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Food-packaging migration models: A critical discussion

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ABSTRACT

The widely accepted and used migration models that describe the mass transport from polymeric packaging material to food and food simulants are confirmed here. A critical review of the most accepted models is presented in detail. Their main advantages and weak points, regarding their predictive accuracy, are discussed and weighted toward their usage extensiveness. By identifying the specific areas where using such models may not provide a strong correlation between theoretical and actual results, this work also aims in outlining some particular directions regarding further research on food – packaging interactions.

Introduction

Migration, sorption, and permeation of substances through the various material phases are of high concern for the food quality as the most important physical–chemical interactions within a food-packaging–environment system (Figure 1). Environmental (S_E) or food (S_F) originating substances may be correspondingly trapped by either foodstuffs or packaging. In the same figure, migration is presented M_F for substances originating from the packaging material to its containing food volume and M_E for the opposite direction transport. All of the above phenomena may potentially impact the overall product quality. The evolution of these processes depends on the physical and chemical characteristics of the polymer, the nature of the substances and the type, composition, and physical characteristics of the foodstuff. Regarding the public health, migration is by far the most significant process, since chemical substances that migrate into foodstuffs could potentially introduce a risk to human health (Sanches-Silva et al., 2008).

Consequently, food-packaging interactions have become a rather important filed to be studied, as it affects the processing, preservation, distribution, marketing and even the cooking preparation of foods. However, although the existing packaging materials' components serving as process aids, colorants, active compounds or functioning means, have to be safe for the consumers. For that, it is the containing food that may or may not interact with the adjoining packaging materials. In result, this might change the initial mechanical and barrier properties of the materials, as well as the safety of the product at consumption. Understanding and controlling the migration process of a potentially toxic substance from a packaging material retains a major role in the selection and use of the materials for food packaging for the possible effect upon human health. Analytical laboratory testing should provide the required knowledge and allow for defining the compliance of the food-contact plastics to the relevant EU regulations (Traiastaru et al., 2013). A broad number of literature citations regarding the levels of migrants, their reaction products and the role of additives can be found in the literature (see for instance, Gilbert et al., 1980; Downes, 1987; Tehrany and Desobry, 2004). Since food-packaging mass transport phenomena may also have a major impact in many particular technological areas, it has also been investigated from experimental and theoretical point of view (Vitrac and Hayert, 2006).

Commonly, the term "migration" refers to the diffusion of chemical substances from a zone of higher concentration (the food-contact layer) to one of a lower concentration (usually the food surface) due to the concentration gradient. In general, the migration process can be considered via all of the following four major steps, namely, the diffusion of chemical compounds through the matrix, the desorption of the diffused molecules from the polymer surface, the sorption of the compounds at the polymer-food interface and the desorption of the migrated compounds in the food volume. The transport of the migrant due to pressure difference in the packaging medium is very much restricted, hence it will not have a significant influence on the overall migration process (Del Nobile et al., 2003; Nollet, 2004; Kanavouras and Coutelieris, 2006).

The main mechanism of the mass transfer during migration of chemical compounds from packaging material to food has been broadly attributed to a diffusion process. Food contamination occurs due to the dissolution of the migrant in the food in contact with the migrated substances on the polymer surface. This process is often influenced by food-packaging interactions as well as by various factors such as the temperature of the system, the concentration of the migrant, the molecular weight, the solubility, time, polymer and food compositions and structures diffusivity and partition coefficients between food and packaging, (Arvanitoyannis and Bosnea, 2004; Tehrany and Desorby, 2004).

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Figure 1. Food–packaging–environment possible mass transfer processes.

However, solubility even though it is not a transport phenomenon, when present in a system affects the rest of mass transport phenomena via the partition coefficient that indicates the polymer – solvent (food) compatibility (Mangaraj, 1963; Tehrany and Desorby, 2004). Solubility parameters were used by Haelck and Luttman (1991), Nielsen (1994) and Paik (1995) to predict the migration values from polymeric packaging to foodstuff. Through the use of solubility, the sorption behavior of migrants and polyolefins to food and foodstuff was discussed by Tehrany and Desorby (2004).

In addition, the loss of compounds from the food phase migrating into a polymeric packaging material has been considered as a sorption mechanism receiving a significant consideration (Risch, 1988; Tehrany and Desobry, 2004; Vitrac and Hayert, 2005; Vitrac and Hayert, 2006). Recently, several migration studies of different experimental techniques aiming in estimating the sorption/migration events and their respective advancements and limitations for plastic packaging materials—a major type of packaging materials for the global markets, as indicated by Robertson (2012)—were reviewed by Kadam et al. (2015). It was suggested that it was both the quality of a product and its shelf life that were affected by either natural and/or superficial factors such as: mechanical stress, temperature, permeability of gases, and vapors. In addition, the physical factors affecting the quality of a packaged food were the properties of the packaging material such as design and compatibility to the food itself, as food-packaging interact occur till the end of the products' use. Interactions such as sorption and migration appeared to be rate dependent by the food-packaging exposure environmental conditions. Categorization and comparison among the different ways to experimentally study sorption and migration should also be a considered (Kadam et al., 2015).

During the last three decades, a rather enormous scientific knowledge has been accumulated concerning the migration process and its behavior on food-packaging materials (Piringer and Baner, 2000). In relation to that, scientific studies have been performed using officially authorized food simulants, avoiding the migration analytical studies with real foodstuffs, for the reason of confirming the materials' compliance under systematic hurdles. The usage of extensive migration datasets using food simulants was established in Europe and USA. Most of the related research developments have been carried out in support of the international and European food-contact materials legislations and guidelines. All of the various investigations performed, demonstrated that migration from food-contact materials could be a both physically and mathematically, predictable and describable, process. In that sense, the mass transfer from a plastic material into food simulants has been considered a foreseeable process that in most cases was suggested to obey the Fick's laws of diffusion (Franz, 2005).

In a review by Poças et al. (2008), the models providing the different mathematical expressions for determining the parameters of the food-package system under study, were presented. In addition to that work, this study aims in an in-depth analysis of the main migration models, with a critical view that is taking into consideration more complex phenomena beyond the "safe" assumption of a Fickian-controlled migration's approximation. Therefore, in this work, a presentation of several mathematical models dealing with the prediction of the substances' migration from packaging material to foodstuffs, or food simulants, under several storage conditions, is attempted. Via the following critical discussion of the widely accepted models, a justified view on their compensations and drawbacks will be presented for to actually identify the lack of existing knowledge. This work wishes to eventually provide indicative directions regarding the forthcoming research approach on that topic.

Accordingly, this work will be developed through the presentation of the main attempts to define the mass transfer coefficients, will present the main migration models, the case studies these models applied and the consequent outcomes and estimations of their applicability. A certain part of relevant interest will be the reposting of main software programs available in the market for the migration estimations. At the end, a broad discussion and a more focused conclusion deriving from this work will be given, regarding the potential future research work on the field.

Migration models

The scope of a mathematical migration model is to predict the concentration of the migrant in the food after contact with the package during a certain time defined as the "shelf-life" of the product. In addition to this mathematical approach, a number of relevant transport phenomena controlling the migration process can be also identified. Knowing these phenomena may allow realistic simulations of the migration process. A reliable and accurate model should, therefore, take into consideration all the participating mass transport phenomena, along with the external factors affecting their evolution processes. Such phenomena involve the diffusion, the transport due to pressure difference and the consequent chemical reactions of the migrant with the receiving phase's substances. It's important to note that a list of these phenomena may not be definitely exhaustive, while such phenomena can occur in both food and packaging phases. Thus, a large number of studies can be found on the development, improvement and testing of migration mathematical models.

In particular, in order to determine the migration levels using migration data, Limm and Hollifield (1996) and Baner et al. (1996) developed certain semi-empirical models for the estimation of diffusion coefficients, based on the nature of the migrant and the properties of the polymer. Other aspects of migration, such as partitioning, mass transfer, polymer morphology, shape/polarity of the migrant, as well as plasticization of the polymer were not considered in full for these models. Nevertheless, these factors should be considered carefully when deriving migration levels to food using modeling techniques since they might cause erroneous values (Franz, 2005). For the plastic materials used in food contact applications, the main

topics of focus have been the adhesives, the urethane polymers, and the repeated-use of packaging (Baner et al., 1996).

Mass transfer coefficients

Usually, the mass transport due to sorption or desorption phenomena was estimated via studies allowing the distinction among the prevailing internal, interfacial and thermodynamic systemic phenomena. A description of the most important of those phenomena follows.

To set up a worst case migration scenario, in a first approximation, the following two assumptions can be made according to Piringer and Baner (2008) and Pennarun et al. (2004):

i.) the solubility of the migrant in food is high,
ii.) as far as the focus is usually on safety rather than on quality control, the diffusion coefficient of the migrant has an "upper bound" value, D^*, which actually represents the worst acceptable case,

where D^* is the value of the overestimated additive diffusion coefficient which, within a given statistical certainty, is larger than any actual additive diffusion coefficient (D_P) for the specific migrant.

Whereas the first assumption leads to a simple relation, $K_{P,F} \leq 1$ (where $K_{P,F}$ is the polymer–food partition coefficient), the second one is much more difficult to quantify. This is because a realistic D_P may range from about 10^{-7} cm^2 s^{-1} down to about 10^{-18} cm^2 s^{-1}. Therefore, the primary target is to find a way for predicting D_p values. That, in combination with the diffusion equations and $K_{P,F} = 1$, can provide an estimated based on calculations migration value, equal or above the actual migration value feasible under the same conditions. In order to be on the safe side and protect the health of the consumer, the equations describing migration tend toward the overestimation of the migrants quantities expected in foods (Helmroth et al., 2002).

Vitrac and Hayert (2006) analyzed the detectability and identification of different diffusion properties that control migration from a single desorption/sorption kinetic, which can be subject to physical constraints. Their study focused in the estimation of standard diffusion coefficients for the additives and monomers in plastic materials, when in contact to food simulants. The results were tested for compliance to the European Directive 2002/72/EC. A novel solution for the general dimensionless mass transport problem controlling desorption/sorption kinetic was presented, resulting to the evolution of the migrant concentration in the food or the packaging phase as shown in a new approximation space called "Kinetic phase diagram". The migrant concentration at equilibrium could be easily extrapolated and internal and external mass transfer resistances could be clearly distinguished. However, the authors pointed out that when the thermodynamic and external mass transfer coefficients were falsely neglected, the results were significantly overestimating the internal mass transport resistance in the solid phase and hence, allowed for a significant underestimation of the real migration values in the solid phase. Finally, they proposed an estimation strategy in order to simultaneously identify the three properties (namely, diffusion; partition coefficient; interfacial mass transfer coefficient) controlling the sorption kinetics.

The vast majority of the relative studies in the migration modeling area employing a deterministic approach were considering the migration process to be controlled by the diffusion of the migrant, through the volume of the packaging materials, as described by Fick's law given in Equation [1] (Crank, 1975; Limm and Hollifield, 1996; Reynier et al., 1999; Pocas et al., 2008):

$$\frac{\partial C}{\partial t} = D\nabla^2 C \quad (1)$$

The above mathematical description indicates that the transient mass flux of a compound through a control volume is proportional to the gradient of the concentration of this compound. It has to be also mentioned that this approach was based on specific assumptions (constant packaging thickness, homogenous media, no boundary effects, no chemical processes, etc.).

Further to diffusion, given chemical reactions taken into account are, accordingly, modify Equation [1], as follows (Bird et al., 2002):

$$\frac{\partial C}{\partial t} = -D\nabla^2 C \pm kC^n \quad (2)$$

where k denotes the reaction rate constant and n is the order of the reaction.

The last Equation [2] describes the Fickian diffusion in combination with the chemical reaction. In order to achieve an analytical solution of this second-order partial differential equation, a number of assumptions should be made. Primarily, the diffusion coefficient is assumed to be constant in both the food and the packaging material (see, for instance, Brandsch et al., 2006a, 2006b). By solving the general diffusion Equation [1], it can be concluded that the diffusion and the partition coefficient of the migrant should be known in order to practically apply the equation. It is often assumed that the solubility of the migrant in the polymer is very high. This, consequently, results to the assumption that the partition coefficient $K_{P/F} = 1$, which avoids any additional difficulties in estimating the partition coefficient for a given migrant–packaging material–food system (Brandsch et al., 2002).

Main migration models

Various models aiming the prediction of diffusion coefficient for a given migrant have been developed and reported through the years (Piringer, 1994; Limm and Hollifield, 1996; Mercea, 2000a, 2000b; Han et al., 2003; Pennarun et al., 2004; Begley et al., 2005), with the Piringer's model (Piringer, 1994) and the Limm and Hollifield model (Limm and Hollifield, 1996) being the two main ones. The way of solving the migration problem by using such mathematical models will now be presented.

The "Piringer's" model is by far the most widely used model up to day. In terms of mathematics, Piringer's approach describes the diffusion coefficients in gases and condensed phases (Helmroth et al., 2002), including the plastic materials, as expressed below (Piringer, 1994; Brandsch et al., 2002):

$$D_P \leq D_P^* = 10000e^{\left(A - a M_i - \frac{b}{T}\right)} \quad (3)$$

where D_p is the actual additive diffusion coefficient, D_p^* is the overestimated additive diffusion coefficient, A is a polymer specific constant, α is an additive molecular weight specific constant, b is a temperature specific constant, M is the molecular weight of the additive i, and T is the temperature.

The diffusion coefficients were determined by the empirical correlation in Equation [3], using the coefficients obtained from literature against the molecular mass of the migrants, with a specific parameter, A_p and with the absolute temperature, T in K (Brandsch et al., 2002). The model can be adapted to different types of polymer, simply by changing the specific polymer parameters (Pennarun et al., 2004).

Reynier et al. (1999) have exploited the applications of Piringer's model, by proposing an empirical correlation between an upper bound value of the diffusion coefficient and the molar mass of the migrant, enabling the calculation of an upper bound value of migration. This approach has also been validated several times as by O'Brien et al. (1999) and O'Brien and Cooper (2001). The results showed that most of the migration values predicted by Piringer's model were indeed overestimated, being greater than approximately 50% of the experimentally reported results (O' Brien et al., 1999; O' Brien and Cooper, 2001; Helmroth et al., 2002).

In a more recent work on the validation of the model performed by Brandsch et al. (2002), it was found that the model results overestimated more than 95% of the experimental values, while the smallest differences between the "worst case" estimations and the experimental values appeared at high temperatures. Also, it is important to underline that according to Reynier et al. (2002), the Piringer's model tends to underestimate the temperature influence on diffusion of high molecular mass components. Experimental tests with high molecular weight components, at high temperatures, generally showed diffusion coefficient values, 2–3 orders of magnitude lower than the values predicted by Piringer's model. This could be explained by considering the effect of the molecules size and molecule shape on the diffusion process. As shown in the work of Chan et al. (2015), the bigger the size of the molecules, the lower the real diffusion coefficient (Pennarun et al., 2004). For the larger molecules, the diffusion rates of planar solutes were reduced or even reversed, as compared to those of the spherical ones of the same size (Chan et al., 2015). Furthermore, the temperature effect on diffusion has been described by Reynier et al. (2002), where they observed that the increase of mobility lead to lower diffusivity sensitivity to the molecular weight.

Brandsch et al. (2002) used an equation for the estimation of the diffusion coefficients that did not rely on experimental data:

$$D_P = D_0 \exp\left(A_P - 0.1351 M_i^{2/3} + 0.003\, M_i - \frac{10454}{T}\right) \quad (4)$$

The equation combined the molecular masses with the parameter, A_P, having the role of a "conductance" of the polymer matrix to the diffusion of the migrant (Brandsch et al., 2002).

To calculate migration rates within a safety margin from the regulations limit it is possible to match the "conductance" in Equation [4] to yield a "worst case" migration estimation. In order to achieve that the polymer specific parameter can be modified by using an upper limit polymer specific diffusion parameter ($A_p^{'}$), the temperature (T), the polymer specific parameter (τ) which is actually a contribution of the polymer matrix to the diffusion activation energy, (A_P):

$$A_P = A_P^{'} - \left(\frac{\tau}{T}\right) \quad (5)$$

Under these assumptions, the migration value of a migrant from the polymer to the food-in-contact can be calculated by the following expression derived when Fick's law equation is analytically solved in planar geometry, as indicated by Brandsch et al. (2002):

$$\frac{M_{F,t}}{A} = C_{p,0}\rho_P\, d_P\left(\frac{a}{1+a}\right)\left[1 - \sum_{n=1}^{\infty}\frac{2a(1+a)}{1+a+a^2q_n^2}exp\left(-D_P t\frac{q_n^2}{d_P^2}\right)\right] \quad (6)$$

where $\frac{M_{F,t}}{A}$ denotes the migration value at time t, A is the contact surface area, $C_{P,0}$ is the initial concentration of the migrant in the polymer, ρ_F and ρ_P are the densities of food and polymer respectively, d_P is the thickness of the polymer, $\alpha = (V_F/V_P)/K_{P,F}$ with V_F and V_P being the volumes of food and polymer respectively, and $K_{P,F}$ is the polymer–food partition coefficient. Finally, the parameters q_n are the positive roots of the equation: $\tan(q_n) = \alpha q_n$.

A comprehensive list of available diffusion coefficient data for LDPE, HDPE, and PP was given by Mercea (2000a, 2000b). The data derived from an extensive literature review of scientific papers. The data were used by Brandsch et al. (2002), to derive the specific diffusion parameter A_P to be used in Equation (4). The authors validated the accuracy of the calculation of a "worst case scenario," using the relation $D_P^* \geq D_P$ at 95% confidence level. Additional migration experiments were carried out in order to validate their work using several migrants from HDPE toward olive oil as a fatty food simulant. In addition to the previous work, Begley et al. (2005) re-evaluated the parameters of Piringer's model in order to estimate the diffusion coefficient. Their results were apparently overestimated the migration value at a rate of 95% of 366 experimental values, while, finally the modeling values of migration were reported to be 26% lower than the actual ones.

Reynier et al. (1999) focused on the determination of the diffusion coefficients by the implementation of advanced constants for the calculation of the upper bound value, by using experimental data instead of the, at that time, available literature data (Reynier et al., 1999). The reason being that the Piringer's model uses data found in literature that were most likely the results of very different type of experiments and were obtained from different mathematical treatments. The results obtained via the Reynier's method showed that this method showed a general trend toward a slight overestimation of the migration values of certain migrants, which coincides with conclusions deriving from similar works (see also Brandsch et al., 2002).

Limm and Hollifield (1996) proposed a semi-empirical model of additive diffusion prediction in polyolefins (POs), as a first step in systematically predicting additives' migration. Their approach utilized the relationships between molecular diameters and activation energies, which have been established for relatively small molecules with molecular weight of 100 daltons. The molecular diffusion of additives through a polymer matrix was considered to be adequately expressed by an Arrhenius-type equation of the following form also found in Helmroth et al. (2002) and Pocas et al. (2008):

$$D = D' e^{\left(\frac{-E_D}{RT}\right)} \quad (7)$$

Limm and Hollifield's model uses this Arrhenius behavior as the basis for quantifying the temperature dependence for various additives' diffusion, given a specific polymer. Furthermore, and in accordance to the Piringer's model, the previously reported work proposed a direct relationship between the diffusion coefficient and the molar mass of the migrant. But, in contrary to Piringer's model, Limm & Hollifield's model required a minimal amount of data, while their deterministic approach was based upon existing physical diffusion theories, such as diffusion theories developed for rubbery polymers to model poly olefin (PO) made packaging materials (Limm and Hollifield, 1996; Pocas et al., 2008). The Limm and Hollifield's model relied on empirical constants from actual migration experiments, therefore the model apparently provided a quite good correlation with experimental values, especially for the migration of additives with high molecular masses into oils when in contact with POs at elevated temperatures (Limm and Hollifield, 1996; Brandsch et al., 2002).

Limm and Hollifield's model has also been tested on a large number of diffusion coefficients found in literature and was found to have prediction deficiencies ranging from 2 times lower, up to 8 times higher levels (Limm and Hollifield, 1996; Helmroth et al., 2002). A significant part of their study relies on that when the thermal expansion was neglected it may lead to a slight overestimation of the activation energy at elevated temperatures, resulting to a much more conservative estimation of diffusion coefficients. However, the main disadvantage of their work has been its applicability, as their model could only be applied to polyolefins, therefore limiting its use as a global packaging-migration tool (Limm and Hollifield, 1996).

To further evaluate their model, Limm and Hollifield (1996) used diffusion coefficient values derived by the work of Johansson and Leufven (1994) regarding weight gain experiments due to the absorption of penetrants. The prediction accuracy was found to be within an order of magnitude quite comparable to the available experimental data. Furthermore, this model was also validated against the data of Sadler and Braddock (1990) for the limonene diffusion in LDPE. A direct comparison of these results demonstrated that this model might be useful in estimating additives' migration at elevated temperatures by using only the molecular weight of the migrant and a rather limited amount of experimental migration data.

Both Piringer's and Limm and Hollifield's models may apparently be prone to a number of limitations, that have to be taken into account consider before models' use. Because of the necessity of an accurate estimation of the diffusion coefficient it is important to note that both of these models can only be applied accurately on polyolefins only. It should be noted that polyolefins are currently the most frequently used material of use in the food packaging industry. On the other hand, it must be noted that when fatty foods are in contact with packaging made of polyolefins, negative migration of triacylglycerols will occur, resulting to a time depended change of the diffusion coefficients of the migrating substance in the polymeric system. This fact can be considered as a big disadvantage of these models (Meulenaer, 2009).

Critical discussion on the main migration models

A series of recently published studies presented below, employed by the two major models discussed above and presented the efforts toward a better understanding of the insufficiencies and inaccuracies mainly due to the over-simplification of the transport phenomena.

Among these studies, the work of O'Brien and Cooper (2001) reported on the polymer additives' migration from polypropylene (PP) to a food simulant (olive oil). In this study, the "Migratest Lite" program was used based on the Piringer's model developed in 1994. The program was designed to overestimate the overall migration value. Accordingly, the results showed that the 97% of the values calculated were overestimated at levels greater than 70%. Confidently, this model was proven inadequate in providing a realistic estimation of migration values.

The same model proposed by Piringer (1994) was also used by Gillet et al. (2009), who studied the migration of a model migrant from plastic materials (HDPE) in a food simulant under the assumptions described by Vitrac and Hayert (2006) and Vitrac et al. (2007). Their results underlined the hypothesis that the model fails to demonstrate a consistency in the calculations of the exact overall migration value. Comparing their results with the literature data of Welle and Franz (2012) a positive difference up to one order of magnitude resulting to the overestimation of the overall migration value when they studied the migration of model migrants from PET bottles to water, was also observed. Furthermore, after using the same model, Reinas et al. (2012) studied the migration of two antioxidants from packaging materials into a solid food (rice) and into a food simulant (Tenax®). Their results showed an overestimation of the overall migration value up to several orders of magnitude. More recently, using the same model, Maia et al. (2016) studied the migration value of a model migrant (BZP) from plastic (LDPE) into different foodstuffs. The values predicted by the model had a large margin of uncertainty making them

improper to reveal accurate overall migration values. Finally, Han et al. (2016) studied the migration of photoinitiators from paper to two fatty food simulants (Tenax® and 95% ethanol) by using the model used by Zulch and Piringer (2010). Their results were found to be higher at approximately 20% more than the actual values, therefore, it was concluded as rather improper for use in estimating a realistic overall migration value.

Nevertheless, the main problem of a realistic estimation of the diffusion coefficients describing the migration process still remains, when a highly realistic estimation of migration is considered as necessary. In that case, the use of the diffusion coefficients deriving from the above reviewed models will lead to rather overestimated migration values, making the practical use of migration models rather impractical and inaccurate (Brandsch et al., 2000; Meulenaer, 2009).

Additional migration models

Additional models were found in the relevant literature aiming in predicting the migration level from a different scope of view, as will be discussed further below.

Among these models, the one of Pennarun et al. (2004) was applied for predict the migration of PET materials in contact with aqueous food simulants at 313 K, using some empirical equations, overestimating the diffusion coefficients. Their method was also applied to poly olefins (POs) and their conclusive empirical equation was given, based on D values from the literature, as:

$$\log D^* = AM + \frac{B}{T} + C \tag{8}$$

where A, B, C are constants, D^* is the worst-case diffusion coefficient determined empirically from a graphical correlation $\log D = f(M)$, M is the molecular weight of the migrant, and T is the temperature.

It is important to note that the experimental conditions, as well as the experimental background theories, found in the literature are in many cases significantly different between each other, thus resulting into different D values. However, the very large number of data used in this work gave a rather high level of confidence and accuracy to Equation [8]. Nevertheless, the parameters found in the literature were overestimated due to the reasons explained above, being therefore suitable for use on the side of the safety and protection of public health (Pennarun et al., 2004).

Han et al. (2003) developed and applied a model based on a numerical treatment method known as finite element method (FME), for quantifying the migration through multilayer structures. According to this approach, there were several assumptions made including that there is no swelling of the polymer, the partition coefficient is time independent, there is a one-dimension mass transfer, the diffusion coefficients are only temperature depended, there is a finite packaging, etc. (Pocas et al, 2008). Based on the assumptions of constant diffusion coefficient and negligible resistance for the mass transfer between the plastic and the food simulant, the diffusion coefficient used in the simulations was obtained through the simplified analytical solution of the Fick's law, expressed as:

$$\frac{M_{F,t}}{A} = 2C_{p,0}\left(\frac{Dt}{\pi}\right)^{0,5} \tag{9}$$

where A is the surface area of the polymer in contact with the food, $C_{P,0}$ is the initial concentration of the migrant in the polymer volume at time $t = 0$, D is the diffusivity of the migrant within the polymer, and $M_{F,t}$ is the amount of mass that has migrated from the polymer into the food after time "t."

As far as this simulation process has been dedicated to the multilayer polymer packaging, its value for the present study was limited on the way they have determined the diffusion coefficient as well as on the fact that the whole process was assumed to be solely diffusion driven.

The same approach was also used by Haldimann et al. (2013), where FME was now used to simulate migration of the heavy metal – antimony in a food simulant (3% acetic acid) and in a foodstuff (ready meals) from PET trays. The diffusion coefficient required for the models were experimentally determined. Their results showed a 95% confidence between the experimental and overestimated theoretical migration measurements. A similar agreement was also reported by Zhang and Zhao (2014), who studied the migration of flavonoids from LDPE to aqueous food simulants. This studied concluded that when comparing the theoretical results with the experimental values, they evidently did not fit very well, apparently due to the complexity of the migration tests.

The diffusion coefficient of the migrant in the outer layer of a multilayer structure was estimated algebraically by Brandsch et al. (2002), using the empirical equation (4). A successful validation of the model using HDPE and LDPE materials in contact to a food simulant (Ethanol) at two bulk concentrations of 100% and 50% and for three temperatures (296 K, 304 K, and 313 K) was performed by comparing their simulated results to experimental data. Model results were found to be quite accurate, as the deviation from the experimental values was negligible (Han et al, 2003).

Lickly et al. (1997) proposed a simple, analytical model, based on the general theory of mass transfer. They assumed a semi-infinite flat layer of polymer in which the additive migrated toward the surface and then into the bulk solution. An analytical model, similarly to the others, was based on the diffusion theory as described by Fick's second law. The main equation describing the migration phenomenon in this study is:

$$M_t = C_{po}aK\left(1 - e^{z^2}erfc(Z)\right) \tag{10}$$

where

$$Z = \frac{(D_p t)^{1/2}}{aK} \tag{11}$$

and M_t is the migrated quantity of the component migrated for time t, a is the volume of simulant, K is the food–polymer partition coefficient, C_{po} is the initial concentration of the

component in the polymer phase, and *erfc*(Z) is the error function term of variable *Z*, given by Eq. (11).

The use of this expression assumes infinite thickness of the polymer phase, homogeneously distributed migrant in the polymer, a temperature-only-dependent diffusion coefficient and no interactions occurring between polymer and external phase. The model was validated by measuring experimentally the migration for specific additives and materials from different sample configurations, where an overestimation of migration was reported (Lickly et al., 1997).

A quite different model was proposed by Fauconier et al. (2001), where the migrated quantity was described as a polynomial function of temperature and time. The influence of time and temperature on the additives was modeled by adopting the well-known statistical method of "response surfaces methodology (RSM)" (Box and Wilson, 1951), where the following polynomial equation was used:

$$z = A + Bx + Cy + Dx^2 + Ey^2 + Fxy, \quad (12)$$

where x and y are temperature and time, respectively, z is the migrated quantity (mg/g), and A to F are coefficients calculated for all migrants in each migration liquid.

In accordance to RSM, modeling of the desorption data was based on a correlation procedure using a polynomial equation. Such a procedure, which is not based on physical principles but on the inter-relation of statistically important variables, was actually built by the extrapolation of the statistical variables into regions, where the results could not be acceptable, thus resulting into false values. Therefore, for avoiding such an erroneous approach it seems quite important to eliminate some critical regions. In order to validate their method, the authors performed a series of experiments using HDPE and three different aqueous food simulants, namely ethanol, lemon-origin terpenes and an emulsion of terpenes. The results showed an accuracy of over 90% for all the phenolic migrants as well as for polymer oligomers migrating into various simulants.

Regulations

An important note concerns the use of migration modeling for plausibility considerations in support of regulatory decisions. Analysis limitations within certain regulations have been set by specific and detailed migration testing rules. Although migration testing in food prevails, migration estimation is usually calculated by using "food simulants," representative for a specific food category. Modeling of potential migration has already been used in the United States as an additional tool to assisting in establishing regulatory decisions, while the European Union uses this tool as a quality assurance mean (Brandsch et al., 2002).

The main principals behind EU and USA regulations for food contact materials have been the protection of consumers against toxic migrating substances. Therefore, agencies producing and designing paced-foods and packaging materials used for food, have to apply and confirm the compliance via appropriate experimental techniques. This created an opportunity for modeling the migration and the use of subsequent models for predicting it (Begley et al., 2005).

The concentrations of migrated contaminants should be below the legally accepted specific migration limits (SML). The verification of the compliance of food packaging materials with the existing regulations can be done by comparing the SML with the values predicted by "generally recognized migration models" (Cruz et al., 2008). The theoretical predictions of migration from packaging to food with the use of models are often made using equations, which are usually not designed especially for the problem attended but for attaining the widest possible range of applications.

Computer programs assisting migration estimations

A series of sophisticated computer programs able to perform the necessary model calculations for the prediction of the migration value have been reported. Such programs are available in the market or can be freely downloaded from the internet. The most commonly used programs are briefly presented below.

MIGRATEST LITE 2001 of FABES, which is continuously been updated and optimized has been revised to MIGRATEST© EXP. In contrary to its predecessor MIGRATEST© EXP has been created using numerical algorithms, which enable the prediction of migration from food packaging materials to foodstuff or food simulants. These numerical algorithms are in fact solving the Fick's Partial Differential Equations (PDEs) for diffusion by using the Finite Difference Method (FDM) (Mercea et al., 2008). It allows a deep understanding of the migration processes within the packaging material. MIGRATEST© EXP uses specific constants of the material under study, in order to predict the migration of substances. MIGRATEST© EXP simulates the time and temperature depending migration of a specific migrant from a packaging material, toward the foodstuff or the food simulants for specific time periods. It is able to compare the calculated results with SMLs as are defined within the EU list into the plastic regulation EU 10/2011 in order to determine the compliance with the existing regulations. MIGRATEST© EXP can also calculate the maximum initial concentration of a substance in the product in order to meet the SML in foodstuff (Mercea et al., 2008; Pocas et al., 2008).

The AKTS–SML is a joint application of the Federal Food Safety and Veterinary Office (FSVO, Switzerland), the company Advanced Kinetics and Technology Solutions AG (AKTS AG, Switzerland) and MDCTec Systems GmbH. It employs an advanced Finite Element Method (FEM – also called Finite Element Analysis, FEA) aiming to predict the migrating amount from the packaging material into the foodstuff or food simulant. It ensures the compliance of plastic food contact materials with the SML's defined within the EU list into the plastic regulation EU 10/2011. It simulates the migration process based on Fick's second law of diffusion under consideration of partitioning between adjacent layers or contact media in closed systems. The temperature dependence of the process is considered by the Arrhenius equation. AKTS-SML can compute the time-dependent migration curves and the concentration profiles inside the packing materials giving a more realistic estimation of the migration in the packaging material (Pocas et al., 2008).

The SMEWISE program developed by INRA in France estimates the magnitude of a migration process from a packaging material into a foodstuff or a food simulant. In order to do that it is necessary to know the time dependence of the migrant concentration profiles in the multilayer material. This can be calculated by solving Fick's Partial Differential Equations (PDEs) for diffusion. In this program, the calculations of concentration are made by using the Finite Element Method. It is essentially based on the diffusion theory and takes under consideration any partitioning effects. The key parameters are the diffusion coefficient of the migrant in the packaging material as well as the partition coefficient of the migrant between the packaging material and the foodstuff or food simulant. The application of this migration model to demonstrate compliance with SML's is permitted in the latest version of the Plastics Directive (2002/72/EC) (Roduit et al., 2005; Pocas et al., 2008).

All of the programs mentioned above basically use the same migration model and the same empirical equations to determine the migration in a specific packaging- migrant system. However, as it can be concluded the numerical methods used to calculate the necessary parameters affecting migration is different. To solve these numerical equations numerically the finite approximations techniques of finite difference and finite elements are used. The development of these techniques became very effective with the development of computers and is nowadays recognized as probably the most powerful tool for approximating the solutions of complex problems (Meulenaer, 2009).

The finite element method (FEM) which probably is the oldest of these methods covers the solution domain by computational cells. At each point of the mesh covering the grid the partial derivatives of the differential equation are calculated approximately by the expressions on terms of the variable values at the grid nodes. This results to the use of Taylor series or polynomial fittings to obtain the approximations of the first- and second-order derivatives. However, a major disadvantage of this method is that the conservation in not enforces except when special methods are applied. Another limitation of this method, in contrary to FEM, is the necessity of using simple geometry (Ranade, 2002).

In the FEM, the computational domain is divided into finite elements or discrete volumes, where the calculations occur into. Then, it solves the equations by first multiplying them with a weight function before they are integrated over the whole domain. This approximation is then substituted into the integral of the conservation law. By minimizing the residual of the calculation, a set of nonlinear algebraic equations is then obtained. An important advantage of this method is its ability to deal with a complex domain consisted by any geometrical scheme. However, when using finite element method to develop a computationally efficient solution for strongly coupled and nonlinear equations, a high difficulty is found in applying FEM (Ranade, 2002).

These computer programs have been shown to provide an estimation of worse-case migration (not total transfer) and are designed so they are able to predict the migration that will occur with sufficient safety margins (overestimated migration). The diffusion coefficients of the migrants in packaging material are estimated by generally recognized estimation procedures as proposed basically by Piringer's model, which will be discussed in detail in the following paragraphs. (Roduit et al., 2005).

Discussion

According to the various case studies mentioned above, the most common approach for practical migration modeling for quality assurance has been the initial use of the two rather simple models, i.e., either the Piringer's model (Piringer, 1994) or the Limm and Hollified's model (Limm and Hollifield, 1996). Piringer's model correlates the diffusion coefficients with the relative molecular mass of the migrant with a specific parameter along with the absolute temperature. This approach seems to be the simpler and most widely used for the purpose of migration modeling. On the other hand, the Limm and Holifield, model proposed a similar approach for migration modeling with the limitation though, of good usage only for polyolefins, which obviously is limiting its potential for selection and applicability of the specific model to migration modeling for other materials. However, on the other hand, in the work of O' Brien et al. (1999), when a direct comparison of the two models for the migration of a number of additives from HDPE in olive oil has been made, it was concluded that Limm and Hollifields model was more accurate in most of the situations.

Additionally, certain theoretical issues need to be addressed. Among the most significant comments to be made at this point, is that all the approaches converge to the fundamental consideration that the migrant mass transfer is diffusion driven, therefore the process may be adequately described by Fick's laws. For that reason, the differences among the most widely used migration predictive models have been actually categorized in such a way that the diffusion coefficient is basically estimated, while models being otherwise essentially similar in their insight. As stated earlier in this present review, the fundamental considerations for the Fick's law valid use are actually dependent on the following specific assumptions:

1. The migrant was distributed homogeneously in either the packaging material or the food phase.
2. There was no boundary resistance in the transfer of the migrant between packaging and food phases.
3. There were no interactions between packaging and food.
4. No swelling phenomena occurred within the food-packaging system.
5. A specific partition coefficient between food and polymer might be assumed.
6. There was no external supply of migrant during migration process, i.e., the sum of the total migrant amount in the food-packaging system is constant.

Although the aforementioned points may be valid for the vast majority of the migration applications in nature, it seems apparently rather less likely for this consideration to be incorporated in more complicated phenomena, such as sorption of specific food contaminants by the packaging material, partitioning on the food-packaging interface, chemical reactions of packaging material or of some of its byproducts with the food content, etc., all of which possess a high potential within real food-packaging systems. We may safely assume then, that the above assumptions cannot be valid, in a universal way.

In general, it seems rather easy to identify a case where at least one of the above assumptions breaks down. For example, within a more precise context of pragmatic hesitations we may report on the assumption #1 which could not be valid for packaging materials other than plastic polymers, on assumption #2 that might not be valid for sticking migrants, and so on.

Ultimately, by summarizing the studies of the aforementioned models and their results regarding their validation on various combinations of materials in contact to food simulants, an apparent non-Fickian behavior of migrants may be concluded. For each and every model the use of oversimplified assumptions was profound, leading to higher inaccuracies, although being acceptable for addressing food – safety issues.

Nonetheless, such a complex mass transport process has to be modeled via more holistic, this more complicated, mathematical expressions, potentially containing nonlinear terms to express the above-mentioned phenomena. In this context, Equation [1] is sufficient either for defining norms, rules and laws, or for a rough estimation of mass transport for industrial purposes, but it seems quite weak in its out coming results when a deeper, a more thorough and highly descriptive and accurate in a scientific way, insight may be in demand. Needless to say, Equation [2] is a significant improvement, although it has found quite a limited apparent applicability, most possibly mainly due to its inevitable complexity.

On top of the above-mentioned shortcoming remarks, another significant drawback has been encountered in the widely accepted published literature. The latter drawback is regarding the following system consideration: the environment is usually considered as the entity which just imposes the conditions (boundary/initial conditions as well as values of the parameters involved in the equations), without being considered as an inherent part of the system. Consequently, environmental influence has not been engaged directly in the transport problem, but only through the conditions and parameters. Therefore, such an involvement could be considered somehow arbitrary. Hence, it is under the opinion of the authors that it could be considered as rather absolute necessity to rework and potentially restructure, the traditionally accepted "packaging-food" system with the now suggested novel approach, being "environment-packaging-food." We wish to support that such a position allows for a more detailed and rather solid consideration of the totality of the transport phenomena occurring within a complete system.

An additional point in need for a further discussion, since it could be considered quite relevant to the previous specific critical discussion, has to do with the main difficulty of modeling the migration process, implying that we should probably no longer work for the purpose of elaborating a model (Han et al, 2003), but it seems rather much more important focus in obtaining those parameters that are requested for the most appropriate, descriptive, and accurate calculations. Such parameters may be summarized as follows:

- the diffusion coefficients D of the migrant in each layer; if not available;
- the partition coefficient between layers as only little data are available. If the different layers are made from the same or from similar polymers, the partition coefficient can be assumed to be $K_{p/fb} = 1$;
- the partition coefficient between functional barrier and food $K_{fb/f}$. Similarly, in the absence of data, a worst-case value must be selected, such as $K_{fb/f} > 10^{-2}$;
- the swelling of the plastic layers by food constituents leads to a continuous increase of D during contact with food: use of D^* values often takes into account swelling;
- the mass transfer coefficient at the interface. In the absence of relevant data, the interface may be assumed to be infinite, as a worst-case scenario.

Conclusions

The major models reviewed in this work are only to predict the migration of known and already characterized migrants from polyolefins. Hence, these models are not quite capable of predicting the total accurate migration of a substance migrating from a different contact material to the food volume, since the material might contain a number of completely unknown compounds. Evidently, as these models tend to overestimate the migration value, they cannot be used in the food manufacturing process, where the migration of an additive might be essential and/or even necessary for the optimum quality of the product, such as in the case of active packaging. In analogous cases, a more accurate value of the migration process must be calculated in order to have the optimum quality. Consequently, the need of a new, accurate model becomes a seeming priority. In that sense, research should take into consideration all the mass transport phenomena, taking place within the "food–packaging–environment" system. This may also be of particular importance for the food industry when a cost-efficient check in terms of compliance with the existing regulations aiming to assure food safety, as well as when a more quality-driven food packaging – system design is in focus. For industrial practices, a tool for assessing the interactions between the food and the packaging and the environment, is becoming in need for to optimize the interplay between the three parts of the system (Food–Packaging–Environment). Therefore, an increased effort and attention should probably be paid in future research and modeling work in order to build a model able to provide accurate results under the conditions and complex assumptions mentioned above.

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