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# Internal bags with barrier layers for foods packed in recycled paperboard: recent progress

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**Abstract** Internal bags for packaging dry foods into boxes of recycled paperboard, collected in Dresden and Zurich in June 2013, were investigated with regard to the layer composition and the barrier efficiency against substances migrating from the recycled fibers. The layers were identified by microtome cuts and Fourier transform infrared spectroscopy, often after wet-chemical separation of the layers. The barrier efficiency was tested with five surrogate substances and classified between 1 and 5, with class 1 having no significant barrier effect, 4 being a virtually tight barrier consisting of polymeric material and 5 including an aluminum foil. Merely 17 of the 87 bags (20 %) consisted of paper or polyethylene that constituted insignificant barriers. Bags of oriented polypropylene, substantially reducing migration (class 2), were encountered in 32 % of the packs; those with more efficient, but still incomplete barriers (class 3) in 16 % and virtually tight barriers (classes 4 and 5) in 32 % of the products. This is a strong move toward efficient barriers compared to the findings in 2010. Efficient or tight barriers were found for nearly all food types, which suggests that there are no important technical obstacles against the inclusion of a barrier layer into all bags to protect the food against contamination from the recycled paper board.

**Keywords** Paperboard boxes · Barrier test · Barrier efficiency · Surrogate substances · Dry foods

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## Introduction

Recycled paperboard is of limited suitability for food packaging, not only because of mineral oil migrating into food [1, 2], but also because of many other substances the safety of which cannot reasonably be ensured due to their number and variation depending on the material entering the recycling process. For most foods stored in boxes of recycled paperboard for more than a few days, the German Federal Institute for Risk Assessment (BfR) recommended to introduce a functional barrier [2]. This barrier should be of an efficiency to restrict migration below the limits determined by regulation, toxicological evaluation or the threshold of concern for unidentified substances.

If foods are packed into an internal bag, this barrier can be integrated into the bag. For foods directly packed into recycled paperboard, a barrier layer could be applied to the internal surface of the box. Also migration from transport boxes, often of corrugated board, or of trays to present products in the store may be a problem if the primary packaging does not include a barrier [3].

Plastics with barrier properties, often multilayer films, are readily available for some time. They were mostly conceived as barrier against gases or humidity. Others, used to prevent permeation of aroma or odorous compounds, are effective against organic substances, which more closely corresponds to the needs for preventing food contamination from recycled paperboard. While aluminum foils are absolute barriers, several plastic materials slow the migration to a sufficient extent to act as a barrier under certain conditions [4–8].

An experimental method for the determination of the breakthrough of mineral oils as used in printing inks through plastic films or coated paperboard was proposed in [9]: a paper spiked with such mineral oil and a dye (Sudan

red II) as donor was fixed to one side of the material to be tested and a polyethylene (PE) film as receptor to the other. Periodically, a section of the PE film was removed and analyzed for mineral oil broken through the barrier. The dye was used to check the distribution of the mineral oil on the donor sheet, but also to optically spot local deficiencies in the barrier, such as pin holes, breaks, scratches or damage from creasing. For efficient barriers, migration was accelerated by heating to 40 or 60 °C. Acceleration was estimated by the Arrhenius equation and the activation energy assumed in EU Regulation 10/2011: it amounted to a factor of 4.6 for the temperature increase from 25 to 40 °C and to a factor of 30 from 25 to 60 °C. However, results obtained at increased temperature must be considered with care, since warming may alter the polymer structure in a way weakening the barrier. This test indicated that at ambient temperature mineral oil breaks through PE films within less than a day. Oriented polypropylene (OPP) acted as a barrier for a few weeks, but this property was lost by an even slight temperature increase. It also revealed that barrier efficiencies were frequently determined by deficiencies in the layer, i.e., that the integrity of the layer may be more critical than the material used.

Ewender, Franz and Welle [10] described a test involving 15 surrogate standards, mainly mineral oil constituents, but also a diisopropyl naphthalene (DIPN), two benzophenones and 2,2,4-trimethyl-1,3-pentanediol-di-iso-butyrate (TXIB). These were applied to a disk of paperboard placed below the polymer film to be tested in a permeation cell kept at 40 °C. From the upper room of the cell, the migrated material was swept onto a trap and analyzed by GC.

Diehl, Seyffer and Pfeiffer [11] introduced a rapid test intended for industrial development or production control. They used hexane as a surrogate, since the small size of the molecule strongly accelerates migration compared to mineral oils. This hexane was introduced into a pot that was covered by the barrier material to be tested. The weight loss by diffusion through the barrier was monitored on a balance over one or a few days. Tiggeleman, Pasch and Hartmann [12] described a similar screening test, using a reversed configuration and n-heptane as mineral oil simulant. A low pot was filled with activated carbon and closed by the barrier material to be tested. It was placed in a desiccator at 23 °C with a heptane-saturated atmosphere. Migration was determined gravimetrically by the increase in the weight resulting from transfer of heptane through the barrier into the adsorbent. Both tests are rapid and convenient to use, but have not been calibrated against mineral oil migration and there is some uncertainty whether there is a simple correlation.

As mineral oil is only one of many compounds of potential concern for the migration from recycled paperboard, in a recently described test [13], it was replaced by 5 surrogate compounds covering a broad range of polarities, i.e.,

n-heptadecane, n-octadecane, 4-methyl benzophenone, dipropyl phthalate and triethyl citrate. Strong selectivity effects were observed. For instance, polyamide and cellulose-based materials were efficient barriers against the migration of hydrocarbons, whereas OPP was most efficient for polar surrogates. Furthermore, migration strongly depended on the molecular mass/volatility of the components.

In April 2010, 119 samples of dry foods packed in paperboard were collected from the German market and analyzed for migration of mineral oil hydrocarbons [14]. The same samples were analyzed a second time after 4 months in August 2010 and a third time either at the end of their shelf life or, if the expiry date was still not reached, in August 2011 [15]. During storage, they were wrapped into aluminum foil to prevent absorption of mineral oil from outside and evaporation from the box to the outer atmosphere, which approximated the situation of the pack in a transport box or piled on a pallet.

In the meantime, many producers reacted. Some changed to fresh fiber paperboard, which, however, may be only a partial solution if these packs are stored in transport boxes made with recycled fibers. Others changed to plastic bags, leaving the paperboard away. Manufacturers of recycled paperboard developed board with an internal coating that acts as a barrier, but up to summer 2013, the efficiencies of these barriers were not yet known well enough and the material was not available in large scale.

Many packers changed to internal bags with a barrier layer, which is subject of this report. In Germany, 29 products of the 2010 campaign with an internal bag and reaching more than 1 mg/kg mineral oil aromatic hydrocarbons (MOAH) in the food were collected again. As there was no such reference in Switzerland, products in recycled paperboard with an internal bag were randomly collected and tentatively compared with those collected from the German market in 2010. The methods applied for evaluation, the type of barrier materials encountered and the efficiencies of these barriers are described.

## Materials and methods

Recycled paperboard was recognized by its grayish taint as well as by the characteristic patterns of mineral oil saturated hydrocarbons (MOSH) and MOAH checked by GC-FID whenever there was uncertainty.

The external and internal sides of the bags were characterized by Fourier transform infrared spectroscopy (FT-IR) on a spectrum one FT-IR spectrometer (PerkinElmer, Schwerzenbach, Switzerland). Films were mounted on the golden gate attenuated total reflection (ATR) insert of the spectrometer with a diamond crystal and single reflection (Specac, Orpington, UK). The penetration depth equals



approximately one wavelength, ranging from approximately 3–10  $\mu\text{m}$  for wave numbers of 3,300–1,000  $\text{cm}^{-1}$ . For identification of the polymers, the IR spectra obtained were compared to commercial and in-house spectral libraries with the PerkinElmer software Spectrum v5.3.1.

Microtome cuts of 5  $\mu\text{m}$  thickness were prepared using a manual rotary microtome (Leica RM 2035, Wetzlar, Germany). The slices were transferred onto a microscope slide using an adhesive film, embedded in a liquid resin (Roti Histokitt II, Roth, Karlsruhe, Germany) and covered by a glass plate. The polymer layers were investigated using a transmitted light microscope with polarized light (Meiji MX 4000L, Axbridge, Great Britain) and 400-fold magnification. The preparations were displayed on a monitor using a digital camera (dhs pixel-fox<sup>®</sup>) mounted on the microscope, then processed and documented by the software pixel-fox<sup>®</sup> 4.01 (dhs Dietermann and Heuser Solution GmbH, Greifenstein-Beilstein, Germany). Thicknesses of the layers were determined after calibration with a stage micrometer.

Multilayers ( $n \geq 3$ ) were separated by partly dissolving one of the layers or the adhesive. Hot or boiling formic acid was used to dissolve polyurethane (PUR)-based adhesives, polyamide and aluminum. Hot toluene dissolved PE, polypropylene (PP; PE faster than PP) and PE vinyl acetate copolymer (EVA).

Laminates with adhesive: After boiling in hot formic acid, the adhesive was dissolved from the edge of the multilayer to peel off the upper film/layer in diagonal direction. The adhesive left on the laminate was identified by FT-IR (4,000–600  $\text{cm}^{-1}$ ) with ATR-element (Thermo Scientific FT-IR Nicolet iS5 with iD5-element, diamond crystal, Dreieich, Germany). Then, the adhesive was removed from the separated parts by further boiling in formic acid and the films next to the adhesive identified by FT-IR.

Multilayers with coextruded PP or PE often consist of more than one PE, EVA or PP layer. The outer ones were swollen and partly dissolved in hot toluene then removed one after another. After solvent evaporation, the consecutively exposed films were identified by FT-IR. Coextruded films with materials other than PE or PP were boiled in hot toluene until all PE or PP was dissolved. The undissolved layer was identified via FT-IR.

From PP films coated with PMMA, the PMMA was removed by wiping with a cotton stick soaked with methanol to identify the film material behind the coating. PVDC coatings were identified by FT-IR and confirmed by the Beilstein test: green flame from some polymer picked up onto a copper wire heated in a flame.

Barrier efficiencies were determined by the test reported in [13]. Briefly, a donor paper with dipropyl phthalate (DPP), 4-methyl benzophenone (MBP), triethyl citrate (TEC), n-heptadecane ( $\text{C}_{17}$ ) and n-octadecane ( $\text{C}_{18}$ ) as surrogates and Sudan red II was attached to the outer surface

of the opened bags, with a piece of clean paper in between to rule out wetting contact. It was sealed against the bag by an aluminum foil and tape. A silicone paper was placed on the other side, serving as receptor for the components that permeated through the barrier. Amounts of the surrogate substances measured in the silicone paper were expressed as percentages of those in silicone paper after equilibration with all components of the test package in a glass vial.

## Results

### Structures of the bags

Structures of the films used for the internal bags were investigated by microtome cuts, FT-IR-ATR and transmission microscopy combined with a digital camera. Thicknesses of the layers were determined using imaging software. First hints on the identity of the polymer were obtained from the color with polarized light. Using this information (number, thickness and position of layers, color), the laminates were separated by dissolving certain layers or adhesives. The polymers of the now exposed layers were identified by FT-IR-ATR.

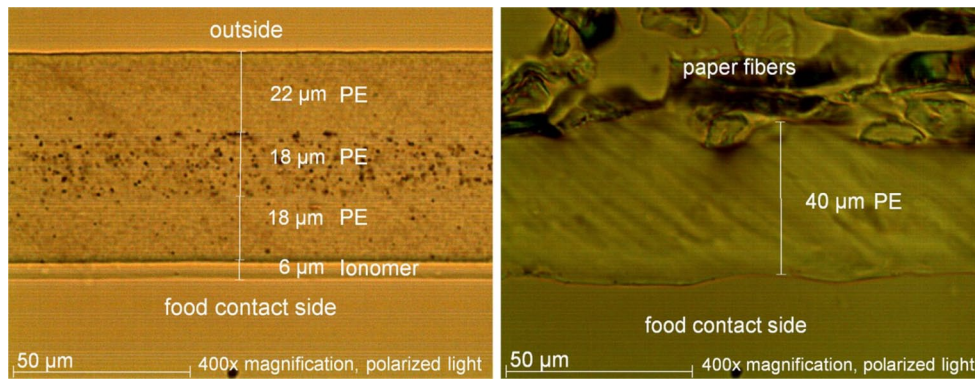
The composition of the bags varied from a PP monolayer to complex laminates with up to seven different layers and polymers. The materials identified were paper, aluminum (Al), PE, PP, polyethylene terephthalate (PET), glycol-modified PET (PET-G), polyamide (PA), polyethylene vinyl alcohol co-polymer (EVOH), EVA, cellophane, polymethyl methacrylate (PMMA) and polyvinylidene chloride (PVDC), the last two applied as lacquers on PP films.

Some of the layers were coextruded, sometimes with adhesion-promoting layers, such as EVA, with a polarity between those of the layers to be combined. Layers of different polarity were also laminated using an adhesive, such as a polyurethane (PUR, isocyanate-polyester type). Below, double slash (//) is used for lamination by an adhesive, and a single slash (/) for co-extrusion.

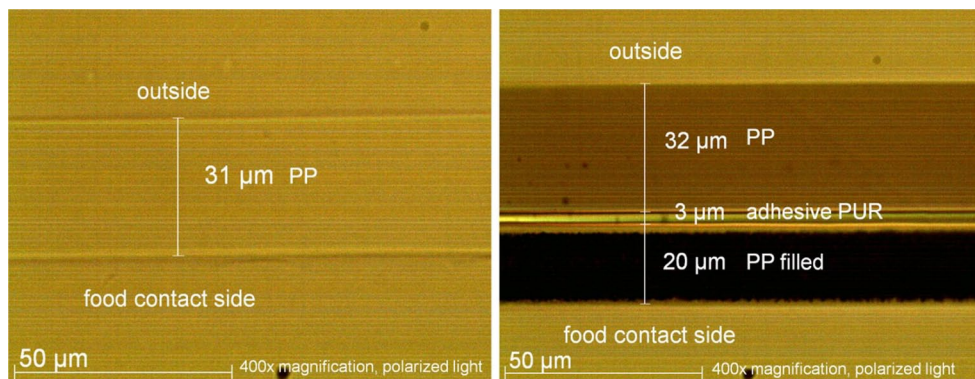
Multi-layer films consisting of two or three PE layers (one of them filled with pigments for an opaque appearance) and an ionomer on the food contact side as sealing layer (Fig. 1 left) were frequently used for cereals and mueslis. PE-coated paper bags were often used for baking mixtures and crispbread (Fig. 1 right).

Thirty of the 87 investigated products were packed in PP-monolayers (Fig. 2 left), PP double layers (Fig. 2 right) or PE/PP double layers. It is assumed that most PP films were biaxially oriented. The thickness of the PP layers varied between 20 and 60  $\mu\text{m}$ .

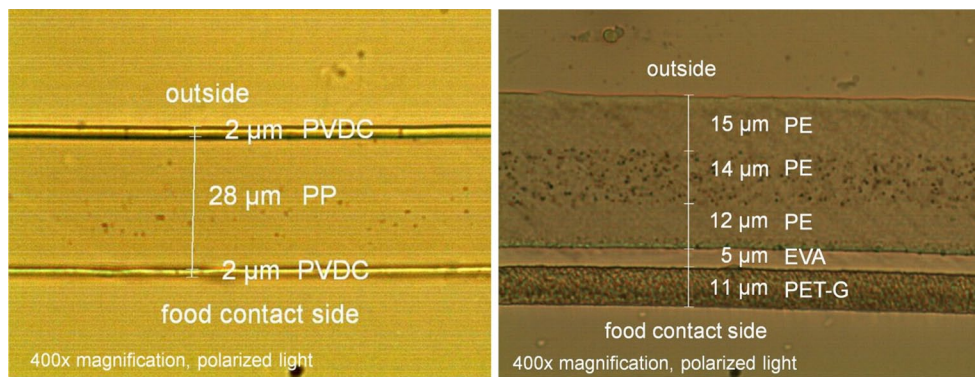
Some PP films were lacquered with PMMA or PVDC. The thickness of the lacquer layers was not accurately measurable by transmission microscopy in the microtome



**Fig. 1** Microtome cuts of an inner bag used for cereals (PE/PE/PE/ionomer; *left*) and a PE-coated paper bag (*right*)



**Fig. 2** Microtome cuts of a PP monolayer (*left*) and a PP double layer laminated with an adhesive (*right*)

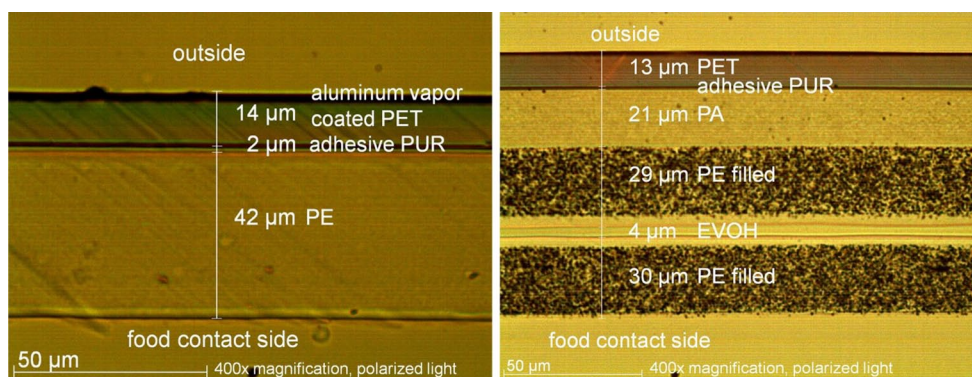


**Fig. 3** Microtome cuts of a PP film lacquered with PVDC on both sides (*left*) and an inner bag for cereals with a sealable polyester (PET-G) on the food contact side (*right*)

cut ( $<3 \mu\text{m}$ ; Fig. 3 left), but the identification of the polymer with FT-IR-ATR in combination with the Beilstein test was unambiguous. PVDC was also used as barrier coating: paper was coated with PE and a PVDC/PMMA copolymer, the latter being in food contact and sealable.

A new development seems to be the use of glycol-modified polyesters (PET-G) as heat-sealable food contact

layer. The inner bags of seven cereal products consisted of a co-extrudate of two or three PE layers, an EVA layer as adhesion promoter and a sealable polyester (Fig. 3 right). The sealability of the polyester depends on the ratio of diethylene glycol to ethylene glycol in the polymer [16]. The homopolymeric PET has a high melting temperature ( $260 \text{ }^\circ\text{C}$ ) due to its regular structure in comparison with



**Fig. 4** Microtome cuts of vapor-deposited aluminum on PET (*left*) and a complex structure of polymers with high barrier efficiency (PET/<sup>PUR</sup>PA/PE/EVOH/PE; *right*)

PET-G in which neighboring chain interactions are reduced due to co-monomers such as diethyleneglycol resulting in a melting temperature below 90 °C. Due to its polar character, PET is often laminated by an adhesive to non-polar layers.

Aluminum can be used as foil (laminated by an adhesive) or as vapor coating on PP, PA or PET (Fig. 4 left). Vapor-coated aluminum is also used for optical reasons. The metal can be located on the outside or in the middle of the laminate, where it is protected against scratches. EVOH layers are used as aroma and gas barrier. As they have to be protected against humidity, they are typically coextruded between PP or PE layers (Fig. 4 right).

#### Classes of barrier efficiencies

Efficiencies of the bags in reducing the migration from the recycled paperboard to the food were evaluated using surrogate substances [13]. Test packs were initially kept at room temperature (RT). If more than 50 % breakthrough within a week was observed for at least one surrogate substance, the test was stopped. Otherwise, it was continued, first at RT, then usually at 40 °C and for some also at 60 °C. OPP must be evaluated at RT, as the barrier efficiency is underestimated when heating to 40 °C [9, 17].

Barrier efficiencies were classified between 1 and 5. Class 1 comprised materials without relevant barrier efficiency, class 5 the complete barriers, namely aluminum foils. Internal bags of class 1 showed strong breakthrough already after a week at RT: breakthrough exceeded 80 % for the n-alkanes, MBP and DPP, but was sometimes lower for the highly polar TEC. They consisted of paper, paper laminated with PE or EVA, or only of PE (see detailed descriptions listed below). For PE films, it was previously shown that they hardly slow migration of mineral oil compared to packing directly in recycled paperboard boxes [15, 18], but reduce it by absorption.

Class 2 comprised OPP as monolayer or in combination with PE. In the barrier test involving a mineral oil for printing inks [9], 1 % breakthrough at ambient temperature occurred after 10–40 days (depending on film thickness) and 10 % breakthrough after 18–70 days. Using surrogate substances [13], for a 30-μm OPP film 10 % breakthrough was measured for C<sub>17</sub> after 6.3 days, for MBP after 5.3 days, for DPP after 27 days; the migration of TEC only reached 3 % after 30 days, pointing out the selectivity in its barrier efficiency. At 40 °C, breakthrough was virtually complete in less than a week. Migration of mineral oil during storage of foods in recycled paperboard boxes with internal OPP bags at RT has been shown to be low during the first about 6 months, but to become significant afterward. After 9 months, it was still roughly ten times lower than with PE bags made of films of comparable thickness and only in the range of a few percent of the potential migration [18]. Products from the market confirmed this result [15].

Class 4 comprised polymeric materials with high barrier efficiency. Calculating with acceleration by a factor of 4.6 for the temperature increase from 25 to 40 °C [9], the 22 weeks at 40 °C assumed as a minimum duration without breakthrough exceeding 1 % suggest tightness at 25 °C for at least 100 weeks. Most films classified as 4 were additionally tested at 60 °C for 5 weeks and still remained tight, which is equivalent to tightness at RT for 150 weeks when using an acceleration factor of 30. On the basis of this, class 4 barriers were considered adequate to protect foods from substances migrating from recycled paperboard whatever rules might be imposed in future.

Class 5 bags included an aluminum foil, usually integrated into a multilayer system, and were qualified as tight without testing. They did not include those with a vapor-deposited metal layer, which were tested and allocated to classes of inferior tightness.

Only relatively few bags belonged to class 3 barriers with a performance situated in the broad range between



**Table 1** Results obtained by the barrier test for internal bags; class 3 films except of samples 8 and 9. Number of weeks the material was tested at the given temperature. Percent of breakthrough compared to equilibrium [13]

	Composition of the bag* Outside → food contact side	Conditions		Breakthrough (%)				
		Weeks	°C	DPP	MBP	TEC	C17	C18
1	Ink (nicell)/25 µm PP foamed/3 µm PVDC	2	40	8	31	2.5	16	13
		4	40	15	44	6	20	17
2	1 µm PMMA/29 µm PP/1 µm PMMA	2	40	2.5	15	1.1	6	5
		6	40	16	53	15	13	11
3	2 µm PVDC/22 µm cellophane/21 µm cellophane/2 µm PVDC	5	40	<1	2.6	<1	3.0	1.4
		11	40	1.7	6	1.4	10	5
		16	40	5	7	3.0	15	8
4	Paper/26 µm PE/15 µm PVDC-PMMA	4	RT	<1	1.8	<1	2.3	1.3
		3	40	1.1	3.3	<1	5	2.7
		10	40	2.2	6	2.4	7	3.7
		15	40	3.7	10	3.5	10	6
5	2 µm PVDC/28 µm PP/2 µm PVDC	2	40	1.0	3.0	<1	<1	<1
		7	40	2.2	6	<1	1.1	<1
		13	40	2.8	11	6	1.4	<1
		18	40	2.2	15	5	1.6	<1
6	16 µm PE/15 µm PE filled/11 µm PE/6 µm EVA/12 µm PET-G	3	40	<1	1.2	<1	1.2	<1
		6	40	1.5	4.2	<1	3.0	2.0
		10	40	3.9	9	3.0	7	5
		15	40	11	18	4.0	17	12
7	13 µm PET// <sup>PUR</sup> 30 µm PE	10	40	<1	<1	<1	<1	<1
		16	40	3.8	4.1	<1	9	5
		21	40	2.7	2.9	1.6	7	3.8
8	2 µm ink (acryl)/paper// <sup>acryl</sup> Alv/17 µm PP/3 µm PE	16	40	<1	<1	<1	<1	<1
		21	40	<1	0.8	<1	1.1	<1
		25	40	<1	0.8	<1	1.2	<1
9	17 µm PA/50 µm PE	2	60	<1	<1	<1	<1	<1
		5	60	1.1	<1	<1	3.6	1.7
		9	60	1.8	1.1	<1	3.9	1.9

\**nicell* nitrocellulose, *PP* polypropylene, *PVDC* polyvinylidene chloride, *PMMA* polymethyl methacrylate, *PE* polyethylene, *EVA* ethylene-vinyl acetate, *PET-G* glycol-modified polyethylene terephthalate, *PET* polyethylene terephthalate (homopolymer), *PUR* polyurethane, *PA* polyamide, / co-extruded, // laminated by adhesive

class 2 (essentially PP) and the unambiguously tight materials of classes 4 and 5. They have in common that there was <1 % breakthrough after 1 week at RT plus 1 week at 40 °C, but substantial breakthrough earlier than class 4 films.

Selected test results covering and delimiting class 3 barriers are presented in Table 1. Samples 1 and 2 were at the low end of class 3 efficiency: they resisted for 1 week at RT plus 1 week at 40 °C, but then breakthrough started immediately. Printing based on nitrocellulose (nicell) and/or a thin PVDC layer (sample 1) as well as a PMMA coating (sample 2) enhanced the barrier properties of OPP. As shown before [13], MBP migrated at a higher rate than the other surrogate substances, while TEC migrated the least.

The limit between classes 3 and 4 was drawn between samples 7 and 8; samples 8 and 9 were the class 4 films with the highest breakthrough. Sample 8, paper printed with an acrylate varnish, glued by an acrylate adhesive to PP with vapor-deposited aluminum and a thin layer of PE on the food contact side, was only tested at 40 °C because of a glass transition temperature of the acrylates being below 60 °C (it was unclear which layer formed the relevant barrier). The first slight (analytically insignificant) breakthrough (1.1 %) was measured after 21 weeks, which was considered borderline for class 4. For sample 10, a polyamide (PA)/PE bilayer, breakthrough reached 3.6 % for C<sub>17</sub> after 5 weeks at 60 °C.

For the PVDC-coated cellulose (sample 3), breakthrough began after around 5 weeks at 40 °C and increased



after 11 and 16 weeks in an exponential manner compatible with expectations. The same applies to bags 4 and 5. Sample 6 stands for several of similar performance. The EVA and PET-G layers did not provide complete tightness. In the heat-sealable PET-G, part of the ethylene glycol was replaced by diethylene glycol [16], which decreased the melting point and apparently also the barrier efficiency.

Bag 7, with a 13- $\mu\text{m}$  PET layer glued by a PUR to PE, deviated from several similar films of class 4: there was significant migration after 16 weeks at 40 °C, but after additional 5 weeks, the values tended to decrease again. The same type of irregular migration was observed in figure 6 of Ref. [13]. It might be explained by local deficiencies in the barrier, as shown in Ref. [9]. Migration would be expected to cause early local breakthrough which slows when the zones close to the deficiencies are depleted. As stripes of about 10 cm<sup>2</sup> of the silicone paper were removed for each analysis, inhomogeneous distributions of the deficiencies result in varying values for the breakthrough. This means that class 3 includes deficient barriers of basically better materials.

#### Products sorted by internal bag

Of the 87 products analyzed, the 17 listed in Table 2 had internal bags without relevant barrier efficiency (class 1). Products in bags of virtually the same composition were grouped and their number is given in the third column. Five bags essentially consisted of paper, 12 of PE, mostly with an ionomer layer in food contact. Flakes (totally 7 samples), cereals (4) and muesli dominated for this type of packaging. Four products were organic (bio).

Internal bags of 28 products were class 2 barriers, essentially consisting of OPP (Table 3). Most of the packed products were of the type bakery ware (cakes, biscuits, crackers, crispbread and grissini).

The composition as well as the efficiency of the 14 internal bags evaluated as class 3 barriers (Table 4) varied widely (some test results in Table 1). Cereals and muesli dominated this group.

Also the 22 products in bags of class 4 (tight) barriers (Table 5) comprised a broad range of multilayers and virtually all types of food, suggesting that there are no technical or serious economic obstacles against using tight internal bags. Among the five products with an aluminum foil in the bag, there were three biscuits for babies, a muesli and a polenta.

#### Samples sorted by food type

Table 6 shows how the 36 products of the type bakery ware packed. Only one was packed into a class 1 bag (PE-laminated paper), of all things an organic cracker (sample 14),

**Table 2** Products with class 1 internal bags, i.e., bags without relevant barrier efficiency

	Food type	Nr.	Internal bag
1	Bread crumbs	1	Paper
2	Baking mix	2	Paper/EVA
3	Crackers bio	1	Paper/27 $\mu\text{m}$ PE/4 $\mu\text{m}$ PE
4	Semolina bio	1	Paper/31 $\mu\text{m}$ PE/3 $\mu\text{m}$ PE
5	Cereals	4	20 $\mu\text{m}$ PE/13 $\mu\text{m}$ PE/12 $\mu\text{m}$ PE/6 $\mu\text{m}$ ionomer
6	Flakes	3	13–22 $\mu\text{m}$ PE/18 $\mu\text{m}$ PE/17 $\mu\text{m}$ PE/6 $\mu\text{m}$ ionomer
7	Flakes	2	13 $\mu\text{m}$ PE/19 $\mu\text{m}$ PE/7 $\mu\text{m}$ ionomer
8	Flakes bio	2	13–24 $\mu\text{m}$ PE/23 $\mu\text{m}$ PE/6 $\mu\text{m}$ ionomer
9	Muesli	1	16 $\mu\text{m}$ PE/4 $\mu\text{m}$ PE/11 $\mu\text{m}$ PE/6 $\mu\text{m}$ ionomer

Number of products (Nr.) with virtually same bag composition. Abbreviations, see Table 1

**Table 3** Products with class 2 internal bags, i.e., bags essentially consisting of OPP

	Food type	Nr.	Internal bag
1	Bakery ware	6	25–47 $\mu\text{m}$ PP
2	Bakery ware	1	3 $\mu\text{m}$ ink/33 $\mu\text{m}$ PP
3	Bakery ware	1	2 $\mu\text{m}$ Ink (nicell)/36 $\mu\text{m}$ PP foamed
4	Bakery ware bio	1	42 $\mu\text{m}$ PP filled
5	Bakery ware bio	1	40 $\mu\text{m}$ PP
6	Bakery ware for babies	1	42 $\mu\text{m}$ PP
7	Crackers	3	30–32 $\mu\text{m}$ PP
8	Crispbread	1	29 $\mu\text{m}$ PP
9	Crispbread	2	30 $\mu\text{m}$ PP// <sup>PUR</sup> 21 $\mu\text{m}$ PP
10	Grissini	5	28–37 $\mu\text{m}$ PP
11	Grissini Demeter	1	30 $\mu\text{m}$ PP
12	Baking mix bio	1	25 $\mu\text{m}$ PP/3 $\mu\text{m}$ PE/43 $\mu\text{m}$ PE
13	Muesli	1	49 $\mu\text{m}$ PP
14	Pasta	2	45–60 $\mu\text{m}$ PP
15	Semolina bio	1	44 $\mu\text{m}$ PP

whereas 25 bags essentially consisted of PP. Two products were in class 3 and six in class 4 bags, none of which organic.

Of the 27 products typically consumed for breakfast (Table 7), 12 were in class 1 bags, among which five of the six flakes and including the two organic products (samples 5). Of the 12 cereals, four were essentially in PE (class 1), another four in bags of class 3 (PET-G as barrier layer) and the last four in bags including a PET layer (class 4). Of the seven muesli, five were well protected (classes 3–5).

Products consisting of fine particles, such as semolina (Table 8), were packed into just about all types of internal

**Table 4** Products with internal bags having class 3 barrier efficiencies

	Food type	Nr.	Internal bag
1	Bakery ware	1	Ink (nicell)/25 µm PP foamed/3 µm PVDC
2	Crispbread	1	1 µm PMMA/29 µm PP/1 µm PMMA
3	Baking mix	1	Paper/26 µm PE/15 µm PVDC-PMMA
4	Cereals	4	15 µm PE/17 µm PE filled/7 µm PE/7 µm EVA/13 µm PET-G
5	Muesli	3	25 µm PE/17 µm PE filled/7 µm EVA/14 µm PET-G
6	Muesli	1	2 µm PVDC/28 µm PP/2 µm PVDC
7	Rice	1	4 µm PA/95 µm PE
8	Rice	1	13 µm PET// <sup>PUr</sup> 30 µm PE
9	Semolina bio	1	2 µm PVDC/22 µm cellophane/21 µm cellophane/2 µm PVDC

bags encountered, covering barrier efficiencies from 1 to 5. For products such as rice, pasta and nuts (Table 9), primarily efficient barriers were used. These types of foods have mostly been packed directly into recycled paperboard and those packers now having introduced a bag might have been aware that only efficient materials would make the difference.

## Conclusions

Internal bags of a broad range primarily of multilayer materials were encountered in boxes of recycled paperboard.

**Table 5** Products with internal bags having class 4 barrier efficiencies

	Food type	Nr.	Internal bag
1	Bakery ware	3	12–15 µm PET// <sup>PUr</sup> Alv/18–21 µm PP
2	Bakery ware	1	14 µm PET/Alv// <sup>PUr</sup> 51 µm PE
3	Crackers	1	14 µm PET/3 µm ink// <sup>PUr</sup> Alv/20 µm PP
4	Crackers	1	Ink (nicell)/31 µm PP filled// <sup>PUr</sup> Alv/13 µm PET
5	Cereals	2	20 µm PE/6 µm PE/4 µm EVA/10 µm PET/8 µm ionomer
6	Cereals bio	1	23 µm PE/7 µm PE/3 µm EVOH/13 µm PE/8 µm ionomer
7	Cereals for babies	1	19 µm PE// <sup>PUr</sup> Alv/38 µm PP/30 µm PE
8	Flakes	1	14 µm PET// <sup>PUr</sup> 21 µm PA/28 µm PE filled/4 µm EVOH/30 µm PE filled
9	Potato flour	2	Alv/12 µm PET// <sup>PUr</sup> 45 µm PE
10	Rice	1	17 µm PA/50 µm PE
11	Rice for babies	1	16 µm PA/Alv// <sup>PUr</sup> 75 µm PE
12	Semolina	1	22 µm PA/28 PE/6 µm EVOH/29 µm PE
13	Semolina	1	Paper/14 µm PE/17 µm PE/8 µm EvOH/50 µm PE
14	Semolina for babies	1	13 µm PET/Alv// <sup>PUr</sup> 60 µm PE
15	Semolina for babies	1	16 µm PA/Alv// <sup>PUr</sup> 70 µm PE
16	Semolina for babies bio	1	15 µm PA/Alv// <sup>PUr</sup> 70 µm PE
10	Polenta	1	2 µm ink (acryl)/paper// <sup>Acryl</sup> Alv/17 µm PP/3 µm PE
17	Nuts bio	1	17 µm PA/50 µm PE

Also for the apparently same type of food, widely varying bags had been used.

Of the 87 products collected from the German and Swiss market in June 2013, merely 17 (20 %) contained bags without significant protection of the foods against migration from recycled paperboard. In 28 packs (32 %), bags essentially consisted of PP. OPP has previously been shown to be fairly tight for several months and substantially reduce migration also for longer storage [15, 17, 18]. It was frequently used for bakery ware with relatively short shelf lives, for which at least thicker OPP bags might keep contamination acceptably low. For the 14 (16 %) products with a class 3 barrier, there is insufficient data for a final evaluation, but the more efficient among these are likely to be adequate at least for many applications. The bags of classes 4 and 5 in 23 and 5 packs, respectively—32 % of all samples—are complete barriers.

For nearly all types of foods, efficient barriers were encountered, which suggests that there are no serious obstacles against the use of internal bags with efficient barriers and at least most of the remaining weak barriers could be replaced. Hence, internal bags including a barrier are a valid option to render recycled paperboard acceptable for food packaging. Lining the internal surfaces of the box is an alternative, but was not subject of this paper.

## Conclusions for German samples

In June 2013, 29 products were collected from the German market which had been packed in recycled paperboard with

**Table 6** Internal bags used for general and more specific bakery ware; number of similar products (Nr.)

	Nr.	Food type	Barrier	
			Class	Composition
1	7	Bakery ware	2	25–47 µm PP
2	1	Bakery ware	2	2 µm Ink (nicell)/36 µm PP foamed
3	1	Bakery ware	2	3 µm ink/33 µm PP
4	1	Bakery ware	3	Ink (nicell)/25 µm PP foamed/3 µm PVDC
5	3	Bakery ware	4	12–15 µm PET// <sup>PUR</sup> 18–21 µm PP
6	1	Bakery ware	4	14 µm PET/Alv// <sup>PUR</sup> 51 µm PE
7	1	Bakery ware bio	2	42 µm PP filled
8	1	Bakery ware bio	2	40 µm PP
9	1	Bakery ware for babies	2	42 µm PP
10	3	Bakery ware for babies	5	Al foil
11	3	Crackers	2	30–32 µm PP
12	1	Crackers	4	14 µm PET/3 µm ink// <sup>PUR</sup> Alv/20 µm PP
13	1	Crackers	4	Ink (nicell)/31 µm PP filled// <sup>PUR</sup> Alv/13 µm PET
14	1	Crackers bio	1	Paper/27 µm PE/4 µm PE
15	1	Crispbread	2	30 µm PP// <sup>PUR</sup> 21 µm PP
16	1	Crispbread	2	29 µm PP
17	1	Crispbread	2	31 µm PP// <sup>PUR</sup> 21 µm PP filled
18	1	Crispbread	3	1 µm PMMA/29 µm PP/1 µm PMMA
19	5	Grissini	2	37 µm PP
20	1	Grissini Demeter	2	30 µm PP

**Table 7** Internal bags used for breakfast products

	Nr.	Food type	Barrier	
			Class	Composition
1	1	Flakes	1	30 µm PE/6 µm ionomer
2	2	Flakes	1	13–22 µm PE/18 µm PE/17 µm PE/6 µm ionomer
3	2	Flakes	1	13–21 µm PE/19–24 µm PE/7 µm ionomer
4	1	Flakes	4	14 µm PET// <sup>PUR</sup> 21 µm PA/28 µm PE filled/4 µm EVOH/30 µm PE filled
5	2	Flakes bio	1	13–24 µm PE/25 µm PE/5 µm ionomer
6	1	Cereals	1	55 µm PE/6 µm ionomer
7	1	Cereals	1	21 µm PE/25 µm PE/6 µm ionomer
8	1	Cereals	1	20 µm PE/13 µm PE/12 µm PE/6 µm ionomer
9	1	Cereals	1	20 µm PE/23 µm PE filled/5 µm ionomer
10	4	Cereals	3	15 µm PE/13–17 µm PE/7–12 µm PE/6 µm EVA/10–13 µm PET-G
11	1	Cereals	4	20 µm PE/6 µm PE 6/4 µm EVA/10 µm PET/8 µm ionomer
12	1	Cereals	4	17 µm PE/7 µm PE/3 µm EVOH/11 µm PE/8 µm ionomer
13	1	Cereals bio	4	23 µm PE/7 µm PE/3 µm EVOH/13 µm PE/8 µm ionomer
14	1	Cereals for babies	4	19 µm PE// <sup>PUR</sup> Alv/38 µm PP/30 µm PE
15	1	Muesli	1	16 µm PE/4 µm PE/11 µm PE/6 µm ionomer
16	1	Muesli	2	49 µm PP
17	1	Muesli	3	2 µm PVDC/28 µm PP/2 µm PVDC
18	3	Muesli	3	25 µm PE/17 µm PE filled/8 µm EVA/12 µm PET-G
19	1	Muesli	5	Al foil

**Table 8** Internal bags used for flour-type products

Nr.	Food type	Barrier	
		Class	Composition
1	Bread crumbs	1	Paper
2	Baking mix	1	Paper/EVA
3	Baking mix	3	Paper/26 µm PE/15 µm PVDC-PMMA
4	Baking mix bio	2	25 µm PP/3 µm PE/43 µm PE
5	Polenta	4	2 µm ink (acryl)/paper// <sup>Acryl</sup> Alv/17 µm PP/3 µm PE
6	Polenta	5	Al foil
7	Potato flour	4	Alv/12 µm PET// <sup>PUR</sup> 45 µm PE
8	Semolina	4	22 µm PA/28 PE/6 µm EVOH/29 µm PE
9	Semolina	4	Paper/14 µm PE/17 µm PE/8 µm EVOH/50 µm PE
10	Semolina bio	1	Paper/31 µm PE/3 µm PE
11	Semolina bio	2	44 µm PP
12	Semolina bio	3	2 µm PVDC/22 µm cellophane/21 µm cellophane/2 µm PVDC
13	Semolina for babies	4	13-16 µm PET/Alv// <sup>PUR</sup> 60-70 µm PE
14	Semolina for babies bio	4	15 µm PA/Alv// <sup>PUR</sup> 70 µm PE

**Table 9** Internal bags for rice, pasta and nuts

Nr.	Food type	Barrier	
		Class	Composition
1	Rice	3	13 µm PET// <sup>PUR</sup> 30 µm PE
2	Rice	3	4 µm PA//95 µm PE
3	Rice	4	17 µm PA/50 µm PE
4	Rice for babies	4	16 µm PA/Alv// <sup>PUR</sup> 75 µm PE
5	Pasta	2	45-60 µm PP
6	Nuts bio	4	17 µm PA/50 µm PE

internal bags without relevant barrier properties in April 2010 [14, 15]. Now 13 of these were in fresh fiber paperboard. The composition of the inner bags of half of the 16 products that were still packed in a recycled board was changed to class 3 or 4 barriers.

In 2010, six of the 29 products had been in internal bags consisting of PE monolayers (four products of rice and two of flour for dumplings). In 2013, all of them were packed in fresh fiber paperboard. In 2010, all ten cereal products had been in multi-layer PE films (one layer filled with pigments for opaque appearance) and an ionomer on the food contact side. In 2013, only four of them were still packed in these class 1 bags. Four products (three baking mixtures, one bakery ware) had been in PE-coated paper bags, of which two were now in bags with better barrier properties. New materials were sealable polyester, multilayers with EVOH and vapor-deposited aluminum.

It is concluded that between April 2010 and June 2013, the packaging of dry foods marketed in Germany was substantially improved for 21 of 29 products, either by

**Table 10** Products collected from the market in Zurich

Product type	Number of samples
Bakery ware	18
Crackers, crispbread	8
Grissini	6
Cereals	5
Flakes	8
Muesli	5
Pasta	2
Rice	4
Semolina, polenta & similar	8
Nuts	1

changing from recycled to fresh fiber paperboard or by introducing a barrier material in the internal bag.

#### Conclusions for samples collected in Zurich

Totally 69 products packed in recycled paperboard with an internal bag were collected from the five main retailers and a major health food store in the area of Zurich, covering all types of dry foods packed in recycled paperboard with internal bags and kept at ambient temperature for more than a few days (Table 10). The table also provides a picture of the products packed in this way. For instance, only few samples of rice and pasta were found: most were packed directly in paperboard.

Table 11 shows that only 12 of the 69 products (17 %) were without a significant barrier layer in the internal bag. A large proportion (39 %) included a class 2 (OPP) bag, influenced by the frequent use of OPP for bakery products



**Table 11** Classification of the barrier efficiency of the internal bags from the 2013 market of Zurich compared to the 2010 German market

Barrier class	2013 Zurich		2010 Germany	
	Number	%	Number	%
1	12	17	50	63
2	27	39	21	27
3	5	7	0	0
4	20	29	3	4
5	5	7	5	6
Sum	69		79	

and the large proportion of these products (Table 10). Second (29 %) were the class 4 barriers including organic polymers considered as tight. Aluminum foils were found in five products, three of which for babies.

Since no data on the composition of the internal bags were available for earlier times, the 79 analogously packed products among the 119 samples collected in April 2010 from the German market [14, 15] were used for comparison. The distribution strongly improved: In 2010, 19 internal bags mainly consisted of paper and 31 of PE, totaling 63 % bags without relevant barriers. In fact, massive migration of mineral oil was determined for most of these products. In June 2013, only 17 % of the foods were poorly protected.

It was not possible to determine for which proportion of products recycled paperboard was replaced by fresh fiber board or plastic bags leaving the paperboard away, but many such products were noted. Some producers indicated that they would return to recycled board once approved barrier materials were available.

A remark to packaging of organic foods: Four out of 13 products (31 %) were with class 1 internal bags, compared to only 8 out of 56 conventional products (14 %), suggesting that the producers of conventional products were more careful. As the producers of organic food prefer recycled paperboard because of sustainability of material use, they should also pay attention to the chemical contamination.

**Conflict of interest** None.

**Compliance with Ethics Requirements** This article does not contain any studies with human or animal subjects.

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