

## Investigation Report

### Investigation of the specific migration of Irganox<sup>®</sup> 1076 and Metilox from PP-plates for a “repeated use” Scenario

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**Contracting body:** PlasticsEurope AISBL  
Ave E. van Nieuwenhuyse 4  
1160 BRUSSELS  
BELGIUM

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<b>Sample:</b>	<b>No.</b>	<b>Specification</b>
	1	Polypropylene homopolymer with Irganox <sup>®</sup> 1076 [2082-79-3]
	2	Polypropylene homopolymer with Metilox [6386-38-5]

## 1. Introduction

The aim of this project was to determine the specific migration of Irganox® 1076 and Metilox from PP-Plates in a “repeated use scenario”. The development of the migration behaviour of those substances was monitored for 20 cycles into two different food simulants to derive parameters for the mathematical modeling of “repeated use” applications of plastic materials. The parameters generated from the experimental results were compared with existing parameters from other projects and the migration modeling guideline.

## 2. Experimental

The following investigations were performed:

Sample	Investigation	Method of analysis	Simulant	Conditions time/ temp.
1	Specific determination of Irganox 1076	HPLC/UV	Ethanol 95% Ethanol 50%	20 x 8 hours/ 60° C (repeated use)
2	Specific determination of Metilox	HPLC/UV	Ethanol 95% Ethanol 50%	20 x 8 hours/ 60° C (repeated use)

### Specific determination of Irganox 1076 and Metilox

For each test series (20 cycles á 8 hours) 3 pieces (3 cm x 6,4 cm) of the provided PP-samples were selected. For each cycle 3 pieces of a sample are immersed in 60 mL preheated food simulant (either 50% ethanol in water or 95% ethanol in water). After 8 hours the samples are removed from the simulant, wiped dry and stored in aluminum foil until the next cycle. The migration solutions were worked-up and analysed by means of high performance liquid chromatography coupled with an UV-detector (HPLC/UV). Quantification of the substances was performed specifically by external calibration curves.

### 3. Results

#### 3.1 Specific determination of Irganox 1076 (sample No. 1)

In the following table the results of the determination of the specific migration are listed.

Substance	Simulant	Cycle	Results sample No.1 - EtOH 95%	
			[µg/dm <sup>2</sup> ]	[mg/kg simulant]
Irganox 1076	Ethanol 95%	1	131,3	3,52
Irganox 1076	Ethanol 95%	2	68,2	1,83
Irganox 1076	Ethanol 95%	3	54,6	1,46
Irganox 1076	Ethanol 95%	4	32,0	0,86
Irganox 1076	Ethanol 95%	5	33,6	0,90
Irganox 1076	Ethanol 95%	6	30,7	0,82
Irganox 1076	Ethanol 95%	7	42,9	1,15
Irganox 1076	Ethanol 95%	8	34,7	0,93
Irganox 1076	Ethanol 95%	9	33,5	0,90
Irganox 1076	Ethanol 95%	10	29,5	0,79
Irganox 1076	Ethanol 95%	11	24,6	0,66
Irganox 1076	Ethanol 95%	12	28,6	0,77
Irganox 1076	Ethanol 95%	13	28,5	0,76
Irganox 1076	Ethanol 95%	14	27,6	0,74
Irganox 1076	Ethanol 95%	15	26,7	0,72
Irganox 1076	Ethanol 95%	16	26,4	0,71
Irganox 1076	Ethanol 95%	17	26,7	0,72
Irganox 1076	Ethanol 95%	18	22,2	0,60
Irganox 1076	Ethanol 95%	19	23,9	0,64
Irganox 1076	Ethanol 95%	20	25,5	0,68

Table 1: Migration results of Irganox<sup>®</sup> 1076 into Ethanol 95%

Substance	Simulant	Cycle	Results sample No.1 - EtOH 50%	
			[µg/dm <sup>2</sup> ]	[mg/kg simulant]
Irganox 1076	Ethanol 50%	1	18,8	0,46
Irganox 1076	Ethanol 50%	2	14,6	0,36
Irganox 1076	Ethanol 50%	3	13,7	0,33
Irganox 1076	Ethanol 50%	4	9,8	0,24
Irganox 1076	Ethanol 50%	5	10,1	0,25
Irganox 1076	Ethanol 50%	6	9,9	0,24
Irganox 1076	Ethanol 50%	7	11,7	0,29
Irganox 1076	Ethanol 50%	8	10,7	0,26
Irganox 1076	Ethanol 50%	9	11,2	0,27
Irganox 1076	Ethanol 50%	10	9,4	0,23
Irganox 1076	Ethanol 50%	11	9,5	0,23
Irganox 1076	Ethanol 50%	12	10,0	0,24
Irganox 1076	Ethanol 50%	13	10,0	0,24
Irganox 1076	Ethanol 50%	14	9,8	0,24
Irganox 1076	Ethanol 50%	15	9,7	0,24
Irganox 1076	Ethanol 50%	16	9,7	0,24
Irganox 1076	Ethanol 50%	17	9,7	0,24
Irganox 1076	Ethanol 50%	18	9,0	0,22
Irganox 1076	Ethanol 50%	19	9,8	0,24
Irganox 1076	Ethanol 50%	20	10,0	0,24

Table 2: Migration results of Irganox<sup>®</sup> 1076 into Ethanol 50%

### 3.2 Specific determination of Metilox (sample No. 2)

In the following table the results of the determination of the specific migration investigations are listed.

Substance	Simulant	Cycle	Results sample No.2 - EtOH 95%	
			[µg/dm²]	[mg/kg simulant]
Metilox	Ethanol 95%	1	210,3	5,64
Metilox	Ethanol 95%	2	110,0	2,95
Metilox	Ethanol 95%	3	84,8	2,27
Metilox	Ethanol 95%	4	54,4	1,46
Metilox	Ethanol 95%	5	52,6	1,41
Metilox	Ethanol 95%	6	47,4	1,27
Metilox	Ethanol 95%	7	64,3	1,72
Metilox	Ethanol 95%	8	55,1	1,48
Metilox	Ethanol 95%	9	52,8	1,41
Metilox	Ethanol 95%	10	43,0	1,15
Metilox	Ethanol 95%	11	36,8	0,99
Metilox	Ethanol 95%	12	42,7	1,15
Metilox	Ethanol 95%	13	37,8	1,01
Metilox	Ethanol 95%	14	35,9	0,96
Metilox	Ethanol 95%	15	37,5	1,00
Metilox	Ethanol 95%	16	36,0	0,97
Metilox	Ethanol 95%	17	35,3	0,95
Metilox	Ethanol 95%	18	31,3	0,84
Metilox	Ethanol 95%	19	30,8	0,83
Metilox	Ethanol 95%	20	31,1	0,83

Table 3: Migration of results Metilox into Ethanol 95%

In the following table the results of the determination of the specific migration investigations are listed.

Substance	Simulant	Cycle	Results sample No.2 - EtOH 50%	
			[µg/dm <sup>2</sup> ]	[mg/kg simulant]
Metilox	Ethanol 50%	1	161,3	3,93
Metilox	Ethanol 50%	2	88,3	2,15
Metilox	Ethanol 50%	3	72,7	1,77
Metilox	Ethanol 50%	4	40,7	0,99
Metilox	Ethanol 50%	5	38,4	0,94
Metilox	Ethanol 50%	6	34,5	0,84
Metilox	Ethanol 50%	7	50,9	1,24
Metilox	Ethanol 50%	8	44,8	1,09
Metilox	Ethanol 50%	9	40,4	0,98
Metilox	Ethanol 50%	10	33,4	0,81
Metilox	Ethanol 50%	11	30,3	0,74
Metilox	Ethanol 50%	12	36,7	0,89
Metilox	Ethanol 50%	13	34,5	0,84
Metilox	Ethanol 50%	14	33,2	0,81
Metilox	Ethanol 50%	15	31,2	0,76
Metilox	Ethanol 50%	16	29,9	0,73
Metilox	Ethanol 50%	17	29,4	0,72
Metilox	Ethanol 50%	18	24,2	0,59
Metilox	Ethanol 50%	19	29,4	0,72
Metilox	Ethanol 50%	20	27,5	0,67

Table 4: Migration results of Metilox into Ethanol 50%

## 4. Migration modeling

### 4.1.1 Repeated migration scenario

Three test plates made of Polypropylene (PP) are immersed for a certain time,  $t$ , in a migration cell containing an ethanol water mixture (EtOH). This will be named referred to as “wet cycle”. The PP-plates are kept separated by distance holders so that the exit of substances from the plates into EtOH is not hindered. The PP-plates contain either an additive or a decomposition product, which may migrate into the EtOH (Figure 1).

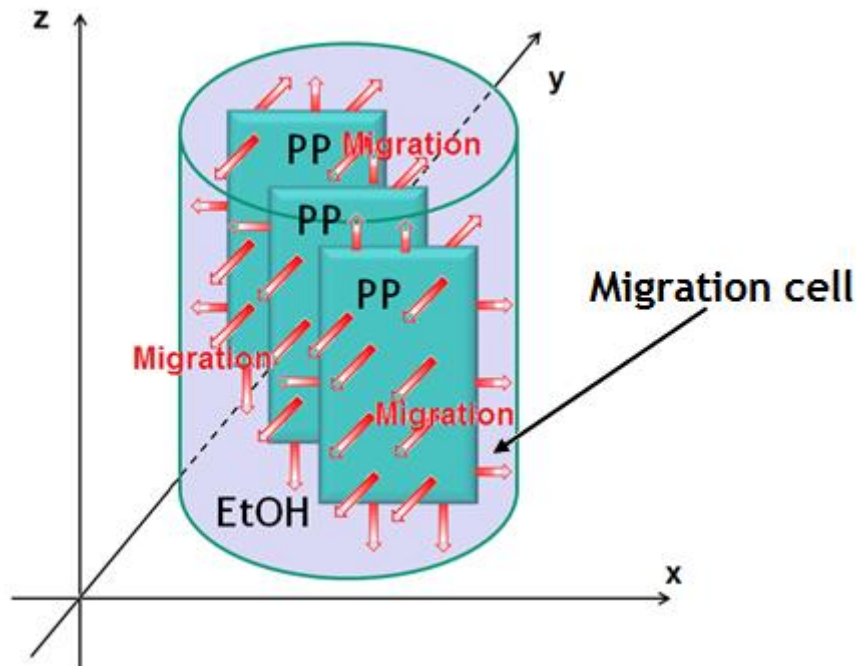


Figure 1. Schematic presentation of migration during a “wet cycle”.

At the end of the “wet cycle” the PP-plates are removed from the vial, wiped dry, wrapped in aluminum foil and then left overnight in a constant temperature chamber. This will be referred to as “dry cycle”. During this cycle it is assumed that no migration of additive or decomposition product from the PP-plates into the surrounding atmosphere takes place (Figure 2).

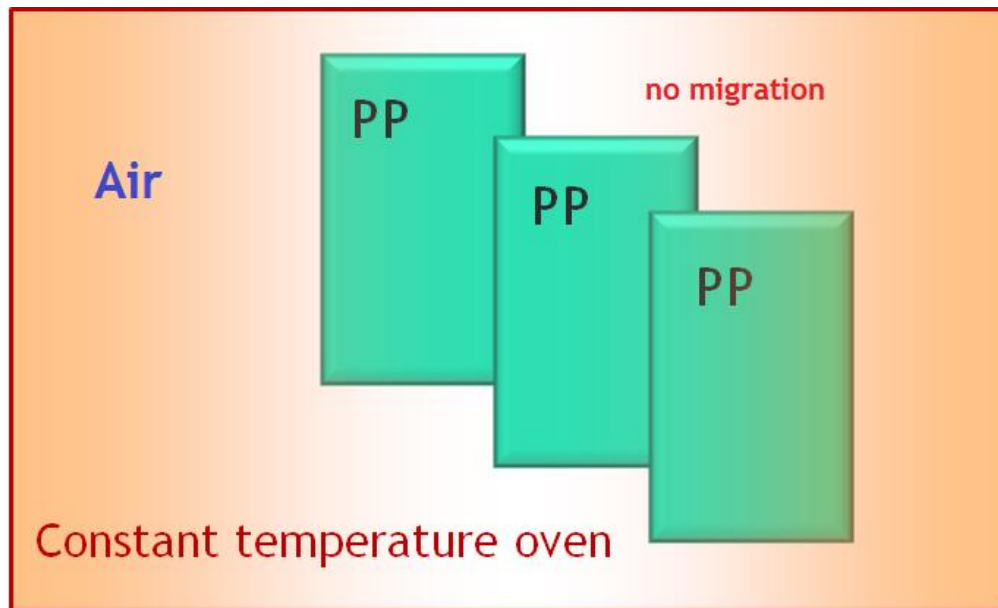


Figure 2. Schematic presentation of set up for a “dry cycle”.

However, due to the additive or decomposition product concentration gradients present under the contact surfaces of the PP-plates, a certain redistribution of these substances takes place in the plates during the “dry cycle”. This redistribution influences the outcome of the migration process during the subsequent “wet cycle”.

The task of the following calculations is to estimate theoretically the repeated use (RU) migration of the additive and respectively decomposition compound into EtOH during 20 successive identical “wet cycles” separated by 19 identical “dry cycles”.

#### 4.1.2 Calculation/estimation of repeated use migration

The calculation/estimation of the migration from a polymeric material into a liquid as shown in Figure 1 can be done by solving Fick's 2<sup>nd</sup> mass transport equation (1) by using the appropriate initial and boundary conditions:

$$\frac{\partial c_k}{\partial t} = D_k \left( \frac{\partial^2 c_k}{\partial x^2} + \frac{\partial^2 c_k}{\partial y^2} + \frac{\partial^2 c_k}{\partial z^2} \right) \quad (1)$$

where:  $C_k$  is a local concentration and  $D_k$  a constant diffusion coefficient in medium  $k$ ,  $x$ ,  $y$  and  $z$  are the Cartesian three dimensional (3D) spatial coordinates,  $t$  the migration time and the index  $k = P$  for the polymer and  $k = F$  for the liquid (food simulant).



In practice, because the migration from a PP-plate into EtOH takes place preferentially in a normal direction ( $90^\circ$ ) to the surface of the plates, one can simplify the mathematical task of solving equation 1 for a real 3D-system by reducing this one to an equivalent one-dimensional (1D) system (Figure 3) with the appropriate mass transport Equation (2):

$$\frac{\partial c_k}{\partial t} = D_k \frac{\partial^2 c_k}{\partial x^2} \quad (2)$$

Thus the 3D picture from Figure 1 can be converted in a 1D picture as shown in Figure 3.

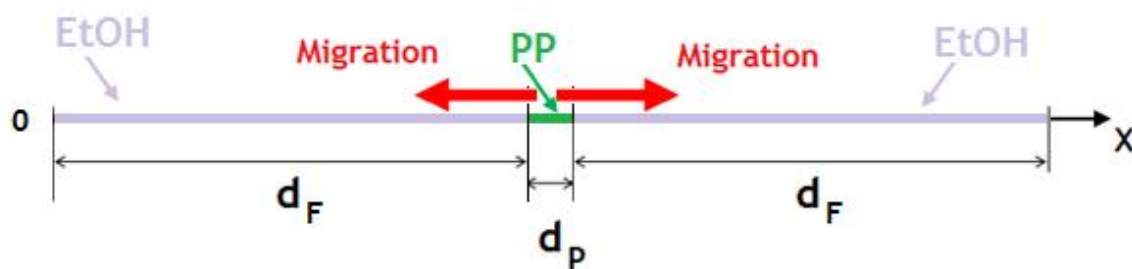


Figure 3. One dimensional (1D) migration during immersion of PP-plates in EtOH (Cartesian coordinates).

In Figure 3 the thickness of the PP-plates,  $d_p$ , is their actual real thickness while the “thickness” of the EtOH media,  $d_F$ , is calculated as the ratio between the total volume  $V$  of EtOH in the vial and the total contact area  $A$  (including the margins) of the PP-plates,  $d_F = V/A$ .

The software **MIGRATEST<sup>®</sup>Exp-RU-2015** developed by FABES-Forschungs GmbH (Ref. 1) can be used to solve equation (2) for the above mentioned migration scenario. This software solves equation (2) with finite differences (FD) numerical methods. It is far beyond the scope of this report to give any details on the actual FD-procedures used in this software but such information can be found for example in Refs. 2 and 3. With **MIGRATEST<sup>®</sup>Exp-RU-2015** it is possible to run calculations for up to 9999 successive RU migration cycles from a mono or multilayer polymeric material (donor) into a contact medium (solid, liquid or gaseous) (acceptor). This software allows both calculation of migration during “wet cycles” from the donor into the acceptor/s as well as calculation of the redistribution of the migrant inside the donor during the “dry cycles”. To run such calculations a series of specific input parameters, initial and boundary conditions for the “wet” and respectively “dry” cycles of the RU scenario must be defined (see below).

### 4.1.3 Input parameters for the calculations

Polymer type,	Polypropylene plates, (PP)
Estimated Density of polymer @23 °C and 60 °C <sup>(+)</sup> ,	$\rho_P = 0.900 \text{ g/cm}^3$
Mean dimension of PP-plates,	$L = 6.4 \text{ cm} \times W = 3.0 \text{ cm}$
Mean thickness of PP-plates,	$d_P = 0.96 \text{ mm} = 960 \text{ }\mu\text{m}$
Number of PP-plates in migration cell,	$N_o = 3$
Total mean contact area of PP-plates in migration cell,	$A = 3 \cdot 2 \cdot [(L \cdot W) + (L + W) \cdot d_P] = 120.61 \text{ cm}^2$
Contact media,	ethanol 95% (w/w), (EtOH95) ethanol 50% (w/w), (EtOH50)
Density of contact media @ 60 °C	EtOH95, $\rho_F \sim 0.750 \text{ g/cm}^3$ EtOH50, $\rho_F \sim 0.825 \text{ g/cm}^3$
Volume of contact media in vial,	$V = 60 \text{ cm}^3$
1D "thickness" of contact media,	$d_F = V/A \sim 4975 \text{ }\mu\text{m}$
Migrants,	(1), Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, (Irganox <sup>®</sup> 1076), CAS 2082-79-3  (2), Methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate , (Metilox), CAS 6386-38-5
Molecular mass of migrants,	$M_r(1) = 530.85 \text{ (g/mol)}$ $M_r(2) = 292.41 \text{ (g/mol)}$
Octanol-water partition coefficient @ 20 °C,	Irganox <sup>®</sup> 1076, $\text{LogK}_{OW} \sim 13.1^{(\text{est.})}$ Metilox, $\text{LogK}_{OW} \sim 5.0^{(\text{est.})}$
Solubility of migrants in pure Ethanol @ 60 °C,	Irganox <sup>®</sup> 1076, well soluble Metilox, soluble
Solubility of migrants in water @ 60 °C,	Irganox <sup>®</sup> 1076, practically not soluble Metilox, poorly soluble
Initial concentrations of migrant (1) in PP-plates,	$C_{P0}(1) = 1000 \text{ mg/kg}$
Initial concentrations of migrant (2) in PP-plates,	$C_{P0}(2) = 500 \text{ mg/kg}$
Initial concentrations of migrant (1) in the EtOH's,	$C_{F0}(1) = 0 \text{ mg/kg}$
Initial concentrations of migrant (2) in the EtOH's,	$C_{F0}(2) = 0 \text{ mg/kg}$
Diffusion coefficients of migrant (1) in PP-plates,	 @ 23 °C, $D_p^*(1) = 7.78 \cdot 10^{-12} \text{ (cm}^2/\text{s)}$ , (see Ref. 4), @ 60 °C, $D_p^*(1) = 7.09 \cdot 10^{-10} \text{ (cm}^2/\text{s)}$ , (see Ref. 4), @ 23 °C, $D_p^*(1) = 1.04 \cdot 10^{-13} \text{ (cm}^2/\text{s)}$ , (see Ref. 5), @ 60 °C, $D_p^*(1) = 4.83 \cdot 10^{-12} \text{ (cm}^2/\text{s)}$ , (see Ref. 5),
Diffusion coefficients of migrant (2) in PP-plates,	 @ 23 °C, $D_p^*(2) = 6.96 \cdot 10^{-11} \text{ (cm}^2/\text{s)}$ , (see Ref. 4), @ 60 °C, $D_p^*(2) = 6.43 \cdot 10^{-9} \text{ (cm}^2/\text{s)}$ , (see Ref. 4), @ 23 °C, $D_p^*(2) = 4.47 \cdot 10^{-12} \text{ (cm}^2/\text{s)}$ , (see Ref. 5), @ 60 °C, $D_p^*(2) = 1.71 \cdot 10^{-10} \text{ (cm}^2/\text{s)}$ , (see Ref. 5),

Partition coefficients of Migrant (1) at the PP-plates - EtOH95 boundary,

@ 60°C,  $K_{P/F}^*(1) = 1.0 \text{ (g/cm}^3\text{)/(g/cm}^3\text{)}$ , (see Ref. 4),

@ 60°C,  $K_{P/F}(1) \sim 0.1 \text{ (g/cm}^3\text{)/(g/cm}^3\text{)}$ , (see Ref. 5),

Partition coefficients of Migrant (2) at the PP-plates - EtOH95 boundary,

@ 60°C,  $K_{P/F}^*(2) = 1.0 \text{ (g/cm}^3\text{)/(g/cm}^3\text{)}$ , (see Ref. 4),

@ 60°C,  $K_{P/F}(2) \sim 1.0 \text{ (g/cm}^3\text{)/(g/cm}^3\text{)}$ , (see Ref. 5),

Partition coefficients of Migrant (1) at the PP-plates - EtOH50 boundary,

@ 60°C,  $K_{P/F}^*(1) = 1000 \text{ (g/cm}^3\text{)/(g/cm}^3\text{)}$ , (see Ref. 4),

@ 60°C,  $K_{P/F}(1) \sim 25 \text{ (g/cm}^3\text{)/(g/cm}^3\text{)}$ , (see Ref. 5),

Partition coefficients of Migrant (2) at the PP-plates - EtOH50 boundary,

@ 60°C,  $K_{P/F}^*(2) = 1.0 \text{ (g/cm}^3\text{)/(g/cm}^3\text{)}$ , (see Ref. 4),

@ 60°C,  $K_{P/F}(2) \sim 4.0 \text{ (g/cm}^3\text{)/(g/cm}^3\text{)}$ , (see Ref. 5),

Migration time for “wet cycle”,

$t = 8 \text{ hours}$

Constant contact temperature during “wet cycle”,

$T = 60^\circ\text{C} = 333.15 \text{ K}$

Migration time for “dry cycle”,

$t = 16 \text{ hours}$

Constant contact temperature during “dry cycle”,

$T = 23^\circ\text{C} = 296.15 \text{ K}$

**Notes:**

*The input data marked with <sup>(+)</sup> are assumptions made by FABES in absence of corresponding data from the commissioner of the report.*

*The above „upper bound“  $D_p^*$  coefficients have been estimated by FABES according to the procedure and parameters given in the “Practical Guidance Document to EU-regulation 10/2011” (Ref. 4.) and (Ref. 5) respectively.*

*The above „lower bound“  $K_{P/F}^*$  partition coefficients have been estimated by FABES according to the practical guidance given in Ref. 4 and respectively “realistic” estimations made using the model described in (Ref.5).*

*The use of the coefficients estimated according to Ref. 4 in the calculations leads to a certain overestimation of the migration processes.*

#### **4.1.4 Initial and boundary conditions for the calculations of the “wet cycles”**

- 1) The migrants are initially homogeneously distributed in the whole matrix of the PP-plates.
- 2) During the migration process there is no degradation/decomposition of the migrant. The total migrant mass in the PP-EtOH System is constant during the whole migration process.
- 3) The diffusion of EtOH into the PP-plates has no influence on the local migration properties (swelling, softening or local diffusion enhancement) of these plates.
- 4) The migration calculation for each “wet cycle” is started from the migrant concentration profile in the PP-plate at the end of the preceding “dry cycle”.

#### **4.1.5 Initial and boundary conditions for the calculations of the “dry cycles”**

- 1) The migration calculation for each “dry cycle” is started from the migrant concentration profile in the PP-plate at the end of the preceding “wet cycle”.
- 2) During the process of redistribution of the migrant inside the PP-plate there is no degradation/decomposition of the migrant.
- 3) During the overnight process of redistribution of the migrant inside the PP-plate there is no evaporation of the migrant to the surrounding atmosphere.
- 4) The total migrant mass in the PP-plates is constant during the overnight storage/redistribution process.

#### 4.1.6 Calculated/Estimated Results

In Figure 4 the migrant (1) concentration profile across the PP-plate is shown at the end of the 1<sup>st</sup> “wet cycle” as well as at the end of the successive 1<sup>st</sup> “dry cycle”.

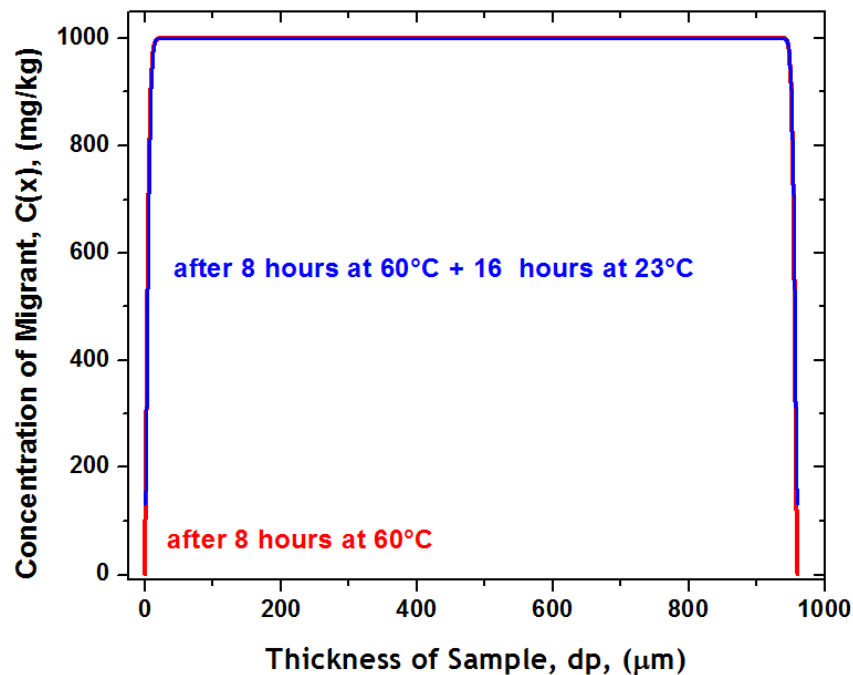


Figure 4. Irganox®1076 concentration profile across the PP-plate at the end of the 1<sup>st</sup> “wet” (contact with EtOH95) and respectively 1<sup>st</sup> “dry” cycles.

In Figure 5 a blow up of the first 25 μm of the PP-plate is shown in order to better illustrate the effect of the overnight redistribution of the Irganox®1076 migrant in a small region just underneath the surface of the PP-plates. Here one can see that during the 16 hours of internal diffusion of the migrant in the PP-plate the concentration of Irganox®1076 at the surface of the PP-plate increases from nearly zero mg/kg to about 170 mg/kg. This is the result of the “flow” of substance from the inner regions of the PP-plate towards its migrant depleted surface (driving force is the migrant concentration gradient present in the PP-plate at the end of the “wet cycle”). The effect of this process during the “dry cycle” is an increased migration rate at the beginning of the subsequent 2<sup>nd</sup> “wet cycle” and a somewhat higher overall migration amount during this cycle. This succession of processes is repeated in each of the 20 “wet” and 19 “dry” cycles of the investigated migration scenario and should be considered in the theoretical estimation of the RU migration in EtOH.

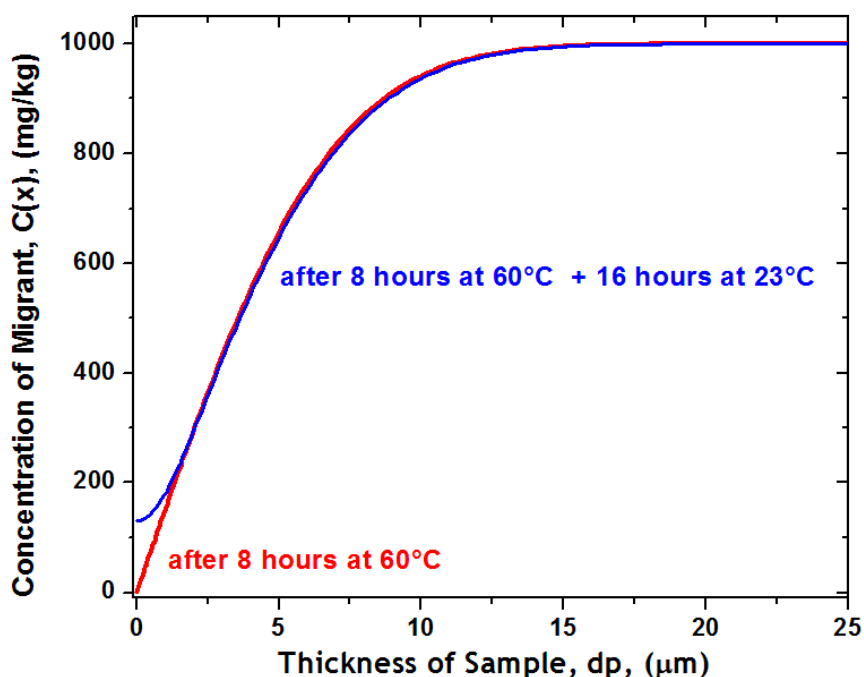


Figure 5. Zoom-in in the Irganox<sup>®</sup>1076 concentration profile just underneath the surface of a PP-plate at the end of the 1<sup>st</sup> “wet” (contact with EtOH95) and respectively 1<sup>st</sup> “dry” cycles.

In Figure 6 the time dependent increase of the contamination of EtOH50 with migrant (1) during the 20 RU “wet” migration cycles is shown. The calculations were performed with the  $D_p^*(1)$  and respectively  $K_{p/F}^*(1)$  coefficients estimated according to the specifications of the Practical Guidance Document to the EU-Regulation 10/2011 (see Ref. 4).

In Figure 7 the time dependent decrease of the contamination of EtOH50 with migrant (1) at the end of the 20 RU “wet” migration cycles is shown. The calculations were again performed with the  $D_p^*(1)$  and respectively  $K_{p/F}^*(1)$  coefficients estimated according to the specifications of the Practical Guidance Document to the EU-Regulation 10/2011 (see Ref. 4) as well as with  $D_p^*(1)$  and respectively  $K_{p/F}^*(1)$  coefficients estimated using the procedures developed in Ref. 5 for polypropylene samples in contact with water. In Figures 8 to 10 similar graphs are shown for the contamination of EtOH50 with migrant (2) and respectively EtOH95 with migrants (1) and (2).

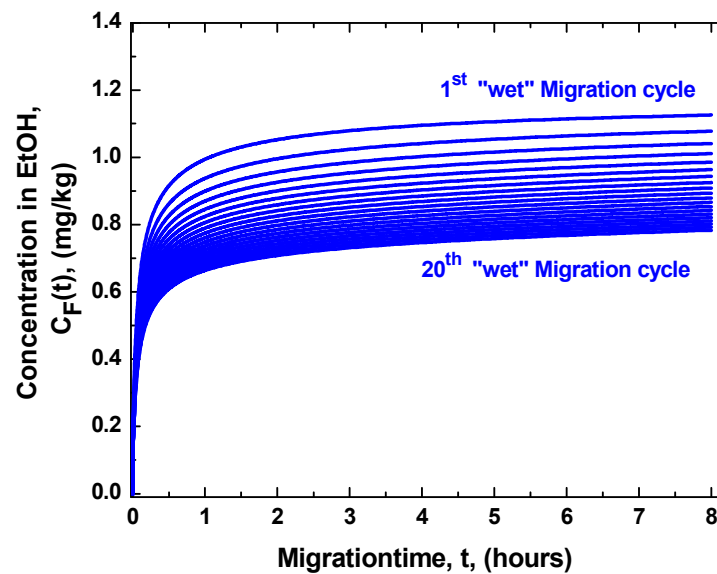


Figure 6. Time dependent migration of Irganox® 1076 in EtOH50% during the 20 RU “wet cycles” at 60 °C and 8 hours.

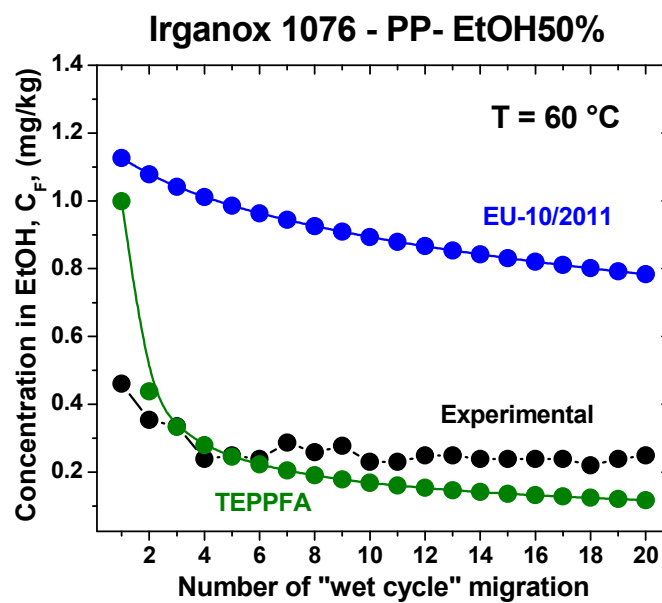


Figure 7. Time dependent decrease of EtOH50% contamination with Irganox®1076 at the end of the 20 RU “wet” migration cycles.

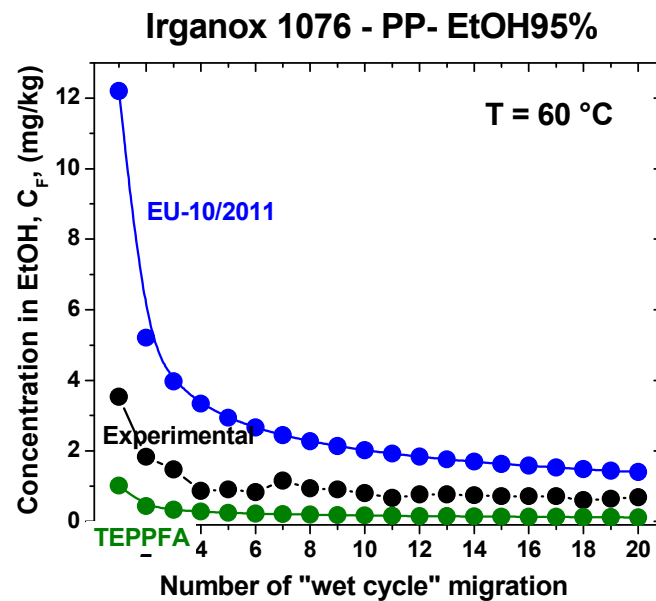


Figure 8. Time dependent decrease of EtOH95% contamination with Irganox®1076 at the end of the 20 RU "wet" migration cycles.

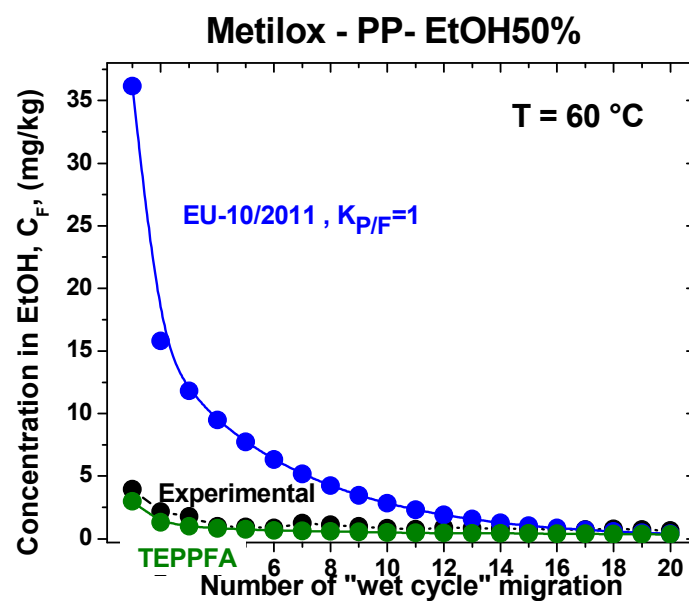


Figure 9. Time dependent decrease of EtOH50% contamination with Metilox at the end of the 20 RU "wet" migration cycles. Assumption Metilox does solve well at 60°C in EtOH50% ( $K^*_{P/F}(2) = 1.0$  see Ref. 4).



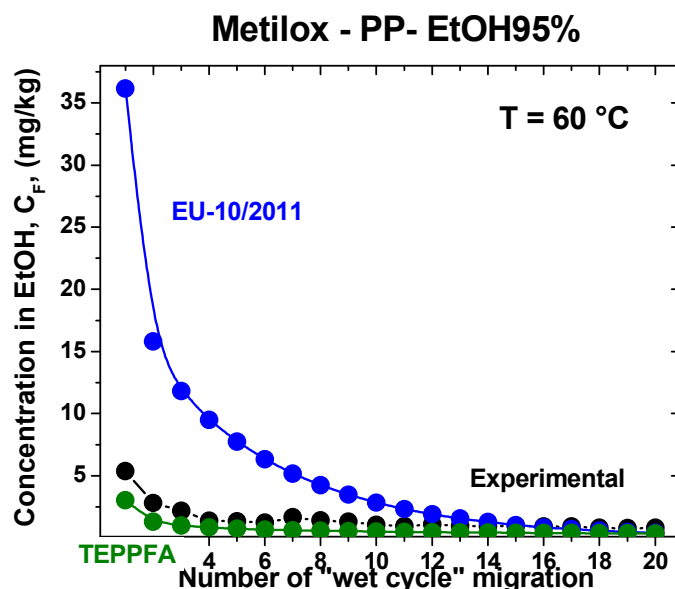


Figure 10. Time dependent decrease of EtOH95% contamination with Metilox at the end of the 20 RU "wet" migration cycles.

From Figures 7 to 10 (as well as from Tables 1 to 4 given in No. 3 "Results") one can see that the experimental results (black dots),  $C_F(t)$ , obtained at the end of the 20 RU use "wet" cycles show in general a decreasing trend similar to that of the corresponding theoretically calculated migration levels (blue and respectively green dots). This is an indication that in reality the repeated migration of Irganox<sup>®</sup>1076 and Metilox from the PP-plates in the EtOH-mixtures follows the pattern described by the idealized theoretical treatment of these migration scenarios. The scatter of the experimental results from the smooth shape of the theoretical curves could be associated to different real phenomena like: i) a cumulated scatter/variability of the experimental procedures used in order to obtain the  $C_F(t)$ -values, ii) additional effects during the migration processes - for example boundary resistances - which have not been considered in the theoretical model and iii) time dependent effects on the diffusion of the migrants in and from the matrix of this polymer due to the uptake of EtOH by the PP-plates.

The theoretical estimations of the investigated RU migration processes show clear overestimations (blue dots and curves) of what happens in reality (black dots) when the  $D^*_p$  and respectively  $K^*_{p/F}$  coefficients use in the calculations are estimated according to the guidance given in Ref.4. This should not be a surprise because the declared intent of migration modeling in the framework of the EU-Regulation 10/2011 in Ref. 4 is to generate results, which overestimate the real migration processes. However as the corresponding graphs in Figures 7 to 10 show, the resulting overestimations are often quite consistent.

In Figure 11 the time dependent decrease of the contamination of EtOH50 with migrant (2) at the end of the 20 RU "wet" migration was calculated assuming that according to Ref. 4 a  $K^*_{p/F}(2) = 1000$  instead of  $K^*_{p/F}(2) = 1.0$  should be considered. This would correspond to an assumption of low solubility at 60 °C of Metilox in EtOH50 (no data was found in the literature

to confirm or deny this assumption). However the results calculated with this  $K_{P/F}^*(2)$  (blue dots) clearly show that this high partitioning effect limits the migration in all 20 RU cycles below 1.25 mg/kg. However the experimental results in the first "wet" cycles (black dots) lie above this level. This would be possible only if at 60 °C in reality the partition coefficient of Metilox between PP and EtOH50 would be lower than  $K_{P/F}^*(2) = 1000$ . The more realistic value  $K_{P/F}^*(2) = 4.0$  estimated according to Ref. 5 leads the correct trend of  $C_F(t)$ 's of the calculated migrations (green dots and curves in Figures 9 and 11).

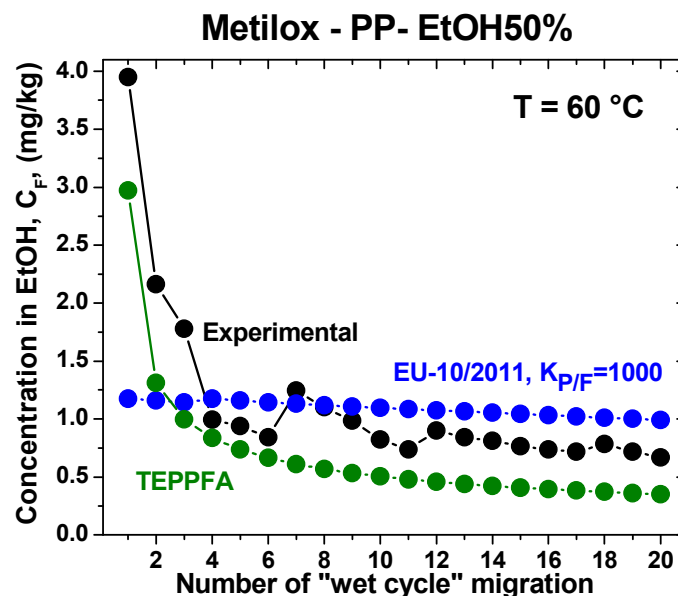


Figure 11. Time dependent decrease of EtOH95% contamination with Metilox at the end of the 20 RU "wet" migration cycles. Assumption: Metilox does not solve well at 60 °C in EtOH50% ( $K_{P/F}^*(2) = 1000$  see Ref. 4).

In Ref. 5 commissioned by TEPPFA FABES developed alternative methods to estimate more realistic  $D_p^*$  and respectively  $K_{P/F}^*$  coefficients for migration estimations from several polyolefine polymer into drinking water. For this experimental data of PP-samples in contact with water were used. The result are less conservative "upper bound"  $D_p^*$ 's and "lower bound"  $K_{P/F}^*$ 's (see above No. 4.1.3 "Input parameters for the calculations"). Using these parameters in the estimation of the 20 RU "wet" migration cycles the graphs with green dots and curves were obtained in Figures 7 to 10. In general these results lie below the experimental ones, which may be mainly attributed to the fact that the estimated  $D_p^*$ 's are in fact lower than the real ones when the PP-plates are in contact with EtOH mixtures instead of pure water. In fact it is known that PP (as a very non polar polymer) also adsorbs small amounts of water (a highly polar liquid), but this has practically no influence on the diffusional properties in the matrix of the polymer. Therefore, the results obtained with EtOH as contact media show that a diffusion of EtOH into the PP-plates, which surely happens during the "wet" cycles, determines an enhancement of the diffusional processes in the matrix of this polymer (a slight swelling of the PP-matrix due to EtOH might be responsible

for this effect). Indeed replacing in the theoretical calculations the  $D_p^*$ 's coefficients estimated according to Ref. 5 with somewhat higher "more realistic"  $D_p^*$ 's (see below) leads to a much better fit between the experimental results and the estimate ones (magenta dots and curves in Figures 12 to 15).

Diffusion coefficients of migrant (1) in PP-plates,

@ 60 °C and 100% water,  $D_p^*(1) = 4.83 \cdot 10^{-12}$  (cm<sup>2</sup>/s), (see Ref. 5),

@ 60 °C and EtOH50%,  $D_p^*(1) = 9.50 \cdot 10^{-12}$  (cm<sup>2</sup>/s), (Data fit)

@ 60 °C and EtOH95%,  $D_p^*(1) = 8.00 \cdot 10^{-11}$  (cm<sup>2</sup>/s), (Data fit)

Diffusion coefficients of migrant (2) in PP-plates,

@ 60 °C and 100% water,  $D_p^*(2) = 1.71 \cdot 10^{-10}$  (cm<sup>2</sup>/s), (see Ref. 5),

@ 60 °C and EtOH50%,  $D_p^*(2) = 4.75 \cdot 10^{-10}$  (cm<sup>2</sup>/s), (Data fit)

@ 60 °C and EtOH95%,  $D_p^*(2) = 6.50 \cdot 10^{-10}$  (cm<sup>2</sup>/s), (Data fit)

The assumption that the diffusion of ethanol into the matrix of the PP-plates enhances the diffusional movements of the migrants is sustained by the fact that for 95% Ethanol in water the  $D_p^*(1)$  and  $D_p^*(2)$  increase relatively to  $D_p^*(1)$  and  $D_p^*(2)$  is larger than for 50% Ethanol in water (see above).

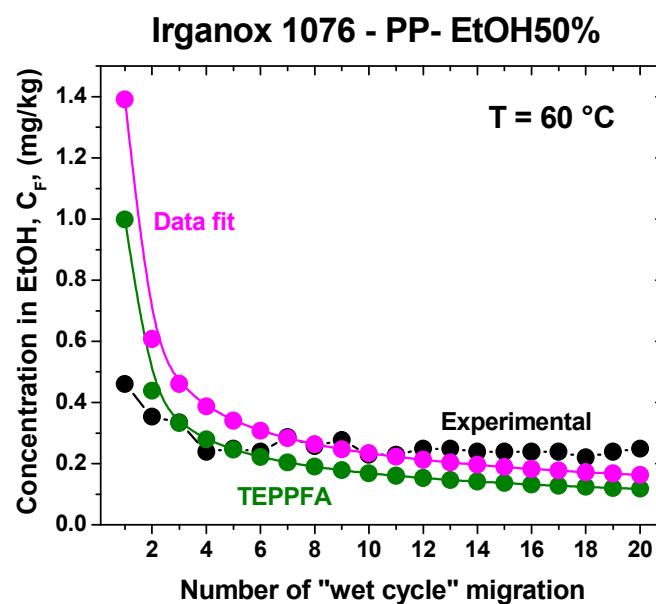


Figure 12. Time dependent decrease of EtOH50% contamination with Irganox®1076 at the end of the 20 RU "wet" migration cycles.

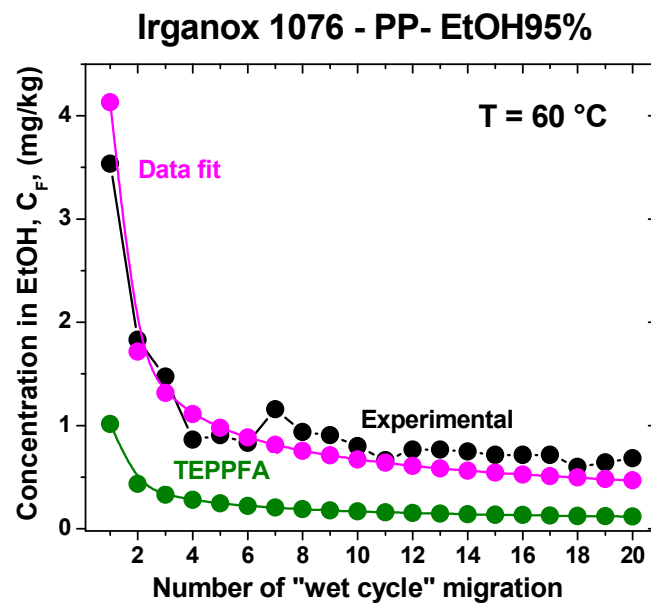


Figure 13. Time dependent decrease of EtOH95% contamination with Irganox®1076 at the end of the 20 RU "wet" migration cycles.

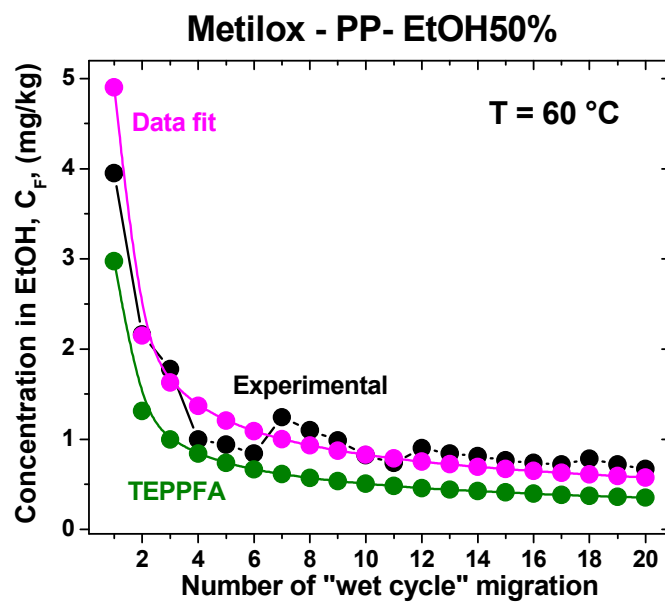


Figure 14. Time dependent decrease of EtOH50% contamination with Metilox at the end of the 20 RU "wet" migration cycles.

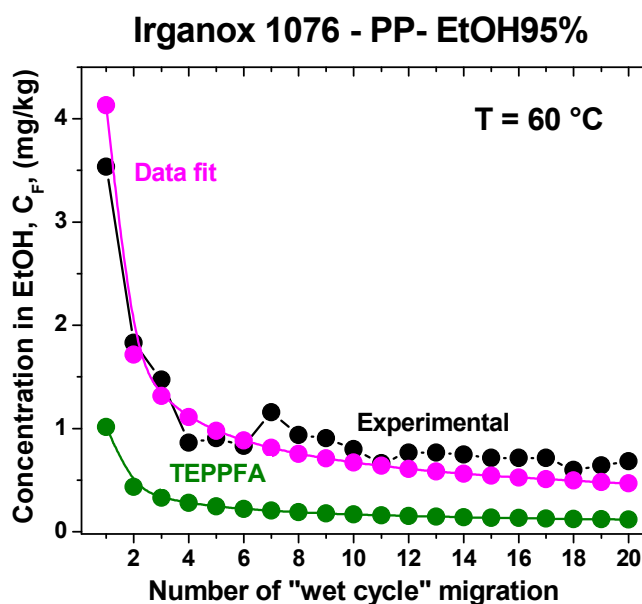


Figure 15. Time dependent decrease of EtOH95% contamination with Metilox at the end of the 20 RU “wet” migration cycles.

## 5. Conclusions

The mathematical modeling with software **MIGRATEST®Exp-RU-2015** developed by FABES GmbH correlates very well with the experimental results, especially when the diffusion coefficients in the polymer are adjusted to a “realistic” “upper bound” level. The developed mathematical modeling is suitable to predict the actual migration when the necessary parameters are known. However, using for the estimation of some of these parameters the guidelines given in connection with the EU-Regulation 10/2011, leads in general to consistent overestimations of the real RU migration processes. On the other hand using for the estimation of the same parameters knowledge derived from the investigation of PP in contact with only water leads to a certain underestimation of the real RU migration processes. Thus the actual outcome of a RU migration process in aqueous food simulants seems to be also dependent on the nature of these simulants. In this respect, in order to improve the understanding of these phenomena and so implicitly the mathematical estimation of RU migrations from plastic materials in food simulants, it might be helpful to extend the present investigations to further food simulants as listed in Annex III Table 1 Regulation (EU) 10/2011 (Ref. 6). Such an additional investigation effort could provide a solid experimental and theoretical evidence and discussion/conclusion basis for a publication of all obtained results in an international journal.

## 6. References

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The results of the investigations and their assessment are limited to the submitted test samples. Retained samples are stored for six months.

Munich, 15.12.2016

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Dr. Peter Mercea  
(author of report)

Christoph Losher  
(project leader)

Matthias Herburger  
(technician)