Oligomers of bisphenol A diglycidyl ether in epoxy can coatings

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INTRODUCTION

A variety of different materials are used for the coatings of food and beverage cans, but epoxy polymers are the types of coatings most widely used. Epoxy resins are obtained by the condensation of epichlorohydrin and bisphenol A (BPA), which yields bisphenol A diglycidyl ether (BADGE). Besides epoxy monomers, migrants from epoxy coatings may also contain BADGE adducts with chain stoppers or reaction products of either solvents or phenolic monomers, which can be formed during the curing process. These substances could be released and migrate into foods.

The objective of this study is the identification of these potential unreacted substances/oligomers that could migrate from epoxy coatings by liquid chromatography coupled to tandem mass spectrometer (LC-MS/MS). It is a difficult task due to the lack of information about the formulations used in the manufacture of the coatings as well as the lack of commercially available standards of these compounds.

The two-piece cans used in this study were provided by industrial partners.

EXPERIMENTAL

Can sample

A known surface of the can was put in contact with a volume of acetonitrile for 24h at 70ºC

0.25 mL extract

+ 0.25 mL water

Filtration and analysis by LC-MS/MS

LC-MS/MS Thermo Scientific

Column	Phenosphere 80A ODS (150 mm × 3.2 mm, 3 µm)
Column Tª	30ºC
Mobile phase	MeOH: ACN (50:50, v/v) and water
Flow rate	0.5 mL/min
Injection volume	10 µL
Gradient elution	55% water and 45% MeOH:ACN (50:50 v/v) for 2 min, MeOH:ACN (50:50 v/v) was increasing until 75% for 14 min, and another gradient to 100% MeOH:ACN for 7 min
Data acquisition	Full scan (400-1000 m/z)
Source	Positive and negative atmospheric pressure chemical ionisation (APCI)
Vaporizer Tª	400ºC
Capillary Tª	350ºC

Table 1: Experimental conditions of LC-MS methods.

RESULTS AND DISCUSSION

- Acetonitrile was selected as solvent for the extraction of the unreacted compounds remaining in the coating based on our laboratory experience and in previous studies.
- Mass spectrometry detection resulted to be a powerful tool for the determination of molecular weight and structure elucidation of unidentified compounds.
- Only compounds with a molecular weight up to 1000 *m/z* were included in the study because it is generally recognized that compounds, except perfluoroalkyl compounds, above this mass range are typically not absorbed through the gastrointestinal tract.
- Several chromatographic peaks with different m/z values were detected in the samples analysed (Figure 1). These masses were compared with the available literature based on the possible starting substances. Several BADGE derivatives were identified including BADGE.H_2O.BPA, cyclo-di-BADGE, BADGE(n=1)H_2O.BPA, BADGE.BPA.BuOH or BADGE(n=1)BPA, among others.

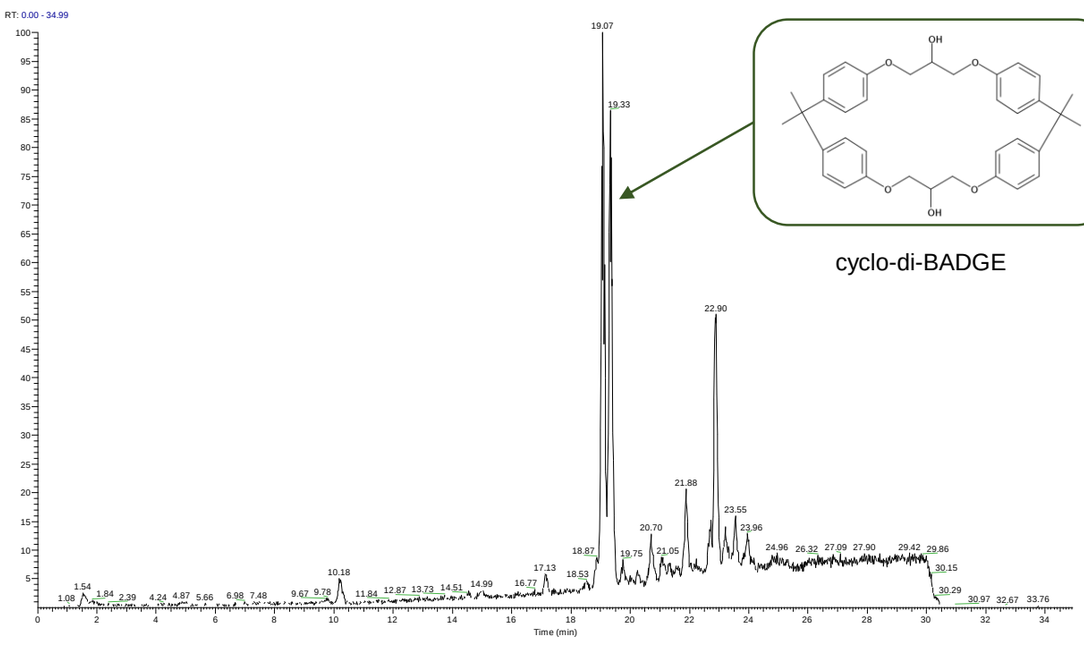

Figure 1: TIC chromatogram for the extract of the beverage can coating in positive mode.

RT (min)	Proposed compound	m/z	Adduct	TC
14.22	BADGE.H_2O.BuEtOH	477.2319 494.2501	H^+ NH_4^+	III
15.00	BADGE.BuEtOH.tBuPh	609.3638 626.3906	H^+ NH_4^+	III
16.89	BADGE.BuEtOH	481.1838 459.2254 476.2500	Na^+ H^+ NH_4^+	III
17.10	BADGE.H_2O.BPA	585.2860	H^-	III
19.00, 19.26	Cyclo-di-BADGE	569.2897 586.2955 567.2750	H^+ NH_4^+ H^-	III
19.72	BADGE(n=1)H_2O.PrOH	701.3696 703.4346 720.4130	H^- H^+ NH_4^+	III
20.52	BADGE.2BuEtOH	577.3464 594.3836	H^+ NH_4^+	III
20.80	BADGE(n=1)H_2O.BPA	869.4258	H^-	III
20.90	BADGE(n=1)	625.3183 642.3581 666.3700	H^+ NH_4^+ ACN	III
21.14	BADGE.BuEtOH.BPA	687.3778 704.4131 685.3751	H^+ NH_4^+ H^-	III
21.34	BADGE.BPA.BuOH	641.3485	H^-	III
21.48	BADGE.2BPA	795.3904	H^-	III
21.90	BADGE(n=2)H_2O	925.4523 927.4670 944.4731	H^- H^+ NH_4^+	III
22.70	BADGE(n=2)	909.4668 926.4797	H^+ NH_4^+	III
22.83	BADGE(n=1)BPA	853.4309 870.4571 851.4160	H^+ NH_4^+ H^-	III

Table 2: Substances tentatively identified in the extracts.

- The results were confirmed by quadrupole time-of-flight mass spectrometry (QTOF).
- As most of them were not toxicologically evaluated yet, the toxicological hazard was estimated according to its molecular structure using the Cramer decision tree: class I (low toxicity), class II (intermediate toxicity) or class III (high toxicity).
- Further, migration assays should be required in order to identify these compounds in foodstuffs.

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