Migration testing of PET bottles

Are 10 d at 60°C suitable contact conditions?

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 [1]. 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. Due to higher activation energies of typical migrants in PET, it is expected that the migration after 10 d at 60°C significantly over-estimates the real migration at the end of the shelf life. In addition, ethanolic food simulants swell the PET polymer and additionally increase the migration.

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

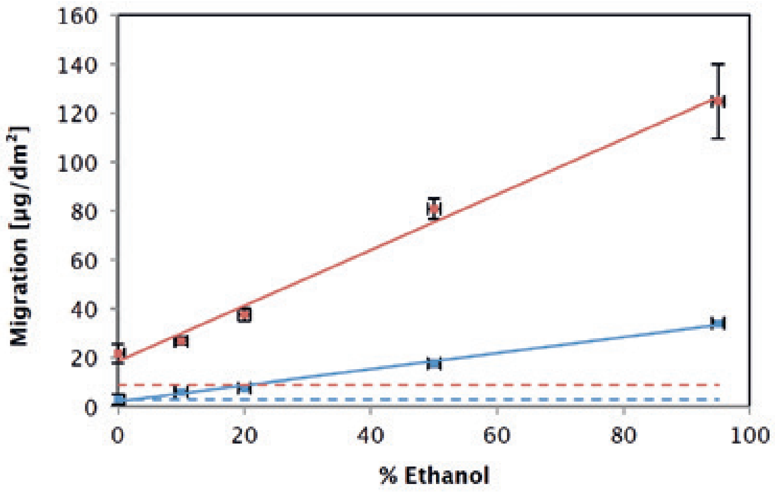
Method

1.5 L PET bottles were provided by a commercial PET bottle manufacturer. The PET material contained the acetaldehyde scavenger 2-aminobenzamide 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.

Results

Terephthalic acid, isophthalic acid, mono- and diethylene glycol were not detectable in any of the investigated migration solutions (40°C and 60°C) at detection limits 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. These migrants are far below the specific migration limits when tested for 10 d at 60 °C [2] due to their low concentrations in PET as well as due to their low diffusion.

On the other hand, the acetaldehyde scavenger 2-aminobenzamide is applied to PET in relatively high concentrations. Therefore a measurable concentration is expected in the food simulants. This makes 2-aminobenzamide to a perfect model substance for the systematic evaluation of the migration into different food simulants. (Figure 1). As



Quelle: IVV

Figure 1: Specific migration of 2-aminobenzamide into ethanolic food simulants at the test conditions 10 d at 40°C and 60°C (red: 10 d at 60°C, blue: 10 d at 40°C, dashed line: migration value without swelling)

expected, migration after 10 d at 60°C was significantly higher than after 10 d at 40°C. Furthermore, a (nearly) linear increase in migration was observed with the increasing ethanol content of the food simulant. The dashed lines given in Figure 1 are the migration into 3% acetic acid (2.9 µg/dm^2 (17.4 µg/L) at 40°C) as well as into isooctane (8.9 µg/dm^2 (53.4 µg/L) at 60°C). Both simulants did not swell PET under the given migration conditions. It is interesting to note, that the specific migration limit of 2-aminobenzamide of 50 µg/L is exceeded for 10 d at 60°C under non-swelling conditions, whereas the migration at 40°C is in compliance with EU Regulation 10/2011.

The linear increase of the migration of 2-aminobenzamide can be explained by the known swelling effect of ethanolic solutions on PET. Based on the experimental data, the swelling of PET can be quantified for the first time. At 40°C the food simulant 50% ethanol and 95% ethanol increases the migration of 2-aminobenzamide by factors of 5.0 and 10.6, respectively. At 60°C the migration is 8.1 and 13.0 times higher compared to non-swelling migration conditions. The experimental results are in perfect compliance with predicted migration values by use of diffusion models [3, 4].

Conclusions

In general, the test conditions of 10 d at 60°C overestimate in most cases real migration at the end of shelf life [4]. This is because the underlying default activation energy of diffusion in PET of 80 kJ/mol is only applicable to very small substances like acetaldehyde [1]. 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. The specific migration of 2-aminobenzamide at typical concentration levels in PET (approx. 350 mg/kg) are exceeded if 10 d at 60°C and non-swelling migration conditions are applied. High ethanolic food simulants increase the migration of 2-aminobenzamide significantly and the PET bottles are not in compliance with the specific migration limit of 2-aminobenazamide. In contrast, under realistic storage conditions at room temperature up to the end of shelf life, the specific migration limit is not exceeded [4]. This indicates that storage conditions for 10 d at 60°C (all simulants) as well as 10 d at 40 °C (high ethanolic food simulants) are unsuitable storage conditions for simulating the end of shelf life of PET bottles.

As a solution approach, the specific migration testing conditions for long-term applications should be estimated by use of migrant- and polymer-specific diffusion parameters such as diffusion coefficients or activation energies of diffusion when designing accelerated migration tests. Non-swelling food simulants or diffusion modeling should be applied whenever possible. ■

Literature

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Information

Abstract

The present European safety regulations for accelerated migration tests of PET bottles neglect the molecular weight of the migrants, being a crucial parameter for activation energy. Correspondingly, the present migration tests showed an over-estimation for most real migration substances such as antimony. Migrations of terephthalic acid, isophthalic acid, mono- and diethylene glycol were even below the detection limit because of their low diffusion. For the highly abundant 2-aminobenzamide in PET, a linear migration increase was found with increasing ethanol concentration. To estimate accelerated migration tests in a more realistic dimension, migrant- and polymer-specific diffusion parameters are proposed being included to the general safety regulations.