Comparison of migration testing conditions for PET bottles – 10 d / 60 °C and 10 d / 40 °C versus a real application

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Introduction

PET bottles are typically used for mineral water, soft drinks, juices and beer. PET materials in contact with food must comply with the general safety requirements of European Framework Regulation (EC) 1935/2004 and, more specifically, with the requirements given in the European Plastics Regulation (EU) 10/2011. This regulation lays down detailed rules for the conditions applied in migration tests. One of the major changes compared to previous regulations was that the time and temperature conditions for accelerated specific migration tests simulating long-term applications should now be calculated using the Arrhenius equation based on a conservative assumption for the underlying activation energy. For real contact times exceeding 30 d at room temperature, the specimen should be subjected to an accelerated test at an elevated temperature for a maximum of 10 d at 60 °C. According to EU 10/2011 these conditions are derived from the default activation energy of 80 kJ/mol, and should cover long-term storage for more than 6 months at or below room temperature. However, for PET it is well known that the activation energy is strongly dependent on the molecular size of the migrating substances. The conditions for an accelerated migration test corresponding to migration at the end of shelf life therefore depend on the molecular size, which is not represented for all kind of migrants by a default activation energy of diffusion of 80 kJ/mol.

The aim of this study was to compare the legally regulated conditions for accelerated migration tests into food simulants with migration into real food at the end of shelf life. Migration tests were carried out under different time and temperature conditions and using different food simulants.

Method

1.5 l PET bottles were provided by a commercial PET bottle manufacturer. The PET material contained the acetaldehyde scavenger 2-amino-benzamide and was partially made of post-consumer recyclate. Migration contact experiments were carried out according to the European Standard EN 1186 part 3 (aqueous simulants by total immersion) and part 14 (substitute tests). The specific migration of selected migrants was determined in the following food simulants: 3% acetic acid, 10%, 20%, 50% and 95% ethanol and isooctane. These simulants were tested for 10 d at 60 °C, which are the test conditions used to represent a storage time of 365 d at room temperature according to Regulation (EU) 10/2011. The simulants were also tested for 10 d at 40 °C, which are the corresponding test conditions according to previous regulations.
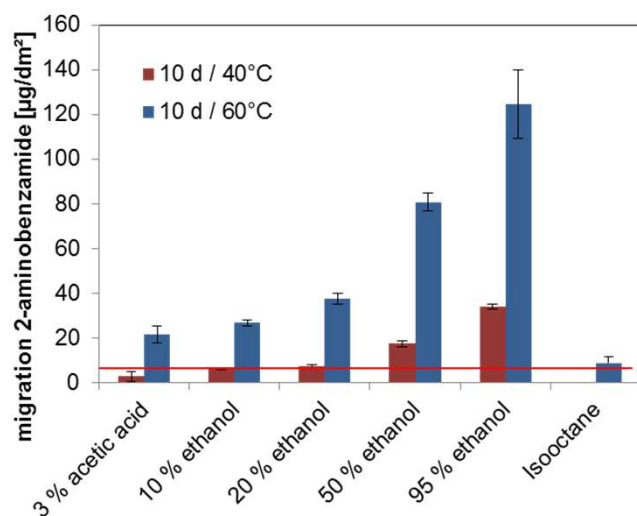

Figure 1: Specific migration of 2-aminobenzamide into different food simulants at the test conditions 10 d @ 40 °C and 10 d @ 60 °C versus calculated migration after a storage of 365 d @ 23 °C (red line)
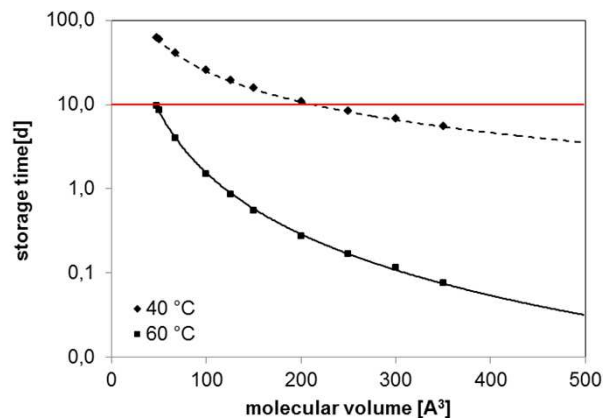

Figure 2: Storage time at 40 °C and 60 °C corresponding to the predicted migration after 365 d @ 23 °C as a function of the molecular volume. Red line shows the effect at 10 d.

Results

Terephthalic acid, isophthalic acid, mono- and diethylene glycol were not detectable in any of the investigated migration solutions at a detection limit of 26 µg/dm² and 200 µg/dm², respectively. Antimony was measured in the 3% acetic acid migration solutions. When tested for 10 d at 40 °C, antimony migration was not detectable at a limit of 0.1 µg/dm². When tested for 10 d at 60 °C, the observed migration was 0.23±0.06 µg/dm². The migration of 2-aminobenzamide was investigated in all simulants (Figure 1). As expected, migration after 10 d at 60 °C was significantly higher than after 10 d at 40 °C. Furthermore, an increase in migration was observed with the increasing ethanol content of the food simulant. This can be explained by the known swelling effect of ethanolic solutions on PET. The migration of 2-aminobenzamide was further calculated by mathematical migration modelling for a real application storage time of 365 d at 23 °C. The diffusion coefficients at 23 °C (4.2 10^{-16} cm²/s) and 40 °C (4.2 10^{-16} cm²/s) are given in the literature [1]. Calculated migration at 23 °C (365 d) was 6.6 µg/dm² and for 10 d at 40 °C 3.4 µg/dm². Both values are in good agreement with the experimental results for 40 °C into non-swelling simulants 3% acetic acid, 10% ethanol and isooctane.

Conclusions

In general, the test conditions of 10 d at 60 °C overestimates in most cases real migration at the end of shelf life (Figure 2). This is because the underlying default activation energy of diffusion in PET of 80 kJ/mol is only applicable to very small substances with a molecular volume of ~50 Å³ (e.g. acetaldehyde). For larger molecules with higher activation energies of diffusion, there is a corresponding significant reduction in the required testing time at 60 °C, equivalent to storage for 365 d at 23 °C. Test conditions 10 d at 40 °C can under- or overestimate real migration, depending on the migrant. To test the specific migration for long-term applications, migrant- and polymer-specific diffusion parameters such as diffusion coefficients or activation energies of diffusion should be considered when designing accelerated migration tests.

References

[1] R. Franz, M. Gmeiner, A. Gruner, D. Kemmer, F. Welle. Diffusion behaviour of the acetaldehyde scavenger 2-aminobenzamide in polyethylene terephthalate for beverage bottles. Food Additives and Contaminants 2016, 33(2), 364-372.

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