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How to determine functional barrier performance towards mineral oil contaminants from recycled cardboard

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ABSTRACT

In recent years migration issues from the cardboard packaging materials into various foods have been reported. Cardboard packaging materials might be contaminated with mineral oil or other contaminants via the fibre recyclate stream. Regarding consumers safety the concentrations of contaminants migrating from recycled fibres into food should be reduced down to levels below of any toxicological concern. At the moment, maximum concentrations of mineral oil components in cardboard packed food were considered to be 2 mg/kg and 0.5 mg/kg for saturated and unsaturated mineral oil components, respectively. But what are efficient barriers towards such mineral oil components and – more important – how to test the performance of a functional barrier? In principle, three experimental set-ups can show the functional barrier performance: (i) migration experiments, (ii) permeation experiments and (iii) lag time experiments. Aim of the study is to evaluate in detail the above mentioned three functional barrier testing options with pros and cons as well as to give recommendations for the performance testing of mineral oil components through functional barriers.

1. Introduction

In recent years migration issues from the cardboard packaging materials into various foods have been reported (Castle, Offen, Bater, & Gilbert, 1997; Gruner and Piringer, 1999; Aurela, Kulmala, & Söderhjelm, 1999; Anderson and Castle, 2003; Jickells, Poulin, Mountfort, & Fernandez-Ocana, 2005; Sturaro, Rella, Parvoli, Ferrara, & Tisato, 2006; Zhang, Noonan, & Begley, 2008; Biedermann and Grob, 2010; Biedermann, Uematsu, & Grob, 2010; Vollmer et al., 2011; Bradley, Stratton, Leak, Lister, & Castle, 2013; Guazzotti, Giussani, Piergiovanni, & Limbo, 2014). Cardboard packaging materials might be contaminated with mineral oil or other contaminants via the fibre recyclate stream. For example, part of the input streams of recycled fibres are newspapers, which are printed with mineral oil based printing inks. Other contaminants of the paper recycling stream are related to substances used for the paper production or recycling processes as well as to printing processes, e.g. UV-cure ink photo-initiators, de-foamers, biocides, slimicides, pesticides, optical brighteners, coating materials or adhesives. Due to the fact, that the above mentioned contaminants are not completely removed during recycling, the contaminants can be determined in recyclate fibres containing cardboard in significant amounts. Another source for mineral oil components might be printing inks of the packaging cardboard itself. Not least because the different input streams and contamination pathways, mineral oil components found in packaging cardboard are complex mixtures of saturated hydrocarbons (MOSH) and unsaturated hydrocarbons (MOAH). MOSH are linear and branched hydrocarbons whereas MOAH are alkyl-substituted poly aromatic compounds. Also other contaminants like di-*iso*-propyl naphthaline, di-*n*-butyl phthalate or di-2-ethylhexyl phthalate are introduced from office or speciality paper into the fibre recycling stream. Typical concentrations of contaminants found in recycled fibres used for food packaging cardboards are given in Table 1 (BMEL, 2012). However, not only the primary packaging materials are responsible for the mineral oil contamination in foodstuffs. The migration into food occurs also from secondary (transport) packaging materials, which are also manufactured from recycled cardboard fibres. The migration from transport boxes is lower than that from recycled paperboard primary packaging but likely to exceed the threshold concentrations (see below) frequently up to 10 times (Biedermann, Ingenhoff, Barbanera, Garbini, & Grob, 2011).

The migration of contaminants from cardboard packaging materials into foodstuffs is a complex process. The contaminants need to be vaporized into the gas phase. From the gas phase the

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Table 1
Average concentrations of contaminants in recycled fibres (BMEL, 2012).

Contaminant	Average content in recycled fibre (mg/kg)	Molecular weight (g/mol)	Source of contaminant
MOSH C16–C24	317	226–339	Newspaper
MOAH <C24	90	<339	Newspaper
Poly alcylated aromates	0.3	150–340	Newspaper, journals
Di-*iso*-propyl naphthaline (DIPN) and derivatives	20	212	Office paper, speciality paper, glued paper
Di-*iso*-butyl phthalate (DiBP)	9	278	Office paper, speciality paper, glued paper
Di-*n*-butyl phthalate (DBP)	5	278	Office paper, speciality paper, glued paper
Di-2-ethylhexyl phthalate	9	391	Promotion prints, journals, decorative paper
Diethlene glycol dibenzoate	13	314	Promotion prints, journals, decorative paper
Benzophenone	3	182	Promotion prints, journals, decorative paper
Di-2-ethylhexyl maleate	2	341	Promotion prints, journals, decorative paper
2-Phenylmethoxy naphthaline	3	234	Thermopaper
Bisphenol A	10	228	Thermopaper
Average sum of contaminants in recycled fibre	481		

contaminants permeated through the functional barrier into the food. This permeation process has a kinetic part that can be described by the diffusion of a contaminant and a thermodynamic sorption/desorption part that can be described e.g. by the solubility of a contaminant in a packaging material or food. The gas phase migration process requires an evaporation of the mineral oil components with subsequent re-condensation onto packaging materials or food. Evaporation at ambient temperature was found to be relevant for hydrocarbons up to tetracosane (*n*-C24) (Lorenzini, Fiselier, Biedermann, Barbanera, Braschi, & Grob, 2010; Biedermann et al., 2011). Higher molecular weight compounds seem to be negligible regarding to migration, because their vapour pressure is too low. Therefore contaminants up to the molecular weight range of *n*-tetracosane are the relevant for migration/permeation.

Regarding consumers safety the migration of contaminants from recycled fibres into food should be reduced down to levels below of any toxicological concern. The German Federal Ministry of Food and Agriculture (BMEL) presented a draft document for the regulation of mineral oil from recycled fibres in cardboard food packaging materials. According to this draft document, the maximum concentration of mineral oil components in cardboard packed food should be 2 mg/kg and 0.5 mg/kg for MOSH and MOAH, respectively. For MOSH the mineral oil components between *n*-C20 to *n*-C35, whereas for MOAH the compounds between C16 and C35 should be considered.

There are several options to reduce the migration of mineral oil components from cardboard food packaging materials into food:

- Substitution of recycled fibres by fresh fibres,
- Elimination of mineral oil components from printing inks for newspapers,
- Sufficient decontamination of mineral oil contaminants during paper and cardboard recycling,
- Optimizing the sorting of the input streams of paper and board recycling and sufficient elimination of newspapers,
- Introducing efficient barrier for mineral oil components into cardboard materials (coatings or inner liners).

According the Ewender, Franz, and Welle (2013) the introduction of efficient barriers towards mineral oil or other contaminants seems to be the only practical and fast solution for the prevention or reduction of contamination of the cardboard packed food. The barrier can be applied as a coating on the food contact side of the cardboard or as an inner liner in the cardboard box. But what are efficient barriers towards mineral oil components and – more important – how to test the performance of a functional barrier?

In principle, three experimental set-ups can show functional barrier performance:

- Migration experiments
- Permeation experiments
- Lag time experiments

Aim of the study is to evaluate in detail the above mentioned three functional barrier testing options with pros and cons as well as to give recommendations for the performance testing of mineral oil components through functional barriers.

2. Materials and methods

2.1. Migration modelling

The calculation of the permeation was performed using the AKTS SML software version 4.54 (AKTS AG Siders, Switzerland). The program is using finite element analysis. The mathematical procedure and the main equations are published by Rodiut, Borgeat, Cavin, Fragniere, and Dudler (2005). Migration modelling was based on constant diffusion (D_P) and partition coefficients (K).

3. Results and discussion

3.1. Parameters influencing the permeation

Permeation through a functional barrier is influenced by several parameters. The main principles of functional barriers are visualized in Fig. 1. First of all, the concentration of the contaminant in the cardboard or the gas phase ($c_{gasphase}$) above and the temperature at which the permeation test is performed are playing a crucial role. As already known, higher temperatures lead to higher permeation rates. On the other hand, the concentration of the permeant in the gas phase ($c_{gasphase}$) is directly proportional to the permeated amount after a certain storage time. The measured

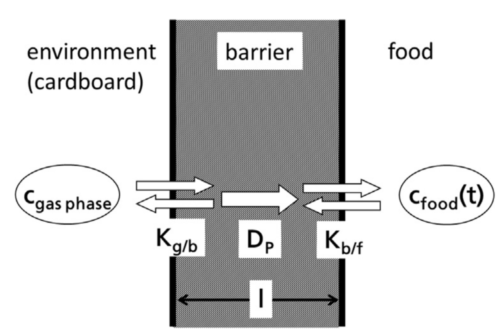

Fig. 1. Schematic diagram of the main parameters influencing the functional barrier performance.