Functional Barriers: properties and evaluation

A. Feigenbaum[1], P. Dole[1], S. Aucejo[2], D. Dainelli[3], C. de la Cruz Garcia[1], T. Hankemeier[2], Y. N'Gono[1], C.D. Papaspyrides[4], P. Paseiro[5], S. Pastorelli[5], S. Pavlidou[4], P.Y. Pennarun[1], P. Saillard[6], L. Vidal[7], O. Vitrac[1], Y. Voulzatis[4]

(1) INRA EMOA, 51687 Reims, France; (2) TNO-Nutrition and Food Research Institute, 3700 AJ Zeist, Netherlands; (3) Sealed Air Corporation Cryovac Division, 20017 Passirana di Rho, Italy; (4) Laboratory of Polymer Technology, National Technical University of Athens, 15780 Athens, Greece; (5) Analytical Chemistry, Nutrition and Bromatology Department, The University, 15782 Santiago de Compostella, Spain; (6) ITOSOPE CTCPA rue Henri de Boissieu 01000 Bourg en Bresse, France; (7) Eco Emballages, 92300 Levallois Perret, France

Abstract

Functional barriers are multilayer structures deemed to prevent migration of some chemicals released by food contact materials into food. Different migration behaviour of mono- and multilayer plastic structures are reviewed, in terms of lag time and of influence of the solubility of the migrants in the food simulant. Whereas barriers to oxygen or to aromas must prevent the diffusion of these compounds in service conditions, functional barrier must also be efficient in process conditions, to prevent diffusion of substances when the polymer layers are in contact at high (processing) temperatures. Diffusion in melted polymers at high temperatures is much slower for polymers which are glassy than in polymers which are rubbery at ambient temperature. To evaluate the behaviour of functional barriers in service conditions, a set of reference diffusion coefficients in the 40-60°C range has been determined for 14 polymers. Conditions for accelerated migration tests have been proposed, on the basis of worst case activation energy in the 40-60°C range. For simulation of migration, numerical models are available. The rules derived can be used both by industry (to optimize a material in terms of migration) or by risk assessment authorities. Differences in migration behaviour between monolayer and multilayer materials are emphasized.

Correspondence to: alexandre.feigenbaum@reims.inra.fr Fax: + 33 -3 26 91 39 16

Introduction

3 Functional barriers are parts of food contact materials, used to prevent migration of contaminants of substances which are either not evaluated by health authorities, or which may cause harm to public health. The major properties of functional barriers are reviewed here, on

6 the basis of knowledge obtained in a .

For compliance purpose, or to protect the health of consumers, is it necessary that a label glued outside a glass bottle complies with the regulations for food contact materials ? To

9 solve this kind of issues, regulations have invented the principle of functional barriers. Functional barriers are used in multilayer structures; they are deemed to prevent migration of undesirable substances from layers beyond the barriers (figure 1). Up to now they are met in

12 three types of situations:

- **for recycled plastics**: recycled plastics may be contaminated by various chemicals available in the environment of consumers; in order to prevent such contaminants to reach the food, a

15 functional barrier is intercalated between the recycled plastic and the food.

- **for substances not approved by regulation**: according to a draft EU regulation, industry will be authorized to use substances which are not approved by the authorities in charge of

18 public health (i) if these substances are nor carcinogenic and (ii) if they are separated from the food by a functional barrier which ensures that they are not detectable in the food. Such substances are named in the regulation "functional barrier substances".

21 - **for active packaging**: in the area of active packaging, functional barriers can prevent migration of active substances or of constituents of the active material.

24 Glass and metal are known to be "absolute" functional barriers. But what about plastics? How do they behave? Are glassy polymers efficient as functional barriers? Can functional barrier properties be predicted considering barrier to oxygen behaviour? The purpose of this paper is

27 to review the situation and to provide the basis of guidance both to plastics converters who put materials with functional barriers on the market as well as to authorities who assess the risk.

30

The background of this paper is a work on functional barriers associated to recycling from two projects: one on PET (sponsored by ADEME and ECO EMBALLAGES) and one on 14

33 other polymers (sponsored by the European Commission, FAIR CT 98-4318 programme). The conclusions drawn are extended here to the other areas of use of functional barriers. We

will review successively: (i) experimental illustration of the interest of functional barriers, (ii) behaviour of functional barriers at high (process) temperature and (iii) in conditions of storage, (iv) selection of polymers for functional barriers, (v) the prediction of the functional barrier efficiency and (vi) ways of tests for functional barriers.

As a preliminary we should emphasize that this paper deals only with functional barriers based on diffusion behaviour. Functional barriers reducing the migration of a substance with which the have little affinity can also be met (for instance a polar substance will not dissolve easily in a polyolefin) but are hardly discussed here.

1. Materials and methods

1.1 Diffusion of surrogates within multilayer PET preforms

In the ADEME – ECO EMBALLAGES project, 17 surrogates have been selected on the basis of different volatility, molecular weight, chemical functionality or polarity (especially solubility in water) (Table 1). Many of them are also in usual lists of recommended surrogates. In order to avoid too large global concentrations of surrogates in PET, and to mind possible chemical reactions, they were divided into three sets (A), (B) and (C) (Table 1). Each set of surrogates was incorporated separately into flakes, thus minimising alteration of PET physical-chemical properties. After drying, the flakes were dried and injected into preforms (Pennarun 2004b).

[Insert table 1 about here]

1.2 Diffusion of surrogates in melted polymer sheets

Two plates of the same polymer (100 to 500 μm thick, depending on the polymer intrinsic UV absorption), one virgin and one loaded, were placed in an aluminium mould facing each other on their smallest cross section. The loaded plate contained DMA as a UV probe (at least 3000 ppm), acid orange (1500 ppm) and an antioxidant (Irganox 1076, 1000 ppm). The mould was sandwiched between two iron plates and heated under a slight pressure up to the testing

temperature during 10 min. After this heating session, the sample was then removed and analysed with a UV microspectrophotomer (Carl Zeiss UV-visible spectrophotometer

3   equipped with a Xenon lamp and a microscope unit for analysis of small areas). The concentration gradient of DMA along the x axis is recorded (maximum absorption at 330 nm); and the diffusion coefficient is then calculated from the fit of the experimental and

6   calculated concentration profiles, assuming Fickian diffusion and a constant diffusion coefficient (Pennarun 2004b).

9   Acid red has a high molecular weight and does not diffuse during the experiment. It allows to locate the initial interface between the two plates; the analysis can be done only on the initially virgin side (uncoloured).

12

1.3 Reference diffusion coefficients at 40°C in polymers

1.3.1 Impregnation of surrogates into tested polymers

15   The objective was to obtain surrogate concentrations around 1000 ppm in plastics, which is a good compromise between the need of a good analytical sensitivity for the different diffusion / migration tests and the request of avoiding unrealistic plasticization. Contamination is

18   obtained through two successive extrusions: (i) preparation of a master batch and (ii) dilution with virgin granules.

21   1.3.2. Measurement of diffusion coefficients

To measure diffusion coefficients D, the general philosophy was to avoid whenever possible a diffusion test involving a contact with a liquid (i) because of possible errors which would

24   minimise D due to mass transfer at the solid / liquid interface, (ii) because of possible errors which would yield an apparent too large D, due to plasticization of the polymer by the liquid (iii) because migration into liquids is efficient (ie leading to a mathematically quantitatively

27   exploitable data) only when the partition coefficient is sufficiently low and (iv) more generally because the first step to take into consideration with functional barriers is the diffusion from the recycled layer to the barrier.

30

The tests used were:

Moisan type test: The Moisan test, a classical method to measure diffusion coefficients, was

33   designed by Moisan (1980). It is based on the measurement of a concentration gradient in a

stack of films after a given time of contact with a **source** of Polyethylene wax spiked (or contaminated) with surrogates.

3

The classical Moisan cell is an open system and obviously it cannot be used to determine diffusion coefficients of volatile compounds. In this project it was necessary to design a special tightly closed cell for volatile surrogates (Paseiro 2002). It allowed to determine D for volatile compounds (European Commission 2003).

The Moisan test is very precise, but the main problem is that when diffusion is slow (e.g. in an efficient barrier), the surrogate does not even reach the second layer of the stack within 15 or 30 days. It is not interesting from a practical point of view to wait for 3 months or more in order for diffusion to progress sufficiently in the stack. Therefore, in principle, the Moisan test is not appropriate for good functional barriers, and is useful only when no more adequate tests are available.

15

[Insert figure 1 about here]

Three-layer test: This test was developed for the projects. It consists in superimposing three films, creating the geometry of a functional barrier. In the earlier experiments of the project, the three layers consisted in an inner film contaminated with surrogates and two outer virgin films (Figure 1). But later, in order to reduce the time needed for the experiments and to obtain a better sensitivity the test was realised with an inner layer of virgin polymer and two outer contaminated layers. As in the Moisan test, an intimate contact between layers is a fundamental condition. This intimate contact is also achieved by applying a slight pressure and heat.

Figure 1 shows a profile of experimental data of diffusion of toluene into a film (typically PS), as the percentage of migration versus time. The equilibrium will be reached with 66 % of the initial concentration ($Q_2/Q_1+Q_2+Q_3$ = 0.33); increasing temperature facilitates the monitoring of kinetics. When films ①, ② and ③ have not been modified by the surrogate impregnation, they are identical, and the 66 % can be assumed, without need of an analytical confirmation. Thus it is not necessary to carry out the test till equilibrium, which is an advantage for high barrier polymers.

3   # 2. Results

2.1 Experimental illustration of the interest of functional barriers

6

Two major differences between monolayer and multilayer materials are emphasised here:

- the lag time behaviour

9   - the influence of solubility on migration.

[Insert Table 2 about here]

12

Before a substance initially located in a layer beyond the barrier is capable of reaching the food, it must cross the functional barrier layer(s), which induces a lag time. The more efficient

15   the barrier, the longer the lag time. Various definitions of lag time are available in literature (equations 1, 2 and 3). A comparison of their background and scope is given in

Table 2. Figure 2 shows an experiment where the lag time can be seen with polypropylene,

18   which is a poor barrier. In order to be able to observe a lag time with this polymer, the time of residence of the polymer at high temperature during its manufacture, as well as the temperature of the process have been minimised. The material was stored in a deep freezer

21   until the migration test was started. The observed lag time corresponds to a few minutes. Similar results were obtained for HDPE (Han *et al.* 2003). With glassy polymers, the lag phase can be of several weeks or months.

24

[Insert Figure 2 about here]

[Insert Figure 3 about here]

27

The lag time depends not only on the polymer, but also on the diffusants studied. Low molecular weight diffusants have the shortest lag times.

30

It can be understood that the solubility of the migrants in the simulants play a much more important role for monolayers than for multilayers, at least in early stages of migration. With

33   monolayers, the most soluble migrants give the largest migration. With multilayers, the first

migrants which reach the food are those which diffuse the fastest in the functional barrier, and the solubility of the migrants plays a much smaller role. This different behaviour is shown for

3   PET in Figure 3 (Pennarun *et al.* 2005): the sequence of migration from monolayers is completely changed from ethanol (where all the surrogates are well soluble) to 3 % acetic acid (where only phenol and pentanedione are well soluble). In contrast, the sequence of migration

6   from a multilayer is hardly affected by the change of solvent.

9   **2.2 Behaviour of functional barriers at process temperatures in PET preforms**

When a functional barrier layer is assembled with other layers of a multilayer structure, the

12   temperature of the process may be high when the process is co-injection or co-extrusion. When lamination with an adhesive is used to assemble the layers, the processing temperature is lower. Even if the time spent at high temperature is very short (a few seconds), a substance

15   initially located in layers beyond the barrier may diffuse into the barrier. If at the end of the process the undesirable substance is evenly distributed all over the layers, then obviously, the barrier layer is not efficient, and the use of a functional barrier is not justified. It could then be

18   useful to assemble the layers by lamination, at a much lower processing temperatures. In contrast, if there is little to no diffusion into the barrier during the process, then the material may be a good functional barrier. The final decision about the efficiency of the functional

21   barrier will depend on its behaviour during contact with food, which will be reviewed in the next section. At this point we must emphasize a major difference between functional barriers and barriers to gases and aromas: a functional barrier must also be efficient at the material

24   processing temperature, whereas barriers to aromas and gases are expected to work in service conditions, which is usually around room temperature.

27   The approach used consisted in observing the behaviour of different polymers with surrogates and to generalize their behaviour using migration modelling. Diffusion in melted polymers has been studied by determining diffusion profiles of surrogates, using two approaches:

30   - different surrogates of different polarities were studied in PET preforms.
- the diffusion of 2,4-dimethoxyacetophenone (DMA, a UV absorbing probe) was monitored in 14 different melted polymers (Pennarun *et al.* 2004b).

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A range of diffusants with different polarities [phenol; 2,6-di-tert-butyl-4-methylphenol; chlorobenzene; 2,5-thiophenediylbis(5-tert-butyl-1,3-benzoxazole); 1-chlorooctane], were

3   incorporated into PET, in the middle layer of three layer preforms [virgin PET/loaded PET/virgin PET]. After co-injection, slices of the preforms were cut parallel to the main axis, extracted with a solvent and analysed by gas chromatography. The diffusion profile was

6   reconstructed in this way by plotting

amount of surrogate = f(distance to the preform outer surface).

No diffusion of any surrogate could thus be detected in the virgin layer, and this was shown to

9   correspond to $D_{280°C} > 10^{-5}$ cm^2/s. The virgin PET layer behaved as an efficient functional barrier.

12   The diffusion in melted polymers was investigated using DMA as a UV absorbing surrogate. Two distinct polymer behaviour could be distinguished:

       - polyolefins and EVA displayed much larger diffusion coefficients than the polar

15   polymers: PET, PA, PVC, PVDC, EVOH, PAN.

       - when a plot of

       $\log D = f(10^3/T)$

18   was displayed, the activation energies of DMA (slopes of these plots) diffusion in

       apolar polymers appeared to be much lower than in polar ones (Figure 4).

21   The polar polymers are much better candidates to functional barriers for two reasons: (i) diffusion is always slower in polar melted polymers, despite higher melt temperatures than apolar polymers and (ii) due to larger activation energy, as soon as the temperature of the

24   mould decreases, the diffusion coefficient of any molecule decreases much faster than in apolar polymers.

27   *[Insert Figure 4 about here]*

30   **2.3 Behaviour of functional barrier polymers in service conditions.**

In the 40-60°C range, the apolar polyolefins and EVA displayed much larger diffusion

33   coefficients than the more polar PET, PA, PVC, PVDC, EVOH and PAN. This result was

obtained for a set of polar and apolar diffusants, covering a molecular weight range from 92 to 431 g/mole (**Table 3**, Table 4).

[Insert Table 3 about here]
[Insert Table 4 about here]

The values of Table 4 have been used to increment the data base of diffusion coefficients managed under the auspices of the European Commission, to assess Ap values. The Ap values are used to predict overestimated (worst case) diffusion coefficients of substances with different molecular weight, according to equation (4) (O'Brian *et al.* 2005):

$$D^* = 10^4 \exp [Ap - 0.8 + Ea/T] \qquad (4)$$

Specially for PET, the large number of data obtained allows to set Ap values and to predict the migration behaviour of any chemical with a margin of safety in monolayer materials (O'Brian *et al.* 2005, Pennarun *et al.* 2004a).

When several substances are incorporated together in a polymer, synergic effects can be observed (Table 3). These effects are similar to plasticization effects, and only the highest molecular weight substances are affected (Pennarun 2004a). This shows that the data obtained for the lower molecular weight surrogates are not influenced by their concentration in the polymers.

These data can also be used to predict the migration behaviour of a known substance in a multilayer system, and to check whether the layer in contact with food behaves as a functional barrier. This is the situation encountered with substances "not approved by the regulation" (see the introduction) or associated to active packaging systems. A software for multilayers has been developed for that purpose (INRA 2003). The relevant parameters are discussed in the next section.

In the case of recycling, the ability of a functional barrier to protect the food from the migration of contaminants coming from an inner layer is less straightforward, since neither the identity nor even the presence of contaminants are known in advance. The assessment can then only rely on modelling of the diffusion in worst case situations. But what is a worst case representative of an unknown contaminant? Is it a very fast diffusing surrogate? Toluene and

pentanedione are among the fastest diffusing surrogates studied, but lower molecular molecular weight chemicals would probably exhibit even larger diffusion coefficients. The situation has to be assessed in line with the request of safety assessment. The EU regulation offers an approach about safety assessment of volatile molecules: despite their large diffusion coefficients, compounds with molecular weight below 80 g/mol are not subject to migration restrictions, unless they are toxic at very low doses (like vinyl chloride): ethylene (M = 28 g/mol), propylene (M = 42 g/mol) and butene (M = 56 g/mol) have no SML in the EU regulation. The SCF who proceeded to safety assessment considered that: *"residues of this gas in plastics are very small … Migration into food will be toxicologically negligible"* (European Commission 2005b). This contrast with hexene (M = 80 g/mol) and higher molecular weight 1-alkenes, which are subject to migration restrictions. The lowest molecular weight of concern is usually around 80 g/mole.

However if toluene (M = 92 g/mole) was the contaminant representative of worst case contaminants, very few materials could behave as functional barrier for recycling.

In fact, many steps of the material processes of the opportunity to eliminate volatiles by evaporation: either drying (as for PET) or "super cleaning" (as for PET and HDPE) (Welle 2005). In this case, the reference diffusion coefficient should be that of a higher boiling surrogate, e.g. phenylcyclohexane, assuming that the more volatile chemicals have been removed.

2.3 Prediction of functional barrier efficiency

In contrast to glass or metals, which are absolute barriers above a minimum thickness, it is not possible to draw general rules for plastics. The efficiency depends on the history or the polymer, of the material and of the finished article as well on their geometric properties, mainly on their thickness. Some general trends can however be drawn:

>	- it is unlikely that polyolefins and EVA can behave as functional barriers, whatever the thickness of the layers

>	- other polymers, PET, EVOH, PVC, PVDC, PAN may behave as functional barriers if the barrier layer is sufficiently thick.

As can be seen from

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Table 2, none of the mathematical expressions available can take into account all the steps of processing and use of functional barriers. Modelling therefore has to rely on numerical analysis. To decide about the minimum thickness there is the need to use a software which takes into account the whole history of the food contact article. The freeware [MULTITEMP & MUTIWISE] (INRA 2003) is able to describe successively:

- diffusion into the barrier during processing (taking into account a cooling rate),
- diffusion into the barrier during storage of the empty package,
- migration during hot filling
- migration during storage of the food (taking into account swelling effects).

This software uses classical equations for diffusion of heat and of matter, and has been validated in the FAIR programme on recyclability (European Commission 2003).

The web site of INRA also offers the possibility to use [PROCESS & STORAGE], which are very quick tools to evaluate diffusion and migration. They do not calculate the result, but search in a data base of pre-calculated situations those which are the most similar to the system investigated.

The main difficulty of modelling is no longer to elaborate a model (Han *et al.* 2003). It is much more important to be able to obtain the parameters requested for the calculation:

- the diffusion coefficients D of the migrant in each layer; if they are not available, upper bound values can be obtained from equation (1). For a functional barrier efficiency to protect food from contaminants, the value of phenylcyclohexane can be used as reference value, as discussed above. Recently, 3,5-di-t-butyl-4-hydroxytoluene (BHT) has been proposed as a reference substance (Han *et al.*, 2003) for modelling diffusion into a functional barrier.
- the partition coefficient between layers. Little data are available. If the different layers are made from the same or from similar polymers, $K_{p/fb} = 1$
- the partition coefficient between functional barrier and food $K_{fb/f}$. Again, in absence of data, a worst case value must be selected, such as $K_{fb/f} > 10^{-2}$ (O'Brian *et al.* 2005).
- swelling of the plastic layers by food constituents leads to a continuous increase of D during contact with food: use of D* values often takes into account swelling. Swelling depends on the diffusivity and on the solubility of the simulant in the polymer (Riquet

et al. 2002). If solvents are used as food simulants, they usually give very fast swelling and a value corresponding to already swollen materials can be taken.

3   -   the mass transfer coefficient at interface H. In absence of data, H= infinite can be taken as a worst case.

The current prediction tools can only be used for a prediction of worst case values. As can be

6   seen, migration modelling still requires much research effort to predict these parameters, and to obtain realistic values.

9

2.5 Activation energy of diffusion at 40°C and design of accelerated tests

12   Multilayers cannot be tested like monolayers, because of the lag phase behaviour. With monolayers, the longest test time in Official tests is 10 days. Assuming that the migration follows strictly a Fickian behaviour with a constant diffusion coefficient, the migration is

15   proportional to the square root of the contact time: a migration in 10 days is only 1/6 of what may occur in 360 days. If we turn to multilayers, the ratio

$\text{Migration}_{10 \text{ days}}$ / $\text{Migration}_{1 \text{ year}}$

18   can be any value. If the barrier is inefficient, the lag time will be short, and the material behaves more or less like a multilayer. But if the barrier is efficient, the lag time may be larger than 10 days, and the ratio can be of several orders of magnitude.

21

Therefore, accelerated test conditions must be designed, in order that the migration measured is at least as large as the actual migration. The acceleration occurs at an accelerated test

24   temperature, up to 60 or even 65°C (if the materials are not too much modified at this temperature) (**Table 5**). However it is not possible to draw precise rules for each situation, and only guidelines can be given:

27   -   if the material is stored empty for a period sufficient to induce diffusion into the functional barrier, the test should include an ageing period by storing the empty material at the accelerated test temperature.

30   -   a migration test can be conducted at the accelerated test temperature. Most solvents withstand 60 or 65°C.

33   *[Insert Table 5 about here]*
[Insert Table 6 about here]

[Insert Figure 5 about here]

3   In order to define an acceleration factor, one has to look at the activation energy of diffusion. Some values are reported for the activation energy of gases. Figure 5 reports the influence of molecular weight on the activation energy of diffusion of gases and of surrogates in PET. It

6   can be seen that although this is yet a purely empirical relationship, the value of 80 kJ can be considered as the lowest value for surrogates and plastics additives. If a test is conducted at 60°C within a test time t_{test}, use of an 80 kJ/mole activation energy is equivalent to an

9   acceleration factor 45.5 compared to 25°C (Table 6). In other words the same diffusion (or migration) is expected at 25°C within 45.5 t_{test}. In this way, 80 kJ/mole appears as a worst case activation energy. Similar results are obtained for some polyolefins, so that the value 80

12   kJ/mole can be considered as general (European Commission 2003), pending more data.

    If there is some precise knowledge of the actual activation energy, or if there are any other

15   good reasons to estimate that the actual activation energy is larger, larger acceleration factors can be used (Table 5).

18   The principle of these activation factors allows to correlate a test time with an actual time of storage, rather with conventional test conditions, as is the case currently. Of course due to the multiplicity of specific cases (some materials may not withstand the 60°C, other can support

21   much higher test temperatures, some are stored empty, others not …), it is not possible to define general test conditions like the current 97/48 directive does.

24

Conclusions

27   The major properties of functional barriers have been pointed out. Diffusion and migration through functional barriers depend on much more factors than with monolayer materials: conditions (time and temperature) of processing, of storage of the empty material, of filling

30   and of storage of the food.

    The assessment of functional barriers efficiency should rely heavily on prediction of

33   migration. The diffusion coefficient of the migrant is here a key parameter. When the

structure of the migrant is known (non authorised substances or components of active packaging systems), its diffusion coefficients can be estimated from data available for

3 compounds with a similar structure or from the Piringer equation, based on the molecular weight. For contaminants (recycled materials), modelling should be carried out in first instance to optimise the materials before running the complex tests with surrogates. Reference

6 values are available, to define an index of polymer behaviour.

With monolayer materials, there is a reasonable correlation between migration in

9 conventional test conditions and in actual storage. This may no longer be true with multilayers and specially with efficient functional barriers. Accelerated test conditions have to be considered for that purpose. Acceleration factors have been proposed on the basis of a

12 worst case activation energy of migrants with molecular weight above 80 g/mole. Rules are given to use more realistic acceleration factors and test conditions if relevant.

15

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List of tables and figures

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Note(2): derived from Einstein relationship for a 3D uncorrelated displacement

9   Note (3): Feigenbaum et al. 1997

Table 3: Mutual influence of surrogates on their diffusion coefficients (cm^2/s) in PP 20 μm at

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Figure 3: Comparison of migration from monolayer (280 μm) and from multilayer [60 μm

27   (barrier)/60 μm (recycled)/100 μm] PET bottles into ethanol and into 3% acetic acid after 6 months at 40°C (adapted from Pennarun 2005)

30   Figure 4: diffusion coefficients of DMA in melted polymers

Figure 5: Activation energy of diffusion of gases and of surrogates in PET (Δ: permanent

33   gases, O: surrogates and additives)

Set	Surrogates	M (g/mole)	Concentration (mg/ kg impregnated PET bottle)
A	1,1,1-Trichloroethane*	M=133	2690
A	Dimethyl sulfoxyde (DMSO)	78	1363
A	Methyl palmitate*	270	704
A	Benzophenone*	182	2910
A	Phenylcyclohexane*	160	1285
A	Ethyl hydrocinnamate	178	587
B	Phenol	94	2616
B	2,6-Di-tert-butyl-4-methylphenol (BHT)	220	872
B	Chlorobenzene*	113	1324
B	2,5-Thiophenediylbis(5-tert-butyl-1,3-benzoxazole) (TDBB)*	431	570
B	1-Chlorooctane	149	1552
C	2,4-Pentanedione	100	785
C	Azobenzene	182	921
C	Nonane	128	624
C	Dibutyl phthalate (DBP)	278	533
C	Phenyl benzoate	198	810
C	Toluene*	92	704

3

Table 1: surrogates used for diffusion in PET at food storage temperature (ADEME – ECO EMBALLAGES project) *: surrogate used in the FAIR

6   programme

Lag time equation	$\tau = \dfrac{L_{fb}^{\;2}}{6\,D}$ **(eq. 1)**	$\tau = \dfrac{L_{fb}^{\;2}}{16\,D}$ **(eq. 2)** *(1)*	$\tau = \dfrac{L_{fb}^{\;2}}{100\,D}$ **(eq. 3)** *(2)*
Meaning of lag time	Average time for a given molecule to cross the barrier, **probability 16 %**	Average time for a given molecule to cross the barrier, **probability 5 %**	Time for the concentration of the migrant at interface to become $C_0/1000$ (arbitrary choice of this value). Two layers of the same polymer assumed, with same D.
Assumption on thickness	Influence of thickness not taken into account (semi-infinite model)	Influence of thickness not taken into account (semi-infinite model)	Eq. (3) valid for $[L_{fb} \geq L/2]$. For other $[L_{fb}/L]$ values, see Feigenbaum *et al.* 1997
Assumption on contact	None (semi-infinite and continuous geometry assumed)	None (semi-infinite and continuous geometry assumed)	No contact with food assumed
Assumption on the volume and concentration of the polluted layer	The concentration in the inner layer is considered constant (expression is for permeation from a large volume of solution through a membrane)	The concentration in the inner layer is considered constant (expression is for permeation from a large volume of solution through a membrane)	The concentration in the inner layer decreases, that in the barrier increases concomitantly.
Influence of material process conditions	Not considered	Not considered	Not considered
Influence of food diffusion	Not considered	Not considered	Not considered

3   Table 2: different expressions of lag time in literature, and underlying assumptions

(Lfb is the thickness of the only functional barrier, L is the thickness of the whole material)

6   Note(2): derived from Einstein relationship for a 3D uncorrelated displacement
Note (3): Feigenbaum et al. 1997

Experiment	D (cm^2/s)			
	TDBB Mw: 430	Methyl margarinate Mw: 284.5	Benzophenone Mw: 182.2	Phenylcyclohexane Mw: 160.3
4 surrogates together	4.5 10^{-10}	1.7 10^{-10}	1.8 10^{-10}	2.6 10^{-10}
Each surrogate separately	9.2 10^{-13}	1.4 10^{-10}	Not determined	2.2 10^{-10}
TDBB / benzophenone	4.4 10^{-12}		3.0 10^{-10}	
TDBB / methyl margarinate	4.6 10^{-12}	2.4 10^{-10}		
TDBB / phenylcyclohexane	4.6 10^{-12}			1.6 10^{-10}

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Table 3: Mutual influence of surrogates on their diffusion coefficients (cm2/s) in PP 20 μm at 40 °C

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Functional Barriers: properties and evaluation

Polymer	Trichloroethane	Toluene	Chlorobenzene	DMSO	Phenylcyclohexane	Benzophenone	Me Margarinate	TDDB	Other data
HDPE	$2.4\ 10^{-9}$ (a) $2\ 10^{-9}$ (d)	$8.5\ 10^{-9}$ (a) $8\ 10^{-9}$ (d)	$8.9\ 10^{-9}$ (a) $15\ 10^{-9}$ (d)		$3.9\ 10^{-9}$ (a) $7\ 10^{-9}$ (d)	$4.3\ 10^{-9}$ (a) $7\ 10^{-9}$ (d)	$2.1\ 10^{-9}$ (a) $2\ 10^{-9}$ (d)	$0.2\ 10^{-9}$ (a) $0.5\ 10^{-9}$ (d)	
LDPE	$20\ 10^{-9}$ (d)	$40\ 10^{-9}$ (d)	$40\ 10^{-9}$ (d)		$21\ 10^{-9}$ (a) $12\ 10^{-9}$ (d)	$33\ 10^{-9}$ (a) $12\ 10^{-9}$ (d)	$5.8\ 10^{-9}$ (a) $3\ 10^{-9}$ (d)	$0.32\ 10^{-9}$ (a) $0.5\ 10^{-9}$ (d)	
LLDPE	$6\ 10^{-9}$ (d)	$6\ 10^{-9}$ (d)	$9.5\ 10^{-9}$ (d)		$7\ 10^{-9}$ (d)	$4.5\ 10^{-9}$ (d)	$6\ 10^{-9}$ (d)		
PP	$0.65\ 10^{-9}$ (a) $0.36\ 10^{-9}$ (c) $0.55\ 10^{-9}$ (d)	$2.4\ 10^{-9}$ (a) $0.94\ 10^{-9}$ (c) $1.5\ 10^{-9}$ (d)	$2.6\ 10^{-9}$ (a) $0.24\ 10^{-9}$ (c) $1.2\ 10^{-9}$ (d)		$0.27\ 10^{-9}$ (a) $0.55\ 10^{-9}$ (c) $0.4\ 10^{-9}$ (d)	$0.18\ 10^{-9}$ (a) $0.49\ 10^{-9}$ (c) $0.47\ 10^{-9}$ (d)	$0.17\ 10^{-9}$ (a) $0.83\ 10^{-9}$ (c) $0.47\ 10^{-9}$ (d)	$0.012\ 10^{-9}$ (a) $0.046\ 10^{-9}$ (a) $0.04\ 10^{-9}$ (d)	
EP	$2.5\ 10^{-9}$ (d)	$4\ 10^{-9}$ (d)			$1.2\ 10^{-9}$ (d)	$2\ 10^{-9}$ (d)	$9.5\ 10^{-9}$ (d)	$0.2\ 10^{-9}$ (d)	
PVC plast	$6.7\ 10^{-9}$ (a)	$6.2\ 10^{-9}$ (a)	$6.4\ 10^{-9}$ (a)		$4.4\ 10^{-9}$ (a)	$3.2\ 10^{-9}$ (a)	$2.7\ 10^{-9}$ (a)	$0.26 - 0.3\ 10^{-9}$ (a)	
EVA	$> 10\ 10^{-9}$ (a)	$> 10\ 10^{-9}$ (a)	$> 10\ 10^{-9}$ (a)		$45\ 10^{-9}$ (a)	$30\ 10^{-9}$ (a)	$15\ 10^{-9}$ (a)	$1.8\ 10^{-9}$ (a)	
PVDC		$9/5\ 10^{-13}$(b)	$10\ 10^{-13}$ (b)		$0.22\ 10^{-13}$ (b)				
EVOH 60 % rh						$12\ 10^{-11}$ (a)	$40\text{-}90\ 10^{-11}$ (a)		
EVOH 38 % rh									$2.2\ 10^{-15}$ (d, e5)
PA 60 % hr *	$25\ 10^{-13}$ (a)	$34\ 10^{-13}$ (a)	$36\ 10^{-13}$ (a)		$120\ 10^{-13}$ (a)	$320\ 10^{-13}$ (a)	$160\ 10^{-13}$ (a)	$0.98\ 10^{-13}$ (a)	
PA dry			$0.1\ 10^{-13}$ (b)			$0.14\ 10^{-13}$ (b)			
PET dry		$38\ 10^{-15}$ (a)	$44\ 10^{-15}$ (a)	$50\ 10^{-15}$ (a)	$0.0008\ 10^{-15}$ (a)	$0.081\ 10^{-15}$ (a)			$77\ 10^{-15}$ (e4)
PET / water									$200\ 10^{-15}$ (e4)
PS		$200\ 10^{-15}$ (d)	$600\ 10^{-15}$ (d)		$0.8\ 10^{-15}$ (d)				$13000\ 10^{-15}$ (e1) $9800\ 10^{-15}$ (e2) $350\ 10^{-15}$ (e3)
PVC rigid									$350\ 10^{-15}$ (e1) $3\ 10^{-15}$ (e3)
PMMA									$1\ 10^{-15}$ (e1) $13\ 10^{-15}$ (e2) $9\ 10^{-18}$ (e3)

(**a**): measured with the Moisan cells   (**b**): measured with a 3-layer test   (**c**): measured by permeation   (**d**): obtained by sorption kinetics

3   (**e1**): n-pentane,   (**e2**): benzene, (**e3**): carbon tetrachloride, values adapted from Berens and Hopfenberg, 1982, calculated from the activation energy and the D at 30 °C given in that paper

(**e4**): pentanedione (from Pennarun *et al.* 2004)   (**e5**): hexanol (from Aucejo *et al.* 1998)

* the differences between compounds are most likely explained by the different methods for moisture control in different laboratories; values for PA 60 % rh are associated to large error bars

6   Table 4: Reference diffusion coefficients (cm2 s-1) of surrogates at 40 °C in all polymers studied

Activation energy (kJ/mol)	65 → 25°C	60 → 40°C	65 → 40°C	40 → 25°C	60 → 25°C
	Acceleration factors				
80 (worst case)	**45.5**	**6.3**	**9.7**	**4.7**	**29.9**
90	73.7	8.0	12.9	5.7	45.7
100	119	10.1	17.2	6.9	69.7
110	193	12.7	22.8	8.4	107
130	499	20.1	40.3	12.4	249

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Table 5: Acceleration factors and activation energy of diffusion

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Time of storage at 25 °C	Test time at 40°C	Test time at 60°C	Test time at 65°C
≤ 1 day	1 day		
1 < t ≤ 7 days		6 h	4 h
7 < t ≤ 14 days		12 h	7.5 h
14 < t ≤ 30 days		1 day	16 h
30 < t ≤ 45 days	10 days	2 days	1 day
45 < t ≤ 180 days		6 days	4 days
180 < t ≤ 300 days		10 days	7 days
300 < t ≤ 700 days		23 days	15 days

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Table 6: correspondence between actual storage conditions and accelerated test times, using a 80 kJ/mole activation energy

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Figure 1: Principle of solid-solid three-layer test and of obtaining D0 (initial conditions: C/V/C)

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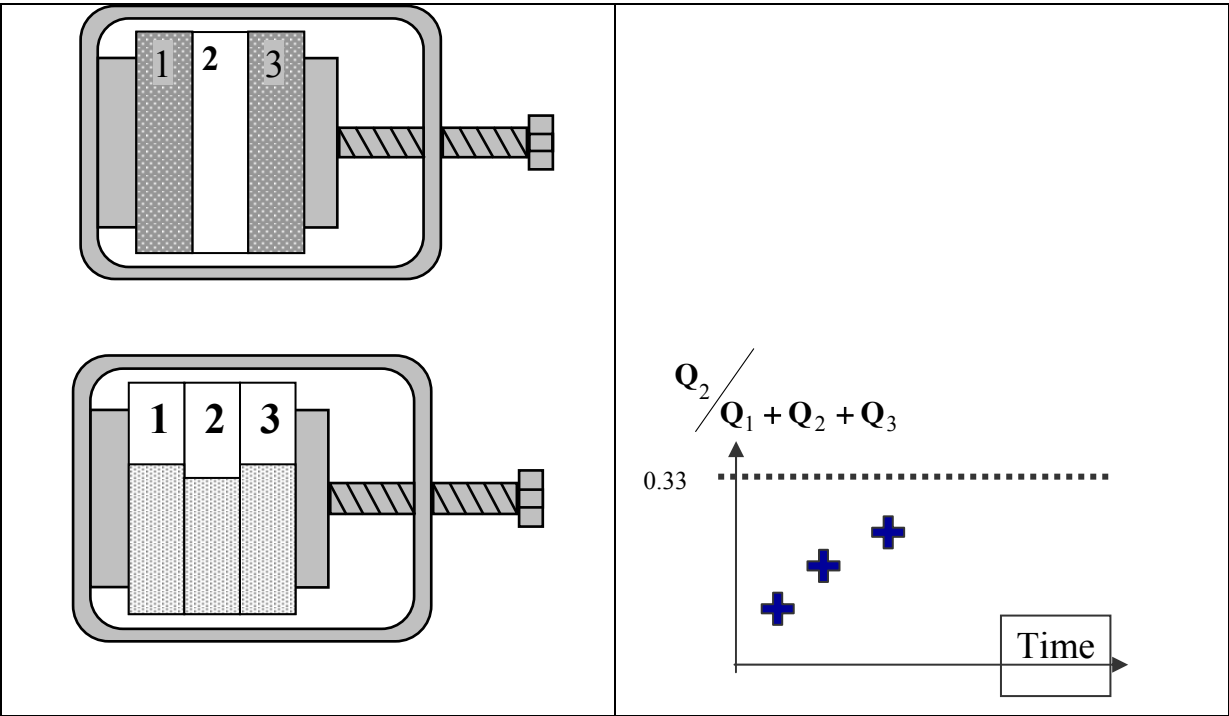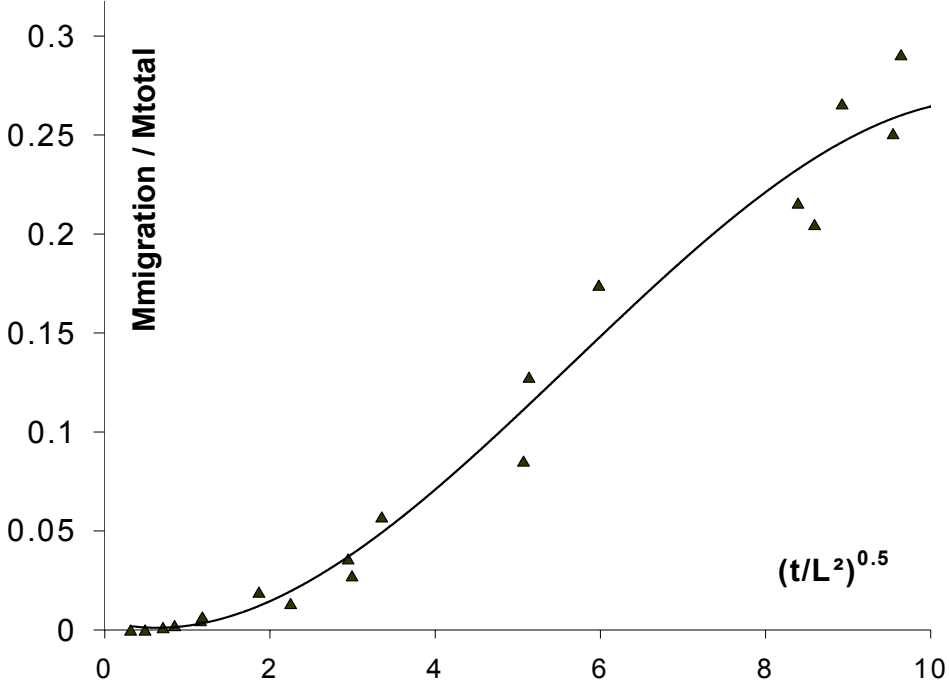
Figure 2: Migration kinetics at 40°C of trichloroethane from [Virgin PP/polluted PP/Virgin

3   PP (300 μm] into olive oil
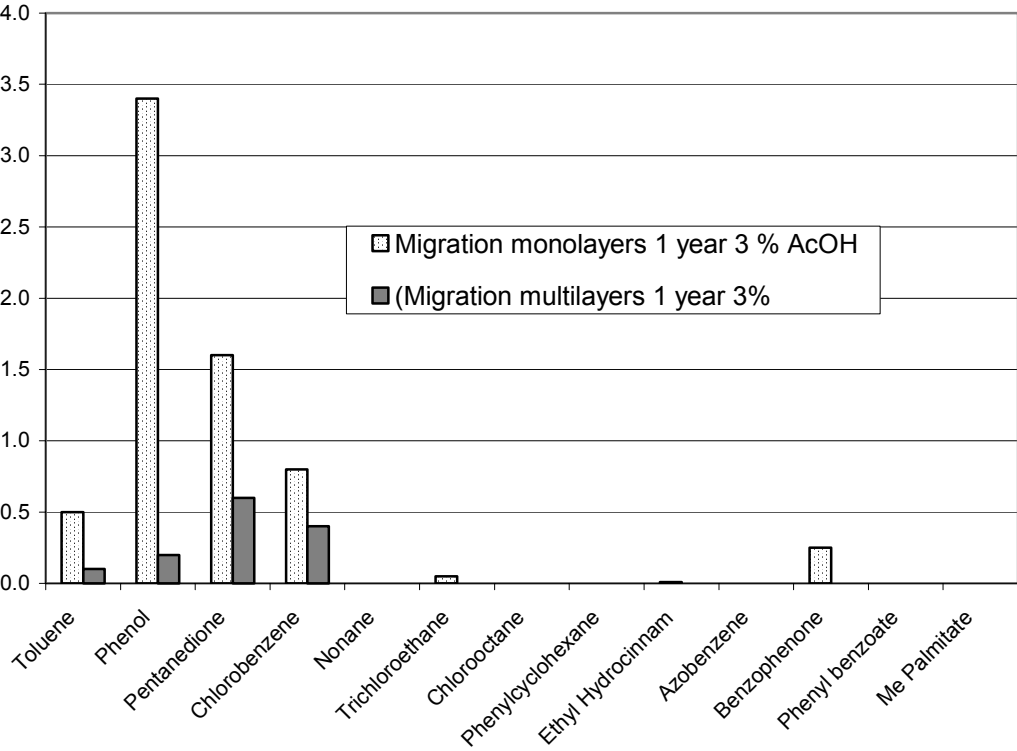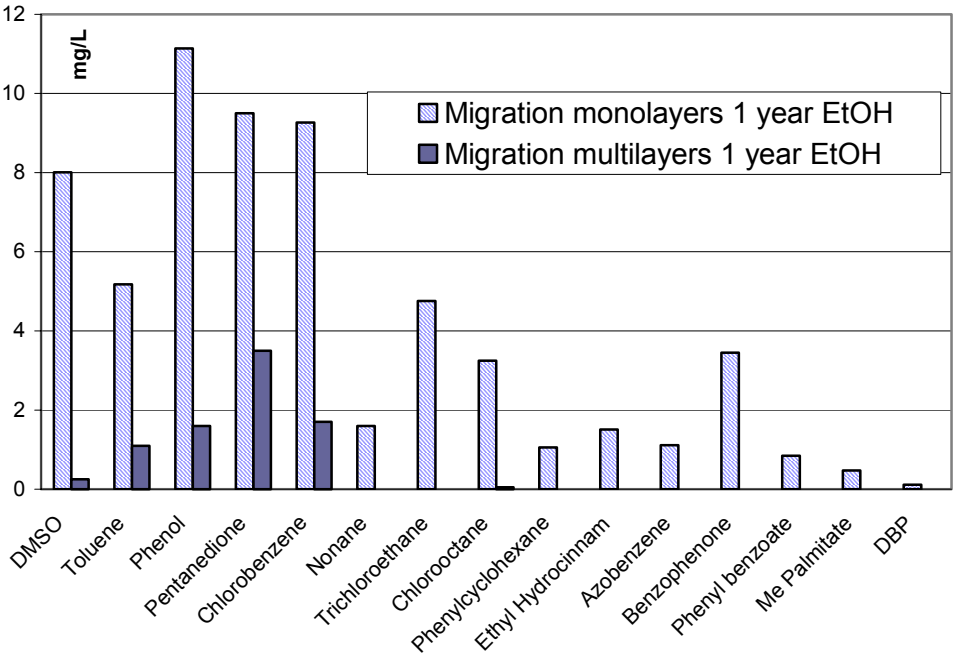
Figure 3: Comparison of migration from monolayer (280 μm) and from multilayer [60 μm (barrier)/60 μm (recycled)/100 μm] PET bottles into ethanol and into 3% acetic acid after 6 months at 40°C (adapted from Pennarun 2005)

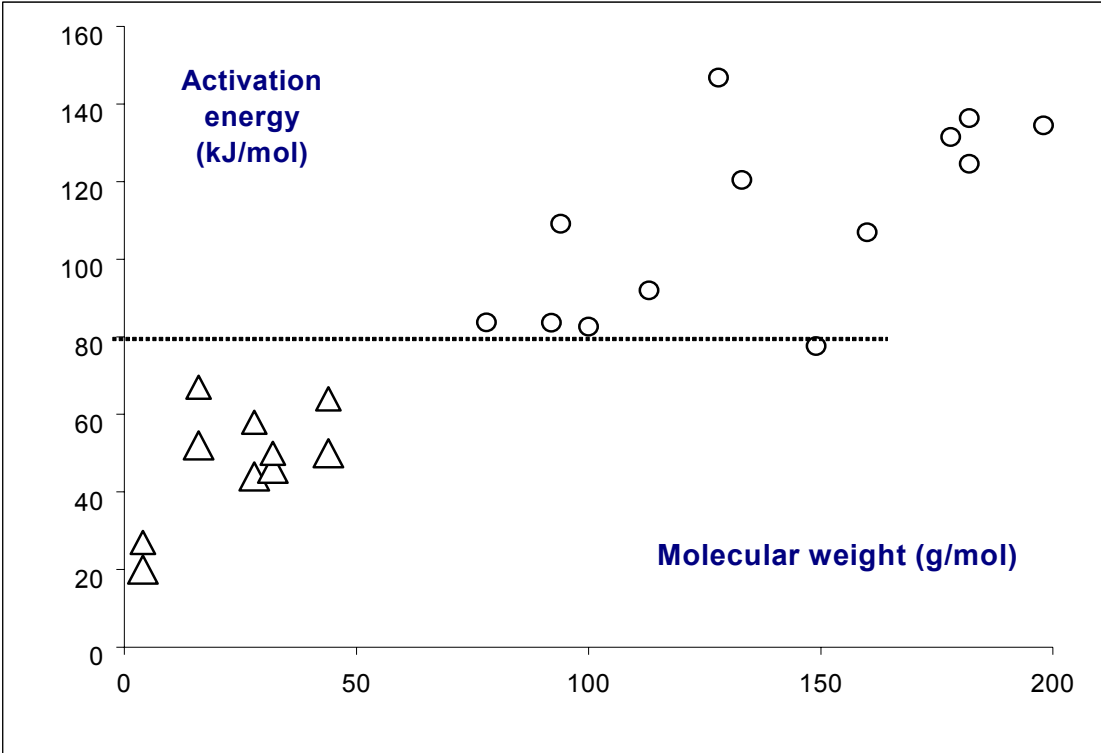Figure 4: diffusion coefficients of DMA in melted polymers

3
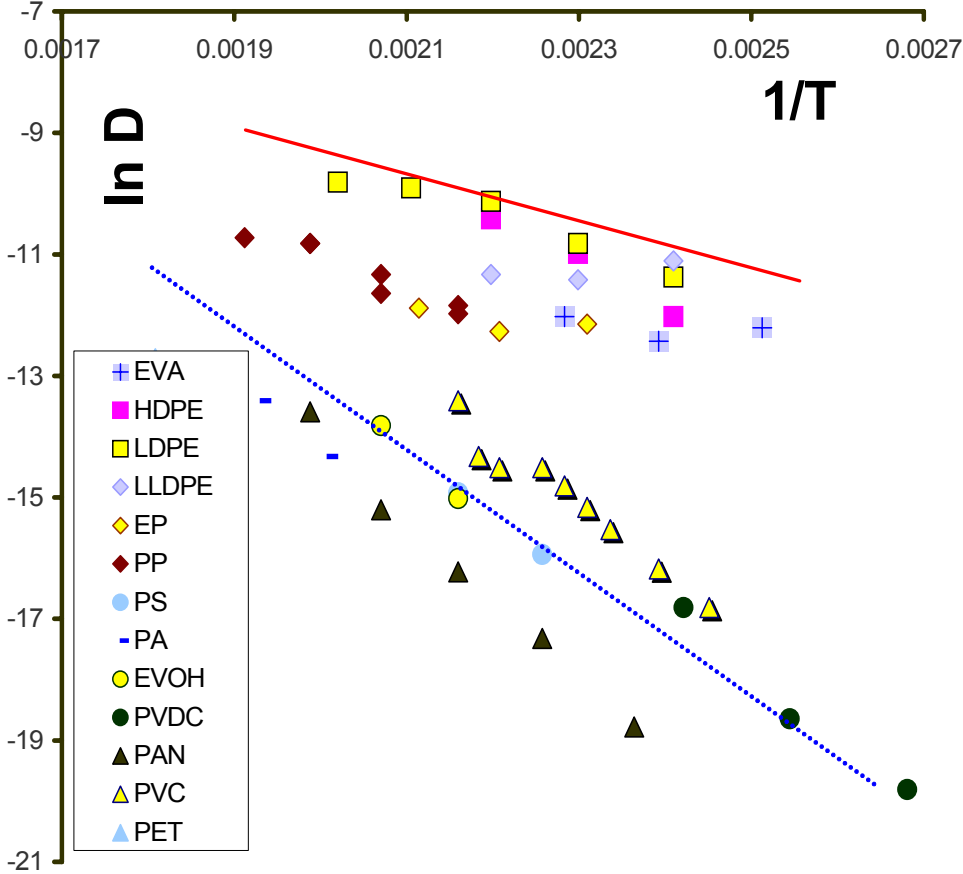
Figure 5: Activation energy of diffusion of gases and of surrogates in PET
(Δ: permanent gases, O: surrogates and additives)S