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Typical diffusion behaviour in packaging polymers – application to functional barriers

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[1]*INRA SquAlE, Reims, France,* [2]*Analytical Chemistry, Nutrition and Bromatology Department, Faculty of Pharmacy, University of Santiago de Compostela (USC), Spain,* [3]*Packaging Research Group, Analytical Sciences Division, TNO-Nutrition and Food Research Institute, Zeist, The Netherlands, and* [4]*Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Greece*

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Abstract
When plastics are collected for recycling, possibly contaminated articles might be recycled into food packaging, and thus the contaminants might subsequently migrate into the food. Multilayer functional barriers may be used to delay and to reduce such migration. The contribution of the work reported here is to establish reference values (at $40°C$) of diffusion coefficients and of activation energies to predict the functional barrier efficiency of a broad range of polymers (polyolefins, polystyrene, polyamide, PVC, PET, PVDC, [ethylene vinyl alcohol copolymer], polyacrylonitrile and [ethylene vinyl acetate copolymer]). Diffusion coefficients (D) and activation energies (Ea) were measured and were compiled together with literature data. This allowed identification of new trends for the $\log D = f$(molecular weight) relationships. The slopes were a function of the barrier efficiency of the polymer and temperature. The apparent activation energy of diffusion displayed two domains of variation with molecular weight (M). For low M (gases), there was little variation of Ea. Focusing on larger molecules, high barrier polymers displayed a larger dependence of Ea with M. The apparent activation energy decreased with T. These results suggest a discontinuity between rubbery and glassy polymers.

Keywords: *Surrogates, functional barrier, diffusion coefficient, activation energy, polymer, migration, recycling, packaging*

Introduction

Stimulated by new regulations, waste plastics are recycled. Since food packaging represents a large percentage of overall plastics consumption, and since they have a short lifetime, an important approach to minimizing waste consists in making new packaging from post-consumer used packaging materials.

In the European Union, all substances used in the manufacture of food packaging must be registered on positive lists of chemicals. However, in addition to the normal constituents of plastics, recycled plastics may be contaminated by chemicals (e.g., petrol, paints, urine etc) linked to consumer re-use and mis-use. How can a manufacturer ensure that such contaminants do not endanger public health, since they are not linked to a process and since they are unpredictable by nature? It is impossible to control the presence and the migration of substances whose identity and whose presence (or absence) are not known. In order to demonstrate that recycled articles are safe, several approaches are available.

Studies in USA (Bayer 2002) and in Europe (Franz et al. 2004) have focused on poly(ethylene terephthalate) (PET) bottles. Their target was to analyse extracts of a large number of post-consumer collected bottles (up to several thousands in each study). The substances identified were not harmful (mainly food aroma compounds); the concentrations detected in collected bottles were very low (highest values of a few tens of $mg\,kg^{-1}$ were reached in exceptional cases) that they were not likely to pose any health problem.

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Another approach for safety assessment consists in showing that the technological steps in the recycling processes are capable of efficiently removing contaminants, if they are present. Numerous papers have studied the removal of contaminants from PET during processes such as washing (Nielsen et al. 1997), depolymerization (Brandrup et al. 1996), post-condensation (Bayer 1997) or extrusion under reduced pressure (Franz & Welle 2002). Solid state post condensation is usually very efficient in removing contaminants.

One can also examine the potential extent of food contamination, if contaminants were not removed. This approach is used in the case of functional barriers. A functional barrier is a protective layer of virgin polymer placed between the recycled material and the food (Begley & Hollifield 1993, Laoubi & Vergnaud 1995, Feigenbaum et al. 1997, Piringer et al. 1998). Theoretically, during the time of diffusion in the functional barrier, no detectable diffusion occurs into the food.

To evaluate the ability of all these recycling routes to reduce migration below a given level, a double approach is usually necessary: (i) monitor the capacity of the recycling process to remove contaminants by testing surrogates in challenge tests, and (ii) correlate the residual level in plastics with the migration in food, using migration prediction. The surrogates of interest have a molecular weight higher than $80 \, \text{g mole}^{-1}$, as lower molecular weight compounds are removed by processing (Feigenbaum et al. 2005).

Hence the idea that predictive approaches should be more general and more useful. The use of migration models requires that reference diffusion coefficients and activation energies are available. Begley et al. (2005) have proposed and improved sets of empirical equations to provide overestimated values of the diffusion coefficient D from the molecular weight for some polymers. The approach is based on a compilation of literature data. The validation of the equations has been made by comparing experimental and predicted migration values.

Some activation energies are available in the literature for gases (from permeation tests) and for additives (from migration experiments). But surrogates are intermediate compounds and very few values are available. The contribution of this work is to establish experimentally reference values of diffusion coefficients and of activation energies of model contaminants (surrogates) for a broad range of polymers in the 20–70°C range. Diffusion coefficients of organic substances available in literature are generally obtained at high concentrations (e.g., by maceration of a polymer in a solvent), due to their high solubility in polymers. Such values are not useful for our purpose and reference values must be determined by dedicated methods. Diffusion

coefficients at low concentration were recently published for PET (Pennarun et al. 2004, Widen et al. 2004) and for polypropylene (Simal-Gandara et al. 2000a, 2000b). In this paper, the aim is to have a larger overview of surrogate diffusion behaviour in most polymers commonly used by packaging industry: LDPE (low density polyethylene), HDPE (high density polyethylene), LLDPE (linear low density polyethylene), PP (polypropylene), PS (polystyrene), PA (polyamide PA-6), PVC [poly(vinyl chloride)], PET [poly(ethylene terephtalate)], PVDC [poly (vinylidene chloride)], EVOH (ethylene vinyl alcool copolymer), PAN (polyacrylonitrile), EVA (ethylene vinyl acetate copolymer). The diffusion behaviour is studied at a reference temperature (40°C). The temperature effect is discussed separately in the second part of the paper.

Materials and methods

Materials

Polymers: All polymers were supplied by Cryovac (except non-plasticized PVC); HDPE: pellets and film; LDPE: pellets and film; LLDPE: pellets and film; PP: pellets and film; EPR: pellets; PVC plast: pellets and film; PVDC: pellets; EVOH: pellets and film; PA: pellets and film; PAN: pellets and film; PET: pellets; PS: pellets and film; EVA: pellets and film; PVC not plasticized: Powder (Dorlyl).

Surrogates: 1,1,1-trichloroethane; toluene; chlorobenzene; dimethylsulfoxide (DMSO); phenylcyclohexane; benzophenone; methyl heptadecanoate; 2,5-thiophenediylbis(5-*tert*-butyl-1,3-benzoxazole) (Uvitex from CIBA, named here TDBB); dimethoxyacetophenone (DMA).

Preparation of contaminated polymers

In earlier work it was shown that in order to obtain a good sensitivity for migration kinetics, a surrogate concentration around $1000 \, \text{mg kg}^{-1}$ in plastics was necessary (Pennarun et al. 2005). This 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 ($1000 \, \text{mg kg}^{-1}$ is reasonable even for glassy polymers, with 2 or 3 surrogates in the same sample. The detailed procedure has been reported (Papaspyrides et al. 2005).

Methods

To measure the diffusion coefficient D, the general philosophy was to avoid whenever possible a diffusion test involving contact with a liquid: (i) because of possible errors which would minimize 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 only when the partition coefficient ($K_{P/L}$) 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 functional barrier.

A test designed by Moisan (1980) has now become a classical test to measure diffusion coefficients. It is based on the measurement of a concentration gradient in a stack of virgin films after a given time of contact with a source of polyethylene wax spiked with surrogates. A homogeneous solid source is obtained by melting PE wax together with the surrogates (representing the contaminants) in an appropriate mould. Usual final concentrations of surrogates in the source are about $1000 \, \mathrm{mg \, kg^{-1}}$.

The stack of films of the polymer to be tested (of known thickness) is obtained under the action of both temperature and pressure. It is essential to check visually that there is an intimate contact between the different films of the stack and that no air bubbles remain, as this could introduce important errors. Source and stack are assembled under slight pressure to get a good contact between them, and are stored at a known temperature ($40°C$ in this project). During the contact, surrogates diffuse from the source into the stack, through the films. In order to obtain a good estimation of D, the diffusing molecules should reach at least film number ten, but not the last film. The diffusion is stopped at a given time (in general determined by preliminary experiments, or estimated through calculation, using correlation of D with molecular weight

of surrogates). Then each film is separated from the stack and extracted with an appropriate solvent, depending on both the polymer and the surrogates (usually extraction is carried out with dichloromethane, at $40°C$ for 1 day). Finally surrogates are determined quantitatively by an appropriate analytical method, usually by GC or HPLC techniques.

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 et al. 2002). The main problem is that when diffusion is slow (e.g. in an efficient barrier), surrogates do not even reach the second layer of the stack within a reasonable time. Therefore, in principle, the test is not appropriate for good functional barriers.

Three-layer test. This has been developed to measure low diffusion coefficients. It consists in superimposing three films (Figure 1), an inner virgin layer and two outer contaminated layers. As in the Moisan test, an intimate contact between layers is achieved by applying a slight pressure and heat. Diffusion into the inner film is monitored by extraction and quantification of surrogates at several contact times. The equilibrium will be reached with 66% of the initial concentration ($Q2/Q1 + Q2 + Q3 = 0.33$), as films (1), (2) and (3) are assumed to be identical. Thus it is not necessary to carry out the test until equilibrium, which is an advantage for high barrier polymers. Modelling the diffusion kinetics obtained allowed an estimation of the diffusion coefficient.
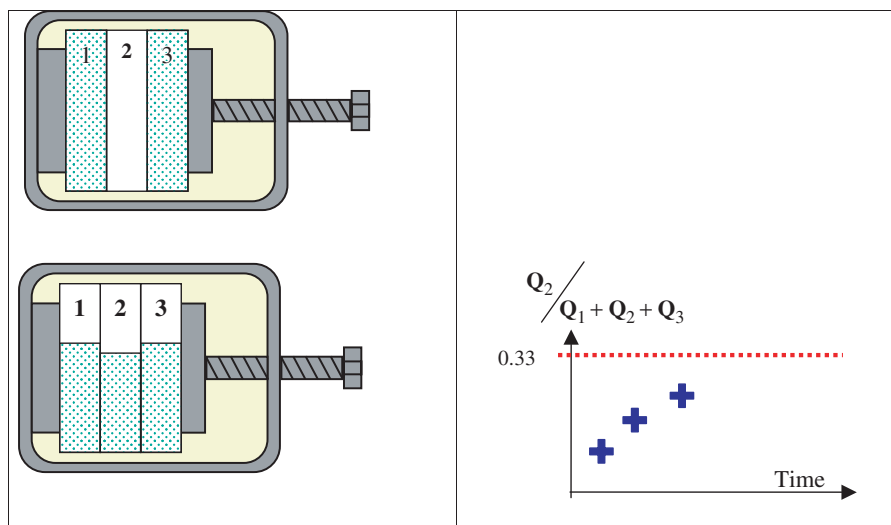

Figure 1. Principle of solid-solid three-layer test and of obtaining D (initial conditions: C/V/C).

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Results

Mutual influence of surrogates

In order to check the effect of the mutual influence of surrogates in the diffusion process, diffusion coefficients of TDBB, benzophenone, methyl margarinate and phenylcyclohexane were measured from two different types of experiments: (i) when the four surrogates are together in the polymer, and (ii) when each surrogate is incorporated separately. The results obtained (Table I) suggest that the diffusion of the largest surrogate, and only of this one, TDBB, is accelerated by the presence of another surrogate by more than two orders of magnitude. There is no detectable influence on the other surrogates.

This is consistent with knowledge on plasticizing effects of rubbery polymers: Only the largest molecules (i.e., those which would not migrate in absence of plasticization) are affected by plasticization effects (Reynier et al. 2001a). In this work, we were interested to identify worst case situations in order to predict migration with a margin of safety. However such mutual plasticization effects are not relevant as in practice, only two types of situations are likely to occur:

- Any type of contaminant may be present. In this case, the diffusion coefficient of small molecules (e.g., toluene) is a worst case. We have seen that the diffusion behaviour of small molecules is not influenced by plasticization through mutual influence.
- Polymers are purified to remove volatile molecules. In this case, a larger molecule is to be used as a worst case, but then plasticization by lower molecular weight (volatile) compounds is no longer possible.

Diffusion data at 40°C in rubbery (poor barriers) and in glassy (good barrier) polymers

Figure 2 shows the variation of experimental diffusion coefficients of the surrogates measured at 40°C, as a function of their molecular weight. A "Piringer like" correlation is observed, showing that molecular weight (M) and polymer type are important factors

influencing D in the range of low molecular weights studied. Effects of molecule geometry and of polymer-molecule interactions are of minor importance for these surrogates (see, for example, the comparison of plasticized PVC with HDPE, which behave similarly, despite very likely different specific interactions with surrogates).

For all glassy polymers, few D values are available, for two reasons: (i) the duration of the experiments is very long, while the most volatile surrogates (those of major interest for our purpose) may be lost, and (ii) the more polar polymers require a strict control of relative humidity over the whole experiment time. The Moisan test can therefore not be used with high barrier polymers. Two tests are then available: The three-layer test and migration experiments. In the latter case, it may be difficult (and sometimes not possible) to find a solvent which strictly does not interact with the polymer.

In the absence of interaction with food, food simulant or solvent, diffusing coefficients in high barrier (generally glassy) polymers depend, like in
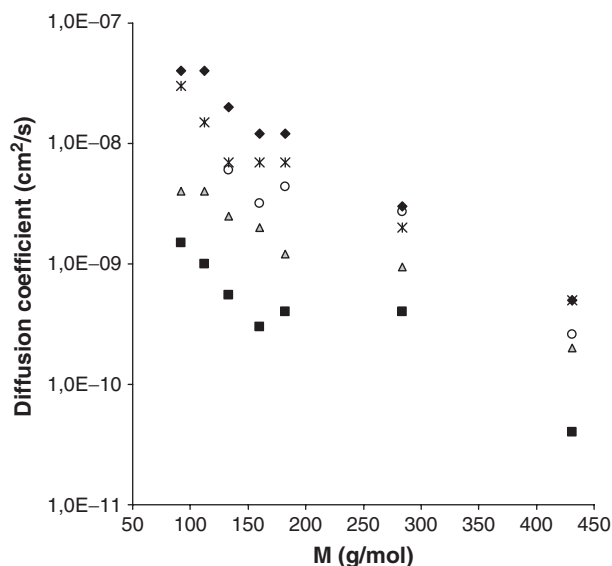

Figure 2. Variation of the diffusion coefficient with the molecular weight M of surrogates in HDPE ✶, LDPE ◆, plasticized PVC ◯, EP △, PP ■, at 40°C.

Table I. Mutual influence of surrogates on their diffusion coefficients ($cm^2 s^{-1}$) in PP 20 μm at 40°C.

Experiment	TDBB M: 430	Methyl margarinate M: 284.5	Benzophenone M: 182.2	Phenylcyclohexane M: 160.3
4 surrogates together	4.5E−10	1.7E−10	1.8E−10	2.6E−10
Each surrogate separately	9.2E−13	1.4E−10	Not determined	2.2E−10
TDBB/benzophenone	4.4E−12		3.0E−10	
TDBB/methyl margarinate	4.6E−12	2.4E−10		
TDBB/phenylcyclohexane	4.6E−12			1.6E−10

TDBB = 2,5-thiophenediylbis(5-*tert*-butyl-1,3-benzoxazole).

poor barriers, on the molecular weight and on the polymer type as main factors. However polymers which are glassy at room temperature display a marked effect of the molecular weight (the $D = f(M)$ correlation displays a larger slope) and of surrogate geometry (Pennarun et al. 2004) (see Figure 3).

To better illustrate these trends we show on Figure 4 a compilation of $D = f(M)$ data for a broad range of polymers. When available, only data from homologous series were selected for a given polymer; for other polymers where few data exist, they were all taken. $Log = f(M)$ correlations shown on Figures 4 and 5 are drawn manually (no mathematical background). The same shape was used for all the data, using a decreasing slope from (i) high to low temperature, (ii) from polyolefins to glassy polymers, (iii) from swollen to non swollen polymers.

Plasticization effects and barrier properties

Glassy polymers are much more sensitive to plasticization. In polyolefins, sorption of 2–3% of oil affects only the diffusion properties of ''higher'' ($>400\,\mathrm{g\,mol^{-1}}$) molecular weight diffusants (Reynier et al. 2001a). In contrast, sorption of 2.5% ethanol by PET and of 3% isopropanol by PS dramatically changes the diffusion behaviour of all surrogates. For PET, all diffusion coefficients are increased by 2–4 orders of magnitude (Pennarun et al. 2004). Similarly, for PS, migration kinetics of DMA, nonane and phenylbutane into isopropanol (fatty simulant recommended by De Kruijf and Rijk (1997)
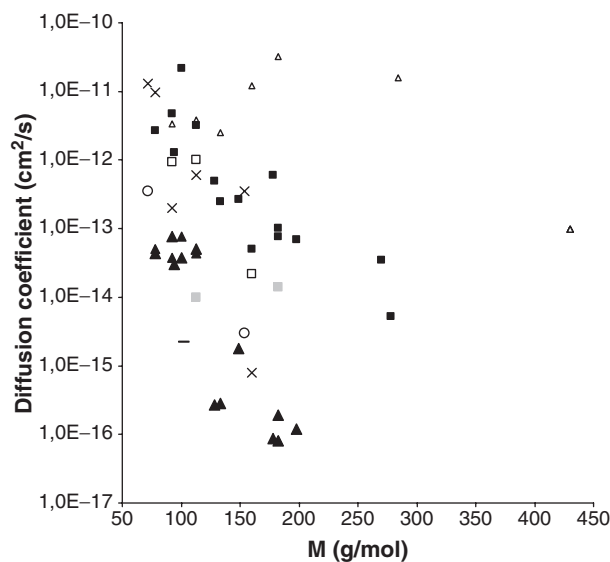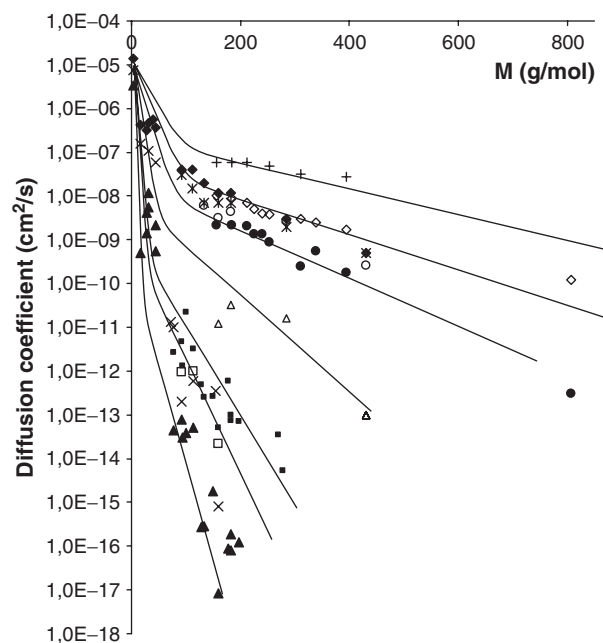

Figure 4. Variation of the diffusion coefficient with the molecular weight of surrogates in PVDC □, PA (at 60% relative humidity) △, PS ×, HDPE ✳, LDPE ◆, plasticized PVC ○, PET (dry conditions) ▲, PET (in contact with ethanol) ■, PP in contact with glyceryl tripelargonate ◇, PP ●, at 40°C. + PP at 70°C. Data from this work and literature data from: Reynier et al. (2001a, 2001b), Brandrup and Immergut (1989, p VI, 443), Pennarun et al. (2004), Flaconnèche et al. (2001).

Figure 3. Variation of the diffusion coefficient with the molecular weight of surrogates in PVDC □, EVOH (at 60% relative humidity) −, PA(at 60% relative humidity) △, PA (dry conditions) ■, PS ×, PET (dry conditions)▲, rigid PVC ○, PET (in contact with ethanol) ■ at 40°C.
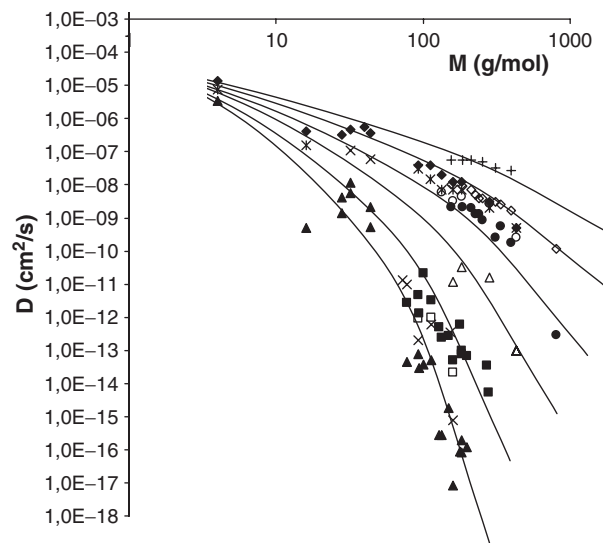

Figure 5. Variation of the diffusion coefficient with the molecular weight (logarithm scale) of surrogates in PVDC □, PA (at 60% relative humidity) △, PS ×, HDPE ✳, LDPE ◆, plasticized PVC ○, PET (dry conditions)▲, PET (in contact with ethanol) ■, PP in contact with glyceryl tripelargonate ◇, PP at 40°C, ●, + PP at 70°C. Data from this work, and literature data from: Reynier et al. (2001a, 2001b), Brandrup and Immergut (1989, p. VI, 443), Pennarun et al. (2004), Flaconnèche et al. (2001).

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were linear with time, indicating a process controlled by plasticization rather than by diffusion rate.

Polar PA and EVOH are highly sensitive to water. Diffusion data must be then given as a function of water content of the polymer and/or relative humidity of the atmosphere in contact. The corresponding data in Table II should be associated to large margin of errors, as it is difficult to control perfectly the water content during very long testing times.

PVC and PVDC were tested as received from the supplier. However it is important to underline that the behaviour of these two polymers is very dependant on their formulation, particularly their plasticizer content. This remark should explain the inconsistently low barrier properties observed with the PVDC samples used in the present study as it is known that it is a better barrier (to oxygen) than PVC.

This work provides sets of diffusion coefficients for a broad range of food packaging polymers. Values for rubbery polymers can be used as reference values for migration prediction. For glassy polymers the values obtained should be used with caution, for the following reasons: (i) intrinsic (in pure, dry polymer) diffusion coefficients are often difficult to obtain; (ii) data available may underestimate practical situations, because these polymers are sensitive to plasticization (atmospheric water, other additives, interaction with food) even at low concentrations.

Activation energy of D for surrogates

To be able to predict migration under various conditions, or to define accelerated test conditions, one needs reference D values (see above) associated to activation energies. Few values were available from this work for polyamide (benzophenone and chlorobenzene) and for polystyrene (phenylcyclohexane) (see Table III).

Figure 6 displays these values, together with a compilation of literature data from gas permeation measurements, diffusion tests and migration kinetics. The abscissa of molecular weight is shown on a log scale to better display the low molecular weights relevant for surrogates. Another way to express the variation of the activation energy is used in Figure 7, where Ea is plotted as a function of log D at reference temperature (40°C). The same kind of representations was used previously.

- The activation energy increases with the molecular weight of the diffusing substance.
- No distinction between polymers is apparent for the lowest molecular weight species (less than $100 \, \mathrm{g \, mol^{-1}}$). For high molecular weight compounds, for a given M, the best is the barrier, the higher is the activation energy (Ea higher in glassy polymers > polypropylene > LDPE). A change of regime is thus observed near $100 \, \mathrm{g \, mol^{-1}}$, suggesting a change of diffusion mechanism. The same change was observed on the D = f(M) relation in Figures 4 and 5. The fact that the activation energy seems mainly to depend on the molecule may suggest a mechanism depending on the intrinsic mobility of the migrant, whereas for higher molecular weight substances, the polymer mobility becomes influent.
- The later observations led us to test whether the activation energy was a direct function of the mobility expressed by a reference diffusion coefficient (D at 40°C), or of the preexponential factor of D as proposed by Koros (1990) and more recently by Klopffer and Flaconnèche (2001). The correlations look better on Figure 7 than on Figure 6 because molecular weight is a poor molecule descriptor, which does not take into account the effect of geometry on diffusion (Reynier et al. 2001a, 2001b); moreover as observed by several authors, rubbery and glassy polymers are separated.

On the other hand, the representation of Figure 7 displays for all polymers a transition around $80 \, \mathrm{kJ \, mol^{-1}}$, at the same energy value as observed in Figure 6 (corresponding nearly to 80–$100 \, \mathrm{g \, mol^{-1}}$). This means that the correlation with molecular weight is nevertheless relevant. The low molecular weight surrogates, which have an M close to this change of regime between gases and organic products, have an activation energy close to $80 \, \mathrm{kJ \, mol^{-1}}$, whatever the polymer. This is why we suggest below, that for regulatory purpose, the value $80 \, \mathrm{kJ \, mol^{-1}}$ should be used as a worst-case underestimation of the activation energy.

Higher molecular weight compounds have a more complex behaviour. A constant activation energy is not possible: If Ea was constant with T, as Ea increases with M (Figure 6), D would become an increasing function of M at high temperature, which is obviously not possible. The apparent Ea is also supposed to decrease with temperature. This means that in Figure 4, Ea is expected to have an overall decrease from the bottom to the top. However, as glassy polymers are less activated for a given log D (Figure 7), a monotonous decrease of Ea with temperature is not possible. Two types of apparent Ea = f(T) decreasing relationships should be expected, one for glassy polymers, the other for rubbery polymers. No data are available in the glass transition region for intermediate behaviour.

In the literature, data showing D variation with temperature are available for gases: but as we have

Table II. Reference diffusion coefficients ($cm^2\ s^{-1}$) of surrogates at 40°C in all polymers studied.

Polymer	Trichloroethane	Toluene	Chlorobenzene	DMSO	Phenylcyclohexane	Benzophenone	Me Margarinate	Uvitex	Other data
HDPE	2.4×10^{-9} (a)	8.5×10^{-9} (a)	8.9×10^{-9} (a)		3.9×10^{-9} (a)	4.3×10^{-9} (a)	2.1×10^{-9} (a)	0.2×10^{-9} (a)	
	2×10^{-9} (d)	8×10^{-9} (d)	15×10^{-9} (d)		7×10^{-9} (d)	7×10^{-9} (d)	2×10^{-9} (d)	0.5×10^{-9} (d)	
LDPE	20×10^{-9} (d)	40×10^{-9} (d)	40×10^{-9} (d)		21×10^{-9} (a)	33×10^{-9} (a)	5.8×10^{-9} (a)	0.32×10^{-9} (a)	
					12×10^{-9} (d)	12×10^{-9} (d)	3×10^{-9} (d)	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)	2.4×10^{-9} (a)	2.6×10^{-9} (a)		0.27×10^{-9} (a)	0.18×10^{-9} (a)	0.17×10^{-9} (a)	0.012×10^{-9} (a)	
	0.36×10^{-9} (c)	0.94×10^{-9} (c)	0.24×10^{-9} (c)		0.55×10^{-9} (c)	0.49×10^{-9} (c)	0.83×10^{-9} (c)	0.046×10^{-9} (a)	
	0.55×10^{-9} (d)	1.5×10^{-9} (d)	1.2×10^{-9} (d)		0.4×10^{-9} (d)	0.47×10^{-9} (d)	0.47×10^{-9} (d)	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)	$0.26–0.3 \times 10^{-9}$ (a)	
EVA	$>10 \times 10^{-9}$ (a)	$>10 \times 10^{-9}$ (a)	$>10 \times 10^{-9}$ (a)		45×10^{-9} (a)	30×10^{-9} (a)	15×10^{-9} (a)	1.8×10^{-9} (a)	
PVDC		$9/5 \times 10^{-13}$ (b)	10×10^{-13} (b)		0.22×10^{-13} (b)				
EVOH 60% rh						12×10^{-11} (a)	$40–90 \times 10^{-11}$ (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; (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); *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.

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Table III. Diffusion coefficients of surrogates in glassy polymers at different temperatures.

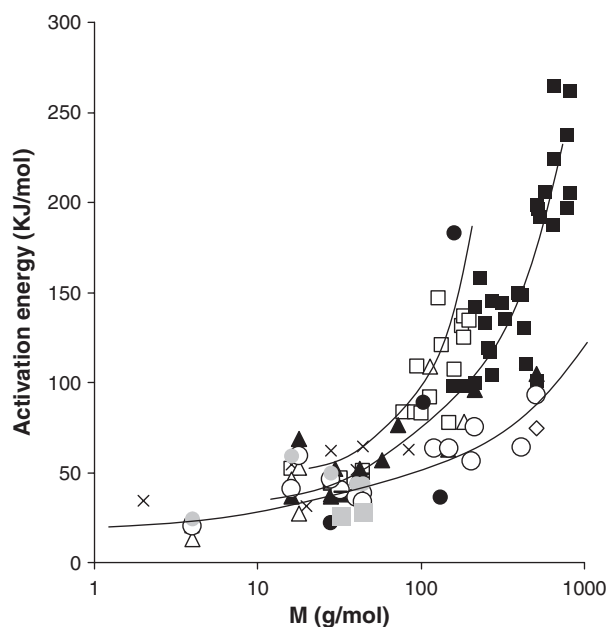| T (°C)	PA dry			PS		
	Chlorobenzene	Phenylcyclohexane	Benzophenone	Phenylcyclohexane	Chlorobenzene	Toluene
40	1×10^{-14} cm^2 s^{-1}		1.4×10^{-14}	8×10^{-16}	6×10^{-13}	2×10^{-13}
55	3.3×10^{-14}	6×10^{-15}	4.0×10^{-14}	2×10^{-14}	$>5 \times 10^{-12}$	$>5 \times 10^{-12}$
70	4×10^{-13}		2.0×10^{-13}	$>5 \times 10^{-12}$	$>5 \times 10^{-12}$	$>5 \times 10^{-12}$

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Figure 6. Variation of E$_D$ (activation energy of the diffusion coefficient near 40°C) as a function of molecular weight of diffusant in PET □, PP ■, HDPE ▲, PVC ×, PA △, PS ●, LDPE ○, LLDPE ◇, Polymethylene oxyde −, polytetrafluoroethylene ■, polyvinylidene fluorure ●. Data from this work, and literature data from: Reynier et al. (2001a), Brandrup and Immergut (1989, p VI, 443), Simpson et al. (1996), Tochin and Sapozhnikov (1974), Quijada-Garrido et al. (1996), Kozhanov et al. (1978), Westlake and Johnson (1975), Hedenqvist and Gedde (1996), Lu and Weiss (1994), Dudler (1993), Pennarun et al. (2004).

shown in Figures 4 and 5, the diffusion mechanism is certainly different for molecular weights higher than $100\,\mathrm{g\,mol^{-1}}$. Some data show non-linear Arrhenius correlations for the diffusion coefficient (apparent Ea decreasing with temperature) in the glassy state, following the free volume model (Begley & Hollifield 1990, Koros & Hopfenberg 1979), but no data are available for large molecules in a wide temperature domain (covering glassy and rubbery states).

We have shown here that: (i) the variation of the apparent activation energy of diffusion with M displays two domains corresponding possibly to two mechanisms. In the first domain (gases) there is little variation of Ea with M, with the polymer and with log $D_{40°C}$, whereas with larger molecules (second domain), high barrier polymers displays a larger dependence of Ea with M, and (ii) the apparent

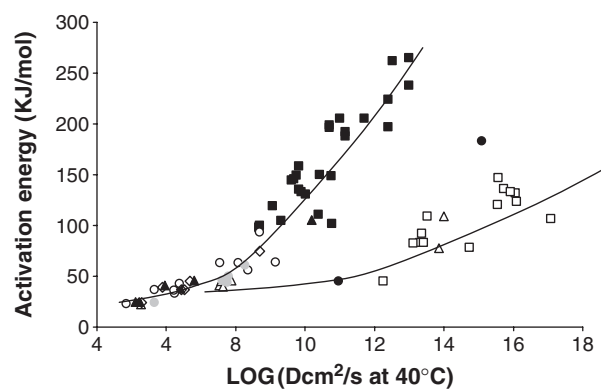Figure 7. Variation of ED as a function of diffusion coefficient at 40°C in PET □, PP ■, HDPE ▲, PA △, PS ●, LDPE ○, LLDPE ◇, polyvinylidene fluorure ●. Data from this work, and literature data from Reynier et al. (2001a), Brandrup and Immergut (1989, p VI, 443), Simpson et al. (1996), Tochin and Sapozhnikov (1974), Quijada-Garrido et al. (1996), Kozhanov et al. (1978), Westlake and Johnson (1975), Hedenqvist and Gedde (1996), Lu and Weiss (1994), Dudler (1993), Pennarun et al. (2004).

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activation energy decreases with T, possibly with a discontinuity between rubbery and glassy polymers. Further studies are necessary to confirm the existence of this discontinuity.

Data are missing (i) to describe the Ea variation within the glass transition region, and (ii) to take into account other variables controlling the activation (e.g., solubility parameters, Vrentas & Vrentas 1998).

Conclusions

The objectives of the work were to establish a reference, worst-case value of D for each polymer, and a reference activation energy.

- Giving reference diffusion coefficients is possible for each polymer as D is mainly a function of the molecular weight (Figures 2 and 3). Two sets of values should be distinguished (see Table IV), depending on whether the polymer is submitted or not to a devolatilization step. For polyolefins, the D values of the most volatile species (trichloroethane, toluene, chlorobenzene) are so large that migration should be high in any situation. A devolatilization step could therefore

Table IV. Worst-case diffusion coefficients at 40 and at 25°C to be used for functional barrier efficiency prediction.

Polymer	Worst-case $D_{40°C}$	Worst-case $D_{25°C}$★
HDPE (1)	7.00×10^{-9}	1.49×10^{-9}
LDPE (1)	3.30×10^{-8}	7.02×10^{-9}
LLDPE (1)	7.00×10^{-9}	1.49×10^{-9}
PP (1)	5.50×10^{-10}	1.17×10^{-10}
EP (1)	9.50×10^{-9}	2.02×10^{-9}
PVC plast (1)	4.40×10^{-9}	9.36×10^{-10}
EVA (1)	4.50×10^{-8}	9.57×10^{-9}
EVOH 60% (1)	2.30×10^{-10}	4.89×10^{-11}
PVDC (2)	1.00×10^{-12}	2.13×10^{-13}
PA 60% hr (2)	3.60×10^{-12}	7.66×10^{-13}
PA dry (2)	1.00×10^{-14}	2.13×10^{-15}
PET dry (2)	7.70×10^{-14}	1.64×10^{-14}
PET contact w. water	2.00×10^{-13}	4.26×10^{-14}
PS (2)	6.00×10^{-13}	1.28×10^{-13}
PVC rigid (2)	3.50×10^{-13}	7.45×10^{-14}
PMMA (2)	1.30×10^{-14}	2.77×10^{-15}

(1) Poor barriers; the worst-case D has been selected from the non-volatile surrogates, assuming that the polymers cannot be used as barrier layers without a devolatilization step;
(2) Good barriers, the worst-case D has been selected, assuming that they can be used without devolatilization;
★$D_{25°C} = D_{40°C}/4.7$ (using the worst-case activation energy 80 kJ mole^{-1}).

be useful. If the process includes such a pre-treatment, the worst-case diffusion coefficient should be that of a higher molecular weight surrogate, ranging from phenylcyclohexane to TDBB. The largest of these values in each row of Table II is introduced in Table IV. For the glassy polymers, no such assumption on a pre-treatment is needed, and the lowest diffusion coefficient in each row of Table II is taken as reference value in Table IV.

• Giving an 80 kJ mol^{-1} reference activation energy is possible for two reasons: (i) the reference Ea must be an underestimated value in order to extrapolate worst-case diffusion coefficients from high test temperature to a lower storage temperature, and (ii) the apparent Ea value is roughly independent on the nature of the polymer for low molecular weight reference surrogates.

Currently worst-case diffusion coefficients D* are calculated according to the Piringer equation (Equation 1) (Begley et al. 2005):

$$\log D^* = a \log A'_P - b(M)^{2/3} + c(M) - d/T \quad (1)$$

where each polymer corresponds to a different set of A'p and d constants. In this work, we confirm that for a given polymer, D* depends mainly on the molecular weight. Equation 1 leads to parallel log D = f(M) curves for different polymers. This is indeed observed for polyolefins (Figure 2), but for other polymers, Figures 4 and 5 display very different

experimental log D = f(M) slopes, increasing with the barrier efficiency. More generally, this slope is also a function of temperature and swelling: b and c should therefore be functions of A'$_p$ (the higher the barrier, the higher the log D = f(M) slope), of T and of swelling. Moreover, d, which refers to an activation energy, should be a function of M and of the polymer (A'$_p$).

This work provides a new view of diffusion behaviour in polymers as many data in a large range of polymers and molecular weight could be compiled. More data are needed at different temperatures to better investigate the activation mechanisms.

The following paper will illustrate practical consequences on functional barriers for recycled materials.

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