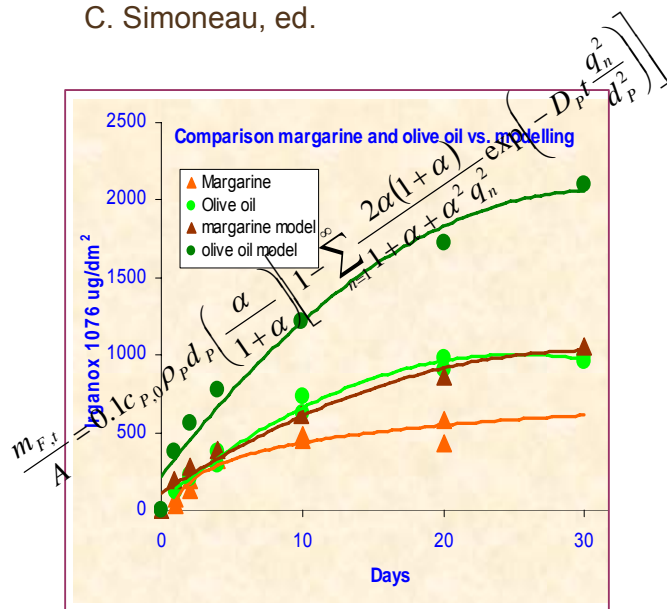




Applicability of generally recognised diffusion models for the estimation of specific migration in support of EU Directive 2002/72/EC

C. Simoneau, ed.



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European Commission
Joint Research Centre
Institute for Health and Consumer Protection

Contact information

Address: DG JRC, IHCP TP 260, I-21020 Ispra
E-mail: catherine.simoneau@jrc.ec.europa.eu
Tel.: 39.0332.785889
Fax: 39.0332.785707

<http://ihcp.jrc.ec.europa.eu/>
<http://www.jrc.ec.europa.eu/>

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EXECUTIVE SUMMARY

The aim of this document is to assist the users of the described model to predict conservative, upper bound migration values for compliance purposes by providing appropriate explanatory guidance, tables for and practical examples of migration modelling.

This document represents the current validity of the models based on constant periodical evaluations of new experimental migration data performed by a task force of experts co-ordinated the EC DG Joint Research Centre on behalf of Commission Services DG SANCO.

The main contributors to this document are (in alphabetical order): R. Brandsch, B. Brands, R. Franz, M. Klatt, MR Milana, O. Piringer, A. Schaefer, C. Simoneau, X. Trier, and O. Vitrac

1 INTRODUCTION

The European legislation requires verification of compliance for migration of substances from polymeric food contact materials with existing specific and overall migration limits. To do so, there are migration tests to carry out using food/food simulants under the test conditions specified in specific Directives 85/572/EEC, 82/711/EEC and amendments (e.g. 97/48/EC).

Numerous scientific investigations during the last two decades have demonstrated that migration from food contact materials into food and food simulants are predictable physical processes. In the absence of specific interactions with food and for monolayer materials, migration is a mass transfer of substances from a plastic material into foodstuffs and obeys in most cases to Fick's laws of diffusion.

Hence, in addition to experimental methods an alternative tool based on theoretical migration estimations can be applicable. Modelling potential migration is recognised by the Food and Drug Administration (FDA) in the USA as an additional tool to assist in making regulatory decisions. The European Union introduced this option to use generally recognised migration models as a novel compliance and quality assurance tool with Directive 2001/62/EC, where the following statement is reported in Article 8(4) of the EU Directive 2002/72/EC

"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 recognised model must be based on scientific evidence. The realisation of this requirement was achieved within the European project SMT-CT98-7513 under the 5th Framework Programme 'Growth' 'Evaluation of Migration Models in Support of Directive 90/128/EEC'.

The major objectives of this project were

- 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 and
- To establish documentation that demonstrates the validity of underlying migration models for compliance purposes. Consequently, parameters used in the migration model were selected in a way that a "worst-case" estimate of migration rate was generated.

The final report of this project was published in a peer-reviewed scientific journal (Begley et al, 2005). This research project established the mathematical equations to be applied and the conditions for their appropriate application with regards to plastics.

Migration modelling has the ability to estimate upper bound migration values, provided the boundary and simplifying assumptions are fulfilled. The model is subjected to a continuous update and refinement process and should be practiced only by users with appropriate skills and training.

According to the current state-of-the-art, the scope and applicability of migration prediction comprises the mass transfer of most of migrants listed in Annex B when in contact with food simulants according to Directive 97/48/EU and its successive amendments.

For other polymers and situations not listed in chapter 3 of this document, migration modelling can be used provided the procedures described in the Technical Guidance Document (in preparation) have been followed and that these are supported by the appropriate documentation to demonstrate that the diffusivity behaviour parameter, A_P values are obtained or that the use of the model in that particular case leads necessarily to an overestimation.

Further reading can be found in the bibliographic references.

This document represents an update on fields of application for the overestimation of diffusion coefficients based on the validation of the model for a given number of polymers and migrants.

2 CONCEPT OF MIGRATION MODELLING

To predict the specific migration from plastic food contact materials for a given substance, one needs a physical description of mass transport (described in paragraph 2.1) a value or a model of the diffusion coefficient in plastics (described in paragraph 2.2), and assumptions on partitioning and conditions at the plastics-food interface.

Currently existing predictive mathematical models for migration estimation are essentially based on diffusion theory and consideration of partitioning effects. The underlying key parameters are the diffusion coefficient of the migrant in the plastic D_P as well as the partition coefficient of the migrant between the plastic and the food (simulant) $K_{P,F}$. Although these models are still under further scientific discussion, refinement or development, they provide an estimation of worst case migration scenarios for monolayer, homogeneous materials, and without any modification in time and interaction with food (simulant). One of these models has been used in an approach to predict upper bound migration values, which has been validated within the EU project SMT-CT98-7513 (Hinrichs and Piringer, 2002; Begley et al, 2005). It is based on some general requirements (see 2.1) and is designed such that it enables migration prediction with sufficient margins of overestimation.

Note: The margin of overestimation can vary with the type of polymer migrant, and contact conditions; it is generally higher in cases of lower diffusion (e.g. high molecular weights migrants, non-polyolefines) but might not always overestimate in all cases. Consequently the model should be used in the range of temperatures and conditions that were experimentally tested. Useful explanations to provide guidance to the user of the model are reported in the following paragraphs.

2.1 General considerations: physical description of mass transport

2.1.1 Boundary conditions and assumptions

Beyond the characterisation of the plastics polymer P and food (simulant) F, the key input parameters for the use of a migration model are the diffusion coefficient, D_P , of the migrant in P, as well as the partition coefficient $K_{P,F}$, of the migrant between P and F. The model relies on the following boundary conditions and assumptions reported below. The choice of these boundary conditions leads to overestimation.

In most cases of practical relevance a plastic food contact material or article (monolayer, homogenous) (P), can be regarded as a polymer film/sheet, of finite and constant thickness (d_P) being in contact with F, of finite volume (V_F) and contact surface area (A).

It is assumed that at the time of bringing P in contact with F ($t=0$), the migrant is distributed homogeneously in P. The possible mass transport resistance on F side is neglected, therefore assuming the migrant is uniformly distributed in F at all times.

It is assumed that the interaction between P and F is negligible and no swelling of P by uptake of F occurs during the migration process. As a result it is assumed that D_P is uniform in P and does not vary with time.

A partition coefficient between F and P is assumed and defined as:

$$K_{P,F} = \frac{c_{P,\infty} \rho_P}{c_{F,\infty} \rho_F} \quad (1)$$

The total amount of the migrant in P and F remains constant during the migration process, that means no chemical formation, decomposition or evaporation will be taken into account.

2.1.2 Mass transport equation

Based on the previous assumptions, the mass transport of the substances is governed by the Fick's 2nd equation -

$$\frac{\partial c}{\partial t} = D_P \frac{\partial^2 c}{\partial x^2} \quad (2)$$

where: c is the concentration of migrant in the food contact material or article (P) at time t at distance x from the origin of the x -axis and D_P is the constant diffusion coefficient in the food contact material or article.

2.1.3 Analytical solution to the diffusion equation

Under the above assumptions, the analytical solution of Eq (2) is Eq (3) (Crank, 1975):

$$\frac{m_{F,t}}{A} = 0.1 c_{P,0} \rho_P d_P \left(\frac{\alpha}{1+\alpha} \right) \left[1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-D_P t \frac{q_n^2}{d_P^2} \right) \right] \quad (3)$$

where:

$$\alpha = \frac{1}{K_{P,F}} \frac{V_F}{V_P} = \frac{c_{F,\infty} \rho_F V_F}{c_{P,\infty} \rho_P V_P} \quad (4)$$

since

$$K_{P,F} = \frac{c_{P,\infty} \rho_P}{c_{F,\infty} \rho_F}$$

and $\tan q_n = -\alpha q_n \quad (5)$

with:

$m_{F,t}$ - mass of migrant transferred from P into F after time t , (mg)

A - area of P in contact with F, (dm^2)

- $C_{P,0}$ - initial concentration of migrant in P, (mg/kg)
- ρ_P - density of P, (g/cm³)
- ρ_F - density of F, (g/cm³)
- D_p - diffusion coefficient of migrant in P, (cm²/s)
- t - migration time, (s)
- d_p - thickness of P, (cm)
- V_P - volume of P, (cm³)
- V_F - volume of F, (cm³)
- $C_{P,\infty}$ - equilibrium concentration of migrant in P (mg/kg)
- $C_{F,\infty}$ - equilibrium concentration of migrant in F (mg/kg)
- $K_{P/F}$ - the partition coefficient of the migrant between P and F
- q_n - the non-zero, positive roots of equation (5)

Equation (3) can be rearranged to give equation (6), 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.

$$MIC = \frac{SML V_F \rho_F}{100 A} \left\{ \rho_P d_P \left(\frac{\alpha}{1+\alpha} \right) \left[1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-D_p t \frac{q_n^2}{d_P^2}\right) \right] \right\}^{-1} \quad (6)$$

where: all parameters as for equation (3) apply, except

SML - Specific Migration Limit, (µg/g = mg/kg)

MIC - Maximum Initial Concentration in P, (µg/g).

2.1.4 Other approaches to calculate the solution of the diffusion equation

These approaches (such as numerical solutions) will be considered in the next edition of this document.

2.2 The key parameters: diffusion coefficient and partition coefficient

As mentioned above the key parameters necessary for migration modelling are the diffusion coefficient of the migrant in the plastic, D_P , as well as the partition coefficient of the migrant between the plastic and the food (simulant), $K_{P,F}$. Both parameters play a crucial role in determining the level of migration in a real food packaging application (Reynier et al, 1999; Piringer and Baner, 2000). Due to a lack of knowledge of their exact values in any specific case, it is recommended to establish these values in more generalised and conservative way so that reliably “worst case” scenarios with respect to migration are estimated which, in fact, is of primary interest from regulatory standpoint. To meet this requirement the described migration model has some important implications:

2.2.1 Diffusion coefficients

The literature reports a series of models for the theoretical estimation of diffusion coefficients in polymers (Mercea, 2000) 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, Hamdani et al, 1997, Limm and Hollifield 1996). To pursue the goal of obtaining a simple formula for the estimation of D_p , a refined equation for polyolefines and some other plastic materials has been developed (Brandsch et al. 2002). With this equation a polymer specific upper-bound diffusion coefficient, D_p^* , of a migrant in the polymer matrix can be estimated and used instead of the actual diffusion coefficient D_p . It must be emphasized that $D_p \leq D_p^*$. Therefore, using such a D_p^* for migration estimations leads to "worst case" values. From phenomenological derivations and a statistical evaluation of experimental diffusion and migration data (Mercea and Piringer, 1998) D_p^* can be estimated by the following Eq. (7) (Piringer and Baner, 2000):

$$D_p^* = 10^4 \exp \left[A_p^* - 0.1351 M_r^{2/3} + 0.003 M_r - \frac{R \cdot 10454}{R \cdot T} \right] \quad (\text{cm}^2/\text{s}) \quad (7)$$

where:

$$A_p^* = A_p'^* - \frac{\tau}{T} \quad (8)$$

- where: M_r : relative molecular mass of migrant (Dalton)
 T : temperature (K)
 $A_p'^*$: an upper bound polymer specific diffusion parameter
 τ : a polymer specific "activation energy" parameter (K)
 $R \times 10454$: $E_{A,ref}$ - reference activation energy (K)

From equation (7) it can be recognised that there are key variables, which determine the diffusion in a polymer. Two of them are not linked to the polymer and are the relative molecular mass of the migrant, M_r , and the absolute temperature, T , respectively.

The parameter, A_p^* , is linked to the polymer and describes the basic diffusion behaviour of the polymer matrix in relation to the migrants. In soft/flexible polymers, such as low density polyethylene (LDPE), A_p^* values are high reflecting a high diffusion behaviour (D_p^*) and hence high migration through the polymer, while stiff chain polymers such as polyesters have lower A_p^* values due to the lower diffusion behaviour, and hence lower migration of the same migrant. Where A_p^* can vary with temperature, $A_p'^*$ is a temperature independent term. A_p^* (and hence $A_p'^*$) are upper-bound values, and have been derived statistically so that equation 7 generates upper-bound experimentally measured D_p^* s. Using these D_p^* s in equations 3 and 6, the migration will be overestimated and consequently worst case migration rates will be calculated by the proposed migration model within certain temperature ranges.

The parameter τ , together with the constant 10454 in equation (7), both contribute to the diffusion activation energy, $E_A = (10454 + \tau) \cdot R$, where $R = 8.3145$ (J/mol K) is the gas constant. Upon analysing E_A data from literature for a large series of migrants in

many polymer matrices, it was concluded that $\tau = 0$ for many polymers. Thus, setting $\tau = 0$ as a first approximation for LDPE gives $E_A = 86,92 \text{ kJ/mol}$, which is in good agreement with the mean value of $E_A = 87 \text{ (kJ/mol)}$ found from literature data (Mercea 2000).

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 value for these matrices is $E_A = 100 \text{ kJ/mol}$ corresponding to $\tau = 1577$.

It is known that in a given polymer and temperature range each migrant has different diffusion activation energy E_A (Mercea 2000). For feasibility reasons the polymer related mean values are used for migration modelling. Deviations of the migrant specific activation energies from the mean value are accounted for during the translation of diffusion data in polymer specific constants followed by the statistical evaluation described in the Technical Guidance Document (in preparation).

2.2.2 Partition coefficient

In absence of specific data, in order to model worst case scenarios, the partition coefficient of the migrant between the polymeric material and F should be taken as $K_{p,F} = 1$ which means that the substance is very soluble in F; this option leads to the highest migration values, i.e. complete transfer of the migrant from the food contact material to food at equilibrium. The question whether this equilibrium partitioning will be reached in a practical application depends on the polymer type and more specifically on the diffusion behaviour of the polymer under the practical contact conditions. For all other cases, that is for which the migrant is only sparingly soluble in F the partition coefficient should be set at $K_{p,F} = 1000$, (e.g. for lipophilic substances when the polymeric material is in contact with aqueous food /simulant)

3 APPLICATION OF MIGRATION MODELLING TO PLASTICS

3.1 Historical context and state of the art:

The experts participating to the European project SMT-CT98-7513 'Evaluation of Migration Models in Support of Directive 90/128/EEC' agreed to consider the prediction tool fully validated for polyolefines (PO), on the basis of the large number of consistent results. During this project, experts agreed that although much less data were available for the non-PO (like polystyrene - PS, high impact polystyrene - HIPS, polyethylene terephthalate - PET, Polyethylene naphthalate -PEN, polyamide - PA) compared to PO, the basis was considered sufficiently solid due to the fact that well-defined migration experiments were selected and performed by internationally recognised laboratories. For the non-PO samples covering the market situation, it could be shown that these equations overestimate the experimental migration values. For polycarbonate - PC and polyvinylchloride - PVC, experts at the time of the SMT project considered the data insufficient to create a reliable set of parameters for migration modelling.

This current update is the result of a dedicated Task Force co-ordinated by the JRC which considered experimental migration data produced since the project SMT (i.e. period 2000-2004) and it takes into the outcome of the evaluation of new (until 2008) available data, which is in particular the case for PET polymer.

Where appropriate, previous values of the key parameters have been refined. In addition, the migration behaviour of new polymers in terms of their polymer specific constant (A_p -value) was evaluated based on experimental data and their relevant parameters introduced in this update.

Consequently, the updated requirements for polymer specific migration modelling are described in the following paragraphs.

3.2 Polyolefines

The most important polyolefines (PO) used for food packaging are: low density polyethylenes (LDPE and LLDPE), high-density polyethylene (HDPE) and various types of polypropylenes (PP-random, PP-homo and PP-rubber)¹. 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,(Table1). Under these temperature conditions and with an initial migrant concentration, $c_{p,0}$, not higher than about 1 %, the migration process in PO's follows the general physical law of diffusion with the solution given in equation (3).

Polymer	T (°C)	Mr (g/mol)	$c_{p,0}$ (%)	$K_{p/F}$
LDPE	≤ 80	30 - 2000		
LLDPE	≤ 100	30 - 2000		1 for high solubility
HDPE	≤ 90	30 - 2000	< 1.0 for all PO	of migrant in food,
PP (homo)	≤ 120	30 - 2000		1000 for low solubility
PP (random)	≤ 120	30 - 2000		of migrant in food
PP (rubber)	≤ 100	30 - 2000		

Table 1: Parameter ranges for the applicability of the migration model for selected PO.

The actual “upper-bond” values of A_p^* and respectively τ from equation (8) for PO's listed in table 2 were first determined empirically using a database with diffusion coefficients reported in the literature over the last four decades (Mercea 2000). In addition, the results from recent migration measurements were used to confirm and validate these A_p^* and τ values. Further details on the methodology of the evaluation of the model were recently published (Begley et al, 2005).

The A_p^* value is based on the overestimation of calculated A_p values²

Polymer	A_p^*	τ
LDPE/LLDPE	11.5	0
HDPE	14.5	1577
PP (homo and random)	13.1	1577
PP (rubber)	11.5	0

Table 2: Parameters for selected Polyolefines

3.3 Polystyrenes

Polystyrenes used for food packaging applications can be roughly subdivided into three general categories: general-purpose polystyrene (PS) high impact polystyrene (HIPS)

¹ The copolymers with non-olefinic monomers (eg acrylics, vinylics, etc) are not yet evaluated.

² The current A_p^* were generated according to Begley et al, 2005. The next edition of this document will revise the approach.

and styrene-butadiene-styrene block-copolymer (SBS). Using an evaluation of experimental migration data of these polymers, the temperature range for the applicability of migration modelling, as required by the general requirements given before, is listed in Table 3. In these cases the migration process in PS's follows the generally accepted physical law of diffusion, Eq. (2), with the solution given in Eq. (3).

Polymer	T (°C)	Mr (g/mol)	$c_{p,0}$ (%)	$K_{P/F}$
PS	≤ 70	104 - 647		1 for high solubility
HIPS	≤ 70	104 - 430	< 1.0 for all PS	of migrant in food,
SBS	≤ 70	84 - 689		1000 for low solubility
PS/SBS blend	≤ 70	84 - 689		of migrant in food

Table 3: Ranges of parameters for the applicability of the migration model for PS , HIPS and SBS.

For PS, HIPS and SBS the actual values of A'_P * and τ could be determined empirically from the data base of diffusion coefficients and verified by well defined migration experiments reported in recent years (Hinrichs and Piringner, 2002; Begley et al, 2005, Brandsch et al., in preparation). Applying these values of A'_P * and τ (see table 4) in Eqs. (7) and (8) results in “upper bound” diffusion coefficients, D_P *. These D_P * when introduced in Eq. 3, lead to overestimations (in most cases largely) of the experimental migration data available.

Polymer	A'_P *	τ
PS	-1	0
HIPS	1.0	0
SBS	10.5	0

Table 4: Parameters for PS, HIPS and SBS

*Note: blending PS with SBS results in a linear relationship of A'_P * value as a function of % SBS added to PS. The upper bound A'_P * value for a blend of PS with SBS can be described by the following relationship:*

$$A'_P(P.S.) = -1 + 0,115 * (\%SBS)$$

*(- max 100% SBS gives A'_P *=10,5 and - min 0% SBS (general purpose PS) gives A'_P *=-1)*

3.4 Polyesters

The polyesters mainly used for food packaging applications are polyethylene terephthalate (PET), and polyethylene naphthalate (PEN). Using an evaluation of experimental migration data of these polymers, the temperature range for the applicability of migration modelling, as required by the general requirements given before, is listed in Table 5. In these cases the migration process in these polyesters follows the generally accepted physical law of diffusion, Eq. (2), with the solution given in Eq. (3).

Polymer	T (°C)	Mr (g/mol)	$c_{p,0}$ (%)	$K_{P/F}$
PET	≤175	>32		1 for high solubility
			< 1.0 for all	of migrant in food,
PEN	≤175	>32	polyesters	1000 for low solubility
				of migrant in food

Table 5: Ranges of parameters for the applicability of the migration model for PET and PEN.

For PET and PEN the actual values of A'_P * and τ from Eq. (8) were determined empirically using migration data from well defined migration experiments reported in

recent years (Hinrichs and Piringer, 2002; Begley et al, 2005) . Using these values of $A_{P'}^*$ and τ (see table 6) in Eqs. (7) and (8) results in “upper limit” diffusion coefficients, $D_{P'}^*$, which, introduced in Eq. (3), lead to overestimations (in most cases largely) of the experimental migration data. This was confirmed very recently by systematic studies on migration from PET bottles into softdrinks (Franz and Welle, 2008). The results from this study support the assignment of $A_{P'}^*$ values for temperatures $\leq 70^\circ\text{C}$ as given in table 6.

The split between two ranges of temperature was derived from an evaluation of new data (Feigenbaum et al, 2005; Pennarun et al, 2005); The temperature cut-off was selected with a safety margin of overestimation to reflect the lowest Tg values for PET on the market; In the case of small molecules (generically referring to below 50 g/mol, the value of $A_{P'}^*$ should be taken as 6.4 in both cases).

Polymer	$A_{P'}^*$	τ
PET >Tg (70 °C)	6.4	1577
PET <Tg (70 °C)	3.1	1577
PEN	5.0	1577

Table 6: Parameters for PET and PEN

3.5 Polyamides

For polyamides only few data are available both for diffusion coefficients and migration data. Furthermore, the water content of the food or food simulant can strongly influence the mechanism of the transfer

As current data had only addressed PA in contact with olive oil and isooctane only, but not PA in the swollen state, this Task Force considers that the current data does not present all the relevant foodstuffs. The model is therefore not considered fully validated for PA. The following tables relating to Simulant D and isooctane are provided for informative purposes only.

Polymer	T (°C)	Mr (g/mol)	$c_{P,0}$ (%)	$K_{P/F}$
PA6	≤ 100	113	< 1	1 for high solubility
PA 6,6	≤ 100	32 - 587	< 1	of migrant in food, 1000 for low solubility
PA12	≤ 100	197	< 1	of migrant in food

Table 7: Ranges of parameters for the applicability of the migration model for Polyamides

Note: The PA was previously equilibrated with air at room temperature, within an approximate range of 40- 65% relative humidity)

For PA6, PA 6,6 and PA12 the actual values of $A_{P'}^*$ and τ from Eq. (8) were determined empirically using migration data from well defined migration experiments reported in recent years (Hinrichs and Piringer, 2002; Begley et al, 2005; Stoffers et al 2005; Stoffers at al. 2003) Using these values of $A_{P'}^*$ and τ (see table 8) in Eqs. (7) and (8) results in “upper limit” diffusion coefficients, $D_{P'}^*$, which, introduced in Eq. (3), lead to overestimations (in most cases largely) of the experimental migration data.

Polymer	$A_{P'}^*$	τ
PA6	0	0
PA6,6	2.0	0
PA12	2.6	0

Table 8: Parameters for PA

3.6 Polyvinylchloride

3.6.1 Rigid PVC

For rigid PVC migration data and diffusion coefficients are available (Brandsch et al, in preparation) for the range of temperatures 20-70°C. Using an evaluation of experimental migration data of these polymers, the temperature range for the applicability of migration modelling, as required by the general requirements given before, is listed in Table 9. In these cases the migration process in PVC follows the generally accepted physical law of diffusion, Eq. (2), with the solution given in Eq. (3).

Polymer	T (°C)	Mr (g/mol)	c _{P,0} (%)	K _{P/F}
PVC (rigid)	≤ 70	>225	< 1	1 for high solubility of migrant in food, 1000 for low solubility of migrant in food

Table 9: Ranges of parameters for the applicability of the migration model for rigid PVC

Polymer	A _P ^{1*}	τ
PVC (rigid)	-1.0	0

Table 10: Parameters for rigid PVC

3.6.2 Plasticised PVC

For plasticised PVC only few data are available both for diffusion coefficients and migration data. Current data has only addressed migration of individual plasticisers. Therefore this Task Force considers that the current data does not present relevance to the presence of mixtures of additives and the model is therefore not considered fully validated for plasticized PVC. The following tables and formula are provided for informative purposes only.

Since plasticisers are used at high concentrations, the diffusion coefficient is expected to vary with the total concentration of plasticiser in PVC. This edition proposes an overestimate of the diffusion coefficient based on the initial total concentration of plasticisers. According to the assumption in point 2, it is assumed that the migration follows the general law of diffusion and that the proposed diffusion coefficient is constant and always overestimates the real diffusion coefficient.

It should be noted that the parameters of the equation given below will vary both with the plasticiser molecular weight as well as its concentration. The formula should be used for plasticisers only with molecular weights above the range tested.

For 30% (w/w) plasticised PVC based on data for 5 plasticisers ranging from mw 370-419, an upper bound A_P^{1*} of 14.6 is considered reasonable.

A linear relationship of A_P^{1} value as a function of % plasticiser added to PVC exists. The upper bound A_P^{1*} value for plasticised PVC can be described by the following relationship:*

$$A_{P}^{1*}(\text{PVC}) = -1 + 0.52 * (\% \text{ plasticiser})$$

(- max 30% plasticizer gives A_P^{1}=14.6 and - min 0% plasticizer (rigid PVC) gives A_P^{1*}=-1)*

3.7 Other polymers, migrants and other parameter range

For other polymers and parameter ranges not listed in chapter 3, migration modelling can be used for compliance purpose provided the mass transfer (migration process) from the plastic in the food or food simulant follows the law of diffusion and the

parameters (A_P^* and τ) were determined according to recognised and validated procedures. Such procedures are described in a Technical Guidance Document (in preparation). The appropriate documentation must demonstrate how the D_P values are obtained and their translation into A_P -values as well as the range of applicability in terms of contact conditions and molecular weights. Furthermore the documentation must bring conclusive proof that the use of the model in that particular case leads necessarily to an overestimation in 95 percent of all applicable cases.

4 PROCEDURES, PRACTICAL APPLICATIONS, EXAMPLES

For migration modelling as described above corresponding in-house computer programmes might be developed and applied. For convenience, there are computer programmes commercially or freely available on the market:

The used software should be checked for reliability of results as described in the Technical Guidance Document (in preparation).

The model allows the following estimations:

- (i) Based on knowledge of the existing initial concentration of a migrant of known molecular weight in a polymer its specific time and temperature dependent migration into a given food simulant or food can be calculated from Eq. (3).
- (ii) Reversely, based on a given migration limit or SML value, the maximum initial concentration (MIC) of a migrant of known molecular weight in a polymer that can be used in a food contact can be estimated from Eq (6).

As a general rule: in cases where the migration estimation scheme outlined above leads to results which are above the legal limits (SML), an experimental test of compliance is compulsory. In case of doubt or if the polymer specific A_P' value is not known or applicable from the tables given in paragraph 3, a kinetic study should be carried out as described in the procedure given in the Technical Guidance Document (in preparation) to establish the Q versus SM relationship (Brandsch et al, 2002).

4.1 Compliance testing of substances with specific migration limits (SML)

One major objective of this document is to give guidance for compliance testing. Consequently, one major field of application concerns the control for compliance of substances listed in the Directive 2002/72/EC and its amendments with respect to their specific migration limit (SML).

It must be emphasised that at the present stage of knowledge the migration model is only suitable for the polymers and under the conditions described in paragraph 3. In addition, Annex B lists the compounds that are theoretically eligible for modelling based on criteria below. However, before applying the model one always has to ensure that the model assumptions (paragraph 2.1) are fulfilled for the compound(s) considered.

The following criteria for inclusion or exclusion from the list were applied:

- All organic, non-gaseous substances with a well-defined molecular weight, soluble in the polymeric matrix, were included in the list.
- All polymeric additives with a well-defined molecular weight distribution were included in the list under reserve. Migration modelling is applicable provided the

actual molecular weight distribution of the polymeric additive is available. Polymeric additives are marked with pa. in Annex B

- All organic compounds known to deliberately bloom out from some polymeric materials, e.g. antistatic or antifogging agents incorporated in polyolefines, were included in the list under reserve. Migration modelling is applicable only in those cases (polymer/migrant combinations), in which blooming does not occur. Substances showing blooming in a given polymer are marked with bl.## in Annex B, where ## is the shortcut for the polymer from which blooming occurs, like iPP for isotactic polypropylene.
- All organic mixtures with undefined molecular weight, typically derived from natural sources like fats and oils, rosins, waxes, starch, proteins, cellulose, cotton were excluded from the list. However a specific substance with well defined molecular weight below 2000 g/mol that is a component of a mixture can be addressed by migration modelling.
- All inorganic compounds, metals, metal oxides, metal salts, etc. were excluded from the list.

Even with these selection criteria, a considerable number of compounds remains. Therefore this list is a useful reference for those users, who need or desire to perform estimations without uncertainty in the adequate selection of the appropriate parameters. Once selected from the list (Annex B), migration modelling can be applied for the substance, provided the substance is contained in one of the polymers specified in paragraph 3 and also the proper value for the worst case partition coefficient, $K_{P,F}$ is applied.

Under these conditions the eventual problem of swelling is not relevant because it is inherently considered in the design of the model (see 2.1 General scientific considerations - general requirement 4.). Accordingly the model cannot be used for migration predictions in iso-octane or other test media with a high swelling power. In such cases it is recommended to consider the approach of Reynier et al (2002).

The problem of blooming must be considered case by case with respect to the polymer/migrant combination investigated. It is well known that antistatic and antifogging agents typically incorporated into polyolefines deliberately migrate at the surface of the polymeric materials. Alternatively the same substance does not bloom out from a more polar polymeric material like polyester or polyamide. The user of the migration model is strongly advised to carefully consider the possibility of blooming, to avoid application of the migration model for special cases out of its scope.

Note: Blooming out of a given component from the plastic occurs if the difference in polarity between the component and the polymeric matrix is high resulting in low solubility of the component in the polymer. Due to blooming the component is migrating in short time at the polymer/air interface resulting in high migration values for short contact times. From migration modelling point of view the assumption (2) from paragraph 2.1 is not fulfilled anymore and accordingly if blooming occurs modelling cannot be applied.

A further point of discussion is the plasticising effect, when higher amounts of low molecular weight components are added to a polymeric material. Substances known to have a plasticising effect in given polymers above a level of use are marked in Annex B with pl.##.5% where ## is the shortcut of the polymer. For these specific cases modelling is not applicable above the level of use specified in %, unless a specific A_P -value accounting for the plasticising effect has been determined by experiments, according to the Technical Guidance Document (in preparation).

Note: For all substances from List A with a level of use above 1%, a plasticising effect in given polymeric materials may be expected. If a plasticising effect is observed, the use of the migration model is possible only with an A_P -value accounting for the plasticising effect.

Finally it should be noted that by using Eq.(6) a value for the maximum initial

concentration (MIC) of a migrant in P can be estimated for which a specific migration limit (SML) for an additive cannot be exceeded.

4.2 Optimising compliance control

When the necessary inputs to the model are available, migration models can be used to optimise compliance control strategies.

Tables of PM/REF-numbers, chemical names, Mr-, SML-values and highest concentrations, $C_{P,0}$ of some additives usually used in polyolefines and non-polyolefines can be found in Annex A.

It is the responsibility for every company involved in the production, conversion, import and retail sale of food contact materials (FCM) to demonstrate compliance with existing EU legislation. National authorities in turn are responsible to enforce that the legislation is followed. To fulfil their obligations both, companies (or the contracted control laboratories) and enforcement employ compliance testing of FCMs, e.g. by experimental chemical testing of migration, by organoleptic testing and/or testing specific migration limits (SML) by migration models (MM).

The results obtained by modelling are however only as good as the data put into the model, and only valid if the assumptions of the model are fulfilled. To use MM successfully it is therefore essential to have a well-described FCM. This typically requires good traceability and information flow through the production chain, from raw material producers, to the food industry and to the “seller” of the finished FCM article. It should also be emphasized, that MM can determine only the migration of known compounds with known initial concentrations.

When testing compliance of a FCM, the first question to ask is which type of polymer is at hand – if in doubt an infrared spectroscopy (FTIR) can possibly be of some help. If the polymer is listed in tables of this guide, migration modelling can be applied. If not, the polymer specific constants (A_P and τ) can be determined by a kinetic study e.g. as described in the procedure in the Technical Guidance Document (in preparation) and then the MM can be applied. Otherwise experimental migration-chemical testing needs to be performed.

Apart from the polymer identity, it is crucial to know

1. Which migrateable substances are present in the objects to test (e.g. additives, residual amounts of monomers)?
2. What are their initial concentrations, $C_{P,0}$ (e.g. amount of additive as seen from recipe, or determined in an experimental test, see guidance in Feigenbaum et al. 2002)?
3. What is the “worst-case” intended use (type of foodstuff, max. temperature and max. packaging time) in practical life, based on function of FCM and any given advisory to the user?
4. What is the intended shape of the final article, specifically what surface area will contact what portion of food (i.e. the surface-to-volume ratio)?
5. Which of these substances can be used in practice in the polymer and fulfil the limitations of substances that can be modelled (e.g. blooming agents are not homogeneously distributed in the polymer and hence cannot be modelled)?

In practice it is a challenge to obtain all the necessary information (Petersen et al, 2005), of which 1, 3 and 4 are inherent requirements to any control laboratories that do experimental testing, but 2 and 5 are specific to MM. Typically two situations exist (figure 1):

- All necessary information is available: An example is when a raw material producer tests the compliance of polymer samples representative for its final intended use, which is known to them e.g. coffee cups.
- Necessary information is missing: Examples are when converters and/or enforcement authorities test the compliance of an unfinished product such as a tray or laminate, or retailers /enforcement authorities test the compliance of a finished product such as a plastic bottle containing milk.

The quality of information received should always be judged critically, as is the case with experimental results. When the data are found to be trustworthy, the application of MM is straightforward and extremely time saving. In particular if the MM predicts migration below the SML and no further action needs to be taken. If the MM predicts migration above the SML, experimental migration testing must be conducted. If migration still is above the SML, an additional useful option offered by the MM to the producers is to use the MM to calculate the maximum allowed $c_{P,0}$ (MIC) and then to reformulate the FCM; otherwise the necessary restrictions of use (e.g. food types, lower contact temperatures, times and/or surface-to-volume ratios) to keep migration below the SML could be put down in the declaration of compliance accompanying the FCM.

As a first step in enforcement the authorities have to make an effort to retrieve the information from the production chain. If the information is available MM can follow as described above. If the migrateable substances are known, but their $c_{P,0}$ are unknown, then the usual max. concentrations ($c_{P,0}$) of additives in various polymers (listed in tables 4.2.1 (PO) and 4.2.2 (non-PO)) can be used. These substances are extracted from the table in Annex B, based on the usual compositions for a given polymer. The tables were prepared by consulting the most important producers of plastic materials and the secondary literature referring additives for plastic materials (Zweifel, 2001). In addition to the identification numbers the upper limits of initial concentrations reported to be used in plastic materials for food contact are shown. Nevertheless, as fully specified in reference (Milana and Piringer, 2002), *this table should be considered only as an example to offer a first guide in selecting specific additives if no other information is available about the composition of a sample to be tested.* Alternatively a quick estimate of compliance can be made by assuming that 100% of the initial concentration migrates. This method might also be applied to known impurities, reaction and breakdown products etc. Whereas enforcement (in principle) has a legal right to obtain all information asked for, private companies may encounter difficulties due to confidentiality issues in relation to the composition.

As shown in figure 1 the endpoint to decide on compliance of a material is the experimental migration testing. This means, that in practice there should be an (accredited for enforcement) experimental migration test available to decide if the FCM is legal or not.

In conclusion, MM can be time saving, in particular to those who have readily access to all necessary information about the FCM, and only if the material is in compliance (>SML) as non-compliance typically leads to experimental testing anyway .

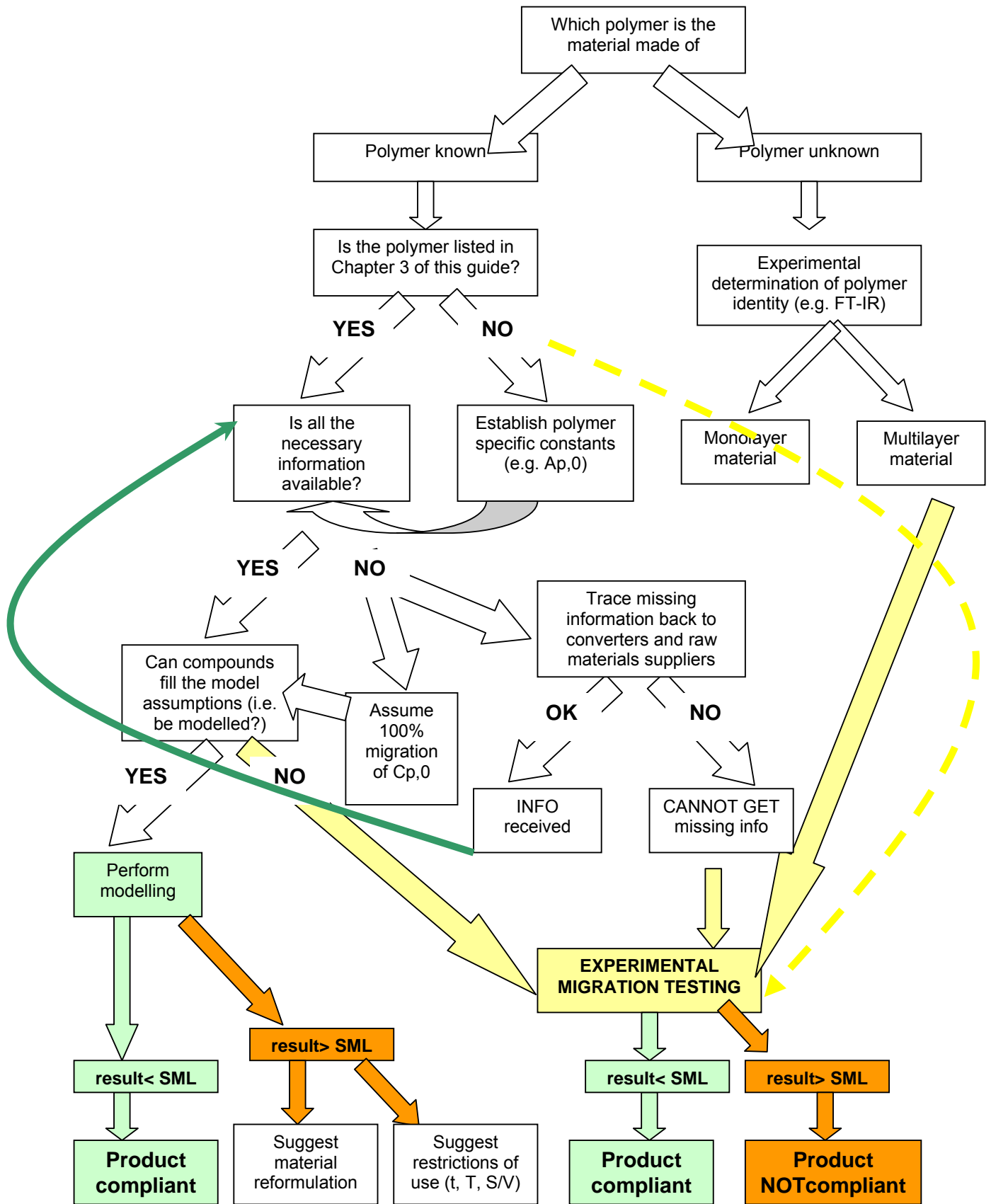


Figure 1: Decision scheme of how to handle a FCM when doing compliance testing.

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ANNEX A:

PM/REF-numbers, chemical names, molecular weights (M_r), SML-values and highest concentrations, $C_{P,0}$ of some additives usually used in polyolefines.

PM/REF	Chemical name	M_r	SML (mg/kg)	$C_{P,0}$ (%)
38560	2,5-bis(5-tert-butyl-2-benzoxazolyl)thiophene	431	0.6	
38800	N,N'-bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl)-hydrazide	553	15	HDPE 0.2
38820	Bis(2,4-di-tert-butylphenyl)penta-erythritol diphosphite	605	0.6	PP 0.1; LDPE 0.06
38840	Bis(2,4-dicumylphenyl)pentaerythritol diphosphite	853	5	LDPE 0.06
39890	Bis(methylbenzylidene) sorbitol	386	60	
46480	Dibenzylidene sorbitol	358	60	
46640	2,6-Di-tert-butyl-p-cresol (BHT)	220	3	PP 0.2
48640	2,4-Dihydroxybenzophenone	214	6	
48720	4,4'-Dihydroxybenzophenone	214	6	
48880	2,2'-Dihydroxy-4-methoxy benzophenone	244	6	
53670	Ethylenglycol-bis(3,3-bis(3-tert-butyl-4-hydroxyphenyl)butyrate)	795	6	PP 0.2; HDPE 0.1
54300	2,2'-Ethylidene-bis(4,6-di-tert-butyl-phenyl)-fluorophosphonite	487	6	PP 0.1; LDPE 0.06
60320	2-(2-Hydroxy-3,5-bis(1,1-dimethylbenzyl)phenyl)benzo-triazole	448	1.5	
60400	2-(2'-Hydroxy-3'-tert-butyl-5'-methyl-phenyl)-5-chlorobenzotriazole	316	30	PP 0.4; HDPE 0.3
60480	2-(2'-Hydroxy-3,5'-di-tert-butylphenyl)-5-chlorobenzotriazole	358	30	PP 0.5
61600	2-Hydroxy-4-n-octylbenzophenone	326	6	PP 0.5; HDPE 0.3; LDPE 0.5
68320	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	531	6	PP 0.2; HDPE 0.1; LDPE 0.3
71680	Pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate]	1178	60	PP 0.2; HDPE 0.25; LDPE 0.03
74010	Phosphorous acid, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl ester	514	5	PP 0.1; HDPE 0.05; LDPE 0.06
74240	Phosphorous acid, tris(2,4-di-tert-butylphenyl)ester	647	60	PP 0.1; HDPE 0.5; LDPE 0.12
80480	Poly(6-morpholino-1,3,5-triazine-2,4-diyl)-[(2,2,6,6-tertamethyl-4-piperidyl)imino]-hexamethylene-[(2,2,6,6-tertamethyl-4-piperidyl)imino]	2600 -	1.8	PP 0.5
81200	Poly[6-[(1,1,3,3-tetramethylbutyl)-amino]-1,3,5-triazine-2,4-diyl]-[(2,2,6,6-tertamethyl-4-piperidyl)imino]-hexamethylene-[(2,2,6,6-tertamethyl-4-piperidyl)imino]	2000-3100	3	PP 0.5; HDPE 0.2; LDPE 0.5
81220	Poly-[[6-[N-(2,2,6,6-tetramethyl-4-piperidyl)-n-butylamino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidyl)imino]-1,6-hexanediy]l[(2,2,6,6-tetramethyl-4-piperidyl)imino]-alpha-[N,N,N',N'-tetrabutyl-N"-(2,2,6,6-tetramethyl-4-piperidyl)-N"-[6-(2,2,6,6-tetramethyl-4-piperidylamino)-hexyl]-[1,3,5-triazine-2,4,6-triamine]-omega-N,N,N',N'-tetrabutyl-1,3,5-triazine-2,4-diamine]	2600-3400	5	PP 0.2; HDPE 0.1; LDPE 0.1
83595	Reaction product of di-tert-butyl phosphonite with biphenyl, obtained by condensation of 2,4 di-tert-butylphenol with Friedel-Crafts reaction product of phosphorus trichloride and biphenyl	991	18	PP 0.1; HDPE 0.05 ; LDPE 0.06
92880	Thiodiethanol-bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)	643	2.4	
93120	Thiodipropionic acid, didodecyl ester	515	5	PP 0.1 – 0.5
93280	Thiodipropionic acid, dioctadecyl ester	683	5	PP 0.5
93520	Alpha-Tocopherol	431	60	
94960	1,1,1-Trimethylol-propane	134	6	
95200	1,3,5-Trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene	775	60	PP 0.2; HDPE 0.1
95270	2,4,6-Tris(tert-butyl)phenyl 2-butyl-2-ethyl-1,3-propanediol phosphite	450	2	HDPE 0.05;LDPE 0.06
95360	1,3,5-Tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione	784	5	PP 0.1; HDPE 0.1
95600	1,1,3-Tris(2-methyl-4-hydroxy-5-tert-butylphenyl) butane	545	5	PE 0.1

PM/REF-numbers, names, Mr-, SML-values and highest concentrations, C_{P,0} of some additives usually used in some non-polyolefines

PM/REF	Chemical name	M _r	SML (mg/kg)	C _{P,0} (%)
PS				
40020	2,4-Bis(octylthiomethyl)-6-methyl-phenol	425	6	0.2
61440	2-(2;-Hydroxy-5'-methylphenyl)benzotri-azole	225	30	0.25
61600	2-Hydroxy-4-n-octylbenzophenone	326	6	0.2
68320	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionate	531	6	0.15
74240	Phosphorous acid, tris(2,4-di-tert-butylphenyl)ester	646	60	0.2
83595	Reaction product of di-tert-butyl phosphonite with biphenyl, obtained by condensation of 2,4 di-tert-butylphenol with Friedel-Crafts reaction product of phosphorus trichloride and biphenyl	595	18	0.2
94400	Triethyleneglycol-bis[3-(3-tert-butyl-4-hydroxy-5-methylphenyl) propionate]	587	18	0.2
95600	1,1,3-Tris(2-methyl-4-hydroxy-5-tert-butylphenyl) butane	545	5	0.2
HIPS				
31520	Acrylic acid, 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methyl-phenyl ester	395	6	0.5
38560	2,5-bis(5-tert-butyl-2-benzoxazolyl)thiophene	431	0.6	0.05
40000	2,4-Bis(octylmercapto)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3,5-triazine	589	30	0.1
40020	2,4-Bis(octylthiomethyl)-6-methyl-phenol	425	6	0.2
61440	2-(2;-Hydroxy-5'-methylphenyl)benzotri-azole	225	30	0.4
68320	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionate	531	6	0.5
94400	Triethyleneglycol-bis[3-(3-tert-butyl-4-hydroxy-5-methylphenyl) propionate]	587	3	0.04
PEN				
51700	2-(4,6Diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)phenol	425	0.05	0.5
60320	2-(2-Hydroxy-3,5-bis(1,1-dimethylbenz-yl)phenyl)benzo-triazole	448	1.5	0.5
71680	Pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate]	1178	60	0.1
74240	Phosphorous acid, tris(2,4-di-tert-butylphenyl)ester	647	60	0.1
94400	Triethyleneglycol-bis[3-(3-tert-butyl-4-hydroxy-5-methylphenyl) propionate]	587	3	0.1
PET				
51700	2-(4,6Diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)phenol	425	0.05	0.2
60320	2-(2-Hydroxy-3,5-bis(1,1-dimethylbenz-yl)phenyl)benzo-triazole	448	1.5	0.2
60480	2,2'-Methylenebis(4-methyl-6-tert-butyl-phenol)	358	30	0.2
71680	Pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate]	1178	60	0.08
PA				
38820	Bis(2,4-di-tert-butylphenyl)penta-erythritol diphosphite	605	0.6	0.125
53200	2-Ethoxy-2'-ethyloxanilide	312	30	0.5
59120	1,6-Hexamethylene-bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide	637	45	0.5
60320	2-(2-Hydroxy-3,5-bis(1,1-dimethylbenz-yl)phenyl)benzo-triazole	448	1.5	0.5
60480	2,2'-Methylenebis(4-methyl-6-tert-butyl-phenol)	358	30	0.5
68320	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionate	531	6	0.5
71680	Pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate]	1178	60	0.5
74240	Phosphorous acid, tris(2,4-di-tert-butylphenyl)ester	647	60	0.5
81200	Poly[6-[(1,1,3,3-tetramethylbutyl)-amino]-1,3,5-triazine-2,4-diy]-[(2,2,6,6-tert-amethyl-4-piperidyl)imino]-hexamethylene-[(2,2,6,6-tert-amethyl-4-piperidyl)imino]	2000-3100	3	0.5
81220	Poly-[[6-[N-(2,2,6,6-tetramethyl-4-piperidyl)-n-butylamino]-1,3,5-triazine-2,4-diy]][(2,2,6,6-tetramethyl-4-piperidyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidyl)imino]-alpha-[N,N,N',N'-tetrabutyl-N''-(2,2,6,6-tetramethyl-4-piperidyl)-N''-[6-(2,2,6,6-tetramethyl-4-piperidylamino)-hexyl]-[1,3,5-triazine-2,4,6-triamine]-omega-N,N,N',N'-tetrabutyl-1,3,5-triazine-2,4-diamine]	2600-3400	5	0.5
83595	Reaction product of di-tert-butyl phosphonite with biphenyl, obtained by condensation of 2,4 di-tert-butylphenol with Friedel-Crafts reaction product of phosphorus trichloride and biphenyl	991	18	0.25
92880	Thiodiethanol-bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)	643	2.4	0.5
93120	Thiodipropionic acid, didodecyl ester	515	5	0.25
94400	Triethyleneglycol-bis[3-(3-tert-butyl-4-hydroxy-5-methylphenyl) propionate]	587	3	0.5
95200	1,3,5-Trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene	775	60	0.5

ANNEX B

List of substances from the positive list system of Directive 2002/72/EC, including 6th Amendment, which are eligible for migration modelling

See excel table provided as attached document

It includes the list of authorised monomers, other starting substances, macromolecules obtained from microbial fermentation, additives and polymer production aids

ANNEX C

Practical examples on migration modelling

In this section the use and potential of migration modelling is demonstrated with 3 examples obtained from reference (Milana and Piringer, 2002). These examples are presented such that first the practical application and the migration problem is described. Then the corresponding necessary input data for any migration modelling software are compiled and finally the results are given and further discussed.

Example 1:

A film of LDPE with a thickness of 100 μm is used for sandwiches with fatty substances on the surface. This kind of food is stored at 4° C for maximum 7 days. It is known that the film contains Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076) and Phosphorous acid, tris(2,4-di-tert-butylphenyl ester (Irgafos 168) as additives.

What information can be obtained about the specific migration of the two additives by mathematical modelling?

Modelling with a software requires to provide the following information as **input data**:

1. Information about the polymer

Polymer thickness: **0.01 cm**
Polymer density: **0.945 g/cm³**
Polymer type: LDPE ($A_P'^* = 11.5$, $\tau = 0$)

NOTE: The density value 0.945 is the highest density for LDPE and gives a worst case for the amount of migrant per volume of PO.

2. Information about the migrant:

Migrant: Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
PM-Ref No: 68320
SML: 6 mg/kg
Molecular weight: **531**
 $c_{P,0}$: **5000** (mg/kg)

NOTE: The initial concentration of 5000 mg/kg can be assumed as an upper limit for all the additives from table 4.2.1 for PO. From a practical and economical standpoint this value is exaggerated

3. Information about the migration contact conditions:

Food simulant: Oil ($K_{P/F} = 1$) (good solubility in food simulant)
Temperature: T_1 (5° C)
Time: t (**10 days**)
Surface/volume ratio: **6 dm² / 1000 ml** food

NOTE: From the above data the software can calculate at T_1 the diffusion coefficient D_1 in the polymer

Calculation of migration under one side contact conditions should give the following result:

$$m_{F,t}/A = 2.8 \text{ mg/dm}^2.$$

Discussion of the result:

Save the above result of modelling in a corresponding file, denoted for example as Ex1.

In conformity with Article 7 (b) of Directive 2002/72/EC, the specific migration limits expressed in mg/kg shall be divided by the conventional conversion factor of 6 in order to express them in mg/dm². For the above additive (Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) the SML= 6 mg/kg. Therefore the area related limit is 1 mg/dm². At this point the calculated migration, 2.8 mg/dm², exceeds the legal limit. However, the sandwiches with fatty substances on the surface belong to the category of food with the reference number 08.08 in the Directive 85/572/EEC and the reduction factor X/5 is applicable. This means in the above example: $(m_{F,t}/A)/5 = 0.56 < 1 \text{ mg/dm}^2$ and, consequently, it is in compliance with the Directive 2002/72/EC.

For the second additive, phosphorous acid, tris(2,4-di-tert-butylphenyl) ester (PM/REF = 74240), with the molecular weight $M_r = 647$ a smaller migration rate results (Eq.2) as for Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate with $M_r = 531$. With the tenfold higher migration limit (SML = 60 mg/kg) no further investigation of the specific migration is necessary.

Example 2:

An empty beaker made of PS is to be evaluated with respect to its compliance when intended for contact with milk products (yoghurt, and such products in association with fruit and fruit products) as categorised with the reference number 07.02 in the Directive 85/572/EEC. The product must be stored at 8°C. The beaker with a volume of 500 ml has a conic geometry and a wall thickness of $\leq 1 \text{ mm}$. The requested test conditions in conformity with the EEC Directives are: 10 days at 20°C with simulant 50% ethanol.

Which information can mathematical modelling provide with respect to specific migration of any additive?

From the 8 additives listed in table 4.2.2 for PS, 2-(2-Hydroxy-5-methylphenyl)benzotriazole (PM 61440, Tinuvin) has the smallest M_r and it can be assumed that it migrates with the highest rate. Therefore it is recommendable to start with this compound. As a reasonable assumption for $c_{p,0}$ a concentration of 5000 mg/kg is made.

Modelling with a software requires to provide the following information as **input data**:

1. Information about the polymer

Polymer thickness: **0.1 cm**
Polymer density: **1.1 g/cm³**
Polymer type: **PS ($A_p'^* = -1, \tau = 0$)**

2. Information about the migrant:

Migrant: 2-(2-Hydroxy-5-methylphenyl)benzotriazole (Tinuvin)
PM-Ref No: 61440

SML: 30 mg/kg
Molecular weight: 225
 $C_{P,0}$: 5000 (mg/kg)

3. Information about the migration contact conditions:

Food simulant: 50% Ethanol ($K_{P/F} = 1$) (good solubility in food simulant is assumed)
Temperature: T_1 (20° C)
Time: t (10 days)
Packaging geometry: conic trunk with $d = 6.8$ cm, $D = 8.8$ cm and $h = 10.5$ cm
Packaging volume: 500 ml

Calculation of migration under one side contact conditions should give the following result:

$$C_{F,t} = 0.42 \text{ mg/kg}$$

Discussion of the result

The modelled migration is by far smaller than the SML value even if the additive is considered to be soluble in the simulant (which is equivalent to a fat test). The other 7 additives from table 4.2.2 have considerably higher molecular weights. It is therefore extremely unlikely that one of these additives exceeds the respective SML value under the above conditions of use.

Example 3:

A steam sterilizable container made from PP polymer with a capacity of 500 ml and a cylindrical form, with a maximum wall thickness of 2 mm is used for liquid or paste with fatty substances on the surface, according to reference number 08.03 in the Directive 85/572/EEC. The additives used are Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (0.06 %) and Phosphorous acid, tris(2,4-di-tert-butylphenyl) ester (0.1 %).

Compliance testing of the above article according to Directive 97/48/EEC requires test conditions of 2 h (t_1) at 121°C (T_1) followed by 10 days (t_2) at 40°C (T_2) using simulant D, olive oil.

Which information can be obtained by mathematical modelling?

In the following **two procedures** are described:

Procedure 1 (two separate migration effects: T_1 separated from T_2):

Modelling with a software requires to provide the following information as **input data**:

1. Information about the polymer

Polymer thickness: 0.2 cm
Polymer density: 0.91 g/cm³
Polymer type: PP ($A_P^* = 13.1$, $\tau = 1577$)

2. Information about the migrant:

Migrant:	Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
PM-Ref No:	68320
SML:	6 mg/kg
Molecular weight:	531
$C_{P,0}$:	600 (mg/kg)

3. Information about the migration contact conditions:

Food simulant:	Oil ($K_{P/F} = 1$) (good solubility in food simulant is assumed)
Temperature:	T_1 (121° C)
Time:	t_1 (2 hours)
Packaging geometry:	cylindric pack with D = 10 cm and h = 6.5 cm
Packaging volume:	500 ml

NOTE: In this way the migration effect attributed by the high temperature condition alone is considered

Calculation of migration under one side contact conditions should give the following result:

$$C_{F,t} = 15.7 \text{ mg/kg}$$

Now, for calculation of the pure low temperature (t_2/T_2) migration effect the t/T input data are changed:

4. Information about the migration contact conditions:

Temperature:	T_2 (40° C)
Time:	t_2 (10 days)

NOTE: In this way the migration effect attributed by the low temperature condition alone is considered

Calculation of migration under one side contact conditions should give the following result:

$$C_{F,t} = 3.38 \text{ mg/kg}$$

Discussion of the result

The sum of the two separate migration effects at 121° C and 40° C amounts to $15.7 + 3.4 = 19.1$ mg/kg, which would exceed the SML (6mg/kg) for Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate. For the conformity check with the Directive 85/572/EEC the reduction factor X/3 is in principle applicable and the result would be $19.1 / 3 = 6.37 > 6$ mg/kg. However, due to the exhaustive migration (more than 80%) which may occur in this case at the high temperature, the reduction factor may not be applicable anymore according to EC directive 2007/19/EC, Annex I.

Now, to calculate the Phosphorous acid, tris(2,4-di-tert-butylphenyl) ester the following input data are changed for both, t_1/T_1 and t_2/T_2 conditions:

5. Information about the migrant:

Migrant:	Phosphorous acid, tris(2,4-di-tert-butylphenyl) ester
PM-Ref No:	74240
SML:	no (i.e. 60 mg/kg)
Molecular weight:	647
$c_{P,0}$:	1000 (mg/kg)

Calculation of migration under one side contact conditions should give the following result:

For 2 hours at 121°C:	16.9 mg/kg
For 10 days at 40°C:	3.6 mg/kg

Discussion of the result

The sum of both migration effects at 121° C and 40° C amounts to 16.9 + 3.6 = 20.5 mg/kg which is lower than the 'SML' of 60 mg/kg = SML for Phosphorous acid, tris(2,4-di-tert-butylphenyl) ester.

The sum of specific migrations of both additives would be lower than the overall migration limit of 60 mg/kg.

Procedure 2 (consecutive migration effect: T₁ followed by T₂):

Modelling of procedure 2 for each additive requires to change the **input data** concerning t₁/T₁ and t₂/T₂ conditions where all other data remain unchanged:

6. Information about the migration contact conditions:

Temperatures:	T ₁ (121°C) followed by T ₂ (40° C)
Time:	t ₁ (2 hours) followed by t ₂ (10 days)

NOTE: In this way the consecutive migration effect attributed by both temperatures and both contact times is considered

Calculation of migration under one side contact conditions should give the following result:

For Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate:	15.8 mg/kg
For Phosphorous acid, tris(2,4-di-tert-butylphenyl) ester:	17.0 mg/kg

Discussion of the result

With the second procedure the result is lower compared to the first one procedure, because in the first procedure the two migrations are considered as independent processes with two separate samples. The calculated specific migration for Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate is likely to exceed the corresponding SML value. Therefore, a migration test is needed for final evaluation of compliance.

The calculated specific migration value for Phosphorous acid, tris(2,4-di-tert-butylphenyl) ester is significantly smaller than the SML value. A migration test is not necessary in this case.

In sum, migration of both additives remains below the overall migration limit.

ANNEX D

Additional notes on remarks on the experimental verification of migration modelling

Since the migration model described in this report has not been fully validated for each and every polymer type or polymer modification or food packaging application, it is essential to provide a possibility for experimental verification of modelled migration results. This requirement is also addressed by Article 5 of the 6th amendment of Directive 2002/72/EC which says that '*...that a relationship between the quantity of a substance in the finished material or article and the value of the specific migration of the substance has been established either by an adequate experimentation...*'

The Technical Guidance Document (in preparation) describes an experimental procedure which allows industry and enforcement laboratories to measure and derive experimentally/theoretically the basic diffusivity behaviour (A_P value) of a given test plastics material using one or more selected test migrants only. Based on the determined A_P value, Q/SM or MIC/SML relationships can be calculated for any other migrant in dependency of its molecular weight and for the applicable temperature range.

This method is not only applicable for verification purposes but could be applied in case of doubt when for instance the polymer specific A'_P value is not known or applicable from the tables given in section 3.

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Abstract

The aim of this document is to assist the users of the described model to predict conservative, upper bound migration values for compliance purposes by providing appropriate explanatory guidance, tables for and practical examples of migration modelling.

This document represents the current validity of the models based on constant periodical evaluations of new experimental migration data performed by a task force of experts co-ordinated the EC DG Joint Research Centre on behalf of Commission Services DG SANCO.

The main contributors to this document are (in alphabetical order): R. Brandsch, B. Brands, R. Franz, M. Klatt, MR Milana, O. Piringer, A. Schaefer, C. Simoneau, X. Trier, and O. Vitrac

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