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Quality control of cured epoxy resins

Determination of residual free monomers (*m*-xylylenediamine and bisphenol A diglycidyl ether) in the finished product

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ABSTRACT

A simultaneous method for extracting residual bisphenol A diglycidyl ether (BADGE) and *m*-xylylenediamine (*m*-XDA) from finished epoxy resins cured with different equivalent ratios of these raw materials (1:1, 1:2 and 1:3) has been developed. Extraction is based on refluxing epoxy–amine formulations in a chloroform–methanol (25:75) mixture for 10 h and quantification is carried out by reversed-phase high-performance liquid chromatography with fluorescence detection, directly for BADGE and previous precolumn derivatization with fluorescamine for *m*-XDA. The relative standard deviation for BADGE chromatography at 200 μg/l was 3.4% and for *m*-XDA derivatization–chromatography 5.7%, the detection limit 5 μg/l for BADGE and 20 μg/l for *m*-XDA and the recovery for six spiked concentrations of 200 μg/l was 98.9 ± 6.5% for BADGE and 89.3 ± 6.0% for *m*-XDA.

INTRODUCTION

The first commercial epoxy resins were obtained by a condensation reaction between epichlorohydrin and bisphenol A [1]. This reaction leads to the diglycidyl ether of bisphenol A and, depending on the epichlorhydrin to bisphenol A molar ratios and the reaction conditions, products of different molecular weights are obtained as indicated in Fig. 1, where *n* is the degree of condensation.

A liquid epoxy resin of low molecular weight has a structure derived from two molecules of epichlorohydrin and one molecule of bisphenol A. Higher molecular weights increase the viscosity of the epoxy resins and solid products are obtained. However, these products are soluble, fusible and without remarkable mechanical and chemical properties. To be converted into insoluble and thermosetting products, the epoxy resins need to undergo reaction with other chemical intermediates, so-called curing agents, which must be of high functionality (at least three) with good hydrogen-releasing activity to ob-

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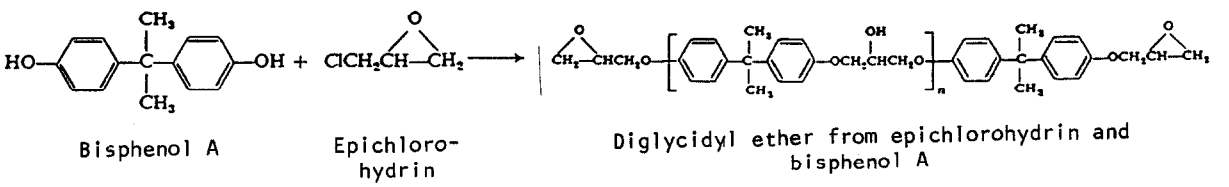

Fig. 1. General reaction forming epoxy resins of the bisphenol A type.

tain a highly cross-linked structure owing to the high reactivity of the hydrogen donor. Amine compounds are most commonly used in epoxy formulations [2].

The degree of toxicity of epoxy compounds depends mainly on the fractional concentration of unreacted epoxy groups. Epoxy compounds are alkylating agents and they have specific cytotoxic actions in tissues with high rates of cell division. Bisphenol A diglycidyl ether [2,2-bis(4-hydroxyphenyl) propanebis(2,3-epoxypropyl) ether (BADGE) causes sensitization of surface tissues, probably owing to the presence of by-product impurities which are toxic. Hardeners probably play a major role. *m*-Xylylenediamine (1,3-benzenedimethanamine) (*m*-XDA) is toxic by inhalation, in contact with the skin and if swallowed. It is necessary to bear in mind that many aromatic amines have been shown to produce toxic effects on animals, *e.g.*, liver, kidney and bone marrow damage [3].

Epoxy-based solution coatings are used many applications. Our interest is centred on their use for lacquer coatings on food cans and food storage vessels [4,5]. Because of their toxicity it is necessary to control the unreacted products to prevent their migration into good.

BADGE (oligomer of molecular weight 340) is contained in list 7 of the Scientific Committee for Food (SCF) 19th Report [6], which includes substances for which some toxicological data exist but for which an admissible daily ingest (ADI) or tolerable daily ingest (TDI) could not be established. The additional specified information should be furnished. The Committee recognizes that priorities will have to be set because of the large number of substances mentioned. The criteria for setting these priorities should include, for example, availability of analytical methods, data on exposure (*e.g.*, usage, extent of migration) and hydrolysis data. *m*-XDA is contained in list 8, which includes substances for which no or only scant and inadequate data were available.

A recent EEC Directive [7] established as the specific migration limit in food or in food simulants a level of 0.02 mg/kg for BADGE and 0.05 mg/kg for *m*-XDA, and set also for BADGE the maximum permitted concentration of the residual substance in the material or article at 1 mg/kg.

Many papers [8–11] have been devoted to aspects of the control of food packaging because of its possible contamination of foods by migration of additives and free monomers. Test conditions (10 days at 40°C) have been approved to determine this transfer of residuals, but it is possible to detect them in the final product fairly rapidly.

The American Society for Testing and Materials (ASTM) include test methods which cover the determination of the epoxy content in the epoxy resins [12]. However, gel permeation chromatography (GPC) permits the coarse separation of epoxidic oligomers [13–17], althouh the best resolution has been achieved using reversed-phase partition techniques, commonly using ultraviolet detection [18–24]. We have determined BADGE by reversed-phase high-performance liquid chromatography (RP-HPLC) with fluorescence detection because of its higher sensitivity, in a similar manner to that reported previously [25].

Low-level detection techniques to determine *m*-XDA based on HPLC with both electrochemical and fluorescence detection have also been reported [26]. We decided to use the latter because of its greater simplicity.

EXPERIMENTAL AND RESULTS

Apparatus

A Perkin-Elmer DSC/7 differential scanning calorimeter, a Perkin-Elmer FT-IR 1720/X Fourier transform infrared spectrometer, a Spectra-Physics

SP8700 XR extended-range LC pump, a Spectra-Physics SP8750 organizer, a Perkin-Elmer PE LS 40 fluorescence detector, a Spectra-Physics SP4290 integrator and SP WINNER software V. 4.00, a Crison micropH 2002 pH meter and an Agimatic heater were used.

Polyester membrane (47 mm × 0.4 μm) was obtained from Nuclepore and glass material from Afora.

Reagents

Water purified with a Milli-Q system (Millipore) was used throughout. Helium (N-48) from SEO was used for degassing the mobile phases. Analytical-reagent grade chemicals were used unless indicated otherwise.

Acetonitrile, methanol and chloroform (LiChrosolv) were obtained from Merck and tetrahydrofuran and fluorescamine from Carlo Erba.

Phosphate buffer (1/15 *M*, pH 8) was prepared as follows:: solution A was 0.9073 g of KH_2PO_4 (Merck) in 100 ml of water, solution B was 11.87 g of $Na_2HPO_4 \cdot 2H_2O$ (Merck) in 1 l of water, and 37 ml of solution A were mixed with 963 ml of solution B and the mixture was filtered through 0.4-μm filter and adjusted to pH 8 with solution A.

A stock solution of *m*-XDA (purity 99%) (Aldrich) containing exactly 500 mg of *m*-XDA in 100 ml of water was prepared under a nitrogen atmosphere with silica gel as desiccant to avoid carbonation. It was stored in the dark in a refrigerator.

Bisphenol A diglycidyl ether was obtained as Epikote 828 from Shell, purified (>99%) by Shell for Gairesa Industry. A product of similar purity can be obtained as described by Paz Abvín *et al.* [27]. A stock solution was prepared containing exactly 500 mg of BADGE in 100 ml of tetrahydrofuran. It was stored in the dark in a refrigerator.

Chromatographic conditions

A stainless-steel column (15 cm × 5 mm I.D.) packed with 5-μm Pecosphere CRT C_{18} RC was used. Guard columns (C_{18}) were used in order to protect the packing in the analytical columns. For injection, the 50-μl loop in a Rheodyne valve was filled with a Hamilton syringe. The eluent flow-rate was 1 ml/min.

Elution was carried out as follows. Gradient elution for BADGE consisted of a 5-min linear gradient from acetonitrile–water (30:70) (30% acetonitrile) to 55% acetonitrile, 5-min isocratic elution at 55% acetonitrile, a 5-min linear gradient to 75% acetonitrile and 5 min isocratic elution at 75% acetonitrile. Isocratic elution for derivatized *m*-XDA was performed with phosphate buffer (1/15 *M*, pH 8)–water–methanol (16:34:50).

For detection, the attenuation factor was 16 with auto-zero, and the response was 4 [equivalent RC (98% FS) response time 2.8 s]. The excitation wavelengths were 275 nm for BADGE and 395 nm for derivatized *m*-XDA and the emission wavelengths were 300 nm for BADGE and 480 nm for derivatized *m*-XDA. The photomultiplier voltage was 750 V.

The integrator attenuation was 4.

Procedure

Before starting the extraction, the details of the curing conditions are very important. Epoxy–amine formulations that have not completely cured contain large amounts of soluble compounds, so it is necessary to predetermine the optimum curing conditions, that is, the time and temperature characteristics for each epoxy–amine equivalent ratio. The time and temperature of curing for a 1:1 equivalent ratio in this reaction was stated to be 10 min at 110°C [27]. Following the same technique, employing differential scanning calorimetry and Fourier transform IR techniques, we found that 16 min at 80°C for a 1:2 and 90 min at 50°C for a 1:3 equivalent ratio produced fully cured resins.

A sample of about 200 mg of the epoxy–amine formulation was treated as follows. The sample was transfered into a 100-ml conical flask and 20 ml of chloroform–methanol (25:75) were added. A reflux column was fitted and the sample was maintained at reflux for 10 h. The mixture was filtered into a 50-ml volumetric flask. The conical flask was washed with methanol and the washings were filtered into the 50-ml flask. Finally, methanol was added to the mark.

For formulations with BADGE to *m*-XDA ratios of 1:2 and 1:3, free BADGE may be directly determined in this solution. If the ratio is 1:1, it is necessary to dilute 25-fold with methanol (2 ml in 50 ml) before chromatographic analysis.

Free *m*-XDA at a BADGE to *m*-XDA ratio of

1:1 is determined by diluting the refluxed solution 25-fold with water (2 ml in 50 ml), derivatizing with fluorescamine and chromatographic analysis. Pre-column derivatization was peformed as follows. A 2-ml volume of the solution was pipetted into a screw-topped tube and 0.4 ml of phosphate buffer (1/15 *M*, pH 8) was added. A 20-μl volume of a solution of fluorescamine in acetone ((2 mg/ml) was added and the mixture was stirred for 1 min and allowed to stand for 10 min before injection. For formulations with BADGE to *m*-XDA ratios of 1:2 and 1:3, this new solution was further diluted with water 10-fold (10 ml in 100 ml) and 100-fold (1 ml in 100 ml), respectively, before derivatization.

Chromatograms obtained in this way are shown for BADGE and *m*-XDA in Fig. 2.

Calibration

Working solutions with concentrations of 1000 μg/l were prepared from the stock solutions of BADGE and *m*-XDA using stepwise dilution steps of 50-fold (1 ml in 50 ml) and 100-fold (1 ml in 100 ml), respectively, with methanol or water.

Aliquots of 1, 2.5, 5, 10, 20 and 40 ml of the BADGE working solution were pipetted into 50-ml volumetric flasks and made up to the mark with methanol to give concentrations of 20 μg/l (limit of quantification of the calibration line) to 800 μg/l (at higher levels the detector signal is saturated under the chromatographic conditions). These six new solutions were utilized to construct the BADGE calibration graph (Fig. 3).

Aliquots of 2.5, 5, 10, 15 and 25 ml of the *m*-XDA working solution were pipetted into 50-ml volumetric flasks and made up to the mark with water. These five solutions and a sample of the working solution were derivatized according to the described procedure and chromatographed to construct the *m*-XDA calibration grpah (Fig. 3).

External standard chromatograms for BADGE and *m*-XDA are shown in Fig. 4.

Calculations

The free BADGE content in the cured epoxy resin was calculated from the equation

$$R = \frac{CF}{200W}$$

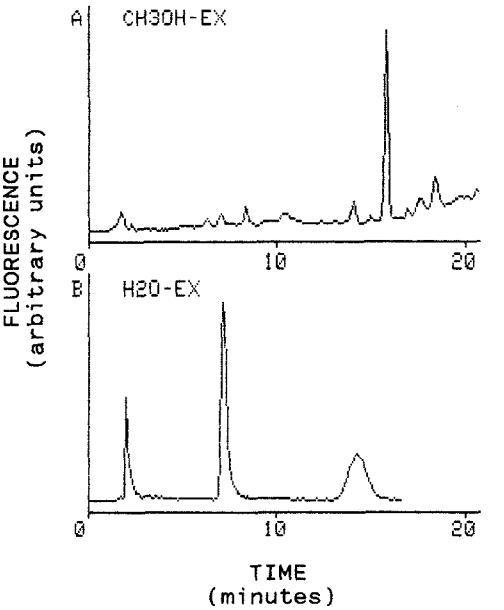

Fig. 2. Chromatograms obtained following the described procedure independently of the raw material ratio in the epoxy resin: (A) BADGE; (B) derivatized *m*-XDA. The late peak results from the reaction of two molecules of fluorescamine with each amine group in *m*-XDA [29].

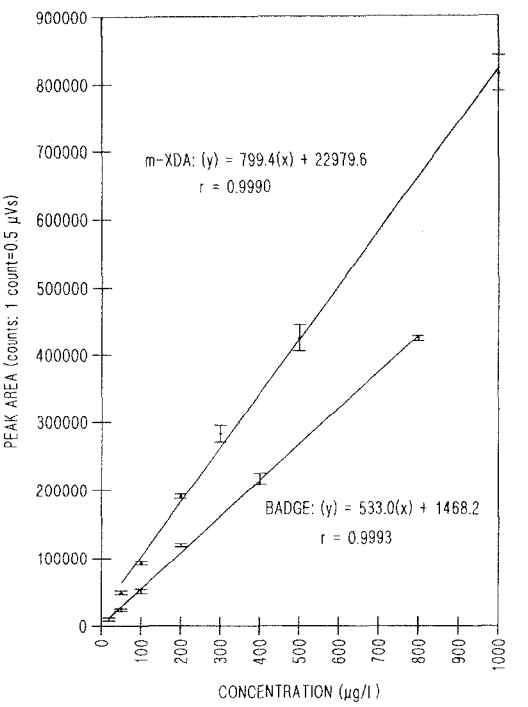

Fig. 3. Calibration graphs for BADGE and *m*-XDA.

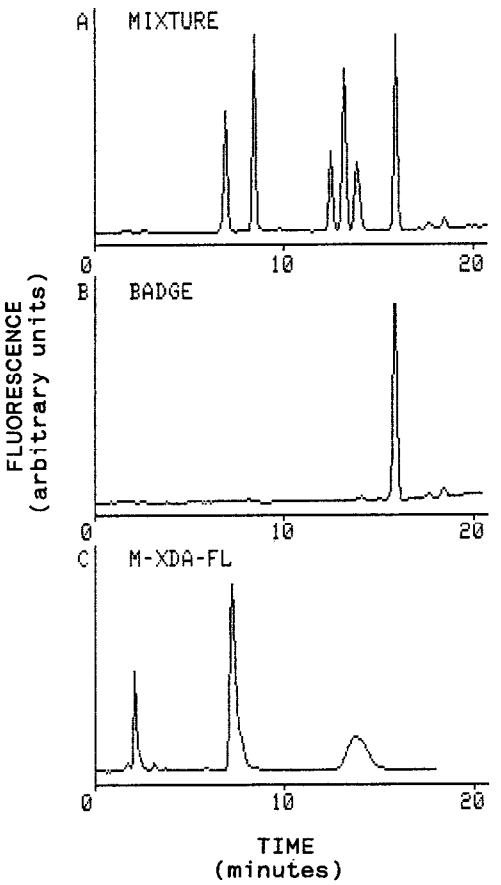

Fig. 4. External standard chromatograms: (A) mixture of, in order of elution, bisphenol F, bisphenol A, three Bisphenol F diglycidyl ether isomers and bisphenol A diglycidyl ether; (B) BADGE; (C) derivatized *m*-XDA.

where R is the free BADGE content (%) in the cured epoxy resin, C is the concentration (μg/l) given by the calibration line, F is a factor, being 25 for a BADGE to *m*-XDA ratio of 1:1 or 1 for a ratio of 1:2 or 1:3, and W is the weight utilized of cured epoxy resin (mg) utilized in the procedure.

The free *m*-XDA content in the cured epoxy resin was calculated from the same equation, but now R is the *m*-XDA content (%) and F is 25 for a BADGE to *m*-XDA ratio of 1:1, 250 for a ratio of 1.2 and 2500 for a ratio of 1:3.

Chromatographic precision (including the derivatization for m-XDA)

A single specimen with a fortified BADGE concentration of 200 μg/l in methanol was chromatographed six times, giving a relative standard deviation of 3.4%. A single specimen containing 200 μg/l of *m*-XDA in water was derivatized and chromatographed six times, giving a relative standard deviation of 5.7%.

Recovery and precision

A 1-ml volume of the stock solution of BADGE in tetrahydrofuran was diluted to 100 ml with methanol, and 0.5 ml of the stock solution of *m*-XDA in water was diluted to 100 ml with methanol. Then 5 or 10 ml of the solution containing 250 μg of BADGE or *m*-XDA, respecitvely, were mixed with 5 ml of chloroform in a conical flask. Refluxing, filtration and washing steps were carried out as in the described procedure and then the methanol solution (50 ml) was diluted 25-fold (2 ml in 50 ml) using methanol to determine BADGE and water to determine *m*-XDA. The final concentration in both solutions is *ca.* 200 μg/l. The results are given in Table I. Table II gives the results of the determination of free levels of BADGE and *m*-XDA in two different kinds of epoxy–amine resin formulations at BADGE to *m*-XDA equivalent ratios of 1:1, 1:2 and 1:3.

Detection limit

The lowest concentration of BADGE observable at a signal-to-noise ratio of 3 was 5 μg/l and the corresponding concentration of *m*-XDA was 20 μg/l. These results were verified experimentally by spiking a blank at these levels.

DISCUSSION

Chloroform–methanol (25:75) was used to extract BADGE and *m*-XDA from cured epoxy resins. Chloroform was chosen by Kwei [28] for vapour sorption studies because of the extensive swelling of highly cross-linked network structures, but a higher proportion of methanol was found necessary in order to prevent the high reactivity of *m*-XDA towards humidity and its tendency to form carbonates.

TABLE I

RESULTS OF RECOVERY EXPERIMENTS FOR BADGE AND *m*-XDA

BADGE			*m*-XDA		
Added (μg)	Found (μg)	Recovery (%)	Added (μg)	Found (μg)	Recovery (%)
250	262	104.8	250	218	87.2
	248	99.2		234	93.6
	226	90.4		217	86.8
	237	94.8		248	99.2
	270	108.0		214	85.6
	241	96.4		208	83.2
Average		98.9			89.3
Relative standard deviation (%)		6.5			6.0

TABLE II

RESULTS OF DETERMINATIONS OF RESIDUAL FREE LEVELS OF BADGE AND *m*-XDA IN CURED EPOXY RESINS

BADGE to *m*-XDA equivalent ratio	First resin		Second resin	
	BADGE (%)	*m*-XDA (%)	BADGE (%)	*m*-XDA (%)
1:1	0.047	0.19	0.098	–
1:2	0.007	1.23	0.001	0.84
1:3	–	2.88	–	6.21

CONCLUSIONS

The proposed method for the determination of free residueal BADGE and *m*-XDA in cured epoxy resins has very good precision. The accuracy is excellent for BADGE and adequate for *m*-XDA in comparison with other methods [26].

This method for the quality control of epoxy resins is not time consuming and is quicker than the migration assays performed on food-simulating solvents. Further, it has an appropriate limit of detection. It can therefore be recommended for determining BADGE monomer and *m*-XDA hardener in epoxy resins with different ratios of these raw materials.

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