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**SiO_x layer as functional barrier for PET bottles towards potential
contaminants from post-consumer recycled poly(ethylene
terephthalate)**

Frank Welle, Roland Franz

Fraunhofer Institute for Process Engineering and Packaging (IVV)
Giggenhauser Straße 35, 85354 Freising, Germany

correspondance: welle@ivv.fraunhofer.de

Abstract

The barrier effect of a silicon oxide (SiO_x) coating on the inner surface of PET bottles, in terms of the ability to reduce the migration of post-consumer compounds from the PET bottle wall into the food simulants 3% acetic acid and 10% ethanol, was investigated. The barrier effect was examined by artificially introducing model substances (surrogates) into the PET bottle wall to represent a worst case scenario. Test bottles with three different spiking levels up to about 1000 mg kg^{-1} per surrogate were blown and coated on the inner surface. The SiO_x coated bottles and the non-coated reference bottles were filled with food simulants. From the specific migration of the surrogates with different bottles wall concentrations the maximum concentrations of the surrogates in the bottle wall corresponding to the migration of $10 \mu\text{g l}^{-1}$ were determined. It was shown that the SiO_x coating layer is an efficient barrier towards post-consumer compounds. The maximum bottle wall concentrations of the surrogates corresponding to the migration of $10 \mu\text{g l}^{-1}$ were in the range of 200 mg kg^{-1} for toluene and about 900 mg kg^{-1} for benzophenone. Consequently, the SiO_x coating allows use of conventionally recycled post-consumer PET flakes (without a super-clean recycling process) for packaging aqueous and low alcoholic foodstuffs (under cold-fill conditions) and prevents the food from migration of unwanted contaminants from post-consumer PET.

Keywords:- Functional barrier, PET recycling, SiO_x coating, challenge test, food packaging, migration

Introduction

The use of post-consumer recycled polyethylene terephthalate (PCR PET) in soft drink bottles has been established for a number of years. Post-consumer PET bottles typically are collected with curbside or deposit collections. Subsequently the PET bottles which have been collected are ground and washed. Labels and closures as well as dirt and surface contamination are removed from the PET recyclates. The resulting conventionally recycled PET flakes can be used for non-food packaging applications (e.g. detergent bottles) or fibres. If the recycled PET flakes are to be re-used in food contact applications, further deep-cleansing recycling processes is necessary. Post-consumer substances or compounds from the possible misuse of PET bottles for the storage of e.g. household chemicals which have been absorbed into the PET material may migrate from the recyclate containing bottle into the foodstuff. In case of a too high concentration of the post-consumer compounds in the bottle wall, the migration might pose a health risk for the consumer. Since measurement of bottle wall concentrations for each and every bottle is impossible, so-called challenge tests have been developed in which model chemicals (also named surrogates) are artificially introduced into a recycling process. As a safety parameter or as cleaning efficiency criterion, for these surrogates a migration limit of 10 µg l⁻¹ in food from a bottle produced in a challenged recycling process has been generally accepted (FDA 1992, ILSI 1998, BgVV 2000, Franz 2004a, Begley and Hollifield 1993, Franz et al 1998, Franz and Welle 1999, 2002). More recently, the French Food Safety Authority AFFSA has defined 1.5 µg l⁻¹ as a target migration limit which should not be exceeded (AFFSA 2006). It is assumed, when taking exposure scenarios also into account, that with these performances a recycling process would remove any unknown contaminant which might be able to migrate and would be capable to produce a recycled PET food contact material which can safely be reused for direct food contact.

In the last decade, several super-clean recycling technologies have been established in industrial or pilot plant scale in several countries (Mueller and Welle 2005). All of these technologies have been shown to be able to reduce the concentration levels of

PET untypical compounds in the PET recycles down to levels which are similar to the concentrations of technical impurities in virgin PET. The output material of a super-clean recycling process has therefore a migration potential which is similar to virgin PET (Franz and Welle 2003). An overview of the different recycling technologies and food contact application conditions is given on the internet homepage of the US FDA (FDA 2007).

Another possibility to prevent the migration of unwanted post-consumer compounds into PET bottled foodstuffs is the use of appropriate functional barriers. A functional barrier is defined as a package construction or barrier layer which limits the extent of migration of a component from the package to the food or food simulant in amounts below an accepted value threshold or migration limit of no concern. However, it should be noted that a functional barrier is not necessarily an absolute barrier but a function of the given food packaging application. The migration kinetics of a functional barrier system is in general characterized by an initial time lag phase followed by a much less steeper migration curve line compared to the functional barrier free package (Feigenbaum et al. 2005, Dole et al. 2006). The lag time is defined as the time which a substance needs to cross a functional barrier package construction and to reach the food contact surface. Typically the lag time is responsible, that during the shelf life of the product the migration limit is not exceeded. In the special case of PET bottles or sheets, an outside and inner layer of virgin PET acts as a functional barrier. In the core layer of such a multi-layer structure conventionally recycled PET is located in a certain amount. The virgin layer on the inner side with contact to the foodstuff can reduce the migration into the foodstuff to levels under the general accepted migration limit of $10 \mu\text{g l}^{-1}$ (Franz et al. 1996, Welle and Franz 2006). In comparison to conventional monolayer PET bottles, the manufacturing of multilayer PET bottles is more expensive. Another problem is that the virgin layer might be contaminated with post-consumer compounds by in-situ diffusion during bottle manufacturing with the consequence that the partially contaminated virgin layer might have then a lower barrier effect (Franz et al. 1997, Piringer et al. 1998). The use of conventionally recycled PCR PET in the core layer

of PET multilayer bottles is therefore today not established on a significant industrial scale in Europe.

Another functional barrier technology is the application of a silicon oxide (SiO_x) coating on the inner surface of PET bottles. Typically this technology is used to reduce the permeation of permanent gases like oxygen or carbon dioxide. Therefore SiO_x coated PET bottles are on the market for oxygen sensitive foodstuffs like beer and juices. On the other hand, the SiO_x layer reduces not only the permeation of gases. The functional barrier might also reduce the migration of post-consumer compounds into the PCR PET bottled foodstuff. If this functional barrier is efficient enough, then it would present an alternative option to super-clean technologies and may allow directly the re-use of conventionally recycled PET without further deep-cleansing of the PCR PET.

In the literature some studies can be found dealing with the barrier properties of SiO_x coatings inside of PET bottles. For instance, a diamond-like carbon (DLC) layer on PET bottles enhances the gas permeation barrier (Boutroy et al 2006, Yamamoto et al 2005, Finch et al 1996). In another study the barrier properties of carbon coated PET against post-consumer contaminants was investigated (Cruz et al. 2006). The results of this study, however, do not reflect the barrier properties potential of SiO_x layers which, in our opinion, might be due to the laboratory coating scale character of the investigated samples. In a study with a SiO_x coated PET film Dimitroulas et al (2004) found that the barrier against the chemical substance methylethyl ketone increases by a factor of 7-8 at room temperature.

The objective of this study was to investigate and to evaluate the barrier effect of a market scale commercially available SiO_x coating process. The barrier effect was examined by artificially introducing model substances (surrogates) into the bottle wall in a worst case scenario. The surrogates were chosen according to the principles recommended by American and European Guidelines (FDA 1992, FDA 2006, ILSI 1998, BgVV 2000, Franz et al. 2004a). After the contamination, the spiked PET bottles were industrially coated with a SiO_x layer. The specific migration of the surrogates into food simulants from the bottle wall through the SiO_x barrier layer was

measured. The difference between the specific migration from the coated and non-coated test bottles represents the barrier effect of the SiO_x coating layer towards the applied surrogates. In order to establish a basis for an extrapolation from the worst case scenario of the challenge test to more realistic concentrations of possible contaminants, the PET test bottles were spiked with three different contamination levels (low, medium, high).

Materials and Methods

Selection of Surrogates

The barrier properties of the SiO_x coating was determined by introducing chemicals (surrogates) into the bottle wall of PET test bottles. The applied surrogates are in compliance with the four categories of organic compounds: high volatile and polar, high volatile and non-polar, low volatile and polar, low volatile and non-polar. The following model compounds were used for the migration tests: toluene, chlorobenzene, phenyl cyclohexane, benzophenone and methyl stearate.

Spiking of the Test bottles

Batches of 1.1 kg of dried PET resin were weighed into glass jars. For the desired amount of preforms several batches were prepared in parallel. Subsequently the target weight of each of the chemicals were added to each of the jars. The jars were tightly sealed and shaken to disperse the chemical mixture onto the surface of the dried PET pellets. The sealed jars were stored at 38 °C for 7 days. Each day, the jars were shaken to thoroughly mix the resin and chemicals. At the end of the seven days storage time, the material was removed from the storage environment and be kept sealed until it is injection molded into 24.5 g preforms. From the preforms 0.3 l PET bottles were blown. Subsequently one part of the bottles was coated with the investigated SiO_x coating process whereas the other part of the (non-coated) bottles was used as reference. The concentrations of each surrogate and contamination level were determined in the coated as well as in the non-coated reference bottles.

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Coating of the test bottles

The coating film is deposited on the surface of PET bottles using a plasma impulse chemical vapour deposition (PICVD) process. Starting substances for the SiO_x coating are hexamethyl disiloxane (HMDSO) and hexamethyl disilazane (HMDSN). The barrier coating is a quartz-like surface with almost the stoichiometric composition of SiO₂. The maximum average thickness of the barrier layer is about 100 nm. The SiO_x coating is approved by the American health authority FDA under food contact substance notification FCN 329.

Migration testing

The specific migration of the surrogates was measured into the food simulants 3% (w/v) acetic acid and 10% (v/v) ethanol. Due to the fact that the SiO_x coating might be sensitive towards high pH values, 5 g citric acid per 300 ml was dissolved in the ethanolic food simulant. For migration testing, the bottles were filled with the food simulants (two bottles for each bottle type and food simulant) and stored for 10 d at 40 °C. The bottles were sealed with HDPE closures with an aluminum film on the contact surface in order to prevent sorption of the surrogates into the closures. For the food simulant 10% ethanol a migration kinetic was established. 50 ml aliquots of the food simulant were drawn after 3 d, 6 d, 10 d, 20 d and 30 d. The bottles were refilled after drawing the 50 ml aliquots with the same amount of simulant. The reduction of the concentration of the surrogates by the refilling with food simulants was considered.

Determination of the bottle wall concentrations of the surrogates

The PET test bottles were cut in small pieces of approximately 0.5 x 0.5 cm. 1.0 g of each PET sample was placed in a 5 ml glass vial. 1.0 ml 1,1,1,3,3,3-hexafluoro-*iso*-propanol (HFIP) was given to the PET material and stored for 1 d at 60 °C in order to swell the PET matrix. Then 2.0 ml *iso*-propanol was added for 1 d at 60 °C to extract the swollen matrix. The extract was decanted from the polymer and stored for 4 h at

4 °C. Then it was decanted again from the precipitate and analyzed by GC/FID. Quantification was achieved by external calibration using the standard addition method. Gas chromatograph: HP 5890II, column: SE 10 - 30 m - 0.32 mm i.d. - 0.32 µm film thickness, temperature program: 40 °C (5 min), rate 15 °C min⁻¹, 240 °C (15 min), pressure: 50 kPa hydrogen, split: 10 ml min⁻¹.

Determination of the surrogate concentration in migration solutions by purge and trap gas chromatography

The concentration of the volatile and medium volatile surrogates toluene, chlorobenzene, phenyl cyclohexane in the food simulants was determined using purge and trap gas chromatography (p&t GC) with flame ionisation detection (FID). Sample preparation: a) Acetic acid: 5 ml of the 3% acetic acid migration solution was neutralised with 1 ml of 20% caustic soda (NaOH) solution in water. Subsequently the solution was analysed by purge and trap gas chromatography (FID). b) 10% ethanol: 10 ml of the 10% ethanol migration solution was analysed by purge and trap gas chromatography (FID). Method: Gas Chromatograph: Carlo Erba 5300 Mega, column: ZB 624, length 60 m, inner diameter 0.32 mm, film thickness 1.8 µm, carrier gas: 120 kPa helium, Temperature program: 35 °C (6 min), rate 5 °C min⁻¹, 90 °C (0 min) rate 10 °C min⁻¹, 260 °C (15 min). Purge and trap conditions (PTA 3000): sample temperature 40 °C, purge time: 20 min, purge flow 20 ml min⁻¹, trap temperature: -65 °C, desorption temperature 200 °C, desorption time 7 min, water trap MWT, Tenax[®] trap. Quantification was achieved by external calibration using standard solutions of the surrogates.

Determination of the surrogate concentrations in migration solutions by GC/MS (SIM)

The 3% acetic acid and 10% ethanol migration solutions were extracted three times with *n*-hexane (20 ml of food simulant with 8 ml, 5 ml and 5 ml of *n*-hexane). Subsequently the concentrations of methyl stearate was determined using GC/MS in the selective ion mode (SIM). The mass fragment $m/z = 74$ was used for quantification. $m/z = 87$ was used as qualification ion. GC/MS System: Shimadzu QP

5000, column: DB VRX - 30 m - 0.32 mm i.D. - 1.8 μ m film thickness, temperature program: 40 $^{\circ}$ C (5 min), rate 15 $^{\circ}$ C min⁻¹, 250 $^{\circ}$ C (15 min), pressure: 64 kPa hydrogen, splitless, interface temperature: 260 $^{\circ}$ C, Injector temperature: 250 $^{\circ}$ C. Quantification was achieved by external calibration using standard solutions of the surrogates.

Determination of the benzophenone concentrations in migration solutions by HPLC (UV)

The migration solutions were analysed by HPLC (UV). HPLC equipment: Dionex, column: Phenomenex, Synergi Fusion RP 150 $\times$ 2.0 mm, 4 μ m particle size, guard column, mobile phase: 60% acetonitrile and 40% water, isocratic elution, flow rate: 0.3 ml min⁻¹, oven temperature: 25 $^{\circ}$ C, detection at 254 nm, injection volume: 10 μ l.

Detection Limits

The detection limits were determined according to DIN 32645. The detection limits of the applied methods for the determination of the surrogates in the different food simulants are given in Table 1.

Place here Table 1

Results and Discussion

Spiking Levels of Test Bottles

The concentration of the surrogates in the bottle wall was analysed after manufacturing of the spiked bottles as well as after coating. The concentrations are measured by extraction of the PET bottle wall with HFIP/*iso*-propanol and gas chromatographic analysis. The results are summarised in Table 2 (mean value from three individual bottles). The contamination levels are slightly higher for the medium and low volatile substances (phenyl cyclohexane, benzophenone, methyl stearate)

than for volatile substances like the solvents toluene and chlorobenzene. During preform and bottle manufacturing of the test bottles, the concentration of the high volatile substances are reduced due to vaporisation.

Place here Table 2

Specific migration testing

The specific migration testing was performed using three different detection methods. Volatile surrogates were quantitatively determined using a purge and trap gas chromatographic method. The method shows detection limits and a good linearity of the calibrations curves. However, the method is limited to the volatile toluene, chlorobenzene and phenyl cyclohexane only. For benzophenone an HPLC/UV method was applied. In the case of methyl stearate, the analytical detection in the migration solutions at detection limits below $10 \mu\text{g l}^{-1}$ failed due to interferences and analytical artefacts. The applied gas chromatographic separation with mass spectrometric determination in the single ion mode (GC MS (SIM)) was not sensitive enough for the determination of methyl stearate in the $10 \mu\text{g l}^{-1}$ range. Therefore the results of methyl stearate were not used for the evaluation of the maximum bottle wall concentrations. However, the concentrations of methyl stearate in the migration solutions after storage for 10 d at 40°C was below the analytical detection limit of $13.0 \mu\text{g l}^{-1}$ (3% acetic acid) and $25.4 \mu\text{g l}^{-1}$ (10% ethanol). The results of the specific migration testing for toluene and chlorobenzene with the contact conditions 10 d at 40°C into 3% acetic acid and 10% ethanol are given in Table 3. For toluene and chlorobenzene the experimental migration kinetics follows the prediction by changing the bottle wall concentration ($c_{P,0}$). The concentration of phenyl cyclohexane in migration simulants after storage for 10 d at 40°C are for all investigated bottle wall concentrations (coated and non-coated) below the analytical detection limits of $0.9 \mu\text{g l}^{-1}$ and $1.1 \mu\text{g l}^{-1}$, respectively. For benzophenone only the bottles with the highest concentrations were measured. The migration was below the analytical detection limit of $8.8 \mu\text{g l}^{-1}$.

Place here Table 3

Migration kinetics into 10% ethanol

For the high level spiked test bottles (non-coated and coated) a migration kinetics was established up to a storage time of 30 d at 40 °C. Table 4 summarizes the results of the migration kinetics for toluene, chlorobenzene, phenyl cyclohexane and benzophenone in 10% ethanol. As a result the surrogates toluene and chlorobenzene follow this linear correlation (Figure 1) between the square root of time and the migration for the non-coated as well as for the SiO_x coated test bottle which indicates that the migration follows Fick's law. For phenyl cyclohexane and for benzophenone, the concentrations in the migration solutions are too low for a correlation.

Place here Table 4

Place here Figure 1

Maximum concentrations of surrogates in the bottle wall

For the evaluation of food law compliance of the PCR PET containing and SiO_x coated PET bottles a maximum migration of 10 µg l⁻¹ into food simulants at 40 °C was applied. It should be noted that this 10 µg l⁻¹ migration limit is not an officially by EU Directives recognised threshold of no concern for potential contaminants from PCR plastics (see introduction). The maximum acceptable concentrations of surrogates in the bottle wall, which corresponds to a 10 µg l⁻¹ migration value in the investigated 300 ml bottle, can be calculated from the correlation between the bottle wall concentration and the resulting specific migration into the investigated food simulants due to the fact that according to migration theory the bottle wall concentration correlates linear with the concentration in food simulant for a specific migrant. Such a correlation after storage for 10 d at 40 °C was established for the surrogates toluene and chlorobenzene for the non-coated test bottles (Table 3). From the slope of the linear correlation the maximum concentration could be estimated directly. The intercept was not taken into account. For phenyl cyclohexane and benzophenone as well as for toluene and chlorobenzene in the SiO_x coated

bottles, the concentrations in the migration solutions were below $10 \mu\text{g l}^{-1}$ even at the highest bottle wall concentrations. The estimated maximum acceptable concentrations in PET material which correlate with a $10 \mu\text{g l}^{-1}$ migration limit in food simulants are summarised in Table 5. In the cases of a migration below the analytical detection limits, the highest concentration level in the spiked test bottles was used as maximum acceptable bottle wall concentration. For the SiO_x coated bottles the maximum concentrations in the bottle wall are much higher due to the additional barrier effect in comparison to the non-coated reference bottle.

Place here Table 5

Conclusions

From analytical screening tests on PET recyclate samples taken from the market, it has been shown, that the concentrations of foreign compounds in production batches of conventionally recycled PCR PET do not exceed a concentration level of about 50 mg kg^{-1} for any individual post-consumer compounds (Franz et al 2003, Franz et al 2004b). Chemical compounds, which are introduced into the bottle wall by misuse of PET bottles for the storage of e.g. household chemicals have high levels in the individual bottle. However, due to the rarity of this event and due to the dilution of the contaminated PET flakes during washing with non-contaminated flakes, the average residual concentration of chemical compounds from misuse are more likely to be $<10 \text{ mg kg}^{-1}$ (Franz et al 2004b). Therefore, the artificially established initial concentrations used in this study and especially at the high spiking level would be far above any relevant concentrations of post-consumer compounds occurring in practice and would represent a worst-case scenario for the input-material.

From the ratios of the slopes of the migration kinetics (concentration in food simulant versus square root of time) the barrier effect for the SiO_x coating layer for reducing the migration of toluene and chlorobenzene in 10% ethanol was determined to 37 and 29, respectively. Therefore, the data shows the SiO_x layer significantly reduces migration. It can be assumed, that the barrier effects for other surrogates or post-

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consumer compounds are in a similar range. The migration tests were performed on a 0.3 l bottle with a surface of about 280 cm². Due to the more favourable surface/volume ratios of larger bottles, the estimated maximum levels given in Table 8 can be considered as worse case. Therefore the maximum levels of possible contaminants in the bottle wall will increase with increasing bottle size (increasing surface/volume ratio).

The experimental data from this study demonstrate that SiO_x coated PET bottles produced from the contaminated test batch would be in accordance with the 10 µg l⁻¹ migration limit as long as the estimated maximum concentrations given in Table 8 are not exceeded. The maximum bottle wall concentrations of the surrogates are in the range of 200 mg kg⁻¹ (toluene) and about 900 mg kg⁻¹ (benzophenone). Therefore the investigated SiO_x coating layer is an efficient functional barrier towards recycle typical compounds. Consequently, this SiO_x coating layer would allow the use of conventionally recycled post-consumer PET flakes without super-clean recycling processes for packaging aqueous and low alcoholic foodstuffs under cold-fill conditions and prevent the food from migration of unwanted contaminants from post-consumer PET. In addition, it should be noted that the drawn conclusions implicate the worst case assumption that 100% post-consumer recycle is used for PET bottle manufacturing.

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Literature

AFFSA. 2006. Opinion of the French Food Safety Agency (AFFSA) on the assessment of health risks associated with the use of materials made from recycled

poly(ethylene terephthalate) intended for or placed in contact with foodstuffs and drinking water. Mandate no 2001-SA-0315, 27. November.

Begley TH, Hollifield HC. 1993. Recycled polymers in food packaging: migration considerations. *Food Technology* 109-112.

BgVV 2000. Use of mechanical recycled plastic made from polyethylene terephthalate (PET) for the manufacture of articles coming in contact with food. Berlin: Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin.

Boutroy N, Pernel Y, Rius JM, Auger F, von Bardeleben HJ, Cantin JL, Abel F, Zeinert A, Casiraghi C, Ferrari AC, Robertson J. 2006. Hydrogenated amorphous carbon film coating of PET bottles for gas diffusion barriers. *Diamond & Related Materials* 15:921-927.

Cruz SA, Zanin M, Nerin C, De Moraes MAB. 2006. Study of barrier properties and chemical resistance of recycled PET coated with amorphous carbon through a plasma enhanced chemical vapour deposition (PECVD) process. *Food Additives and Contaminants* 23:100-106.

Dimitroulas GD, Badeka AB, Kontominas MG. 2004. Permeation of methylethylketone, oxygen and water vapor through PET films coated with SiOx: Effect of temperature and coating speed. *Polymer Journal*. 36:198-204.

Dole P, Voulzatis Y, Vitrac O, Reynier A, Hankemeier T, Aucejo S, Feigenbaum A. 2006. Modelling of migration from multi-layers and functional barriers: Estimation of parameters. *Food Additives and Contaminants* 23:1038-1052.

FDA 1992. Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations. HFF-410. Washington, DC: US Food and Drug Administration, Center for Food Safety and Applied Nutrition.

FDA 2006, Guidance for Industry: Use of Recycled Plastics in Food Packaging: Chemistry Considerations. HFS-275, Washington, DC: US Food and Drug Administration, Center for Food Safety and Applied Nutrition.

1
2
3
4
5
6 FDA 2007. Recycled plastics in food packaging. US Food and Drug Administration.
7 Center for Food Safety & Applied Nutrition, Office of Premarket Approval. Internet:
8 <http://vm.cfsan.fda.gov/~dms/opa-recy.html> [March 2007].
9

10
11 Feigenbaum A, Dole P, Aucejo S, Dainelli D, Garcia dIC, Hankemeier T, N'Gono Y,
12 Papaspyrides D, Paseiro P, Pastorell S, Pavlidou S, Pennarum PY, Saillard P, Vidal
13 L, Vitrac O, Voulzatis Y. 2005. Functional barriers: Properties and evaluation. Food
14 Additives and Contaminants 22:956-967.
15
16

17
18 Finch DS, Franks J, Randall NX, Barnetson A, Crouch J. Evans AC, Ralph B. 1996.
19 Diamond-like Carbon, a barrier coating for polymers used in packaging applications.
20 Packaging Technology and Science. 9:73-85.
21
22

23
24 Franz R, Huber M, Piringer OG, Damant AP, Jickells SM, Castle L. 1996. Study of
25 functional barrier properties of multilayer recycled poly(ethylene terephthalate)
26 bottles for soft drinks. Journal of Agricultural and Food Chemistry 44:892-897.
27
28

29
30 Franz R, Huber M, Piringer O. 1997. Presentation and experimental verification of a
31 physico-mathematical model describing the migration across functional barrier layers
32 into foodstuffs. Food Additives and Contaminants 14:627-640.
33
34

35
36 Franz R, Huber M, Welle F. 1998. Recycling of post-consumer poly(ethylene
37 terephthalate) for direct food contact application - a feasibility study using a simplified
38 challenge test. Deutsche Lebensmittel-Rundschau 94:303-308.
39
40

41
42 Franz R, Welle F. 1999. Post-consumer poly(ethylene terephthalate) for direct food
43 contact applications - final proof of food law compliance. Deutsche Lebensmittel-
44 Rundschau 95:424-427.
45
46

47
48 Franz R, Welle F. 2002. Post-consumer Poly(ethylene terephthalate) for Direct Food
49 Contact Application - Challenge-Test of an Inline Recycling Process. Food Additives
50 and Contaminants 19:502-511.
51
52

53
54 Franz R, Welle F. 2003. Recycling packaging materials. In: Ahvenainen R, editor.
55 Novel food packaging techniques. Cambridge Woodhead, pp 497-518.
56
57
58
59
60

1
2
3
4
5 Franz R, Bayer F, Welle F. 2004a. Guidance and criteria for safe recycling of post
6 consumer polyethylene terephthalate (PET) into new food packaging applications.
7 Report No. 21155. Luxembourg: Office for Official Publications of the European
8 Communities.
9
10
11

12
13 Franz R, Mauer A, Welle F. 2004b. European survey on post-consumer
14 poly(ethylene terephthalate) materials to determine contamination levels and
15 maximum consumer exposure from food packages made from recycled PET. Food
16 Additives and Contaminants 21:265-286.
17
18
19

20
21 ILSI 1998. Recycling of plastics for food contact use. Guidelines prepared under the
22 responsibility of the International Life Sciences Institute (ILSI) European Packaging
23 Material Task Force. Brussels: ILSI.
24
25
26

27
28 Mueller K, Welle F. 2005. PET in beverage packaging. Plast Europe 95(10):120-125.
29

30
31 Piringier O, Huber M, Franz R, Begley TH, McNeal TP. 1998. Migration from food
32 packaging containing a functional barrier: Mathematical and experimental evaluation.
33 Journal of Agricultural and Food Chemistry 46:1532-1538.
34
35

36
37 Welle F, Franz R. 2006. Recycled Plastics and Chemical Migration into Food. In: K.
38 A. Barnes, C. R. Sinclair, D. H. Watson, editors. Chemical migration and food
39 contact materials. Woodhead Publishing Cambridge, pp 205-227.
40
41

42
43 Yamamoto S, Kodama H, Hasebe T, Shirakura A, Suzuki T. 2005. Oxygen
44 transmission of transparent diamond-like carbon films. Diamond & Related Materials
45 14:1112-1115.
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Figure 1: Migration kinetics of toluene and chlorobenzene into 10% ethanol at 40 °C (high level bottles)

Table 1: Detection limits of the applied model compounds in food simulants

Surrogate	Detection limit [$\mu\text{g l}^{-1}$] (method)				
	Toluene (p&t GC)	Chlorobenzene (p&t GC)	Phenyl cyclohexane (p&t GC)	Benzophenone (HPLC/UV)	Methyl stearate (GC MS SIM)
3% Acetic acid	1.0	0.7	1.1	8.8	13.0
10% Ethanol	0.4	0.3	0.9	8.8	25.4

Table 2: Concentration of the surrogates in the bottle wall of the spiked PET bottles determined after extraction with HFIP/*iso*-propanol (mean values of the concentrations and standard deviation from three individual bottles)

Test bottle type	Concentration [ppm]				
	Toluene	Chlorobenzene	Phenyl cyclohexane	Benzophenone	Methyl stearate
low level, non-coated	17.6 ±0.6	26.2 ±0.5	35.3 ±1.0	91.4 ±2.4	107.0 ±2.9
low level, coated	18.7 ±0.3	26.1 ±0.4	32.2 ±0.4	88.9 ±0.7	104.6 ±1.0
medium level, non-coated	70.6 ±0.6	101.3 ±0.8	261.7 ±1.7	394.3 ±3.2	400.9 ±3.0
medium level, coated	57.0 ±0.1	87.6 ±0.3	240.9 ±1.6	396.1 ±2.7	412.5 ±3.4
high level, non-coated	297.5 ±1.2	357.8 ±1.5	782.3 ±1.4	973.9 ±3.5	1029.1 ±16.3
high level, coated	203.6 ±1.5	249.5 ±1.8	601.3 ±4.9	882.5 ±7.7	904.1 ±11.5

Table 3: Concentration of toluene and chlorobenzene in migration simulants after storage for 10 d at 40 °C determined by purge and trap gas chromatography

Simulant	Migrant	bottle type	concentration in food simulant [µg l ⁻¹]			slope	Intercept	Correlation coefficient R ²
			low level	medium level	high level			
3% acetic acid	Toluene	non-coated	1.4	2.3	14.5	0.0489	-0.2170	0.9862
10% ethanol	Toluene	non-coated	2.3	8.6	43.4	0.1488	-1.0284	0.9987
3% acetic acid	Chlorobenzene	non-coated	3.2	5.7	32.6	0.0928	-1.1818	0.9803
10% ethanol	Chlorobenzene	non-coated	4.5	17.1	65.4	0.1848	-0.9022	0.9996
3% acetic acid	Toluene	coated	<1.0	<1.0	<1.0	/	/	/
10% ethanol	Toluene	coated	<0.4	<0.4	1.1	/	/	/
3% acetic acid	Chlorobenzene	coated	<0.7	<0.7	<0.7	/	/	/
10% ethanol	Chlorobenzene	coated	<0.3	0.3	1.7	0.0086	-0.4875	/

Table 4: Results of the migration kinetics of the model compounds from the test bottles into 10% ethanol at 40 °C

storage time [d]	concentration [$\mu\text{g l}^{-1}$] (bottle wall concentration [ppm])							
	Toluene		Chlorobenzene		Phenyl cyclohexane		Benzophenone	
	non coated (297.5 $\pm$ 1.2)	SiO _x coated (203.6 $\pm$ 1.5)	non coated (357.8 $\pm$ 1.5)	SiO _x coated (249.5 $\pm$ 1.8)	non coated (782.3 $\pm$ 1.4)	SiO _x coated (601.3 $\pm$ 4.9)	non coated (973.9 $\pm$ 3.5)	SiO _x coated (882.5 $\pm$ 7.7)
3	24.7	<0.4	32.7	0.3	<0.9	<0.9	not determined	not determined
6	38.6	0.7	53.8	1.1	<0.9	<0.9	not determined	not determined
10	43.4	1.1	65.4	1.7	<0.9	<0.9	<8.8	<8.8
20	63.0	2.1	99.0	3.2	<0.9	<0.9	14.8	<8.8
30	98.5	2.1	146.4	4.0	1.6	<0.9	21.2	<8.8

Table 5: Estimated maximum concentrations [ppm] of the investigated model compounds in the bottle wall of the test bottles corresponding to a migration of $10 \mu\text{g l}^{-1}$ in food simulant (contact conditions: 10 d at 40 °C)

Surrogate	Estimated maximum concentrations [ppm] in the bottle wall			
	non-coated bottle		SiO _x coated bottle	
	3% acetic acid	10% ethanol	3% acetic acid	10% ethanol
Toluene	204	67	>204	>204
Chlorobenzene	108	54	>250	>250
Phenyl cyclohexane	>782	>782	>601	>601
Benzophenone	>974	>974	>883	>883