Evaluation of different mineral oil barriers for cardboard packed food

Johann Ewender, Frank Welle

Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany, email: ewender@ivv.fraunhofer.de, phone: ++49 8161 491 742

Introduction

Paper and cardboard are important food packaging materials. In the last few years, however, migration issues have been reported in the scientific literature. Especially the migration of mineral oil components from the cardboard packaging materials into various foodstuffs were investigated in detail. The problem behind the mineral oil contamination of cardboard packed foodstuffs is that most of the paper and cardboard packaging materials are containing recycled fibres. One main input material of the paper recycling processes is newspapers. The newspaper printing inks contain mineral oil components which is the main source of the mineral oil components in cardboard packaging materials. Due to the fact, that the printing ink components are not removed completely during cardboard recycling, the mineral oil components can be determined in recyclate containing cardboard in significant amounts. Unprinted cardboard with recycled fibres contains about 300 to 1000 mg kg-1 mineral oil components up to n-C28^[1]. In another study an average value of mineral oil of 338 mg kg⁻¹ was reported^[2]. Barrier materials will provide an option to reduce the migration of compounds from the cardboard packaging materials into the foodstuff. However, reference values for barrier improvement factors for different barrier materials against mineral oil components are not available in the scientific literature.

Aim of the study was therefore to develop a fast and reproducible method for the determination of the permeation of mineral oil components through food packaging film materials. With this method the barrier properties of inner liner materials as well as two cardboard coatings were determined at 40 $^{\circ}\text{C}$.

Method

A list of the model compounds used for the method development and for the permeation tests is given in Table 1. A disk of the cardboard with 15.4 cm in diameter (5.5 g) was spiked with approximately 750 mg kg⁻¹ of each substance in the cardboard. The films were placed in special permeation cells. In the lower side of the cells the spiked cardboard was placed. The tested films had direct contact with the cardboard. The upper side of the cells was rinsed with pure nitrogen. The constant nitrogen flow moved the permeated substances out of the cell. The nitrogen stream was analysed for the substances by using a 16-position

valve that passes the gas stream of each cell one after the other to a pre-trap with a connected enrichment unit and gas chromatograph with flame ionisation detection (GC/FID). Calibration was performed with injections of known amounts of the applied substances. Permeation was measured at a constant temperature (40 °C) in a climate chamber. Further details are given in Lit.^[3].

Results and Discussion

Within the study an automated method for the determination of mineral oil permeation through packaging films was developed. The method is using 15 defined standard substances instead of mineral oil. The reason for application of standard substances instead of mineral oil is that the mineral oil typically used for newspaper printing contains hundreds of different and potentially unknown substances. A separation is not possible with current available analytical methods. Therefore when analysed by gas chromatography, the mineral oil components result in a huge peak with a low resolution. As a consequence,

Table 1: Model substances used for the permeation measurements und their physical properties

Substance	Molecular weight [g mol ⁻¹]	Boiling point [°C]	log (vapour pressure) [hPa]
Dodecane	170.3	216	-0,81
Naphthalene	128.2	218	-0,69
1-Methyl naphthalene	142.2	245	-1,05
Tetradecane	198.4	254	-1,84
1-Ethyl naphthalene	156.2	260	-1,49
2,7-Di-iso-propyl naphthalene	212.3	279	-3,14
TXIB	286.4	280	-2,51
Hexadecane	226.4	287	-2,82
Benzophenone	182.2	305	-2,85
Octadecane	254.5	316	-3,85
4-Methylbenzophenone	196.3	326	-3,45
Phenanthrene	178.2	332	-3,54
Eicosane	282.6	343	-4,91
Docosane	310.6	369	-5,91
Tetracosane	338.7	391	-6,92

Poster presentation at the 5th international Symposium on Food Packaging, 14-16 November 2012, Berlin

100000
10000
10000
10000
10000
10000
1000
1000
1000
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
100
10

Figure 2: Correlation between the logarithm of the vapour pressure and the permeation rate for a HDPE film (44 µm)

Table 1: Experimenatlly determined barrier improvement factors for different barriers system in comparison to HDPE at 40 C

Barrier	Application	Barrier improvement factor				
		Tetradecane	Hexadecane	Octadecane	Eicosane	
HDPE 44 µm	Inner liner	1	1	1	1	
OPP 43 µm	Inner liner	0.7	0.7	0.6	0.5	
OPP 40 µm metallized	Inner liner	n.d.	2.1	1.0	0.5	
PE/PET 13 μm/6 μm	Inner liner	6.6	3.6	1.8	1.1	
PE/PET 18 μm/8 μm	Inner liner	n.d.	40.8	44.0	22.7	
Ultramid, 10 g m ⁻²	Coating	32600	4530	275	97.0	
Ecovio, 18 g m ⁻²	Coating	24000	3710	478	89.0	
PET 12 μm	Inner liner	>156000	>20400	>2200	>204	
PA 15 μm	Inner liner	>156000	>20400	>2200	>204	

the permeation rate can only be measured as a sum parameter for the whole mineral oil peak. For an evaluation of the barrier properties, however, this makes no sense because low molecular weight compounds with higher vapour pressures will permeate much faster in comparison to the high molecular weight compounds with lower vapour pressures. The logarithm of the vapour pressure correlates with the permeation rates (Figure 1). As a result, the correlation for the *n*-alkanes can be considered as the worst-case in comparison to all other tested compounds. Barrier improvement factors for different barrier materials are given in Table 1. From the results of this study it can be concluded, that inner layer films like 12 µm oriented PET or 15 µm oriented PA are effective barriers towards mineral oil components. In addition, cardboard coatings based on PA (Ultramid®) or biodegradable polyesters (Ecovio®) provide also a good barrier towards mineral oil or printing ink components. On the other hand, the barrier effect of pure or metallized polyolefin films are negligibly poor.

References

[1] M. Biedermann, K. Grob, Is recycled newspaper suitable for food contact materials? Technical grade mineral oils from printing inks, European Food Research and Technology, **2010**, *230*(5), 785-796.

^[2] A. Vollmer, M. Biedermann, F. Grundbock, J.E. Ingenhoff, S. Biedermann-Brem, W. Altkofer, K. Grob, Migration of mineral oil from printed paperboard into dry foods: survey of the German market, European Food Research and Technology, **2011**, *232(1)*, 175-182.

[3] J. Ewender, R. Franz, F. Welle, Permeation of mineral oil components from cardboard packaging materials through polymer films, Packaging Technology and Science, in press, doi:10.1002/pts.1990.

