Migration Of MOSH/ MOAH Through Multi-layered Packaging Into Food

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Abstract: MOSH/ MOAH components are toxic and potentially carcinogenic substances which migrate from food packaging into foodstuffs. A model to simulate the migration of these substances through plastic packaging material was developed using the LiveLink to MATLAB. The model can describe a wide variety of packaging solutions, as arbitrary numbers of packaging layers and migrating substances can be simulated. The migration is simulated using the Transport of Diluted Species interface. Additionally, the model can describe adsorption layers and evaporation of MOSH/ MOAH components to the surroundings, using the domain ODE interface, or the boundary ODE interface, respectively. Furthermore, temperature changes during storage can be included by using stepwise and analytical functions for the parameters. Further work will include simulation of non-plastic packaging materials and estimation of parameters by comparison with experimental results.

Keywords: MOSH, MOAH, Migration, Diffusion, Food packaging

1. Introduction

Mineral oil saturated hydrocarbons (MOSH) and Mineral oil aromatic hydrocarbons (MOAH) are groups of substances which are frequently found in foodstuffs [2, 3, 4, 17]. These substances originate from arrears of printing ink in recycled paper and board used for food packaging [2, 3, 4, 17]. As they are toxic and potentially carcinogenic, the amount of MOSH and MOAH components in food may not exceed a certain limit, to be defined by legislation [7, 10].

As experimental determination of migration kinetics is very time-consuming and expensive, there is a need for numerical models which can describe the migration of these substances from packaging materials to foodstuffs.

The aim of this work is, therefore, to develop a model, which can simulate a broad variety of packaging solutions, to eliminate the need for excessive experimental work. Effects, like adsorption, evaporation, or temperature changes will be included.

This work will concentrate on designing a model to describe the migration of an arbitrary number of substances through an arbitrary number of plastic packaging layers, including the effects mentioned afore.

2. Methods

As the aim of this work is to develop a model which can simulate a wide variety of packaging situations, the model is build using the LiveLink to MATLAB. This enables the simulation of an arbitrary numbers of packaging layers and diffusing substances, as well as additionally including evaporation to the surroundings, adsorption layers and temperature changes. The exact packaging situation to be simulated can be defined by simply entering a few parameters in the MATLAB code. This will be explained in more detail in the following subsections.

2.1 Definition of Variables in MATLAB

The variables to be defined in MATLAB are:

- Number of packaging layers, their respective material and thickness.
- Number of substances, their respective name and initial concentration.
- Partition- and mass transfer coefficients for all substances and boundaries.
- Length of the interval representing the foodstuff.
- Beginning and end time, as well as time-step at which results will be shown.
- Number of different temperatures during the simulation, their respective temperature value and duration.
- A Boolean variable to check if evaporation of substance to the surroundings is to be included in the simulation. If so, the respective parameters (i.e. Arrhenius parameters of mass transfer coefficient for

evaporation) also need to be entered for each substance.

- A Boolean variable to check if an adsorption layer is to be included in the simulation. If so, the respective parameters (i.e. location of the adsorption layer in the multi-layer packaging and Arrhenius parameters of the rate and partition coefficient of adsorption) also need to be entered for each substance.

The diffusion coefficients of the substances in the different materials are estimated by an empirical correlation, which will be described in section 3.

2.2 Analytical and Stepwise Functions

If the simulation is to be non-isothermal, a stepwise function is created for the change in temperature. This function serves as the input to the analytical functions describing the temperature dependency of the parameters.

Analytical functions are created for the temperature dependent diffusion coefficients, mass transfer coefficients and, if included in the simulation, the parameters for the adsorption layer and evaporation to the surroundings. The equations describing their temperature dependence will be shown in section 3.

2.3 Geometry and Mesh

As in most practical cases the packaging is relatively small compared to the food, the problem is considered to be one-dimensional [11]. For each packaging layer of the exact packaging situation, an interval with the respective length is created. A further interval is then created, representing the foodstuff.

For each interval a user-defined mesh is created, according to the following specifications:

- Exponential growth/ decline of the mesh elements, according to the "geometric" distribution in COMSOL.
- Symmetrical distribution of mesh elements in all interior intervals, non-symmetrical in the outer layers, so that the smallest elements are located at the interior boundaries.
- Growth rate of the mesh elements is set to 3 percent.
- Minimum element size is 100 nanometers. For some simulations it is decreased to 1 nanometer, if a good resolution of the initial solution can not be achieved with bigger element sizes.

2.4 Physics

For each interval and each substance a Transport of Diluted Species (TDS) interface is created. The initial concentrations are set in the MATLAB code. Convection is disabled for all simulations. The diffusion coefficients are estimated by the analytical function mentioned afore. Flux nodes are created for all interior boundaries of the system. The equations describing these boundary conditions will be shown in section 3.

If evaporation of substance to the surroundings is included in the simulation, a flux node is also added for the left outer boundary of the system. Furthermore, a boundary ordinary differential equation (ODE) node for the amount of evaporated substance is created and connected to the left outer boundary.

If an adsorption layer is included in the simulation, a reaction node is added to the TDS interface of the respective interval. A domain ODE node for the amount of adsorbed substance is then created and connected to this interval. The corresponding equations will also be shown in section 3.

2.5 Solver Configurations

Interactions between different diffusing substances are neglected, as their parameters are usually several orders of magnitude lower than the diffusion coefficients [9, 12]. Therefore, each substance is simulated independently by creating a solution node for each substance and connecting it to the respective Physics interfaces. This approach also leads to a drastic decrease in computing time.

3. Governing Equations

3.1 Fick'ian Diffusion

The TDS interface uses Fick's laws of diffusion to describe mass transport [8]. Migration through plastic packaging materials

can be described by Fick's laws of diffusion [6], which are shown for one-dimensional diffusion and constant diffusion coefficients in equations 1 and 2.

$$F = -D * \frac{\partial c}{\partial x} \quad (1)$$

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

F denotes the Flux of substance per unit cross sectional area, D the diffusion coefficient, c the concentration, x the axis direction, along which the diffusion occurs, and t the time.

3.2 Estimation of Diffusion Coefficients

The diffusion coefficients are estimated using an empirical correlation for plastic materials [5, 6], shown in equation 3.

$$D = D_{ref} * \exp(A_p - \frac{\tau}{T} - 0.1351M^{\frac{2}{3}} + 0.003M - \frac{10454}{T}) \quad (3)$$

D_{ref} denotes a reference diffusion coefficient with a value of 1 m^2/s, M the molar mass of the given substance in Da and T the absolute temperature in K. The parameters A_p and τ are specific values of the packaging material used. The A_p parameter describes the "conductivity" of the material for diffusion, whereas the τ parameter accounts for the contribution of the packaging material to the activation energy of diffusion [6]. Their values are preassigned to yield a slight overestimation of the diffusion coefficients, accounting for a margin of safety when calculating the amount of migration to a foodstuff [6, 16]. For the plastic materials most-commonly used in food packaging, their values can be found in [16].

3.3 Boundary Conditions

Flux boundary conditions are used for all interior boundaries of the model. The boundary conditions to describe the mass transfer of substance between different packaging layers, and from the packaging to the food, is shown in equation 4.

$$D * \frac{\partial c}{\partial x} = h * (c_i - K_i * c_{i+1}) \quad (4)$$

The parameter K_i is the partition coefficient of the substance between the i-th and the i+1-th layer. It is defined as shown in equation 5 [1, 14].

$$K_i = \frac{c_{i,\infty}}{c_{i+1,\infty}} \quad (5)$$

$c_{i,\infty}$ is the equilibrium concentration of the substance in packaging layer i and $c_{i+1,\infty}$ is the equilibrium concentration in the subsequent packaging layer, or the foodstuff, if the innermost packaging layer is concerned.

The mass transfer coefficient h for all boundaries is set to an arbitrary high value between 1 and 100 m/s for all simulations, which corresponds to situations where the overall flux is not limited by mass transfer resistance at the boundary [15]. The mass transfer coefficients are calculated depending on temperature by a simple Arrhenius equation (equation 6).

$$h = A * \exp(\frac{E_a}{R*T}) \quad (6)$$

The Arrhenius parameters were chosen arbitrarily to yield a mass transfer coefficient in the range mentioned before, which increases with increasing temperature. R in equation 6 is the ideal gas constant.

For the outer boundaries of the model, a no-flux condition is used (equation 7), except when evaporation of substance to the surroundings is included in the simulation. In that case, a flux boundary condition is applied to the left outer boundary. The equation for this boundary condition is similar to equation 4, except that it is assumed that the evaporated substance diffuses away from the packaging rapidly, yielding a concentration in the surroundings of effectively zero. This leads to the slightly modified boundary condition shown in equation 8.

$$D * \frac{\partial c}{\partial x} = 0 \quad (7)$$

$$D * \frac{\partial c}{\partial x} = h * c_i \quad (8)$$

The mass transfer coefficient for the evaporation is also calculated by the Arrhenius dependence shown in equation 6.

3.4 Adsorption Layers

For simulations including an adsorption layer, a reaction term, according to equation 9, is added to the respective TDS Interface.

$$\frac{\partial c_{ads}}{\partial t} = h_{ads} * (c_i - K_{ads} * c_{ads}) \quad (9)$$

The parameter h_{ads} is the rate of adsorption, c_i is the concentration of freely diffusing substance in the adsorption layer and c_{ads} is the adsorbed concentration. The parameter K_{ads} is a partition coefficient between the free and adsorbed concentrations in the adsorption layer, defined equivalently to equation 5.

An Arrhenius equation (equation 6) was used for the temperature dependence of the parameters h_{ads} and K_{ads}. Adsorption can be assumed to decrease with increasing temperature [13]. The Arrhenius parameters are therefore chosen to yield an increased rate of adsorption and an increased partition coefficient of adsorption with increasing temperature, leading to an overall decrease in the concentration of adsorbed substance in the adsorption layer with increasing temperature.

4. Results and discussion

4.1 Arbitrary Number of Intervals

Figure 1 shows time-dependent concentration profiles in a five-layer packaging. The names of the packaging materials used in the simulation are also shown in Figure 1

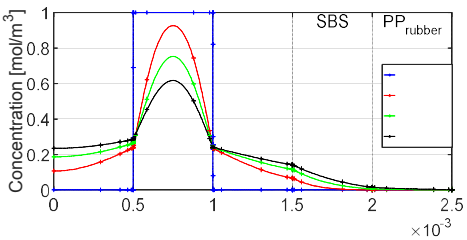

Figure 1: Concentration profiles in a five-layer packaging

As can be seen from Figure 1, the concentration increases over time in the intervals where the initial concentration was zero and decreases over time in the interval where the initial concentration was greater than zero.

To validate the model, a simulation was carried out with uniform initial concentrations in all packaging layers and partition coefficients of the interior boundaries set to a value of one. The amount of migrated substance of this simulation was then compared to the amount of migrated substance of a simulation which was carried out with a one-layer model of the same overall-thickness. The results (not shown) were practically the same for both simulations.

4.2 Arbitrary Number of Species

Figure 2 shows the amount of migrated substance in the food as a function of its molar mass and time.

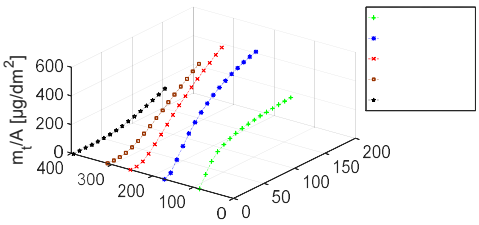

Figure 2: Amount of migrated substance as a function of molar mass and time

As can be seen from Figure 2, it takes longer for substances of higher molecular weight to migrate to the food, as their diffusion coefficients are lower (compare equation 3). For substances of low molecular weight, an equilibrium amount of migration is reached within the simulated time.

A similar approach as described in the previous subsection was used for validation. Two simulations were carried out, one where an initial concentration of 1 mol/m^3 of one substance was applied. For the other simulation, two equal substances with an initial concentration of 0.5 mol/m^3 each were used. The results (not shown) were practically the same for both simulations.

4.3 Evaporation and Adsorption Layers

Figure 3 shows concentration profiles for a simulation which included evaporation of substance to the surroundings.

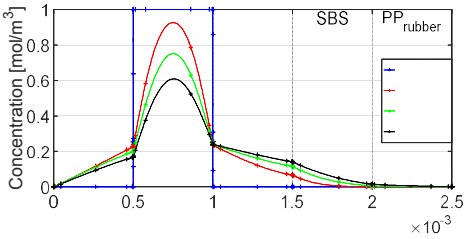

Figure 3: Concentration profiles of a simulation including evaporation

As can be seen from Figure 3, there is an almost linear concentration gradient in the outer packaging layer, as substance is continuously removed from the outer boundary

Figure 4 shows the amount of adsorbed and free substances in an adsorption layer as a function of time. The packaging consisted of three layers, with the adsorption layer as the innermost.

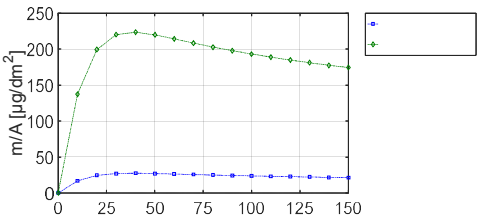

Figure 4: Amount of adsorbed and free substance in an adsorption layer

The amount of adsorbed substance increases at the beginning of the simulation, as more and more substance has migrated up to the adsorption layer. For later times, there is a decline in the adsorbed amount, as the free substance continues to migrate further into the foodstuff. The ratio between the adsorbed and free amounts is constant for all times unequal zero, corresponding to the partition coefficient of the adsorption.

4.4 Non-isothermal Simulations

Figure 5 shows the amount of migrated substance as a function of time for a non-isothermal simulation. The respective temperature values are also depicted in Figure 5.

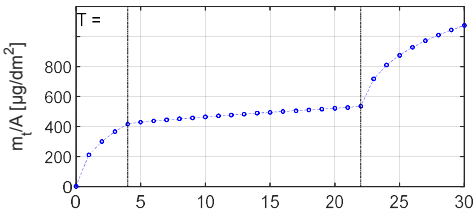

Figure 5: Amount of migration as a function of time and temperature

As can be seen from Figure 5, the amount of migrated substance increases during the first temperature-interval. During the second temperature interval, there is only a slight increase in the amount of migrated substance, due to the low temperature in this interval, which leads to a lower diffusion coefficient. As the temperature is increased by 50 K for the third temperature-interval, the amount of migrated substance increases drastically.

5. Conclusion

Our model is able to simulate packaging situations with an arbitrary numbers of packaging layers and contaminating substances. Evaporation of substances to the surroundings and adsorption layers can optionally be included in the simulations. Non-isothermal simulations are also possible, corresponding to changes in temperature during storage. The results obtained so far are feasible concerning the underlying physical laws (e.g. increasing amount of migration for increasing diffusion coefficients or increasing temperature).

Further work will include estimation of parameters by comparison with experimental results, which will enable the simulation of "real-life" food packaging situations. Modeling of diffusion in porous networks, like paper packaging, will also be included in further work, as diffusion in those systems can only in some cases be adequately described by Fick'ian diffusion [18].

6. References

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11. Appendix

Abbreviations:

MOAH	Mineral oil aromatic hydrocarbons
MOSH	Mineral oil saturated hydrocarbons
ODE	Ordinary differential equation
TDS	Transport of diluted species

Symbols:

A	Arrhenius preexponential factor	[-],[m*s^{-1}],[s^{-1}]; depending on application
A_p	Empirical polymer-specific value	[-]
c	Concentration	[mol*m^{-3}]
D	Diffusion coefficient	[m^2*s^{-1}]
E_a	Arrhenius activation Energy	[J*mol^{-1}]
F	Flux	[mol*m^{-2}*s^{-1}]
h	Mass transfer coefficient	[m*s^{-1}]
h_{ads}	Rate of Adsorption	[s^{-1}]
K	Partition coefficient	[-]
M	Molar mass	[Da]
R	Ideal gas constant	[J *mol^{-1}*K^{-1}]
T	Absolute temperature	[K]
τ	Empirical polymer-specific value	[K]
x	Axis direction of migration	[m]