Migration from Food Packaging Containing a Functional Barrier: Mathematical and Experimental Evaluation

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A model for predicting the functional barrier properties of layered films based on Fickian diffusion is presented along with experimental migration data from layered poly(ethylene terephthalate) films (PET) to test the model. Three-layered coextruded PET films were produced in which the center layer contained model solutes/contaminants and the outer layers were made with virgin material. The contaminants in the center layer were toluene and chlorobenzene. The PET films, which were 400 μm thick, had barrier layers of 20, 30, 40, and 60 μm of virgin coextruded PET. The center or core layer had thicknesses between 360 and 280 μm. The amount of migration was measured into water, 3% acetic acid, and isooctane at temperatures up to 60 °C. The measured amount of migration through the different barrier thicknesses was predictable on the basis of the model presented. The effects of diffusion from the center layer to a virgin barrier layer during the coextrusion process must be considered if reliable predictions of migration are to be obtained.

Keywords: *Migration; functional barrier; diffusion; food packaging; recycled polymers*

INTRODUCTION

Over the past 20 years numerous studies have shown that chemical components of food packaging migrate to food. Reseach has also shown that this migration (mass transfer) to food obeys Fick's laws of diffusion and that this migration is generally predictable. The actual effect of a functional barrier on the amount of migration, however, has not been addressed in the literature. The deficiency of research in this area is probably due to the lack of a clear definition of a functional barrier as it relates to the amount of migration.

A functional barrier can be generally defined as a package construction that limits the amount of migration of a component from the package to food or food-simulating liquids in amounts below a threshold value. This threshold value is usually established by regulatory institutions and is generally derived from toxicological evaluations. In the United States, the Food and Drug Administration (FDA) has established a dietary concentration of 0.5 μg/kg as the threshold. This value is derived from toxicological data on oral feeding studies (Rulis, 1986; FDA, 1993, 1995a,b). The migration of any noncarcinogenic compound in an amount that corresponds to a dietary concentration of $\leq$0.5 μg/kg is not considered a significant health risk. Therefore, a package construction (usually a multilayer construction) that reduces the migration of a component of the package to an amount which corresponds to $\leq$0.5 μg/kg would be considered acceptable in the United States. For example, 10 μg/kg of a chemical component could migrate to food or a food simulant from a package with a food contact surface of poly(ethylene terephthalate) (PET) and still fall at or below the 0.5 μg/kg dietary concentration. The 10 μg/kg migration concentration takes into account the fraction of food (5%) in contact with PET in the United States (FDA, 1995a,b). A PET package construction that permits 10 μg/kg or less migration of a component is still considered acceptable.

The functional barrier concept can also be defined in practical food quality terms instead of toxicological terms. An example is the reduction of lipid oxidation in food oils stored in a plastic bottle by preventing the migration of a UV absorber used in making the bottle (Pascall et al., 1995). Pascall et al. (1995) placed the UV absorber in a regrind layer sandwiched between two virgin polypropylene layers of a bottle. This package configuration limited the migration of the UV absorber into the food and prevented or limited UV light from reaching the food. This reduced lipid oxidation and maintained food quality.

Over the past few years a number of publications have discussed the functional barrier concept (Begley and Hollifield, 1993, 1995; Franz et al., 1993; Castle, 1994; Franz et al., 1994, 1996; Johns et al., 1995; Laoubi et

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al., 1995; Laoubi and Vergnaud, 1995, 1996; Gerding et al., 1996). The functional barrier concept in relation to recycled polymers for food contact use has been discussed on a theoretical basis in these studies, but few have provided systematic experimental evidence to show the practical effect (that is, limitations on the amount of migration) of a functional barrier. Franz et al. (1996) and Franz and Huber (1996) have shown, using three-layered high-impact polystyrene (HIPS) structures, that when using a coextrusion process to create a functional barrier, the assumed virgin layer becomes contaminated from components of the core layer during manufacturing. This is a direct result of solute diffusion between polymer layers for the few seconds at coextrusion temperatures, which can be as high as 280 °C for some of the major food-packaging polymers. This same effect can occur if the polymer sheets are stored for long time periods before the food contact application begins. Therefore, all mathematical models that neglect this physical process could significantly underestimate the actual amount of migration.

This paper is part of a continuing systematic study on characterizing the effectiveness of a functional barrier. Here we show the effectiveness of a coextruded virgin PET layer acting as a functional barrier over a contaminated PET core layer. Also, a general mathematical model is presented that permits the amount of migration through a functional barrier to be predicted even when the barrier layer becomes contaminated during package manufacturing or storage. In addition, the mathematical model can be used to determine the maximum concentration that can be present in the core layer for a given barrier thickness and still meet threshold amount requirements or specific migration limits. The practical application of the mathematical model was verified by conducting migration studies at two independent laboratories using different experimental protocols.

MIGRATION MODEL

Let us consider a plain sheet of a laminate made of a solute containing a core layer (P) and a virgin layer (B) of the same polymer type. The thickness of P and B are d and b, respectively, and $l = d + b$. The virgin layer is in contact with a liquid layer (F). The thickness of the virgin layer (B) is such that it acts as a barrier against the diffusing solute out of the core layer.

When the food-simulating liquid comes in contact with the laminate, the following two extreme situations can occur:

(i) The solute is homogeneously distributed in the core layer with the concentration $C'_{P,0}$ (w/v) or $C_{P,0}$ (w/w) with the density ρ_P of the polymer. The concentration of the solute in B, $C_{B,0}$, is 0.

(ii) The solute is already homogeneously distributed in the whole laminate with the equilibrium concentration ($C_{P,e}$), $C_{P,e} = C_P = C_B = C_{P,0}[d/(d + b)] = C_{P,0}(d/l)$.

The starting point for modeling the migration to the liquid is this second case (ii). This is because it represents the well-studied diffusion of a solute from a polymer of limited volume (V_P) into a stirred solution (worst case) of limited volume (V_F). A suitable equation for all of these cases can be derived from the diffusion theory under the following principal assumptions (Crank, 1975):

(1) The solute or migrant is homogeneously distributed in the polymer (that is, no surface blooming effect).

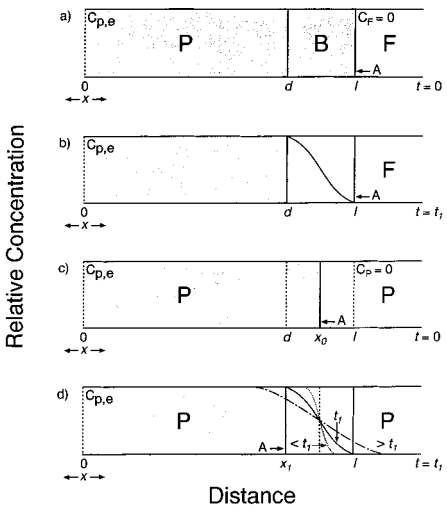

Figure 1. Illustration of the mass transfer through a layered package.

(2) There is a constant coefficient of diffusion (D_P) in the polymer (no interaction between the polymer and the food).

(3) The concentration of the solute migrating to the liquid depends only on time [that is, no mass transfer resistance of the solute to the liquid (F)].

(4) The total amount of solute in the liquid/food and in the polymer remains constant (no chemical degradation of solute in the liquid/food or loss into the atmosphere).∞

With these assumptions the amount of the solute in the liquid $m_{F,t}$ at time t is related to the corresponding amount at infinite time $m_{F,\infty}$ (equilibrium) by

$$\frac{m_{F,t}}{m_{F,\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^{\,2}} \exp(-D_P q_n^2 t/l_P^2) = 1 - (\Sigma)_t \quad (1)$$

where

$$\alpha = \frac{1}{K_{P/F}} \frac{V_F}{V_P} = \frac{C_{F,\infty}}{C_{P,\infty}} \frac{V_F}{V_P}$$

and q_n are the nonzero positive roots of $\tan q_n = -\alpha q_n$. The dimensionless parameter α is a function of the ratio V_F/V_P (volume of the food and volume of the polymer), and the partition coefficient $K_{P/F} = C'_{P,\infty}/C'_{F,\infty}$ is a dimensionless ratio of the solute concentration in the polymer (P) and the liquid (F) at equilibrium. For a food package, A is the area of the interface B/F and $l = d + b$ is the thickness of P and B, respectively.

By using eq 1 and starting with an initial solute concentration $C_{P,e}$, the amount of solute that migrates at time t through the unit of area (A) is

$$\frac{m_{F,t}}{A} = C_{P,e}\rho_P l\left(\frac{\alpha}{1+\alpha}\right)[1 - (\Sigma)_t] \quad (2)$$

Let us consider the laminate system for situation ii with $\alpha \gg 1$ and a very short contact time $t = t_1$. This means the initial solute concentration in the vicinity of $x = l$ at $t = 0$ is $C_P = C_{P,e}$ and $C_{F,t} \cong 0$ (Figure 1a). This illustration is the case of a system with diffusion between two semi-infinite media (Crank, 1975) for which eq 2 reduces to

$$\frac{m_{F,t}}{A} = 2C_{P,e}\rho_P\sqrt{\frac{D_P t}{\pi}} \quad (3)$$

A more realistic situation for diffusion in a laminate is illustrated in Figure 1b, which shows the solute concentration profile in the barrier layer after a short contact time $t = t_1$. In this illustration the concentration profile of the solute just reaches the polymer/food interface and $C_{F,t} \cong 0$. If we now consider a similar case with a semi-infinite polymer system with the initial solute concentration ($C_{P,e}$) at the distance $x \leq x_0 = d + b/2$ and $C_P = 0$ at $x > x_0$ and $t = 0$ (Figure 1c), then the possible concentration profiles for three different times, $t < t_1$, $t = t_1$, and $t > t_1$ can be illustrated in Figure 1d. If we assume a mass transfer through the interface A at $x = x_1$ at $t = t_1$ in Figure 1d, then $m_{P,t}/A = 0.5C_{P,e}\rho_P(l - x_1)$, which corresponds to $m_{P,t}/A = C_{P,e}\rho_P(x_0 - d) = C_{P,e}\rho_P b/2$ in Figure 1c. If we combine this result with eq 3 for $t = t_1$, then we obtain the time

$$t_1 = (\pi/16)[(l - x_1)^2/D_P] \quad (4)$$

If we allow diffusion to continue until $t = t_2 > t_1$, then under the same assumptions of a semi-infinite system, the mass transfer during $\Delta t = t_2 - t_1$ is

$$\frac{m_{F,\Delta t}}{A} = (2/\sqrt{\pi}C_{P,e}\rho_P\sqrt{D_P}(\sqrt{t_2} - \sqrt{t_1}) \quad (5)$$

As mentioned in the begining of this section, the real concentration of the solute in the laminate at the first moment of laminate/liquid contact lies between the two extremes (i) and (ii). Let us now consider the special case shown in Figure 1b, where the front of the solute just reaches the barrier/food layer interface B/F. By comparing Figure 1b with Figure 1d, we see similar situations are illustrated. Therefore, using eq 4 and the notations $l - x_1 = b$ and $t_1 = \Theta$, a time $\Theta = (\pi/16)(b^2/D_P)$ is defined, which is a little greater than the well-known "time lag" $= b^2/6D_P$ (Crank 1975). If such a system comes into contact with the liquid-phase F, then the mass transfer after the time $\Delta t = t_2 - \Theta = t$ that results from eq 5 is

$$\frac{m_{F,t}}{A} = \frac{2}{\pi}C_{P,e}r_P\sqrt{D_P}(\sqrt{t + \Theta} - \sqrt{\Theta}) \quad (6)$$

The specific case in Figure 1b and Figure 2a can be considered as a general reference case for all other practical cases between the extremes (i) and (ii). Depending on the degree of solute diffusion into the barrier layer before it comes in contact with the liquid-phase F, a fictive time (Θ'), which is shorter (Figure 2b) or longer (Figure 2c) than Θ described in Figure 2a, can be determined. By relating this Θ' to Θ, a relative time can be defined which is a measure of the efficiency of the barrier layer (B) (Franz et al., 1996, 1997). The value of Θ' can be deduced from the relation in eq 7, where

$$\sqrt{D_P^* t} = \sqrt{D_P\Theta'} \quad \text{or} \quad \Theta' = (D_P^*/D_P)t^* \quad (7)$$

D_P^* is the diffusion coefficient of the solute at some temperature (T^*) for time t^*, for example, the extrusion temperature of the laminate, where the diffusion of the solute into the barrier layer is most significant. D_P is the diffusion coefficient of the solute in the polymer at the temperature during the contact with liquid/food. By

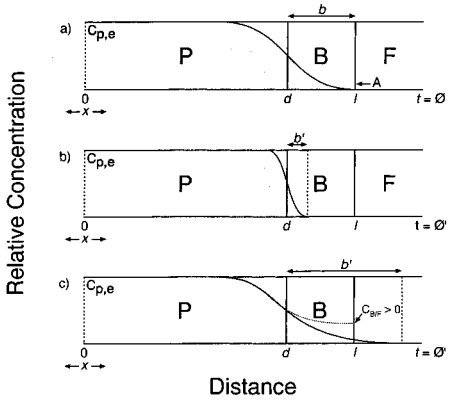

Figure 2. Illustration of the relative mass transfer for different amounts of contamination of the barrier layer.

using the relative time Θ_r instead of Θ and the general valid eq 2 instead of eq 3, a final equation for the migration of the solute from the core layer P through the barrier layer B after the contact time t can be written similar to the form of eq 6:

$$\frac{m_{F,t}}{A} = C_{P,e}\rho_P l\left(\frac{\alpha}{1+\alpha}\right)[(\Sigma)_{\Theta_r} - (\Sigma)_{t+\Theta_r}] \quad (8)$$

In eq 8

$$\Theta_r = \frac{\Theta^2}{\Theta'} = \left(\frac{\pi}{16}\right)^2\frac{b^4}{D_P^* D_P t} \quad (9)$$

and

$$C_{P,e} = C_{P,0}[d/(d + b)] = C_{P,0}(d/l) \quad (10)$$

In the extreme case (ii) of complete diffusion of the solute into the barrier layer (B), $\Theta_r = 0$, eq 8 reduces to eq 2.

If a threshold of regulation can be established, for example, in the form of a specific migration limit (SML)

$$\text{SML} = C_{F,t} = \frac{m_{F,t}}{A}\frac{A'}{M} \quad (11)$$

where A' and M represent the area (cm^2) of the laminate/food interface and the mass (g) of the food, respectively, then a maximum concentration (QM) of the solute in the core layer P can be calculated from eq 8 by replacing $C_{P,0}$ with QM:

$$\text{QM} = \text{SML}\frac{M}{A}\left\{\rho_P d\left(\frac{\alpha}{1+\alpha}\left[\sum_{n=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2}\exp\left(\frac{-D_P q_n^2\Theta_r}{l^2}\right) - \sum_{n=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2}\exp\left(\frac{-D_P q_n^2(\Theta_r + t)}{l^2}\right)\right]\right)\right\}^{-1}$$

$$= \text{SML}\frac{M}{A'}\left\{\rho_P d\left(\frac{\alpha}{1+\alpha}\right)[(\Sigma)_{\Theta_r} - (\Sigma)_{t+\Theta_r}]\right\}^{-1} \quad (12)$$

EXPERIMENTAL PROCEDURES

Materials. The functional barrier experiments were carried out using artificially contaminated food quality PET films. The films, which had a symmetric three-layer structure with

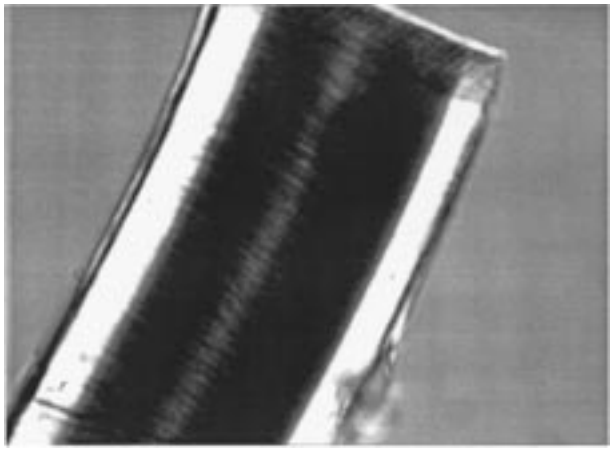

Figure 3. Photomicrograph of a cross section of a three-layered coextruded PET film. The clear sections are the barrier layers shown here to be 60 μm thick. The center layer (core layer) is 270 μm thick.

a contaminated PET core layer and coextruded virgin PET cover layers acting as functional barriers, were manufactured in the following way: 11 kg of PET agglomerate was contaminated by adding 1 L of toluene and 300 mL of monochlorobenzene and keeping the mixture in a closed container for 6 weeks at 40 °C. This highly contaminated PET material became the master batch that was used for manufacture of the core layer of the coextruded PET films as well as the homogeneously contaminated monofilm by diluting the master batch with plain virgin PET agglomerate at the industrial plant. The dilution was carried out by controlled addition of the master batch to the virgin PET material stream such that the contaminant concentration was nominally ~100 mg/kg (ppm) in the contaminated layer. The core layer was colored with a food grade brown pigment, which is commercially used for confectionary trays. The coextruded virgin cover layers were of the same commercial quality PET but without any pigment addition to permit measurement of layer thicknesses. During the coextrusion process the extrusion parameters were adjusted such that the different virgin layers were prepared with thicknesses of 0, 20, 30, 40, and 60 μm; the total polymer sheet thickness was kept constant at 400 μm. From these, the thicknesses of the resulting core layers were 400, 360, 340, 320, and 280 μm, respectively. Figure 3 shows a typical cross section of the PET sheets. Following the sheet production, the PET roll stock was divided and tested separately in the two laboratories.

Determination of the Residual Amounts of Contaminants. The PET test materials were cut into small pieces. One gram of PET was weighed into a tared vial and swelled with 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (from Merck, Darmstadt, Germany) for 14 h at 50 °C. To the swelled polymer was added 1 mL of 2-propanol containing the internal standard *n*-decane, and the polymer solution was held for an additional 24 h at 50 °C in a sealed vial. The solvent was removed, and the solution was stored overnight at 4 °C to precipitate the solvated oligomers. The solvent was filtered and the solutes in the solution were quantified by gas chromatography (GC). Each PET test film was extracted in triplicate.

Migration Tests Using Compression Type Cells for Single-Sided Contact. The test sheets were held in migration cells where 45.0 g of water was in contact with 95.4 cm^2 of polymer surface. This amount of water to surface area produced a value of $\alpha = 25$ for the case when the partition coefficient ($K_{P/F}$) was assumed to be unity. The cells were placed in a convection oven set at 60 °C. Duplicate test cells were removed from the oven at specific time intervals, and the amount of migration into water was measured by headspace GC with a flame ionization detector (FID). Each test cell corresponded to a specific time interval, and all tests were run in duplicate. Analyses were made by placing 5.0-mL aliquots of water from the test cell into 20-mL headspace vials. All vials were crimp-sealed with Teflon-faced septa and analyzed with a Perkin-Elmer AutoSystem GC equipped with an HS 40 automated headspace sampler. Data acquisition and instrumental control were accomplished with a PE Nelson model 1022 chromatographic data system. The precision of the migration tests into water and the headspace GC procedure were determined by placing five cells in the oven set at 60 °C for 5 days followed by analysis. The coefficients of variation for toluene and chlorobenzene are 6.2 and 10.4%, respectively.

Table 1. Typical Equilibrium Concentrations, $C_{P,E}$, of Contaminants in the Whole Films

barrier thickness (μm)	toluene (mg/kg)	chlorobenzene (mg/kg)
0	76	59
20	62	60
30	116	79
40	131	83
60	60	53

Migration Tests with the Pouch Method. The films were cut and formed into pouches of 2 dm^2 inner surface. The pouches were filled with 20 mL of food simulant, sealed, and stored at 20, 40, and 50 °C, respectively. Using this amount of simulant to surface area and the thickness of the polymer sheets produced a value of $\alpha = 5$ for the case when the partition coefficient ($K_{P/F}$) was assumed to be unity. The food simulants used were 3% acetic acid (w/v) in water and isooctane. After defined contact time intervals, the concentration of the migrants in the simulants were determined by GC. GC analyses were performed with an HP 5890 series II gas chromatograph with FID detection. The analyses for the target compounds in isooctane were performed by liquid injection. The analyses of the contaminants in 3% acetic acid were performed on the same GC using a Perkin-Elmer HS 40 automated headspace sampler. The detection limits (LODs) of the method for the target contaminant in each simulant were ≈0.1 μg/dm^2 in 3% acetic acid and 0.5 μg/dm^2 in isooctane. The LOD is based on a signal-to-noise ratio of 5 above the control.

RESULTS

Amounts of Solutes/Contaminants in the Core Layer. The extraction method described above yields the solutes' concentration in the whole PET film, that is, the equilibrium concentration $C_{P,e}$ according to the model definitions described in the previous section. The typical values determined in the test sheets are listed in Table 1. The high moisture content of the contaminated raw material caused technical processing problems. Therefore, the solute/contaminant concentrations in the core layers of the different sheets are not exactly the same. Additionally, in some cases the barrier layer thicknesses of the test sheets varied. In one case, measurements of the barrier layer thickness gave a value of 35 μm instead of 40 μm. All thicknesses used for calculations were those actually measured on the test sheets.

Migration Testing. The results for the amount of migration into water at 60 °C in the cells are shown in Tables 2 and 3. Table 4 lists the results for the migration of chlorobenzene into isooctane. Toluene could not reliably be determined in isooctane because of an interference/contaminant present in this simulant. Neither migrant was detectable after 131 days at 20 °C. After 2 months at 40 °C, only very low amounts of migration into the simulants were found. However, the amount of migration was significantly above the detection limits of the pouch method at 50 °C. Therefore, only those migration results at ≥50 °C are shown.

Table 2. Migration of Toluene into Water at 60 °C

	concentration (μg/dm^2)								
	$b = 60$ μm $C_{P,e} = 116$ μg/g			$b = 35$ μm $C_{P,e} = 155$ μg/g			$b = 20$ μm $C_{P,e} = 108$ μg/g		
time (days)	exptl	calcd	$b = 0$	exptl	calcd	$b = 0$	exptl	calcd	$b = 0$
5	7.3	6.3	15.2	3.8	3.2	20.4	1.1	0.8	14
9							2.4	1.4	19
10	9.7	11.1	21.5						
12				10.3	7.4	31.5			
22	14.9	20.1	32	17.1	13.1	43	5.1	3.4	30
32				20	18.3	51	7	4.9	36

Table 3. Migration of Chlorobenzene into Water at 60 °C

	concentration (μg/dm^2)								
	$b = 20$ μm $C_{P,e} = 68$ μg/g			$b = 35$ μm $C_{P,e} = 87$ μg/g			$b = 60$ μm $C_{P,e} = 69$ μg/g		
time (days)	exptl	calcd	$b = 0$	exptl	calcd	$b = 0$	exptl	calcd	$b = 0$
5	3.9	3.4	8.9	2.3	1.6	11.4	0.85	0.45	9
9							1.4	0.80	12
10	5.3	6.1	12.6						
12				5.0	3.8	17.7			
22	7.3	11.2	18.7	7.7	6.7	24	2.9	2.0	19
32				8.9	9.5	29	4.0	2.8	23

Additionally, at these higher temperatures (≥50 °C) some strong interactions between PET and the acetic acid solution were observed during the long contact times. These interactions produced changes in structure and color of the PET films that could be visually observed. Visually the test sheets became opaque due to the polymer's crystallizing. Nevertheless, the effect of the barrier layer on reducing the migration into acetic acid is shown in Table 5 using the migration results for a 60 μm barrier layer and a PET film without barrier layer.

DISCUSSION

A series of conclusions can be derived from the migration model and the experimental results.

1. Owing to the long times needed for diffusion of a solute through a barrier layer of PET at normal food storage conditions, migration testing must be done under accelerated conditions. These accelerated conditions can have some pitfalls for producing meaningful migration data. One pitfall occurs when food simulants and/or temperatures used produce strong interactions with the barrier polymer. In this case such an interaction was observed with acetic acid in contact with PET at high temperatures (≥50 °C). The test films became opaque, and increased crystallization was demonstrated by differential scanning calorimetry (DSC). This crystallization was solvent-induced: it occurred only in the presence of acid and not with water or isooctane. This solvent-induced crystallization indicates the film must have been plasticized by the acid solution. A plasticization could be expected because acetic acid has Hildebrand solubility parameters similar to those of PET. Strong interaction effects were also observed with ethanol (50%) and PET. Reliable predictions of the diffusion rates are not possible under these types of interactions because of the competition between crystallization and plasticization. Nevertheless, it is important to stress that the effect of the barrier layer can be seen (Table 5) even for the case when the solvent affects the polymer. The data in this table indicate that the film with a barrier layer will always have less migration even when there is a strong interaction between the food and polymer. This is especially apparent at the shorter time intervals. Some of the reduced migration can be explained by the slightly lower $C_{P,e}$ in the 60-μm barrier film as listed in Table 1, but because eq 8 indicates migration is directly proportional to $C_{P,e}$, the magnitude of the reduced migration cannot be explained by small differences in $C_{P,e}$ alone. Predicting migration in the presence of strong polymer/food simulant interactions is beyond the scope of this particular study.

2. One important result of this investigation is the confirmation that the "virgin" barrier layer becomes partially contaminated during the extrusion process. This contamination must be taken into account if reliable estimates of migration are to be obtained. The approximate error in assuming an ideal extrusion process, that is, no contamination of the barrier layer during extrusion, can be estimated by comparing the experimental results with theoretical estimates based on an ideal barrier layer (Begley and Hollifield, 1995; Laoubi and Vergnaud, 1995). For example, at 50 °C, the calculated migration value using the ideal senario from the above references for chlorobenzene through 30-μm PET into isooctane is ~0.05 μg/dm^2. This value is at least 10 times less than the experimentally measured migration value in Table 4. In general, a considerable underestimate can occur if an ideal extrusion process is assumed.

3. To calculate the migration values according to eq 8, data for the diffusion coefficients at the extrusion and the test temperatures are needed. Additionally, the extrusion time and the real thickness of the barrier layer are also needed. Although these parameters are not generally available, one can start with a first approximation based on some assumptions about the production process of the laminate. Information supplied by the industry on the extrusion lamination of PET indicates an extrusion time of 1 s at 270 °C is realistic. Using the method by Baner et al. (1996) with a coefficient of $A_P = -3$ for PET and an extrusion temperature of 270 °C, the diffusion coefficients $D_P^* = 8.7 \times 10^{-7}$ and 7.1×10^{-7} cm^2/s in eq 7 can be estimated for toluene and chlorobenzene, respectively. For the migration experiments at 60 °C the diffusion coefficient (D_P) for toluene was measured to be 1.6×10^{-12} cm^2/s. The same value was also assumed for chlorobenzene. Using the corresponding barrier thickness (b) and initial solute/contamination concentrations ($C_{P,e}$) in the tested PET films, Tables 2 and 3 show comparative calculated and experimental migration values for toluene and chlorobenzene (in units of μg/dm^2) from the PET films. The efficiency of the barrier layers in reducing migration is illustrated in these tables by calculating migration values without the barrier layer ($b = 0$). These same calculations can be performed for the migration of chlorobenzene into the food simulant isooctane at 50 °C. In this case the diffusion coefficient for chlorobenzene in PET was measured to be $D_P = 2.13 \times 10^{-13}$ cm^2/s. The calculated and experimental migration values for chlorobenzene migration into isooctane are shown in Table 4. Additionally, Table 4 shows the corresponding calculated values for migration without a barrier layer ($b = 0$).

4. Although good agreement exists between the experimental and calculated migration results listed in Tables 2−4 using the above assumptions, further improvement in the correlation between the experimental and calculated values can be obtained by refining the estimates of the unknown migration parameters. The

Table 4. Migration of Chlorobenzene into Isooctane at 50 °C[a]

time (days)	concentration (μg/dm^2)											
	$b = 20\ \mu$m, $C_{P,e} = 60\ \mu$g/g			$b = 30\ \mu$m, $C_{P,e} = 79\ \mu$g/g			$b = 40\ \mu$m, $C_{P,e} = 83\ \mu$g/g			$b = 60\ \mu$m, $C_{P,e} = 53\ \mu$g/g		
	exptl	calcd	$b = 0$	exptl	calcd	$b = 0$	exptl	calcd	$b = 0$	exptl	calcd	$b = 0$
10	<0.5	0.9	4.1	<0.5	0.5	5.4	<0.5	0.3	5.6	<0.5		
39	1.3	3.1	8.0	1.0	2.1	10.6	0.8	1.2	11.0	<0.5	0.4	7.1
69	2.2	5.0	10.7	2.4	3.5	14	2.0	2.2	14.8	<0.5	0.6	9.4
91	3.3	6.3	12.3	3.1	4.6	16		2.9	17.0	<0.5	0.8	10.8
110	3.9	7.3	13.5	3.9	5.5	17.8	3.0	3.4	18.7			
130	4.9	8.3	14.7	5.0	6.3	19.3	4.0	4.0	20.2			

[a] Performed using the pouch method.

Table 5. Experimental Migration of Toluene and Chlorobenzene from PET without ($b = 0$) and with ($b = 60\ \mu$m) a Functional Barrier into 3% Acetic Acid at 50 °C

contact time (days)	concentration (μg/dm^2)			
	toluene		chlorobenzene	
	$b = 0$	$b = 60\ \mu$m	$b = 0$	$b = 60\ \mu$m
10	4.1	<0.1	<0.1	<0.1
40	25.5	0.2	9.2	2.4
70	29.9	7.1	12.6	5.4
92	30.8	9.8	14.6	6.6
111	32.3	14.7	15.3	9.1
131	33.3	20.7	17.0	12.3

Table 6. Experimental and Calculated Migration Values of Toluene and Chlorobenzene from PET with a Functional Barrier of 60 μm into Water at 60 °C[a]

contact time (days)	concentration (μg/dm^2)			
	toluene		chlorobenzene	
	exptl	calcd	exptl	calcd
5	1.1	1.2	0.85	0.75
9	2.4	2.1	1.4	1.3
22	5.1	5.0	2.9	3.2
32	7.0	7.2	4.0	4.6

[a] Calculated values obtained by using refined values for $D_P\Theta_r$.

product $D_P\Theta_r$ in eq 9 contains two unknown parameters, D_P^* and t^*, which have been estimated using the assumptions described above. By treating this product, $D_P\Theta_r$, as a constant that must be determined empirically, improving the correlation between the calculated and experimental migration values by varying this constant leads to a better understanding of the diffusion process that takes place during the extrusion process. For example, the constant value, $D_P\Theta_r$, for toluene in the 60-μm barrier layer in Table 2 is 5.7×10^{-5} cm^2. An improved correlation between the calculated migration values and experimental migration values is obtained by reducing this constant value to 2.5×10^{-5} cm^2. This is illustrated in Table 6, in which calculated values with a reduced constant are listed against the measured migration values. In effect, the reduced constant, $D_P\Theta_r$, indicates more solute diffusion into the barrier layer during the extrusion process than was given in the original estimate. Similar results are obtained for chlorobenzene using the same constant as for toluene. These comparative values are also listed in Table 6. For very thin barrier layers, the quality of the correlation between the theory and experiment is also a function of the uniformity of the barrier layer. This refining procedure is recommended as a general approach for comparing experimental migration results to those calculated using the model for the functional barrier.

5. Although eq 8 is the most generalized equation for this migration model, eq 6 is simpler and gives the same results for the experimental conditions used in this investigation. However, Θ_r must be used instead of Θ. Use of eq 6 must be verified to produce a ratio $m_{F,t}/m_{P,0} < 0.6$ from the mass balance, $m_{P,e}/A = C_{P,0}\rho_P d$, before this simplification can be used. For illustration, consider the following example with $D_P = 3 \times 10^{-10}$ cm^2/s, $D_P^* = 1 \times 10^{-8}$ cm^2/s, $t = 10$ days, $t^* = 1$ h, $b = 25\ \mu$m, $d = 100\ \mu$m, $C_{P,0} = 100\ \mu$g/g, and $\rho = 1$ g/cm^3. A calculation based on eq 6 leads to a value of $m_{F,t}/A = 143\ \mu$g/dm^2, but the total available amount $m_{P,0}/A = 125\ \mu$g/dm^2, and gives a ratio of $m_{F,t}/m_{P,0} > 1$. In this case eq 8 should be used.

6. From the regulatory point of view, estimating a worst case analysis is the most important objective. Therefore, testing the effectiveness of functional barrier layers using solutes (impurities) with low molecular masses such as toluene would represent the worst case. If, as a first approximation, one uses the experimentally determined constant $D_P\Theta_r = (\pi/16)^2 b^4/D_P^* t^*$ as a general characteristic parameter for the laminate, then eq 10 can be used to estimate the maximum concentration of solute/contaminants in the core layer (QM values) for all impurities with higher molecular masses under worst case conditions. For example, to fulfill an SML criteria of 1 μg/kg into the food simulant after 10 days from a package design with the following parameters $d = 400\ \mu$m, $b = 100\ \mu$m, or $l = d + b = 500\ \mu$m, and if the diffusion in the package of polymer density, $\rho = 1$ g/cm^3, is given by $D_P = 1 \times 10^{-10}$ cm^2/s, and $D_P^* = 1 \times 10^{-6}$ cm^2/s, with a coextrusion processing time $t^* = 1$ s, then a Θ_r is calculated to be 3 855 314 s or 44.6 days. Using this value of Θ_r, eq 10 can be used with an $\alpha = 1$ and a mass of food to package surface area of 1.55 g/cm^2 to calculate a QM value in the polymer. The calculated QM value for this package design is 1.6 mg/kg. Therefore, under this threshold scenario the amount of solute/contaminant in the core layer must not exceed 1.6 mg/kg. If the solute of the core layer is already homogeneously distributed in both core and functional barrier layers, that is, a package with no barrier, then the concentration of potential migrants in the package, that is, QM value, must not exceed 0.15 mg/kg. Therefore, the functional barrier under this scenario would allow 10 times more contamination than the single-layer package.

CONCLUSIONS

A functional barrier limits the amount of migration of a food-packaging component from the package to food or food-simulating liquids to amounts below a threshold value. A general mathematical model is presented that permits the prediction of the amount of migration through a functional barrier even when the barrier becomes contaminated during package maufacturing or

storage. When using a coextrusion process to create a functional barrier, the assumed virgin layer becomes contaminated from components of the core layer (recycled polymer layer) during manufacturing. These effects of diffusion from a contaminated core layer into a virgin barrier layer during the coextrusion process must be considered if reliable predictions of migration are to be obtained.

The practial application of the mathematical model was verified by conducting migration studies using common test sheets at two independent laboratories using different experimental protocols. The effectiveness of a coextruded virgin PET layer as a functional barrier over a contaminated PET core layer was shown. The experimental migration data through the PET barrier layers presented in the tables agree with the calculated values based on the model parameteres for a functional barrier described here. Additionally, the data presented here are also consistent with the same effects on migration as for the case of a virgin layer of polystyrene coextruded as a functional barrier over contaminated polystyrene (Franz et al., 1997).

Although this work presents data using diffusion of nonpolar contaminats in PET, the presence of polar contaminants, which also diffuse through PET, will not alter the significance of these results. This is because PET is a polar polymer in which polar contaminats will generally diffuse slower in the polymer because of slight interactions with the polymer. This effect would be greatest for contaminats that can hydrogen bond with the polymer. Evidence for this effect can be seen in work by Sadler et al. (1996), who showed that the diffusion of butryic acid in PET is 85 times slower than the diffusion of *d*-limonene in PET. Therefore, diffusion of nonpolar contaminats in a polar polymer should represent a worst case in estimating the migration potential to food. Thus, the mathematical model presented here can be used to determine the maximum concentration that could be present in the core layer for a given barrier thickness while still fulfilling threshold or specific migration limit requirements.

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