulted in an increase in equilibrium migration value of DEHA by 15.8% and 18.5% respectively. Irradiation as a result of energy transfer to the polymer probably disrupts some polymer–plasticizer or polymer–polymer bonds resulting in increased migration of plasticizer. In each case, though, the obtained values are within the limits for DEHA migration from plastic packaging materials into foods/food simulants set by the EU (18 mg/L or 3 mg/dm^2). The above results indicate that in the case of isooctane the migration of DEHA from the film is rapid regardless the dose of the applied radiation, but remains at acceptable levels.

The results showed that all radiation doses induced statistically significant differences ($P < 0.05$) in migrating amounts of ATBC into isooctane. For non-irradiated samples and samples irradiated at a dose of 5 kGy detectable amount of ATBC was determined after 3 h of PVC/isooctane contact, while for samples irradiated at doses of 10 and 25 kGy detectable amount of ATBC was determined after 15 and 5 min respectively. Irradiation at doses of 5, 10 and 25 kGy resulted in an increase in equilibrium migration value of ATBC by 17.4%, 58.3% and 87.4% respectively. From the above results it is obvious that the irradiation-induced increase of ATBC migration was significantly higher than the corresponding increase of DEHA migration.

In our previous studies (Goulas et al., 1995, 1998) the low dose gamma radiation (4 and 9 kGy) had no effect on the migration of DEHA and ATBC from PVC and PVdC/PVC films respectively into olive oil at 4–5 °C. In contrast e-beam absorbed doses of 20 and 50 kGy resulted in increased DEHA migration values into olive oil, while ATBC migration slightly increased after 50 kGy only.

Of course direct comparison between present results and those reported in our previous work is not realistic because experimental conditions used differ substantially in the initial plasticizer content in the film, irradiation conditions (dose rate, temperature, radiation source), storage temperature as well as simulant used.

Very little information exists in the literature on the effect of ionizing radiation on the migration of plasticizers into food simulants or other solvents and absorbed doses used are significantly higher than those used in food irradiation applications.

Killoran (1972) reported that e-beam irradiation of plasticized PVC and PVdC/PVC films at doses in the range of 59–75 kGy increased global migration into *n*-heptane after contact at 38 °C for 6 weeks. The migrant was mainly an ester-type and an ether-type plasticizer for PVC and PVdC/PVC films respectively.

Mendizabal et al. (1996) investigated the effect of gamma radiation (100–700 kGy) on plasticized PVC and reported that plasticizer extraction resistance into various solvents increased after irradiation treatment as a result of irradiation-induced crosslinking in the polymer structure. Crosslinking was observed after a dose of 100 kGy and increased as the radiation dose increased.

Finally, Krylova et al. (1979) reported that during gamma irradiation (50–500 kGy) of plasticized PVC both the polymer and phthalic acid ester plasticizer undergo breakdown but this effect is insignificant up to a dose of 50 kGy.

3.2. Determination of diffusion coefficients

The diffusion of a substance in a polymer generally obeys Fick's second law (Little, 1983; Reynier et al., 2002):

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \quad (1)$$

where D is the diffusion coefficient.

Eq. (2) can be used instead of Eq. (1) for the initial stages of migration assuming long migration times and a D value independent of concentration (Goulas & Kontominas, 1996; Lau & Wong, 2000; Little, 1983; Till et al., 1982):

$$M_t = 2C_{p0}(Dt/\pi)^{1/2} \quad (2)$$

where M_t is the amount of plasticizer migrated in time t, expressed in mg/cm^2 and C_{p0} is the initial concentration of plasticizer in the film expressed in mg/cm^3. Time t is expressed in s.

A plot of M_t/C_{p0} against $2(t/\pi)^{1/2}$ is initially linear and has a slope of $D^{1/2}$ (Figs. 3–6). The diffusion coefficient (D) represents the migration rate of a molecule within the packaging material.

D values for irradiated and non-irradiated samples are given in Table 3 for both DEHA and ATBC plasticizers. As shown in Table 3 the irradiated samples exhibit greater D values compared to non-irradiated samples. Absorbed doses of 5, 10 and 25 kGy produced an increasing trend in D values of ATBC by 2, 15 and 19 times. In contrast, the same doses produced no significant differences in D values of DEHA. The above reported differences can be attributed to the different chemical nature as well as molecular weight of the two plasticizers.

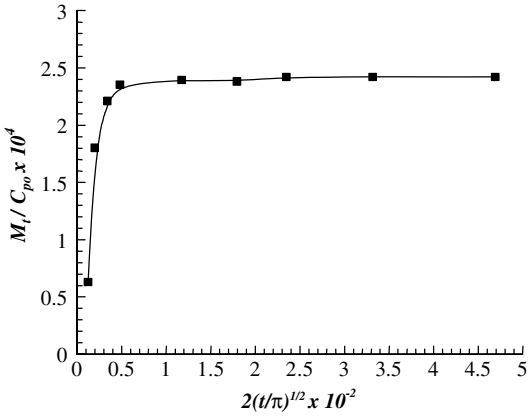

Fig. 3. Plot of $x = (t/\pi)^{1/2}$ versus $y = M_t/C_{p0}$ for DEHA from non-irradiated PVC film into isooctane at 20 °C.

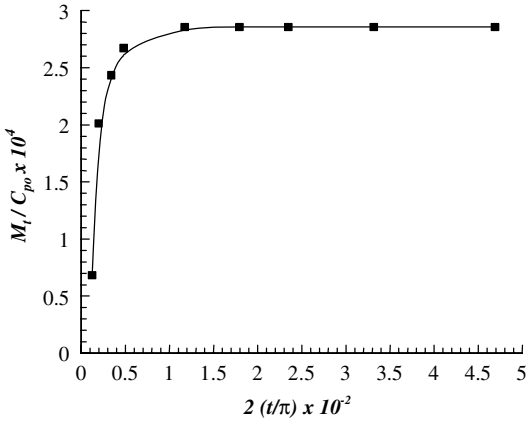

Fig. 4. Plot of $x = (t/\pi)^{1/2}$ versus $y = M_t/C_{p0}$ for DEHA from irradiated (25 kGy) PVC film into isooctane at 20 °C.

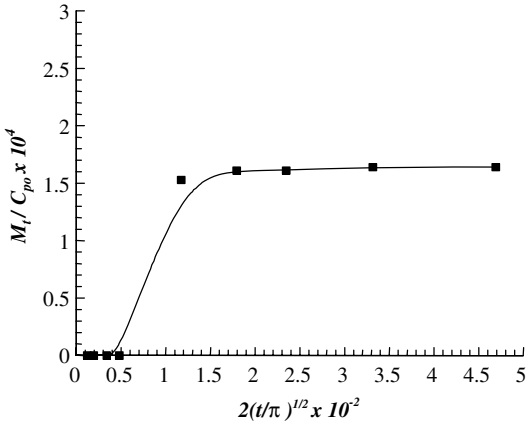

Fig. 5. Plot of $x = (t/\pi)^{1/2}$ versus $y = M_t/C_{p0}$ for ATBC from non-irradiated PVC film into isooctane at 20 °C.

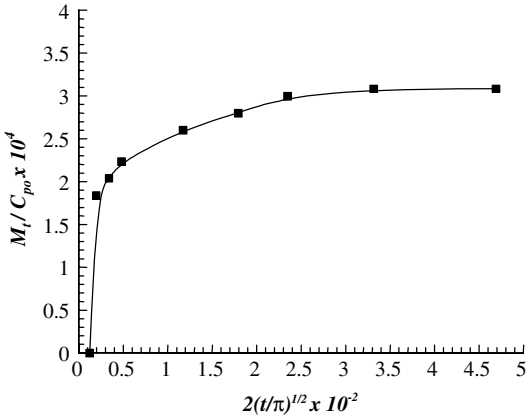

Fig. 6. Plot of $x = (t/\pi)^{1/2}$ versus $y = M_t/C_{p0}$ for ATBC from irradiated (25 kGy) PVC film into isooctane at 20 °C.

Table 3
Diffusion coefficient (D) values for control and irradiated samples

Plasticizer	D (cm^2/s)			
	Non-irradiated	Irradiated		
		5 kGy	10 kGy	25 kGy
DEHA	4.5×10^{-11}	4.9×10^{-11}	5.2×10^{-11}	5.5×10^{-11}
ATBC	2.0×10^{-14}	3.2×10^{-14}	29.0×10^{-14}	38.0×10^{-14}

There are no results in the literature for D values of DEHA after contact of plasticized PVC film with isooctane. Till et al. (1982) reported a value of 2.3×10^{-12} cm^2/s after contact of plasticized (DEHA) PVC film with corn oil at 4 °C, while Kondyli, Demertzis, and Kontominas (1990) reported a value of 3.0×10^{-14} cm^2/s after contact of plasticized (DEHA) PVC film with olive oil at 6 °C.

4. Conclusions

Based on present experimental results, the amount of DEHA plasticizer that migrated into food simulant isooctane from PVC cling-film (containing 5.3% w/w DEHA

and 3.0% w/w ATBC) after 2 days of contact at 20 °C is within the limit set by the EU (18 mg/L or 3 mg/dm^2). These results concern intermediate (5 and 10 kGy) and high doses (25 kGy) of γ-radiation. Also, lower than DEHA was the amount of ATBC plasticizer that migrated into isooctane after all absorbed doses. There is no reported limit for ATBC in the literature.

From a practical point of view and given that conditions used in the present study can be considered as a worst case scenario (in most food irradiation applications the dose used does not exceed 10 kGy, isooctane is an aggressive solvent in terms of migration testing, two side contact PVC/isooctane) one may state that this plasticized PVC film can be used in food irradiation applications.

Implications of the above results for the food packaging industry may include: (1) a trend toward partial substitution of monomeric by polymeric plasticizers (that exhibit lower migration potential in fatty foods) into PVC films, (2) a trend towards using alternative flexible films with low plasticizer content such as PVdC/PVC copolymer (Saran) film containing approximately 5% w/w ATBC.

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