Experimental direct evaluation of functional barriers in PET recycled bottles
Comparison of migration behaviour of mono and multilayers

P. Y. Pennarun a , P. Saillard b , A. Feigenbaum a , P. Dole a

a: INRA UMR FARE, Moulin de la Housse, 51687 Reims, France
b: ITOSOPE - CTCPA Technopole Alimentec, 01060 Bourg en Bresse, France

Abstract

Recycling of used bottles into new bottles is associated with possible migration of pollutants arising from the previous life of the packages. To reduce or to delay such migration, the recycled resin is depolluted, or a functional barrier layer, made of virgin plastics, is used. Testing migration from such recycled bottles relies on the use of model pollutants (surrogates). In order to enable modelling of migration kinetics, each step of the use of surrogates is carefully investigated here in the case of PET. In a first part, criteria underlying the selection of surrogates are carefully examined; besides volatility, polarity and diffusion behaviour, it is shown here that their solubility in the food simulant and their chemical stability strongly influence migration results. For aqueous test media, 2,4-pentanedione and phenol should be used as surrogates. In a second part, a procedure is developed to impregnate surrogates at very large concentrations (several thousands mg/kg PET) which are necessary to monitor migration kinetics. This procedure, which uses dichloromethane as solvent, allows a quick and reproducible impregnation, not sensitive to temperature between 11 and 23 °C, factors which favour its use at a plant scale. In a third part, flakes impregnated with this procedure are processed into bottles, and their physico-chemical properties are compared to those of commercial bottles. In a last part, monolayer and tri-layer polluted bottles (model pollutants in inner layer) are tested for migration for more than 1.5 year. With multilayers, the migration lag time of the fastest surrogates is 6 months with 3 % acetic acid, and 3 months with ethanol as simulant, due to plasticization of PET by ethanol. The sequence of migration of surrogates is different with
monolayer and with multilayer bottles, which shows that partition effects (solubility) play an essential role, especially with monolayer materials.

Keywords

Functional barriers, PET, recycling, surrogates, food simulant, consumer exposure, migration

Introduction

Recycling plastics waste has become a major issue in most developed countries. A very good outcome for used food packaging materials is to make new packages from old packages. However, this may raise food safety considerations, as post-consumption collected packages may be polluted by common chemicals available to households or to any consumers (detergents, petrol, garden herbicides or pesticides...) [1]. In order to prevent such chemicals from contaminating foodstuffs packaged in recycled plastics, various processes are available to purify the materials or to reduce migration: washing and reuse [2], depolymerisation [3, 4], post-condensation [5], use of a functional barrier [6, 7] or on line decontamination during processing [8].

Testing foodstuffs packaged in such materials for non contamination by these chemical pollutants is an impossible task, since neither the identity nor even the presence of pollutants are known. An interesting approach was proposed years ago by the Food and Drugs Administration [9]. This consists in incorporating model chemicals -or surrogates- into a resin, in order to evaluate the ability of a recycling process to purify the material and of a multilayer packaging structure to delay and to reduce migration. Resins impregnated with surrogates undergo all the steps of manufacture of new containers, including washing, drying, extrusion and/or injection. At the end of the process, the materials are extracted to determine the amount of residual surrogates and the cleaning
efficiency of the process. In addition, the finished packages can be filled with food simulants, and
the migration of residual surrogates is then monitored [10, 11, 12].

The efficiency of a functional barrier can be evaluated by the migration lag time, which is the time
needed for a surrogate to cross the barrier layer. The lag time depends on several factors, like nature
of the polymer and of the pollutant [13, 14], dimension and heterogeneity of the barrier [15], nature
of the food in contact, possible pollution of the barrier layer during processing [16]. Two
approaches are possible to evaluate the lag time: experimental evaluation of migration on materials
spiked with surrogates and prediction using numerical simulation of pollutant migration. Prediction
is of course a very good approach; however models require experimental parameters representative
of all relevant phenomena.

In this work, we will evaluate experimentally the migration from recycled mono and tri-layer
bottles with a classical geometry. The experimental data obtained will be used in another paper to
feed simulation model. We focus here on poly(ethylene terephthalate) (PET), a good candidate for
large scale recycling. Migration of model pollutants through PET functional barriers has almost
never been detected, and it has been questioned whether the physical properties of surrogates could
influence the results and the assessment of the materials [6]. FDA paid attention to polarity and
volatility, and surrogates used in most studies have been selected mainly on the basis of these
criteria (table 1).

In the current study, full migration kinetics were obtained for the first time for PET functional
barriers, which required migration data well above quantification limits. This was achieved here:
- by using a sufficient pollutant concentration in PET: since migration is proportional to the
  initial concentration in the polymer, high concentrations of surrogates were used: high
  enough to enable detection in test media, but not too high, to avoid unrealistic modifications
of PET. The concentrations used are driven by the need to be able to measure kinetics, and
are independent on any “realistic” level of pollution.

- by choosing pollutants which are likely to migrate in aqueous food simulants (surrogates
  must be soluble in test media)
- by choosing pollutants adapted to the process of artificial pollution (surrogates should not
  react with the polymer during processing at high temperature)
- by recording migration kinetics over very long contact times (over 1.5 year).

Independently of migration simulation, it will be possible to extrapolate the results obtained here
(with concentrations around 1000-1500 ppm surrogate in PET), to predict the migration from PET
polluted at “realistic” levels (around 1-3 ppm) considering that migration is proportional to the
initial concentration.

The kinetics described here will allow characterizing experimentally the properties of functional
barriers. The influence of the food simulant (ethanol and 3 % acetic acid were used here) will be
assessed, both for mono- and tri-layers. The results will provide experimental parameters which will
be used in a next paper for migration modelling [17, 18, 19], in order to support prediction of the
behaviour of PET materials.
Materials and methods

I. Materials

17 surrogates (table 2) have been selected on the basis of different volatility, molecular weight, chemical functionality or polarity (especially solubility in water). Most of them are also in usual lists of recommended substances. In order to avoid too large global concentrations of surrogates in PET, they were divided into three sets (A), (B) and (C). Each set of surrogates was incorporated separately, thus minimising alteration of PET physical-chemical properties. The sets were defined in order to prevent reactions between surrogates.

2,5-Thiophenediylibis(5-tert-buty-1,3-benzoxazole) (Uvitex OB) (>96%) was supplied by CIBA (France). Phenol (99%), chlorobenzene (99%), 2,6-dibutyl-4-methylphenol (BHT) (99%), azobenzene (99%), phenyl benzoate (99%), toluene (99%), nonane (99%), dimethyl sulfoxide (DMSO) (99%), benzophenone (99%), phenylcyclohexane (98%) were supplied by Acros (France). Chlorooctane (99%), dibutyl phthalate (99%), 2,4-pentanedione (99%) and ethyl hydrocinnamate (99%) were supplied by Aldrich (France). 1,1,1-Trichloroethane (99%) was supplied by Fluka. Methyl palmitate (>96%) was supplied by ICN Biomedicals Inc (France). PET flakes from an industrial processing recycling plant were supplied by Amcor PET Packaging Recycling France (Dunkerque, France).

II. Thermal analysis

Modulated Differential Scanning Calorimetry (MDSC) was performed with MDSC2920 (TA Instruments) to evaluate reversible and non reversible heat flow. PET samples (10 mg), taken at a distance X from the bottom of bottles were placed in aluminium pans closed with a sealed cap to prevent modifications of sample contact surface with DSC sensors during experiment.
modifications are due to relaxation of orientation during heating [20]. The heating rate was 5°C/min, the oscillation period was 60 seconds and the amplitude was 0.796°C (heat only mode).

Melt Flow Indexes (MFIs) were determined on a Davenport Melt Viscosimeter (Farcham, UK).

III. Impregnation by surrogates and processing of model materials:

Experimental conditions differ for each experiment, as they were optimised progressively to achieve a target concentration. Changing the concentration of a single surrogate in the dichloromethane solution affects the final concentrations of all the other surrogates in the polymer. However, when the conditions are well defined, the final concentrations are well reproducible.

Solvent effects on impregnation kinetics

PET samples taken from bottle walls (sides of the bottles) were immersed in a solution of surrogates in dichloromethane or heptane.

Impregnation in dichloromethane: several concentrations in impregnation solution were used (see conditions in following paragraphs).

Impregnation in heptane: 2.5 g of PET pieces of bottle walls were placed in 20 ml of a solution of toluene and 1,1,1-trichloroethane in heptane at 40°C. This solution contained 66.2% (w/w) heptane, 20.5% (w/w) 1,1,1-trichloroethane and 13.3% (w/w) toluene. At regular intervals of time, PET pieces were removed from the mixture, rapidly washed superficially with ethanol (1 min), and extracted by dichloromethane.

Rinsing of flakes: when flakes are washed by immersion into ethanol on a pilot plant scale, it may be difficult to control the washing time. Therefore, different rinsing times (1-10 minutes) were
checked on a laboratory scale. It allowed ascertaining that washing did not significantly modify the concentration of the surrogates in the flakes.

Temperature effect on impregnation

A dichloromethane solution of set B [phenol (1.1 % w/w), BHT, chlorobenzene, chlorooctane, 1,3 – butanediol (each 1 % w/w), Uvitex OB (0.54 % w/w)] was used to evaluate the effect of temperature on impregnation. 1 g of flakes was placed in a flask with 50 ml of the dichloromethane solution. The flasks were immersed in a bain-marie at 11, 17 and 23°C. After 5 days, flakes were separated and washed with ethanol at the same temperature for 1 minute, and then extracted as described below.

Reactivity of surrogates in dichloromethane at 40°C

50 ml of solutions of each of the 3 set of surrogates (500 mg each/l) in dichloromethane were stirred for 7 days at 40°C. Samples of 1 µl were analysed by GC-FID at regular interval of time. The internal standard was tetradecane for sets A and B, and toluene (non reactive substances) for set C.

Effects of drying at 150°C and injection at 280°C processes

26 g of PET flakes were introduced in a flask with 92 g of each surrogate solution. The system was stirred regularly. After 5 days at room temperature, the PET flakes were washed twice with 20 ml of ethanol.

Solutions of surrogates for impregnation into flakes were prepared as shown in table 3:

Simulation of drying at 150°C was realised in an oven, under air aspiration. Samples of the flakes were removed periodically, and the surrogates were extracted by dichloromethane and analysed as described below (section IV).
To evaluate injection process effects, impregnated PET flakes (0.4 g) were first dried for 3 hours at 150°C, then placed in a pyrex tube (8 cm long x 6 mm diameter). The top of the tube was sealed under vacuum while the flakes were cooled with ice, to prevent evaporation of the surrogates. The sealed tubes were then heated at 280°C for 5 minutes. After cooling, surrogates were extracted with dichloromethane (32 hours at 40°C), and analysed as described below (section IV).

Manufacture of impregnated bottles:

Impregnation conditions are described in table 3. After 5 days incubation in the solution, the flakes were removed and washed twice with ethanol (2 x 8 l). The flakes were heated at 150°C for 3 hours in a ventilated oven to remove dichloromethane and water. They were then sent to the plant, where they were dried again at 150°C for 3 hours. Preforms were injected by Amcor PET Packaging Recycling France (Dunkerque, France) and bottles were blown. Monolayer (100% of impregnated PET) and tri-layer (25% of impregnated PET) bottles were obtained. The materials were stored at –20°C to prevent evaporation of surrogates and their diffusion.

IV. Extraction and quantification of surrogates in PET.

Flakes (less than 0.5g) were extracted with 10 ml of dichloromethane in a closed vial (SVL screw stopper tube, diameter 15) for 32 hours at 40°C. It was checked in separate experiments that this time was needed for a quantitative extraction of the cyclic PET trimer (molecular weight 576 g/mol, larger than that of any surrogate) [21]. 1 ml of tetradecane internal standard solution in dichloromethane (50 mg/l) was then added. Results were expressed as a function of PET mass after flakes drying at 150 °C for 3 h. Extracts were analysed by GC-FID (on column mode) as follows:

1,1,1-Trichloroethane, phenylcyclohexane: The column was a DB5-MS J&W Scientific (15 m x 0.32 mm x 1 µm). Carrier gas (He) flow was 2 ml/min at 40 °C. FID temperature was 300 °C, H₂ and air flows were 25 and 250 ml/min respectively. The oven program was: 40 °C for 4 minutes,
ramp 15 °C/min up to 132 °C, isotherm for 6 minutes, heating 15 °C/min up to 270 °C and isotherm for 3 minutes.

DMSO, methyl palmitate, benzophenone, ethyl hydrocinnamate: the column was a DB-WAX J&W Scientific (30 m x 0.25 mm x 0.25 µm). Carrier gas (He) flow was 1.8 ml/min at 40 °C. FID temperature was 240 °C, H₂ and air flows were 25 and 250 ml/min respectively. The oven program was: 40 °C for 5 minutes, ramp 15 °C/min up to 230 °C, isotherm for 3 minutes.

BHT, Uvitex OB: The column was a DB5-MS J&W Scientific (15 m x 0.32 mm x 1 µm). The carrier gas (He) flow was 2 ml/min at 40 °C. FID temperature was 330 °C, H₂ and air flows were 25 and 250 ml/min respectively. The oven program was: 40 °C for 5 minutes, ramp 15°C/min up to 320°C, isotherm for 11 minutes.

Phenol, chlorobenzene, 1-chlorooctane: The column was a DB-WAX J&W Scientific (30 m x 0.25 mm x 0.25 µm). Carrier gas (He) flow was 1.8 ml/min at 40°C. FID temperature was 240°C, H₂ and air flows were 25 and 250 ml/min respectively. The oven program was: 40°C for 5 minutes, ramp 15°C/min up to 210°C, isotherm for 3 minutes.

Azobenzene, nonane: The column was a DB5-MS J&W Scientific (15m x 0.32mm x 1µm). Carrier gas (He) flow was 2 ml/min at 40°C. FID temperature was 300°C, H₂ and air flows were 25 and 250 ml/min respectively. The oven program was: 40°C for 8 minutes, ramp 15°C/min to 170°C, ramp 2°C to 180°C, ramp 15°C/min up to 240°C, isotherm for 2 minutes.

2,4-Pentanedione, DBP, phenyl benzoate, toluene: The column was a DB-WAX J&W Scientific (30m x 0.25mm x 0.25µm). Carrier gas (He) flow was 1.8 ml/min at 40°C. FID temperature was 240°C, H₂ and air flows were 25 and 250 ml/min respectively. The oven program was: 40°C for 4 minutes, ramp 15°C/min up to 230°C, isotherm for 4 minutes.
Migration tests

Migration from model bottles into 3 % acetic acid

Acetic acid/water (3% w/v) is used as food simulant. Ultrapure water and acetic acid Normapur for analysis (PROLABO) are used. Each bottle is filled with 1.5 l of simulant, closed tightly with a screw stopper and placed at 40°C. Each bottle gives only one migration measurement at time t.

Samples of 75 ml are neutralised with 10 M sodium hydroxide. 20 g of sodium chloride are added and the solution is extracted for 12 hours in a closed vial with 3 ml dichloromethane containing 50 mg/l tetracane. Control extraction tests showed that recovery rate of every surrogates is close to 100%, except for DMSO (0%), 2,4-pentanedione (66%) and phenol (33%).

Extracts are analysed directly by on-column GC-FID (on column mode) as follows:

\textbf{1,1,1-Trichloroethane, phenylcyclohexane:} The column is a DB5-MS J&W Scientific (15 m x 0.32 mm x 1 µm). Carrier gas (He) flow is 2 ml/min at 40°C. FID temperature is 300°C, H$_2$ and air flows are 25 and 250 ml/min respectively. The oven program is: 40°C for 4 minutes, ramp 15°C/min to 132°C, isotherm for 6 minutes, heating 15°C/min up to 270°C and isotherm for 3 minutes.

\textbf{DMSO, methyl palmitate, benzophenone, ethyl hydrocinnamate:} The column is a DB-WAX J&W Scientific (30 m x 0.25 mm x 0.25 µm). Carrier gas (He) flow is 1.8 ml/min at 40°C. FID temperature is 240°C, H$_2$ and air flows are 25 and 250 ml/min respectively. The oven program is: 40°C for 5 minutes, ramp 15°C/min up to 230°C, isotherm for 3 minutes.

\textbf{BHT, Uvitex OB:} The column is a DB5-MS J&W Scientific (15 m x 0.32 mm x 1 µm). The carrier gas (He) flow is 2 ml/min at 40°C. FID temperature is 330°C, H$_2$ and air flows are 25 and 250 ml/min respectively. The oven program is: 40°C for 5 minutes, ramp 15°C/min up to 320°C, isotherm for 11 minutes.
Phenol, chlorobenzene, 1-chlorooctane: The column is a DB-WAX J&W Scientific (30 m x 0.25 mm x 0.25 µm). Carrier gas (He) flow is 1.8 ml/min at 40°C. FID temperature is 240°C, H₂ and air flows are 25 and 250 ml/min respectively. The oven program is: 40°C for 5 minutes, ramp 15°C/min up to 210°C, isotherm for 3 minutes.

Azobenzene, nonane: The column is a DB5-MS J&W Scientific (15m x 0.32mm x 1µm). Carrier gas (He) flow is 2 ml/min at 40°C. FID temperature is 300°C, H₂ and air flows are 25 and 250 ml/min respectively. The oven program is: 40°C for 8 minutes, ramp 15°C/min to 170°C, ramp 2°C to 180°C, ramp 15°C/min up to 240°C, isotherm for 2 minutes.

2,4-Pentanedione, DBP, phenyl benzoate, toluene: The column is a DB-WAX J&W Scientific (30m x 0.25mm x 0.25µm). Carrier gas (He) flow is 1.8 ml/min at 40°C. FID temperature is 240°C, H₂ and air flows are 25 and 250 ml/min respectively. The oven program is: 40°C for 4 minutes, ramp 15°C/min up to 230°C, isotherm for 4 minutes.

Detection limits (and recovery yields): 1,1,1-Trichloroethane: 10 ppb (100 %), 1-chlorooctane: 5 ppb (100 %), 2,4-pentanedione: 10 ppb (66 %), azobenzene: 15 ppb (100 %), benzophenone: 10 ppb (100 %), BHT: 2 ppb (100 %), chlorobenzene: 5 ppb (100 %), DBP: 5 ppb (100 %), DMSO: (0 %), ethyl hydrocinnamate: 5 ppb (100 %), methyl palmitate: 5 ppb (100 %), nonane: 3 ppb (100 %), phenol: 10 ppb (33 %), phenyl benzoate: 5 ppb (100 %), phenylcyclohexane: 5 ppb (100 %), toluene: 5 ppb (100 %).

Migration from model bottles into ethanol

Absolute ethanol (pure for analysis, SDS) is used as a simulant. Each bottle is filled with 1.5 l of simulant and placed at 40°C. Samples (10 ml) are regularly taken from bottles. 100 µl of ethanol containing 1527 g/l of tetradecane as internal standard are added to the samples. These samples (6 µl) are analysed by GC-FID with Split/Splitless injection technique (Splitless time is 20 s and flow is 20 ml/min) as follows:
**1,1,1-Trichloroethane:** The column is a DB1-MS J&W Scientific (15 m x 0.53 mm x 5 µm). Carrier gas (He) flow is 2 ml/min at 40°C. Injector temperature is 230°C, FID temperature 280°C, H₂ and air flows are 25 and 250 ml/min respectively. The oven program is: 70°C for 5 minutes, ramp 25 °C/min to 280°C, isotherm for 7 minutes.

**DMSO, methyl palmitate, benzophenone, ethyl hydrocinnamate, phenylcyclohexane:** The column is a DB-WAX J&W Scientific (30 m x 0.25 mm x 0.25 µm). Carrier gas (He) flow is 1.8 ml/min at 40°C. Injector temperature is 220°C, FID temperature is 240°C, H₂ and air flows are 25 and 250 ml/min respectively. The oven program is: 70°C for 5 minutes, ramp 15°C/min to 230°C, isotherm for 6 minutes.

**Phenol, chlorobenzene, 1-chlorooctane, BHT:** The column is a DB-WAX J&W Scientific (30 m x 0.25 mm x 0.25 µm). Carrier gas (He) flow is 1.8 ml/min at 40°C. Injector temperature is 220°C, FID temperature is 240°C, H₂ and air flows are 25 and 250 ml/min respectively. The oven program is: 70°C for 5 minutes, ramp 15°C/min to 230°C, isotherm for 6 minutes.

**Nonane, 2,4-Pentanedione, toluene:** The column is a DB1-MS J&W Scientific (15 m x 0.53 mm x 5 µm). Carrier gas (He) flow is 2 ml/min at 40°C. Injector temperature is 230°C, FID temperature is 280°C, H₂ and air flows are 25 and 250 ml/min respectively. The oven program is: 70°C for 6 minutes, ramp 25°C/min to 280°C, isotherm for 7 minutes.

**DBP, phenyl benzoate, azobenzene:** The column is a DB-WAX J&W Scientific (30m x 0.25mm x 0.25µm). Carrier gas (He) flow is 1.8 ml/min at 40°C. Injector temperature is 230°C, FID temperature is 240°C, H₂ and air flows are 25 and 250 ml/min respectively. The oven program is: 70°C for 5 minutes, ramp 25°C/min to 230°C, isotherm for 7 minutes.

In the case of mechanical recycling, when collected bottles are washed, chopped and their flakes are mixed with those of clean bottles, the concentration of adventitious pollutants drops to very low amounts, probably well below the detection limits of the most common analytical methods. However, when the purification efficiency of a process has to be determined, or if the aim is to model migration kinetics, much larger concentration of surrogates are needed, well above the detection limits. We decided that a target concentration of 1000 (± 50 %) ppm of each surrogate in the recycled layers was necessary to obtain migration kinetics with a good sensitivity. Since we intended to test a large number of surrogates, this lead to split them into three series, which were incorporated separately, to avoid overload of the PET matrix. Surrogates used should cover a broad range of molecular weight, shape, functionality and solubility in food simulants.

I. Selection of surrogates.

**Volatility**: Low molecular weight migrants usually migrate the fastest and are therefore those of major concern for safety assessment. On the other hand, the more volatile the surrogates, the easier is their evaporation during the drying of flakes, in an air stream at 150 - 180°C. This was addressed by using surrogates covering a broad range of molecular weights (table 2), up to 431 g/mol (Uvitex OB). Dedicated experiments will be shown in the section “influence of drying” [22].

**Polarity**: Polarity both influences the compatibility of surrogates with the polymeric matrix and the solubility in food simulants. To have surrogates capable to migrate into aqueous test media, we have investigated the behaviour of very hydrophilic compounds, namely triethylamine, dodecylamine, 1,3-butanediol, DMSO, 2,4-pentanedione and phenol. Triethylamine, dodecylamine and 1,3-butanediol were removed from our sets after testing for their reactivity (see below, they graft on PET) and they do not appear in table 2.
Suitability of analytical methods: some surrogates are introduced in the list for specific methods, as azobenzene, to visualize the functional barrier under a microscope. In another work, 2,4-dimethoxyacetophenone was used to monitor diffusion in molten polymers [23].

Reactivity of surrogates: organic chemicals may be reactive at PET process temperatures. Surrogates may undergo rearrangements, oxidation or grafting on polymer chains. Reactive surrogates would be non detectable in migrates, for reasons other than food safety, and they must be discarded. Hydroxyl and amine functional groups enhance the solubility of surrogates in water. However they are also very reactive and may induce reactions with other surrogates or with the solvent used for impregnation of flakes; at high temperatures, they may also undergo transesterification or ester-amide exchange reactions with PET, and this must be carefully checked. The reactivity of surrogates was monitored without trying to identify reaction products, only by checking whether the surrogates could be extracted after being submitted to the following conditions:

- at 40°C, in solution in dichloromethane (without flakes), for 7 days. Dichloromethane is the solvent used both for impregnation and for extraction of PET flakes. These experiments cover the conditions used for both extraction of surrogates prior to their analytical determination (1.5 days at 40 °C) and for the impregnation step (5 days at 20 °C).
- at 150°C for 3 hours, simulating the drying
- at 280 °C (after drying 150°C for 3 hours) for 5 minutes in a sealed tube, for simulation of the injection conditions (without allowing evaporation of the surrogates).

a) In dichloromethane at 40°C, all surrogates were stable over the 7 days, except triethylamine, which slowly reacted with dichloromethane (50 % loss). It could therefore not be used as surrogate, as it was incompatible with the use of dichloromethane as impregnation and extraction solvent.
b) Reactivity of surrogates in conditions simulating drying at 150°C followed by injection at 280°C:

Impregnated flakes were dried at 150°C for 3 hours and heated at 280°C for 5 minutes (2-3 times longer than the industrial process). Surrogates eliminated because they were not recovered are not in table 4.

Results are shown in table 4. In all cases, except for Uvitex OB, the concentrations of surrogates are affected mainly by treatment at 150°C. The surrogates are either evaporated, or did undergo degradation by reaction with PET or with another surrogate.

After heating at 280°C, the DMSO concentration (initial concentration at 20 °C in PET was 4900 ppm) was too low to be quantified. However, increasing its initial concentration in the solution (its concentration in PET was 7600 ppm before drying) enabled the incorporation of 1363 ppm of DMSO in monolayer bottles. Only then was its quantification possible in migrates, at the end of the study (our target) (table 4).

With triethylamine and dodecylamine surrogates, PET became brown and none of these amines could be extracted anymore. The colour did not disappear after extraction, suggesting that amines are probably reacting with PET (grafting or amidation). Similarly, 1,3-butanediol was not recovered after any of the process simulation experiments (esterification, transesterification). These compounds were eliminated from the list of surrogates.

Some surrogates are selected to be used as microscopy UV probes, e.g. azobenzene and Uvitex, in order to measure the thickness of the recycled layer by observation under UV light. After successive
trials, a target of 1000 mg ± 50% of surrogates /kg finished PET materials was selected for an easy detection of the probe in simulants and bottles.

To obtain 1000 ppm surrogate in the finished PET article, allowing to monitor migration kinetics, we had to start with much higher initial concentrations (IC in table 4) just after impregnation. We stress again that these levels are well above any realistic level of pollution, but that it is needed to be able to monitor migration kinetics.

This shows that the normal PET processing conditions already contribute significantly to clean the material, and to remove pollutants, if they were present.

**Distribution in the mass:** for repeatability and reproducibility of analytical determinations, surrogates should be uniformly distributed over the mass of the material. Moreover, if the aim is to test the efficiency of industrial washing procedures (using aqueous solutions), it is essential to have a distribution of surrogates in the core of the material. Otherwise, if surrogates are only adsorbed on the surface, the efficiency of the washing steps might be overestimated [4, 28], which would reduce the safety margin for risk assessment of consumer’s exposure.

To check that surrogates do not influence in an unrealistic manner the characteristics of the final PET material studied, a viscosity control at injection temperature is necessary. Reactions (grafting and/or degradation) and plasticization could affect this viscosity, which will also be investigated through glass temperature controls. Orientation and cristallinity should be reasonably close to those of commercial PET bottles.
II. Impregnation of Surrogates

For impregnation of PET by surrogates, PET flakes were placed in a solution of surrogates in a solvent. The choice of the solvent strongly affects PET resin properties and leads to different impregnation results.

Solvent effects:

Impregnation of surrogates is expected to be more reproducible when the kinetics reach a plateau. The choice of the impregnation solvent is critical in this case. Impregnation kinetics were therefore monitored with two solvents having completely different behaviours: heptane, which is considered as chemically and physically inert [29], and dichloromethane, known for its remarkable swelling and plasticizing effect on PET [30].

Conditions (1): heptane has been used as a vehicle for surrogates at 40°C for 14 days, and uptake kinetics of toluene and 1,1,1-trichloroethane by PET bottle walls pieces was monitored (figure 1).

Conditions (2): dichloromethane was chosen, in order to reduce the testing time. It was used at ambient temperature. In order to have measurable kinetics, we monitored uptake of the highest molecular weight surrogate, namely Uvitex OB, whose uptake rate is expected to be the slowest, whatever the solvent (diffusion coefficients are more or less proportional to exp[M]).

Using heptane, impregnation is still continuing after 26 days, following apparent Fickian diffusion kinetics (figure 1). In contrast, a plateau was reached with dichloromethane after 2.5 days for the highest molecular weight surrogate: Uvitex OB (figure 1). The data compiled in figure 1 are of different experimental design. No kinetic conclusion is drawn, even though lines are drawn for the kinetics. However there is such a difference between the behaviour of heptane and that of dichloromethane that it can be concluded that use of dichloromethane is as a very fast means to impregnate PET.
Dichloromethane thus appears as a good candidate for large scale treatments of flakes. The effect of dichloromethane on processability was also assessed, using Melt Flow Indexes (MFI). MFIs of both type of virgin flakes and of flakes swollen with dichloromethane, and then dried (150 °C, 3 h) were compared. No significant difference could be observed between the two types of PET (0.75 dl/g).

It thus appeared that despite the strong physical modifications of the PET structure induced by dichloromethane during impregnation, drying of the flakes removed most of the solvent. TGA data (not shown here) demonstrate that the level of volatiles (water and dichloromethane) was below 1% after this first treatment. A second identical treatment was applied just before injection to remove residual water, as usual in PET processing. The concentration of volatiles was not measured after this second treatment, but from the yields of evaporation (table 4) of other volatile compounds, the residual concentration of dichloromethane is expected to be very low (probably even lower than the other surrogates which are less volatile).

Temperature effect on impregnation:

Since impregnation tests often have be run on a large scale (when a process has to be assessed), it is important to know whether the procedure requires a strict temperature control. Therefore, impregnation of PET flakes by dichloromethane was run at 11, 17 and 23 °C for set (B) surrogates, for 5 days (conditions corresponding to figure 1). No sensible difference was observed in the concentrations of the surrogates in PET flakes at the different temperatures, even for Uvitex OB (the highest molecular weight, corresponding to the slowest sorption kinetics). The impregnation procedure using dichloromethane (5 days, till the plateau) can thus be run at room temperature, and is not sensitive to temperature fluctuations.

The use of dichloromethane as vehicle for surrogates impregnation at room temperature, allowed reaching a plateau within 2.5 days at 20°C for the sorption of Uvitex OB which has the highest
molecular weight corresponding to the lowest diffusion coefficient (figure 1). Then, in all experiments reported below, the PET flakes were incubated in the solution of surrogates for 5 days.

III Influence of high temperature drying on residual levels of surrogates

Typically, PET is dried in any industrial processes for 6 to 8 hours at 150 –180 °C under air circulation. In this section, we investigate about possible evaporation of pollutants during drying. Impregnated flakes were dried in an oven at 150 °C for 3 hours to remove dichloromethane and were then sent to the industrial converter in tightly closed barrels. Once on the plant, a second drying step (150 °C, 3h) was applied just before preform injection. The effect of drying time on surrogates concentrations was monitored (example of set B is given on figure 2). Except Uvitex, a strong initial decrease of the concentrations of all surrogates by a factor 3 [DMSO, chlorobenzene, phenol, chlorooctane] to 8 [2,4-pentanedione, toluene] was observed, mainly during the first 3 hours at 150 °C. These results show that drying contributes considerably to the removal of volatile pollutants from PET, and, finally, to consumers safety.

IV Characterisation of bottles impregnated with surrogates

Two types of bottles and of preforms were processed: monolayers (made from 100% impregnated PET) and tri-layers (with 25% impregnated PET).

Determination of surrogate’s distribution in the bottles:

The concentrations of surrogates in monolayer bottles (table 4) effectively correspond to those targeted (1000 ppm ± 50%). Exceptions are 1,1,1-trichloroethane, benzophenone and phenol, which exceeded 2500 ppm. Losses during processing were lower than in model experiments. Our test in
the sealed tube at 280°C was probably more stringent than reality (5 minutes instead of around 2 min). Surrogates were indeed lost by reactivity and by evaporation, but losses were less important than expected from the preliminary model experiments.

In tri-layer bottles, the concentrations of the surrogates were determined in the neck, in the bottom and at four places in the wall, identified by their distance X (cm) to the bottom (figure 3). Necks do not contain any surrogate. This arises from the fact that in commercial bottles, the manufacturer does not introduce any recycled PET in the neck, as this part of the bottle could be in contact with mouth of consumers. In the bottom of bottles, concentrations of surrogates are lower than in the body because at the end of injection, virgin PET is injected to compensate for thermal retract during cooling.

Along the walls of the bottles, the concentrations were not homogeneous showing that the thickness of the virgin and impregnated layers is not constant. However, the average value of the four points of measurement in the wall (X=3, 10.5, 18 and 25.5 cm) was equal to 25% of the value of concentrations in the monolayer bottle. This corresponded indeed to the ratio of impregnated/virgin PET in tri-layer bottles.

**Physical characterisation of bottles**

Samples, taken in the wall of our model bottles (between X=3 and 25.5 cm), were compared to commercial bottles by MDSC. Results are shown in figures 4 and 5. The glass temperature of test bottles (70°C) was lower than that of commercial bottles (80°C). These differences also appeared in reversible and irreversible heat flow thermograms. Transition temperatures of model bottles were lower, showing a plasticization by the surrogates. Since diffusion is accelerated by plasticization effects, these characteristics of model bottles should lead to slightly overestimated migration and
will then enable evaluation of consumer’s exposure with an additional safety margin for public health protection.

Tri-layer bottles and preforms were cut into slices (by transversal microtomy) and their cross sections were analysed by visible light microscopy (to observe azobenzene) and fluorescence (for Uvitex). The thickness of the layer was not constant, which was quantitatively consistent with results shown in figure 5. No clear diffusion gradient could be observed for azobenzene and Uvitex OB, then it seemed that limited diffusion of those surrogates occurred during the preform and bottle manufacturing steps. Moreover, it can be concluded that little or no blending of virgin and recycled PET occurs during preform injection. The impregnated layer was not in the middle of the bottle wall. However, the thickness of the functional barrier in bottles was ranging from 60 to 75 µm for these two dying substances.

**IV Migration testing.**

*Monolayer bottles*

Figures 6 and 7 show migration kinetics from monolayer bottles into ethanol and into 3 % acetic acid. The migration rate of surrogates from monolayers is function of the initial pollutant concentration in the polymer, of their diffusion coefficient in PET and of their partition coefficient between packaging and simulant. In a first approximation, to compare the results, we can assume that all initial concentrations in PET (500 – 1500 ppm) are in the same order of magnitude. Partition effects are not expected to play an important role with ethanol, as (i) ethanol is a good solvent of all the surrogates studied and (ii) the large [simulant / packaging] volume ratio favours the transfer into the simulant. As a consequence, migration into ethanol is expected to be mainly dependent on the diffusivity of the surrogates, which itself is known to be more or less a decreasing function of the molar volume [6, 31, 32]. This is indeed the case, as we have the sequence:
In ethanol (figure 7): Phenol (94) > DMSO (78) ≃ pentanedione (100) > chlorobenzene (113) > toluene (92) ≃ trichloroethane (133) > benzophenone (182) > chlorooctane (149) > nonane (128) ≃ ethyl hydrocinnamate (178) > phenyl benzoate (198) > phenylcyclohexane (160) > dibutyl phthalate (278 g/mole).

The migration behaviour is different in 3 % acetic acid, partition obviously playing an important role, besides diffusivity. Consequently, the largest migration values are obtained for molecules which are both fast diffusing and water soluble.

In 3 % acetic acid (figure 6): Phenol (94) >> pentanedione (100) > chlorobenzene (113) > toluene (92) > benzophenone > trichloroethane > ethyl hydrocinnamate (178) > nonane (128), chlorooctane (149), phenylcyclohexane (160), phenyl benzoate (198) and dibutyl phthalate (278 g/mole).

There seems to be an influence of molecular weight, as the lower molecular weight compounds are most likely more soluble in aqueous media. Thus, the hierarchy between migration of phenol, 2,4-pentanedione, chlorobenzene and toluene is the same in the case of a contact with ethanol and of a contact with 3 % acetic acid. For higher molecular weight compounds (between 130 and 200 g/mol), migration behaviour is totally different in both simulants: polar molecules lead to larger migrations, and partition plays a major role. Despite a 182 g/mol molecular weight, benzophenone migrates more than trichloroethane (133 g/mol), as its solubility is likely to be larger in 3 % acetic acid (the simulant) than in distilled water (see table 2). In the same way, ethyl hydrocinnamate (178 g/mol) is detected in 3% acetic acid after 500 days, while the apolar nonane (128 g/mol), chlorooctane (149 g/mol) and phenylcyclohexane (160 g/mol) are not detected. Surrogates with molecular weight above 200 g/mol are not detected, even after 300 days of contact, because both their solubility in water and their diffusivity in PET are too low.
DMSO was not recorded for analytical reasons (easy to analyse in pure water by several GC or LC experimental methods; it was not recovered in the presence of 3 % acetic acid).

**Tri-layer bottles**

Figures 8 and 9 show migration behaviour of tri-layer bottles in contact with 3 % acetic acid and ethanol. As expected from results above, only fast and water soluble molecules migrate into the aqueous simulant. Surrogates are detected in the aqueous simulant only after 6 months of contact. If we now try to foresee the possible migration of real pollutants, recent studies have shown that the highest realistic levels of pollution of PET flakes are in the 1-3 ppm range [33, 34]. Since migration is proportional to the initial concentration of the pollutants in PET, a worst case realistic migration can be extrapolated from the data in figure 8: with an initial concentration of a pollutant in PET around 1500 ppm, any migration at \( t = 625 \) days \( \left( t^{0.5} = 25 \text{ days}^{0.5} \right) \) is always below 0.016 ppm. With a 3 ppm concentration, the migration would be 500 times lower (i.e. 0.32 ppb), which is well below any threshold of concern. With ethanol (figure 9), the largest measured migration at \( t = 6 \) months is 0.5 ppm, which corresponds to 1 ppb migration for a concentration in PET of 3 ppm. Consumer protection from accidental contamination is therefore also at least 6 months with ethanol, and 2 years with aqueous acidic beverages.

Comparing migration of tri-layers and monolayers, a remarkable result is that the hierarchy between surrogates migration rates is different: this is due to the fact that during the lag phase, only diffusion plays a role (diffusion from the inner layer through the barrier), while migration (which occurs after the lag phase) is also connected to packaging / food partition effects, as for monolayers.

In 3% acetic acid (figure 8): pentanedione (100) > chlorobenzene (113) > Phenol (94) > toluene (92) >> chlorooctane (149 g/mole).

In ethanol (figure 9): pentanedione (100) > chlorobenzene (113) ≃ Phenol (94) > toluene (92) > DMSO >> chlorooctane (149 g/mole).
Higher molecular weight lipophilic surrogates, which are both slow and insoluble in the aqueous test medium, do not migrate in detectable levels.

This confirms that the solubility of the surrogates in the simulant may play an important role, mainly for monolayer materials.

Influence of ethanol

Migration into ethanol is always much larger than into 3 % acetic acid. This can be attributed to its good solvent properties. However this does not explain all results. Even surrogates which are well soluble in water migrate more and faster in ethanol than into 3 % acetic acid (compare figures 6 and 7, 8 and 9). With multilayers, the lag times are always much shorter with ethanol (around 80 days for pentanedione, chloroethane and toluene) than in 3 % acetic acid (around 170 days for these surrogates). Since lag times are influenced by diffusion coefficients, this shows that ethanol plasticizes PET by swelling effects. Swelling effects strongly contribute to the larger migration into ethanol observed both with mono and with multilayers.

Conclusion.

Monolayer and tri-layer bottles containing large concentrations of surrogates were obtained. Dichloromethane, a strongly swelling solvent was used as a vehicle for surrogates impregnation into PET. It enables a quick impregnation (≤ 5 days) at room temperature, with a homogeneous concentration in the mass of the flakes. The impregnation levels were not sensitive to temperature
fluctuations. Drying of these flakes enabled evaporation of dichloromethane and of water prior to injection.

Surrogates have been chosen with different criteria in order to cover all possible properties of real potential pollutants: volatility, polarity, functionality, stability and solubility in the simulant. Surrogates with amine and hydroxyl groups were tested, since these functional groups tend to increase the solubility in water. Unfortunately, these polar functional groups also react with dichloromethane during impregnation of flakes or with PET in process conditions. Only DMSO, phenol and 2,4-pentanediol were suitable as surrogates highly soluble in water.

A 1000 ppm concentration was a good compromise between the requirement of a good analytical sensitivity for the migration test and the need not to alter the polymeric matrix properties. To obtain such concentrations of surrogates in finished materials, there was the need to pollute at high levels. 60 to over than 90 % of the surrogates were eliminated after processing, which shows that the normal PET handling already cleans the resin, and contributes to safer materials.

Bottles processed from impregnated PET flakes had physical properties which were reasonably close to those of commercial PET bottles, and the procedure can be considered as acceptable. Due to plasticization by the surrogates, diffusion phenomena should be faster in model bottles than in commercial bottles, which provides again a safety margin to evaluate consumer exposure.

The surrogates can be classified into groups with different migration behaviour, defined by molecular weight ranges. Besides migration properties, these classes correspond also roughly to volatility scales, and also to the ability of any surrogate to be possibly (M<130g/mol) or not easily (M>130g/mol) removed by a suitable recycling process. Migration kinetics of polluted bottles (with
and without functional barrier) in contact with 3 % acetic acid and with ethanol at 40 °C show the following:

- only low molecular weight compounds (<130 g/mol) migrate into 3 % acetic acid after 1 year of contact when a functional barrier is present
- before 6 months of contact, any migration is close to zero
- only M < 200 g/mol compounds could migrate into 3 % acetic acid, even for large (at least 1.5 year) contact times at 40 °C

The migration of higher molecular weight lipophilic surrogates is not detectable (most detection limits are below 10 ppb, which illustrates the need to use surrogates soluble in water. As worst case substances, 2,4-pentanedione and phenol should be incorporated in the classical lists of surrogates;

The sequence of migration of surrogates depends on their diffusion properties and on interface partition effects. Solubility of surrogates in the simulant plays an important role, specially with monolayer materials: surrogates which are insoluble in 3 % acetic acid do not migrate in this medium. With multi-layers, the differentiation of the surrogate occurs during the lag phase, where the surrogates cross the functional barrier, and surrogates reach the surface in the sequence of fastest diffusion behaviour.

Acknowledgements

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Table 1: Surrogates most frequently used in literature for PET impregnation

<table>
<thead>
<tr>
<th>Surrogates</th>
<th>Properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>Polar, volatile</td>
<td>[4]</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>Polar, volatile</td>
<td>[4, 9]</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>Polar, non volatile</td>
<td>[4, 9]</td>
</tr>
<tr>
<td>Phenyldecane</td>
<td>-</td>
<td>[4]</td>
</tr>
<tr>
<td>Toluene</td>
<td>Non polar, volatile</td>
<td>[9, 4, 10, 12]</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>Polar</td>
<td>[10]</td>
</tr>
<tr>
<td>Phenylcyclohexane</td>
<td>Non polar, non volatile</td>
<td>[9, 12]</td>
</tr>
<tr>
<td>Diazinon</td>
<td></td>
<td>[4, 12]</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>Polar, volatile</td>
<td>[9, 12]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Polar, volatile</td>
<td>[9]</td>
</tr>
<tr>
<td>Iso-amyl acetate</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>n-hexanol</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>Polar, non volatile, water soluble</td>
<td>[9, 10]</td>
</tr>
<tr>
<td>Surrogates (set)</td>
<td>Set</td>
<td>Properties (Volatile, Polarity, Mass, Boiling temp °C)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----</td>
<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>(A)</td>
<td>V, P, M=133 g/mol, BP=75°C</td>
</tr>
<tr>
<td>Dimethyl sulfoxide (DMSO)</td>
<td>(A)</td>
<td>NV, P, M=78 g/mol, BP=189°C</td>
</tr>
<tr>
<td>Methyl palmitate</td>
<td>(A)</td>
<td>NV, NP., M=270 g/mol, BP= N.c.</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>(A)</td>
<td>NV, P, M=182 g/mol, BP=305°C</td>
</tr>
<tr>
<td>Phenylcyclohexane</td>
<td>(A)</td>
<td>NV, NP, M=160 g/mol, BP=240°C</td>
</tr>
<tr>
<td>Ethyl hydrocinnamate</td>
<td>(A)</td>
<td>MV, NP, M=178 g/mol, BP=247°C</td>
</tr>
<tr>
<td>Phenol</td>
<td>(B)</td>
<td>NV, P, M=94 g/mol, BP=182°C</td>
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<tr>
<td>2,6-Di-tert-butyl-p-cresol (BHT)</td>
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<td>NV, MP, M=220 g/mol, BP=265°C</td>
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<tr>
<td>Chlorobenzene</td>
<td>(B)</td>
<td>V, P, M=113 g/mol, BP=131°C</td>
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<tr>
<td>2,5-Thiophenediylbis(5-tert-butyl-1,3-benzoazole) (Uvitex OB)</td>
<td>(B)</td>
<td>Fluorescent dye, M=431 g/mol</td>
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<tr>
<td>1-Chlorooctane</td>
<td>(B)</td>
<td>MV, NP, M=149 g/mol, BP=183°C</td>
</tr>
<tr>
<td>2,4-Pentanedione</td>
<td>(C)</td>
<td>NV, P, M=100 g/mol, BP=133°C</td>
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<tr>
<td>Azobenzene</td>
<td>(C)</td>
<td>Dye, M=182 g/mol</td>
</tr>
<tr>
<td>Nonane</td>
<td>(C)</td>
<td>NV, P, M=128 g/mol, BP=151°C</td>
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<td>Dibutyl phthalate</td>
<td>(C)</td>
<td>NV, MP, M=278 g/mol, BP=340°C</td>
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<td>Phenyl benzoate</td>
<td>(C)</td>
<td>NV, MP, M=198 g/mol, BP=299°C</td>
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<tr>
<td>Toluene</td>
<td>(C)</td>
<td>V, NP, M=92 g/mol, BP=110°C</td>
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Table 2: Surrogates used in the current study
<table>
<thead>
<tr>
<th>Name of series A surrogates</th>
<th>Weight of chemicals (g) for simulation of</th>
<th>Drying at 150°C</th>
<th>Bottle processing</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>[3h at 150°C+5 min at 280°C]</td>
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<td></td>
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<tr>
<td>1,1,1-Trichloroethane A</td>
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<td>5.30</td>
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<td>DMSO A</td>
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<td>Methyl Palmitate A</td>
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<td>Benzophenone A</td>
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<td>935</td>
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<td>Phenylcyclohexane A</td>
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<td>Ethyl Hydrocinnamate A</td>
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<td>1.02</td>
<td>485</td>
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<td>Dichloromethane A</td>
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<td>100.00</td>
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<td>PET A</td>
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<td>Uvitex B</td>
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<td>1-Chlorooctane B</td>
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<td>Dichloromethane B</td>
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<td>100.00</td>
<td>34300</td>
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<tr>
<td>PET B</td>
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<td>-</td>
<td>10000</td>
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<td>2,4-Pentanedione C</td>
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<td>Azobenzene C</td>
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<td>Nonane C</td>
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<td>DBP C</td>
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<td>Dichloromethane C</td>
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<tr>
<td>PET C</td>
<td>-</td>
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Table 3: Quantities of chemicals (surrogate, solvent and PET) used to impregnate the PET for different tests.
<table>
<thead>
<tr>
<th>Surrogate</th>
<th>Initial concentration (IC) (ppm)</th>
<th>Drying at 150°C for 3 hours Concentration (ppm)</th>
<th>Recovery % versus IC</th>
<th>Drying (150°C/3h) + 5 min at 280°C Concentration (ppm)</th>
<th>Recovery % versus IC</th>
<th>Conc. in flakes after impregnation (ppm)</th>
<th>Concentrations in monolayer bottles (ppm)</th>
</tr>
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<tbody>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>7648</td>
<td>2105</td>
<td>28</td>
<td>745</td>
<td>10</td>
<td>6840</td>
<td>2 690</td>
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<tr>
<td>DMSO</td>
<td>4911</td>
<td>702</td>
<td>14</td>
<td>&lt; 70</td>
<td>-</td>
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<td>Methyl Palmitate</td>
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<td>164</td>
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<td>Benzophenone</td>
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<td>Ethyl Hydrocinnamate</td>
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<td>Uvitex OB</td>
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**Table 4:** Concentrations at the different simulating steps of the process: initial concentration after impregnation (IC), after drying at 150°C for 3 hours, and after drying at 150°C for 3 hours and 5 min at 280°C. Concentration of surrogates in PET during bottle manufacture: concentrations of surrogates in PET flakes after impregnation and in bottles after processing (standard deviation less than 8%)
**List of figures**

**Figure 1:** Impregnation kinetics at 40°C of PET flakes (1 cm x 1 cm x 280 µm) by toluene (13.3% w/w) (●) and 1,1,1-trichloroethane (20.5% w/w) (▲) in solution in heptane, and by Uvitex OB (0.54% w/w) in dichloromethane (□).

**Figure 2:** Evolution of serie B surrogates in function of drying time at 150°C: chlorobenzene ▲, chlorooctane ■, BHT - - Δ - - - , phenol ◆, uvitex OB ●.

**Figure 3:** Serie C surrogates concentrations in function of their location in the bottle (x cm is the distance from the bottom B): toluene ◆, 2,4-pentanedione ●, azobenzene ▲, phenylbenzoate - - □ - - , DBP - - ◊ - - , nonane ■.

**Figure 4:** Mono (100%) and tri-layer (25%) bottle reversible heat flow for series A (○); comparison with a commercial bottle (□).

**Figure 5:** Mono (100%) and tri-layer (25%) bottle non reversible heat flow for series A (○); comparison with a commercial bottle (□).

**Figure 6:** Migration kinetics of monolayer bottles (series A, B C) into 3 % acetic acid. Straight lines suggest apparent fickian behaviour. Toluene ▲, Pentanediol ●, Nonane *, Chlorobenzene □, Chlorooctane ◊, Phenol X, DMSO +, Phenylcyclohexane *, Ethyl hydrocinnamate Δ, Methyl palmitate ◊, Benzophenone O, Azobenzene ●, Phenyl benzoate △, DBP ◊, Trichloroethane ■. Detection limits are below 15 ppb.

**Figure 7:** Migration kinetics of monolayer bottles (series A, B and C) into ethanol. Straight lines are put to illustrate apparent fickian behaviour. Same symbols as in Figure 6. Detection limits are below 120 ppb (except trichloroethane, 400 ppb).

**Figure 8:** Migration kinetics from tri-layer bottles into 3 % acetic acid (series A, B and C). Same symbols as in figure 6. Detection limits below 120 ppb.

**Figure 9:** Migration kinetics from tri-layer bottles into ethanol (series A, B and C). Same symbols as in figure 6. Detection limits below 120 ppb (except trichloroethane 400 ppb)
Square root of time (hours$^{1/2}$)

Concentrations of surrogates in PET (ppm).

Figure 1

$t = 26$ days
Conc $= 1000$ ppm
Concentrations of surrogates in PET (ppm)

Figure 3
Figure 4
Figure 6
Figure 7
Figure 8