Studies on the migration of per- and polyfluorinated compounds from paper based packaging into real food and food simulants

Karsten Müller, Romy Fengler, Mona Still, Martin Schlummer, Ludwig Gruber, Gerd Wolz, Dominik Fiedler

Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany,
email: martin.schlummer@ivv.fraunhofer.de, phone: ++49 8161 491 750

Introduction

Grease proof packaging and other food contact materials (FCM) have been reported to contain fluorine-based organic coatings. As previously shown by Begley et al. [1] these fluorinated substances or their degradation products may migrate from FCM into food items and may become a source of per- and polyfluorinated compounds (PFAS) in diet. As diet is the major pathway of exposure towards PFAS in the not occupationally exposed population [2], exposure via FCM has been analysed in detail in the current EU research Project PERFOOD (www.Perfood.eu).
In a previous study we screened up to 600 samples of FCM for the presence of fluorine. Fluorine positive samples were analyzed for volatile fluorotelomer alcohols (FTOHs) and anionic perfluoroalkyl carboxylates (PFCAs). The results showed that each fluorine positive sample contained a significant amount of FTOHs. This is reasonable as most polyfluorinated coating compounds contain FTOH moieties and thus, FTOHs were evaluated as a general indicator for the presence of larger polyfluorinated molecules [3,4].

Method

In this study we explored the migration of PFCAs and FTOHs from paper-based FCM. The selection of FCM was performed with respect to the use pattern of typically fluorine-containing FCM. Four application profiles were investigated: long-term packaging at 5°C and 20°C, short-term packaging at (80°C, 30 min) and baking applications (up to 220°C). Migration trials were performed with real food items and food simulants, including polar and non-polar solvents as well as poly(oxy-2,6-diphenyl-1,4-phenylene). The kinetic of migration of FTOHs was studied at 60 °C, 120 °C and 220 °C. Before and after the migration contact, FCM, food items and food simulants were analyzed for PFCA by LC-ESI-MS/MS and for FTOH by GC-CI-MS. Quantification was based on $^{13}C_{12}$ labeled internal standards.

Results and Discussion

Results of these investigations reveal, that migration into polar and non-polar liquids (Mthanol and olive oil) over- or respectively underestimate the migration into real food (e.g. butter) and that poly(oxy-2,6-diphenyl-1,4-phenylene) can be applied as a suitable food simulant especially at elevated temperatures. Furthermore, migration of PFCAs is rather low compared to the migration of FTOHs [5]. Migration of FTOH is visible even at 5 °C and increases with temperature [6]. At baking temperatures, migration values exceeded the migration potential, i.e. the total amount present in the original packaging, by far. This clearly indicates a formation of FTOH from high molecular precursors at typical use conditions (Table 1). This net production of FTOHs was confirmed in kinetic studies at 60 °C (10 days) (Figure 1), 120 °C (6 h) (Figure 2) and 220 °C (2 h). However, after an initial increase of FTOH levels we observed a release of FTOHs into the environment within the stated study duration.

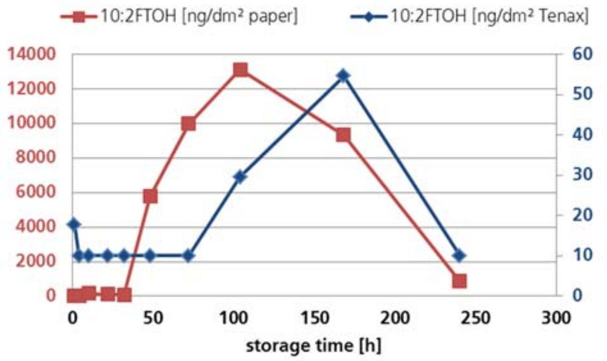

Figure 1: Concentration changes of 10:2 FTOH in paper and food simulant poly(oxy-2,6-diphenyl-1,4-phenylene) during 240 h at 60 C

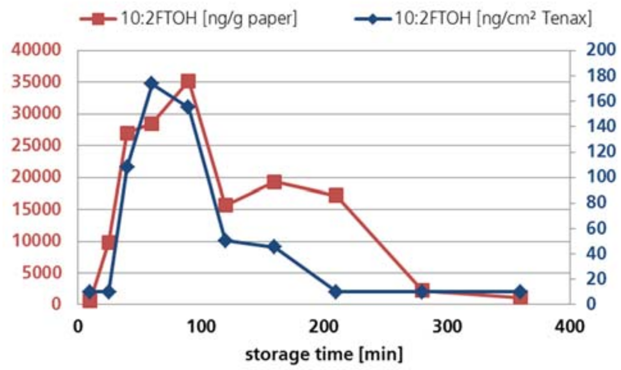

Figure 2: Concentration changes of 10:2 FTOH in paper and food simulant poly(oxy-2,6-diphenyl-1,4-phenylene) during 360 min at 120 C

References

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Table 1: Results of PFAA and FTOH migration at different time-temperature combinations into food or simulants

FCM/Food/Time	8:2 FTOH [ng/dm²]	10:2 FTOH [ng/dm²]	PFOA [ng/dm²]
	T=5 °C		
Butterwrap 1 c_{p0}	1114,6	598,7	5,6
Methanol 20 d	1725	662	6,12
Isooctan 20 d	49,81	108,5	3,42
Butterwrap 2 c_{p0}	2739,9	924,1	7,8
Butter 21 d	683,4	251	0,35
	T= 20 °C		
Sandwich wrap c_{p0}	1574,4	1034,3	13,56
Butter 10 d	1335,7	788,2	n. d.
poly(oxy -2,6-diphenyl-1,4-phenylene) 10 d	113,6	280,4	0,89
	T= 80 °C		
Cardboard c_{p0}	1897,4	2121,5	761
Burger 30 min	< 27,18	58,57	n. d.
poly(oxy -2,6-diphenyl-1,4-phenylene) 30 min	275,5	894,3	0,6
	T= 200 °C		
Muffincup c_{p0}	635,9	373,1	0,85
Muffin 2 20 min	3594,4	1436,8	n. d.
poly(oxy -2,6-diphenyl-1,4-phenylene) 220 °C 60 min	61861,5	26287,3	2,46

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