Migration measurement and modelling from poly(ethylene terephthalate) (PET) into softdrinks and fruit juices in comparison with food simulants

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Introduction

Poly(ethylene terephthalate) (PET) bottles are widely used for beverages. Knowledge about the migration of organic compounds from the PET bottle wall into contact media is of interest especially when post-consumer recyclates are introduced into new PET bottles. Using migration theory, the migration of a compound can be calculated if the concentration in the bottle wall is known. On the other hand, for any given specific migration limits or maximum target concentration for organic chemical compounds in the bottled foodstuff, the maximum allowable concentrations in the polymer $C_{P,0}$ can be calculated. Since a food simulant cannot exactly simulate the real migration into the foodstuff or beverages, a worse case simulation behaviour is the intention. However, if the migration calculation should not be too over-estimative, the polymer specific kinetic parameter for migration modelling, the so-called A_P value, should be established appropriately.
The objective of the study was the kinetic determination of the specific migration behaviour of low molecular weight compounds (toluene, chlorobenzene, phenyl cyclohexane) with relatively high diffusion rates and therefore with high migration potential from the PET bottle wall into food simulants in comparison with real beverages. From the experimental migration kinetic curves, the diffusion coefficients for the applied model compounds were determined.

Results

The model compounds toluene, chlorobenzene, phenyl cyclohexane, benzophenone and methyl stearate were spiked into the test bottles at three concentration levels. This was achieved by introducing the model compounds on the PET pellet level before preform manufacture. In this way a homogeneous distribution of the model compounds in the bottle wall was ensured. Application of different contamination levels allows an extrapolation of the experimental migration data to other concentration levels, due to the fact that migration of a compound into a contact media is directly linked to the concentration of the compound in the bottle wall. For the migration kinetics, the test bottles (300 ml, 280 cm^2 inner surface) were filled with beverages and juices as well as food simulants. The specific migration of the model compounds toluene, chlorobenzene and phenyl cyclohexane into the food simulants as well as the investigated beverages and juices were determined by purge and trap gas chromatography. The results of the migration kinetic for toluene are given in Figure 1. For chlorobenzene similar results were found. The migration of benzophenone and methyl stearate was below the experimental detection limit. Phenyl cyclohexane shows only for 50% ethanol and 95% ethanol measurable values. From the experimental data the diffusion coefficients of the model compounds were calculated. As a result 10% ethanol does not cover beverages like ACE juice and disqualifies for being a generally suitable food simulant for beverages, soft drinks and juices. For the beverages and the food simulant 10% ethanol a linear behaviour of the concentration versus the square root of migration time was found. On the other hand, 95% ethanol as well as 50% ethanol show an increasing diffusion behaviour with increasing storage time. This can be explained such that ethanol penetrates into the PET surface quicker than the migrants diffuse in the food direction.

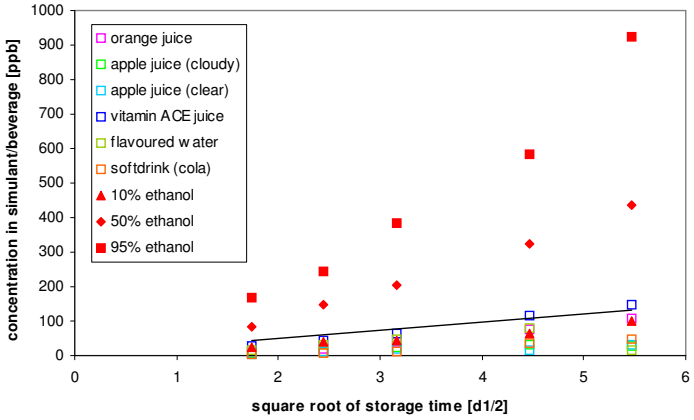

Figure 1: Migration kinetics of toluene from spiked PET bottle (298 ppm) into food simulants, soft drinks and juices at 40 °C

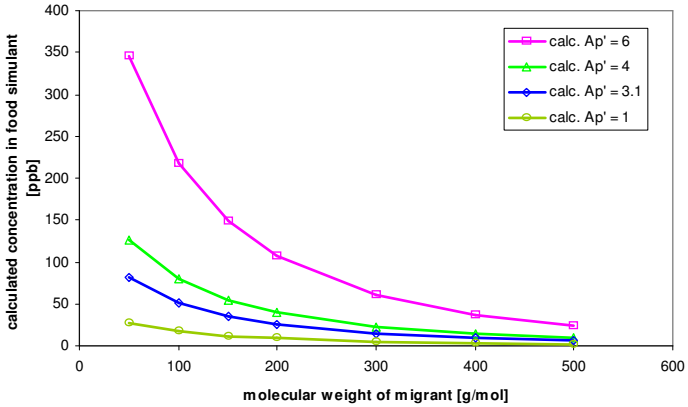

Figure 2: Calculated migration versus experimental data for 10 d at 40 °C at a bottle wall concentration ($C_{P,0}$) of 100 ppm for the "EU cube" (600 cm^2, 1000 ml) and A_P' = 6 (currently generally recognized modelling parameter), A_P' = 4, A_P' = 3.1 and A_P' = 1 (K = 1, τ = 1577 K)

Conclusions

The currently recognized modelling parameter for PET (A_P' = 6) was found to be too conservative. An A_P' value of 1 was derived from the experimental migration data for non-swelling food simulants like 3% acetic acid, 10% ethanol or *iso*-octane. For more swelling condition e.g. 95% ethanol as food simulant an A_P' value of 3.1 seems to be suitable for migration calculation.
In relation to PET recycling safety aspects, maximum concentrations in the bottle wall corresponding to a migration limit of 10 ppb were established for migrants / contaminants with different molecular weights. From the experimental data obtained using food simulants and in comparison with beverages, the most appropriate food simulant for PET packed foods with a sufficient but not too over-estimative worse case character was found to be 50% ethanol. In addition, it can be shown that mass transport from PET is generally controlled by the very low diffusion in the polymer and, as a consequence, partitioning coefficients ($K_{P/F}$ values) of migrants between the polymer material and the foodstuff do not influence the migration levels significantly. An important consequence is that migration levels from PET food contact materials are largely independent from the nature of the packed food which on the other hand simplifies exposure estimations from PET.

Reference

R. Franz, F. Welle, Migration measurement and modelling from poly (ethylene terephthalate) (PET) into softdrinks and fruit juices in comparison with food simulants, *Food Additives and Contaminants*, **2008**, *25(8)*, 1033-1046.

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