Functional Barriers in PET Recycled Bottles. Part I. Determination of Diffusion Coefficients in Bioriented PET with and Without Contact with Food Simulants

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ABSTRACT: A major outcome for recycled plastics consists of making food packaging materials. However, any contamination of collected plastics with chemicals may then be of concern for public health. A solution to mind migration is to use a layer of virgin polymer, named functional barrier, intercalated between the recycled layer and the food. This article aims to provide experimental values of diffusion coefficients (D) of model pollutants (surrogates) in poly(ethylene terephthalate) (PET) to be used for modeling migration through functional barriers. Diffusion coefficients of a large set of surrogates at low concentrations in PET were measured in various conditions. A solid-to-solid diffusion test was designed to avoid the use of a solvent that may induce plasticizing of the material and partitioning effects at the interface. Using [Log $D = f$(molecular weight)] correlations, the values of diffusion coefficients and activation energies of the surrogates measured by this method were shown to be consistent with the literature data obtained for gases, in permeation experiments, where no plasticization occurred. Migration from PET into food simulants was then studied. Migration into an aqueous medium is largely influenced by the solubility of the surrogates, the less soluble ones being not detected, despite high D values. With ethanol solvent, there were no partitioning effects, and the high plasticization effect of PET by ethanol considerably increases the apparent diffusion coefficients. The effects of temperature and plasticization on the relationship between diffusion coefficients and molecular weight are discussed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2845–2858, 2004

Key words: PET; diffusion of surrogates; functional barrier; modeling; food packaging; activation energy

INTRODUCTION

Recycling plastic waste has become a major issue in most developed countries. A good approach for postconsumer food packaging materials is to make new packages from old packages. However, this raises food safety considerations, because postconsumption collected packages may be polluted by common chemicals, available to households (detergents, petrol, garden herbicides, or pesticides, etc.). To prevent chemicals from contaminating foodstuffs packaged in the recycled plastics, the following two main routes are available: (1) the use of monolayer materials made from a recycling process that includes cleaning steps where contaminants of concern are removed; or (2) the use of multilayer structures, where the recycled layer is separated from the food by a layer of virgin polymer (functional barrier), which can reduce the migration of possible residual contaminants. Numerous articles have studied the elimination of contaminants during processes such as washing,[1] depolymerization,[2] postcondensation,[3] or extrusion under reduced pressure.[4] In these studies, surrogate contaminants are incorporated into the plastics, and their concentrations are monitored along the process.

The ability of functional barriers to prevent or reduce the migration of possible contaminants was discussed.[5–8] Functional barriers introduce a lag time to migration, and testing their efficiency to reduce migration requires that kinetic information is known. Hence, most articles agree that migration modeling should be used. The currently agreed approaches to predict migration from monolayer materials have not been extended to multilayer structures. In addition, if a predictive approach is used, there is a need of reference diffusion coefficients to be introduced in the calculations. Many data have been published for elastomeric polymers, but only few data exist for glassy polymers, which are of major interest as functional barriers.

With monolayers, the migration rate is a function of the initial pollutant content,[9] and the purification efficiency of the process can be related to a maximum tolerable pollution level in the feedstock[10] as well as to a tolerable level in food. This upper-bound migration level can be calculated through migration modeling.[6,8,11–17]

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Migration modeling requires knowledge of the following parameters:

- Initial pollutant concentration: This can be given by the usual purity specifications of the recycling industry; alternatively, average values can be determined from studies on real recycled materials.[10]
- Partition coefficient of the potential contaminant between food and packaging: It must be overestimated; generally total migration or equipartition ($K = 1$) are assumed.
- The diffusion coefficient, D: In recent years, Piringer et al.[18] have proposed and improved a set of empirical equations to provide overestimated values of D. The general approach is to correlate D and the molecular weight. Such values are not available for poly(ethylene terephthalate) (PET).
- The initial distribution of contaminant in the material[19,20]: This point is especially important when the recycled material is used with a functional barrier. During processing (coextrusion or coinjection), the contaminant may diffuse into the functional barrier, which is then more or less polluted already when the package is set in contact with the food.

The contribution of this work is to establish reference values of diffusion coefficients of model pollutants (surrogates) in PET. In further articles, we demonstrate by experiments and modeling that no detectable diffusion occurs during coinjection of PET preforms. In our last article, we will apply reference data to migration overestimation and propose a model for safety assessment.

The determination of diffusion coefficients in PET is not easy because of (1) its high barrier properties, which require very long experiment times and (2) the dependence of diffusion coefficients with concentration. Miltz et al.[21] determined diffusion coefficients in PET in contact with pure liquids (toluene, benzyl alcohol). They emphasized that their values had to be considered as upper limits for diffusion coefficients in PET, because pure liquids have a high solubility and plasticize the polymer matrix. Bove et al.[22] studied the variation of dichloromethane diffusion coefficient in PET as a function of its concentration. Sadler et al.[12] studied the diffusion properties of benzene. In both cases, 5 to 7 orders of magnitude are observed between diffusion coefficients measured at high concentrations of the liquid in PET and values extrapolated to a zero concentration. The diffusion properties of PET, which is glassy at room temperature, are expected to be strongly influenced by the liquid (solvent or food simulant) in contact, as well as by the nature and the concentration of the surrogates.

High, unrealistic levels of contamination are achieved to obtain measurable migration levels, to monitor kinetics, and to determine parameters controlling the migration. These parameters then can be used with mathematical models to predict the behavior of the material over its desired shelf life and to establish the requirements in order that the migration remains below a tolerable level.

In this work, to measure their diffusion properties in PET, the model contaminants were introduced in PET at low concentrations. To determine the possible influence of the solvents, we measured diffusion coefficients in different conditions of contact (solid/solid contact and solid/liquid contacts). We evaluated the influence of water and ethanol on the diffusion properties.

EXPERIMENTAL

Materials

Surrogates

The model pollutants used in this work (Aldrich, Strasbourg, France) are presented in Table I. The selection of the surrogates was presented elsewhere.[9] The molecules of concern are those with low molecular weight, as higher molecular weight pollutants diffuse too slowly to migrate.

Model bottles

Three-layer (virgin/recycled-contaminated/virgin and virgin/virgin/virgin) and monolayer (only recycled-contaminated) PET bottles were manufactured by Amcor PET Packaging Recycling France (Dunkerque, France). The recycled-contaminated PET was impregnated with surrogates by immersing PET flakes with either one of three different groups of surrogates (see Table I) in dichloromethane. Dichloromethane was used as a carrying solvent, because it strongly plasticizes PET.[9] PET virgin flakes are soaked in dichloromethane solution of surrogates (concentration of surrogates between 0.5 and 5% in dichloromethane depending on the affinity of the pollutant with PET). Dichloromethane could be efficiently removed by allowing the PET to dry, first in air, then by using two conventional PET 3 h drying steps at 150°C (1% after the first drying step, determined by TGA). The residual level of dichloromethane was less than 800 ppm in preforms, estimated by assuming the same yield of evaporation as toluene, which is even less volatile. PET bottle physical properties were similar to those of bottles processed directly from virgin flakes: similar melt flow index (MFI), glass transition temperature, and modulus at room temperature. The concentrations of the surrogates in the recycled layer of the wall of PET bottles were adjusted in the range of 500-1500 ppm for each surrogate, to have measurable amounts migrating, and that kinetics can be monitored.

TABLE I
Surrogates Incorporated in PET, Their Limits of Detection in Water and Ethanol, and the Initial Concentration in Monolayer Bottles

Model substance (Group)	LOD in μg/l in ethanol	LOD in μg/l in AcOH/water 3%	Concentration in monolayer bottles (ppm)
1,1,1-Trichloroethane (A)	400	10	2690
Dimethyl sulfoxide (DMSO) (A)	120	—	1363
Methyl palmitate (A)	80	5	704
Benzophenone (A)	80	10	2910
Phenylcyclohexane (A)	50	5	1285
Ethyl hydrocinnamate (A)	80	5	587
Phenol (B)	20	10	2616
BHT (B)	20	2	872
Chlorobenzene (B)	130	5	1324
1-Chlorooctane (B)	100	5	1552
2,4-Pentanedione (C)	90	10	785
Azobenzene (C)	60	15	921
Nonane (C)	50	3	624
DBP (C)	50	5	533
Phenyl benzoate (C)	50	5	810
Toluene (C)	50	5	704

The total thickness of monolayer bottles was 280 μm. The total thickness of trilayer bottles was 220 μm. The average thickness of the functional barrier (internal virgin layer) was 60 μm; the average thickness of the external virgin layer was 100 μm, and the average thickness of the recycled layer was 60 μm. The functional barrier was not polluted after coinjections, as will be shown in the next article.

Model films for the determination of diffusion coefficients without contact with a solvent

Thin PET films were obtained by thermoforming. The objective of this operation is to obtain a very thin (around 10 μm) material which could be used in Moisan-type tests, and whose physical structure (orientation and crystallinity) would be as close as possible to that of the oriented bottle walls.

Films were made by thermoforming amorphous PET sheets (200 μm thick) with a ILLIG SB53c apparatus. PET sheets were heated 7 s under infrared lamps. After removing the lamps, the sheet was blown to the bottom of a cylindrical mold with a quick vacuum. Resulting bioriented PET films (taken at the bottom of the thermoformed box) were 90 mm in diameter and 10 ± 1 μm thick.

Methods

Evaluation of model films

Physical properties of thermoformed films and bioriented bottles were compared by thermal analysis.

Modulated differential scanning calorimetry. Measurements were run with an MDSC 2920 (TA Instruments). Nitrogen flow is 50 mL/min. Average heating rate is 5°C/min; the oscillation period is 60 s, and the amplitude is 0.796°C (heating only).

Shrinkage measurements. DMA 2980 (TA Instruments) was used in thermal mechanical analysis (TMA) mode. The length of the sample is measured for a temperature scan of 1°C/min from 0 to 300°C. A minimum force (0.010*N*) is applied to the sample to avoid being drawn.

In the bottles, because longitudinal and axial orientations are not identical, measurements were carried out in both the parallel and the perpendicular directions of bottle axes. In the films, measurements are done in two different perpendicular directions of the film. Results are expressed by the product of both shrinkage measurements; in that way, nonisotropic bottles can be compared directly to isotropic films.

Diffusion through PET model films (nonswollen PET)

The diffusion experiments were conducted at 40°C (temperature of most test conditions in the regulation for food contact materials) and at 60°C because the diffusion is too slow at 40°C to reach the equilibrium plateau in a reasonable time. Experiments consisted of alternating in a stack 40 virgin thin films (model virgin films, 10 μm thick) and 40 contaminated thick plates (from the walls of contaminated monolayer bottles, 280 μm). At given times, a plate and a film were removed, and the concentrations of the surrogates in the plate and the film were determined. The diffusion coefficients of the surrogates were then calculated from the fit of experimental kinetics of film contamination.

Because the concentration at equilibrium is known in advance, it is not necessary to wait very long for

equilibrium: because the virgin films and polluted bottles have the same physical properties, it can be assumed that an identical concentration of each surrogate in the films and in the plates is reached at equilibrium.

Circular virgin PET films (27 mm diameter, thickness L_2 = 10 μm) and polluted plates that were cut from monolayer bottles (L_1 = 280 μm) were placed alternatively in a hermetically sealed copper cylinder (40 pieces of each). This stack was homogeneously pressed at 40 or 60°C. At given times, a plate and a film were removed from the stack, and the film was extracted for 12 h with 70 μL dichloromethane containing 15 mg/L of tetradecane (internal standard).

Surrogates in extracts were quantified by injection of 2 μL in GC-flame ionization detector (FID) (Fisons Instruments GC 8160) with a split/splitless injection technique. Injector temperature was 250°C. Splitless time was 15 s and flow was 20 mL/min. The column is a DB5-MS J&W Scientific (15 m × 0.32 mm × 1 μm). Carrier gas (He) flow was 2 mL/min at 40°C. FID temperature was 320°C; H_2 and air flows were 25 and 250 mL/min, respectively.

Oven program for surrogate group A (Table I) was conducted as follows: 40°C for 4 min, ramp 15°C/min to 132°C, isotherm for 6 min, 15°C/min until 270°C and isotherm for 3 min.

Oven program for surrogate group B (Table I) was carried out as follows: 40°C for 4 min, ramp 10°C/min to 145°C, 15°C/min to 200°C, 30°C/min to 320°C, and isotherm for 13 min.

Oven program for surrogates group C (Table I) was as follows: 40°C for 8 min, ramp 15°C/min to 170°C, 2°C/min to 180°C, ramp 15°C/min to 240°C, and isotherm for 2 min.

Sorption test in PET model films (swollen PET)

Virgin PET films (27 mm diameter; model films prepared by thermoforming as described above) were sorbed by immersion in ethanol at 40°C until a constant weight was attained (15 days to reach equilibrium). These films were then placed in surrogate solutions containing 1% of each surrogate (three batches were done in correspondence to surrogate groups A, B, and C) in ethanol. The concentration used for UVITEX was the lowest (0.4%) because of its limited solubility in ethanol. At given times, films were then extracted and analyzed by GC as described above.

Migration into an aqueous simulant from model bottles

Acetic acid/water (3% w/v) is used as a food simulant. Ultrapure water and acetic acid Normapur for analysis (PROLABO) was used. Each PET bottle was filled with 1.5 L of the simulant and subsequently placed in an oven at 40°C. Each bottle gives only a single migration measurement at any time t.

Samples of 75 mL were neutralized with 10M sodium hydroxide. Twenty grams of sodium chloride were added into the mixtures and the solution was extracted 12 h in a closed vial with 3 mL dichloromethane containing 50 mg/L tetradecane. Extraction tests showed that recovery rate of every surrogate was close to 100% except for DMSO (0%), 2,4-pentanedione (66%), and phenol (33%).

Extracts were analyzed directly on-column by GC-FID as follows.

1,1,1-Trichloroethane, phenylcyclohexane. The column was a DB5-MS J&W Scientific (15 m × 0.32 mm × 1 μm). Carrier gas (He) flow rate was 2 mL/min at 40°C. FID temperature was 300°C; H_2 and air flows were 25 and 250 mL/min, respectively. The oven temperature program was as follows: 40°C for 4 min, ramping 15°C/min to 132°C, isotherm for 6 min, heating 15°C/min until 270°C, and isotherm for 3 min.

Dimethyl sulfoxide, methyl palmitate, benzophenone, ethyl hydrocinnamate. The column was a DB-WAX J&W Scientific (30 m × 0.25 mm × 0.25 μm). Carrier gas (He) flow was 1.8 mL/min at 40°C. FID temperature was 240°C; H_2 and air flows were 25 and 250 mL/min, respectively. The oven program was as follows: 40°C for 5 min, ramp 15°C/min to 230°C, isotherm for 3 min.

BHT, Uvitex OB. The column was a DB5-MS J&W Scientific (15 m × 0.32 mm × 1 μm). The carrier gas (He) flow was 2 mL/min at 40°C. FID temperature was 330°C; H_2 and air flows were 25 and 250 mL/min, respectively. The oven program was as follows: 40°C for 5 min, ramp 15°C/min to 320°C, isotherm for 11 min.

Phenol, chlorobenzene, 1-chlorooctane. The column was a DB-WAX J& Scientific (30 m × 0.25 mm × 0.25 μm). Carrier gas (He) flow was 1.8 mL/min at 40°C. FID temperature was 240°C; H_2 and air flows were 25 and 250 mL/min, respectively. The oven program was as follows: 40°C for 5 min, ramping 15°C/min to 210°C, isotherm for 3 min.

Azobenzene, Nonane. The column was a DB5-MS J&W Scientific (15 m × 0.32 mm × 1 μm). Carrier gas (He) flow was 2 mL/min at 40°C. FID temperature was 300°C; H_2 and air flows were 25 and 250 mL/min, respectively. The oven temperature was as follows: 40°C for 8 min, ramping 15°C/min to 170°C, ramp 2 to 180°C, ramping 15°C/min to 240°C, isotherm for 2 min.

2,4-Pentanedione, DBP, phenyl benzoate, toluene. The column was a DB-WAX J&W Scientific (30 m × 0.25 mm × 0.25 μm). Carrier gas (He) flow was 1.8 mL/min at 40°C. FID temperature was 240°C; H_2 and air flows were 25 and 250 mL/min, respectively. The oven program was as follows: 40°C for 4 min, ramping 15°C/min to 230°C, isotherm for 4 min.

Migration into ethanol from model bottles

Absolute ethanol (pure for analysis, SDS) was used as a simulant and as a moderate plasticizing liquid. Each bottle was filled with 1.5 L of simulant and placed at 40°C. Aliquots (10 mL) were regularly taken from bottles. Each bottle gave only a single migration measurement at any time t (each data point was taken from a different bottle).

Ethanol (100 μL) containing 1527 g/L of tetradecane as an internal standard was added to the aliquots. Samples (6 μL) were analyzed by GC-FID with split/splitless injection technique (splitless time was 20 s and flow was 20 mL/min) as follows.

1,1,1-Trichloroethane. The column was a DB1-MS J&W Scientific (15 m × 0.53 mm × 5 μm). Carrier gas (He) flow was 2 mL/min at 40°C. Injector temperature was 230°C; FID was temperature 280°C, and H_2 and air flows were 25 and 250 mL/min, respectively. The oven program was as follows: 70°C for 5 min, ramp 25°C/min to 280°C, isotherm for 7 min.

Dimethyl sulfoxide, methyl palmitate, benzophenone, ethyl hydrocinnamate, phenylcyclohexane. The column was a DB-WAX J&W Scientific (30 m × 0.25 mm × 0.25 μm). Carrier gas (He) flow was 1.8 mL/min at 40°C. Injector temperature was 220°C; FID temperature was 240°C, and H_2 and air flows were 25 and 250 mL/min, respectively. The oven program was as follows: 70°C for 5 min, ramp 15°C/min to 230°C, isotherm for 6 min.

Phenol, chlorobenzene, 1-chlorooctane, BHT. The column was a DB-WAX J&W Scientific (30 m × 0.25 mm × 0.25 μm). Carrier gas (He) flow was 1.8 mL/min at 40°C. Injector temperature was 220°C; FID temperature was 240°C, and H_2 and air flows were 25 and 250 mL/min, respectively. The oven program was as follows: 70°C for 5 min, ramp 15°C/min to 230°C, isotherm for 6 min.

Nonane, 2,4-pentanedione, toluene. The column was a DB1-MS J&W Scientific (15 m × 0.53 mm × 5 μm). Carrier gas (He) flow was 2 mL/min at 40°C. Injector temperature was 230°C; FID temperature was 280°C, and H_2 and air flows were 25 and 250 mL/min, respectively. The oven program was as follows: 70°C for 6 min, ramp 25°C/min to 280°C, isotherm for 7 min.

DBP, phenyl benzoate, azobenzene. The column was a DB-WAX J&W Scientific (30 m × 0.25 mm × 0.25 μm). Carrier gas (He) flow was 1.8 mL/min at 40°C. Injector temperature was 230°C; FID temperature was 240°C, and H_2 and air flows were 25 and 250 mL/min, respectively. The oven program was as follows: 70°C for 5 min, ramp 25°C/min to 230°C, isotherm for 7 min.

Numerical treatments of migration and diffusion data

The numerical methods and assumptions have been presented in a previous article.[16] An easy freeware is available on INRA web site ("MULTIWISE"). (INRA 2001 Multiwise program can be downloaded on the INRA web site at: http://www.inra.fr/Internet/Produits/securite-emballage.) Assuming liquid contact or not, three-layer or monolayer structure, initial pollution outside or inside the polymer, presence/absence or progressive sorption of plasticizing agent, all the geometries tested in this work can be exploited by the freeware to calculate diffusion coefficients.

Taking into account experimental errors and scatter of experimental values, diffusion coefficients were obtained with a 50% uncertainty margin.

RESULTS AND DISCUSSION

During a migration experiment, the diffusion coefficient may increase progressively due to the interaction of the polymer with the food stimulant. To fit the experimental kinetics, it is necessary to determine the initial and the final values of the diffusion coefficients. To obtain reference diffusion coefficients in PET not plasticized by any solvent, we have produced very thin virgin PET model films, the thermomechanical properties of which are as close as possible to those of the wall of bottles. Diffusion kinetics are monitored in stacks of films to obtain the diffusivities in nonswollen PET. Next, diffusivities in fully swollen PET are determined taking into account these reference values.

Physical characterization of model films

A set of seven films with the appropriate thickness (10 ± 1 μm) was compared with commercial bottle properties by thermal analysis. Results are presented in Figures 1 and 2.

MDSC thermograms show that physical properties of films and commercial bottles are very similar (glass transition temperature, recrystallization during melting, melting temperature, shape of heat flow, transition intensity). Comparing reversible and nonreversible heat flows suggests a very close crystallinity rate, which is one of the major parameters influencing diffusion properties.

TMA results show larger differences (Fig. 3). Shrinkage of films is quicker, which can be at least partly explained by the different thicknesses of amorphous PET sheets and preform (ratio ≈ 20) (affecting temperature profiles governing the shrinkage). However, orientation must be considered as less important than crystallinity for diffusion properties: orientation may modify diffusivity about only 10 to 15%,[23] whereas diffusivity could be divided by 16.5 from 4 to 25% crystallinity rate.[24] Then, we conclude that our films have properties as close as possible to those of bottles and that they can be used for model diffusion tests.

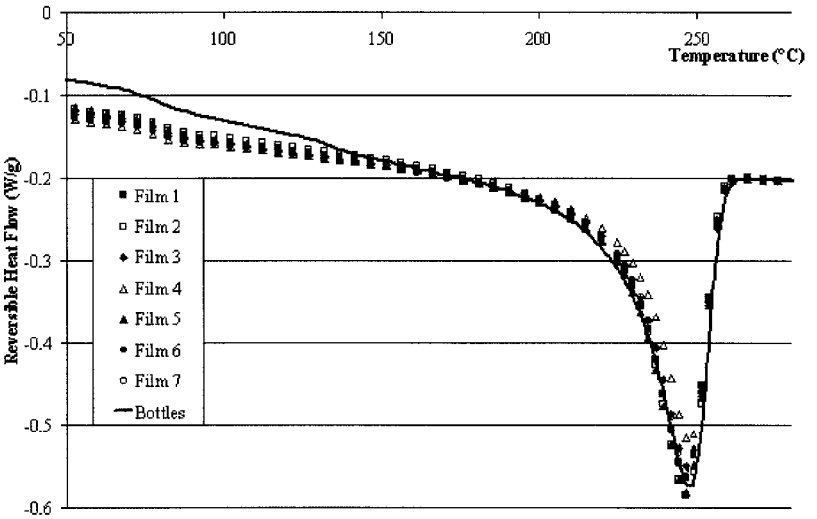

Figure 1 Modulated differential scanning calorimetry, reversible heat flow for seven films of virgin model PET. Comparison with average value of wall samples of six commercial PET bottles.

Diffusion coefficients in nonswollen PET

An example of diffusion kinetics at 60°C is shown in Figure 4 for phenol. A plateau is reached at only 33% of theoretical plateau. This phenomenon is observed for the five lowest molecular weight compounds and the plateaus vary from 25 to 45% of theoretical values. The phenomenon is commonly encountered with solid/solid diffusion tests.[25] Reasons for this could be multiple, and some explanations are given in a previous article.[25]

The kinetics of other surrogates were less advanced and did not reach the plateau. When experiments are not performed until the plateau is reached, the diffusion coefficient must be calculated assuming two extreme plateau values: the upper plateau is the theoretical value (100%); the lower plateau has been chosen taking arbitrarily an average value of experimental plateaus (i.e., 33% of theoretical value). Diffusivities are thus calculated at 40 and 60°C, both for 100% theoretical plateau (D_{100}) and for 33% (D_{33}) (Table II). The ratio between calculated diffusivities from 33 and 100% plateau is around one order of magnitude.

Nevertheless, Figure 5 shows the correlation between diffusion coefficient and molecular weight. Data for gases (very low molecular weight compounds) taken from literature[26] are added. The good continuity between our values and those of gases supports our experimental approach. The literature data selected were obtained from gas permeation measurements (i.e., generally at low concentration, and with low or negligible plasticizing effects). This also sup-

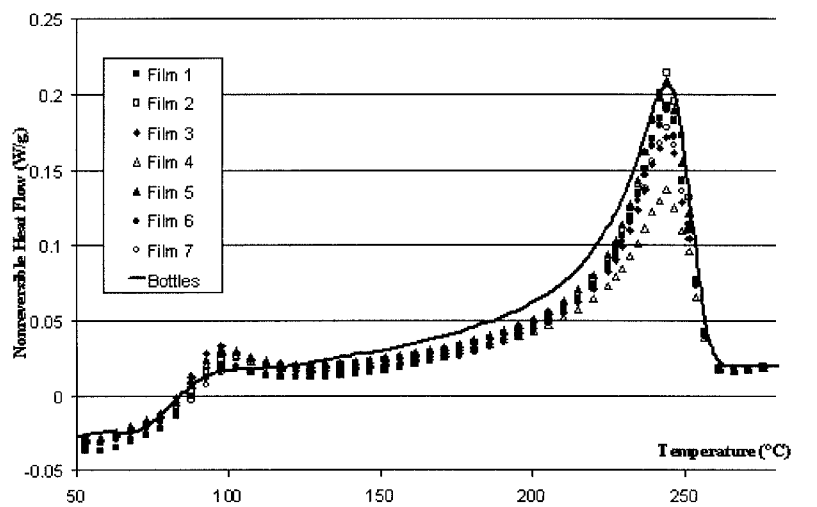

Figure 2 Modulated differential scanning calorimetry, nonreversible heat flow, for seven films of virgin model PET. Comparison with average value of wall samples of six commercial PET bottles.

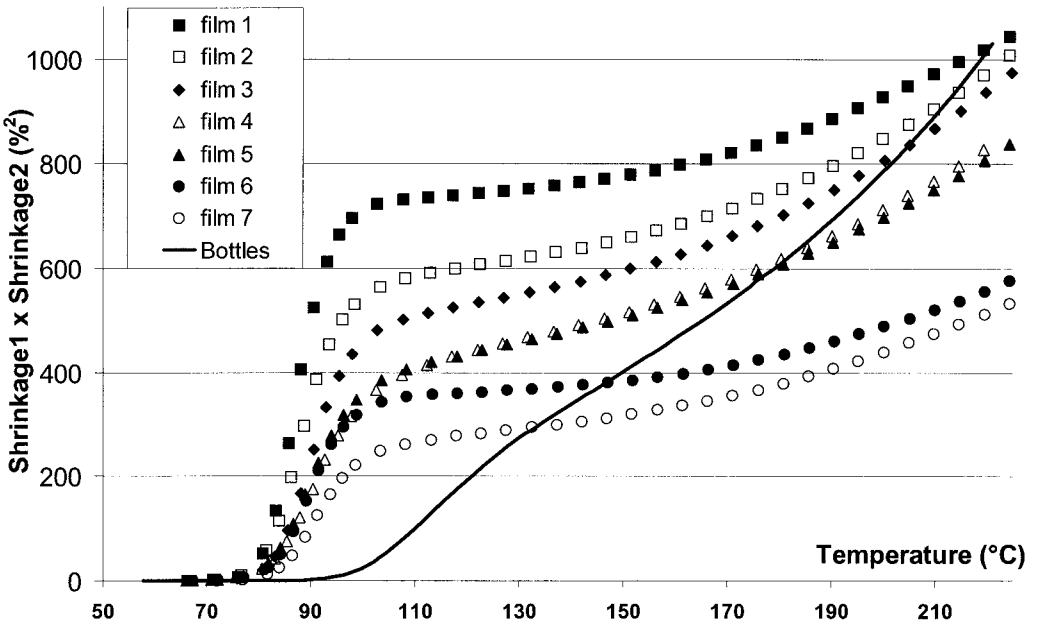

Figure 3 Thermal mechanical analysis for seven films of virgin model PET. Comparison of perpendicular shrinkages with average value for wall samples of six commercial PET bottles.

ports our expectation that in our experimental conditions (1000 ppm surrogate concentration) low or negligible plasticization effects occurred.

The pseudo-linear decrease of log D with molecular weight (M_W) shows that a Piringer type [Log $D = f(M_W)$] empirical correlation[18] can be applied to PET. A major difference is, however, observed compared to other polymers already studied for such correlation (mainly polyolefins): the slope of the Log $D = f(M_W)$ relation is very large. From $M_W = 0$ to $M_W = 250$ g/mol, the diffusion coefficient decreases by 13 orders of magnitude, in contrast, for example, to the two decades for low-density polyethylene (LDPE). Diffusion coefficients in PET are thus very sensitive to the molecular weight of the diffusant.

As diffusion coefficients have been measured at two temperatures, an activation energy can be calculated assuming an Arrhenius relation. The results are obviously the same considering either a 100% or a 33% plateau at each temperature. The activation energy can be plotted as a function of molecular weight (or as a function of the preexponential factor of D, which is

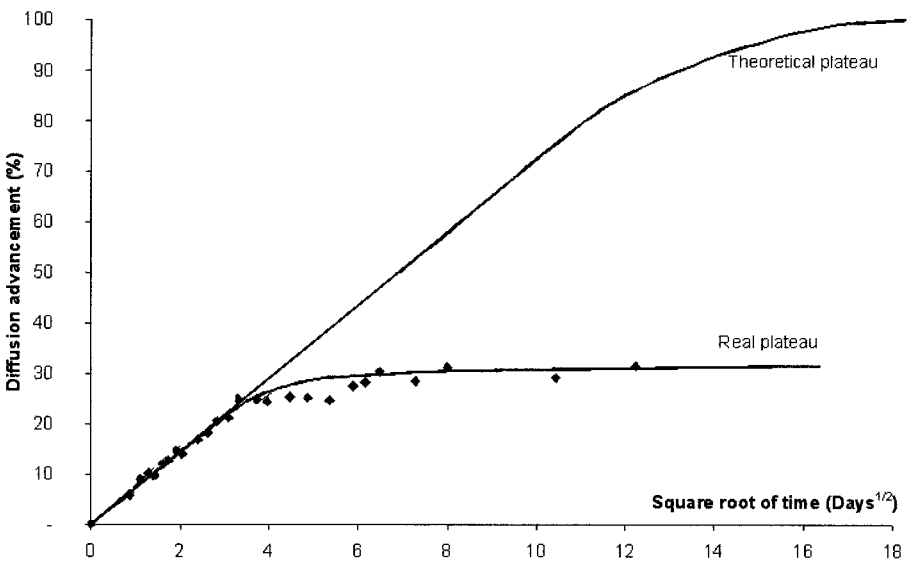

Figure 4 Diffusion advancement in PET films at 60°C for phenol.

TABLE II
Diffusion Coefficients of Surrogates in PET

Surrogates	No.	M_w (g/mol)	D_{100} (40°C)	D_{33} (40°C)	D_{100} (60°C)	D_{33} (60°C)	$D_{Aq,tri}$ (40°C)	$D_{Aq,mono}$ (40°C)	$D_{Et,film}$ (40°C)	$D_{Et,tri}$ (40°C)	$D_{Et,mono}$ (40°C)
Dimethylsulfoxide (DMSO)	1	78	5.5×10^{-15}	5.0×10^{-14}	3.8×10^{-14}	3.4×10^{-13}	—	—	4.6×10^{-13}	3.0×10^{-13}	2.7×10^{-12}
Toluene	2	92	4.2×10^{-15}	3.8×10^{-14}	2.9×10^{-14}	2.6×10^{-13}	9.5×10^{-14}	3.8×10^{-14}	6.3×10^{-13}	2.1×10^{-12}	4.8×10^{-12}
Phenol	3	94	3.3×10^{-15}	3.0×10^{-14}	4.1×10^{-14}	3.7×10^{-13}	9.0×10^{-14}	7×10^{-14}	2.1×10^{-13}	1.1×10^{-12}	1.3×10^{-12}
2,4-Pentanedione	4	100	8.6×10^{-15}	7.7×10^{-14}	5.8×10^{-14}	5.2×10^{-13}	2.0×10^{-13}	2.0×10^{-13}	9.8×10^{-13}	6.0×10^{-12}	2.2×10^{-11}
Chlorobenzene	5	113	4.9×10^{-15}	4.4×10^{-14}	4.1×10^{-14}	3.7×10^{-13}	1.3×10^{-13}	3×10^{-14}	5.8×10^{-13}	2.3×10^{-12}	3.2×10^{-12}
Nonane	6	128	3.0×10^{-17}	2.7×10^{-16}	8.9×10^{-16}	8.0×10^{-15}	—	—	1.2×10^{-13}	—	5.0×10^{-13}
1,1,1-Trichloroethane	7	133	3.1×10^{-17}	2.8×10^{-16}	5.0×10^{-16}	4.5×10^{-15}	—	—	7.8×10^{-14}	—	2.5×10^{-13}
Chlorooctane	8	149	2.0×10^{-16}	1.8×10^{-15}	1.2×10^{-15}	1.1×10^{-14}	—	—	9.6×10^{-14}	2.7×10^{-13}	2.7×10^{-13}
Phenylcyclohexane	9	160	9.3×10^{-19}	8.4×10^{-18}	1.1×10^{-17}	9.9×10^{-17}	—	—	$\leq 2.4 \times 10^{-14}$	—	5.0×10^{-14}
Ethyl hydrocinnamate	10	178	9.6×10^{-18}	8.6×10^{-17}	2.0×10^{-16}	1.8×10^{-15}	—	—	$\leq 4.5 \times 10^{-14}$	—	6.0×10^{-13}
Benzophenone	11	182	9.0×10^{-18}	8.1×10^{-17}	1.6×10^{-16}	1.4×10^{-15}	—	1.5×10^{-15}	$\leq 2.9 \times 10^{-14}$	—	1.0×10^{-13}
Azobenzene	12	182	2.1×10^{-17}	1.9×10^{-16}	4.9×10^{-16}	4.4×10^{-15}	—	—	$\leq 5.9 \times 10^{-14}$	—	7.6×10^{-14}
Phenyl benzoate	13	198	1.3×10^{-17}	1.2×10^{-16}	2.9×10^{-16}	2.6×10^{-15}	—	—	$\leq 5.4 \times 10^{-14}$	—	7.0×10^{-14}
BHT	14	220	—	—	—	—	—	—	$\leq 3.2 \times 10^{-14}$	—	—
Methyl palmitate	15	270	—	—	—	—	—	—	$\leq 3.7 \times 10^{-14}$	—	3.5×10^{-14}
Dibutyl phthalate	16	278	—	—	—	—	—	—	$\leq 3.4 \times 10^{-14}$	—	5.3×10^{-15}
Uvitex	17	431	—	—	—	—					

D_{100} (40°) and D_{33} (40°C) are the diffusion coefficients in model virgin films, assuming a 100 or a 33% plateau, respectively, by the trilayer test. $D_{Aq,mono}$ (40°C) is the diffusion coefficient at 40°C after complete solubilization of aqueous simulant from monolayer bottles, $D_{Aq,tri}$ (40°C) is obtained from trilayer bottles. $D_{Et,film}$ (40°C) is the diffusion coefficient obtained from sorption into preswollen (by ethanol) model films. $D_{Et,tri}$ (40°C) and $D_{Et,mono}$ (40°C) are the diffusion coefficients after complete solubilization of ethanol. They are obtained from migration in ethanol from monolayer and trilayer bottles.

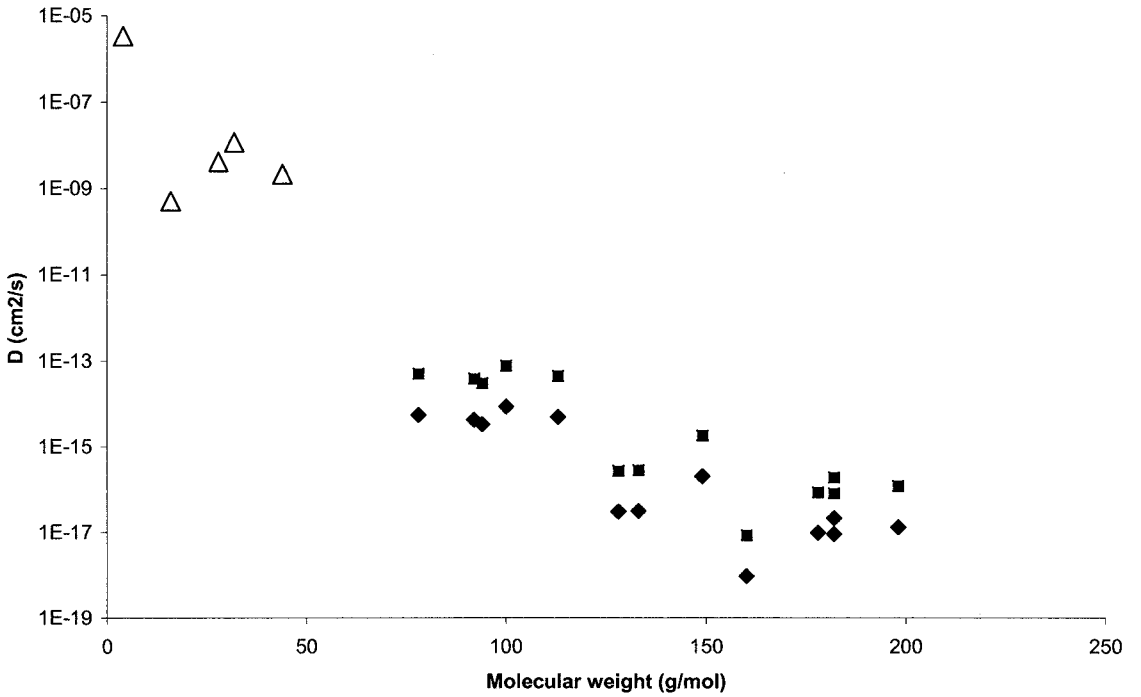

Figure 5 Diffusion coefficient at 40°C as a function of molecular weight; △, literature data.[26] For each surrogate, two values are given: ■, D_{33}, and ♦, D_{100}, corresponding to different assumptions for equilibrium in solid/solid diffusion tests (Table II).

itself a function of molecular weight; see ref. 25). Here again (Fig. 6), a good continuity is obtained between our data ($78 \leq M_W \leq 198$ g/mol) and literature values (gases, $M_W \leq 50$ g/mol), showing a good consistency between gas permeation experiments and our solid/solid diffusion test.

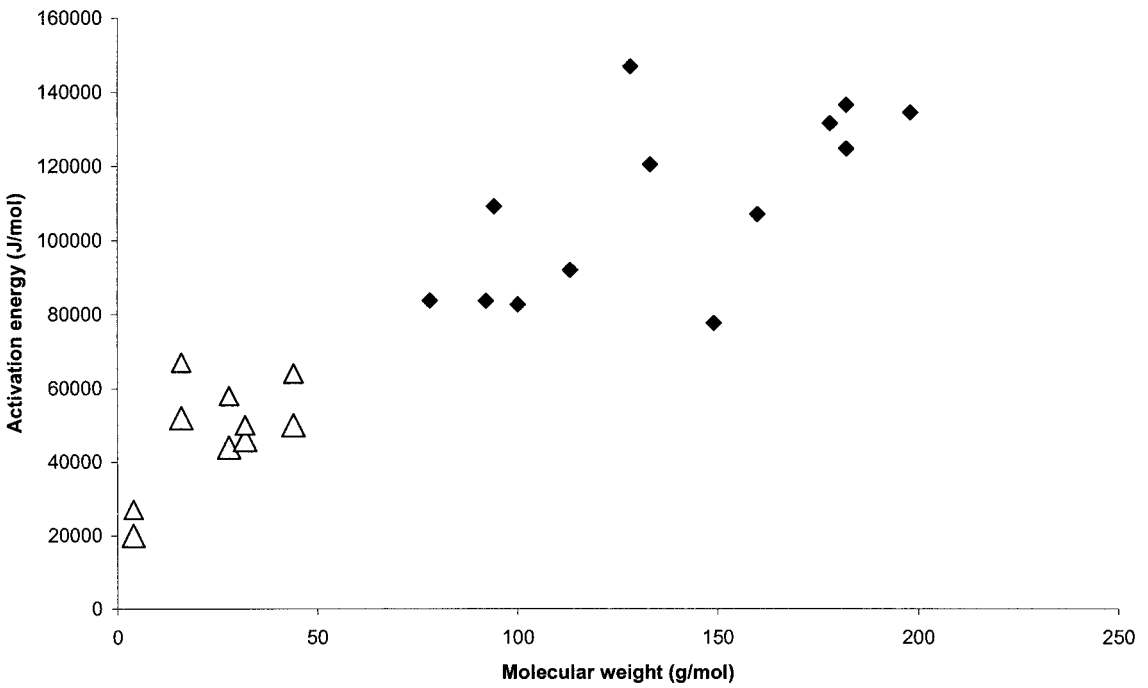

Figure 6 Activation energy as a function of molecular weight. △, literature data.[26] ♦, activation energy calculated from diffusion data at 40 and 60°C.

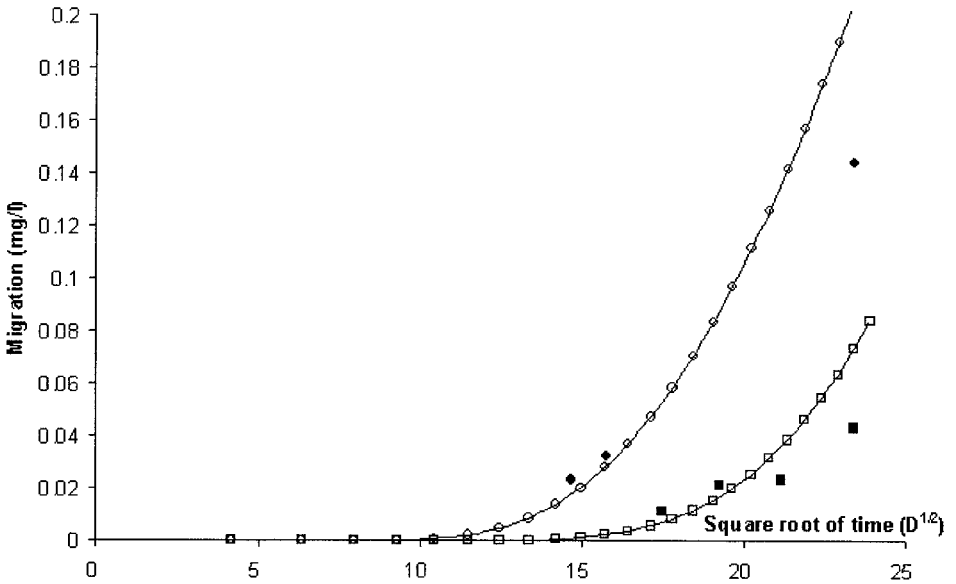

Figure 7 Migration (filled squares) and simulation of migration (open symbols) from model bottles of 1.5 L PET containing a 60-μm-thick functional barrier in acetic acid/water 3% (w/v) at 40°C for 2,4-pentanedione (● and ○) and phenol (■ and □).

Diffusion coefficients of surrogates in PET in contact with water

Diffusivities have been determined directly by monitoring over 18 months the migration from contaminated (mono- and three-layer) bottles into aqueous 3% acetic acid, simulant for most nonalcoholic beverages. The diffusion coefficient is considered to increase exponentially with water concentration in the PET.[27] The value at zero concentration is taken from the above measurement (D_{33} is taken arbitrarily) (Table II). The values at 40°C after complete solubilization of aqueous simulant is called $D_{\mathrm{Aq,mono}}$ (40°C) (mono for values obtained from monolayer bottles, tri for values obtained from trilayer bottles). They are obtained from (1) the fit of experimental and calculated migration kinetics, (2) D_{33}, (3) the diffusivity of water sorption in PET.

The diffusivity of water used to model the sorption of the aqueous simulant in PET was $D_{\mathrm{water}} = 5.2 \times 10^{-10}$ cm^2/s, according to literature.[24] This value is given for a 25% crystallinity rate, similar to that of our PET bottles, and at 25°C. Diffusivities of surrogates are determined by assuming total migration at equilibrium. Two values are determined from migration of mono- and three-layer bottles (Table II).

Examples of fitted data are given in Figure 7 for 2,4-pentanedione and for phenol from a bottle with a functional barrier (three-layer). As expected, migration kinetics show a lag phase, corresponding to the time needed by surrogates to cross the functional barrier. The corresponding diffusion coefficients are listed in Table II: $D_{\mathrm{Aq,tri}}$ (determined from the lag time) and $D_{\mathrm{Aq,mono}}$ (determined by assuming a 100% migration at the plateau) values obtained from the migration of mono- and three-layers are reasonably close. This confirms that the plasticization by surrogates does not play a major role (the 100% polluted bottle behaves similar to the 25% polluted bottle). It also validates the assumption of total migration for the five water-soluble surrogates.

The comparison of these diffusion coefficients with the values determined from the solid/solid method shows a very low plasticizing effect by water. This probably has to be related to the low water solubility in PET (around 0.5%).

No value is given for DMSO because it could not be quantified at very low levels in the presence of acetic acid.

No detectable migration occurs for surrogates which are either apolar or with a higher molecular weight, even with monolayer bottles and after 1.5 years of contact with simulant (limits of detection are given in Table I). Two characteristics of most surrogates with $M_W > 130$ g/mol should be underlined: their solubility in water is low (resulting in PET/water partition coefficients strongly in favor of PET at equilibrium), and their diffusivity is supposed to be very low, on the basis of solid/solid results (Table II). As a consequence, they are not detected in aqueous solution.

We have, therefore, used another liquid in contact with PET to be able to study molecular weight effects independently of solubility effects. Because all surrogates are soluble in pure ethanol, we monitored their migration into ethanol.

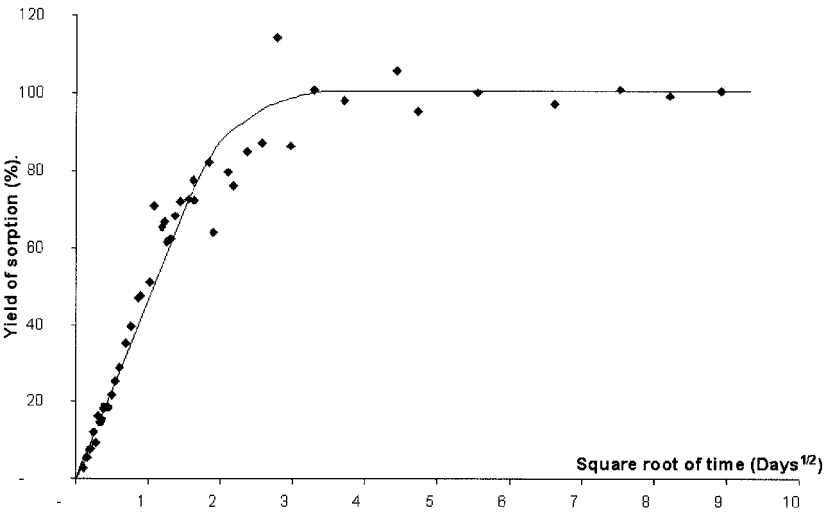

Figure 8 Sorption of chlorobenzene at 40°C in model film preswollen by ethanol.

Moreover, the solubility of ethanol in PET is higher than the solubility of water, and also an acceleration by plasticization effects is expected.

Diffusion coefficients of surrogates in PET in contact with ethanol

As previously shown for contact with water, the diffusivity of ethanol in PET is necessary to describe the migration phenomena: the diffusion coefficient is supposed to increase exponentially with ethanol concentration. The value at zero concentration again is taken from solid/solid measurements (D_{33} is taken arbitrarily) (Table II).

The values at 40°C after complete solubilization of ethanol are called $D_{\text{Et,mono}}$ (40°C) (mono for values obtained with migration from monolayer bottles, tri for values obtained with migration from trilayer bottles, film for values obtained by sorption test in model films). They are obtained from (1) the fit of experimental and calculated migration and sorption kinetics, (2) D_{33}, (3) the diffusivity of ethanol sorption in PET.

Diffusivity of ethanol ($D_{\text{ethanol}} = 9.4 \times 10^{-12}$ cm^2/s, Solubility = 2.7%) has been determined at 40°C by immersion of PET plates (thickness 280 μm) cut from the walls of commercial bottles.

Diffusivities of surrogates have been determined in different ways:

By monitoring sorption of surrogates into preswollen films (see example of Fig. 8 for chlorobenzene): Samples were first immersed in ethanol until equilibrium, and then in a solution of surrogates. The sorption kinetics are then monitored. In this case, the ethanol sorption step is not taken into account for the calculation.

By monitoring migration both from monolayer and from three-layer bottles (see the example of data for toluene, chlorobenzene, and phenol, Fig. 9).

Diffusion coefficients of surrogates in swollen PET are given in Table II and their evolution with molecular weight is given in Figure 10.

Diffusion coefficients from sorption tests could not be determined in all the range of surrogate molecular weights, because high molecular weight samples did not reach equilibrium, and as the partition coefficients are not known. In these cases, D is overestimated by assuming that the plateau corresponds to the last experimental value (underestimation of the plateau leads to overestimation of D). As previously (for migration in water), total migration is assumed.

Apparent diffusivities obtained with monolayer bottles are about the same order or slightly higher than those obtained with trilayers. The main explanation can be the following: in the monolayer bottles, the neck and the bottom have the same concentrations as in the wall but these parts (15% of the total surface in contact with simulant) are amorphous. As a consequence, (1) in these parts, the solubility of simulant is higher; (2) the local diffusivity of simulant is higher; (3) local diffusivities of surrogates (in nonswollen and swollen material) are also higher. The apparent diffusion coefficient measured in monolayer bottles is an average one. Even if the diffusivities obtained for both types of bottles are relatively identical, this shows that the presence of only 15% of amorphous parts may strongly influence migration kinetics. This influence is less important in the case of contact with water because the plasticization effect is lower.

Besides the slight differences between films and bottles, two main remarks must be made concerning diffusivities in contact with ethanol. First, the diffu-

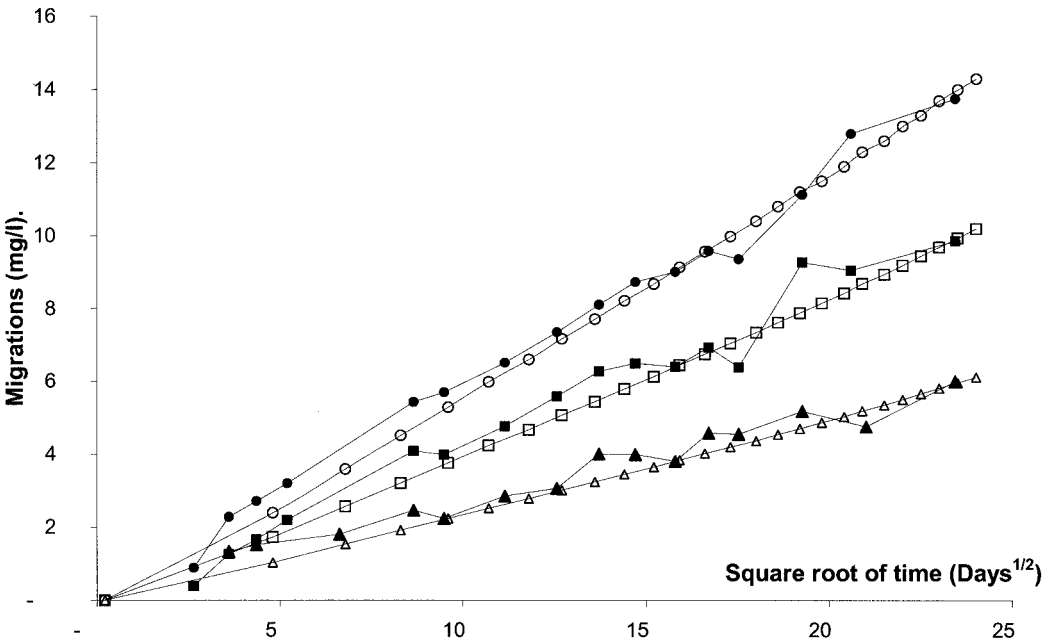

Figure 9 Migration (filled symbols) and simulation of migration (open symbols) from model bottles of 1.5 L PET in direct contact with ethanol at 40°C for toluene (△ and ▲), chlorobenzene (■ and □), and phenol (● and ○).

sion coefficients of surrogates are much higher (at least 25 times) than those obtained by the solid/solid method and than those obtained from migration in water. This illustrates the strong plasticizing effect of ethanol, whereas its solubility is 2.7% at 40°C. In previous work,[28] we have compared diffusion coefficients

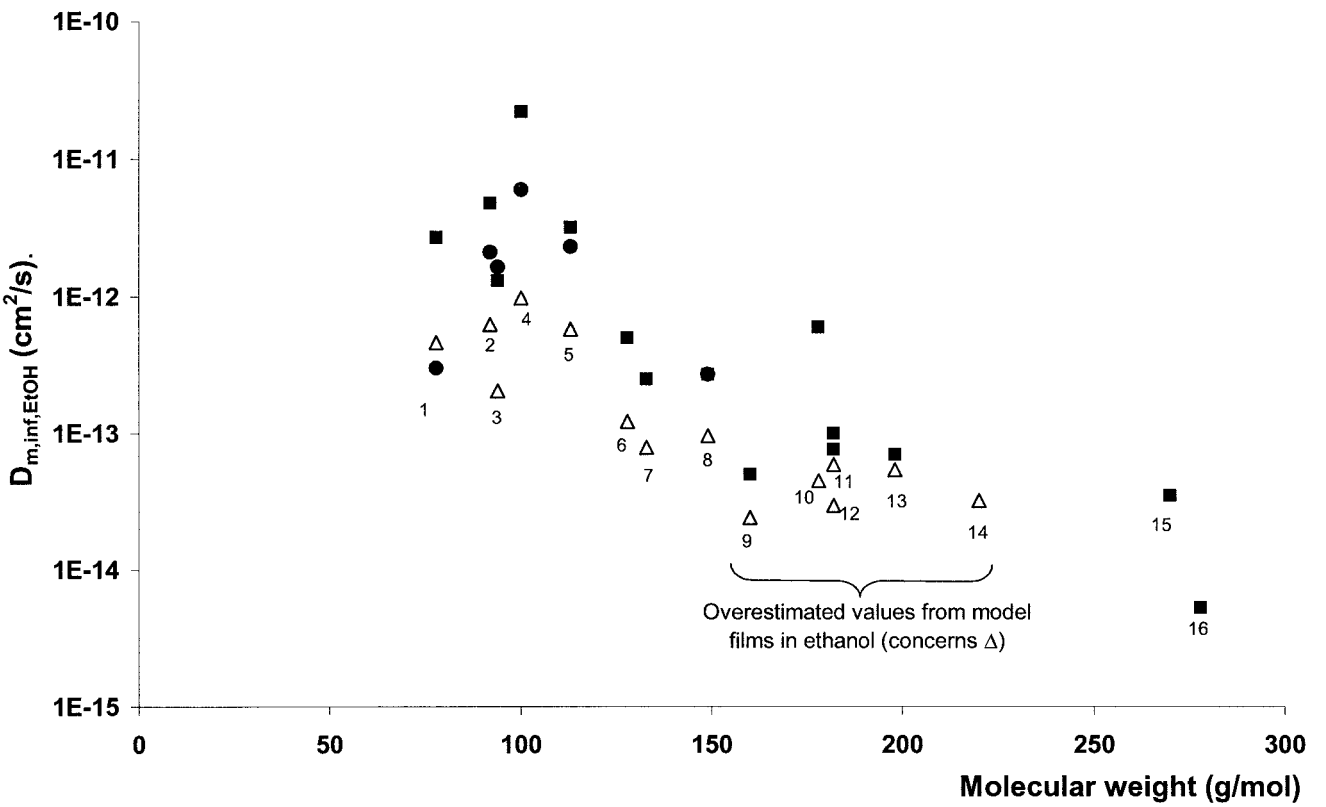

Figure 10 Diffusivities of surrogates (see number code in Table II) in PET preswollen by ethanol as a function of their molecular weight in model films (■), in three-layer bottles (●), and in monolayer bottles (△).

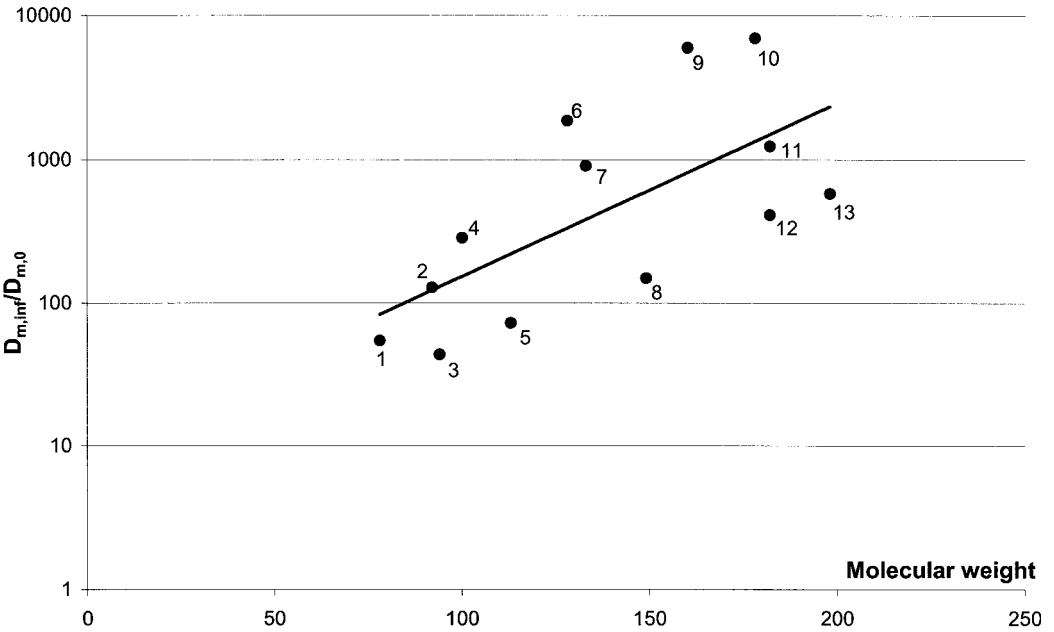

Figure 11 Ratio of diffusion coefficients obtained at 40°C with monolayer bottles swollen by ethanol and with virgin films as a function of molecular weight.

in polyolefins nonswollen and swollen by glyceryl tripelargonate; for similar low molecular weight compounds, the plasticization effect is much smaller in elastomeric than in glassy polymers. Second, the dependence of D with M_W is lower for swollen PET. As a consequence, the swelling effect, which can be expressed by the ratio of diffusion coefficient in contact with ethanol and the diffusion coefficient from the solid/solid test, is an increasing function of molecular weight (Fig. 11). The same type of behavior was observed by Reynier et al.,[28] who studied the plasticization effect of a triglyceride on PP, as a function of diffusing probe molecular weight. More generally, as observed in this work, the decrease of D with molecular weight is less and less important when mobility increases [e.g., (1) comparing PET to LDPE behavior; (2) comparing diffusion at 40 and 60°C; (3) comparing diffusion without and with plasticizing simulant in contact].

CONCLUSION

In this study, we measured diffusion coefficients of a large set of surrogates at low concentration levels in PET. The solid/solid test performed avoids the use of a liquid simulant as well as the associated plasticizing and partitioning effects. Diffusion parameters (diffusion coefficients and activation energies) measured in this work for surrogates ($M_W \geq 78$ g/mol) are in agreement with the literature data for gases ($M_W \leq 48$ g/mol), measured by permeation experiments (no plasticization).

Diffusion behavior was also determined by putting PET in contact with water and ethanol. Concerning diffusion/migration in contact with water, only low molecular weight surrogates soluble in water could be quantified in the aqueous simulant. On the basis of their molecular weights and the corresponding diffusion coefficients, other apolar or semipolar volatile surrogates (1,1,1-trichloroethane and phenylcyclohexane) were also expected to migrate significantly. However, with these poorly soluble in water surrogates, partition effects at the PET/water interface play a major role. These molecules have been widely used in other studies to test the efficiency of functional barriers, but as it is shown here, even with their relatively high concentration in bottles, they give no migration because of their low solubility in water and high partitioning effect. In such tests, they are not suitable to evaluate the efficiency of the functional barriers.

The use of ethanol as a second simulant allowed us to get a complete set of diffusion coefficients in swollen PET, as ethanol is a good solvent of all the surrogates used. As shown in previous studies, the larger the molecular weight of the surrogate, the more important is the plasticization effect on the diffusion coefficients.

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