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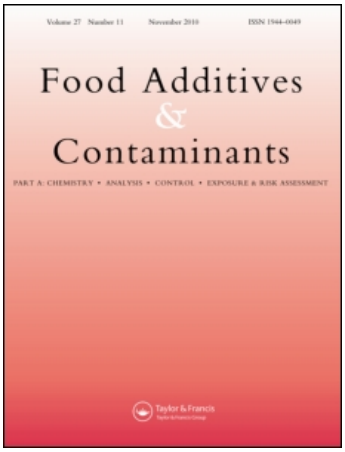

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Evaluation of migration models that might be used in support of regulations for food-contact plastics

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Abstract
Materials and articles intended to come into contact with food must be shown to be safe because they might interact with food during processing, storage and the transportation of foodstuffs. Framework Directive 89/109/EEC and its related specific Directives provide this safety basis for the protection of the consumer against inadmissible chemical contamination from food-contact materials. Recently, the European Commission charged an international group of experts to demonstrate that migration modelling can be regarded as a valid and reliable tool to calculate 'reasonable worst-case' migration rates from the most important food-contact plastics into the European Union official food simulants. The paper summarizes the main steps followed to build up and validate a migration estimation model that can be used, for a series of plastic food-contact materials and migrants, for regulatory purposes. Analytical solutions of the diffusion equation in conjunction with an 'upper limit' equation for the migrant diffusion coefficient, D_P, and the use of 'worst case' partitioning coefficients $K_{P,F}$ were used in the migration model. The results obtained were then validated, at a confidence level of 95%, by comparison with the available experimental evidence. The successful accomplishment of the goals of this project is reflected by the fact that in Directive 2002/72/EC, the European Commission included the mathematical modelling as an alternative tool to determine migration rates for compliance purposes.

Keywords: *Food-contact plastics, migration, modelling, diffusion, polyolefin, polystyrene, polyester, polyamide*

Introduction

To check the compliance of a polymeric food-contact material with the existing European Union (EU) regulations, specific and overall migration tests should be carried out using food simulants under specified test conditions. However, the experimental determination of the specific migration into food or food simulants requires a considerable amount of time and is even in many cases impossible due to technical/analytical problems or non-availability of corresponding analytical methods.

Numerous scientific investigations have demonstrated during the last two decades that migration from food-contact materials into food and food simulants are predictable physical processes. Mass transfer from plastic material into foodstuffs in most cases obeys Fick's laws of diffusion. Hence, in addition to the experimental methods, a new alternative tool appears to be applicable which is based on theoretical migration estimations. Modelling of potential migration is already used by the US Food and Drug Administration (FDA) as an additional tool to assist in making regulatory decisions. The EU

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has recently introduced this option to use generally recognized migration models in EU Directive 2002/72/EC as a novel conformity and quality assurance tool with the following statement in Article 8 (4):

> *The verification of compliance with the specific migration limits provided for in paragraph 1 may be ensured by the determination of the quantity of a substance in the finished material or article, provided that a relationship between that quantity and the value of the specific migration of the substance has been established either by an adequate experimentation or by the application of generally recognised diffusion models based on scientific evidence. To demonstrate the non-compliance of a material or article, confirmation of the estimated migration value by experimental testing is obligatory.*

A generally recognized model must be based on scientific evidence. The realization of this requirement has been recently achieved within EU Project SMT4-CT98-7513 under the 5th Framework Programme 'Growth Evaluation of Migration Models in Support of Directive 2002/72/EC'.

The major objectives of this project were as follows:

- To demonstrate that a correspondence between the specific migration limit (SML) and a permitted maximum initial concentration (MIC) of a substance in the finished product can be established.
- To establish documentation that demonstrates the validity of underlying migration models for compliance purposes. Consequently, parameters used in the migration model have been selected in a way that a 'worst-case' estimate of migration rate is generated.

The final report of this project has been compiled recently (Hinrichs and Piringer 2002).

This research project has established the mathematical equations to be applied and the conditions for their appropriate application with regards to plastics in contact with food. All these conditions and equations have been published in detail in the Practical Guide of the EU Commission in Annex 1, Mathematical Models, as well as in previous publications (Hamdani et al. 1997, Brandsch et al. 2002). The main objective of the present paper is to present a collection of previously unpublished migration data together with their modelling constants for verification of migration modelling and thus show the domain in which the migration model can be used at present. This data collection is a result of contributions from the various authors of this paper, provided from their laboratories by using up-to-date experimental migration methods and from known migration data banks.

Migration modelling

Beyond the characterization of the polymer and food (simulant), the key input parameters for the use of a migration model are the diffusion coefficient, D_P, of the migrant in the plastic material P, as well as the partition coefficient $K_{P,F}$, of the migrant between the plastic and F (food simulant). It is assumed that at the beginning of the mass transfer, the migrant is homogeneously distributed in the plastic matrix P and that there is no boundary resistance for the transfer from the surface of P to F. The migrant is then homogeneously distributed in F and the total amount of the migrant in P and F remains constant during the migration process, that means no chemical decomposition or evaporation will be taken into account. With these assumptions, Fick's second diffusion equation has the following analytical solution (Crank 1975, Brandsch et al. 2002):

$$\frac{m_{F,t}}{A} = c_{P,0}\rho_P d_P\left(\frac{\alpha}{1+\alpha}\right) \times\left[1-\sum_{n=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2}\exp\left(-D_P t\frac{q_n^2}{d_P^2}\right)\right] \quad (1)$$

$$\text{with } \alpha = \frac{1}{K_{P,F}}\frac{V_F}{V_P} = \frac{c_{F,\infty}}{c_{P,\infty}}\frac{\rho_F}{\rho_P}\frac{V_F}{V_P};$$

$$K_{P,F} = \frac{c_{P,\infty}}{c_{F,\infty}}\frac{\rho_P}{\rho_F}; \quad \text{and} \quad \tan q_n = -\alpha\, q_n$$

where $m_{F,t}/A$ ($\mu g\,cm^{-2}$) represents the amount of the migrated substance after the contact time t (s) of P with F. The contact area of the food-contact plastic is A (cm^2); the initial concentration of the migrant in P is $c_{P,0}$ ($\mu g\,g^{-1}$); the densities of P and F are ρ_P ($g\,cm^{-3}$) and ρ_F ($g\,cm^{-3}$), respectively, and the thickness of P is d_P (cm). With the volumes V_P (cm^3) and V_F (cm^3) of polymer and food, $\alpha = (V_F/V_P)/K_{P,F}$, where the partition coefficient $K_{P,F} = c_{p,\infty}\rho_P/c_{F,\infty}\rho_F$ is the ratio of the migrant concentrations (w/v) in P and F at equilibrium. The parameters q_n are the positive roots of the transcendent equation: $\tan q_n = -\alpha\, q_n$.

Equation (1) can be rearranged to give Equation 2, which can be used to estimate the maximum initial concentration of migrant (MIC) in the food-contact material or article based on specific migration limits for compliance checks.

$$\text{MIC} = \frac{\text{SML}}{100}\frac{V_F\rho_F}{A} \times\left\{\rho_P d_P\left(\frac{\alpha}{1+\alpha}\right) \times\left[1-\sum_{n=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2}\exp\left(-D_P t\frac{q_n^2}{d_P^2}\right)\right]\right\}^{-1} \quad (2)$$

All parameters apply in the same way as for Equation 1, except the specific migration limit SML ($\mu g\,g^{-1} = mg\,kg^{-1}$) and the maximum initial concentration MIC ($\mu g\,g^{-1}$).

As mentioned above, D_P as well as $K_{P,F}$ play a crucial role in determining the level of migration in a real food packaging application. Due to a lack of knowledge of the exact values in any specific case, it is recommended to establish these values in a more generalized way so that reliably 'worst case' scenarios with respect to migration are estimated which, in fact, is of primary interest from a regulatory stand point. To meet this requirement the described migration model has the two following implications:

- In absence of specific data, the partition coefficient should be taken as $K_{P,F} = 1$, which means that the substance is very soluble in food (simulant); this option leads to the highest migration values. For all other cases, that is for which the migrant is relatively insoluble in the food (simulants) the partition coefficient could be set at $K_{P,F} = 1000$. Because these conservative values could strongly influence the estimated migrations, it is recommended to use experimental $K_{P,F}$ values whenever available.
- The literature reports a series of sophisticated models for the theoretical estimation of diffusion coefficients in polymers (Mercea 2000a) but these models are, at least today, too complicated for practical applications. Therefore, a simpler approach was developed. A first approximation to estimate D_P was to correlate this coefficient with the relative molecular mass, M_r, of the migrant, with a matrix-specific (polymer) parameter, A_P and the absolute temperature T, based on empirical data. This approach had been used before (Piringer 1994, Limm and Hollifield 1996). To pursue the goal of obtaining a simple formula for the estimation of D_P, a refined equation for polyolefins and some other plastic materials has been developed (Brandsch et al. 2002). With this equation a polymer specific upper-bound diffusion coefficient, D_P^*, can be estimated and used instead of the actual diffusion coefficient, $D_P \leq D_P^*$, of a migrant in the polymer matrix:

$$D_P^* = 10^4 \exp\left[A_P - 0.1351 M_r^{2/3} + 0.003 M_r - \frac{10454}{T}\right] \quad (cm^2\,s^{-1}) \quad (3)$$

$$\text{with} \quad A_P = A'_P - \frac{\tau}{T}. \quad (4)$$

The parameter, A_P, is linked to the polymer and describes the basic diffusion behaviour or a 'conductance' of the polymer matrix towards the diffusion of migrants. In Equations 3 and 4, A_P should now be regarded as an 'upper-bond' conductance of the polymer. Higher values of A_P in such polymers as low density polyethylene lead to increased D_P^* values and increasing migration while in stiff chain polymers such as polyesters, A_P values account for smaller diffusion coefficients for the same migrant and thus lower migration. The dimensionless term $A_P = A'_P - \tau/T$ can also be a function of temperature, where A'_P is an athermal term. In Equations 3 and 4, A'_P should also be regarded as an 'upper-bond' athermal term for a given class of polymers.

The parameter τ, together with the constant 10 454 in Equation 3, both with the formal dimension of temperature, contribute to the diffusion activation energy, $E_A = (10454 + \tau) \times R$, where $R = 8.3145\ (J\,mol^{-1}\,K^{-1})$ is the gas constant. By analysing from literature E_A data for a large series of migrants in many polymer matrices, it was concluded that one can take $\tau = 0$ for many polymers. Thus, taking $\tau = 0$ for low-density polyethylene (LDPE) one obtains $E_A = 86.92\,kJ\,mol^{-1}$, which is in good agreement with the mean of $E_A = 87\ (kJ\,mol^{-1})$ found from literature data (Mercea 2000b).

For other important groups of plastics relevant to food packaging, e.g. high-density polyethylene (HDPE) and polyethylene terephthalate (PET), a higher activation energy is generally observed. A good mean for these matrices is obtained with $E_A = 100\,kJ\,mol^{-1}$, which requires $\tau = 1577$.

To ensure that the proposed migration model leads to estimations that offer the safety margin required by the EU consumer protection laws, the 'upper-bond' A'_P values for different polymers were selected in such a way that real 'upper-bond' $D_P^\star$ values are obtained in Equation 3. The results obtained are shown in Tables I and II, which are also given in the Practical Guide to the EU Directive 2002/72/EC. Using now these A'_P in Equation 3

Table I. 'Upper-bond' A'_P values for selected polyolefins.

Polymer	A'_P	τ	T (°C)
LDPE/LLDPE	11.5	0	<90
HDPE	14.5	1577	<100
PP (homo and random)	13.1	1577	<120
PP (rubber)	11.5	0	<100

Table II. 'Upper-bond' A'_P values for PS, HIPS, PET, PEN and PA 6,6.

Polymer	A'_P	τ	T (°C)
PS	0.0	0	<70
HIPS	1.0	0	<70
PET	6.0	1577	<175
PEN	5.0	1577	<175
PA (6,6)	2.0	0	<100

and from here the $D_P^\star$ values in Equations 1 and 2 will overestimate the migration and consequently worst-case migration rates will be calculated by the proposed migration model within certain temperature ranges.

To keep Equation 3 functional and to work only with a minimum number of specific variables, to a first approximation τ was fixed at 0 and 1577, which has corresponding activation energies of $E_A = 87$ and 100 (kJ mol^{-1}), respectively. It is known that in a given polymer and temperature range each migrant has a different diffusion activation energy E_A (Mercea 2000b). Therefore, each migrant has a small specific contribution to E_A and thus influences also A'_P. However, analysing the available experimental data, one finds out that the main contribution to these values come from the specific structure of the polymer matrix and thus the influence of the migrant on E_A and respectively A'_P may be neglected in a first approximation.

Polymer-specific migration modelling

Polyolefins. The most important polyolefins (PO) used for food packaging are low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylenes (PP). These materials have specific temperature ranges for which the integrity of the food package is maintained. Using product knowledge of these packages, the temperature range to use PO is generally limited to less than 100°C, which is also valid for the applicability of migration modelling (for details, see Table I). Under these temperature conditions and with an initial migrant concentration, $c_{P,0}$, not higher than about 1%, the migration process in POs follows the general physical law of diffusion with the solution given in Equation 1.

The actual 'upper-bond' values of A'_P and respectively τ from Equation 4 for POs listed in Table I have been determined empirically using a database with diffusion coefficients reported in the literature over the last four decades (Mercea 2000b). In addition, the results from recent migration measurements into olive oil (a simulant used to mimic fatty foods) over a wide temperature range for additives presently used in POs (O'Brien et al. 1997, 1999, O'Brien and Cooper 2001, 2002) confirm these A'_P and τ values. Measured diffusion coefficients for some alkanes and additives in PO (Reynier et al. 1999) were used for comparison with estimated values according to Equation 3 and found to support the A'_P and τ values as listed in Table I.

To validate further the polymer-specific A'_P values in Table I as 'upper-bond' values, migration rates were collected from different sources in the context with the EU project to validate the migration model. All data were obtained from recent measurements using additives from the positive list of substances permitted under Directive 2002/72/EC (Table III). The migration measurements were carried out by following the conditions of Directive 97/48/EC for fatty food (simulants), in most cases olive oil, where solubility for the additives is to be found. The measured migration amounts are listed in Tables IV.I–IV.III.

To establish the 'upper-bind' values for $A_P = A'_P - \tau/T$ (Equation 4), which would provide an 'upper-bond' estimate for $D_P^\star$, the following procedure has been applied. For each migration value in Tables IV.I–IV.III, the corresponding real A_P has been calculated now using Equation 3 for 'real' D_P's instead of 'upper-bond' $D_P^\star$. This means that the real D_P is determined in a first step from the experimental migration results using Equation 1 and assuming no partitioning or $K_{P,F} = 1$. With this real D_P, the corresponding 'real' A_P and respectively A'_P can be calculated with Equations 3 and 4 taking into account that $\tau = 0$ is assumed for LDPE and $\tau = 1577$ for HDPE and PP. The 'real' A'_P values obtained for LDPE, HDPE and PP are listed in Tables IV.I–IV.III. By using this approach, it is possible to build representations that reflect the distribution of the number of experimental migrations from the tables as a function of the athermal 'real' parameter A'_P. In this way, a representation of the characteristic migration behaviour of a polymeric matrix is possible from a collection of experimental data obtained under very different conditions, at different temperatures including migrants of very different structures and molecular weights. In a next step the mean, $\bar{A}'_P$, and the corresponding standard deviation, s, are calculated. To select an upper boundary at the 95% confidence limit for the 'real' A'_P ($A'^\star_P$), the mean is increased by adding the standard deviation multiplied with the Student t-factor (t) for a one (right)-side 95% confidence level or $A'^\star_P = \bar{A}'_P + s \times t$, where N is the number of samples. These $A'^\star_P$ values are listed in Table VI. A comparison between the $A'^\star_P$ values and the 'real' A'_P values from Table I shows a satisfactory match. This is because migration from a food package has a square-root dependence on the diffusion coefficient, therefore small differences in the 'real' A'_P do not translate into large differences in migration.

Other polymers

Similar analysis was performed using data from important non-polyolefins polymers used in food packaging. Polystyrenes used for food packaging applications can be roughly subdivided into two general categories: general-purpose polystyrene (PS) and high-impact polystyrene (HIPS). The polyester with the largest application range for food packaging

Table III. Trade names and the corresponding chemical names of the additives used for migration measurements in the following tables.

Trade name	PM-reference number	CAS number	Chemical name
CG 30-1389	74010	145650-60-8	see Irgafos 38
CGA 012	68145	80410-33-9	see Irgafos 12
CGL 2020	81220	192268-64-7	see Chimassorb 2020
Chimassorb 2020	81220	192268-64-7	Poly((6-(N-(2,2,6,6-tetramethyl-4-piperidinyl)-*n*-butylamino)-1,3,5-triazine 2,4-diyl) ((2,2,6,6-tetramethyl-4-piperidinyl)imino)-1,6-hexanediyl ((2,2,6,6-tetramethyl-4-piperidinyl)imino))-α-(N,N,N′,N′-tetrabutyl-N‴-(2,2,6,6-tetramethyl-4-piperidinyl)imino)
Chimassorb 81	61600	1843-05-6	2-Hydroxy-4-*n*-octylbenzophenone
Cyasorb UV-2908	46800	67845-93-6	3,5-Di-*tert*-butyl-4-hydroxybenzoic acid, hexadecyl ester
Hostavin N 30	92700	78301-43-6	Polymer of 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-20-(2,3-epoxypropyl)dispiro [5.1.11.2]-heneicosane-21-one
Irgafos 12	68145	80410-33-9	2,2′,2″-Nitrilo(triethyl-*tris*(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite)
Irgafos 168	74240	31570-04-4	Phosphorous acid, *tris*(2,4-di-*tert*-butylphenyl)ester
Irgafos 38	74010	145650-60-8	Phosphorous acid, *bis*(2,4-di-*tert*-butyl-6-methylphenyl)ethyl ester
Irganox 1010	71680	6683-19-8	Pentaerythritol tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate)
Irganox 1076	68320	2082-79-3	Octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate
Irganox 1330	95200	1709-70-2	1,3,5-Trimethyl-2,4,6-*tris*(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene
Irganox 245	94400	36443-68-2	Triethyleneglycol-*bis*(3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionate)
Irganox 3052	31520	61167-58-6	Acrylic acid, 2-*tert*-butyl-6-(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl ester
Irganox E 201	93520	59-02-9	d,l-alpha-Tocopherol
Irganox MD 1024	38800	32687-78-8	N,N′-*bis*(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyl)-hydrazide
Isonox 129	39060	35958-30-6	1,1-*Bis*(2-hydroxy-3,5-di-*tert*-butylphenyl)ethane
Mark AO 80	38565	90498-90-1	see Sumilizer GA 80
Mark PEP-36	38810	80693-00-1	*Bis*(2,6-di-*tert*-butyl-4-methylphenyl)pentaerithritol diphosphite
Sanol LS-770	85280	52829-07-9	see Tinuvin 770
Sumilizer GA 80	38565	90498-90-1	3,9-*Bis*(2-(3-(*tert*-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-*tert*-butyl)-2,4,8,10-tetraoxaspiro[5,5]undeca
Sumilizer GM	31520	61167-58-6	see Irganox 3052
Tinuvin 234	60320	70321-86-7	2-(2-Hydroxy-3,5-*bis*(1,1-dimethylbenzyl)phenyl)benzotriazole
Tinuvin 326	60400	3896-11-5	2-(2′-Hydroxy-3′-*tert*-butyl-5′-methylphenyl)-5-chlorobenzotriazole
Tinuvin 770	85280	52829-07-9	Sebacic acid, *bis*(2,2,6,6-tetramethyl-4-piperidyl)ester
TIPA	94560	122-20-3	Triisopropanolamine
Topanol AO 14	95600	1843-03-4	see Topanol CA
Topanol CA	95600	1843-03-4	1,1,3-*Tris*(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane
Ultranox 626	38820	26741-53-7	*Bis*(2,4-di-*tert*-butylphenyl)pentaerythritol diphosphite
Ultranox 640	95270	161717-32-4	2,4,6-*Tris*(*tert*-butyl)phenyl 2-butyl-2-ethyl-1,3-propanediol phosphite
Uvitex OB	38560	7128-64-5	2,5-*Bis*(5-*tert*-butyl-2-benzoazolyl)thiophene
	31920	103-23-1	Acid adipic, *bis*(2-ethylhexyl)ester
	34850	143925-92-2	Amines, *bis*(hydrogenated tallow alkyl) oxidized (mixture)
	54300	118337-09-0	2,2′-Ethylidene *bis*(4,6-di-*tert*butyl-phenyl)fluorophosphonite
	38950	79072-96-1	*Bis*(4-ethylbenzylidene)sorbitol
	52880	23676-09-7	4-Ethoxybenzoic acid, ethylester
	39280	120-40-1	N,N-*Bis*(2-hydroxyethyl)lauramide
	75120	84-66-2	Phthalic acid, diethyl ester
	74560	85-68-7	Phthalic acid, benzylbutyl ester

is polyethylene terephthalate (PET) and to a much smaller extent is polyethylene naphthalate (PEN). Polyamide (PA(6,6)) plays also an important role as a food packaging material.

Using product knowledge of the various polymer types the temperature range for the applicability of migration modelling, are listed in Table II. In these cases the migration process in the above-mentioned non-polyolefins follow the physical law of diffusion with the solution given in Equation 1.

In comparison with the POs, the quantity of available migration and diffusion data is much smaller. It should also be noted that the inherent low diffusivity in these polymers produces numerous migration experiments with non-detectable results. These non-detectable results cannot be included in the validation procedure. As a consequence, an initial estimate of corresponding A_P values following the stochastic approach was not possible. Therefore, using the procedure as described above, the upper-bond limits of A'_P values have been determined using a statistical evaluation. This evaluation was based directly on available migration values. As in the case of POs, only migration data obtained for additives from the positive list (Table III), from well-designed migration measurements done in one of the author's

Table IV.I. Migration data from LDPE.

PM/reference number	CAS number	Additive	M_r	d_P (cm)	$c_{P,0}$ (mg kg^{-1})	T (°C)	t	$m_{F,t}$ (mg kg^{-1}) exp.	A'_P	Polymer: remarks[1]
68320 (1)	2082-79-3	Irganox 1076	531	0.05	930	40	10 days	2.6	7.0	LLDPE; 0.91
68320 (2)	2082-79-3	Irganox 1076	531	0.2	220	40	1 day	0.85	9.7	0.918
							2 days	1.26	9.8	
							4 days	1.74	9.8	
							10 days	2.75	9.8	
95200 (2)	1709-70-2	Irganox 1330	775	0.2	585	40	1 day	1.13	10.1	0.918
							2 days	1.55	10.1	
							4 days	2.20	10.1	
							10 days	3.56	10.1	
74240 (2)	31570-04-4	Irgafos 168	646	0.2	760	80	1 h	3.20	10.2	0.918
							2 h	4.54	10.2	
							3.5 h	5.87	10.1	
							6 h	7.86	10.1	
74240 (2)	31570-04-4	Irgafos 168	646	0.2	540	80	1 h	3.22	10.9	LLDPE; 0.905
							2 h	4.72	10.95	
74240 (2)	31570-04-4	Irgafos 168	646	0.2	540	80	3.5 h	6.46	11.05	LLDPE; 0.905
							6 h	8.39	11.05	
92700 (3)	78301-43-6	Hostavin N 30	840[2]	0.1	450[2] 670 670	49	1 day	1.2	9.8	0.93
			1680							
			2000							
			840		450 670 670		2 days	2.02	10.2	
			1680							
			2000							
			840		450 670 670		5 days	3.65	10.4	
			1680							
			2000							
			840		450 670 670		10 days	5.34	10.5	
			1680							
			2000							
92700 (3)	78301-43-6	Hostavin N 30	840	0.1	450 670 670	66/49	0.5 h/1 day	1.4	10.0	0.93
			1680							
			2000							
			840		450 670 670		0.5/5 days	4.79	11.0	
			1680							
			2000							
			840		450 670 670		0.5/10 days	6.65	11.0	
			1680							
			2000							
93520 (3)	59-02-9	d,l-α-Tocopherol; Irganox E 201	431	0.4	1000	40	10 days	16.74	9.5	0.93
94560 (3)	122-20-3	Triisopropanolamine (TIPA)	191	0.015	270	40	10 days	0.35	7.6	0.92
			191	0.015	270	100	1 h	0.49	8.2	0.92

Experimental migration data in fat simulants were collected from different sources, expressed as mg kg^{-1} (1 kg simulant with the density $\rho_F = 0.9$ g cm^{-3} in contact with 6 dm^2 polymer with thickness d_P) and the corresponding 'real' A'_P values calculated with Equations 1 and 3; $\tau = 0$.

[1]Density ρ_P (g cm^{-3}) of the corresponding polymer.

[2]Relative molecular masses, M_r, and the corresponding initial concentrations, $C_{P,0}$, of the oligomers in an additive mixture were calculated from the distribution curve of the mixture obtained by GLP. Number in parentheses in column 1 indicates the source of the experimental data: (1) Istituto Superiore de Sanita (ISS), Rome; (2) FABES, Munich; and (3) Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin (BgVV), Berlin.

laboratories and migration results collected from recognized authorities have been considered. These experimental data are compiled in Tables IV.IV–IV.VIII. For all these data, the corresponding 'real' A'_P values have been calculated using Equations 1 and 3. With regards to the activation energy of diffusion, $\tau = 0$ is assumed for PS, HIPS and PA 6,6 and $\tau = 1577$ for PET and PEN, respectively. Based on these results as listed in Table VI, the 'upper-bond' A'_P values for PS, HIPS, PET, PEN and PA (6,6) as shown in Table II have been proposed to the EU Commissions. These A'_P values lead to 'upper-bond' D_P⋆ values and respectively 'worst-case' migration estimations, which in fact is

Table IV.II. Migration data from HDPE.

PM/reference number	CAS number	Additive	M_r	d (cm)	$c_{P,0}$ (mg kg^{-1})	T (°C)	t	$m_{F,t}$ (mg kg^{-1}) exp.	A'_P	Polymer: remarks[1]
74240 (2)	31570-04-4	Irgafos 168	646	0.2	1070	80	1 h	0.89	11.3	0.946
							2 h	1.26	11.3	0.946
							3.5 h	1.70	11.4	0.946
74240 (2)	31570-04-4	Irgafos 168	646	0.2	1070	80	6 h	2.36	11.5	0.946
68320 (2)	2082-79-3	Irganox 1076	531	0.2	2000	40	4 days	3.84	11.9	0.948
							10 days	6.06	11.9	0.948
							20 days	8.70	11.9	0.948
68320 (2)	2082-79-	Irganox 1076	531	0.2	2000	60	1 day	8.70	12.6	0.948
							2 days	11.82	12.55	0.948
							4 days	15.90	12.5	0.948
74240 (2)	31570-04-4	Irgafos 168	646	0.2	2000	60	1 day	2.64	11.1	0.948
							2 days	3.84	11.2	0.948
							4 days	5.58	11.2	0.948
34850 (4)	143925-92-2	Amines, *bis*(hydrogenated tallow alkyl) oxidized (mixture)	537	0.1	960	40	10 days	1.02	9.8	–
38565 (3)	90498-90-1	Sumilizer GA 80; ADK STAB AO-80; MARK AO-80	741	0.1	3000	65.5/49	0.5 h/2 h	0.14	7.9	0.95
							0.5/1 day	0.24	7.3	
38565 (3)	90498-90-1	Sumilizer GA 80; ADK STAB AO-80; MARK AO-80	741	0.1	3000	65.5/49	0.5/4 days	0.61	7.9	
							0.5/10 days	0.85	7.6	
38800 (3)	32687-78-8	Irganox MD 1024	553	0.06	1000	40	10 days	0.09	5.0	0.962
			553	0.06	1000	100	1 h	0.76	8.6	0.962
			553	0.06	2000	40	10 days	0.23	5.5	0.962
			553	0.06	2000	100	1 h	2.03	9.2	0.962
38820 (3)	26741-53-7	Ultranox 626	604	0.05	500	40	10 days	<0.42	<9.9	0.95
			604	0.05	500	100	1 h	<0.42	<9.2	0.95
			604	0.05	1000	40	10 days	<0.42	<8.5	0.95
			604	0.05	1000	100	1 h	<0.42	<7.8	0.95
39060 (3)	35958-30-6	Isonox 129	439	0.13	1000	40	10 days	1.03	9.0	0.949
			439	0.13	1000	100	1 h	2.90	10.4	0.949
54300 (4)	118337-09-0	2,2′-Ethylidene *bis*(4,6-di-*tert*butyl-phenyl)fluoro-phosphonite	487	0.1	750	40	10 days	0.33	7.6	–

(*continued*)

Table IV.II. Continued.

PM/reference number	CAS number	Additive	M_r	d (cm)	$c_{P,0}$ (mg kg^{-1})	T (°C)	t	$m_{F,t}$ (mg kg^{-1}) exp.	A'_P	Polymer: remarks[1]
68145 (3)	80410-33-9	CGA 012; TK12878	1465	0.1	3000	40	10 days	0.60	12.2	0.95
			1465	0.1	3000	100	2 h	0.72	11.2	0.95
74010 (3)	145650-60-8	CG 30-1389; Irgafos 38	515	0.1	1500	40	10 days	1.46	9.5	0.95
			515	0.1	1500	70	2 h	1.20	10.5	0.95
74010 (3)	145650-60-8	CG 30-1389; Irgafos 38	515	0.1	1500	70	2 h	1.92	11.5	MDPE; 0.94
81220 (3;4)	192268-64-7	CGL 2020	1060[2]	0.1	51[2] 372 1518	60	3.5 h	0.038	12.1	0.95
			1710		1338					
			2360							
			3660							
81220 (3;4)	192268-64-7	CGL 2020	1060	0.1	85 620 2530 2230	60	3.5	0.066	12.1	0.95
			1710							
			2360							
			3660							
85280 (4)	52829-07-9	Sanol LS-770	481	0.1	3000	40	10 days	4.80	10.2	–
			481	0.1	3000	60	1 h	2.04	11.6	–
			481	0.1	3000	110	0.17 h	5.76	10.8	–
92700 (3)	78301-43-6	Hostavin N 30	840[2]	0.1	420[2] 620 620	100/49	0.5 h/1 day	0.084	8.0	0.95
			1680							
			2000							
			840		420 620 620		0.5/4 days	0.114	8.1	
			1680							
			2000							
92700 (3)	78301-43-6	Hostavin N 30	840	0.1	420 620 620	100/49	0.5/10 days	0.288	9.4	
			1680							
			2000							
92700 (3)	78301-43-6	Hostavin N 30	840	0.1	770 1150 1150	100/49	0.5/1 day	0.150	7.9	
			1680							
			2000							
			840		770 1150 1150		0.5/4 days	0.252	8.5	
			1680							
			2000							
			840		770 1150 1150		0.5/10 days	0.522	9.3	
			1680							
			2000							
95270 (3)	161717-32-4	Ultranox 640	450	0.254	1000	65.5/40	2 h/0 days	1.11	11.1	0.95
							2 h/1 day	1.72	11.5	
							2 h/4 days	2.17	11.1	
							2 h/10 days	2.74	10.9	

Experimental migration data in fat simulants were collected from different sources, expressed as mg kg^{-1} (1 kg simulant with the density $\rho_F = 0.9$ g cm^{-3} in contact with 6 dm^2 polymer with thickness d_P) and the corresponding 'real' A_P' values calculated with Equations 1, 3 and 4; $\tau = 1577$.

[1]Density ρ_p (g cm^{-3}) of the corresponding polymer.

[2]Relative molecular masses, M_r, and the corresponding initial concentrations, $C_{P,0}$, of the oligomers in an additive mixture were calculated from the distribution curve of the mixture obtained by GLP. Number in parentheses in column 1 indicates the source of the experimental data; (2) FABES, Munich; (3) BgVV, Berlin; (4) European Union Commission, Brussels.

Table IV.III. Migration data from PP.

PM/reference number	CAS number	Additive	M_r	d (cm)	$c_{P,0}$ (mg kg^{-1})	T (°C)	t	$m_{F,t}$ (mg kg^{-1}) exp.	A'_P
38820 (1)	26741-53-7	Ultranox 626	605	0.05	950	40	10 days	<0.5	<9.0
			605	0.05	950	40	10 days	<0.5	<9.0
			605	0.05	1000 (theoretical)	40	10 days	<0.5	<8.9
			605	0.05	972	40	10 days	<0.5	<9.0
68320 (1)	2082-79-3	Irganox 1076	531	0.05	995	40	10 days	0.2	6.5
			531	0.05	915	40	10 days	0.2	6.7
			531	0.05	1064	40	10 days	1.1	9.8
34850 (4)	143925-92-2	Amines, *bis*(hydrogenated tallow alkyl) oxidised	537	0.1	1040	40	10 days	<1.02	<9.8
			537	0.1	1040	100	2 h	1.86	9.6
38565 (3)	90498-90-1	Sumilizer GA 80; ADK STAB AO-80; MARK AO-80	741	0.1	2000	65.5/49	0.5 h/2 h	0.19	9.4
							0.5/1 day	0.22	8.0
							0.5/4 days	0.47	8.2
							0.5/10 days	0.88	8.6
38810 (3)	80693-00-1	Mark PEP–36; (ADK STAB PEP–36)	633	0.2	2500	71/49	2 h/0 days	1.39	10.7
							2 h/1 day	1.60	10.2
							2 h/4 days	1.62	9.3
							2 h/10 days	1.89	8.8
38820 (3)	26741-53-7	Ultranox 626	604	0.05	2500	40	10 days	1.91	9.8
			604	0.05	1000	40	10 days	0.99	10.3
			604	0.05	1000	100	1 h	3.71	12.2
38950 (3)	79072-96-1	*Bis*(4-ethylbenzylidene)sorbitol	414	0.06	3000	40	10 days	1.62	7.5
			414	0.06	3000	70	2 h	2.10	9.5
			414	0.06	3000	100	0.5 h	1.44	7.3
39060 (3)	35958-30-6	Isonox 129	439	0.06	1000	40	10 days	0.37	7.0
			439	0.06	1000	121	0.5 h	4.70	10.4
39280 (4)	120-40-1	N,N-*bis*(2-hydroxyethyl)lauramide	288	0.0375	1900	40	10 days	0.96	6.2
			288	0.0375	1900	70	2 h	1.56	6.5
46800 (4)	67845-93-6	Cyasorb UV-2908	475	0.05	3000	40	10 days	2.88	9.2
			475	0.05	5000	40	10 days	5.22	9.4
			475	0.05	5000	70	2 h	4.45	10.5
52880 (4)	23676-09-7	4-Ethoxybenzoic acid, ethyl ester	194	0.2	57	40	10 days	1.09	12.3
			194	0.2	57	70	2 h	0.54	12.4
			194	0.2	92	40	10 days	1.75	12.4
52880 (4)	23676-09-7	4-Ethoxybenzoic acid, ethyl ester	194	0.2	92	70	2 h	0.84	12.2
			194	0.2	322	40	10 days	4.41	11.7
			194	0.2	322	70	2 h	1.94	11.5
54300 (4)	118337-09-0	2,2′-Ethylidene *bis*(4,6-di-*tert*-butyl-phenyl)fluorophosphonite	487	0.1	750	40	10 days	0.52	8.65
68145 (3)	80410-33-9	CGA-012 (TK 12878)	1465	0.1	3000	40	10 days	0.60	12.3
			1465	0.1	3000	100	2 h	0.90	11.7

(*continued*)

Table IV.III. Continued.

PM/reference number	CAS number	Additive	M_r	d (cm)	$c_{P,0}$ (mg kg^{-1})	T (°C)	t	$m_{F,t}$ (mg kg^{-1}) exp.	A'_P
71680 (3)	6683-19-8	Irganox 1010	1178	0.0025	10 000	40	10 days	1.08	9.5
74010 (3)	145650-60-8	CG 30-1389; Irgafos 38	515	0.1	3000	40	10 days	1.2	7.8
			515	0.1	3000	70	2 h	1.2	9.2
81220 (3)	192268-64-7	CGL 2020	1060[1]	0.1	51[1] 372 1518	60	3.5 h	0.05	12.7
			1710		1338				
			2360						
			3660						
			1060	0.1	85 620 2530 2230	60	3.5 h	0.096	12.9
			1710						
			2360						
			3660						
85280 (4)	52829-07-9	Sanol LS-770	481	0.1	5000	60	1 h	1.20	9.7
			481	0.1	5000	110	0.17 h	3.90	9.1
92700 (3;4)	78301-43-6	Hostavin N 30	840[1]	0.1	400[1] 600 600	40	10 days	0.042	7.1
			1680						
			2000						
			840	0.1	700 1060 1060	40	10 days	0.072	7.0
			1680						
			2000						
93520 (3)	59-02-9	d,l-α-Tocopherol	431	0.4	1000	40	10 days	1.14	9.2
95270 (3)	161717-32-4	Ultranox 640	450	0.254	1000	65.5/40	2 h/0 days	0.28	8.4
							2 h/1 day	0.43	8.7
							2 h/4 days	0.45	8.1
							2 h/10 days	0.62	8.0

Experimental migration data in fat simulants were collected from different sources, expressed as mg kg^{-1} (1 kg simulant with the density $\rho_F = 0.9$ g cm^{-3} in contact with 6 dm^2 polymer with thickness d_P) and the corresponding 'real' A_P' values calculated with Equations 1, 3 and 4; $\tau = 1577$.

[1]Relative molecular masses, M_r, and the corresponding initial concentrations, $C_{P,0}$, of the oligomers in an additive mixture were calculated from the distribution curve of the mixture obtained by GLP. Number in parentheses in column 1 indicates the source of the experimental data: (1) ISS, Rome; (3) BgVV, Berlin; and (4) European Union Commission, Brussels.

Table IV.IV. Migration data from PET.

PM/reference number	CAS number	Additive	M_r	d_P (cm)	$c_{P,0}$ (mg kg^{-1})	T (°C)	t	$m_{F,t}$ (mg kg^{-1})	A'_P
60320 (4)	70321-86-7	Tinuvin 234 (olive oil)	448	0.1	2500	40	10 day	0.006	−3.6
			448	0.1	2500	100	1 h	0.11	1.6
						100	2 h	0.13	1.2
			448	0.1	5000	40	10 day	0.008	−4.3
			448	0.1	5000	100	1 h	0.25	1.8
						100	2 h	0.31	1.6
60320 (2)	70321-86-7	Tinuvin 234 (ethanol 95%)	448	0.1	1400	40	10 day	0.01	−1.4
60320 (5)	70321-86-7	Tinuvin 234 (olive oil)	448	0.1	903	175	2 h	3.6	4.4
			448	0.1	880	175	2 h	4.2	4.8
60320 (6)	70321-86-7	Tinuvin 234 (i-octane)	448	0.025	2360	70	3 day	0.05	−2.0
						60	10 day	0.07	−2.5
		(ethanol 95%)	448	0.025	2360	60	5 day	0.145	1.0
60320 (6)	70321-86-7	Tinuvin 234 (ethanol 95%)	448	0.025	2360	60	10 day	0.26	1.5
(6)		Tinuvin 234 ... (iso-octane)	448	0.025	2360	50	15 day	0.053	−1.0
(2)		Tinuvin 234 (ethanol 95%)	448	0.025	2360	50	10 day	0.15	1.5
			448	0.025	2360	40	13 day	0.01	−3.0
(4)	–	Pentaerythrit (olive oil)	136	0.03	400	40	10 day	0.028	−0.4
			136	0.03	400	49	7 day	0.028	−0.9
51700 (6)	147315-50-2	Tinuvin 1577 (oil)	425	0.0025	5000	121/49	2 h/10 days	0.42	−0.4
61600 (5)	1843-05-6	Chimassorb 81 (olive oil)	326	0.1	896	175	2 h	7.6	4.8
			326	0.1	937	175	2 h	10.0	5.3
(2)	–	Tinuvin 571 (i-octane)	394	0.1	3000	60	1.5 h	0.016	0.3
68320 (5)	2082-79-3	Irganox 1076 (olive oil)	531	0.1	4184	175	2 h	11.8	4.4
			531	0.1	3812	175	2 h	17.6	5.5

Experimental migration data in fat simulants were collected from different sources, expressed as mg kg^{-1} (1 kg simulant with the density $\rho_F = 0.9$ g cm^{-3} in contact with 6 dm^2 polymer with thickness d_P) and the corresponding 'real' A'_P values calculated with Equations 1, 3 and 4: $\tau = 1577$.
Number in parentheses in column 1 indicates the source of the experimental data: (2) FABES, Munich; (4) European Union Commission, Brussels; (5) PIRA, Leatherhead; and (6) FDA, Washington, DC.

Table IV.V. Migration data from PEN.

PM/reference number	CAS number	Additive	M_r	d_P (cm)	$c_{P,0}$ (mg kg^{-1})	T (°C)	t	$m_{F,t}$ (mg kg^{-1})	A'_P
60320 (5)	7 h0321-86-7	Tinuvin 234 (olive oil)	448	0.1	860	121	2 h	<0.2	2.4 (sample 1)
			448	0.1	870	121	2 h	<0.2	2.4 (2)
			448	0.1	780	121	2 h	0.34	3.7 (3)
			448	0.1	850	121	2 h	<0.2	2.4 (4)
			448	0.1	840	121	2 h	<0.2	2.4 (5)
			448	0.1	809	121	2 h	<0.2	2.4 (6)
74560 (5)	–	Benzylbutylphthalate (olive oil)	312	0.1	8700	121	2 h	0.2	−3.4 (sample 1)
			312	0.1	8700	121	2 h	0.2	−3.4 (2)
			312	0.1	7100	121	2 h	5.3	3.5 (3)
			312	0.1	8600	121	2 h	0.2	−3.5 (4)
			312	0.1	8600	121	2 h	0.1	−4.9 (5)
			312	0.1	8200	121	2 h	<0.1	−5.5 (6)
			312	0.1	8700	40	10 d	0.1	−1.8 (sample 1)
			312	0.1	8700	40	10 days	0.1	−1.8 (2)
			312	0.1	7100	40	10 days	0.1	−1.5 (3)
			312	0.1	8600	40	10 days	0.1	−1.7 (4)
			312	0.1	8600	40	10 days	0.1	−1.7 (5)
			312	0.1	8200	40	10 days	0.1	−1.6 (6)

Experimental migration data in fat simulants were collected from different sources, expressed as mg kg^{-1} (1 kg simulant with the density $\rho_F = 0.9$ g cm^{-3} in contact with 6 dm^2 polymer with thickness d_P) and the corresponding 'real' A_P' values calculated with Equations 1, 3 and 4; $\tau = 1577$.
Number in parentheses in column 1 indicates the source of the experimental data: (5) PIRA, Leatherhead.

Table IV.VI. Migration data from PS.

PM/reference number	CAS number	Additive	M_r	d_P (cm)	$c_{P,0}$ (mg kg^{-1})	T (°C)	t	$m_{F,t}$ (mg kg^{-1})	A'_P
74240 (4)	31570-04-4	Irgafos 168 (olive oil)	647	0.1	1000	40	10 days	0.012	−3.5
			647	0.1	2000	40	10 days	0.053	−1.8
68320 (4)	2082-79-3	Irganox 1076 (olive oil)	531	0.1	1000	50	1 h	0.004	−2.1
							4 h	0.006	−2.6
			531	0.1	1000	60	1 h	0.007	−1.8
							4 h	0.012	−2.1
							1 day	0.031	−2.0
31520 (5)	61167-58-6	Irganox 3052 (olive oil)	395	0.2	5000	40	10 days	0.043	−5.6
			395	0.2	5000	70	2 h	0.30	0.0
94400 (4)	36443-68-2	Irganox 245 (HB307)	587	0.1	2000	40	10 days	0.0185	−4.3
			587	0.1	2000	10	10 days	0.0076	−2.5
(1)		Styrene (olive oil)	104	0.2	220	40	10 days	0.046	−3.0
(1)			104	0.2	210	40	10 days	0.060	−2.5
95600 (5)	1843-03-4	Topanol CA (HB 307)	545	0.05	2000	50	48 days	0.06	−5.0
(4)		Styrene (trimer) (HB 307)	312	0.16	9700	40	10 days	0.108	−6.5
24610	000100-42-5	Styrene ... (Tenax)	104	0.1	300	40	11 days	0.04	−3.0
						50	11 days	0.10	−3.0
24610 (2)	000100-42-5	Styrene ... (Tenax)	104	0.1	300	60	10 days	0.19	−2.5
						70	11 days	0.31	−2.7
					370	40	10 days	0.07	−3.0
						50	10 days	0.12	−3.0
						60	10 days	0.17	−3.3
						70	11 days	0.33	−3.0
		Styrene ... (olive oil)				60	10 days	0.16	−3.7
		Styrene ... (Tenax)			300	40	11 days	0.07	−2.7
						50	11 days	0.16	−2.3
						60	10 days	0.32	−1.8
					200	40	10 days	0.08	−1.8
						50	10 days	0.12	−2.0
						60	10 days	0.18	−2.0
						70	11 days	0.34	−1.9
		Styrene ... (olive oil)				60	10 days	0.30	−1.3

Experimental migration data in fat simulants were collected from different sources, expressed as mg kg^{-1} (1 kg simulant with the density $\rho_F = 0.9$ g cm^{-3} in contact with 6 dm^2 polymer with thickness d_P) and the corresponding 'real' A'_P values calculated with Equations 1 and 3; $\tau = 0$.
Number in parentheses in column 1 indicates the source of the experimental data: (1) ISS, Rome; (2) FABES, Munich; (4) European Union Commission, Brussels; and (5) PIRA, Leatherhead.

Table IV.VII. Migration data from HIPS.

PM/reference number	CAS number	Additive	M_r	d_P (cm)	$c_{P,0}$ (mg kg^{-1})	T (°C)	t	$m_{F,t}$ (mg kg^{-1})	A'_P
38560 (7)	7128-64-5	Uvitex OB (olive oil)	430	0.2	400	70	6 h	0.01	−3.0
			430	0.2	500	40	10 days	0.01	−4.3
			430	0.2	500	70	6 h	0.01	−3.5
			430	0.2	500	70	6 h	0.03	−1.3
			430	0.2	300	70	6 h	0.01	−2.4
61600 (7)	1843-05-6	Chimassorb 81 (olive oil)	326	0.2	6100	40	10 days	0.13	−5.1
			326	0.2	6100	70	6 h	0.34	−2.4
			326	0.2	7200	40	10 days	0.18	−4.8
			326	0.2	7200	70	6 h	0.29	−3.1
			326	0.2	6900	40	10 days	0.28	−3.8
			326	0.2	6900	70	6 h	0.60	−1.5
			326	0.2	6700	40	10 days	0.09	−6.0
			326	0.2	6700	70	6 h	0.12	−4.7
			326	0.2	5000	40	10 days	0.10	−5.2
			326	0.2	5000	70	6 h	0.27	−2.4
75120 (7)	84-66-2	Diethylphthalate (olive oil)	222	0.2	4100	70	6 h	0.15	−4.4
			222	0.2	4700	70	6 h	0.07	−6.2
			222	0.2	4400	70	6 h	0.26	−3.4
			222	0.2	3200	70	6 h	0.15	−3.8
(4)		Styrene (dimer) (HB 307)	208	0.16	600	40	10 days	0.288	0.0
(4)		Styrene (trimer) (HB 307)	312	0.16	9700	40	10 days	0.975	−1.9
(1)		Styrene (olive oil)	104	0.2	360	40	10 days	0.168	−1.0
(1)			104	0.2	160	40	10 days	0.084	−1.0
24610 (2)	000100-42-5	Styrene … (Tenax)	104	0.2	300	40	11 days	0.10	−2.0
						50	11 days	0.25	−1.5
						60	10 days	0.38	−1.5
						70	11 days	0.65	−1.5
		Styrene … (olive oil)				60	20 days	0.40	−2.0
		Styrene … (Tenax)			380	40	10 days	0.35	−0.2
						50	10 days	0.37	−1.0
						60	10 days	0.44	−1.6
						70	11 days	0.77	−1.4
		Styrene … (olive oil)				60	10 days	0.44	−1.5

Experimental migration data in fat simulants were collected from different sources, expressed as mg kg^{-1} (1 kg simulant with the density $\rho_F = 0.9$ g cm^{-3} in contact with 6 dm^2 polymer with thickness d_P) and the corresponding 'real' A'_P values calculated with Equations 1 and 3; $\tau = 0$.
Number in parentheses in column 1 indicates the source of the experimental data: (1) ISS, Rome; (2) FABES, Munich; (4) European Union Commission, Brussels; (5) PIRA, Leatherhead; (7) DOW, Midland and PIRA, Leatherhead.

Table IV.VIII. Migration data from PA.

PM/reference number	CAS number	Additive	M_r	d_P (cm)	$c_{P,0}$ (mg kg^{-1})	T (°C)	t	$m_{F,t}$ (mg kg^{-1}) exp.	A'_P
94400 (4)	36443-68-2	Irganox 245 (olive oil)	587	0.1	5000	40	10 days	0.009	−7.7
			587	0.1	5000	100	1 h	0.128	−2.2
			587	0.1	5000	49	3 h	0.012	−3.7
							8 h	0.012	−4.6
							1 day	0.030	−3.9
							4 days	0.066	−3.7
							10 days	0.096	−3.9

Experimental migration data in fat simulants were collected from different sources, expressed as mg kg^{-1} (1 kg simulant with the density $\rho_F = 0.9$ g cm^{-3} in contact with 6 dm^2 polymer with thickness d_P) and the corresponding 'real' A'_P values calculated with Equations 1 and 3, $\tau = 0$.
Number in parentheses in column 1 indicates the source of the experimental data: (4) European Union Commission, Brussels.

Table V.I. D_P values (8) and the corresponding 'real' A'_P values for PET; $\tau = 1577$.

	M_r	T (°C)	E_D (kJ mol^{-1})	D_P (cm^2 s^{-1})	A'_P
Acetaldehyde	44	90	45	1.7E–9	5.3
		55		3.4E–10	7.2
Toluene	92	155	107	6.1E–9	2.5
		125		6.4E–10	2.3
Limonene	136	155	147	1.5E–9	1.75
		140		3.4E–10	1.3
Ethyl-butyrate	116	150	131	4.4E–9	2.9
		125		4.2E–10	2.3
Chloroform	119	160	113	2.2E–8	3.9
		95		8.8E–11	3.2
Citral	152	160	73	8.7E–10	1.1
		140		3.3E–10	1.5
Linalool	154	160	92	8.7E–10	1.1
		140		2.5E–10	1.2
Ethylene-glycol	62	140	86	4.5E–9	2.6
		115		8.9E–10	2.9
Methanol	32	85	46	1.0E–9	7.1
		55		4.2E–10	4.9
Ethanol	46	160	63	1.9E–8	2.4
		130		5.1E–9	3.2
Benzaldehyde	106	155	78	4.7E–9	2.4
		125		9.1E–10	2.9
Dimethyldisulfide (DMDS)	94	165	92	1.4E–8	2.7
		130		1.6E–9	2.9
Tetracosane	339	160	194	2.8E–8	6.7
		145		4.0E–9	5.8
Methyl-dioxolane	88	160	87	1.5E–8	3.0
		135		3.3E–9	3.2
m-Xylene	106	155	109	4.6E–9	2.4
		123		4.6E–10	2.4
a-Terpineol	154	155	166	1.2E–9	1.8
		140		2.2E–10	1.1
Lindane	291	160	84	1.8E–9	3.5
		135		4.3E–10	3.8

(8) F. Bayer, The Coca-Cola Co., Atlanta, GA.

in agreement with the goal of a consumer protection legislation.

In addition to the migration data as listed Tables IV.IV–IV.VIII, some recent experimental diffusion coefficients, obtained with up-to-date experimental methods, were available for PET, PEN and PA and covered the temperature range of interest for food packaging materials (Tables V.I–V.III). Using these 'real' D_P's in conjunction with Equation 3, one can calculate for each D_P the corresponding 'real' A_P and respectively 'real' A'_P. The values obtained, taking $\tau = 1577$ for PET and PEN and $\tau = 0$ for PA, are shown in Tables V.I–V.III and can be compared with the 'upper-bond' A'_P values given in Table II.

Table V.II. D_P values (8) and the corresponding 'real' A'_P values for PEN; $\tau = 1577$.

	M_r	T (°C)	E_D (kJ mol^{-1})	D_P (cm^2 s^{-1})	A'_P
Acetaldehyde	44	120	54	9.7E–10	2.2
		90		2.5E–10	3.4
Toluene	92	175	120	9.1E–10	−0.7
		145		9.1E–11	−1.1
Limonene	136	160	151	3.7E–11	−2.3
		180		2.4E–10	−1.6
Ethyl butyrate	116	150	117	6.0E–11	−1.5
		180		5.5E–10	−1.1
Chloroform	119	135	146	4.0E–11	−0.8
		160		4.8E–10	0.0
Ethylene glycol	62	150	106	2.7E–10	−0.9
		125		4.1E–11	−1.0
Methanol	32	130	39	2.4E–9	2.1
		95		8.0E–10	3.8
Ethanol	46	160	82	1.9E–9	0.1
		130		3.4E–10	0.4
Dimethyldisulfide (DMDS)	94	165	98	3.8E–10	−0.9
		140		7.5E–11	−0.9
Methyl dioxolane	88	170	124	1.4E–9	0.0
		150		2.7E–10	−0.4

(8) F. Bayer, The Coca-Cola Co., Atlanta, GA.

Table V.III. D_P values (8) and the corresponding 'real' A'_P values for PA (6.6); $\tau = 0$.

	M_r	T (°C)	E_D (kJ mol^{-1})	D_P (cm^2 s^{-1})	A'_P
Acetaldehyde	44	95	77	2.6E–9	1.0
		110		6.8E–9	0.8
Toluene	92	140	107	1.7E–9	−1.6
		120		3.5E–10	−1.9
Limonene	136	150	117	4.7E–10	−2.8
		165		1.5E–9	−2.5
Ethyl-butyrate	116	150	100	2.2E–9	−1.6
		120		2.6E–10	−1.8
Chloroform	119	140	100	4.0E–9	−0.3
		125		1.3E–9	−0.5
Ethylene-glycol	62	150	72	4.1E–9	−1.9
		120		8.6E–10	−1.6
Methanol	32	110	38	8.6E–9	0.8
		75		2.6E–9	2.3
Ethanol	46	105	66	1.3E–9	−0.4
		130		4.6E–9	−0.9
Benzaldehyde	106	150	22	1.1E–9	−2.4
		115		6.1E–10	−0.8
Methyl-dioxolane	88	155	76	8.7E–9	−0.9
		120		1.3E–9	−0.7
m-Xylene	106	150	72	4.1E–9	−1.1
		120		8.6E–10	−0.8
Lindane	291	155	73	3.1E–9	0.7
		125		6.6E–10	1.0

(8) F. Bayer, The Coca-Cola Co., Atlanta, GA.

For example, for PET, an 'upper-bond' $A'_P = 6$ has been proposed based on a separate evaluation of $N = 24$ migration values listed in Table IV.IV whose migrants are defined in Table III. These data were generated following regulatory requirements for fatty food (simulants) and produced a mean ($A'_P = 0.84$ with $s = 2.9$ and $A'_{P(max)} = 5.5$. Therefore, $A'^{\star}_P$ is deduced to be $A'^{\star}_P = 0.84 + 2.9 \times 1.7 = 5.8$.

Conclusion and outlook

Summarizing the results presented above, it can be stated that the scope of the EU project that initiated the work will have been accomplished and the following occurred:

- A series of initial and boundary conditions for the use of migration estimations from plastic food-contact materials were defined.

Table VI. Statistical evaluation of A'_P values for migration modelling under 'worst-case' conditions.

Polymer	A'_P	S	$A'_{P(max)}$	$A'_{P(min)}$	N	t	$A'_P{}^\star$	τ
LDPE	10.0	1.0	11	7.0	27	1.7	11.7	0
HDPE	10.0	1.9	12.6	5.0	49	1.68	13.2	1577
PP	9.4	1.8	12.9	6.2	53	1.68	12.4	1577
PET	2.2	2.5	7.2	−4.3	58	1.67	6.35	1577
PEN	−0.34	2.4	3.8	−5.5	38	1.7	3.7	1577
PS	−2.8	1.25	0.0	−6.5	32	1.7	−0.7	0
HIPS	−2.7	1.67	0	−6.2	33	1.7	0.1	0
PA (6,6)	−1.54	2.0	2.3	−7.7	31	1.7	1.9	0

- For applications in agreement with this framework of initial and boundary conditions, analytical algorithms for the calculation of a 'worst-case' migration level were proposed. The development of a scheme to estimate 'upper-bond' diffusion coefficients by using only readily available experimental data played a crucial role.
- For a series of plastic food-contact materials, which in fact represent the bulk of polymers used nowadays in food packaging, specific parameters needed for the migration calculations were derived. The use of these parameters in migration modelling leads to 'worst-case' estimations that ensure, in at least of 95% of cases, a broad consumer safety margin.
- Based on existing and recently generated up-to-date migration data, a validation scheme for the proposed mathematical framework and polymer-specific parameters was proposed and proofed.
- The fact that the results of this work were considered as a reliable tool to verify the compliance with current food-contact material legislation was eventually certified by the EU Commissions that implemented this migration modelling scheme in Directive 2002/72/EC.

Note that the encouraging results reported here should be regarded only as a first step in a longer process of refinement of migration estimation models for compliance purposes.

As soon as new experimental results, obtained with up-to-date techniques, are available, more precise 'upper-bond', $A_P{}^\star$, values could be estimated. The goal is to produce migration estimations that approach increasingly the real value and thus reduce the over estimations of the model to the safety margin required by the law-maker.

The spectrum on migration processes from plastic food-contact materials is much wider than what is covered by those given nowadays in the Practical Guide accompanying Directive 2002/72/EC. One can mention here only migration from other types of polymers that those given in Tables I and II and, respectively, migration from multilayer food-contact materials.

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