Migration of antimony from poly(ethylene terephthalate) bottles into beverages

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Introduction

Plastics bottles made from polyethylene terephthalate (PET) are increasingly used for beverages like softdrinks, mineral water, juices and beer. In comparison to other packaging plastics, PET is one of the most inert polymers with good barrier properties against moisture, oxygen and carbon dioxide and with a very low migration tendency of its constituents. However, migration of substances from PET bottles into beverages is not completely negligible. For example, antimony trioxide (Sb_2O_3) is widely used as polycondensation catalyst for manufacturing of polyethylene terephthalate because it offers a high catalytic activity and has a low tendency to catalyse side reactions. Within the last decade, several studies on the migration of antimony from PET bottles into beverages and on exposure levels in mineral water, softdrinks and juices have been published. For prediction of such exposure levels, the diffusion coefficients of antimony in PET at different temperatures are helpful.

The objective of this study[1] was to determine experimentally the diffusion characteristics, i.e. activation energy and diffusion coefficients of antimony in PET beverage bottle materials. For this purpose it was also necessary to measure and compile the typical concentration range of antimony present in PET beverage bottles on the European market. Based on the results, the migration of antimony into beverages should be predicted by mathematical modelling for different surface/volume ratios and antimony bottle wall concentrations.

Materials and Methods

Altogether 67 PET bottle and preform samples were collected from European preform and PET bottle manufacturers. Information about the virgin material supplier, the recyclate manufacturer and the recyclate content as well as the use of oxygen or acetaldehyde scavengers was provided by the manufacturers in all cases. 200 mg of the PET bottle wall or perform material was treated with 8 ml conc. nitric acid for 15 min at 200 °C in a microwave-assisted digestion (similar to EN 13656). Subsequently the concentration of antimony was determined quantitatively by ICP-MS according to DIN EN ISO 17294-2. Calibration was achieved by external calibration with antimony standards.

For the determination of the antimony specific migration into 3% acetic acid a commercially available 1.5 l PET softdrink bottle was used. The bottle was supplied from the bottle manufacturer directly after blowing. The antimony bottle wall concentration was determined to 260 ppm by ICP-MS (see above). The thickness of the bottle wall was determined to 0.27 mm. The crystallinity of the investigated bottle was determined by differential scanning calorimetry (DSC) to 43%. The bottle was cut into 5.0x5.0 cm pieces. The 5.0x5.0 cm pieces are further cut into 1.0x5.0 cm stripes. Five stripes of 1.0x5.0 cm (surface area 51.62 cm²) were given into a steel cell. Glass pellets of 3 mm diameter were added in order to reduce the death volume of the steel cell. The steel cell was placed into a Büchi Speed Extractor E-916. The steel cells were filled with 3% acetic acid at a pressure of 100 bar and were heated up to temperatures between 30 °C and 150 °C. After the heating time, the migration solution was purged into a glass vial. Subsequently the steel cell was filled and heated again with 3% acetic acid. Due to the fact, that the volume of the 3% acetic acid solution after the Büchi Speed Extractor was not exactly the same, all migration solutions were filled to exactly 40.0 ml in a volumetric flask before analysing.

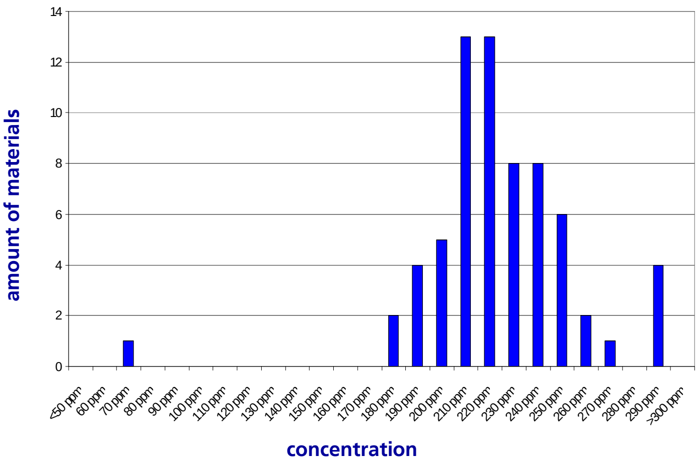

Figure 1: Antimony concentrations indifferent PET beverage bottles and preforms from the European market (n = 67)

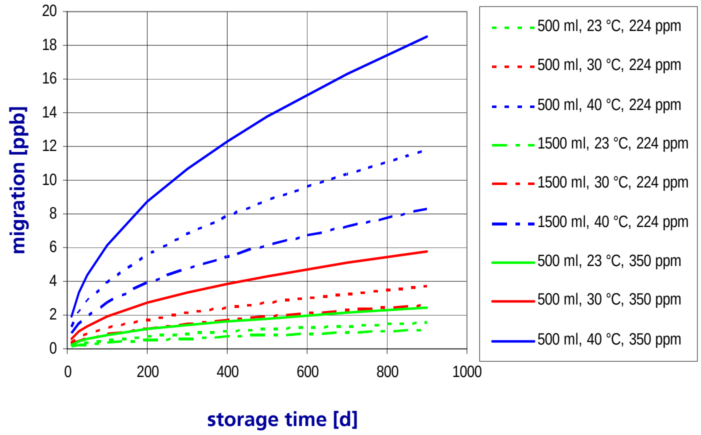

Figure 2: Calculated migration from the PET bottle into beverages as a function of the storage time and storage temperature (bottle wall concentration $c_{P,0}$ = 224 ppm and 350 ppm, activation energy E_A = 184 kJ mol^{-1}, D_0 = 1 10^{14}, K = 1, internal bottle wall surface 420 cm² (500 ml bottle) and 880 cm² (1500 ml bottle), wall thickness d = 300 µm)

Results and Discussion

Figure 1 shows the antimony concentrations in PET bottles from the European market. A mean value of 224 ±32 ppm was found, the median was 220 ppm. Diffusion coefficients for antimony in PET bottle materials were experimentally determined at different temperature between 105 °C and 150 °C. From these data the activation energy of diffusion for antimony species from the PET bottle wall into beverages and food simulants was calculated. The obtained value 189 kJ mol^{-1} was found to be in good agreement with published data on PET microwave trays[2] (184 kJ mol^{-1}). Based on these results the migration of antimony into beverages was predicted by mathematical migration modelling for different surface/volume ratios and antimony bottle wall concentrations (Figure 2). The results were compared to literature data as well as international legal limits and guidelines values for drinking water as well as migration limit set from food packaging legislation. From the calculations within this study, it was shown that antimony levels in beverages due to migration from PET bottles can never reach nor exceed the European specific migration limit of 40 ppb. Maximum migration levels caused by room temperature storage even after 3 years will never be essentially higher than 2.5 ppb and will be in any case below the European limit of 5 ppb for drinking water. In addition, the exposure of the consumer by antimony migration from PET bottles into beverages and even into edible oils reaches only about 1% of the current TDI established by WHO. An important conclusion from this study is that compliance testing for antimony from PET bottles for beverages is superfluous. Migration modelling considerations can fully replace this cost and time expensive undertaking.

References

[1] F. Welle, R. Franz, Migration of antimony from PET bottles into beverages: Determination of the activation energy of diffusion and migration modelling compared to literature data, Food Additives and Contaminants, **2011**, *28(1)*, 115-126.

[2] A. Alt, M. Haldimann, V. Dudler, Diffusion coefficient of antimony catalysts in polyethylene terephthalate (PET) materials, Poster Presentation, 4th International Symposium on Food Packaging, 19.-21. November **2008**, Praque, Czech Republic.

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