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Migration of Bisphenol A from Can Coatings into Beverages at the End of Shelf Life Compared to Regulated Test Conditions

Carina Stärker and Frank Welle *

Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Straße 35, 85354 Freising, Germany; carina.staerker@ivv.fraunhofer.de

* Correspondence: welle@ivv.fraunhofer.de

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Abstract: Beverage cans are used for energy drinks, soft-drinks, sparkling waters, and beer. Bisphenol A is still part of the formulation of epoxy coatings of beverage cans. Due to concerns that bisphenol A acts as an endocrine-active substance, the migration of bisphenol A is restricted. Typically, the migration from beverage cans is tested at elevated temperatures into food simulants, like 20% ethanol in water. However, comparison tests of the migration of bisphenol A at the end of shelf life, with the migration into ethanolic food simulants, are not available in the scientific literature. The aim of the study was to determine the migration of the migration of bisphenol A into real beverages, compared to routine migration tests into the European official food simulant of 20% ethanol at 40 °C and 60 °C after storage for 10 days. As a result, bisphenol A-containing coatings show a considerably higher migration when tested at 60 °C in comparison to 40 °C. On the other hand, migration into energy drinks and coke, from the same coatings at the end of shelf life when stored at room temperature, was below the detection limit in either case. As expected, migration values of bisphenol A below the analytical detection limits were observed for any test conditions from the coating labeled bisphenol A-free. Spiking tests show that bisphenol A is stable in real beverages. Therefore, it can be concluded that the accelerated migration tests with 20% ethanol at the test conditions 10 d at 40 °C and 10 d at 60 °C significantly overestimate the real migration into beverages at the end of shelf life. This overestimation of the migration of bisphenol A is due to swelling of the epoxy can coating by the ethanolic food simulant. These findings were supported by migration modeling based on diffusion coefficients predicted for polyethylene terephthalate.

Keywords: beverage cans; epoxy coatings; bisphenol A; migration testing; food simulants

1. Introduction

The global demand for beverage cans grew around 4% in 2018, and reached about 350 billion units, mostly due to the increase of beverage packaging. The market is driven by an increased consumption soft-drinks and beer in developing countries (China, in the Middle East, and India). Globally, >90% of beverage cans are made out of aluminum, and the rest are made from steel. Bisphenol A is still part of the formulation of epoxy coatings of beverages cans and, therefore, bisphenol A might migrate from packaging materials into food. A review with concentrations of bisphenol A in food and consumer exposure is available in the scientific literature [1]. Due to concern that bisphenol A acts as an endocrine-active substance, the migration of bisphenol A is restricted. The migration of constituents from beverage can coatings are typically tested by the use of ethanolic food simulants. Simulants like 20% ethanol in water are used, in general, to exclude interferences of beverage components with substances migrating from the coating, which might result in masking some of the migrants, which

poses a risk for false negative results of migration testing. Ethanolic simulants are good matrixes for gas chromatographic analysis of migrated organic substances. In addition, good solubility of organic migrants increases the sensitivity of the migration test or gives the test a worse- or worst-case character compared to the migration into real aqueous beverages. On the other hand, it is known that ethanolic solutions show strong interactions between polyester materials like epoxy can coatings. These interactions result in a swelling of the polyester matrix which significantly increases the extent of migration, especially if the migration test is performed at elevated temperature [2]. This increased migration is part of the safety concept, that ethanolic solutions act as worst-case simulants compared to real beverages, which results in a safety factor. On the other hand, contact migration testing conditions that are too overestimative might pose the risk that the specific migration limits for migrants like bisphenol A are exceeded, which results in the non-compliance of the simulant-tested beverage cans.

Bisphenol A has been in focus of toxicologists and the European legal bodies during the last decades, and some countries forbade use of bisphenol A in food packaging. In Europe, until September 2018, the use of bisphenol A as a monomer in the production of plastic materials and articles in contact with food, except infant feeding bottles, was authorized with a specific migration limit (SML) of 600 µg/kg food, according to Regulation (EU) No 10/2011 [3]. As a reaction to new toxicological data [1], and considering the fact that non-dietary sources of bisphenol A also contribute to the overall exposure, the SML was reduced to 50 µg/kg food for plastic materials in 2018 [4]. This limit is applicable from 6 September 2018, and also applies to varnishes and coatings intended to come into contact with food. France even went further and prohibited any food packaging intended to come into direct contact with food containing bisphenol A [5]. In order to assure compliance with the migration limit, migration tests using food simulants shall be carried out, or, as an alternative, the migration can be calculated based on the residual content of the substance in the material applying generally recognized diffusion models based on scientific evidence that are constructed, such as to overestimate real migration [3].

To our knowledge, comparison tests of real-life storage at the end of shelf life with simulant test using ethanolic food simulants at elevated temperatures (e.g., 10 days (d) at 40 °C or 10 d at 60 °C) are not available in the scientific literature. It is therefore not known which maximum shelf life of the real beverage is covered by the migration test into ethanolic solutions performed at 40 °C or 60 °C.

The aim of the study was to determine the migration of the migration of bisphenol A into real beverages, compared to routine migration tests into the European official food simulant of 20% ethanol at 40 °C and 60 °C after storage for 10 d.

2. Material and Methods

2.1. Sample Material

Cans with inside epoxy coatings were provided by a commercial supplier. Each can type was provided in an empty, unused state, as well as filled with energy drink or coke. The filled cans had already reached the corresponding end of shelf life. Two of the coatings contain bisphenol A (BPA), one is a BPA-free coating. The investigated samples are given in Table 1.

Table 1. Sample material used for the study.

Sample No	Description
1a	empty cans, BPA-based epoxy coating, filling volume 250 mL
1b	cans filled with energy drink, BPA-based epoxy coating, filling volume 250 mL
2a	empty cans, BPA-based epoxy coating, filling volume 250 mL
2b	cans filled with energy drink, BPA-based epoxy coating, filling volume 250 mL
3a	empty cans, BPA-free epoxy coating, filling volume 330 mL
3b	cans filled with coke, BPA-free epoxy coating, filling volume 330 mL

2.2. Migration Contact Experiments

Migration contact experiments were carried out according to the European Standard EN 13130-1 [6]. The cans were filled corresponding to the nominal volume with 20% ethanol in water (*v*/*v*), which is the food simulant allocated to clear drinks, such as energy drinks or coke, according to the European Plastics Regulation (EU) No 10/2011. The filled cans were stored for 10 d at 40 °C or 60 °C in a temperature-controlled cabinet. Aliquots of each migration solution were then spiked with a defined amount of the internal standard $^{13}C_{12}$-bisphenol A prior to analysis. Each migration contact was performed in triplicate.

2.3. Preparation of Food Samples

One hundred milliliters of the energy drinks/coke were weighed into a beaker, spiked with a defined amount of the internal standard $^{13}C_{12}$-bisphenol A, and degassed for 5 min in an ultrasonic bath in order to avoid experimental interference with the carbonization. Subsequently, the samples were purified and concentrated by solid phase extraction (Chromabond HR-P). The resulting eluates were evaporated to dryness in a stream of nitrogen, redissolved in a mixture of acetonitrile/water in a ratio of 1:1, and filtrated prior to analysis. A triplicate determination was performed for each sample.

2.4. Extraction of Samples for the Determination of the Residual Content of BPA

From the empty cans, test specimens with a contact surface of 0.5 dm^2 were cut out, spiked with a defined amount of the internal standard $^{13}C_{12}$-bisphenol A, and extracted with acetonitrile using a Büchi® speed extractor (temperature: 100 °C; pressure: 100 bar; number of cycles: 3; duration of static phase: 3 min). Aliquots of the extracts were diluted with ultrapure water (<0.055 µS/cm) in a ratio of 1:1, and filtrated prior to analysis. A triplicate determination was performed for each sample.

2.5. Quantification of Bisphenol A

The quantitative determination of bisphenol A in the prepared samples was achieved by HPLC using mass spectrometric detection (Thermo TSQ Quantum Ultra AM). The chromatographic separation was carried out on a Thermo Accucore Polar Premium (2.6 µm, 100 × 2.1 mm at 40 °C) column. Mass spectrometric detection was performed after negative heated electro spray ionization (HESI) on a Thermo TSQ Quantum Ultra AM triple quadrupole mass spectrometer using multiple reaction monitoring (MRM) mode. The samples were measured both against external standard solutions and against the internal sample preparation standard $^{13}C_{12}$-bisphenol A.

2.6. Recovery Experiments

In order to determine whether bisphenol A might react with the energy drinks/coke during storage in the coated cans, recovery experiments were carried out. Degassed drink samples (20 mL) were spiked with different concentrations of bisphenol A (58.95, 234.2, and 1171 µg/L) and the recovery was determined according to the method described in Section 2.5.

2.7. Migration Modeling

Migration was modeled using AKTS SML software v4.54 (AKTS AG Siders, Siders, Switzerland) [7]. The diffusion coefficients were calculated based on the activation energy of diffusion of the corresponding migrants [8]. For the calculation, a thickness of the inner coating of 10 µm was used. As a worst case, good solubility of bisphenol A in the beverages was assumed for all predicted values which represents a partition coefficient between polymer and food of K = 1.

3. Results and Discussion

Within this study, the migration of bisphenol A into the food simulant 20% ethanol was determined at the test conditions 10 d at 40 °C and 60 °C, respectively, in comparison to the real migration into

energy and coke drinks after storage until the corresponding end of shelf life. The results of the migration tests are summarized in Table 2. In addition, the concentration of free bisphenol A in the can coatings was determined. From the concentrations in the can coatings and from the dimensions of the cans, the maximum total transfer into the filling good was calculated (Table 3). The applied migration test conditions, 10 d at 60 °C, are the test conditions used to represent a storage time of 365 d at room temperature (end of shelf life) according to Regulation (EU) 10/2011. The test conditions 10 d at 40 °C are the corresponding test conditions according to previous regulations.

Table 2. Results of the migration of bisphenol A into the food simulant 20% ethanol and into energy drinks.

Sample	Storage Conditions	Migration [µg/L]
1a	10 d at 60 °C	9.40 ± 1.40
2a	10 d at 60 °C	4.84 ± 0.84
3a	10 d at 60 °C	<0.99
1a	10 d at 40 °C	0.76 ± 0.22
2a	10 d at 40 °C	0.60 ± 0.07
3a	10 d at 40 °C	<0.99
1b	end of shelf life, energy drink	<0.14
2b	end of shelf life, energy drink	<0.14
3b	end of shelf life, coke	<0.14

Table 3. Migration potential of bisphenol A in the can coatings and calculated total transfer to the filling good.

Sample	Migration Potential (µg/dm^2)	Calculated Total Transfer [µg/L]
1	1.00	10.2
2	0.52	5.3
3	<0.16	<1.4

Three different cans from commercial suppliers were tested. One supplier provided cans with bisphenol A-free coatings, as well as conventional bisphenol A coatings. The other two suppliers provided cans with bisphenol A coatings. As a result, migration values of bisphenol A below the analytical detection limits were observed for all test conditions from the coating labeled bisphenol A-free. For the bisphenol A containing coatings, however, the migration was considerably higher when tested at 60 °C in comparison to 40 °C. On the other hand, migration into the energy drinks and coke from the same coatings, at the end of shelf life when stored at room temperature, was below the detection limit in either case.

In order to exclude that bisphenol A might have reacted with the drinks during storage in the coated cans, the drinks were spiked with different concentrations of bisphenol A, and the recovery was determined. Recovery was in the range of 99–112% for all three drinks. This result indicates that bisphenol A is stable in energy drinks and coke, and that the non-detectable migration from epoxy coated cans were correct and not due to a loss of bisphenol A during the migration test. Thus, it can be concluded that the accelerated migration tests with 20% ethanol at the test conditions 10 d at 40 °C and 10 d at 60 °C overestimate the real migration into food at the end of shelf life. The shelf life at room temperature for the energy drinks and coke was 365 d and 180 d, respectively. The test at 60 °C even led to concentrations in the drinks that are close to a total transfer of bisphenol A from the coating (Figure 1).

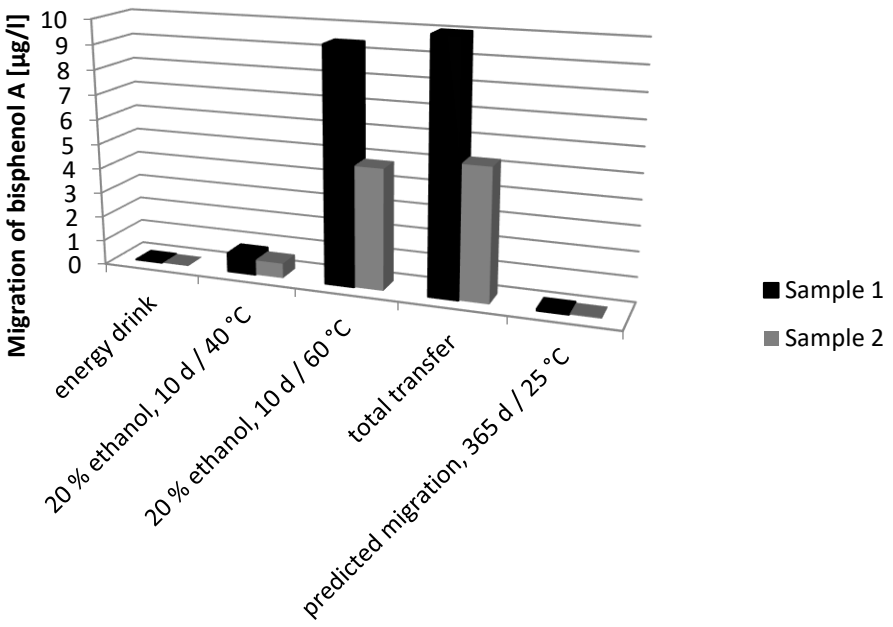

Figure 1. Migration of bisphenol A from the epoxy-coated cans sample 1 and 2 into different test media and calculated migration at the end of shelf life.

It has also been observed for polyethylene terephthalate (PET) materials that ethanolic food simulants lead to an increased migration due to swelling effects [2,9,10]. Similar effects are expected to have occurred in the investigated epoxy resins. Furthermore, a strong dependency of the activation energy of diffusion on the molecular size of the migrating species has been observed for PET [11]. Thus, for PET materials, the test conditions 10 d at 60 °C have been found to be increasingly overestimative compared to storage until the end of shelf life at room temperature with increasing molecular size [8]. For the diffusion of bisphenol A in the investigated epoxy resins, no activation energies are available from the literature. However, as an approximation, the same model for the prediction of the activation energy and diffusion coefficient was applied as has been developed for PET materials [8]. Using this model, from the molecular volume of bisphenol A of 221.11 Å^3, an activation energy E_A of 165.8 kJ/mol (pre-exponential factor $D_0 = 1.22 \times 10^{11}$ cm^2/s) and a diffusion coefficient D_P of 1.11×10^{-18} cm^2/s at 25 °C was predicted. This diffusion coefficient was used to calculate the migration from the investigated cans at room temperature for a storage time of 365 d (end of shelf life) based on the concentrations of bisphenol A determined in the epoxy resins. The modeled migration was 0.068 µg/L for sample 1 and 0.035 µg/L for sample 2. In both cases, the predicted migration was below the detection limit of 0.14 µg/L in the energy drinks and coke, respectively. Even though the results cannot be compared directly, the modeled migration is in good agreement with the findings of the experimental migration test into energy drinks.

4. Conclusions

The present study has shown that migration tests using 20% ethanol as food simulant at the accelerated test conditions of 10 d at 60 °C highly overestimate the migration into real food (in this case, energy drinks) at the end of shelf life. The migration of bisphenol A into 20% ethanol at 60 °C is a factor of >67 (sample 1) or >35 (sample 2), respectively, higher than the migration into real beverages at the end of shelf life. This overestimation of the migration is due to swelling of the epoxy can coating by the ethanolic food simulant. Water-based food simulants, or the energy drink itself, is less swelling and, therefore, the migration into real foods is much lower and, in the case of this study, below the experimental detection limits. Migration into 20% ethanol at 60 °C results in a migration value which is close to the total migration (Figure 1), which indicates that the applied contact conditions represent,

more likely, extraction conditions than migration conditions. The test conditions 10 d at 40 °C also turned out to be overestimative, though to a lesser degree. However, compared to real food, the migration is overestimated by a factor of 4, at minimum. The overestimative effect due to swelling should be considered when performing compliance tests for coated cans with 20% ethanol as simulant. However, it should also be noted that in none of the performed overestimative migration tests was the specific migration limit of bisphenol A of 50 µg/L, according to Regulation (EU) No 10/2011, exceeded. The migration potential of bisphenol A in the can coating, which assumes a complete transfer of bisphenol A into the beverage, was only 10.2 µg/L (sample 1) and 5.3 µg/L (sample 2), respectively, which is a factor of approximately 5 and 10 below the specific migration limit of bisphenol A. Prediction of the migration of bisphenol A from its residual concentration in the epoxy can coating by use for migration modeling, with the published modeling parameters of PET [8], results in a much more realistic migration value compared to the migration into swelling ethanolic simulants like 20% ethanol. The determination of bisphenol A in non-filled cans is therefore a useful test for production control. Empty bottle coatings might be tested for their residual bisphenol A concentration. Assuming total transfer of bisphenol A into the can-packed beverages, the worst-case concentration can be compared to the legal specific migration limit of 50 µg/L. If the migration potential of bisphenol A exceeds the specific migration limit, migration modeling, as applied in this study, can be used for the prediction of the migration at the end of shelf life. Such a procedure avoids that food simulants and elevated storage conditions, like 20% ethanol for 10 d at 60 °C, result in non-realistic, very overestimative migration values for bisphenol A.

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