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Stability of bisphenol A diglycidyl ether and bisphenol F diglycidyl ether in water-based food simulants

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Abstract Varnishes used for 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 these also contain bisphenol A diglycidyl ether (BADGE) or bisphenol F diglycidyl ether (BFDGE) as stabilising components. These compounds may break down during storage and also by the influence of food simulants. The stability of BADGE and BFDGE were studied using reverse-phase gradient high-performance liquid chromatography (RP-HPLC) with ultraviolet detection (UV). Three experimental conditions for spiked simulants were compared: (1) the storage at 25 °C (C1), (2) the storage at 40 °C (C2) and (3) the storage at 25 °C after 15 min heating at 120 °C (C3). Distilled water, 3% acetic acid and 10% ethanol were used as food simulants. It was observed that BADGE is more stable than BFDGE. The loss of BADGE and BFDGE were minimal in 10% ethanol (39 and 46% at 25 °C, 60 and 69% at 40 °C, respectively) and highest in 3% acetic acid (60 and 63% at 25 °C, 76 and 82% at 40 °C, respectively). At experiment (C3), the hardest conditions, significant degradation was not shown in comparison with conditions (C1) and (C2), contrariwise BADGE and BFDGE in 10% ethanol were minimal degraded at conditions (C3) from all these experiments (loss of 5 and 8%, respectively).

Keywords Bisphenols · Hydrolysis and chlorohydroxy derivatives · Migration · Food simulants · Liquid chromatography

Introduction

One of the ways of the can's inner coating preservation employs varnishes is based on epoxy resins or vinylic organosols. These resins can be produced from bisphenol A (BPA, CAS 80-05-7) and bisphenol F (BPF, CAS 620-92-8) and these also contain bisphenol A diglycidyl ether (BADGE, CAS 1675-54-3) or bisphenol F diglycidyl ether (BFDGE, CAS 2095-03-6) as stabilising components [1, 2] (Fig. 1). Epoxy resins are used as maintenance and product finishes, structural steel coatings, tank coatings, can linings or furniture finishes. Epoxy resins also can be useful in applications such as printing inks, and in dental, surgical and prosthetic applications. Because of their use for lacquer coatings on food cans and food storage vessels, the amount of bisphenol-type compounds should be monitored [3, 4].

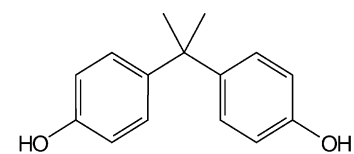
Unreacted residues of raw compounds (in the case of imperfectly thermally stabilised can lacquers) can migrate from the epoxy-based packing materials into the food. A similar situation in the case of the usage of higher temperatures during technological processing (sterilisation, microwave heating) can be encountered—the migration of bisphenols from packaging to food can be more intensive and accelerated. During storage, BADGE and BFDGE may break down to hydrolysis and chlorohydroxy derivatives [5, 6, 7] (Fig. 2). As regards the toxicity, BADGE is related to cytotoxic effects in tissues. It is listed as a carcinogen and mutagen, the potential target tissues are the central neural system, kidney, liver and sweetbread [8].

Migration tests of food packaging are usually realised by means of food simulants. The simulants are chosen as models of the basic food categories (i.e. aqueous, acidic, alcoholic and fatty). In the Czech directives 38/2001 and 186/2003 Collection of Laws are included these limits: (1)

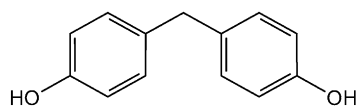
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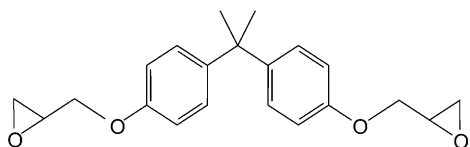
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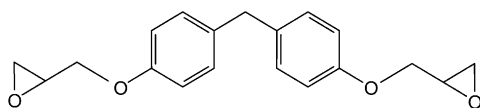
BPA



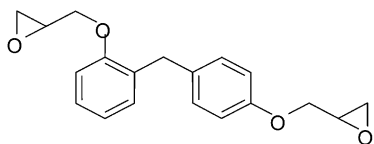
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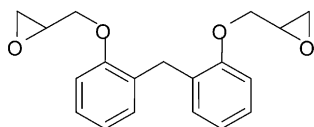
BADGE



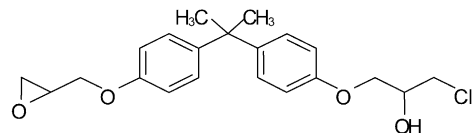
para-para BFDGE



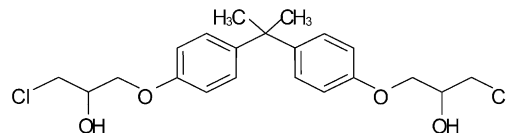
ortho-ortho BFDGE



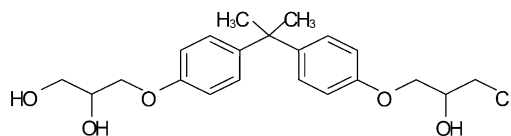
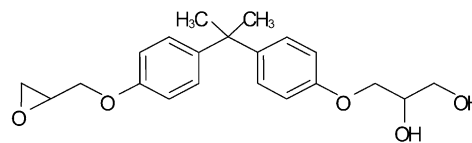
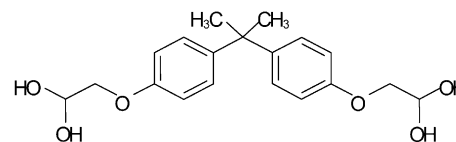
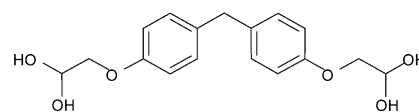
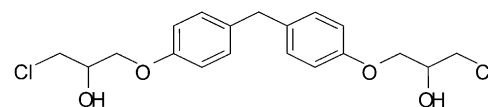
ortho-para BFDGE



BADGE.HCl



BADGE.2HCl

BADGE.HCl.H₂OBADGE.H₂OBADGE.2H₂OBFDGE.2H₂O

BFDGE.2HCl

Fig. 1 Molecular structures of BPA, BPF, BADGE and BFDGE

Fig. 2 Molecular structures of BADGE and BFDGE hydrolysis and chlorohydroxy derivatives

for BADGE and certain of their derivatives—the sum of the migration levels of the following substances: BADGE, BADGE.H₂O, BADGE.HCl, BADGE.2HCl, BADGE.H₂O.HCl shall not exceed the following limits: 1 mg/kg in foodstuffs or in food simulants or 1 mg/6 dm² of food package surface; this value should also include BADGE.2H₂O unless the material or article is labelled for use in contact only with those foods and/or beverages for which it has been demonstrated that the sum of the migration levels of the five BADGE substances cannot exceed the limits described above; (2) for BFDGE and certain of their derivatives—the limits are 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 harmonized with European Community Commission Directives [11, 12, 13, 14, 15, 16, 17].

In work presented the stability of BADGE and BFDGE in acetonitrile and in three water-based food simulants (distilled water, 3% acetic acid and 10% ethanol) under different temperature conditions using RP-HPLC with UV detection was investigated. The aim of this study was to evaluate the significance of the degradation of bisphenols in food simulants during can lacquers testing.

Materials and methods

Chemicals

The following standard compounds from Fluka, Switzerland were used: bisphenol A diglycidyl ether (BADGE, 97%), bisphenol A-bis-(2,3-dihydroxypropyl)-ether (BADGE.2H₂O, 97%), bisphenol A-(3-chlor-2-hydroxypropyl)-(2,3-dihydroxypropyl)-ether (BADGE.H₂O.HCl, 95%), bisphenol A-glycidyl-(3-chlor-2-hydroxypropyl)-ether (BADGE.HCl, 95%), bisphenol A-glycidyl-(2,3-dihydroxypropyl)-ether (BADGE.H₂O, 95%), bisphenol A-bis-(3-chlor-2-hydroxypropyl)-ether (BADGE.2HCl, 99%), bisphenol F diglycidyl ether (BFDGE, 97%, a mixture of 3 isomers: ortho-ortho, ortho-para, para-para), bisphenol F-bis-(2,3-dihydroxypropyl)-ether (BFDGE.2H₂O, 95%, a mixture of 3 isomers: ortho-ortho, ortho-para, para-para), bisphenol F-bis-(3-chlor-2-hydroxypropyl)-ether (BFDGE.2HCl, 97%, a mixture of 3 isomers: ortho-ortho, ortho-para, para-para).

Reagents

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

Experimental

Standard stock solutions in acetonitrile were prepared for all the compounds investigated at concentration level 1 mg/ml. These solutions were sub-diluted to a concentration of 50 µg/ml. These diluted solutions were used for HPLC method optimization of analytes and for testing of stability of BADGE and BFDGE in acetonitrile. The solutions of BADGE and BFDGE in three water-based simulants (distilled water, 3% acetic acid and 10% ethanol) were prepared in a concentration of 50 µg/ml of each compound

from standard stock solutions (150 µl of standard stock solution were added to 2,850 µl of food simulant).

The stability of BADGE and BFDGE in acetonitrile was tested by means of samples measurements each 24 h during 14 days at three different temperature conditions: (1) the storage at 25 °C (C1), (2) the storage at 40 °C (C2) and (3) the storage at 25 °C after 15 min heating at 120 °C (C3). The samples for BADGE and BFDGE stability testing in food simulants were observed at the same conditions as acetonitrile solutions during 48 h with four-hour interval samplings. All stability tests were carried out in amber vials.

Instrumentation

The HPLC system consisted of a high-pressure gradient pump (Perkin-Elmer Series 200, PE Instruments, USA), an analytical column (LiChroCART R 125-4 HPLC Cartridge (Merck, Germany) with Spherisorb R ODS-2 (5 µm) (Merck, Germany) as stationary phase) mounted in a thermostat and an ultraviolet detector (Perkin-Elmer Series 200 UV/VIS Detector, PE Instruments, USA). System control and data acquisition were performed using interface (Perkin-Elmer Nelson NCI 900 Network Chromatography Interface, PE Nelson, USA). For chromatographic data evaluation, Turbochrom 4 (PE Nelson, USA) software was used. The mobile phase consisted of distilled water (solvent A) and acetonitrile (solvent B). The flow rate was set to 1 ml/min and five different HPLC methods (four isocratic and one gradient) were tested to find the best separation: (1) isocratic elution with a mixture of 50(A):50(B); (2) isocratic elution with a mixture of 40(A):60(B); (3) isocratic elution with a mixture of 35(A):65(B); (4) isocratic elution with a mixture of 48(A):52(B); (5) gradient elution: 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. The injection loop was 20 µl, and the wavelength used was 225 nm.

Results and discussion

Chromatographic separation

The best chromatographic separation was reached using a gradient method (Fig. 3) inspired by a published paper [1] ((v) - see Materials and methods). In the case of BFDGE and its derivatives, there was a problem with satisfactory resolution of individual isomers. Also, BADGE.H₂O and BADGE.HCl.H₂O were the critical compounds to be separated. It was difficult to observe changes in derivatives amount; on the other hand, the monitoring of BADGE and BFDGE was not complicated because of well-separated peaks. In accordance with legislative requirements, the total sum of BADGE and its derivatives is important, therefore this gradient method showed as sufficient not only for our experiments, but for all next observation related with analysis of the other derivatives in food simulants extracts.

Stability of BADGE and BFDGE in acetonitrile

These storage experiments are illustrated in Fig. 4 for BADGE and Fig. 5 for BFDGE. At 25 °C (C1), BADGE was relatively stable until the seventh day, then the loss was larger. At 40 °C (C2), the BADGE amount decreased the most during the first 2 days, then the diminution was

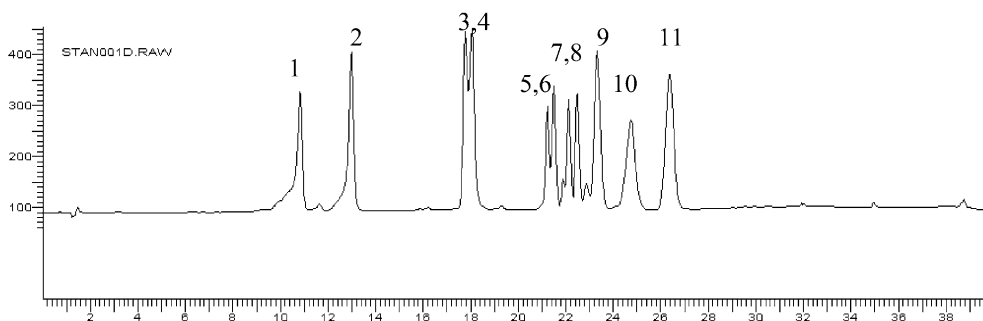


Fig. 3 The chromatogram of the mixture of investigated compounds analyzed using gradient elution (See Materials and methods, (v)) Elution order: 1 BFDGE.2H₂O; 2 BADGE.2H₂O; 3

BADGE.HCl.H₂O; 4 BADGE.H₂O; 5, 6 BFDGE.2HCl; 7,8 BFDGE; 9 BADGE.2HCl; 10 BADGE.HCl; 11 BADGE

Fig. 4 Stability of BADGE in acetonitrile during 14 days

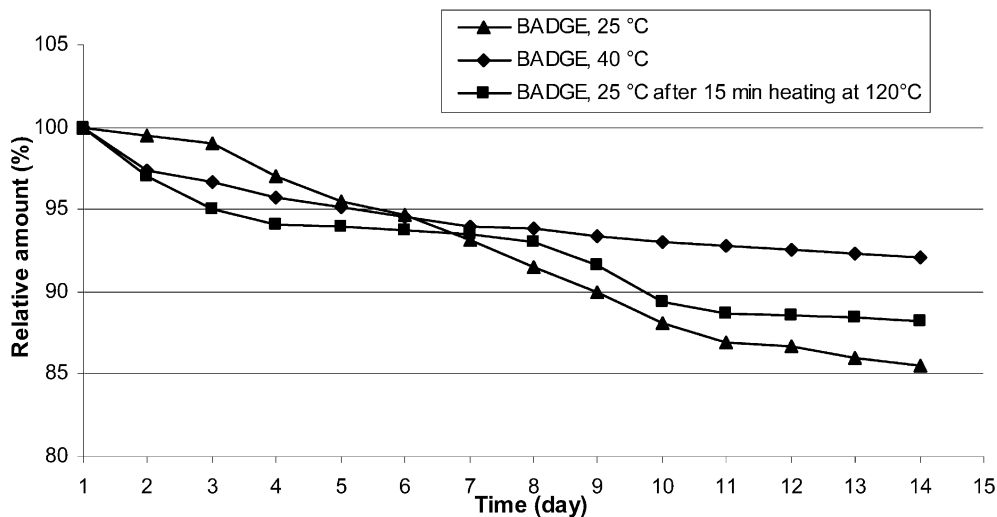
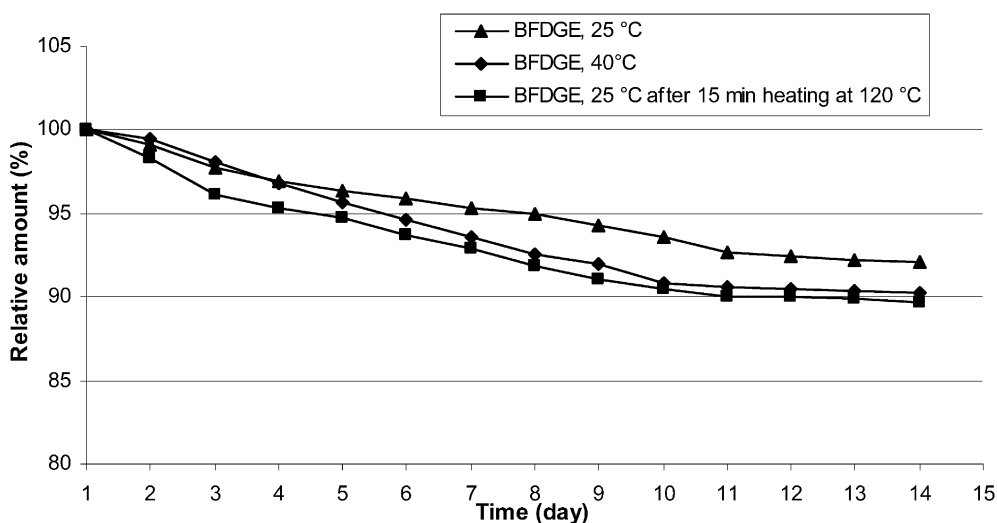


Fig. 5 Stability of BFDGE in acetonitrile during 14 days



slower. After 15 min of heating, the BADGE solution was stored at 25 °C (C3). After the seventh day the decrease was slower, too. In the case of BFDGE, at 25 °C (C1) the diminution was smaller than at 40 °C (C2) or after heating (C3). Generally, at 25 °C (C1) the BADGE and BFDGE

amount did not significantly change over 7 days, it was found approximately 93 and 95%, respectively, and after 14 days was found 85 and 92%, respectively. We can suppose that during storage of the standard solution in the refrigerator (4 °C) the dynamic of the decrease will be

Fig. 6 Stability of BADGE and BFDGE in three food simulants during 48 h at 25 °C

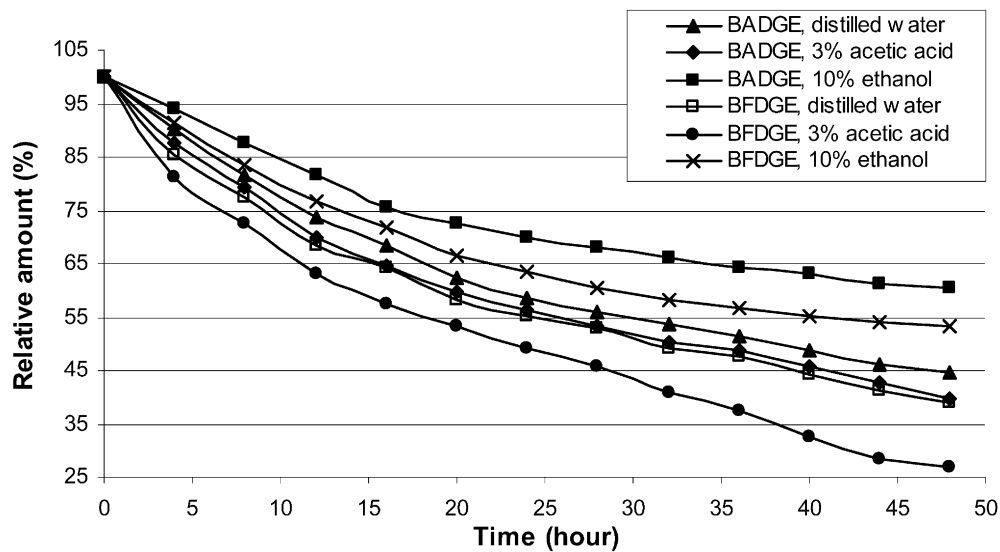


Fig. 7 Stability of BADGE and BFDGE in three food simulants during 48 h at 40 °C

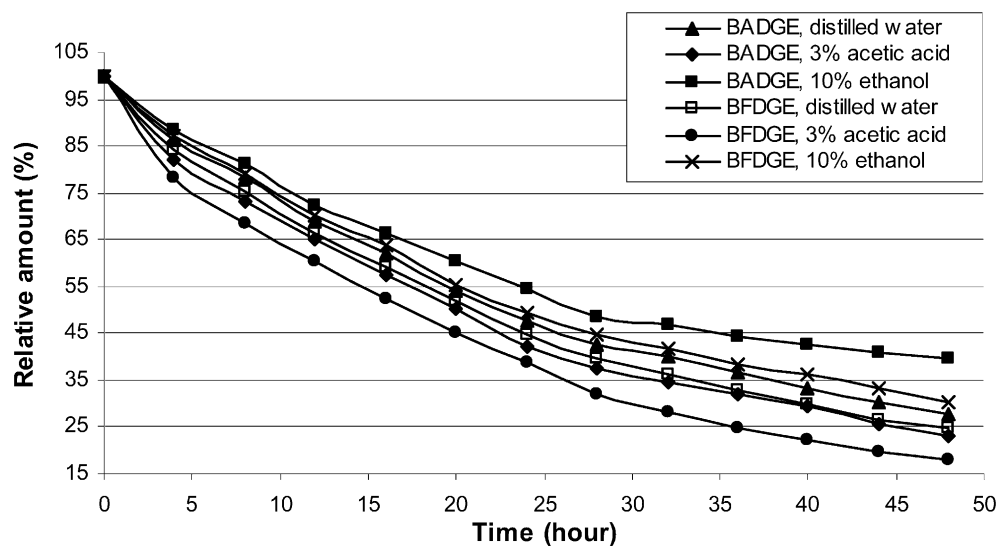
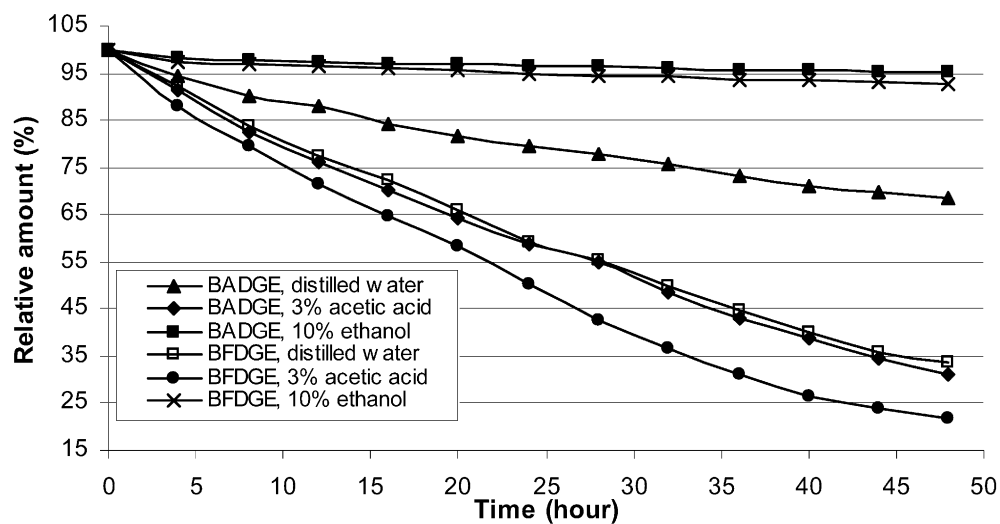


Fig. 8 Stability of BADGE and BFDGE in three food simulants during 48 hours at 25 °C after 15 min heating at 120 °C



slower than during storage at 25 °C (C1) or higher, which proved the suitability of acetonitrile for standard solution preparation.

Stability of BADGE and BFDGE in food simulants

These stability experiments are presented in Figs. 6, 7, and 8 for three different conditions (C1, C2, C3). The BADGE in 10% ethanol was most stable after heating (C3) (95%). The BADGE amount at 40 °C (C2) after 48 h was nearly one-half of the BADGE amount at 25 °C (C1) (39 and 60%, respectively). The BADGE in the distilled water was most stable after heating too (C3) (68%), but the difference between the values of 25 °C (C1) and 40 °C (C2) storage was not so significant (44 and 27%, respectively). The highest BADGE amount loss was observed in 3% acetic acid solution at 40 °C (C2) (77%) over against storage at 25 °C (C1) and after heating (C3) (61 and 69%, respectively). The fastest diminution BFDGE in 3% acetic acid at 40 °C (C2) and after heating (C3) (the loss of 83 and 79%, respectively) demonstrated, while at 25 °C (C1) the loss was 72%. Similar to BADGE, BFDGE in 10% ethanol was the most stable after heating (C3) (92%), at 25 °C (C1) and 40 °C (C2) were observed amounts of BFDGE as 53 and 30%, respectively. As regards BFDGE solutions in distilled water, BFDGE was the most stable at 25 °C (C1) (39%), at 40 °C (C2) and after heating (C3) was the decrease larger (24 and 33%, respectively). The decrease trends were practically constant for all analytes.

Conclusions

As can be seen from measured data evaluation, acetonitrile solutions of BADGE and BFDGE stored at ambient temperature are relative stable, so it can be predicted that their degradation does not influence results. 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 the simulant used. The highest stability of BADGE and BFDGE in 10% ethanol (the food simulant of alcoholic foodstuffs) was observed. In the case of 3% acetic acid and distilled water, tested bisphenols were decomposed after 10 h. Based on the results obtained, it is necessary to assure minimal degradation of investigated

bisphenols by appropriate arrangement of analytical procedure (prompt storage of food simulant extracts at lower temperature or their immediate analysis).

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