FABES Forschungs-GmbH
für Analytik und Bewertung von Stoffübergängen

Investigation Report

Migration/permeation investigation on barrier properties of Aluminium foils against organic molecules

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assignment date : 03.07.2003

commission number : **516/03**

test samples :
Sample 1: PET(12µm)/Adh(5g/m²)/Al(7µm)/Adh(5g/m²)/cPP(60µm)
Sample 2: PET(12µm)/Adh(5g/m²)/cPP(60µm)
Sample 3: (not relevant)
Sample 4: PET(12µm)/Adh(5g/m²)/Al(6µm)/Adh(5g/m²)/cPP(60µm)

1 Introduction

Aim of the project is to demonstrate by scientific evidence through migration/ permeation investigations on aluminium laminates that an Aluminium foil with a certain thickness is an absolute barrier for organic molecules.

2 Experimental investigations

The migration/permeation experiments were performed in migration cells (Figure 1) in which a surrogate of volatile to semi-volatile substances is situated in the beaker and a food simulant is situated in the lid of the cell. The laminate is mounted between lid and beaker hold together by a metal clamp tightened against both with two FEP coated sealing rings.

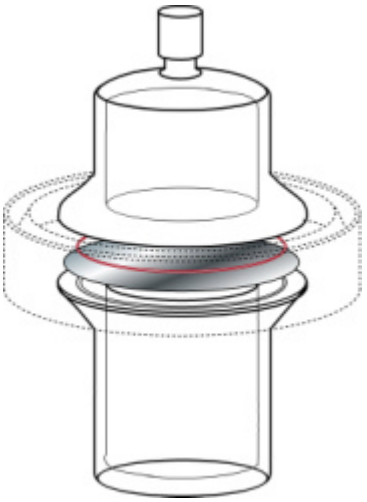

Figure 1 Migration/permeation cell.

The brake through of surrogate species is monitored time dependent on the upper side (PET) of the laminate, using in the lid iso-octane or Tenax as food simulant. A surrogate of three substances (1 g of each species) was used, i.e. Dodecane, Benzophenone and Di(ethylhexyl)adipate, chemical species which differ in their molecular weight and polarity. Three different laminates were investigated: two laminates with an aluminium foil, having 6 µm and 7 µm thickness respectively, as one layer (PET/Adh/Al/Adh/cPP) and a third laminate without aluminium foil (PET/Adh/cPP). The migration/permeation experiments were performed at 40°C and 70°C with iso-octane. At each time point a sample of 200 µl iso-octane was taken, the internal standard added and analysed by GC/FID. The permeation experiment at 100°C was performed with Tenax. After the storage time was expired Tenax was extracted twice with ether, brought to the mark in a volumetric flask, internal standard added and analysed by GC/FID

The concentration of the three species is given by their vapour pressure and is summarized for the three test temperatures in Table 1.

Table 1 Concentration of surrogate species in the gas phase at 40°C, 70°C and 100°C.

species/ temperature	40°C	70°C	100°C
	[µg/cm³]	[µg/cm³]	[µg/cm³]
Dodecane (C12)	4,9	29	120
Benzophenone	0,002	0,3	2,5
Di-(ethylhexyl)-adipate	$8,0\ e^{-7}$	$2,0\ e^{-4}$	$7,0\ e^{-3}$

3 Results

3.1 Permeation at 40°C

At 40°C the permeation of all species through all laminates was for all time points (up to 38 days) below the determination limit of 0,2 mg/dm².

3.2 Permeation at 70°C

At 70°C the permeation of all species through the laminates with an Al-layer (sample no. 1 and 4) was for all time points (up to 38 days) below the determination limit of 0,2 mg/dm².The permeation of the surrogate species through the laminates at 70°C is summarised in Table 2.

Table 2 Permeation of surrogate species through the test laminates at 70°C.

laminate no.	time	C12	Benzoph.	DEHA
	[days]	[mg/dm²]	[mg/dm²]	[mg/dm²]
1. PET/Al(7µm)/cPP	< 38	< 0,2	< 0,2	< 0,2
2. PET/cPP	0	0,0	0,0	0,0
	8	2,0	16,0	< 0,2
	14	2,2	17,4	< 0,2
	19	3,1	23,2	< 0,2
	26	4,5	20,4	< 0,2
	60	141,4	553,6	1,6
4. PET/Al(6µm)/cPP	< 38	< 0,2	< 0,2	< 0,2

3.3 Permeation at 100°C

The permeation of the surrogate species at 100°C is summarised in Table 3. Due to the high test temperature and different expansion coefficients of the two plastic layers the samples are subjected to shear stress through which the Al-layer in the laminates is damaged locally after 6 days. Because of this observation only the permeation data measured until 21 days with sample 2. (PET/cPP) are reported.

Table 3 Permeation of surrogate species through the test laminate PET/cPP at 100°C.

laminate no.	time	C12	Benzoph.	DEHA
	[days]	[mg/dm²]	[mg/dm²]	[mg/dm²]
1. PET/Al(7µm)/cPP	< 6	< 0,2	< 0,2	< 0,2
2. PET/cPP	0	0,0	0,0	0,0
	6	7,2	5,1	< 0,2
	13	23,2	74,2	0,43
	21	32,9	75,6	0,95
4. PET/Al(6µm)/cPP	< 6	< 0,2	< 0,2	< 0,2

4 Evaluation

4.1 Theoretical considerations

The time dependent permeation data obtained at 100°C were evaluated as follows. The amount m_t [µg] of a diffusing substance, which passes through a laminate of thickness d_P [cm] in time t [s] per surface area A [dm²] can be calculated with the equation /1/ (Crank):

$$\frac{m_t}{A} = 100 \cdot d_p \cdot c_{P,1} \cdot \left(\frac{D_P \cdot t}{d_P^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(\frac{-D_P \cdot n^2 \cdot \pi^2 \cdot t}{d_P^2} \right) \right) \qquad /1/$$

For long times this series converges rapidly to equation /2/:

$$\frac{m_t}{A} = 100 \cdot d_p \cdot c_{P,1} \cdot \left(\frac{D_P \cdot t}{d_P^2} - \frac{1}{6} \right) \qquad /2/$$

were $c_{P,1}$ [µg/cm³] represents the constant concentration of the diffusing substance in the laminate at position x = 0. $c_{P,2}$ = 0 [µg/cm³] represents the concentration at position x = d_P and D_P [cm²/s] is the diffusion coefficient. After rearrangement the lag time θ [s] can be calculated with equation /3/:

$$\theta = \frac{1}{6} \cdot \frac{d_P^2}{D_P} \qquad /3/$$

On the other hand with the above relationship the diffusion coefficient can be calculated from the lag time determined experimentally with a permeation experiment. The accurate determination of the lag time is only possible if the curve shows a linear increase of the concentration with time and is not the time point were a given migration limit (e.g. 10 ppb) is exceeded.

This procedure has been applied for the permeation experiments at 100°C by linear extrapolation of the experimental data points as shown in Figure 2 and Figure 3.

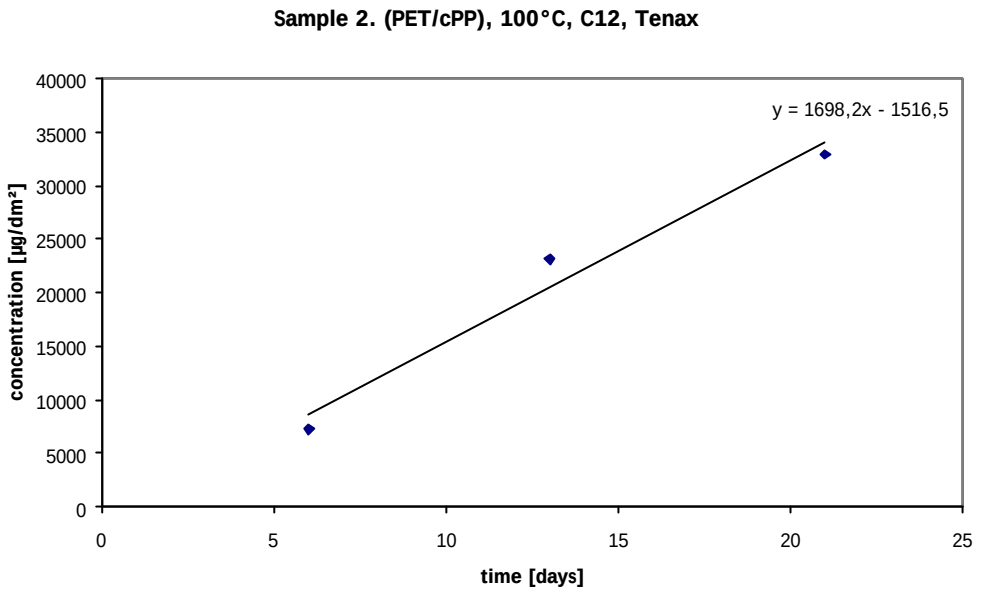

Figure 2 Permeation data for Dodecane (C12) through sample 2. (PET/cPP) at 100°C.

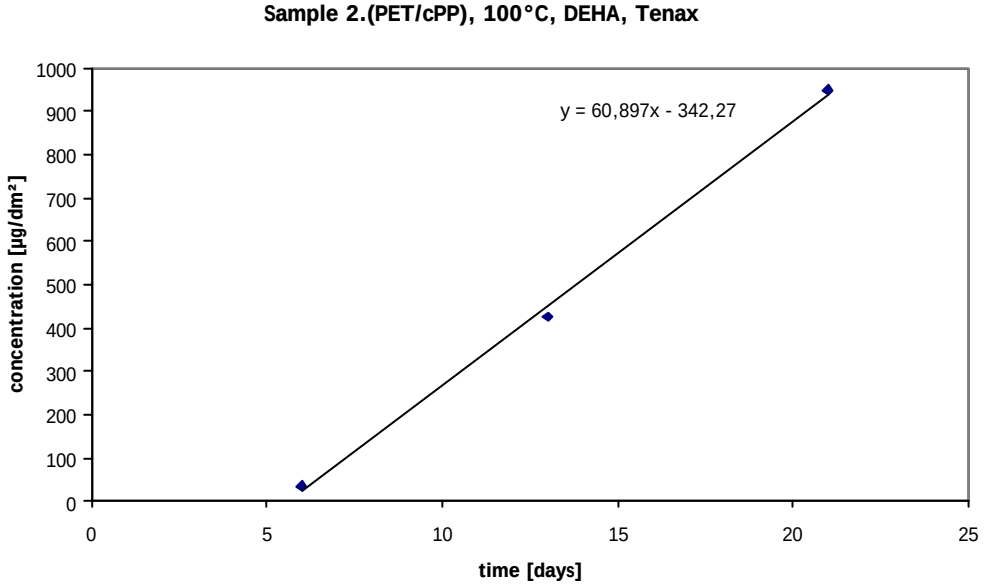

Figure 3 Permeation data for Di-(ethylhexyl)-adipate (DEHA) through sample 2. (PET/cPP) at 100°C.

The intercept of the regression line with the time axis gives the lag time which is θ = 16 hours for C12 and θ = 6 days for DEHA. From these lag times the diffusion coefficients in PET at 100°C were calculated as follows: D_P = 4,2e-12 for C12 and D_P = 4,6e-13 for DEHA. From the diffusion coefficients finally the polymer specific constant A_P = 0,5-1577/T for PET was derived with equation /4/ (Piringer):

$$D_P = D_0 \exp\left(A_P - 0.1351 M_r^{2/3} + 0.003 M_r - \frac{10454}{T} \right) \qquad /4/$$

D_0 - 1 m²/s = 10^4 cm²/s
M_r - relative molar mass of migrant in dalton
T - temperature in K
A_P - polymer specific constant

4.2 Validation of 70°C and 40°C measurements

With the A_P-value for PET derived from the permeation experiments at 100°C the diffusion coefficients (eq. 4) and lag times (eg. 3) of the surrogate components in PET can be estimated for 40°C and 70°C as well (Table 4).

Table 4 Lag time of surrogate species for sample 2. (PET/cPP) laminate at 40°C, 70°C and 100°C.

species/ temperature	40°C	70°C	100°C
	[days]	[days]	[hours]
Dodecane (C12)	325	11	16
Benzophenone		13	18
Di-(ethylhexyl)-adipate		100	144

The polymer specific constant, A_P derived from the 100°C permeation experiment is in full agreement with the A_P-value derived from experimental migration data obtained with PET.

The estimated lag times for C12, Benzophenone and DEHA at 70°C (Table 4) are in satisfiable agreement with those determined experimentally (Table 2, approx. θ = 26 days for C12 and Benzophenone and θ > 60 days for DEHA). In practice the lag times at 70°C are even higher because the concentration of the surrogate components in the PET layer of the laminate is higher at 100°C compared to 70°C which results in an increased diffusion coefficient at 100°C.

From eq. 2 the concentration of C12 at the vapour/PET layer interface under steady state permeation conditions can be calculated to be $c_{P,C12}$ = 3,8 % (w/w) (53,7 mg/cm³).

From eq. 1 a thickness of 45 µm for a PET layer can be calculated based on C12 migration below m_t/A = 0,2 mg/dm² at 100°C after 6 days. Sample 4 behaves at least like a pure PET film with a thickness of 45 µm. When subtracting the 12 µm thick PET layer present in the laminate the barrier properties of the 6 µm Al-foil alone are at least better than those of a 33 µm PET film.

The knowledge of the surrogate concentration at the vapour/PET layer interface during the steady state permeation regime gives the possibility to calculate for a laminate with a certain diffusion behaviour(e.g. 6 µm Al-foil with barrier properties at least better than a 33 µm PET-film) at a given temperature the time point at which a defined migration limit (e.g. 10 ppb) is exceeded. The calculation with eq. 1 showes that at 100°C the migration limit of 10 ppb will not be exceeded before 30 hours.

A worst case scenario for the use of a packaging material will never reach these sever conditions and those it could be demonstrate unambiguously by scientific evidence that an Al-foil of at least 6 µm thickness must be considered an absolute barrier in terms of food contact applications.

5 Conclusions

The permeation of the surrogate through the laminate without Al-layer (sample 2. / PET/cPP) is determined by the PET layer. At 40°C no break through of surrogate components within a reasonable time frame can be observed as demonstrated experimentally and validated by estimations based on the diffusion behaviour of the surrogate in the PET-layer. The diffusion coefficients of the surrogate components were derived from the 100°C permeation measurement were a clear break through of the surrogate components could be observed experimentally. Additional information's on the diffusion behaviour of organic molecules in PET were available as well. Consequently the presence of an Al-layer in a laminate containing an PET-layer and its barrier properties can not be assessed experimentally at 40°C as long as the test period is shorter than approximately 1 year (break through time point estimated by modelling).

For sample 2. (PET/cPP) at 70°C the break through of surrogate components can be observed as demonstrated experimentally. Compared to the pure plastic laminate, the two samples containing an Al-layer (sample 1. and 4.) show no migration and no break through of surrogate components after 38 days.

Based on the theoretical evaluation of the experimental data, especially those obtained from permeation experiments performed at 100°C, it could be demonstrated for the laminates containing an Al-foil with a thickness of at least 6 µm that at 100°C the migration limit of 10 ppb will not be exceeded before 30 hours.

A worst case scenario for the use of a packaging material will never reach these sever conditions and those it could be demonstrate unambiguously by scientific evidence that an Al-foil of at least 6 µm thickness must be considered an absolute barrier in terms of food contact applications.

The results of the investigations and their assessment are limited to the submitted test samples.

Munich, 03.03.2004

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