# Investigation of Bisphenol A Diglycidyl Ether, Bisphenol F Diglycidyl Ether and their Hydroxy and Chlorohydroxy Derivatives Stability in Water-Based Food Simulants

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**Abstract**: Varnishes used as the inner coatings of food cans are often based on epoxy resins or vinylic organosols. The epoxy resins can be produced from bisphenol A (BPA) and bisphenol F (BPF) and they also contain bisphenol A diglycidyl ether (BADGE) of bisphenol F diglycidyl ether (BFDGE) as stabilising components. These compounds may break down during storage and also by influence of food simulants. The stability of BADGE and BFDGE was studied using reverse-phase gradient high performance liquid chromatography (RP-HPLC) with fluorescence detection (FLD). Four experiments were compared: (*i*) BPA solution at the concentration 3 μg/ml of each food simulant, (*ii*) BADGE solution at the concentration 3 μg/ml of each food simulant, (*iii*) BFDGE solution at the concentration 3 μg/ml of each food simulant and (*iv*) mixture of all bisphenols solution at the concentration 3 μg/ml of each food simulant. Distilled water, 10% ethanol, 95% ethanol and 3% acetic acid were used as food simulants. It was observed that BPA, BADGE and BFDGE were most stabile in 95% ethanol and least stabile in 3% acetic acid. Creation of hydroxy and chlorohydroxy derivatives was in each food simulant different so it cannot be predicted.

**Keywords**: bisphenols; hydroxy and chlorohydroxy derivatives; food simulants; migration; liquid chromatography

## INTRODUCTION

One of the ways of the can inner coating preservations employs varnishes based on epoxy resins or vinylic organosols. These resins can be produced from bisphenol A (BPA) and bisphenol F (BPF) and they also contain bisphenol A diglycidyl ether (BADGE) or bisphenol F diglycidyl ether (BFDGE) as stabilising components [1, 2]. Because of its use for lacquer coatings on food cans and food storage vessels, amount of bisphenol-type compounds should be monitored [3–5].

Unreacted residues of raw compounds (in the case of imperfectly thermally stabilised can lacquers) can migrate from epoxy-based packaging materials into the food. A similar situation can be encountered in the case of the usage of higher temperature during technological processing (sterilisation, microwave heating) – the resin can be decomposed and the migration of bisphenols from packaging to food can be more intensive and rapid. During storage BADGE and BFDGE may break down to hydrolysis and chlorohydroxy derivatives [6, 7]. As regards the supposed toxic effects of the compounds mentioned, BPA shows estrogenic activity, BADGE is related to cytotoxic effects in tissues, it is classified as a carcinogen and mutagen [8].

Migration tests of food packages usually utilise food simulants which present models of the basic food categories. In the Czech directives 38/2001 and 186/2003 Collection of Laws are included these limits: (*i*) for BPA – specific migration limit in food or in food simulants 0.5 mg/dm$^2$ of food package surface; (*ii*) limit for BPF have not been established yet; (*iii*) for BADGE and certain of their derivatives – the sum of the migration levels shall not exceed the limit 0.17 mg/dm$^2$ of food package surface; (*iv*) for BFDGE and certain of their derivatives – the limit is the same as in the case of BADGE. The use and/or presence of BADGE and BFDGE in the manufacture of those materials and articles may only be continued until 31 December 2004 [9, 10]. These limits are full harmonised with already known European Community Commission Directives (90/128/EEC, 1999/91/EC, 2001/61/EC, 2001/62/EC, 2002/16/EC, 2002/17/EC, 2002/72/EC).

In this paper, an evaluation of significance of bisphenols degradation in used food simulants during can lacquers testing is reported.

## EXPERIMENTAL

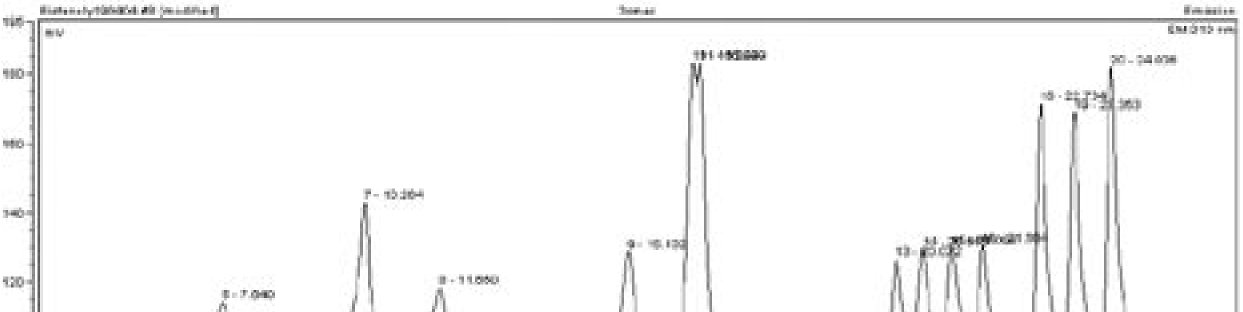
***Chemicals***. The following standard compounds from Fluka, Switzerland were used: bisphenol A diglycidyl ether (BADGE, 97%), bisphenol A-bis-(2,3-dihydroxypropyl)-ether (BADGE.2$H_2O$, 97%), bisphenol A-(3-chloro-2-hydroxypropyl)-(2,3-dihydroxypropyl)ether (BADGE.$H_2O$.HCl, 95%), bisphenol A-glycidyl-(3-chloro-2-hydroxypropyl)ether (BADGE.HCl, 95%), bisphenol A-glycidyl-(2,3-dihydroxypropyl)ether (BADGE.$H_2O$, 95%), bisphenol A-bis-(3-chloro-2-hydroxypropyl)ether (BADGE.2HCl, 99%), bisphenol F diglycidyl ether (BFDGE, 97%, a mixture of 3 isomers: *o-o*, *o-p*, *p-p*), bisphenol F-bis-(2,3-dihydroxypropyl)ether (BFDGE.2$H_2O$, 95%, a mixture of 3 isomers: *o-o*, *o-p*, *p-p*), bisphenol F-bis-(3-chlor2-hydroxypropyl)ether (BFDGE.2HCl, 97%, a mixture of 3 isomers: *o-o*, *o-p*, *p-p*). Bisphenol A (BPA, 99%) and bisphenol F (BPF, 98%) were obtained from Sigma, Germany.

***Reagents***. Acetonitrile (99%) was purchased from Fluka, Switzerland. The 99% acetic acid was obtained from Penta, Czech Republic, 10% and 95% ethanol were obtained from Lachema, Czech Republic.

***Experimental***. Standard stock solutions in acetonitrile were prepared of all the compounds investigated separately at concentration level 1 mg/ml, these solutions were first subdiluted to concentration 50 μg/ml. A standard stock mixture solution was prepared from all standard stock solutions of each bisphenol (500 μl of each standard stock solutions were added to 4500 μl of acetonitrile). The solutions of BPA, BADGE and BFDGE in four simulants (distilled water, 10% ethanol, 95% ethanol and 3% acetic acid) were prepared in concentration 3 μg/ml of each compound from standard stock solutions (60 μl of standard stock solution were added to 940 μl of food simulant). Mixture solutions of all bisphenols were prepared in concentration 3 μg/ml of each food simulant (60 μl of standard stock mixture solution were added to 940 μl of food simulant).

The stability of BPA, BADGE and BFDGE in acetonitrile and in food simulants and creation of their derivatives were tested by means of samples measurements with four-hour interval during 48 h. Mixture solutions of bisphenols in food simulants were analysed at the same conditions. All stability tests were carried out at the temperature of 23°C.

***Instrumentation***. The HPLC system consisted of a high pressure gradient pump (P580, Gynkotek,



Retention times: 7.64, 8.85 – BFDGE.2$H_2O$; 10.26 – BADGE.2$H_2O$; 11.65 – BPF; 15.13 – BPA; 16.18 – BADGE.$H_2O$.HCl; 16.32 – BADGE.$H_2O$; 19.62, 20.07, 20.55 – BFDGE.2HCl; 21.09, 21.66, 22.16 – BFDGE; 22.73 – BADGE.2HCl; 23.35 – BADGE.HCl; 24.04 - BADGE

Figure 1. Chromatogram of mixture solution of bisphenols in acetonitrile (3 μg/ml)

Germany), an analytical column (LiChroCART 125-4, 5 µm, Merck, Germany) mounted in a thermostat and a fluorescence detector (RF2000, Gynkotek, Germany). The mobile phase consisted of distilled water (solvent A) and acetonitrile (solvent B). The flow rate was set to 1 ml/min and gradient elution was used: 0–25 min 10–60% B, 25–30 min 60–100% B, 30–35 min 100% B, 35–38 min 100–10% B, 38–40 min 10% B (Figure 1). The injection was 10 µl (using autosampler GINA 50T, Gynkotek, Germany), wavelengths were set at 225 nm for excitation and 295 nm for emission.

## RESULTS AND DISCUSSION

After 48 hours BPA, BADGE and BFDGE were least stabile in 3% acetic acid (79%, 33% and 25%, respectively) and most stabile in 95% ethanol (85%, 96% and 8%, respectively).

In the mixture of all bisphenols (initial concentration 3 µg/ml of food simulants) these trends of increase or decrease of each compounds were observed (Figure 2): BADGE and BFDGE amounts decreased at most in 3% acetic acid, at least in 95% ethanol; BPA and BPF amounts increased at most (due to decomposition of the other derivatives to BPA and BPF) in 3% acetic acid, at least in 95% ethanol; BPA and BPF amounts were increased at most (decomposition of the other derivatives to BPA and BPF) in 3% acetic acid, at least in 95% ethanol; BADGE.2HCl and BFDGE.2HCl were produced at most in distilled water; BADGE.2$H_2O$ and BADGE.HCl amounts were highest in distilled water and 10% ethanol; the highest amounts of BFDGE.2$H_2O$, BADGE.$H_2O$.HCl and BADGE.$H_2O$ in 3% acetic acid were observed.

In simulants containing only BADGE (3 µg/ml) at the beginning, BADGE was broken down fast-

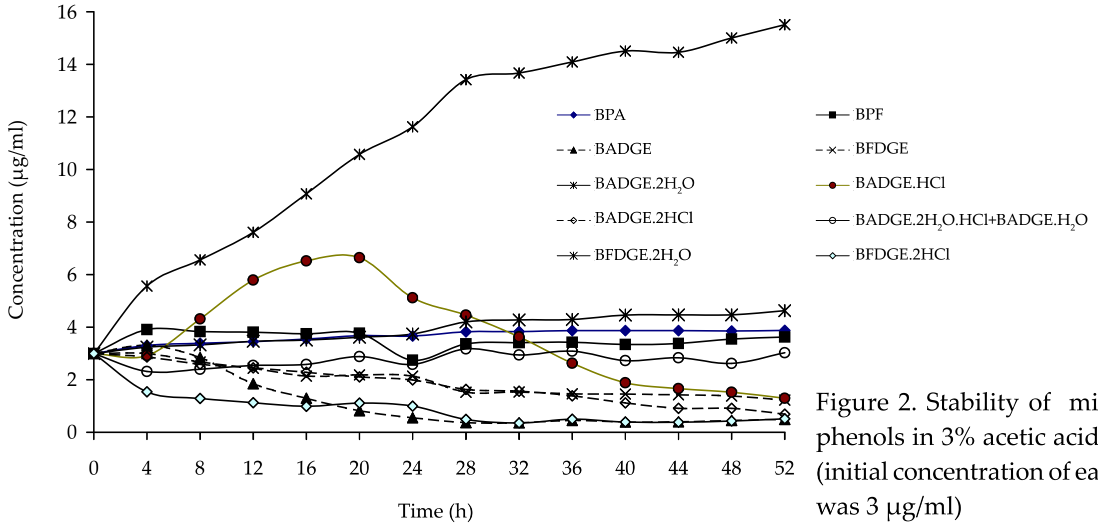


Figure 2. Stability of mixture of bisphenols in 3% acetic acid during 48 h (initial concentration of each bisphenol was 3 µg/ml)

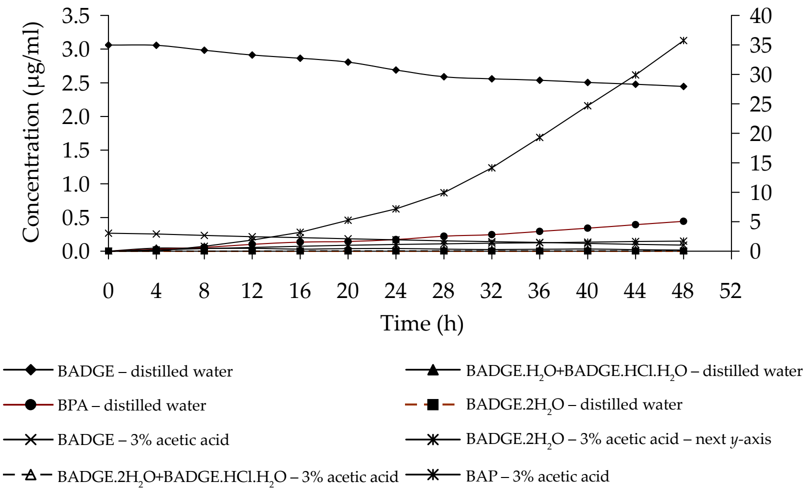


Figure 3. Creation of BADGE derivatives in distilled water and 3% acetic acid during 48 h (initial concentration of BADGE was 3 µg/ml)

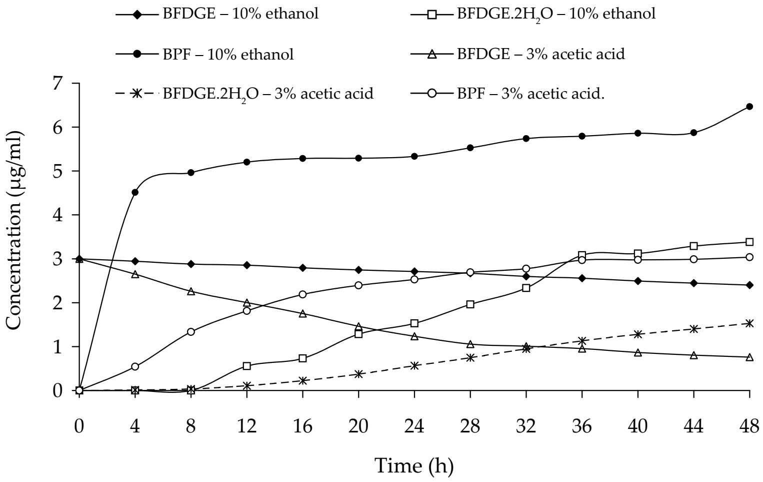


Figure 4. Creation of BFDGE derivatives in 10% ethanol and 3% acetic acid during 48 h (initial concentration of BFDGE was 3 µg/ml)

est in 3% acetic acid (Figure 3), BADGE.$2H_2O$ was progressed only in 3% acetic acid, the other compounds (BPA, BADGE.$H_2O$.HCl and BADGE.$H_2O$) were created at most in 3% acetic acid, too. This food simulant seemed as critical for BADGE and production of its derivatives.

The last experiment (Figure 4) was aimed to monitoring of BFDGE derivatives presence from BFDGE solution in food simulants (initial concentration was 3 µg/ml). BFDGE was broken down most in 3% acetic acid, BPF was created at most in 10% ethanol, at least in 95% ethanol, and BFDGE.$2H_2O$ amount was highest in 10% ethanol whereas in 95% ethanol did not create at all. For BFDGE decomposition are most sensitive food simulants 10% ethanol and 3% acetic acid.

## CONCLUSIONS

Because the package stability is indirectly tested by means of food simulants, it is necessary to verify stability of bisphenols under conditions of migration testing to avoid false positive/negative results caused by their possible decomposition in used simulant. Time progress of each bisphenol derivative presence was in each food simulant different, it can not be predicted. Generally, we can say the most sensitive food simulants relative to risk of decomposition and creation of derivatives were 3% acetic acid and 10% ethanol. Contrariwise 95% ethanol was the most neutral for derivatives formation.

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