Specific migration testing - a comparison of experimental data and values predicted by a migration model

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Introduction

Migration modelling is a cost-efficient alternative to experimental testing when allowed by legislation. For migration modelling, two fundamental pieces of information are needed: the diffusion coefficient D_P and the coefficient $K_{P,F}$ describing a migrant's partitioning between polymer and food. For the latter, a worst case approach can easily be implemented by setting $K_{P,F} = 1$, thus assuming a high solubility of the migrant in the food. The diffusion coefficient D_P however, depends on several factors, e.g.

- the molecular weight of the migrant M_r
- the temperature T
- and the matrix (polymer).

The experimental determination of D_P values is time-intensive and costly and as a result, only a limited number of diffusion coefficients exists. With this in mind, a polymer specific empirical diffusion "conductance" coefficient was introduced by Piringer (1994). An Arrhenius-type relationship of the diffusion coefficient with the relative molecular weight of the migrant, the temperature and the polymer type was established and a polymer coefficient A_P describing the diffusion "conductance" of a polymer was introduced. A worst case diffusion coefficient D_P^* can be estimated for any migrant that is toxicologically relevant for a given temperature applying the following equation:

$$D_P^* = 10^4 \cdot e^{A_P - 0.1351 \cdot M_r^{2/3} + 0.003 \cdot M_r - 10454/T}$$

In the EU funded project "Specific Migration" (G6RD-CT-2000-00411, see poster by Störmer *et al.* on this conference), reference materials for specific migration testing were developed. One major objective of the project was the determination diffusion coefficients, D_P, and partitioning coefficients $K_{P,F}$.

Objectives

This poster presents a comparison of migration values experimentally determined in a small-scale interlaboratory study, with values determined by migration modelling. The D_P and $K_{P,F}$ values applied for the migration modelling approach have been determined experimentally during the same EU funded project by the four participating laboratories.

Results

Table 1: Comparison of experimental and predicted data from Phase 1

No.	Polymer	Migrant	D_P	$K_{P,F}$	Time	Temp.	Food Simulant	Migration exp.	Migration predicted	Deviation
			[cm²/s]			[°C]		[mg/dm²]	[mg/dm²]	[%]
01	LDPE	Irganox 1076	2.3E-07	0.1	2 h	100	olive oil	2.20	2.384	8.4
01	LDPE	Irgafos 168	7.0E-08	0.1	2 h	100	sunflower oil	1.35	1.260	-6.7
02	LDPE	DPBD	1.2E-09	5	6 h	20	olive oil	0.05	0.049	-2.0
03	HDPE	Irganox 1076	4.0E-11	15	10 d	40	sunflower oil	0.44	0.403	-7.8
03	HDPE	Irgafos 168	2.2E-12	80	10 d	40	sunflower oil	0.16	0.094	-41
04	HDPE	Chimassorb 81	7.0E-09	0.1	1 h	70	olive oil	0.58	0.493	-12
04	HDPE	Uvitex OB	1.6E-09	0.1	1 h	70	olive oil	0.12	0.118	-1.7
05	PP (homo)	Irganox 1076	1.9E-08	0.1	1 h	100	olive oil	0.83	1.133	37
05	PP (homo)	Irgafos 168	1.3E-09	0.1	4 h	100	sunflower oil	0.83	0.714	-14.
06	PP (random)	Chimassorb 81	1.1E-08	0.1	1 h	70	olive oil	0.65	0.632	-2.8
06	PP (random)	Uvitex OB	2.6E-09	0.1	1 h	70	olive oil	0.14	0.154	10
07	PP	Trimethylolpropane	2.1E-10	1	4 h	70	water	0.030	0.036	20
07	PP	Erucamide	4.2E-09	0.1	2 h	70	olive oil	0.72	0.745	3.5
09	HIPS(oil)	Styrene	8.3E-14	1	10 d	20	olive oil	0.014	0.016	14
10	GPPS	Styrene	3.0E-13	1	1 d	40	olive oil	0.005	0.007	40
12	PET	Tinuvin 1577	1.4E-11	0.1	2 h	121	olive oil	0.29	0.849	193
14	soft PVC	DEHA	1.7E-11	0.1	1 d	20	olive oil	10.00	13.095	31
15	PA6	Caprolatam	7.0E-12	0.1	2 h	40	water	1.55	0.071	-95
16	PA12	Laurolactam	5.1E-11	0.1	1 d	70	water	0.77	0.548	-29

Results

The experimental and predicted data of materials 1 to 16 in phase 1 (Table 1) and 01-2 to 15-2 in phase 2 (Table 2) fit together quite well. Of the 28 migration values predicted, 93% were in the range of ±40% compared to the experimental migration values.

Table 2: Comparison of experimental and predicted data from Phase 2

No.	Polymer	Migrant	D_P	$K_{P,F}$	Time	Temp.	Food Simulant	Migration exp.	Migration predicted	Deviation
			[cm²/s]			[°C]		[mg/dm²]	[mg/dm²]	[%]
01-2	LDPE	Irganox 1076	1.7E-07	0.9	2h	100	sunflower oil	1.8	2.1	15
01-2	LDPE	Irgafos 168	9.5E-08	1.0	2h	100	sunflower oil	1.2	1.5	22
02-2	LDPE	DPBD	5.4E-09	0.5	4h	20	olive oil	0.17	0.11	-36
04-2	HDPE	Chimassorb 81	1.3E-08	1.5	2h	70	olive oil	0.91	0.90	-1
04-2	HDPE	Uvitex B	2.9E-09	0.5	2h	70	olive oil	0.20	0.22	7
05-2	PP(homo)	Irganox 1076	1.4E-08	0.1	4h	100	sunflower oil	1.6	1.8	20
05-2	PP(homo)	Irgafos 168	3.5E-09	0.1	4h	100	sunflower oil	1.0	1.3	25
09-2	HIPS(oil)	Styrene	1.8E-13	1.0	10d	40	olive oil	0.013	0.017	31
15-2	PA6	Caprolactam	1.0E-12	844	2h	40	water	0.99	0.02	-98*

*due to swelling of the polymer

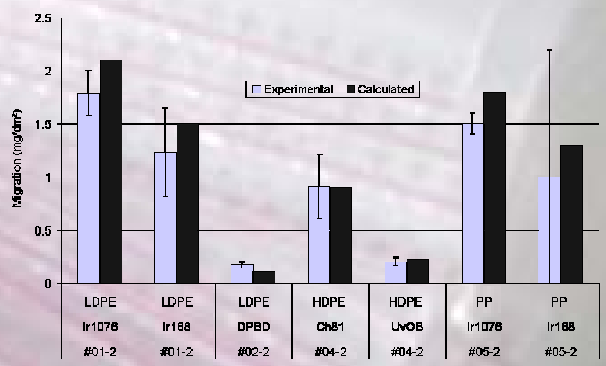

Figure 1: Comparison of experimentally determined migration values and those predicted by migration modelling for some polyolefins

Conclusions

For the first time, diffusion coefficients were determined in a small scale interlaboratory comparison study, meaning that the data established here can be considered the most reliable values relevant for this purpose available to date.

A validation of the migration modelling approach itself was possible as it was possible to compare reliable experimental migration data on one side and predicted migration data on the other.

Deviations observed are likely to originate from analytical variations or in different solubilities of the migrants in oil (applied during specific migration testing) and food simulants (applied during diffusion testing). .

References

Piringer, O.G., 1994, Evaluation of plastics for food packaging. *Food Additives and Contaminants*, 11, 221-230.

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