Final report (FEICA study)

Extraction, migration simulation and storage test regarding oligomeric hydrocarbons from hotmelt adhesives used in cardboard packaging

Index

1. Introduction

The contamination of food with hydrocarbons is a topic of ongoing discussion. The pathways by which hydrocarbons are introduced into food are wide-ranging and can occur at all stages of the production chain from farm to fork. The main focus is still on mineral oil hydrocarbons (MOH), which were observed to migrate from food contact materials, such as jute bags and recycled cardboard, into food. MOH can also enter the food in earlier stages of the production chain. In 2012, EFSA[1] released an 'scientific opinion on mineral oil hydrocarbons in food', which sets no Tolerable Daily Intake (TDI) for those substances and recommends further research into the toxicology of MOH. EFSA stated also that MOH, especially the polycyclic aromatic hydrocarbons are of potential concern. Other food contact materials like hotmelt adhesives can also release hydrocarbons into food[2], which can be also detected during the routine analysis of MOH. These oligomeric hydrocarbons originate mainly from synthetic tackifier resins, which are one of the main constituents of the adhesive formulation. However, during the routine method for MOSH/MOAH (HPLC-GC-FID)[3], these oligomers are frequently misinterpreted as mineral oil hydrocarbons.

Hotmelt adhesives (HMA) are widely used in food packaging applications, such as gluing folding cartons. The main components in a typical formulation of such packaging hotmelts are polyolefins (base polymer), paraffinic waxes (adjusting melt index/viscosity) and hydrocarbon resins (tackifier). For the synthesis of hydrocarbon resins, feed stocks of unsaturated compounds from cracking petroleum streams, such as naphtha, are used (by-products of ethylene production). According to Mildenberg et al.[4], the predominant resin feedstocks are C5, C9 and DCPD[5] (further details see annex I). Mixtures of these feedstocks, such as aromatic-modified aliphatic resins (addition of C9 to DCPD monomers), can be used to adjust physical properties like softening point and solubility. After synthesis, the hydrocarbon resins are commonly hydrogenated to decolorize them and to increase their stability. The degree of hydrogenation varies between partially and fully hydrogenated, which is depending on the required application.

Despite the potential concerns of MOSH/MOAH, some hydrocarbon resins can be used in plastics in accordance with the Plastics Regulation EU 10/2011. "Petroleum hydrocarbon resins, hydrogenated" are listed in the Regulation as FCM (food contact material) 97 without an SML (Specific Migration Limit). The structures of saturated resin oligomers can be differentiated to most of the MOSH species (see Annex II).
Saturated resin oligomers usually show a high number of cyclic moieties (polycyclics), whereas petroleum derived MOSH consists mainly of linear/branched alkanes and a substantial share of alkylated mono- and di-cyclics. In addition, the structures of aromatic resin oligomers can be differentiated from most of the MOAH species (see Annex II). Aromatic resin oligomers usually exhibit a high number of cyclics with only 1-2 non-conjugated aromatic rings, whereas mineral oil derived MOAH consists of alkylated mono-, di- tri- and poly-aromatics. The tri- and polyaromatics (conjugated) are assumed to be the most toxicologically critical MOAH structures. Furthermore, the number of oligomeric species is limited due to the usage of only a few specific monomers ($\rightarrow$ annex I), which is an additional distinctive feature compared to the large variety of different MOSH and MOAH species. This effect can also be observed during chromatographic analysis. Resin oligomers show mainly distinct oligomeric clusters

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[1] EFSA, EFSA Journal 10 (2012) p. 2704
[2] M. Lommatzsch et al., Food Addit. Contam. A 33 (2016) p. 473
[3] MOSH - Mineral oils saturated hydrocarbons; MOAH – Mineral oil aromatic hydrocarbons
  HPLC-GC-FID - High-performance liquid chromatography- gas chromatography with flame ionization detector
[4] R. Mildenberg et al., Hydrocarbon Resins, Weinheim VCH (1997)
[5] DCPD - Dicyclopentadiene

instead of a broad mineral oil hump.

The aim of this study was to investigate the migration from hotmelt adhesives systematically and to introduce relation/correlation factors. As hotmelts are mainly used for paper and paper board packaging, any migration can only take place via the gaseous phase. Therefore, this study focuses on the MOH fractions with C16-C25, as hydrocarbons with higher molecular weights are hardly able to migrate. Firstly, three different approaches were performed: Extraction of hotmelt, migration simulation of hotmelt (gaseous phase) and real storage tests (food stored in a folding carton closed with a hotmelt). Secondly, the results obtained were compared and related to each other. Hotmelts based on several raw materials were used and correlation factors between the analytical approaches were introduced. Thirdly, a calculation model to estimate the migration of hydrocarbons from hotmelt under realistic conditions was suggested (user perspective).

2. Conduct of the study

To investigate hydrocarbon migration from hotmelts, typical hotmelt formulations were prepared and tested (for details of the hotmelts, see Table 1 below). The composition of the sample "Standard 0" was chosen as the most representative mixture of polymer, wax and resin fraction used in typical cardboard closing and packaging applications. However, it must be noted, that this study cannot cover all hotmelt variations and applications in the food packaging market.

While keeping the polymer content constant, the content of resin and wax was varied to cover a wider range of typical hotmelt compositions. In addition, various polymers, waxes and resins were used in these mock-up formulations to investigate any influence from their different chemical properties.
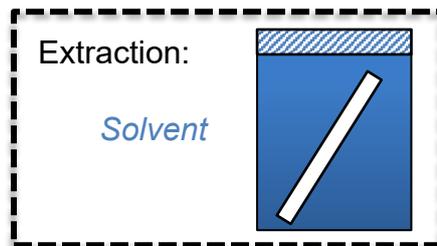
Test specimen (Std 0-13)

Hydrocarbon resins (30-40%)	Waxes (25-35%)	Polymer (35%)
Fully-hydrogenated C9 resin	Paraffin wax A (melting point: 54-70°C)	Polyethylene
Partially-hydrogenated C9 resin		EVA
Fully-hydrogenated C5 resin	Paraffin wax B (melting point: 70-90°C)	
Fully-hydrogenated DCPD resin	Synthetic wax (melting point: >90°C)	
Partially-hydrogenated DCPD resin		

Three approaches were used to measure saturated hydrocarbons (MOSH fraction) and aromatic hydrocarbons (MOAH fraction) in this study:
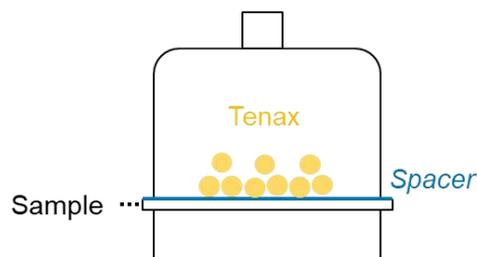
- Extraction of hotmelts

Being a quick routine procedure for analytical labs, hotmelts are extracted with an organic solvent (n-hexane extraction for 1 hour at 50°C + ultrasonic bath in this study) to further investigate the hydrocarbon content. Due to the chemical properties of the hotmelt ingredients, the complete amount of hydrocarbons will be dissolved resulting in exaggerated values in the MOSH and MOAH fraction. These values shall be compared with migration simulation results.

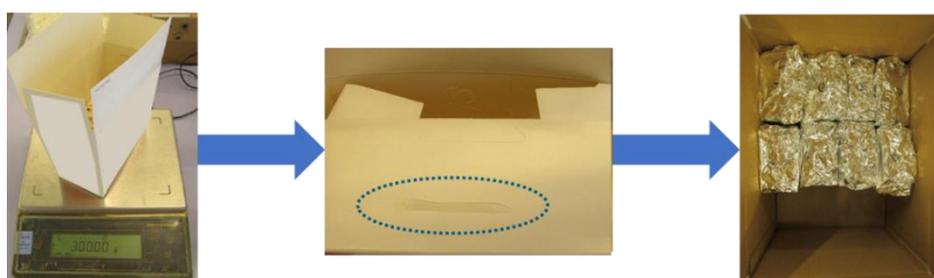- Migration simulation: Migration into food simulant

This method focuses on the typical cardboard packaging used for dry foodstuff. The organic polymer modified polyphenylene oxide (MPPO), 60-80 mesh, is a widely used food simulant for this kind of application. Performing a migration test at 40°C for 10 days on a free hotmelt film (vapour phase transition of hydrocarbons from hotmelt to MPPO) is expected to be a compromise between rapid extraction tests and long-term storage studies.

Reference: gassner-glastechnik.de

- Storage test: Migration on foodstuff under real conditions

Naturally, a storage test with real food will come closest to the real substance transfer of packaging constituents onto the foodstuff. However, as these storage tests last for several months or even years, it would be too time-consuming to perform these tests for every new packaging design and application. For that reason, the most important question is how simulation tests can mimic and replace real storage tests. In this study, typical cardboard boxes have been prepared using virgin fibre cardboard and different hotmelt samples as indicated in *Table 1.* They have been filled with oat flakes and stored at ambient temperature for one year.

More experimental details for all three approaches can be found in Annex III.

The study was focussed on the comparison between extraction and migration simulation as well as between migration simulation and storage test.
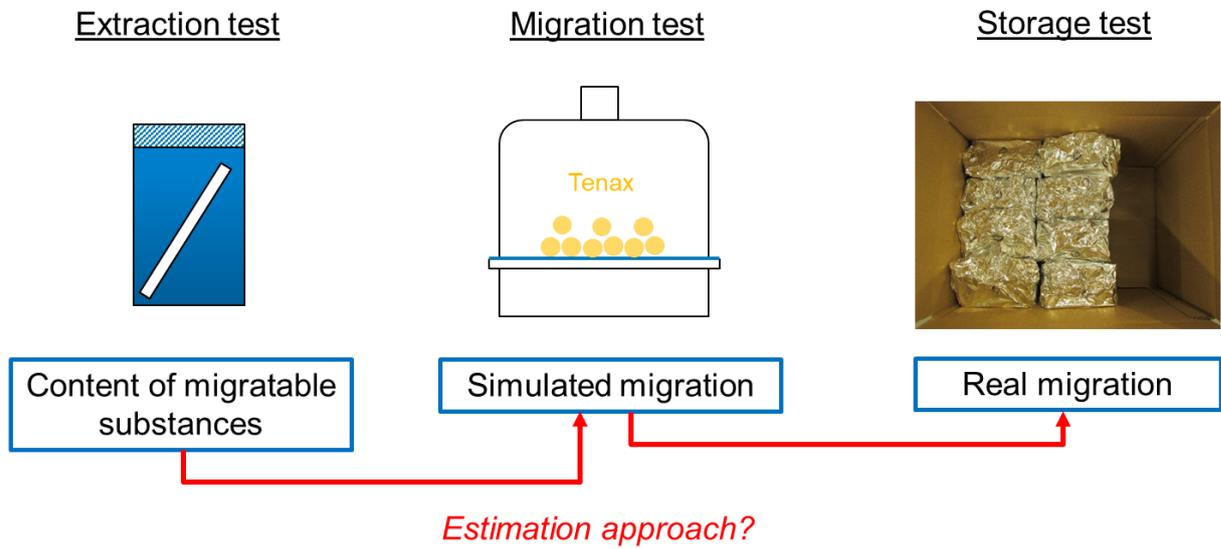
Extraction test	Migration test	Storage test

Content of migratable substances	Simulated migration	Real migration

Estimation approach?

Table 1: Sample description

Sample	Weight / area ration [g/dm²]	Adhesive formulation		
		Polymer	**Wax**	**Resin**
Std 0	≈ 9,5	35% polymer 2	25% syn. wax	40% C9 resin f-H_2
Std 1	≈ 8,9	35% polymer 2	25% p. wax A	40% C9 resin f-H_2
Std 2	≈ 9,1	35% polymer 2	25% p. wax B	40% C9 resin f-H_2
Std 3	≈ 10,2	35% polymer 1	25% syn. wax	40% C9 resin f-H_2
Std 4	≈ 9,3	35% polymer 2	35% syn. wax	30% C9 resin f-H_2
Std 5	≈ 9,0	35% polymer 2	35% syn. wax	30% C9 resin p-H_2
Std 6	≈ 9,4	35% polymer 2	25% syn. wax	40% C9 resin p-H_2
Std 7	≈ 9,5	35% polymer 2	35% syn. wax	30% C5 resin f-H_2
Std 8	≈ 9,5	35% polymer 2	25% syn. wax	40% C5 resin f-H_2
Std 9	≈ 10,7	35% polymer 2	35% syn. wax	30% DCPD resin f-H_2
Std 10	≈ 9,3	35% polymer 2	25% syn. wax	40% DCPD resin f-H_2
Std 11	≈ 9,5	35% polymer 2	35% syn. wax	30% DCPD resin p-H_2
Std 12	≈ 9,8	35% polymer 2	25% syn. wax	40% DCPD resin p-H_2
Std 13[6]	≈ 9,5	35% polymer 2	25% syn. wax	40% C9 resin f-H_2

Polymers: Polymer 1 = EVA (ethyl vinyl acetate)
            Polymer 2 = PE (polyethylene)

Waxes: Wax A = paraffinic wax (54-70 °C)
            Wax B = paraffinic wax (70-90 °C)
            Synthetic wax

Resins: f-H2[7] and p-H2[8] for typical chemical structures
            concerning C5, C9 and DCPD resins, please refer to Annex I.

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[6] Std 0 and Std 13 represent the same formulation. The test set up varies.
[7] f-H2: fully hydrogenated
[8] p-H2: partially hydrogenated

3. Results

3.1. Comparison of migration from hotmelts into food simulant versus the hotmelt extraction

In *Table 2*, the results of both the hotmelt extraction tests and migration simulation tests are listed, separated into MOSH and MOAH fractions. Due to the differing experimental procedures, it should be noted that the dimensions of the reported values are different:

- In migration simulation, the detected hydrocarbon amount is related to the contact surface area, leading to results expressed in µg/dm² of contact area.
- In the hotmelt extraction test, the detected hydrocarbon amount is related to the weighed sample of adhesive used for n-hexane extraction, leading to results expressed in µg/g adhesive.

In order to compare the results, it is assumed that the average weight of 1 dm² hotmelt film is 10 g. The ratio between migration values from the hotmelt films (migration simulation test) and concentration of the substances in the hotmelts (extraction test) is called "proportional migration" and reported in weight percentage in Table 2.

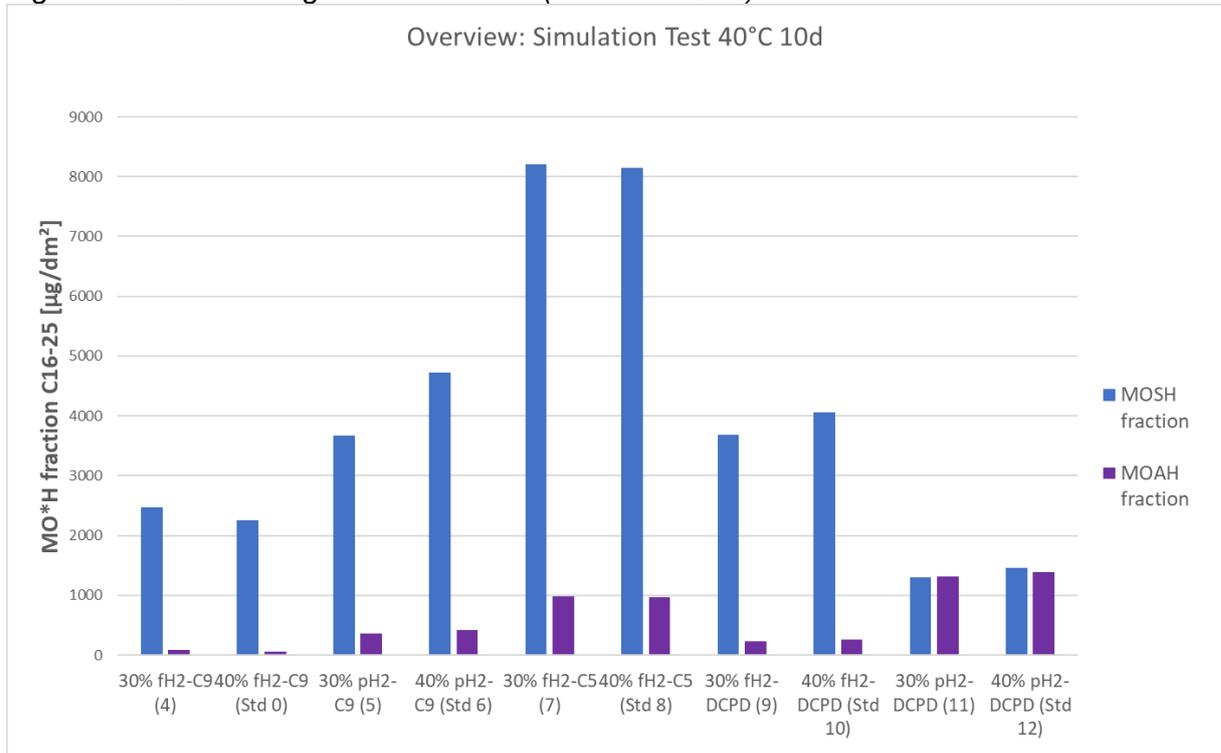*Table 2: Results of migration simulation and hotmelt extraction test*

Std #	MOSH fraction C16-25			MOAH fraction C16-25		
	Simulation 10d 40°C [µg/dm²]	Extraction [µg/g adhesive]	Proportional migration*	Simulation 10d 40°C [µg/dm²]	Extraction [µg/g adhesive]	Proportional migration*
0	2260	11200	2.0%	55	200	2.7%
1	3910	11200	3.5%	105	200	5.2%
2	3010	11200	2.7%	160	200	7.9%
3	3290	11200	2.9%	75	200	3.9%
4	2470	8400	2.6%	90	150	6.0%
5	3680	9400	3.9%	355	900	3.9%
6	4720	12500	3.8%	420	1200	3.5%
7	8200	35600	2.3%	980	3500	2.8%
8	8150	47500	1.7%	970	4700	2.1%
9	3690	29200	1.3%	225	700	3.2%
10	4060	38900	1.0%	265	900	2.9%
11	1300	5000	2.6%	1320	4400	3.0%
12	1450	6700	2.2%	1380	5900	2.3%
13	6350	11200	5.7%	135	200	6.7%

*…   *Proportion of migrated hydrocarbons: Migration simulation related to Extraction involving a weight/area ratio of 10 g adhesive per dm²*

⇨   Exemplary calculation (proportional migration) for "Std 0" (MOSH fraction C16-25):
- ○ 2260 µg (MOSH fraction) per dm² contact surface were determined in the migration simulation
- ○ 1 dm² of "Std 0" weighs approximately 10 g/dm²
- ○ Therefore, 2260 µg MOSH fraction originate from 10 g of hotmelt film, which is 226 µg MOSH fraction per g adhesive

- In the extraction test, 11200 µg (MOSH fraction) per g adhesives has been determined
- Comparing migration simulation with extraction (MOSH fraction), only 226 µg/g are related to 11200 µg/g
- Leading to 226 µg / 11200 µg × 100% = 2.0% of proportional migration

Figure 1: Results of migration simulation (different resins)

Although in the tables and graphs reference is made to "MOSH and MOAH fraction", the migrated hydrocarbons are saturated and aromatic resin oligomers which mainly contribute to the results. These oligomers should not be mistaken for mineral oil hydrocarbons (MOSH/MOAH) with different structures (see Annex 2). The differences in the migration simulation results reflect the differences in the composition of the hotmelt samples and in particular the various resins used during manufacture. However, the migration results of all resins remain in the same order of magnitude.

Figure 2: Results of migration simulation and hotmelt extraction (MOSH fraction)
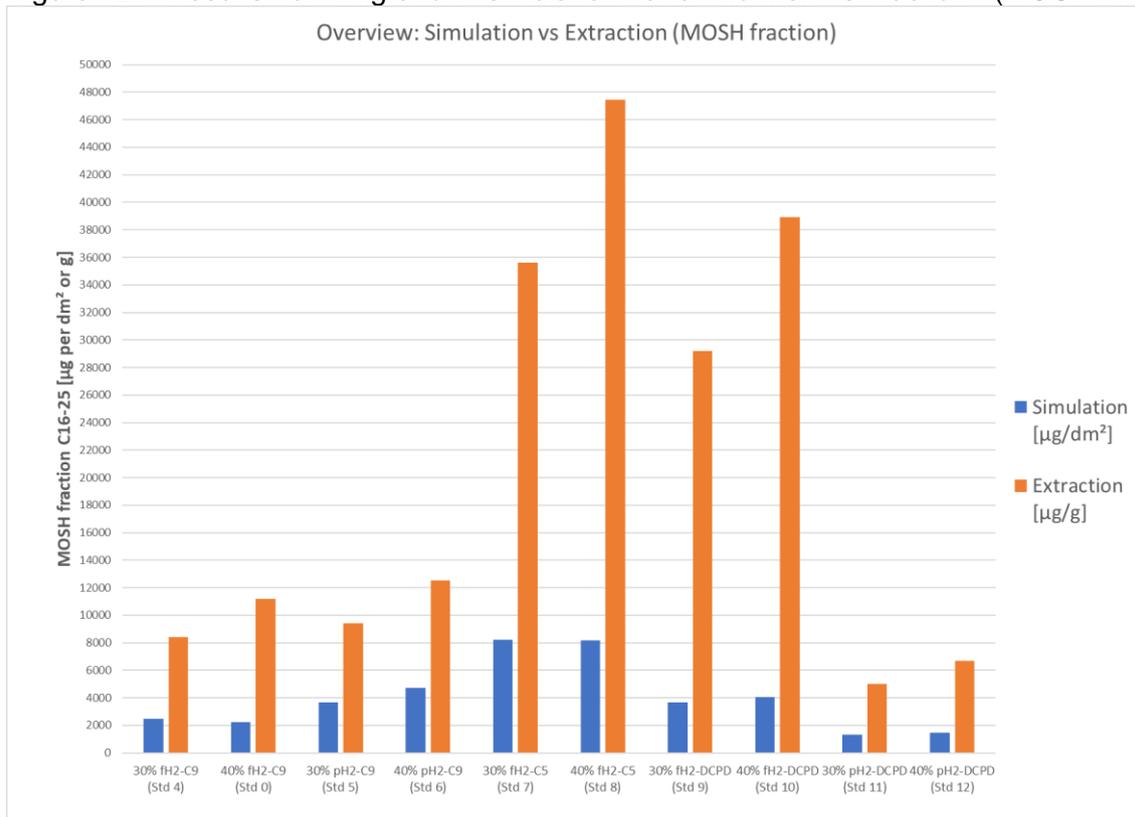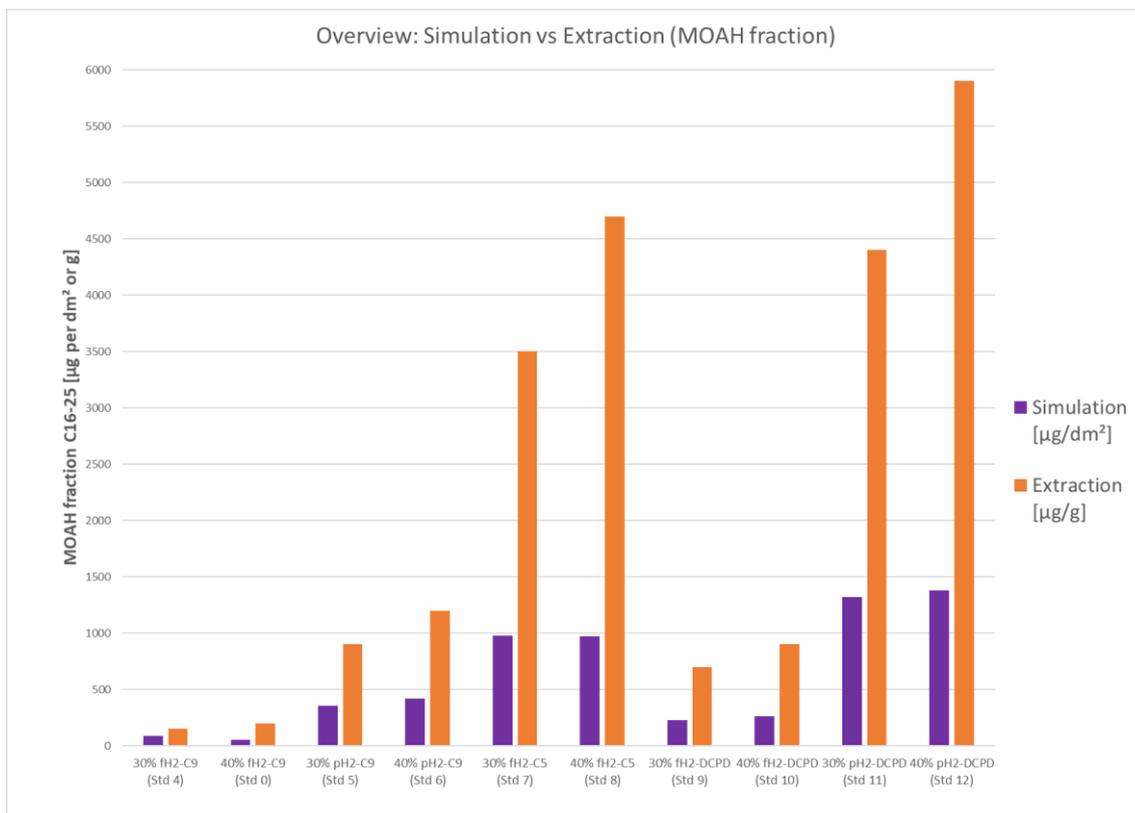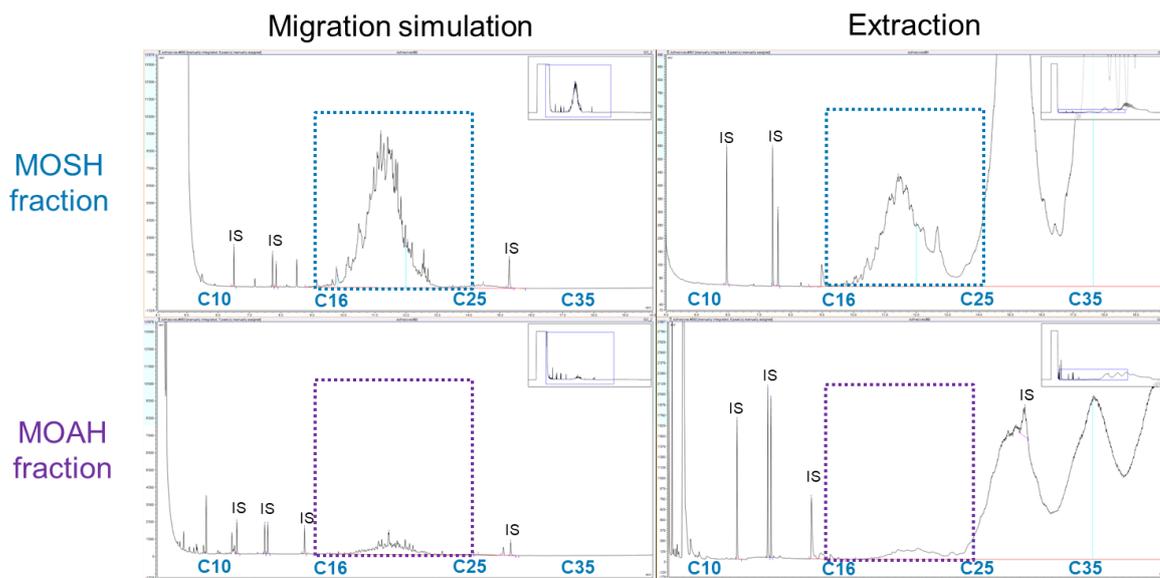

Overview: Simulation vs Extraction (MOSH fraction)

Figure 3: Results of migration simulation and hotmelt extraction (MOAH fraction)

Overview: Simulation vs Extraction (MOAH fraction)

If the migration simulation results are put in relation to extraction results, a certain correlation can be observed for saturated resin oligomers (MOSH fraction) and aromatic resin oligomers

(MOAH fraction). However, in these graphics a comparison is made between the extraction related to 1 g adhesive, whereas the simulation is related to 1 dm² which can be roughly assumed to 10 g of adhesive, as explained above. If for comparison reasons the simulation results are referenced to only 1 g of adhesive the purple bars (see figure 2 and 3) would be 10 times smaller and thus reflecting an even bigger gap between extraction and migration simulation. This could be an indication that the absolute results obtained from the hotmelt extraction test might not be suitable for the evaluation of the expected migration into food.

Figure 4: Chromatographic example (Std 6) obtained from HPLC-GC-FID

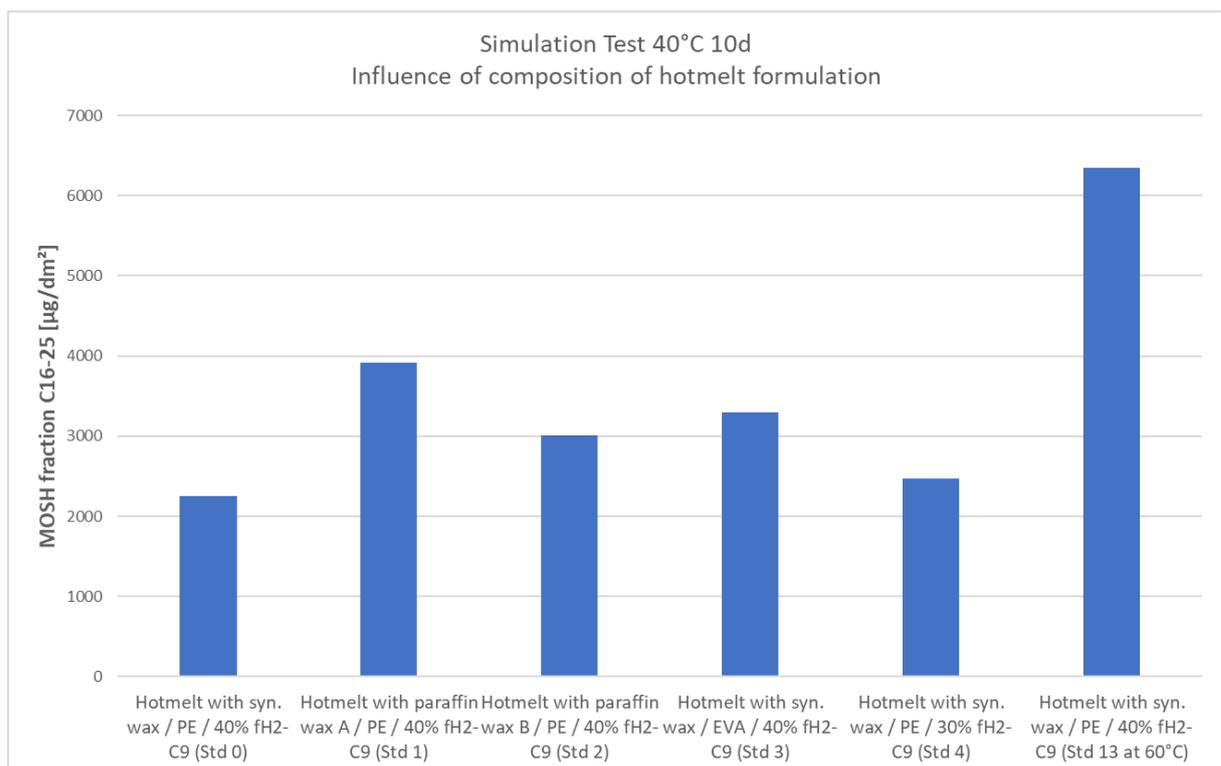## 3.2. Influence of the composition of the hotmelt formulation

As outlined in Chapter 2, hotmelt formulation "Std 0" was modified by changing the wax type or the polymer type. *Figure 1* below shows how migration of the saturated resin oligomers (MOSH fraction) was influenced when the synthetic wax of "Std 0" was changed to paraffinic wax A or B ("Std 1" and "Std 2"). Similarly, the polymer was changed from PE to EVA ("Std 3"). In summary, for both modifications an increased migration (MOSH fraction) could be observed (increase by factor 1.35 to 1.70, see matrix factors below).

When changing the resin content from 40 % in "Std 0" to 30 % in "Std 4", the amount of migrating MOSH fraction did not change noticeably.

Migration into food simulant was also performed at 60 °C ("Std 13") instead of 40 °C. As expected, increased migration temperature leads to increased migration compared to Std 0 (in this case by a factor of 3).

The results of the aromatic resin oligomers (MOAH fraction) were not compared due to the very low initial amount in the resin type. Although the tendencies are similar, the analytical variation of these traces (55 – 160 µg / dm², see table 2) is relatively high and would not lead to a reliable comparison.

Figure 5: Influence of hotmelt composition (MOSH fraction)

Matrix factors: ➢ *Increase of migration by a factor of 1.70 using paraffin wax A (Std 1)*

(MOSH fraction)   ➢ *Increase of migration by a factor of 1.35 using paraffin wax B (Std 2)*

   ➢ *Increase of migration by a factor of 1.45 using polymer EVA (Std 3)*

   ➢ *No noticeable change of migration using 30% resin (Std 4)*

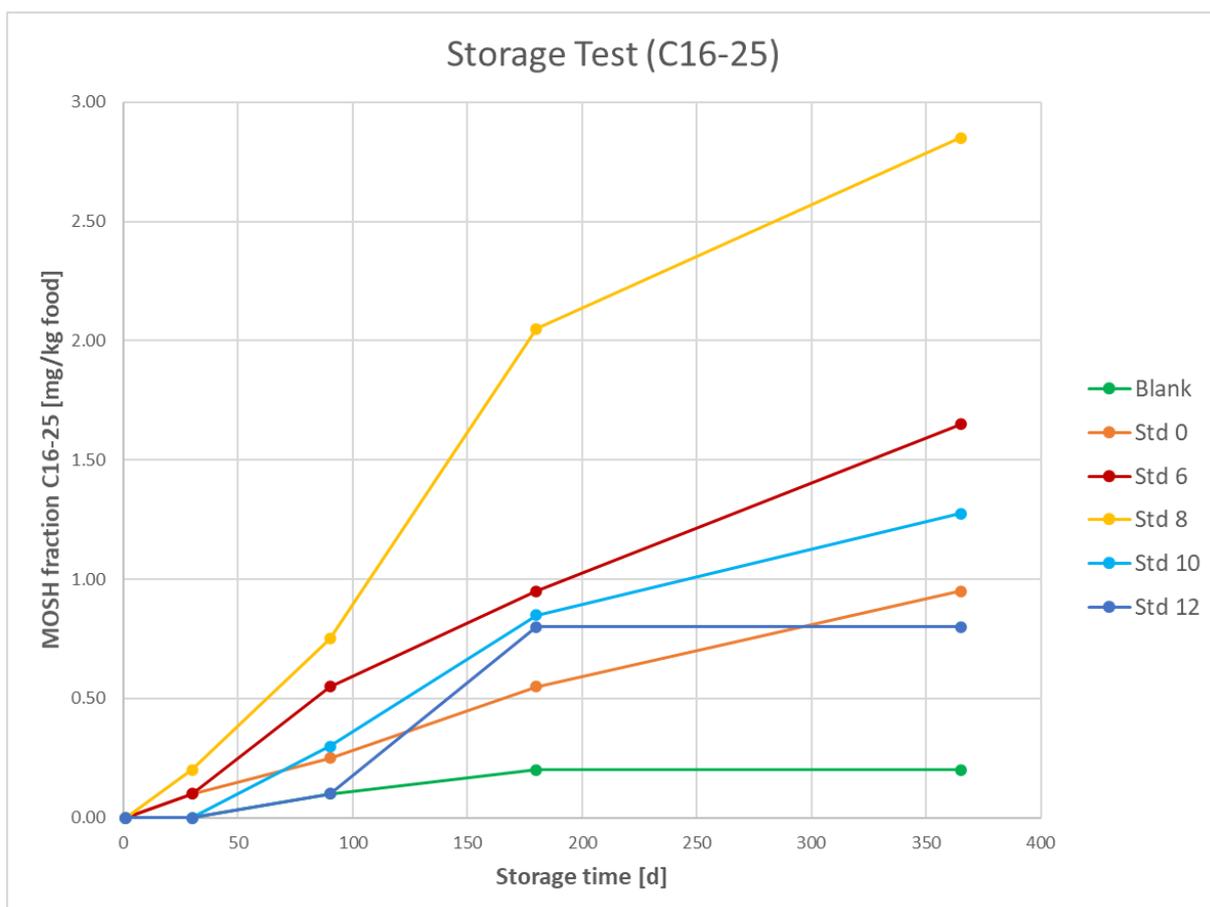   ➢ *Possible underestimation of migration by a factor of 3 for conditions 10 d @ 40 °C vs 60 °C (Std 13)*

3.3. Storage Test

Table 3: Results of storage test

Sample	MOSH fraction C16-25 [mg/kg food]				MOAH fraction C16-25 [mg/kg food]			
	30 d	90 d	180 d	365 d	30 d	90 d	180 d	365 d[9]
Blank	< 0.20	< 0.20	0.20	**0.20**	< 0.20	< 0.20	< 0.20	**< 0.10**
Std 0	< 0.20	0.25	0.55	**0.95**	< 0.20	< 0.20	< 0.20	**< 0.10**
Std 6	< 0.20	0.55	0.95	**1.65**	< 0.20	< 0.20	< 0.20	**0.20**
Std 8	0.20	0.75	2.05	**2.85**	< 0.20	< 0.20	< 0.20	**0.22**
Std 10	< 0.20	0.30	0.85	**1.30**	< 0.20	< 0.20	< 0.20	**0.15**
Std 12	< 0.20	< 0.20	0.80	**0.80**	< 0.20	< 0.20	< 0.20	**0.27**

Cardboard boxes filled with oat flakes were sealed with different hotmelt adhesives and stored for one year. Frequent tests on the MOSH fraction revealed an increase in hydrocarbon migration over the storage period. The results of the MOAH fraction remained below the detection limit most of the time.
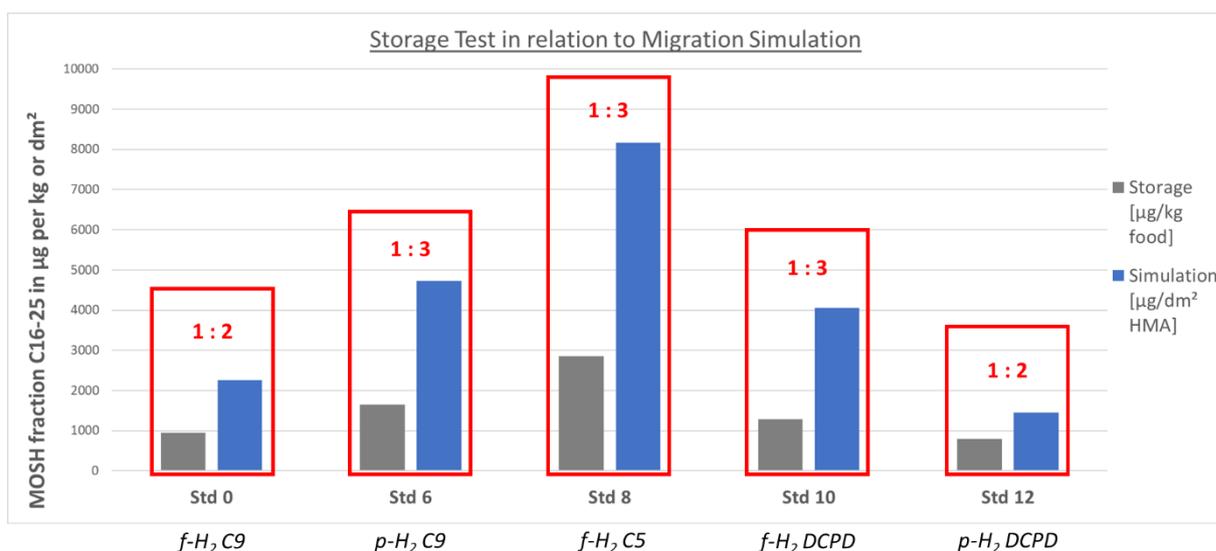
Figure 6: Graphic evaluation of storage test

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[9] For the 365 days value, a lower detection limit of 0.10 mg/kg food was established via adapted sample preparation, so that at least for this storage time a comparison of the MOAH fractions originating from the different hotmelts was possible.

3.4.   Comparison of storage tests and migration simulation

The obstacle of migration simulations has always been the question of whether the testing conditions accurately reflect reality. Therefore, the simulation results were compared to a realistic storage test. It should be noted that although the units from the two tests are not directly comparable (µg resin oligomers / kg of food versus simulation µg resin oligomers / dm^2 hotmelt film), a certain correlation of the numbers is still possible in the case that the test conditions remain constant. Chapter 3.5 "Consideration of the hotmelt application area" provides further detail and deals with the comparison of the actual migration obtained from the storage test with the calculated migration obtained from the simulation.

The standard formulations Std 0, 6, 8, 10 and 12 show a good correlation between the results obtained from the storage test (µg/kg food) and simulation test (µg/dm² hotmelt film). Both sets of values increase in a similar way, showing the lowest migration potential from Std 12 over Std 0, Std10, Std 6 up to Std 8 with the highest migration potential. The relative ratio between both sets of values differs by a factor of 2 for Std 0 and Std 12, and a factor of 3 for Std 6, Std 8 and Std 10. The similarity of the relative difference factors 2-3 underlines the plausibility of the comparison between the two methods and suggests that there is no fundamental difference in migration patterns that occur during the migration simulation from a hotmelt in comparison to the real migration from a hotmelt.

Figure 7: Results of storage test and migration simulation (MOSH fraction)

3.5.   Consideration of hotmelt application area

The estimation of migration regarding a hotmelt adhesive used in a cardboard box can be related to the contact area of the hotmelt film. In general, the use of actual surface of food contact material (FCM) in contact with a defined amount of food is one important parameter to generate migration testing results reflecting the transfer/diffusion from the FCM closer to reality. However, the suggested parameter of 6 dm² packaging for 1 kg food, given in EU regulation (EC) No 10/2011 for non-specified applications is not applicable for hotmelt adhesives. Hotmelts are only applied to a small portion of the total surface area of food contact material. In the conception of this study, 300g oat flakes were packed in a cardboard folding box. The application area of the hotmelt, between the overlapping cardboard layers of the cardboard, was roughly 0.2 dm², which reflects a typical application for this kind of adhesives.

It should be noted that the application area of the hotmelt remains the limiting factor for migration, meaning the migration occurs through the cardboard layer. The relationship to the

weight of hotmelt via the weight/area ratio can only be used if the thickness of the hotmelt test specimens for migration simulation is similar to the real application.

In table 4, the measurement values of migration simulation (indicated in µg/dm²) were divided by factor 5 to calculate the absolute amount of saturated hydrocarbons (MOSH fraction) originating from 0.2 dm² of HMA application area representing the packaging system for 300 g food used in the storage test. This value was multiplied by factor 3.33 to relate this absolute amount to 1 kg of food. The calculated value can be considered as the expected migration into food (indicated in µg/kg). It is a measure based on migration simulation, intended to predict the real migration expected into food in the course of food packaging and storage.

Exemplary calculation for Std 0:
Migration simulation: 2260 µg per 1.0 dm²
- ➢ Step 1:   452 µg MOSH per 0.2 dm²
- ➢ Step 2:   452 µg MOSH per 0.3 kg food
- ➢ Step 3: 1510 µg MOSH per 1.0 kg food

Table 4: Calculating the expected migration into food based on migration simulation

Std #	MOSH fraction C16-25		
	Migration simualtion [µg/dm² hotmelt film]	Absolute amount from 0.2 dm² hotmelt contact area [µg]	Expected migration [µg/kg food]
	C_{sim}	A_O x C_{sim}	C_{expect}
0	2260	452	1510
6	4720	944	3150
8	8150	1630	5430
10	4060	812	2710
12	1450	290	970

A_o…   Surface area of the hotmelt [dm²]
c_{sim}…   Concentration from the migration simulation (10 d / 40 °C) [µg/dm²]
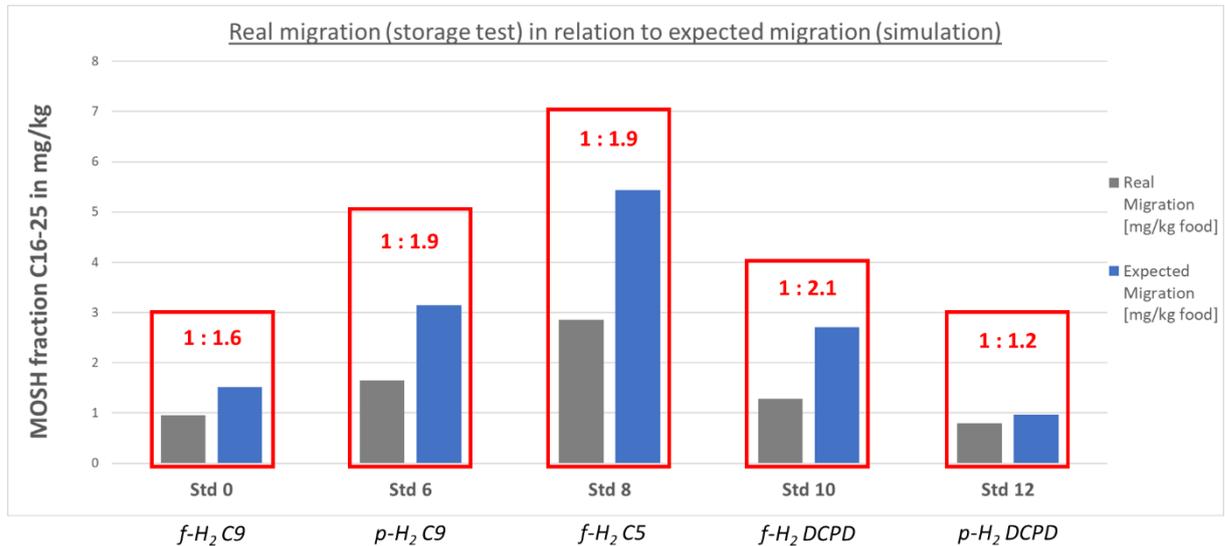*c_{expect}… Concentration of the expected migration [µg/kg]*

In Table 5, the expected migration calculated from migration simulation was compared to the actual migration values obtained for the stored oat flakes (storage time up to 365 days). The results can be expressed as recovery (%) or recovery factor.

Table 5: Comparing the real migration results from oat flaks storage test with the expected migration derived from migration simulation

Std #	MOSH fraction C16-25		
	Expected migration [µg/kg food]	Real migration (365d storage) [µg/kg food]	Recovery (expected migration / real migration)
0	1510	950	159 %
6	3150	1650	191 %
8	5430	2850	191 %
10	2710	1300	208 %
12	970	800	121 %

Recovery factors from 1.2 to 2.1 were calculated, indicating the expected migration derived from migration simulation overestimates the real migration in all investigated samples. Figure 8 illustrates the determined recovery factors when comparing the expected migration derived from migration simulation with real migration results obtained for the oat flakes.

Figure 8: Comparison real migration in relation to expected migration (MOSH fraction)

Since the recovery rate of the migration simulation always exceeded the real migration of the storage tests, the expected migration is appropriate as parameter to assess the worst-case migration. The following formula can be used to calculate the expected migration for the final hotmelt application using the results of a migration simulation carried out on MPPO (Tenax).

<u>Estimation of expected migration using migration simulation</u>

$$c_{expect} = \frac{Ao \times c_{sim} \times 1000}{W}$$

Ao…   Surface area of the hotmelt [dm²]
c_{sim}…   Concentration from the migration simulation (10 d / 40 °C) [µg/dm²]
c_{expect}… Concentration of the expected migration [mg/kg]
W…   Weight of food [g]

4. Conclusion

The FEICA study on the migration of substances / oligomers from packaging hotmelts into dry food demonstrated, that typical packaging hotmelts such as used in this study are in accordance with the EU framework regulation on food contact materials. The various hotmelt formulations showed a low impact on the concentration of saturated hydrocarbons (MOSH fraction) and aromatic hydrocarbons (MOAH fraction) in food and food simulants. These fractions are defined by the commonly applied MOSH/MOAH method for routine analysis via HPLC-GC-FID, but it should be noted that the migrated hydrocarbons are resin oligomers, which cannot be considered as mineral oil hydrocarbons (MOSH/MOAH). However, the analysed aromatic resin oligomers (MOAH fraction) stayed below or close to the detection limit (0.2 mg/kg).

Moreover, the study provides an insight into the contribution to the values of the MOSH fraction and the MOAH fraction from hotmelt over storage time. An appropriate testing approach for the food and food packaging industry was demonstrated when worst case assumptions fail. The correlation of three different approaches was compared. The best correlation was observed between the migration simulation and the storage test (real migration into the food). The migration into a simulant could be considered as the method of choice to deduce the actual migration. If a simulation test is carried out, a calculation model can be used to calculate the expected migration.

Extraction tests on hotmelt samples are not suitable to estimate the migration of saturated hydrocarbons (MOSH fraction) and aromatic hydrocarbons (MOAH fraction) onto packed foodstuff. Extraction tests severely overestimate migration, as the hotmelt formulation will be dissolved and partly decomposed when being exposed to organic solvents. As result the extraction test shows the total amount of hydrocarbons available in the hotmelt and not only the part with a migration potential. Compared to the migration simulation, the MOSH and MOAH results from the extraction tests were about 10 to 50 times higher and therefore not suitable as a meaningful approach.

The **migration simulation** as introduced and described in this study gives a worst-case picture of possible migration under applied storage conditions. In this study the simulation test can overestimate the actual migration up to a factor of 2. In addition, this approach integrates the parameters of volatility, type of components, matrix effect and contact area in the best way.

The migration results from the **storage test** demonstrates that the migration of the aromatic hydrocarbons / resin oligomers (MOAH fraction) remained below the detection limit in the first nine months. Since the detection limit of 0.2 mg/kg food did not show any results during the first nine months, the detection limit was lowered to 0.1 mg/kg for the 365 days value. Following this, a minor difference between the various hotmelts could be noticed.

Over time, the various storage tests showed a slight increase of saturated hydrocarbons / resin oligomers (MOSH fraction) found in the food. This indicates that diffusion processes took place as expected. The migration was ranging at a low ppm level (1 – 3 mg/kg) and none of the samples exceeded 3.0 mg/kg food (C16-C25, MOSH fraction). This value remains below to suggested "MOH Orientation Values" from the German working group ALB[10] for dry food, such as cereals (MOSH <6 mg/kg food).
The nature and quantity of the used resin led to changes in the MOSH and MOAH results. However, taking expected legal restriction for MOAH migration[11] into account (MOAH <0.5 mg/kg food), the variations between the resins could be considered as negligible.

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[10] Draft for MOH Orientation Values of Working Group Consumer Protection for Food and Food Contact Materials, Wine and Cosmetics (ALB) from June 2020
[11] BfR Draft on Notified draft of German 22nd Ordinance amending the Consumer Goods from August 2020

The evaluation of the hotmelt matrix effects involving the variation of polymer types and wax types used in the various hotmelt formulations resulted in slightly different migration values. All remain in the same order of magnitude (deviation less than 50 % from the mean).

The FEICA study was carried out to give an insight on influences of typical hotmelt applications for cardboard packaging regarding the migration of hydrocarbons. The influence especially of aromatic resin oligomers (MOAH fraction) originated from the hydrocarbon resins in hotmelt packaging adhesives could be shown to remain negligible. These results may help the users to get a picture about the safety of the applied hotmelt adhesive, also in consideration of existing and upcoming regulations. Migration simulation can be considered to be the most appropriate method to determine the possible contribution of hotmelt adhesives to the migration of saturated hydrocarbons (MOSH fraction) and aromatic hydrocarbons (MOAH fraction).
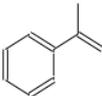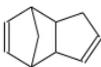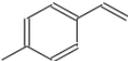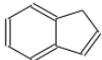
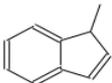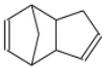*Cologne, 23rd September 2020*

Dr. Martin Lommatzsch

ANNEX I Chemical structures

<u>Chemical structures and share of the predominant resin monomers in the feedstocks:</u>

(According to Mildenberg et al.)

Feedstock	C5	C9	DCPD
Main Monomers	**69 %** Piperylene (C_5H_8)	**2 %** Styrene (C_8H_8)	Cyclopentadiene (C_5H_6)
	18 % Cyclopentene (C_5H_8)	**4 %** α-Methylstyrene (C_9H_{10})	Dicyclopentadiene ($C_{10}H_{12}$)
	2 % Cyclopentadiene (C_5H_6)	**20 %** Vinyltoluene (C_9H_{10})	***65-98 %*** *mixture of both*
		20 % Indene (C_9H_8)	
		5 % Methylindene ($C_{10}H_{10}$)	
		6 % Dicyclopentadiene ($C_{10}H_{12}$)	
Residual compounds	**< 13 %** C4/C6 species	**< 43 %** non-reactive aromatics	***2-35 %*** *species involving butadiene, isoprene, methyl-CPD*

ANNEX II - Structural comparison of mineral oil hydrocarbons and resin oligomers:

Hydrocarbon type	Saturated compounds	Aromatic compounds
Mineral oil hydrocarbons *according to EFSA*		
Resin oligomers *according to Lommatzsch et al.*		
➢ C5 Tetramers		
➢ C9 Dimers		
➢ DCPD Dimers		

ANNEX III experimental

Methods

- Test for the content of hydrocarbons (C10-C50) according to Grob and Biedermann (2009[12], 2012[13]) for mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH)
  - ➢ *In compliance with the JRC Guidance[14] on sampling, analysis and data reporting for the monitoring of mineral oil hydrocarbons in food and food contact materials.*

- Migration simulation with modified polyphenylene oxide (MPPO, Tenax) is derived from DIN EN 14338:2004-03 and DIN SPEC 5010:2018-05

Internal standard (IS) solution

Substance	Conc.	Function
n-Undecane (C11)	300 mg/l	Low-boiler MOSH fraction
Cyclohexylcyclohexane (Cycy)	300 mg/l	Quantification MOSH fraction
n-Tridecane (C13)	150 mg/l	Quantification MOSH fraction
Cholestane (Cho)	600 mg/l	End of MOSH fraction
Pentylbenzene (5B)	300 mg/l	Low-boiler MOAH fraction
1-Methylnaphtaline (1MN)	300 mg/l	Quantification MOAH fraction
2-Methylnaphtaline (2MN)	300 mg/l	Quantification MOAH fraction
Tritertbutylbenzene (TBB)	300 mg/l	Start MOAH fraction
Perylene (Per)	600 mg/l	End of MOAH fraction

Chemicals

All solvents used for analysis were GC-FID grade supplied by Merck. The internal standard solution for MOSH/MOAH analysis was supplied by Restek.

Sample preparation

Adhesive extraction:
- 50 mg of adhesive were extracted with 20 ml n-hexane in an ultrasonic bath at 50 °C for 1 h
- 40µl of internal standard solution were added
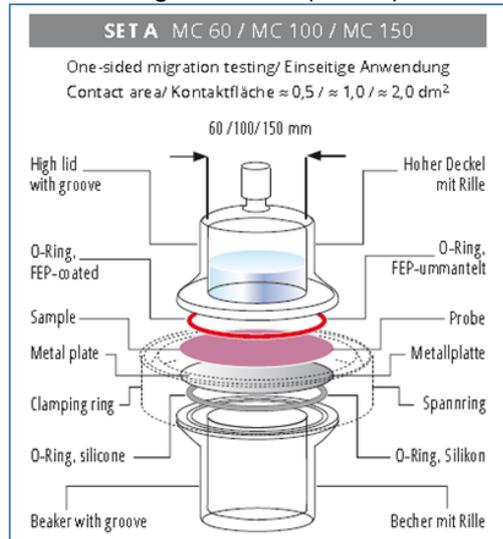
Migration simulation:
- 0.5 dm² of the individual test specimens (ca. 10g/dm² with1.5 mm thickness) were positioned into a migration cell
- A glass fibre filter was used as spacer
- 2 g of MPPO (Tenax® 60/80 mesh) were used as simulant
- Simulation conditions: 10 d at 40 °C or 10 d at 60 °C
- The complete simulant was extracted with 20 ml n-hexane (+ 20 µl IS-solution) for 24 h at ambient temperature

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[12] M. Biedermann, K. Fiselier, K. Grob; J. Agric. Food Chem. 57 (2009) p. 8711
[13] K. Grob, M. Biedermann; J. of Chromatography A 1255 (2012) p. 56
[14] JRC Technical Reports: http://dx.doi.org/10.2760/208879

Migration cell (MC60)

Storage Test:
- 300 g of oat flakes were used as model food
- 8 dm² virgin fibre cardboard boxes were used as packaging
- Each folding box was sealed with 0.3 g (± 0.1 g) of the individual hotmelt adhesive (caterpillar dimension: 4 cm length and 5/32" thickness) + Blank involving staples
- The folding boxes were stored for up to 12 months at ambient temperature

Oat flakes extraction:
- Duplets for each type and sampling date were prepared – the complete oat flakes (300 g) were homogenized
- 2 x 20 g were extracted with 30 ml of n-hexane for 24 h at RT for each duplet
    - 30 µl of internal standard solution were added

<u>HPLC-GC-FID</u>

The supplier of the LC-GC-FID system was Brechbuehler AG (Thermo Scientific). 10–90 µl of the sample extract was injected into the HPLC. The normal phase LC was used for the separation of saturated (MOSH) and aromatic hydrocarbons (MOAH). Polar components remained on the HPLC-column and were eluted into the waste during the backflush of the column. No interference with MOSH and MOAH occurred. The fraction of interest was transferred (on-line) into GC-FID.

HPLC setup
Column: Allure Silica (5 µm, 250 x 2.1 mm, Restek)
Flow: 0.3 ml/min (backflush 0.5 ml/min)
Gradient: Eluent A – n-hexane, 100 % 0.0-0.9 min, 65 % 1-6 min, 100 % 15-30 min
              Eluent B – dichloromethane, 35 % 1-6 min, 100 % 6-15 min
              Backflush 6-15 min
Transfer: MOSH -fraction 2.0 – 3.5 min
              MOAH-fraction 3.8 – 5.3 min

GC setup
Column: 7 m x 0.53 mm ID uncoated precolumn and 15 m x 0.25 mm ID Rxi-1HT separation
              column (Restek)
Injection: On-column (Y-piece) or PTV
Carrier: Hydrogen
Pressure: 60 kPa (80-90 kPa during concurrent solvent evaporation)
Program: 55 °C (5.0 min) – 20 °C/min – 360 °C (5.0 min)
FID: 370 °C, 350 ml/min air, 35 ml/min hydrogen, 20 ml/min nitrogen (make-up)

<u>*Remark for analysis of dry foods (storage test):*</u>
All peaks (set of peaks) on top of the hump(s) were subtracted and not included in the integration, such as n-alkanes for the MOSH fraction and biogenic terpenes for the MOAH fraction. The LoQ is generally < 0.2 mg/kg for dry foods (e.g. oat flakes) and was improved for the determination of the MOAH fraction for the 365 d samples to < 0.1 mg/kg.