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Diffusion coefficient of antimony catalysts in polyethylene terephthalate (PET) materials

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Introduction

Antimony trioxide is extensively used by the polymer industry as a polycondensation catalyst in the production of PET. Consequently, contamination of food by antimony from PET packaging has raised concerns about consumer safety. Unfortunately the lack of data on diffusion characteristics of antimony compounds used in the production of PET makes the simulation of migration and the assessment of the risk difficult. A method to assess the migration from PET trays for heating of ready meals into food simulant (3% acetic acid) over a wide temperature range (45 to 150°C) is presented.

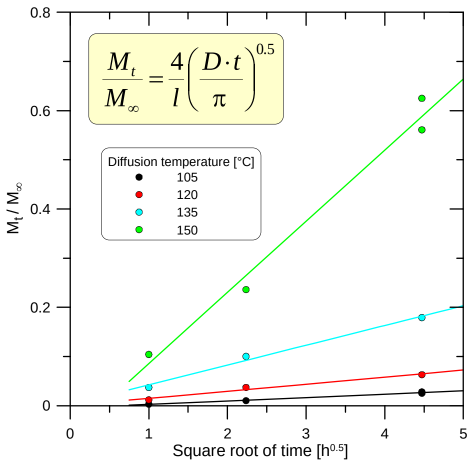
Experimental

Migration: Slabs with the dimension of 0.04 x 6 x 3 cm were cut out from CPET commercial trays and immersed in 90 ml 3 % acetic acid in quartz vessels with a Teflon lid. The vessels were placed in the reactor chamber of a microwave autoclave for high-pressure (UltraClave III). The release of antimony was measured after 1, 5, and 20 h at pressures and temperatures up to 100 bar and 150 °C. Aliquots of the acetic acid solution were diluted by factors of 10 to 100 with 2.5 % nitric acid.
Mineralization of PET: For the determination of total antimony in PET 20 - 40 mg were weighed into PFA-tubes and mineralized in 2ml 65 % nitric acid and 0.2 ml hydrofluoric acid for 2 h at 220 °C in the same microwave autoclave as stated above.
Measurement of Antimony: A sector-field ICP-MS was operated in the low resolution mode (m/Δm = 300) to measure antimony at m/z = 121 in acetic acid solutions and mineralized PET solutions. Energy dispersive XRF was used as a reference method for the measurement of antimony in PET. The PET sample was grounded (< 0.5 mm) under liquid nitrogen conditions and pressed to pellets. Pellets of finely dispersed antimony trioxide in a "Sb-free" PET were used as calibrants.
Modeling: Simulation of migration was carried out with the program SML v. 4.36 of AKTS AG.

Results

The total antimony concentration in the PET under study measured by ICP-MS and XRF was 357 ± 8 mg/kg and 326 ± 6 mg/kg, respectively, which represents an excellent agreement. Long-time experiments (> 40 h) at 150 °C revealed that the fraction antimony available for migration (**M_∞**) was about 60% of the initial concentration. The actual amounts of antimony in the food simulant (**M_t**) were measured at three different times (**t**) in the temperature range from 45 °C to 150 °C. A linear relationship between **M_t/M_∞** and **$t^{0.5}$** was obtained for temperatures above 90 °C (Figure 1), which confirms the hypothesis of a diffusion following the Fick's law .

Figure 1. M_t/M_∞ versus $t^{0.5}$ for Sb migrating from PET to 3 % acetic acid.



The temperature dependence of the apparent diffusion coefficient was analyzed by an Arrhenius plot (Figure 2). In the low temperature domain deviation from linearity was observed, particularly for the short-time (1 h, 5 h) experiments. The results suggest a migration with two kinetic steps:

- a rapid release of the Sb present on the CPET surface
- followed by a Fickian diffusion .

For the long-time experiment (20 h) different temperature dependences of the apparent diffusivity are observed above and below the glass transition temperature of PET (Figure 2), but linearity may be assumed over the whole temperature range.

The average diffusion coefficients (D) for Sb migration from PET to 3% acetic acid at different temperatures (20 h experiments) are listed in the adjoining table. The resulting regression line was:

Ln(D) = (32.6 ± 1.3) - (22246 ± 468)* 1/T [K]

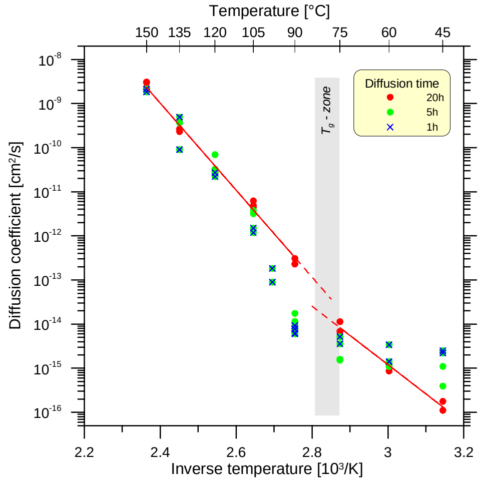
Thereof the pre-exponential factor (D_0) and the activation energy (E_a) for diffusion were derived:

D_0 = 1.38 x 10^{14} cm²/s

E_a = 184.9 kJ/mol

Temperature [°C]	D [cm²/s]
45	1.4 x 10^{-16}
60	1.0 x 10^{-15}
75	9.1 x 10^{-15}
90	2.7 x 10^{-13}
105	4.7 x 10^{-12}
120	3.0 x 10^{-11}
135	2.5 x 10^{-10}
150	3.0 x 10^{-09}

Figure 2. Arrhenius plots for the apparent diffusion coefficient of antimony migrating from PET to 3 % acetic acid. The glass transition (T_g) temperature is indicated as grey shaded zone.

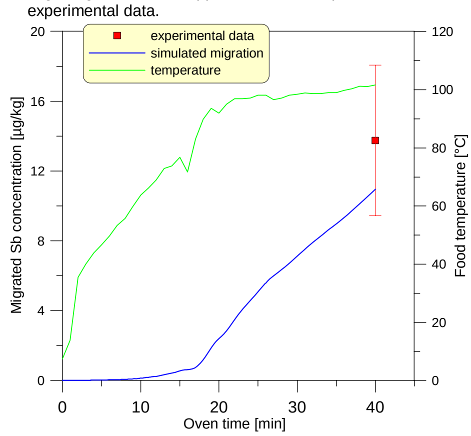


Application of the Arrhenius parameters

The experimentally obtained data were used in a simulation of non-isothermal migration of antimony from PET into a retail apple cake product (see photo).

The apple cake was baked in an oven at a nominal temperature setting of 180 °C. Temperature and migration profiles are shown in Figure 3. The simulated Sb concentration profile falls in the one σ -range of the experimentally verified (ICP-MS) end-point concentration.

Figure 3. Simulated concentration profile of antimony migrating from PET to apple-cake and comparison with experimental data.



Concluding remarks

The chemical form of the migrating antimony is unknown, e.g. antimony glycolate, antimony trioxide or antimony acetate, nevertheless diffusion according to Fick's law has been observed. In the discussion above the actual situation is reduced to a simple migrant system with a defined thickness and a homogeneously distributed antimony concentration, i.e. the initial conditions are fulfilling the assumptions for the equation in Figure 2.

Long-term migration from PET bottles

For comparison the antimony migration from bottled for mineral water or soft drinks into 3 % acetic acid was observed over a long time at 40 °C. Initially, a very fast rate of Sb release into food simulant was always observed. As in the case of the PET tray this may be attributed to a surface effect. Afterwards, the bottles can be subdivided into two categories, which exhibit distinctly different migration kinetics (Fickian or non Fickian).

Figure 4. Concentration profiles of Sb migrating from PET bottles to 3 % acetic acid