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Effect of ionizing radiation treatment on the specific migration characteristics of packaging - food simulant combinations: effect of type and dose of radiation

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Abstract

Migration levels of acetyl tributyl citrate (ATBC) plasticizer from polyvinyl chloride (PVC) film into the EU specified aqueous food simulants (distilled water, 3% w/v acetic acid and 10% v/v ethanol) were monitored as a function of time. Migration testing was carried out at 40 °C for 10 days (EEC 1993). Determination of the analyte was performed by applying an analytical methodology based on surfactant (Triton X-114) mediated extraction prior to gas chromatographic-flame ionization detection. PVC cling film used was subjected to ionizing treatment with a [⁶⁰Co] source, as well as to electron-beam irradiation at doses equal to 5, 15 and 25 kGy, with the aim to compare the effect of type and dose of radiation on PVC specific migration behaviour. Equilibrium concentrations of acetyl tributyl citrate into the aqueous solvents covered the ranges 173–422 µg L⁻¹ and 296–513 µg L⁻¹ for gamma and electron-irradiated PVC, respectively. Hence, e-beam irradiation resulted in significantly higher ATBC migration compared to gamma treatment. The highest extraction efficiency of the 10% ethanol solution was common in both gamma and e-beam treatments; distilled water demonstrated the lowest migration. Gamma irradiation at intermediate doses up to 5 kGy produced no statistically significant (*p*>0.05) effect on ATBC migration into all three aqueous simulants; however, this does not apply for high-energy electrons. Both ionizing treatments were similar in that they resulted in statistically significant (*p*<0.05) differences in plasticizer migrating amounts between non-irradiated and irradiated at doses of 15 and 25 kGy samples. Gamma radiation did not affect the kinetics of plasticizer migration. On the contrary, electron-beam radiation produced shorter equilibration times for all food-simulating solvents tested at 40 °C. Above

values regarding ATBC migration into aqueous food simulants are far below the EU proposed upper limit of specific migration (5 mg kg^{-1}) for both types of ionizing radiation. Thus, PVC cling film may be used in food irradiation applications in contact with aqueous foodstuffs.

Keywords: PVC; ATBC; migration; aqueous food simulants; gamma radiation; electron beam radiation; gas chromatography

Introduction

Ionizing radiation is currently used at various dose levels for food preservation as well as sterilization of packaging materials and medical products. Ionizing treatment of food products by gamma rays of ^{60}Co , ^{137}Cs , or accelerated electrons of a maximum energy of 10 MeV is an alternative to thermal and chemical preservation methods (Molins 2001; Morehouse 1998; Wilkinson and Gould 1996).

Since the item to be irradiation processed is usually pre-packaged in order to prevent microbial re-contamination, the effect of radiation on plastic packaging materials is of prime importance, given the fact that it is directly related to the quality and / or safety of the packaged foodstuff. Plastics are affected in several ways when exposed to high-energy ionizing radiation. The polymer chains exhibit scission or cross-linking inducing changes in mechanical, thermal, and physicochemical properties. The dominant effects depend on the particular material, nature of the additives used to compound the plastic, processing history and specific conditions of irradiation (absorbed dose, dose rate, temperature, and atmosphere) (Buchalla et al. 1993a, 1993b, 2000; Deschenes et al. 1995; Gheysari et al. 2001; Goulas et al. 2004; Sears and Darby 1982; Zygoura et al. 2007).

Although the main interaction of radiation energy with matter is basically the same for gamma and high-energy electrons, minor differences between the two modes exist i.e. gamma radiation exhibits a far greater penetration power than accelerated electrons. Furthermore, typical gamma irradiators deliver dose rates approximately between 3 and 20 kGy/h, while electron accelerators deliver dose rates as much as ten thousand times higher. Under such high dose rate conditions, significant thermal effects may arise modifying the packaging material's properties. Secondly, due to this huge dose rate difference, irradiation exposure times are also vastly different. While it

is common for a gamma facility to deliver a specific dose in several hours, the electron accelerator delivers the same dose in seconds. Differences in oxygen diffusion and oxidative degradation during the exposure times constitute another differentiating factor between the two treatments (Woo and Sandford 2002).

Among potential migrants, plasticizers have raised much concern from the food safety point of view, since they are present in plastics films in significant amounts (up to 30% w/w in PVC). The plasticizers most widely used in polyvinyl chloride for food contact applications are di-(2-ethylhexyl) adipate (DEHA), di-(2-ethylhexyl) phthalate (DEHP), acetyl tributyl citrate (ATBC), epoxidized soybean oil (ESBO), and polymeric species. PVC films (cling and shrink) are clear, flexible and exhibit good resistance to water, acid, fats, and oils (Brody and Marsh 1997).

In order to avoid migration testing for a particular plastic in contact with each and every foodstuff, the use of food simulants was introduced. Directive 82/711/EEC (and its amendment Directive 97/48/EC) lists the following food simulants: (a) distilled water or water of similar quality (simulant A) for aqueous foods with a pH above 4.5, (b) 3% w/v acetic acid in water (simulant B) for acidic aqueous foods (pH below 4.5), (c) 10% v/v ethanol in water (simulant C) for alcoholic products, and (d) rectified olive oil or a synthetic mixture of triglycerides (e.g. HB 307) or sunflower seed oil or corn oil (simulant D) for fatty foods. In addition, substitute media were defined for simulant D; namely, iso-octane, 50% and 95% aqueous ethanol, and modified polyphenylene oxide (MPPO) (EC 1997; EEC 1982).

The migration of plasticizers into water and aqueous solutions is limited, yielding final concentrations in the low $\mu\text{g L}^{-1}$ range. Thus, a pre-concentration step is necessary to precede analysis. The use of pre-concentration schemes based on surfactant mediated phase separation offers an interesting alternative to conventional extraction systems. To date, cloud point extraction (CPE) has been successfully employed for the GC determination of plasticizers, polychlorinated biphenyls, 1,4-dichlorobenzene, polybrominated diphenyl ethers, organophosphorous pesticides, herbicides, alkaloids, phenothiazine, and disulfoton (Faria et al. 2007; Fontana et al. 2009; Froschl et al. 1997; Giokas et al. 2005; Paleologos et al. 2006; Shen and Shao 2006; Takagai and Hinze 2009; Zygoura et al. 2005).

The aim of the present study was to investigate the effect of type of radiation (gamma vs. e-beam), as well as absorbed dose, on specific (ATBC) migration

behaviour of polyvinyl chloride film into aqueous simulants due to radiochemical changes induced in the polymer matrix.

Materials and methods

Materials and reagents

Plasticized food-grade PVC film, 10 μm in thickness, containing $(3.0 \pm 0.1) \% \text{ w/w}$ ATBC was used. PVC was chosen as a substrate for plasticizer migration since it is one of the two commercial synthetic resins, the other being PVDC, that contains plasticizers. According to the supplier (Alex Pak SA, Athens, Greece), the film also contained both a monomeric and a polymeric plasticizer based on adipic acid. The level of acetyl tributyl citrate was determined by chloroform extraction of the film followed by capillary GC analysis.

The internal standard (octadecane) was of analytical grade, purchased from Fluka (Buchs, Switzerland). Analytical grade ATBC was purchased from Unitex Chemical (NC, USA). An appropriate amount of plasticizer was diluted with methanol to prepare a 105 mg L^{-1} stock solution, which was further diluted with double distilled water to prepare working solutions. Methanol, ethanol, acetic acid (glacial), isooctane, anhydrous sodium sulphate and potassium acetate were of analytical grade, purchased from Merck (Darmstadt, Germany). Water used was HPLC grade (Merck). Triton X-114 (Aldrich, Cat. No. 36,934-9) was used, without further purification, to prepare a 100 g L^{-1} aqueous solution.

Irradiation and migration experiments

Rectangular strips of PVC cling film (6 cm x 10 cm) were stretched on stainless steel screens in order to avoid clumping and folding. The film/screen combinations were placed into wide-mouthed glass jars (of ca. 250 mL capacity) with screw caps.

Two groups of cell assemblies were prepared. Group A was subjected to ionizing treatment using a gamma irradiator (Nordion JS 9600 model, Canada) with a 861 kCi [^{60}Co] source at doses equal to 5, 15 and 25 kGy. Irradiation was carried out at room temperature, in the presence of air. Absorbed doses were measured using Harwell Amber 3042 and Red Acrylic Perspex 4034 dosimeters; mean dose rate was 0.81 Gy/s for all samples. Irradiation was conducted at the GAMMA-PAK AS plant (Tekirdag, Turkey). Group B was subjected to high-energy electron beam irradiation using a linear accelerator (LINAC-CIRCE III, Linac Technologies SA.; Orsay, France, 10

MeV) at above-mentioned doses. Irradiation was also carried out at room temperature and in the presence of air. Absorbed doses were measured using an Alanine-ESR dosimeter and mean dose rate was 10^7 Gy/s for all samples. Electron irradiation was conducted at the Federal Research Center for Nutrition and Food (Karlsruhe, Germany).

Following ionizing treatments, the jars were filled with 200 mL of the selected simulant, sealed and placed in a temperature controlled cabinet at 40 ± 1 °C. The solvent simulants used were conditioned at the same temperature prior to the experiments. Sampling for plasticizer determination was carried out at predetermined time intervals. All experiments were carried out in triplicate with three measurements per replicate in order to ensure, as far as possible, reproducible conditions. Identical non-irradiated (control) samples were also analyzed for ATBC content under the same conditions for comparison purposes.

Directive 93/8/EEC (EEC 1993) lists time-temperature combinations to be applied to migration experiments with simulants. It should be stressed that standardized migration test conditions are, in fact, accelerated testing conditions which are used to overcome the problem of the long contact times often required in practice for packaged food migration measurements. The most general conditions used for migration testing are 40 °C for 10 days, in order to simulate storage at ambient temperature for unlimited duration. In addition, a two-sided film-simulant contact was applied in the present study, while the ratio of film area to volume of simulant was 6 dm^2 to 1 L, based on the EC Directive 90/128 (EEC 1990).

Plasticizer analysis

Cloud point extraction from aqueous simulants

The analytical procedure along with optimization experiments, are described in our previous study (Zygoura et al. 2005). Slight modifications made, in order to allow sampling of a representative portion of the simulant, are described herein: Forty milliliters of the standard or sample solution were placed in a Sarstedt centrifugal vial. Four hundred microliters of Triton X-114 stock solution, 5 mL of 1M acetate buffer pH 7.0 and 5 mL of concentrated Na_2SO_4 solution were subsequently added and mixed. Then, the mixture was left to stand for 10–15 min in a water bath at 50 °C.

Centrifugation (10 min at 4000 rpm) was performed, using a Biofuge primo R centrifuge (Heraeus, Kendro Laboratory Products GmbH, Germany), to separate the

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surfactant-rich phase from the bulk aqueous supernatant. The vials were then placed into an ice bath for 5 min to increase viscosity of the micellar phase and the aqueous supernatant was decanted by inverting the tube. One thousand microliters of isooctane containing 0.01 mg mL⁻¹ of the internal standard (octadecane) were added and the preconcentrated analyte was extracted by applying microwaves (700 W) for 2 min. Two distinct layers were formed: the surfactant-rich phase containing some water remnants (lower) and the iso-octane phase (upper).

Gas Chromatographic conditions

One microliter of the iso-octane phase was injected into a gas chromatograph model HP 5890 series II (Hewlett-Packard, Wilmington, USA) with a flame ionization detector (FID). 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 carrier gas was helium at 75 kPa (2 mL min⁻¹).

The temperature of the injector was maintained at 250 °C, while the detector was set at 300 °C. The temperature program of the GC oven was the following: 200 °C, held 1 min; rating 20 °C min⁻¹ to a temperature of 280 °C (6 min hold). Detection was performed at a split (1:5) mode.

Statistical analysis

Migration experiments were run in triplicate with three determinations per replicate ($n=9$). Average values and standard deviations were calculated for all data. Differences between pairs were defined by Student's t test and were considered to be significant at the $p \leq 0.05$ level.

Results and discussion

Analytical features of the CPE method

A stock solution of ATBC at a concentration of 105 mg L⁻¹ was prepared in methanol. Working standards were prepared by adding 5, 10, 25, 50, 80, 100, 200 and 300 µL of the stock solution to 40 mL of double distilled water. The analytical characteristics of the CPE methodology applied to the standard solutions are summarized in Table 1.

It is obvious that the analyte can be determined satisfactorily at µg L⁻¹ levels. In order to evaluate the accuracy of the method, recovery tests were carried out (Zygoura et al. 2005). Distilled water (250 mL), 3% w/v acetic acid and 10% v/v ethanol were

spiked with different volumes of a standard solution containing ATBC at a concentration of 105 mg L⁻¹. The extraction and subsequent analysis of the plasticizer was performed as described above. It was found that for water and acetic acid, the recoveries obtained were over 95% for all tested concentrations of the analyte, while for aqueous ethanol recoveries were somewhat lower, especially at high plasticizer concentrations. This was expected as, according to the literature, increased amounts of organic solvents impair micellization and extraction efficiency of surfactant aggregates (Mittal 1979).

Migration results

Kinetic study

The equilibrium migrating values of ATBC into distilled water, 3% w/v acetic acid and 10% v/v ethanol as a function of time for non-irradiated and gamma-irradiated PVC are shown in Table 2. Respective migration levels for electron-irradiated PVC are depicted in Table 3.

The concentrations of ATBC plasticizer in distilled water at equilibrium state ranged from 171 µg L⁻¹ for non-irradiated to 252 µg L⁻¹ for gamma-irradiated at 25 kGy PVC, corresponding to a migration of 285 x 10⁻⁴ to 420 x 10⁻⁴ mg dm⁻². Since the film contained 1.8 mg dm⁻² of ATBC, such migration levels represent losses which cover the range 1.6 to 2.4% of the available plasticizer. Respective values for the 3% acetic acid solution were 189 to 272 µg L⁻¹; thus, 1.8–2.5% of the available plasticizer migrated at equilibrium. In addition, after contact (40 °C) of control and gamma-processed PVC with the 10% ethanol, ATBC concentrations ranged from 331 to 422 µg L⁻¹ (3.1 to 3.9% loss) at equilibrium state.

By comparing ATBC migration data for all three food simulants tested, it becomes apparent that for untreated, as well gamma-treated PVC film the most aggressive simulant seems to be 10% ethanol, while distilled water demonstrated the lowest migration. Specifically, ATBC concentration into the alcoholic medium at equilibrium state was almost twice of that observed for the other two simulants. These differences become less significant with increasing radiation dose, but still 10% ethanol exhibits the highest extraction efficiency.

The equilibrium concentrations of ATBC in distilled water ranged between 171 and 377 µg L⁻¹ for non-irradiated and electron-irradiated (25 kGy) PVC, respectively.

Such migration levels represent losses from the polyvinyl chloride film of ca. 1.6 to 3.5% of the available plasticizer. Respective values for the acidic medium were 189 to 428 $\mu\text{g L}^{-1}$; thus, 1.8–4.0% of the available plasticizer migrated at equilibrium. In the case of the 10% ethanol solution, contamination levels ranged from 328 to 513 $\mu\text{g L}^{-1}$ (3.1 to 4.8% loss) at equilibrium state.

The highest extraction efficiency of the 10% ethanol is a common fact in both gamma and electron beam ionizing treatments. As already mentioned, such efficiency, which is more significant in untreated samples, becomes less evident with increasing radiation dose. Except for the dose, the type of ionizing radiation also narrows the gap between the three food-simulating solvents as far as their extraction efficiency is concerned; electron-irradiated PVC films exhibit less significant differences in equilibrium plasticizer concentrations between the three simulating solvents compared to gamma-irradiated films.

In addition to the above, electron beam irradiation resulted in higher ATBC equilibrium concentrations into all aqueous solvents at 40 °C compared to gamma treatment; i.e. plasticizer losses from PVC were 2.4 to 3.9% and 3.5 to 4.8% due to gamma and electron irradiation at 25 kGy, respectively. The differences in plasticizer migrating amounts observed between gamma and electron irradiated material were statistically significant ($p < 0.05$) for each of the simulants tested.

An interesting observation to be made is the higher rate of ATBC transfer from electron-irradiated PVC into all aqueous simulants at 40 °C, compared to that from gamma-treated material. More specifically, an average of $233 \times 10^{-4} \text{ mg dm}^{-2}$ of plasticizer migrated from electron-irradiated PVC within just 1 hour of contact with distilled water. This value corresponds to ca. 1.3% loss of the initial plasticizer content (total mean 3.1% loss was achieved within 12 h). In the case of gamma-irradiated film, 1.2% plasticizer loss was observed within approximately 12 hours of PVC/water contact (total mean 2.0% loss was achieved within 72 h).

Moreover, gamma irradiation at intermediate doses up to 5 kGy had no statistically significant ($p > 0.05$) effect on ATBC migration from PVC into all three aqueous simulants; however, this does not apply for high-energy electrons, since an increase in ATBC concentrations ranging from 21 to 91% was observed at such a dose. Both ionizing treatments are similar in that they result in statistically significant ($p < 0.05$) differences in plasticizer migrating amounts between non-irradiated and irradiated at doses of 15 and 25 kGy samples. Specifically, gamma irradiation at high

doses of 15 and 25 kGy led to an enhancement in total migration level of ATBC by ca. 17–28% and 27–45%, respectively. Respective values for electron-irradiated PVC were considerably higher; concentration boost reached ca. 105% (15 kGy) and 126% (25 kGy). It is worth mentioning that the 10% ethanol solution demonstrated at the same time the highest migration levels and the least significant differences between treated (gamma and electron-irradiated) and untreated samples.

Gamma radiation did not affect the kinetics of plasticizer migration. On the contrary, electron beam radiation produced shorter equilibration times for all food-simulating solvents tested at 40 °C; for example, equilibrium conditions for untreated as well as gamma-treated PVC in contact with distilled water were attained within 72 hours, whereas electron-irradiated samples reached equilibrium state within 12 hours. Furthermore, detectable amounts of ATBC were obtained after ca. eight hours of PVC-simulant contact for gamma-treated polymer, whereas ATBC concentrations exceeded the detection limit in less than one hour after electron-irradiated PVC was brought into contact with the food-simulating solvents.

Irradiation, as an energy transfer process, induces changes in the polymer matrix, which affect, among others, its migration characteristics. As reported in the literature, such treatment may result in (a) formation of cross-links and (b) scission of polymer chains. The first phenomenon is expected to repress additive migration, while the second one is expected to enhance it. The dominant effect depends on the type of polymer along with the specific conditions of irradiation. With regard to the above, it is most probable that the dominant effect in PVC treated with gamma rays or accelerated electrons at doses up to 25 kGy is scission of its macromolecular chains. Besides, according to the literature, PVC cross-linking prevails at doses much higher than those used in food irradiation applications (> 100 kGy) (Brody and Marsh 1997; Mendizabal et al. 1996). Electron beam radiation, compared to gamma radiation, is characterized by an extremely higher dose rate (10^7 vs. 0.81 Gy/s for the present study); hence, this radiation intensity delivered to the polymer at such short time period, affected its migration characteristics in a distinct mode.

It should be stressed at this point, that ATBC equilibrium concentrations into all three aqueous food simulants tested at 40 °C were extremely low for both ionizing treatments; respective ranges were 173–422 $\mu\text{g L}^{-1}$ and 296–513 $\mu\text{g L}^{-1}$. Such low contamination levels are due to (a) the ester's hydrophobic nature, high compatibility

with vinyl resins, low initial content in PVC, and (b) low percentage of absorption of the aqueous solvents by the polymer matrix (slight swelling effect).

To the best of our knowledge, limited information exists in the literature with regard to the effect of irradiation on plasticizer migration into food simulants or other solvents; also, most of these studies deal with irradiation at significantly higher doses than those used in food applications.

Data of the present study are comparable to those reported by other researchers. Till et al. (1982) reported that DOA migration from PVC to various solvents tested was higher in 8% aqueous ethanol compared to distilled water. The most efficient extracting agent, though, was heptane.

Schwöpe et al. (1986), as well as Matos et al. (1987) studied the migration of organotin compounds, used as stabilizers, from rigid PVC to food simulants followed by a 10-day contact period at 45 °C. According to the study, migration levels followed the order: isooctane > 8% aqueous ethanol > 3% aqueous acetic acid \approx water.

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

According to Goulas et al. (1998), electron beam irradiation at 20 and 50 kGy resulted in a significant increase in migration levels of DEHA and ATBC plasticizers from PVC and saran films into olive oil at 20 °C.

As reported by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE 1999), ATBC ($\leq 5\%$ w/w) loss from PVC after 48 hours of contact (25 °C) with distilled water was 1.2%; the results are in good agreement with those of the present study given the variation of experimental conditions.

The migration of a substance from a packaging material into the food or simulant in contact is a mass transfer phenomenon which depends on kinetic (i.e. diffusion of the substance into the polymer and into the food phase) along with thermodynamic (i.e. partition of the substance between the polymer and the food phase at equilibrium) parameters. Hence, in order to evaluate the rate, as well as the total amount of specific mass migration, diffusion coefficient D and partition coefficient K should be taken into consideration.

Partition coefficient (K) values may be determined experimentally or predicted via several methods. As reported in the literature, predicted K values for ATBC plasticizer follow the order: $K_{\text{PVC/ethanol}} < K_{\text{PVC/acid}} < K_{\text{PVC/water}}$ (Piringer and Baner 2000). Hence, K values with respect to ATBC migration from PVC indicate that the 10% ethanol should be the most aggressive simulant among aqueous simulants used, which is the case of the present study.

Thermodynamic properties, such as polarity and solubility, play an important role on migration due to interactions between polymer, migrant and food simulant. For example, if a migrant has a poor solubility in the food simulant, it will tend to be retained by the polymer than to migrate into the simulant. In addition, if the food simulant itself has a high affinity for the polymer, it will tend to be strongly absorbed by the polymer. Absorption of certain organic solvents causes swelling of the polymer matrix, thereby enlarging the gaps between molecules and enhancing additive migration. In the case of PVC, which is a slightly polar polymer, absorption of the non-polar isooctane at ca. 50% (25 °C) results in high migration amounts due to swelling (Zygoura et al. 2007), while for ethanol and water the absorption percentage is equal to 2.4 and 1.5%, respectively (Baner et al. 1994).

Calculation of diffusion coefficients

The diffusion of a substance within a polymer generally obeys *Fick's second law of diffusion* (Little 1983):

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

where D is the diffusion coefficient of the migrant within the polymer. Equation (1) can be used in its simplified form (2) for the initial stages of migration assuming long migration times and a D value independent of concentration (Little 1983):

$$M_t \approx 2C_{po}(D t / \pi)^{1/2} \quad (2)$$

where M_t (expressed in mg cm^{-2}) is the amount of substance migrated in time t (expressed in s) and C_{po} (expressed in mg cm^{-3}) is the initial concentration of the migrant in the polymer.

A plot of M_t/C_{po} against $2(t/\pi)^{1/2}$ is initially linear and has a slope of $D^{1/2}$. Diffusion coefficient D represents the migration rate of a molecule within the packaging material and is expressed in $\text{cm}^2 \text{s}^{-1}$ units.

Table 4 presents diffusion coefficient (D) values of ATBC into non-irradiated and irradiated PVC films in contact with the aqueous food simulants. Apparently, D values follow the same trend as equilibrium migration values; that is, the 10% ethanol produces the highest ATBC diffusion rates into the polymer matrix by causing the greatest swelling due to the highest affinity for PVC. Gamma irradiation renders lower diffusion rates, while treatment of PVC film with accelerated electrons results in an enhancement in ATBC diffusion rates by one order of magnitude. It seems that irradiation with high-energy electrons at intermediate and high doses up to 25 kGy leads to increased polymer chain mobility, due to a temperature rise, and thereby in increased diffusion rates.

To the best of our knowledge, there are no data in the literature concerning D values of plasticizers after contact of irradiated plastics materials with aqueous food simulants. In our previous study (Zygoura et al. 2007) we reported D values of ATBC into gamma-irradiated (up to 25 kGy) PVC in contact with isooctane ranging from 3.2×10^{-14} to $38 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$.

Conclusions

The migration of ATBC plasticizer into the EU official aqueous food simulants tested was limited, yielding final concentrations in the low $\mu\text{g L}^{-1}$ range; namely, 173–422 $\mu\text{g L}^{-1}$ and 296–513 $\mu\text{g L}^{-1}$ for gamma and electron-irradiated PVC film, respectively. Above values regarding ATBC migration are far below the EU proposed upper limit of specific migration (5 mg kg^{-1}) for both types of ionizing radiation. Thus, the specific film's compliance with EU specifications with respect to ATBC specific migration from plastic packaging materials into aqueous foods or aqueous food simulants, should not pose any safety concern; PVC cling film may be used in food irradiation applications in contact with aqueous foodstuffs.

Apparently PVC treatment with gamma rays of ^{60}Co or accelerated electrons at doses up to 25 kGy causes scission of its macromolecular chains. Such polymer degradation is followed by changes in physicochemical properties and thereby in increased additive diffusion rates. The extremely higher rate of energy transfer to the polymer during e-beam irradiation, compared to gamma treatment, corresponds to significantly higher diffusion rates of ATBC plasticizer within the PVC matrix, as well as significantly higher additive migration levels into the surrounding medium.

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Table 1. Analytical characteristics of the CPE method

Parameter	ATBC
Retention time (min)	5.72 ± 0.05
LOD ^a (µg L ⁻¹)	7.5
LOQ ^b (µg L ⁻¹)	25.0
RSD ^c (%)	4.2
Regression equation	$E = 5.3 \times 10^{-3} C (\mu\text{g L}^{-1}) + 1.56 \times 10^{-2}$ ^d
Correlation coefficient (r)	0.9996

Notes: ^a Limit of detection, defined as three times the signal- to- noise ratio

^b Limit of quantitation, defined as ten times the signal- to- noise ratio

^c Relative standard deviation obtained from three extractions and three injections each

^d Peak area (arbitrary units)

Table 2. Migration values of ATBC from control and gamma-irradiated PVC film into aqueous food simulants at 40 ± 1 °C

Contact time (d)	Migrated amount ^a of ATBC							
	Non-irradiated		5 kGy		15 kGy		25 kGy	
	($\mu\text{g L}^{-1}$)	(mg dm^{-2}) ($\times 10^{-4}$)	($\mu\text{g L}^{-1}$)	(mg dm^{-2}) ($\times 10^{-4}$)	($\mu\text{g L}^{-1}$)	(mg dm^{-2}) ($\times 10^{-4}$)	($\mu\text{g L}^{-1}$)	(mg dm^{-2}) ($\times 10^{-4}$)
Distilled water								
0.5	69 \pm 3	115 \pm 5	103 \pm 4	172 \pm 7	128 \pm 5	213 \pm 9	145 \pm 6	242 \pm 10
1	120 \pm 5	200 \pm 8	154 \pm 7	257 \pm 11	173 \pm 7	288 \pm 12	196 \pm 8	327 \pm 14
3	173 \pm 7	288 \pm 12	173 \pm 7	288 \pm 12	222 \pm 9	370 \pm 16	251 \pm 11	418 \pm 17
5	173 \pm 7	288 \pm 12	174 \pm 7	290 \pm 12	220 \pm 9	367 \pm 15	249 \pm 11	415 \pm 17
7	171 \pm 7	285 \pm 12	173 \pm 7	288 \pm 12	221 \pm 9	368 \pm 15	251 \pm 11	418 \pm 17
10	175 \pm 7	292 \pm 12	174 \pm 7	290 \pm 12	223 \pm 9	372 \pm 16	252 \pm 11	420 \pm 18
3% w/v acetic acid								
0.5	81 \pm 3	135 \pm 6	132 \pm 6	220 \pm 9	144 \pm 6	240 \pm 10	154 \pm 7	257 \pm 11
1	143 \pm 6	238 \pm 10	177 \pm 7	295 \pm 12	188 \pm 8	313 \pm 13	231 \pm 10	385 \pm 16
3	189 \pm 8	315 \pm 13	212 \pm 9	353 \pm 14	232 \pm 10	387 \pm 16	268 \pm 11	447 \pm 19
5	190 \pm 8	317 \pm 13	218 \pm 9	363 \pm 15	239 \pm 10	398 \pm 16	271 \pm 11	452 \pm 19
7	191 \pm 8	318 \pm 13	223 \pm 9	372 \pm 15	250 \pm 10	417 \pm 18	272 \pm 11	453 \pm 19
10	191 \pm 8	318 \pm 13	214 \pm 9	357 \pm 15	235 \pm 10	392 \pm 17	270 \pm 11	450 \pm 19
10% v/v ethanol								
0.5	149 \pm 6	248 \pm 10	176 \pm 7	29 \pm 12	195 \pm 8	325 \pm 14	268 \pm 11	447 \pm 19
1	230 \pm 10	383 \pm 16	271 \pm 11	452 \pm 19	289 \pm 12	482 \pm 20	340 \pm 14	567 \pm 24
3	270 \pm 11	450 \pm 19	303 \pm 13	505 \pm 21	343 \pm 14	572 \pm 24	391 \pm 16	652 \pm 27
5	331 \pm 14	552 \pm 23	344 \pm 14	573 \pm 24	382 \pm 16	637 \pm 27	418 \pm 18	697 \pm 29
7	328 \pm 14	547 \pm 23	346 \pm 15	577 \pm 24	390 \pm 16	650 \pm 27	422 \pm 18	703 \pm 29
10	330 \pm 14	550 \pm 23	345 \pm 14	575 \pm 24	387 \pm 16	645 \pm 27	420 \pm 18	700 \pm 29

Note: ^a Values represent the mean of three extractions and triplicate runs \pm SD

Table 3. Migration values of ATBC from control and electron-irradiated PVC film into aqueous food simulants at 40 ± 1 °C

Contact time (h)	Migrated amount ^a of ATBC							
	Non-irradiated		5 kGy		15 kGy		25 kGy	
	(µg L ⁻¹)	(mg dm ⁻²) (x 10 ⁻⁴)	(µg L ⁻¹)	(mg dm ⁻²) (x 10 ⁻⁴)	(µg L ⁻¹)	(mg dm ⁻²) (x 10 ⁻⁴)	(µg L ⁻¹)	(mg dm ⁻²) (x 10 ⁻⁴)
Distilled water								
1	< 7.5	–	111 ± 5	185 ± 8	131 ± 6	218 ± 9	177 ± 7	295 ± 12
2	< 7.5	–	170 ± 7	283 ± 12	193 ± 8	322 ± 14	246 ± 10	410 ± 17
5	< 7.5	–	248 ± 10	413 ± 17	269 ± 11	448 ± 19	329 ± 14	548 ± 23
8	< 7.5	–	290 ± 12	483 ± 20	310 ± 13	517 ± 22	369 ± 16	615 ± 26
12	69 ± 3	115 ± 5	296 ± 12	493 ± 21	319 ± 13	532 ± 22	376 ± 16	627 ± 26
24 (1d)	120 ± 5	200 ± 8	297 ± 12	495 ± 21	319 ± 13	532 ± 22	375 ± 16	625 ± 26
72 (3d)	173 ± 7	288 ± 12	297 ± 12	495 ± 21	318 ± 13	530 ± 22	376 ± 16	627 ± 26
168 (7d)	171 ± 7	285 ± 12	298 ± 13	497 ± 21	318 ± 13	530 ± 22	377 ± 16	628 ± 26
240 (10d)	175 ± 7	292 ± 12	296 ± 12	493 ± 21	319 ± 13	532 ± 22	376 ± 16	627 ± 26
3% w/v acetic acid								
1	< 7.5	–	132 ± 6	220 ± 9	161 ± 7	268 ± 11	234 ± 10	390 ± 16
2	< 7.5	–	201 ± 8	335 ± 14	237 ± 10	395 ± 17	316 ± 13	527 ± 22
5	< 7.5	–	294 ± 12	490 ± 21	330 ± 14	550 ± 23	382 ± 16	637 ± 27
8	< 7.5	–	344 ± 14	573 ± 24	380 ± 16	633 ± 27	428 ± 18	713 ± 30
12	81 ± 3	135 ± 6	361 ± 15	602 ± 25	388 ± 16	647 ± 27	428 ± 18	713 ± 30
24 (1d)	143 ± 6	238 ± 10	360 ± 15	600 ± 25	389 ± 16	648 ± 27	427 ± 18	712 ± 30
72 (3d)	189 ± 8	315 ± 13	360 ± 15	600 ± 25	388 ± 16	647 ± 27	427 ± 18	712 ± 30
168 (7d)	191 ± 8	318 ± 13	361 ± 15	602 ± 25	388 ± 16	647 ± 27	428 ± 18	713 ± 30
240 (10d)	191 ± 8	318 ± 13	361 ± 15	602 ± 25	388 ± 16	647 ± 27	428 ± 18	713 ± 30
10% v/v ethanol								
1	< 7.5	–	152 ± 6	253 ± 11	188 ± 8	313 ± 13	250 ± 11	417 ± 18
2	< 7.5	–	198 ± 8	330 ± 14	224 ± 9	373 ± 16	340 ± 14	567 ± 24
5	< 7.5	–	253 ± 11	422 ± 18	275 ± 12	458 ± 19	418 ± 18	697 ± 29

8	< 7.5	–	316 ± 13	527 ± 22	336 ± 14	560 ± 24	502 ± 21	837 ± 35
12	149 ± 6	248 ± 10	377 ± 16	628 ± 26	403 ± 17	672 ± 28	512 ± 22	853 ± 36
24 (1d)	230 ± 10	383 ± 16	396 ± 17	660 ± 28	427 ± 18	712 ± 30	512 ± 22	853 ± 36
72 (3d)	270 ± 11	450 ± 19	396 ± 17	660 ± 28	426 ± 18	710 ± 30	513 ± 22	855 ± 36
168 (7d)	328 ± 14	547 ± 23	396 ± 17	660 ± 28	427 ± 18	712 ± 30	512 ± 22	853 ± 36
240 (10d)	330 ± 14	550 ± 23	396 ± 17	660 ± 28	427 ± 18	712 ± 30	513 ± 22	855 ± 36

Note: ^aValues represent the mean of three extractions and triplicate runs ± SD

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Table 4. Diffusion coefficient values of ATBC into control, gamma-irradiated, and electron-irradiated PVC film in contact with aqueous food simulants at $40 \pm 1\text{ }^{\circ}\text{C}$

	D_{ATBC} ($\text{cm}^2 \text{s}^{-1}$) ($\times 10^{-16}$)							
	<i>Gamma-irradiated PVC</i>				<i>Electron-irradiated PVC</i>			
	0 kGy	5 kGy	15 kGy	25 kGy	0 kGy	5 kGy	15 kGy	25 kGy
10% v/v ethanol	15.5	16.0	20.9	22.3	15.5	126	138	182
3% w/v acetic acid	9.1	10.8	11.6	13.0	9.1	80	86	103
distilled water	6.1	6.2	7.4	8.5	6.1	57	62	80