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ORIGINAL PAPER

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Modelling of simultaneous two-sided migration into water and olive oil from nylon food packaging

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Abstract Nylon 6 and nylon 12 food packaging materials used as sausage casings are typically exposed to fatty food on one side and boiling water on the other during the cooking process. To simulate the migration behaviour under these conditions, a special migration cell was constructed and filled with olive oil on one side of the polymer and water on the other to find out what amounts of the migrants will transfer to either side and phase at 100 °C. Results show that when a nylon 6 film is exposed to the conditions as described above, total mass transfer of the monomer—caprolactam—into the water phase occurs after 2 h at 100 °C. Nylon 12 sausage casings release similar amounts of their monomer—laurolactam—into both the aqueous and oil phase. An existing computer migration model was adapted to simulate the situation of simultaneous two-sided migration applying previously determined diffusion and partitioning coefficients. The suitability of the model was confirmed by experimental data.

Keywords Nylon · Caprolactam · Laurolactam · Migration · Food packaging · Diffusion · Partitioning · Modelling

Introduction

Nylon 6 (polyamide 6, polycaprolactam) and nylon 12 (polyamide 12, polylaurolactam) are the most frequently used polyamides for food packaging applications. Their monomers caprolactam (Ref No. 14200, CAS No. 0105-60-2) and laurolactam (Ref No. 19490, CAS No. 00947-04-6) are listed in section A of directive 2002/72/EC [1] with specific migration limits (SML) of 15 mg kg^{-1} and 5 mg kg^{-1}, respectively (2.5 mg dm^{-2} and 0.833 mg dm^{-2} considering that 1 kg of food is packaged in 6 dm^2 of film according to the EU cube model). Figure 1 shows the chemical structures of caprolactam and laurolactam.

Typical applications of nylon 6 and nylon 12 films are sausage and cooked-meat casings. Such meat products usually contain 20–40% fat. During the process of cooking meat or sausages, the nylon film will be exposed to hot water or steam on the outside as well as the fatty food on the inside. In order to show compliance with EU legislation, specific migration into water and olive oil, the official fatty food simulant, has to be evaluated. Typical migration testing conditions are 2 h at 100 °C. While previous research has always focussed on the migration of monomers into either water or fatty food simulants [2, 3, 4, 5, 6], during practical applications, the film will be exposed to hot water and fatty food simultaneously. The idea behind our investigations was therefore to find a way to simultaneously test specific migration into two totally different food simulants at either side of a food packaging material. We have furthermore tried to simulate this situation by computer modelling and draw conclusions about the partitioning of nylon monomers in the multi-phase system: fatty phase–polymer–water.

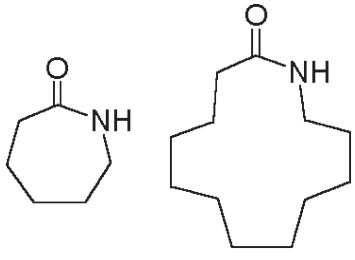

Fig. 1 Structures of nylon 6 and nylon 12 monomers (caprolactam *left* and laurolactam *right*)

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Theory of two-sided diffusion

The basic principles of modelling migration from a polymer into foods have been described in detail in literature [7, 8]. In short, C_P the concentration of a migrant in a food contact polymer at time t at a distance x from the origin of the x-axis is described by Fick's second law of diffusion [9]. D_P is the diffusion coefficient and $K_{P,F}$ is the partitioning coefficient (between polymer and food) in this system. A few assumptions have to be made in order to use this model:

1. There is no chemical interaction between food and polymer
2. The migrant initially is homogeneously distributed in the polymer
3. Both phases (water phase on one side and oil phase on the other side of the polymer) are initially migrant-free
4. No mass-transfer limitation in the foods, so the migrant is always homogeneously distributed in the respective phases

In a previous paper [6] these assumptions have been translated into formulas. In the case of two-sided migration, the transport phenomena from the polymer into the oil phase can be described as:

$$K_{P,O}\left(\frac{V_O}{A}\right)\frac{\partial C_O}{\partial t} = -D_P\frac{\partial C_P}{\partial x}\,\text{at}\,x = 0 \quad t > 0 \tag{1}$$

where $K_{P,O}$ is the coefficient describing the partitioning of the migrant between the polymer and the oil, C_O is the concentration of the migrant in the oil, V_O is the volume of oil, A is the contact area. Diffusion from the polymer into the water phase can similarly be described as:

$$K_{P,W}\left(\frac{V_W}{A}\right)\frac{\partial C_W}{\partial t} = D_P\frac{\partial C_P}{\partial x}\,\text{at}\,x = L_P \quad t > 0 \tag{2}$$

where $K_{P,W}$ is the coefficient describing the partitioning of the migrant between the polymer and the water, C_W is the concentration of the migrant in the water, V_W is the volume of water and L_P is the thickness of the polymer. Figure 2a illustrates the situation described above.

In addition, a new coefficient is introduced describing the partitioning between the oil and water phases, both phases being separated by a polymer film layer.

$$K_{W,O} = \frac{K_{P,O}}{K_{P,W}} \tag{3}$$

This partitioning coefficient gives information about the affinity of a certain migrant for the water or oil phase. Values of $K_{W,O} > 1$ indicate a higher affinity of the migrant for water or an aqueous phase, values $K_{W,O} < 1$ indicate a higher affinity for oil or fatty foods. Information given by this partitioning coefficient is especially interesting for the development of a new migration modelling tool that is currently taking place in the EU funded project "Foodmigrosure" (http://www.foodmigrosure.com).

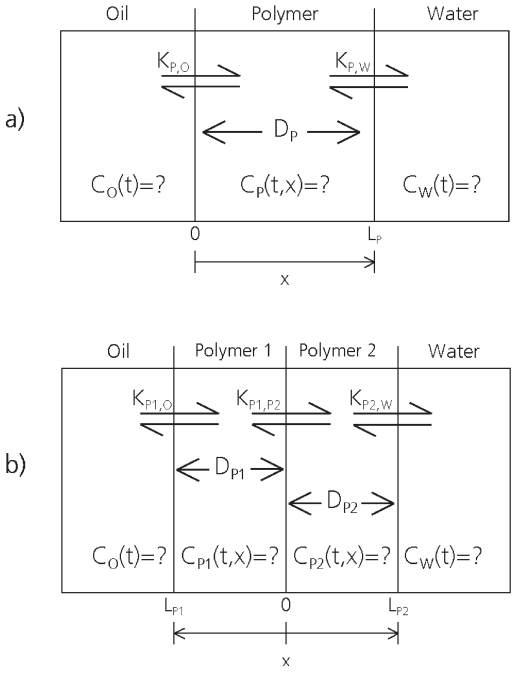

Fig. 2 Schematic diagram of two-sided diffusion into oil and water from monofilm (**a**), multilayer film (**b**)

Since one multilayer film (next to three monolayers) was used in this study, the model described above had to be extended such that this kind of film could be described properly. First of all, it had to be considered that different diffusion coefficients (D_{P1} and D_{P2}) apply in the two layers. Furthermore, it had to be assumed that partitioning processes take place between the two layers: a partitioning coefficient $K_{P1,P2}$ describes the partitioning of a migrant between the two polymers. This, and the coefficients describing the partitioning between the polymers and food simulants are illustrated in Fig. 2b.

Experimental

Sample materials

Four different nylon films were used. Two of them were commercial sausage casing, the other two materials originated from an EU project for the development of a reference material for specific migration testing [10]. A short description of the materials used can be found in Table 1.

Reagents and apparatus

All reagents and solvents were of analytical quality unless stated otherwise: water was HPLC grade from Fluka, Bucks, Switzerland. Virgin olive oil was from Minerva, Voghera, Italy. The glass migration cells were purchased from Gassner Glastechnik GmbH, Munich, Germany. All details concerning the analysis of laurolactam in water

Table 1 Thickness of films A, B, C and D as well as their $C_{P,0}$ considering one-sided migration testing [6, 10]

Film	Film thickness (μm)		Migration potential (mg dm^{-2})	
	Nylon 6	Nylon 12	Caprolactam	Laurolactam
A[a]	-	39	-	1.0
B[a]	19	29	0.4	0.8
C	-	196	-	4.7
D	107	-	2.2	-

[a] Commercial sausage casings

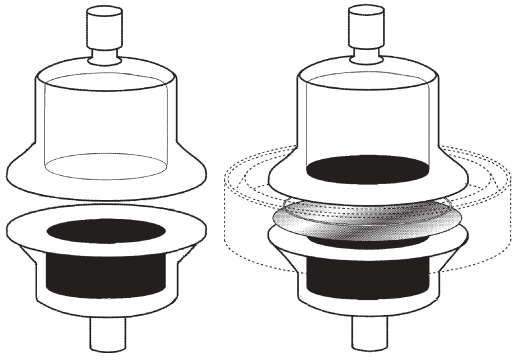

Fig. 3 Migration cell used in this study

and olive oil have been described earlier [6, 11]. In short: aqueous samples containing laurolactam were directly analysed by LC-MS. Olive oil samples containing laurolactam were first cleaned-up by size exclusion chromatography (SEC) and then analysed by LC/MS. For water samples containing caprolactam, the same method as for laurolactam was applied. For the analysis of caprolactam in olive oil, the method of Franz and Rijk [12] was used: olive oil containing known amounts of caprolactam and olive oil samples used during migration experiments were first diluted with heptane, then extracted with a mixture of ethanol and water. Instead of analysing by GC/FID, the aqueous phase was injected into the LC/MS system.

Two-sided migration into olive oil and water

Migration tests were carried out according to the principles of European Standard EN1186-1 [13]. But instead of exposing the films to a food simulant on one side only, both sides of the cells were filled with food simulants. For this, two upper parts of glass migration cells were combined to one as can be observed in Fig. 3.

Prior to the incubation period, migration cells, water and olive oil were preheated to the testing temperature (100 °C). The lower part of the migration cell was completely filled with water (approximately 85 ml, the exact weight was recorded). The film with a diameter of 7 cm having an area of 0.385 dm^2 was then placed in the cell, the upper part was assembled and the cell was closed. Next, a thin layer (approximately 8.5 ml, the exact weight was recorded) of olive oil was filled into the upper part of the cell. The cell was then incubated at 100 °C for 2 h. All experiments described were carried out in triplicate. After the incubation period, two 1-ml water aliquots were filled into autosampler vials, two olive oil aliquots per replicate were prepared to determine levels of caprolactam and/or laurolactam as described in the section above.

Migration modelling

Numerical integration of Fick's second law was performed using the software Athena Visual Workbench (http://www.athenavisual.com). The initial and boundary conditions applied here have been described in detail earlier [6]. Values for diffusion as well as partitioning coefficients (D_P and $K_{P,F}$) originated from the EU project "Specific Migration" [6, 10]. For the multilayer film system as described in the theory section, a numerical model written in Microsoft Excel was used. In this model, the polymer-layers were discretised as a grid model, which was integrated in time using Fick's second law and the Eqs. (1) and (2) by Euler's method.

Results

The method for two-sided migration testing as described in the experimental section worked quite well and was very reproducible. Coefficients of variations between three replicates were typically around 5%. All results reported below are means of three replicate migration tests.

Laurolactam migration from films A and C into water and olive oil

The results from the two-sided migration experiments using monolayered films A and C are presented in Fig. 4a and Fig. 4c and show that similar amounts of laurolactam have migrated into the two phases. In both cases, a mean of 0.3 mg migrated into the water phase, and 0.2 mg migrated into the oil phase. From film A (39 μm), almost total mass transfer took place. Film C (196 μm) contained 1.8 mg meaning that 26% of the laurolactam migrated.

The diffusion coefficient D_P and the partitioning coefficient $K_{P,F}$ values determined in previous studies [6, 10] were used to model the two-sided migration from nylon 12 (Table 2). The slightly higher migration on the water side observed could not be simulated by our model, as only one constant D_P for the complete film was applied. Figure 5a and Fig. 5b show concentration profiles in the polymer at different times between t 0=0 and t 6=2 h. It becomes visible that the application of the two-sided model with two liquids having the same partitioning coefficients gives, as is to be expected, the same profiles as full immersion testing in one food or solvent. Furthermore, the graphs obtained using the coefficients from the previous study do correspond to the experimental data quite well. Almost total mass transfer can be observed in

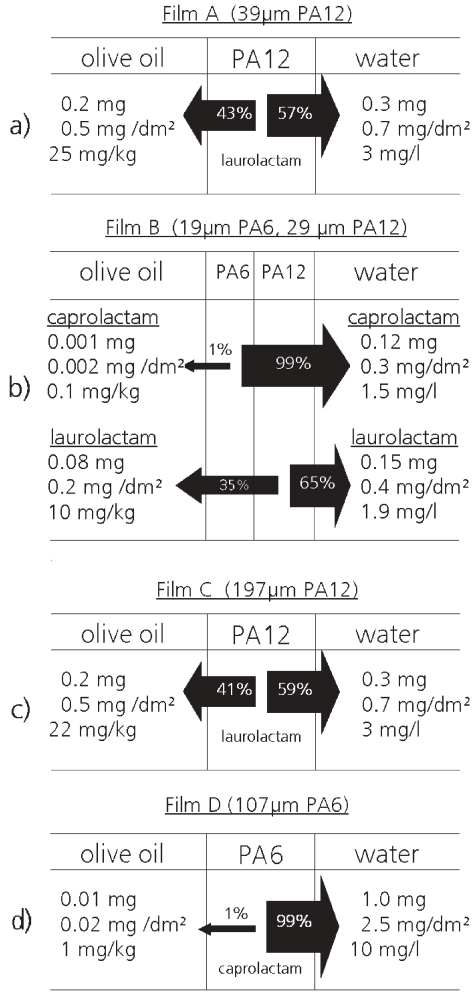

Fig. 4a–d Observed migration of monomers from films A, B, C and D (all 2 h at 100°C)

Table 2 Diffusion and partitioning coefficients applied for migration modelling [6, 10]

Film	Coefficients applied		
	DP (cm2/s)	KP,O	KP,W
A	5 E-10	1	1
B (caprolactam)	5 E-10	1000	1
B (laurolactam)	5 E-10	1	1
C	5 E-10	1	1
D	3 E-08	100	1
D (one-sided)	5 E-10	100	-

the concentration profile for film A looking at t6 (2 h) whereas only a minor fraction of the laurolactam migrated out of the thicker film C at t6. When regarding the concentration in the liquids during the testing period, the effect of the different volumes applied becomes obvious. The same amounts of laurolactam migrated into either direction, but different volumes of food simulants were present, thus the concentration in the olive oil was calculated to be higher. This also matches the experimental observations. A practical consequence of these findings is that if a high solubility of a migrant in a food simulant is given, lower volumes of food simulant can be or even should be applied to increase the sensitivity of the migration test without affecting the masses migrating.

Describing the results in a partitioning coefficient between oil and water phase as suggested in the theory section, for nylon 12 the coefficient is $K_{W,O}$ =1, based upon the assumed other K-values.

Caprolactam migration from film D into water and olive oil

The results from the two-sided migration experiment using film D show that 99% of the caprolactam migrated into the water phase (see Fig. 4d). The total migration of 1 mg from film D into the water means that nearly quantitative mass transfer of caprolactam from the film took place under the testing conditions applied here. Since nylon 6 has a much more hydrophilic character than nylon 12, in contact with water—especially boiling water—the water rapidly penetrates the polymer and swelling occurs. Therefore, the diffusion process takes place at a much higher rate due to the increased D_P in the swollen matrix. The D_P for this matrix was determined in a separate experiment (details not shown). It was found to be two orders of magnitude higher than in the dry polymer. We used the partitioning coefficient between the polymer and water $K_{P,W}$ =1 as given by Baner [14] and a value of $K_{P,O}$=100 was assumed for the partition between polymer and oil. Looking at the outcome of the model using these coefficients, (Fig. 5c) the assumption seems to be correct. Describing the results in a partitioning coefficient between oil and water phase as suggested in the theory section, for nylon 12 the coefficient is $K_{W,O}$=100. Interestingly, the model shows that the caprolactam concentration in the oil initially would rise up to a value of about 13 mg kg^{-1} before decreasing to a value of 1 mg kg^{-1} after 2 h. This means that the caprolactam initially having migrated into the oil would permeate back through the swollen film into the water phase. In order to compare this situation of contact on both sides with one-sided contact, we have modelled the situation that the film has a one-sided contact with oil and no swelling occurs (D_P taken from [10], see Table 2 for details). As Fig. 5 shows, the migration itself would be slower than during two-sided migration due to the usage of a lower D_P. The concentration of caprolactam in oil would reach the 9 mg kg^{-1} after 2 h, meaning that the migration into olive oil measured by one-sided testing would be considerably higher than the respective migration determined by two-sided testing.

Caprolactam and laurolactam migration from film B into water and olive oil

Fig. 4b shows the results from the two-sided migration experiment using multilayered film B. As becomes visi-

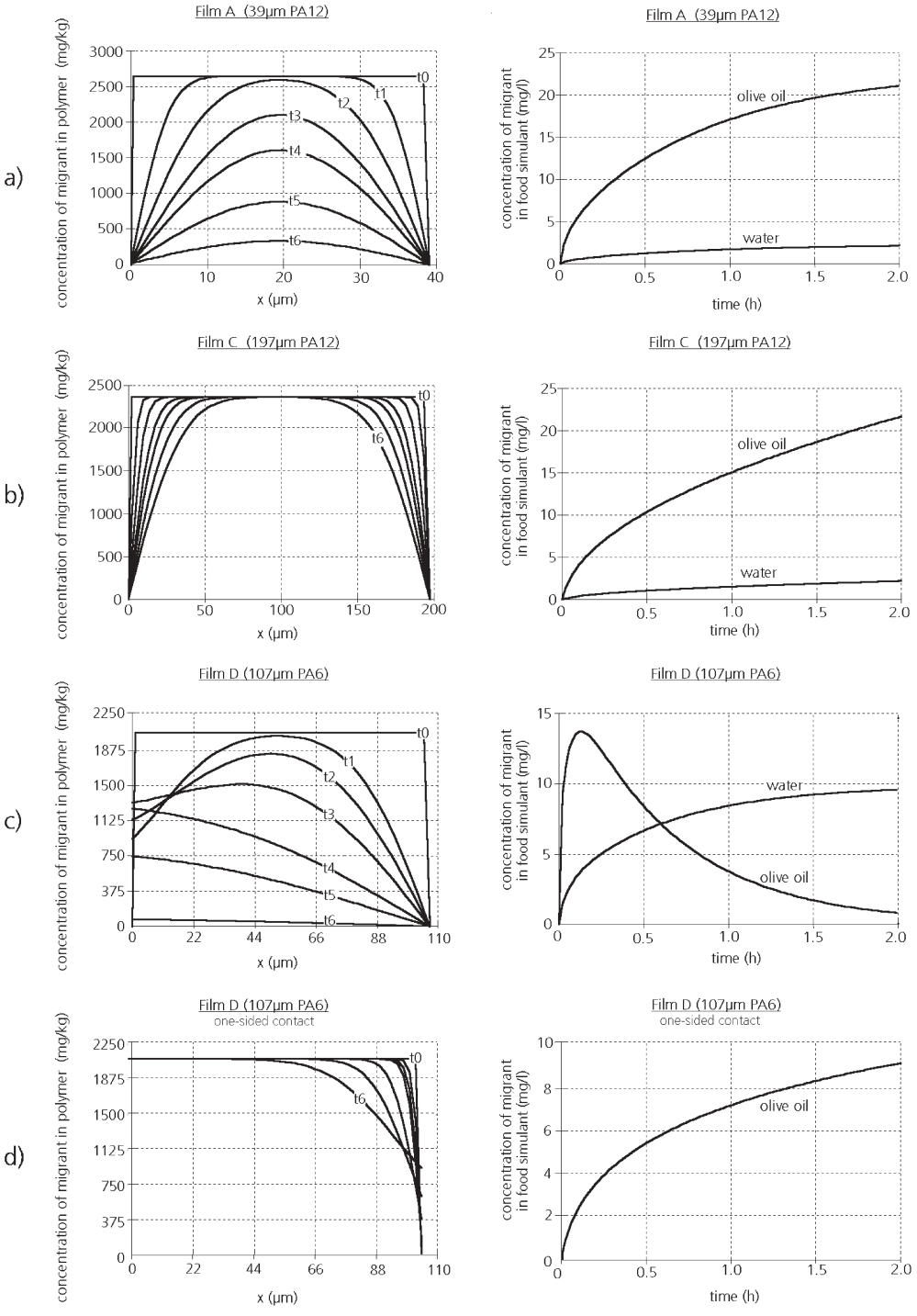

Fig. 5a–d Modelled migration of monomer from films A, C and D (diffusion and partitioning coefficients given in Table 2; t0=0 h, t6=2 h)

ble, roughly two thirds of the laurolactam migrated into the water phase, one third migrated through the nylon 6 layer into the oil phase, confirming once again that laurolactam has similar affinities for water and olive oil. Due to its hydrophilic character 99% of caprolactam migrated through the nylon 12 layer into the water phase, while only 1% could be found in the oil phase. As for the modelling of this multilayer-system, no swelling was assumed since the hydrophilic nylon 6 layer was not in direct contact with water. It was also assumed that both monomers caprolactam and laurolactam have similar affinities for both polymers, translating into partitioning coefficients $K_{P1,P2}$=1 (Table 2.) Figure 6 shows the outcome. Figure 6a describes the diffusion of caprolactam from the nylon 6 layer into the nylon 12 layer and into the two food simulants. Figure 6b shows the respective migration of laurolactam from the nylon 12 layer (t6=1 h for illustration purposes). The phenomenon of caprolactam first migrating into the oil and then permeating back through the polymer into the water can be observed here

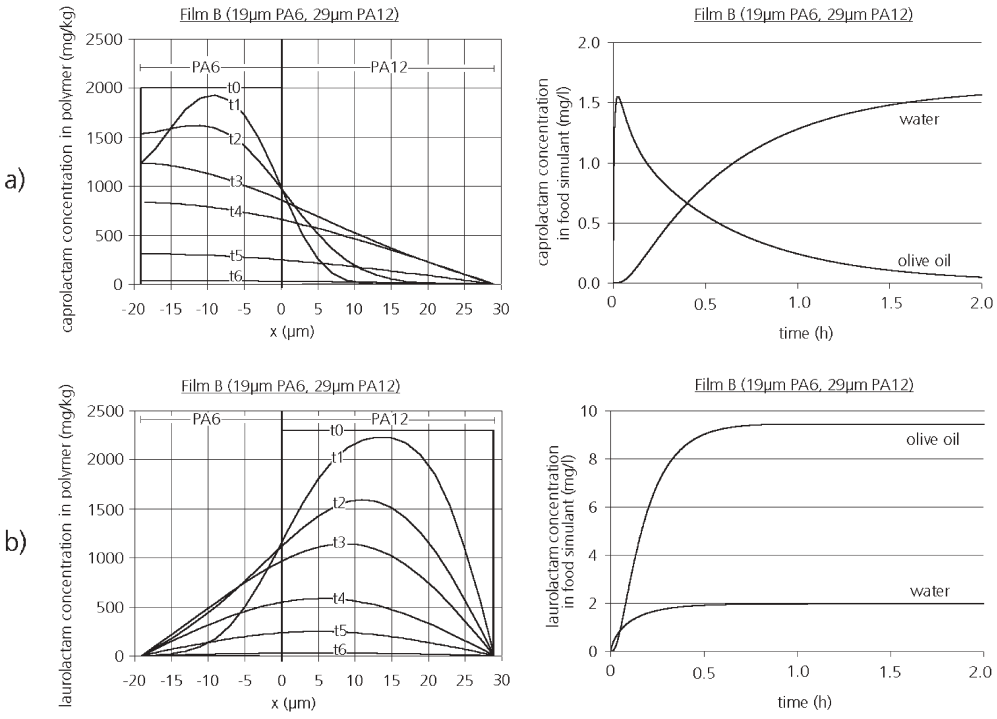

Fig. 6 Modelled migration of monomers from film B (diffusion and partitioning coefficients given in Table 2; **a** t0=0 h, t6=2 h, **b** t6=1 h). (a) caprolactam, (b) laurolactam

as it could with film D. Also, it can be seen that the coefficients applied here seem to be in the right order of magnitude since the results of the model match the experimental observations quite well.

Discussion

It was shown that the approach of simultaneous two-sided migration testing is technically feasible and can generally provide information about the fate of migrants from a polymer film in between two different foods, food simulants or other liquids. The partitioning coefficient $K_{W,O}$ introduced here is a convenient tool that can instantly give information about the fate of migrants (in equilibrium) being subjected to such a two-sided system.

The results on two-sided migration from nylon 12 films here confirm the outcome from a previous study where specific migration of the same films had been investigated by full immersion testing [6]. The migration of laurolactam into water and oil—tested individually—had been similar, and in a range of ±20% compared to results found here. This confirms our recent suggestion [6] to consider water as an appropriate olive oil substitute for nylon 12 specific migration testing.

Even though the respective results are similar, there is an evident difference in laurolactam migration into water (mean 0.7 mg dm^{-2}) and oil (mean 0.5 mg dm^{-2}) phases. It is very unlikely that the lower migration into the oil phase is the result of limited solubility in oil. $K_{P,O}$ would have to be in the range of several hundred to see this kind of effect, but it was determined in olive oil at 80 °C as $K_{P,O}$ =34±20 [6]. Hence, a slightly higher diffusion coefficient on the water side caused by penetration of water into the polymer can be assumed. A short experiment was performed to test this assumption. During 48 h contact time with water at 100 °C, it was shown that the mass of film C increased by 0.5%, while that of a film that had been in contact with olive oil decreased by 0.3%. These data suggest that water penetrates nylon 12 and likely causes higher diffusion.

Migration of caprolactam from film D into water was 1 mg, which means that almost total mass transfer of the monomer from the film took place after 2 h at 100 °C. This is even though the film is significantly thicker than sausage casings usually are (the model film used here is more than 100 µm thick as opposed to the normal 30–50 µm for commercial products). This is in itself nothing new [2]. It has, however, been shown here that if a nylon 6 film is simultaneously exposed to water and olive oil on either side, still all of the caprolactam will migrate to the water side. As for the modelling applied for nylon 6 films, we want to emphasize that applying a constant D_P does not describe the process taking place in the film correctly. The diffusion coefficient increases two orders of magnitude during the migration process along with change from dry to the swollen wet polymer. However, this swelling process takes place very quickly. Therefore, using a high D_P from the beginning will approximate reality using this model as much as possible. The outcome of our model suggests that the migration testing time is of very high importance. When comparing the concentrations of caprolactam in olive oil in Fig. 5c and Fig. 5d, it becomes obvious that one-sided migration testing gives an overestimation compared to two-sided migration. A kinetic study in a two-sided system would be necessary to validate the outcome given in Fig. 5c.

It has furthermore been shown that migration modelling in a multi-layer system is possible when using assumptions as described in the theory section. It would be interesting to extend the investigations in this paper to a system where a multilayer film consists of at least two totally different polymers. In that case, the effect of partitioning between the two polymer layers could become more obvious A comment about the situation in real life seems appropriate: As sausages as well as bacon and meat have a water content of 20–50%, mass transport and partitioning processes between water and oil phase are taking place also in the food itself. Furthermore, sausage casings usually have a maximum thickness of 50 μm, and we have measured monomer concentrations in the range of a maximum of 3,000 mg kg^{-1}. This means that in a worst-case situation, total mass transfer from the film expressed in amounts per area would be roughly 1.5 mg dm^{-2}. This itself would exceed the SML of laurolactam being 0.83 mg dm^{-2}, but not the one of caprolactam at 2.5 mg dm^{-2}. But considering directive 85/572/EEC [15] giving products in category 06.04—processed meat products (ham, salami, bacon and others)—a reduction factor of X/4 is applicable, which means that the result of the migration tests X can be divided by 4. Assuming the above, this means that the corrected maximum migration after full mass transfer of the films would be 0.4 mg dm^{-2}, well below the SML values for caprolactam and laurolactam. This means that if the thickness of a nylon 6 or nylon 12 sausage casing is less than 50 μm, and the concentration of the monomer is less than 3,000 mg kg^{-1}, then no migration testing is necessary, because the SML of caprolactam or laurolactam cannot be reached.

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