Study of Functional Barrier Properties of Multilayer Recycled Poly(ethylene terephthalate) Bottles for Soft Drinks

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Poly(ethylene terephthalate) (PET) flakes were ground, contaminated, washed, manufactured into multilayer preforms and bottles, and then tested for migration. The model contaminants were toluene, trichloroethane, chlorobenzene, phenyldecane, benzophenone, phenylcyclohexane, and copper(II) acetylacetonate. No migration was detected through a barrier of virgin PET (186 ± 39 μm) into 3% acetic acid food simulant using general methods of testing with a detection limit of 1 μg kg^{-1}. Migration was <1 μg kg^{-1} even for 6-month-old bottles placed in contact with the simulant for a further 6 months; that is, a test period considerably in excess of the shelf life of soft drinks. Neither was migration detectable in the more severe simulating solvents (e.g., 50% aqueous ethanol and 100% ethanol). Targeted analysis by gas chromatography−mass spectroscopy was then used to achieve a sub microgram per kilogram limit of detection and establish the performance of the barrier. Three-layer bottles with the contaminated PET buried were compared with 1-layer bottles in which contaminated PET contacted the food simulant directly. Migration into 3% acetic acid from 1-layer bottles was from <0.2 to 57 μg kg^{-1}, and the worst-case substance was chlorobenzene. Migration from 3-layer bottles was from <0.2 up to 0.4 μg kg^{-1}, and the worst-case substance was toluene. Therefore, the virgin PET layer reduced migration from an already low level, by more than 2 orders of magnitude.

INTRODUCTION

Under the influence of environmental considerations (EEC, 1993), plastic recycling is a growing economic activity. Plastics for recycling may be waste from manufacturers, semiclean plastics waste, and waste recovered from bottle banks and other sources (APME, 1993). The acceptable use of recycled plastics for food contact materials and articles will depend in part on the source of the waste (Begley and Hollifield, 1993). The control of recycled paper and plastics for food contact use causes considerable problems for migration testing because the number of potential contaminants is high and their identity unknown (Castle, 1994). It will not be possible in the foreseeable future to devote sufficient analytical facilities to determine the identity and migration level of all potential contaminants in all batches of recycled food contact materials. It should be noted that virgin materials can pose similar problems because of the presence of technical impurities and other sources of contamination. One way to reduce the burden of analytical work involves the concept of a functional barrier. If it can be demonstrated that a barrier to chemical migration exists, substances beyond (outside) that barrier are of no concern and need not be tested for. The debate then centers on the degree to which migration should be reduced [i.e., *a threshold of regulation* (Rulis, 1986)], and how to demonstrate the presence of an effective functional barrier (Franz et al., 1993, 1994; Johns et al., 1995). This threshold can be described either from a toxicological basis, as a level of no concern (Frawley, 1967; Munro, 1990), or from an analytical chemistry basis, as the level of detection for unknown substances by current analytical methodology.

The studies described here were designed to investigate the effectiveness of a virgin layer of poly(ethylene terephthalate) (PET) in limiting chemical migration from recycled PET. Single-layer bottles were prepared from virgin PET and also from PET that was deliberately polluted with a range of model contaminants (NFPA, 1992; FDA, 1992). Similarly, three-layer bottles were prepared with an inner core (buried layer) of either virgin PET or PET that was deliberately contaminated. These bottles were then tested for migration with the acidic food simulant 3% (w/v) acetic acid in distilled water (EEC, 1985). A comparison of migration from single-layer and multilayer bottles then quantified the effectiveness of the barrier layer to restrict migration of the model contaminants.

MATERIALS AND METHODS

Contaminated PET Material A. Clean PET bottles (2 L) produced from virgin PET resin, were ground to a flake-size of ~6 × 6 mm. The flakes (60 kg) were then contaminated by contact with a mixture of toluene and 1,1,1-trichloroethane (5 L each) along with phenyldecane, benzophenone, and copper (II)-acetylacetonate (500 g each). For this purpose, PET flakes and contaminants were filled into three metal drums and stored for 14 days at 40 °C. After this time, the contaminants were removed from the surface of the PET flakes by a short immersion (10 s) in an isopropyl alcohol/water mixture. It was noted that copper residues could not be removed completely and remained on the surface of the flakes. The contaminated flake was washed under conditions typical of those in a commercial recycling cleaning and flaking facility. Flake was washed at 90−92 °C for 20 min with a wash solution of 2.5% (w/v) sodium hydroxide and 1% (w/v) Triton X-100 detergent

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in water, with stirring at 600 rpm. A wash ratio of 10:1 (v/w) was used. The flake was then washed at 90−92 °C for 10 min with fresh water at a 20:1 ratio (v/w). Following washing, the flake was dried at 170 °C for 2 h before filling into polyethylene bags for transport to the industrial plant for bottle manufacture.

Contaminated PET Material B. Ground PET flakes (30 kg) were contaminated in a similar fashion as for material A, but with toluene and trichloroethane (1.5 L each), chlorobenzene (300 mL), phenylcyclohexane and benzophenone (150 g each), and no copper compound. The contaminated master batch was a nearly colorless material (pale yellow) without any solids on the surface of the flakes. The master batch was dried in air at room temperature, and then 6 kg was mixed with 54 kg of uncontaminated PET flakes to yield material B. This material B was filled into polyethylene bags for transport to the bottle fabricator.

Bottle Manufacture. The contaminated flakes were further dried at 170 °C for 4 h and crystallized at the industrial plant prior to making bottle preforms. A Hofstetter 8-cavity mould with Twin Hot Runner system was used in development work to make bottle preforms and a 32-cavity mould was used for production thereafter. For 1-layer bottles, the normal manufacturing process was followed. For 3-layer bottles, each cavity had a valve to control the flow and distribution of the plastics, and the materials were kept completely separate throughout the process up to the point of injection. The materials were stored in silos from where they were transferred to individual dryers. From the dryers they were fed to the individual plasticizing units and then injected in sequence. Virgin material was injected first, and then the recycled material was injected into the center of the virgin material. Finally, more virgin material was injected to seal the envelope around the recycled material. According to the manufacturer, material A was extremely difficult to process and the injection pressure had to be reduced from 150 to 40 bar. The operator noted that material B was much easier to process. The preforms were then blown into 1- and 3-layer bottles that were 45 or 48 g (±0.5) in mass and 1.315 g/cm^3 in density, with a volume of 1.5 L and an inner (contact) surface area of 8.2 dm^2.

Polymer Analysis. The concentration of contaminants was measured in all granulates, preforms, and bottles. Polymer (1 g) was swelled with hexafluoroisopropanol (0.5 mL) for 12 h at 40 °C and then extracted with isopropyl alcohol (1−10 mL, according to the expected concentration) for 24 h at 60 °C. The extracts were chilled overnight to precipitate the polymer and then filtered (regenerated cellulose acetate; pore size, 0.2 μm). Analysis for the contaminants was done by gas chromatography (GC) with external standards. The polymer extracts were analyzed by GC with a flame ionization detector (FID) with a Hewlett-Packard HP 5890 II gas chromatograph fitted with a CarboWax 10 (Supelco, polyethylene glycol phase) column of dimensions 30 m × 0.32 mm i.d. and a 0.5-μm film thickness. The carrier gas was hydrogen at 50 kPa. Injections were 1 μL, and the split flow was 80 mL/min. The injector block was held at 220 °C, and the FID block was held at 250 °C. The column temperature was programmed from 50 °C (held for 5 min) to 220 °C (held for 15 min), rising at a rate of 10 °C/min. Quantification was by external calibration.

Migration Testing. The EEC official migration test conditions (EEC, 1985, 1990) for soft drink bottles were employed: 3% (w/v) acetic acid in water, with test conditions of 10 days at 40 °C. In addition, more severe migration tests conditions, with 50% (v/v) aqueous ethanol and 100% ethanol, were applied. Bottles were rinsed with a small portion of simulant for a few seconds (5−10 s) prior to filling. Migration tests were conducted in triplicate, with the bottles closed with the normal screw caps. In experiments where the bottles were only partially filled, the bottles were shaken/rotated periodically to bring the simulant into contact with all the inner surface.

Simulant Analysis for Toluene and Chlorobenzene. These contaminants were determined by headspace-GC (HS-GC) with an FID. This procedure was also used for phenylcyclohexane (50% ethanol simulant only). The GC was a Hewlett-Packard HP 5890 II fitted with a DB 624 (J&W, phase for volatile halocarbons, no details issued on the phase) column of 30 m × 0.32 mm i.d. and 1.8-μm film thickness. The carrier was hydrogen at 80 kPa, the FID was set at 250 °C, and the injector was set at 220 °C. The column was programmed from 50 °C (held for 5 min) to 220°C (held for 15 min) rising at a rate of 10 °C/min. The split flow was 30 mL/min. Injections were made with a Perkin-Elmer AS headspace analyzer operated at a pressure of 100 kPa and a needle and transfer line temperature of 110 °C. Samples (10-mL portions of simulant) were equilibrated for 60 min at 65 °C. The injection period was 0.2 s, with a pressure setup time of 3 min. Quantification was by external calibration.

Simulant Analysis for Trichloroethane. Ethanolic simulants were injected directly into a GC fitted with an electron capture detector (ECD). Acetic acid simulant (1 mL) was neutralized with aqueous sodium hydroxide (10 M, 40 μL) and then analyzed by GC-ECD. Analysis was done with a Carlo Erba Vega series gas chromatograph fitted with a DB1 (J&W, polydimethylsiloxane phase) column of dimensions 30 m × 0.32 mm i.d., with a 5-μm film thickness. The carrier gas was hydrogen at 50 kPa. Injections were 6 μL, and the split flow was 30 mL/min. The injector block was held at 220 °C, and the ECD block was held at 270 °C. The column temperature was programmed from 70 °C (held for 5.5 min) rising at 10 °C/min to 90 °C, then rising at 35 °C/min to 240 °C (held for 15 min). External standards were employed.

Simulant Analysis for Phenylcyclohexane, Phenyldecane, and Benzophenone. Ethanolic simulants were injected directly into the GC-FID. Acetic acid simulant was subjected to solid-phase extraction (SPE) with octadecyl (C18) reversed-phase sorbent. The SPE cartridge (Baker, 200 mg bed size) was preconditioned with two volumes of methanol and then distilled water. A portion of simulant (100 mL) was neutralized with sodium hydroxide (10 M, 5 mL) and then passed through the SPE cartridge. The support was washed with a small volume of methanol (100 μL) to assist the next step of drying by pulling air through the SPE column by reduced pressure (20 min). The retained analytes were then eluted with hexane (2 × 0.5 mL) and the combined hexane extracts were analyzed by GC-FID with external calibration. The recovery of the concentration step for the 3% acetic acid simulant was determined with spikes at 1, 10, and 100 μg/kg. Recovery values were 78 ± 8% (phenylcyclohexane), 98 ± 4% (phenyldecane), and 84 ± 12% (benzophenone). Results were not corrected for recovery. The GC used for analysis was a Hewlett-Packard HP 5890 II gas chromatograph fitted with a CarboWax 10 column of dimensions 30 m × 0.32 mm i.d., with a 0.5-μm film thickness. The carrier gas was hydrogen at 50 kPa. Injections were 5 μL, and the split flow was 30 mL/min. The injector block was held at 220 °C and the FID block was held at 250 °C. The column temperature was programmed from 120 °C to 220 °C (held for 15 min), rising at 10°C/min.

Simulant Analysis for Copper. A portion of simulant (1 L) was evaporated to a small volume (10 mL) with a rotary evaporator at a bath temperature of 40 °C and 72 mbar of pressure. This solution was then analyzed for copper with a Perkin-Elmer 2100 flame atomic absorption spectrometer fitted with a cylindrical cathode lamp (operated at 324.8 nm and 13 mA) and with a flame of acetylene (1.2 L/min) and air (6.9 L/min).

GC-MS Analysis for Organic Migrants. Aliquots of the acetic acid simulant (10 mL) were extracted with dichloromethane (DCM, 500 μL) by shaking for 12 h, following the addition of internal standards (10 μL of a 1 μg/mL solution). Following extraction, the sample tubes were centrifuged for 3 min at 3000 rpm, and the DCM layer was removed, transferred to a GC sample vial, and analyzed by GC-MS. Samples were analyzed with a Fisons MD800 mass spectrometer in the electron-impact mode, monitoring ions at 50−300 amu and 2.5 cycles/s. The injector and MS interface temperatures were held at 200 and 280 °C, respectively, throughout. Helium (0.8 mL/min) was used as the carrier gas. Injections were made in the splitless mode (splitless time, 45 s) onto a 60 m × 0.25 mm × 0.25 μm RTX-1 column (Thames Chromatography, a dimethylsiloxane phase). Following injection, the GC oven was held at 35 °C for 5 min and then programmed at 30 °C/min to 150 °C, and then at 20 °C/min to 250 °C (held for 10 min). The concentration of analytes was determined by interpolation from calibration graphs constructed from standard solutions (0−100 μg/mL). The quantification ions and internal standards used for each model contaminant are shown in Table 1.

Table 1. Analyte−Internal Standard Pairings and Selected Ions Used for GC-MS

model contaminant	*m/z*	internal standard	*m/z*
trichloroethane	97	carbon tetrachloride	117
toluene	91	toluene-d_8	98
chlorobenzene	112	chlorobenzene-d_5	117
phenylcyclohexane	160	phenylheptane	176
benzophenone	182	benzophenone-d_5	187
phenyldecane	218	phenylnonane	204

RESULTS AND DISCUSSION

Design of the Study. This work was conducted in two phases. In the first, the multilayer bottles were analyzed to establish the level of contaminants incorporated and then the bottles were tested for chemical migration with food simulating solvents. The aim of this first phase was to establish if the barrier of virgin PET limited migration to less than a 1-μg kg^{-1} threshold of detection. In the second phase, the multilayer bottles were tested alongside 1-layer bottles made from the same batch of contaminated PET. The aim here was to measure the effect of the barrier layer separate from the already low intrinsic diffusion and migration characteristics of PET (Franz, 1993; Ashby, 1988; Tice, 1988; Begley and Hollifield, 1989). For this phase of work, a more sensitive analytical method was required to measure migration to sub microgram per kilogram levels.

Choice of Model Contaminants. Model contaminants for the buried PET layer were chosen according to guidelines given by the U.S. Food and Drug Administration (US-FDA; NFPA, 1992; FDA, 1992; Begley and Hollifield, 1993). Inclusion of the organometallic copper salt caused considerable technical difficulties because of its poor solubility. This poor solubility caused a very inhomogenous distribution in the metal drums used as contamination vessels. Small-scale laboratory studies with zinc stearate and copper(II) ethylhexanoate gave similar problems. The copper salt also gave difficulties when the PET was washed. In the alkaline wash at 90 °C, the organometallic copper salt was converted to small brown and black particles. These particles were not completely removed during the washing and rinsing process, but were still present in the blown bottles. Because of these problems, a parallel study was conducted with PET granulate B that was contaminated with only organic model contaminants.

Effect of the Washing Procedure. Granulate A was washed, dried, and crystallized, whereas granulate B was prepared with an intermediate master batch and was not washed but only dried and crystallized. Concentrations of organic chemicals decreased, as expected, on converting contaminated flakes to bottles. A real washing effect (in the sense that the surface could be cleaned) was seen only for the copper salt for PET material A, because it was not able to penetrate the PET plastic. As shown in Tables 2 and 3, there was a decrease in organic contaminants during the washing and rinsing process at a temperature of 90 °C. However, the largest loss occurred during the drying process at 170 °C for several hours. Because water can hydrolyze PET at elevated temperature (e.g., during fabrication), PET is dried rigorously to a water content of typically 0.005% or less. A normal drying regime would be 4−8 h at 170 °C, and a total of 4 or 6 h was used in this work (*vide supra*, for contamination phase + bottle manufacture, 2 + 4 h for material A, 0 + 4 h for material B). The decrease in contaminant concentration clearly depended on the volatility of the contaminants. In small-scale lab tests on the PET masterbatch B, the volatiles trichloroethane (boiling point, 75 °C), toluene (111 °C), and chlorobenzene (132 °C) were lost by 80−90% after washing and drying, with the major loss on drying. By contrast, the less volatile phenyldecane (293 °C), phenylcyclohexane (240 °C), and benzophenone (305 °C) were reduced by 40−45% on washing, but with little further reduction on drying.

Manufacture of Bottles with a Buried Contaminated Layer. In the injection moulding procedure to make 3-layer PET bottles, the first injection into the mold is virgin PET (V). This injection is followed immediately by recycled PET (R) which flows within a sleeve of virgin polymer by virtue of viscous drag at the walls of the mould. At this stage, the mould is partially full, with a 3-layer laminate (VRV). The injection nozzle, etc., is then cleaned with virgin PET (to prevent any carry-over, ready for the next bottle), which flows within the earlier plastic and pushes a plug ahead of itself. The bottle wall has now five layers around the injection port (VRVRV) and three layers (VRV) at locations far from the port (Figure 1). It is possible, by adjusting the temperature, pressure, and speed parameters of the process, to alter the positioning and distribution of the recycled inner layer. This alteration allowed the inner layer to be stretched over the whole length of the preform, compacted over a short length, or both compacted and stretched as required. For brevity and clarity, these multilayer bottles (with both 3- and 5-layer sections) will be called 3-layer, hereafter.

Physical Characteristics of the Functional Barrier. Inspection of the 3-layer preforms revealed that the point of minimum thickness of the barrier virgin layer occurred at bottom-dead-center, opposite the injection point. This location was verified by measurements made with a microtome and microscope. The thinnest part was in the portion of the preform that is not significantly stretched when subsequently blown into bottles. All preforms from three consecutive injection shots under production conditions ($3 \times 32 = 96$ in total) were measured to determine the variation coming from the mould and the process (short-term variation). The average thickness of the barrier layer was 186 μm, with a standard deviation (SD) of 39 μm. The thickness of the barrier layer could be controlled by the relative quantity of materials used in the 3-stage injection procedure. Thus, the manufacturing process used to prepare multilayer PET bottles with a recycled PET content was perfectly capable of maintaining an intact inner layer of virgin PET of a minimum thickness of 25 μm (Begley and Hollifield, 1993) under developmental and production conditions.

Level of Contaminants in Bottle Preforms. The results in Tables 2 and 3 indicate that the drop in contaminant concentration on forming preforms from granulate was much higher for bottles A than bottles B. Material A contained the copper compound, and it is known that copper is a catalyst for PET degradation. Injection moulding granulate A was only possible because the machine operator lowered the injection pressure from 150 (normal pressure) to 40 bar. It is postulated that this decrease in pressure gave a lower viscosity of the molten resin and resulted in a higher diffusivity of the contaminants in the molten PET; this, in turn, gave a higher loss of contaminants due to volatilization.

Loss of Contaminants in Bottle Blowing. There was no significant decrease of contaminants from preforms to blown bottles (Tables 2 and 3). At this stage, the contaminants are encapsulated within the PET matrix and the absence of an appreciable loss can be taken as a early indication of the barrier properties of the virgin material.

Table 2. Concentration of Model Contaminants in PET Material A

PET material A	concentration, mg kg^{-1}				
	trichloroethane	toluene	phenyldecane	benzophenone	copper
granulate A (before washing at 90 °C)	15800	11900	4450	3957	2800
granulate A (washed, dried, and crystallized)	2570	735	490	1375	210
preforms A (3-layer)	13	15	49	88	110
bottles A (3-layer)	14	17	68	98	62

Table 3. Concentration of Model Contaminants in PET Material B

PET material B	concentration, mg kg^{-1}				
	trichloroethane	toluene	chlorobenzene	phenylcyclohexane	benzophenone
master batch B	14400	20930	9870	7120	8360
dried granulate B (6 kg of MB + 54 kg of PET)	1240	445	155	210	455
preforms B (1-layer)	445	140	35	90	190
bottles B (1-layer)	400	88	46	110	212
preforms B (3-layer)	114	76	9	26	54
bottles B (3-layer)	79	42	7	24	42

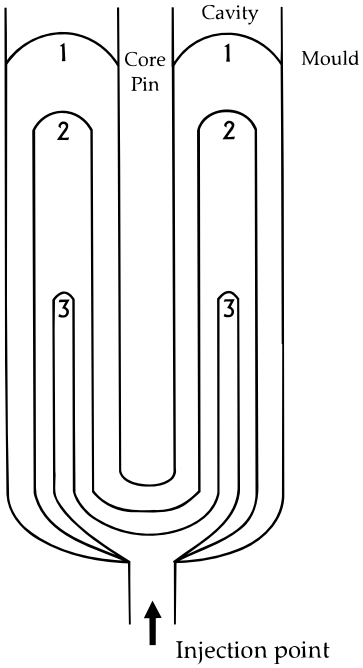

Figure 1. Cross section of multilayer PET bottle in injection mold: (1) first injection, virgin PET; (2) second injection, recycled PET; (3) third injection, virgin PET.

Migration Testing. Soft drink bottles fall in the category of articles filled and stored at room temperature with no thermal treatment in the container. The appropriate EEC test procedure (EEC, 1985, 1990) is to use a food simulant of 3% (w/v) acetic acid in water, with test conditions of 10 days at 40 °C. The US-FDA test protocol (FDA, 1990) is to test with an 8% ethanol solution for 10 days at 49 °C. The tests used in this work were oriented toward the EC, but also covered the FDA protocol. In addition to the 3% acetic acid/10 day/40 °C test, 50 and 100% ethanol were used at 40 °C. For migration testing, a detection limit of 1 μg kg^{-1} was achieved in most cases (Table 4) with routinely used (i.e., not MS-based, see later) analytical instruments. In some cases, even lower *effective* detection limits could be obtained with fill volumes of only 140 and 270 mL in place of the normal (full) fill volume of 1.5 L for the bottles in question. For this procedure, it is presupposed that the extent of migration is effectively the same for a given surface area exposed. Consequently, a higher contaminant concentration can be expected (meaning a more favorable detection limit) for the smaller fill volume. For example, if the migration is 15 μg of substance per bottle, for a 1.5-L fill, the concentration will be 10 μg kg^{-1}. In contrast, for a 270-mL "fill" contacting the same total surface area, 15 μg of substance migrating will give a concentration in the simulant of 56 μg kg^{-1}. Calculating this concentration back for the normal filling volume of 1.5 L, one obtains the same migration value per bottle, but on the basis of a lower effective detection limit.

Choice of Analytical Methods. Two approaches were taken for the analysis of exposed food simulant, and it is important here to identify their relative strengths and weaknesses. The first approach (used in phase I) was rather nonspecific using GC-FID and GC-ECD. In contrast, the second approach (used in phase II) employed the highly specific technique of GC-MS in the selected ion mode. The less specific detectors of FID and ECD can be used to analyze for unknown migrants, which would be the case if recycled PET of an unknown composition were employed. These detectors therefore represent the situation in most analytical laboratories *vis a vis* screening for unknown contaminants. The limit of detection was ~1 μg kg^{-1}. However, it should be noted that the model contaminants were selected (in part) for their ease of analysis and that for the more general case, effective limits of detection would be higher (poorer) than the limits given in Table 4.

In the second analytical approach using GC-MS, extra sensitivity is achieved by monitoring selected ions. This approach gave sub microgram per kilogram limits of detection, which was desirable, so that very low levels of migration could be measured to establish the effectiveness of the functional barrier. The extra sensitivity comes at a cost, however. Where the contaminants are known (as here), appropriate ions can be selected. This selection is not the case, however, when screening for the possible presence of unknown contaminants. For unknown substances, so-called full-scan (or total-ion current) MS detection would have to be used, and MS in this mode is no more sensitive than GC-FID or GC-ECD.

Migration from 3-Layer Bottles As Measured by GC-FID and GC-ECD. *Migration into 3% Acetic Acid.* There was no migration measurable by GC-FID and GC-ECD with the detection limits given in Table 4. Two isolated values of 3.2 and 5.9 μg kg^{-1} trichloroethane were observed for one bottle only (type A), but this was attributed to copper particles that injured the integrity of the inner layer. Bottles with such solid particle

Table 4. Detection Limits (LOD)[a] for Model Contaminants in Food Simulants Determined by GC-FID and GC-ECD

substance	filling volume, mL	LOD, μg kg^{-1} 3% HOAc	50% EtOH	100% EtOH
trichloroethane	1500	0.5	np	np
	270	0.1	0.1	0.1
	140	np	0.05	0.05
toluene	1500	1	np	np
	270	0.2	1.1	18
	140	np	0.7	9
chlorobenzene	1500	1	np	np
	270	0.2	1.1	12
	140	np	0.7	6.3
phenylcyclohexane	1500	1	np	np
	270	0.2	5	36
	140	np	2.6	18
benzophenone	1500	1	np	np
	270	0.2	54	27
	140	np	28	14
phenyldecane	1500	1	np	np
	270	0.2	72	36
	140	np	37	18
copper (by AA[c])	1500	0.1	np	np

[a] Effective detection limit calculated for a fill volume of 1.5 L (see text). [b] np, Not performed. [c] Measured by atomic absorption.

inclusions are of no practical relevance as they can easily be sorted and rejected by optical control devices.

Migration into 50% Ethanol. The limits of detection for this simulant are shown in Table 4. No migration was detected by GC-FID and GC-ECD. There was a low background of toluene in some samples, of ~1 μg kg^{-1}, that was attributed to a contaminant of the solvent.

Migration into 100% Ethanol. Again, limits of detection for this simulant are shown in Table 4. Even with this severe food simulating solvent, there was no migration measurable. The detection limit of 1 μg kg^{-1} was only achieved for the most volatile contaminant trichloroethane. Taking the basic knowledge of migration theory into account, however, it seems that migration of the other contaminants with a higher molecular weight (hence diffusivity) but with comparable concentration in the bottle wall cannot exceed the migration of trichloroethane (i.e., would also be not higher than 1 μg kg^{-1}). This conclusion is supported by the results obtained with 3% acetic acid and also by the GC-MS results discussed later.

Comparison of 1-Layer and 3-Layer Bottles. Migration data established by the highly sensitive GC-MS technique are given in Table 5 for the conventional test with a 10-day exposure at 40 °C. The mean limit of detection for the model contaminants was 0.2 μg kg^{-1}. Migration levels in Table 5 are reported both in units of micrograms per kilogram simulant (ppb) and in units of μg/dm^2, assuming the food contact area of a bottle as 8.2 dm^2. Finally, the migration, if observed, calculated as a factor (fraction) of the contaminant present in the bottle is shown in Table 5.

For the 1-layer bottles prepared from PET material B, migration of all five incorporated contaminants was observed, ranging from 0.5 to 57 μg kg^{-1}. The fraction of contaminant migrating was from 0.00015 for phenyl cyclohexane up to 0.0213 for toluene, which showed the greatest tendency to migrate. By comparison with contaminated PET-B as a buried layer in the 3-layer bottles, only one of the five contaminants migrated to detectable levels and this was toluene (0.38 μg kg^{-1}), with a migration factor of 0.0003. The PET-B material was the same in both bottles, so the ratio of migration levels gives a measure of the effect of placing the virgin PET barrier between the contaminated plastic and the food simulant. For toluene, migration was reduced by a factor of 70.

It is interesting to compare migration results for 3-layer bottles A with 3-layer bottles B. It was already noted that PET-A suffered from inclusions of solid copper residues, and it was thought that this could impair the barrier properties of the overlying virgin PET. There was no evidence for this, however, and as for bottles B, only toluene migrated from bottles A above the LOD of 0.2 μg kg^{-1}. This result indicates that the barrier properties of virgin PET are quite robust and can tolerate even gross particulate contaminants in the buried recycled layer.

Test for a Lag Period in the Migration. It is well known that any permeation process through a polymer shows a characteristic time-lag behavior until breakthrough of the permeant (Barrer, 1968; Crank, 1968). Therefore, caution should be exercised concerning this aspect when testing functional barrier properties. The functional barrier may delay chemical migration while the pollutant diffuses through the layer, but thereafter migration can be observed. If the test period employed, coupled with the time between manufacture and testing, is less than the time the material is actually used in contact with food, then null test results could be misleading. Diffusion coefficients within PET are known to be very low (Begley and Hollifield, 1993). For instance, for a substance like limonene (molecular weight, 136) a diffusion coefficient (D of 7 × 10−14 cm^2 s^{-1}) has been measured at 23 °C (Franz, 1993). Taking as an example this value D and assuming a barrier thickness (l of 100 μm), then according to the time-lag equation $t_L = l^2/6D$ (Crank, 1968), a lag-time (t_L) of 7.5 years can be calculated for a temperature of 23 °C. Even when the test temperature was increased to 40 °C (which was the actual test temperature in this study), the lag-time for limonene can be expected to be reduced approximately by not more than one order of magnitude

Table 5. Migration into 3% Acetic Acid over 10 Days at 40 °C

	1-layer bottle PET-B				3-layer bottle PET-B				3-layer bottle PET-A			
	bottle	migration			bottle	migration			bottle	migration		
contaminant	μg/dm^2	μg/kg	μg/dm^2	factor[a]	μg/dm^2	μg/kg	μg/dm^2	factor	μg/dm^2	μg/kg	μg/dm^2	factor
trichloroethane	2220	15.5	2.8	0.00126	430	<0.2	<0.04	na[b]	80	<0.2	<0.04	na
toluene	480	56.5	10.3	0.02130	230	0.38	0.07	0.00030	90	0.16	0.03	0.00032
chlorobenzene	250	16.6	3.03	0.01200	40	<0.2	<0.04	na	ne[c]	ne	ne	na
phenylcyclohexane	610	0.5	0.09	0.00015	100	<0.2	<0.04	na	ne	ne	ne	na
benzophenone	1170	7.4	1.4	0.00120	230	<0.2	<0.04	na	540	<0.2	<0.04	na
phenyldecane	ne	ne	ne	na	ne	ne	ne	na	370	<0.2	<0.04	na

[a] The fraction of contaminant that migrates (migration level divided by the level in bottle, both in units of μg/dm^2). [b] na, not applicable. [c] ne, not employed.

to an estimated t_L of 0.8 years. Therefore, the question of time lag was not likely to be a factor for the laminates studied here. Nevertheless, as a precaution, the multilayer bottles were tested 6 months after manufacture by filling them with 3% acetic acid and storing them at room temperature for a further 6 months. No migration ($<1\ \mu g\ kg^{-1}$) of the model contaminants was observed.

CONCLUSIONS

These results allow several conclusions concerning contamination-related safety of multilayer PET bottles in general and specifically for the bottles investigated here. First, however, it must be stressed that the contamination levels applied are far higher than any conceivable in real life. The intention was to investigate the effectiveness of a virgin PET layer as a functional barrier. This goal was achieved in the best and most efficient way by excessive and deliberate contamination of a whole batch of recycled PET flakes and by using this highly contaminated material to make bottles for testing. Even if in the real-life situation a series of highly contaminated bottles were returned and processed to raw material for new bottles, the dilution effect would provide contaminant concentrations far below (orders of magnitude) those used here.

A general conclusion is that adventitious contaminants can be effectively reduced by the normal washing and drying processes applied before manufacture of preforms and bottles. Although a thorough rinsing is obligatory for surface cleaning of PET flakes, the crucial step for removal of the most migratable (mobile) contaminants (basically the small volatile substances) was the drying process, where time and temperature act as appropriate control parameters for volatilization. This assumption was confirmed by the dramatic loss of contaminants during the process to make bottle preforms. The concentration of contaminants remained nearly constant thereafter, during blowing of bottles from preforms, thus already indicating the outstanding barrier properties of the virgin PET layer.

The migration results also confirm the good barrier properties of PET in the test bottles. Taking all results as well as knowledge of migration theory into account, the PET food contact layer limited migration of each of the model contaminants to $<1\ \mu g\ kg^{-1}$ in food simulants under the official test conditions of 10 days at 40 °C, and even for the most severe system of 100% ethanol. In addition, a long-term migration experiment with 3% acetic acid at room temperature did not result in detectable migration. Control migration tests with single-layer bottles in direct contact with contaminants gave clearly measurable (but nevertheless quite low) migration, and this result validated the functional barrier findings.

Finally, it is concluded that an intact PET layer represents an efficient functional barrier against migration from any other possible contaminant encapsulated in a recycled PET material under normal conditions of use for soft drinks. The results allow the conclusion that the 25% recycled material employed here could be increased to any technically feasible percentage, provided that the characteristics of the functional barrier layer remained unchanged.

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